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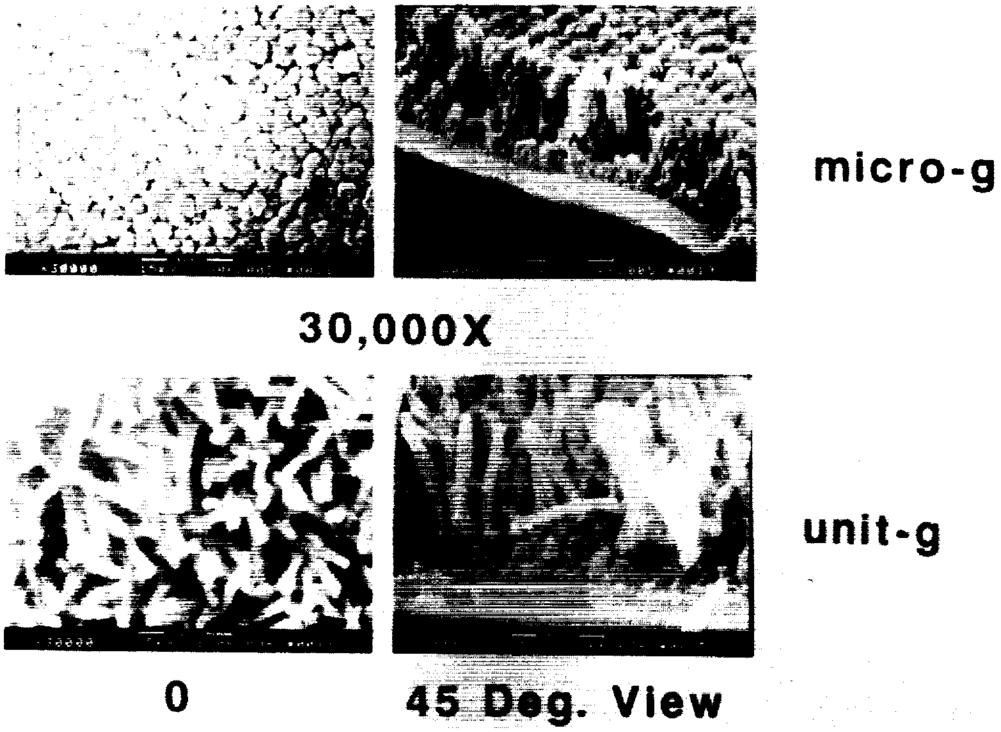
Microgravity Studies of Organic and Polymeric Materials



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Microgravity Studies of Organic and Polymeric Materials

Edited by
D.O. Frazier and C.E. Moore
NASA George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama

and

B.H. Cardelino
Spelman College
Atlanta, Georgia

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TABLE OF CONTENTS

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TABLE OF CONTENTS (Continued)

I. PREFACE

MICROGRAVITY STUDIES OF ORGANIC AND POLYMERIC MATERIALS

Organic and polymeric materials processing is a new and, heretofore, understudied discipline in the Microgravity Science and Applications Division of NASA. Part of the reason for this has been the perception that most interesting polymers are too viscous for convective and Stokes flows to be important within the critical timeframe of a processing event. Whereas this is probably true for high molecular weight organic and polymer melts, it is false for solution polymerizations and a variety of lower molecular weight organics, polymers, and composites. For example, although the scaling behavior of commercial impact polyolefin copolymer phase coarsening is reportedly in agreement with a diffusional mechanism for particle growth, the reported coarsening rate is orders of magnitude faster than one would expect from coarsening by traditional diffusion.[1] Aside from the viscosity issue, similar rationale which allows support of microgravity research in other disciplines applies to these materials. Furthermore, the microgravity environment may be ideal for the unraveling of particular fundamental issues of interest to the "organic and polymer contingent" of the science community. Even though low thermal conductivity may be problematic for some organic solidification processes, organo-metallics, some of which have very interesting optical properties, may not exhibit low thermal conductivity.

Polymers have a number of properties which may be of interest for fundamental microgravity study. Because of orientational constraints, polymers typically supercool before solidification. Furthermore, solidification often accompanies polymerization. For these reasons, thermal profiles of parent matrices can be quite interesting during traveling front polymerizations as observed by Mathias. The reported rapid coarsening of copolymers is suggestive of unique processes occurring in these materials. Coupling between polymerization and convection could significantly affect copolymerization products yielding materials having properties which depend on gravity levels during processing. In many cases involving competing reactants, mass transport to a reactive site is the rate limiting step. A thermodynamically factored reactant may become less competitive with other reactants as mass transport decreases and a depletion region of the favored reactant begins to develop. In general, microgravity should reduce the selectivity of reactions and may be an important tool in elucidating the effect of mass transport on reaction rate and products.

Other suggestions for using the microgravity environment include property measurements such as measurement of tensile stress, a containerless process, for determination of elongational viscosity of polymers, as suggested by Carruthers of Purdue. Accurate measurement of diffusion coefficients, difficult in unit gravity because of the distorting effects of convection and complexity of thermal profiles in polymers, is important to the polymer chemist.

In recent years there has been tremendous interest in the field of nonlinear optics (NLO). Important applications such as optical switching, optical communications, and optical computing all require devices containing materials that possess large nonlinear optical responses. At present, however, NASA has had limited involvement in developing and supporting research in this field. Knowledge suggesting the relevance of space-based research on such materials may increase advocacy both within and outside NASA. Indeed, there are two major reasons why NLO research could be of considerable importance to NASA. One is in optical communications, where NLO devices may be used in laser communications satellites deployed in space. The other area is in microgravity science where basic research into the mechanical and optical properties of organic and polymeric NLO materials could benefit from removal of the gravitational force. There is also the potential that microgravity studies of these materials could enable their properties to be significantly optimized. Eventually, microgravity processing of NLO materials may lead to devices with superior properties to those currently produced on Earth.

One current area of laser technology has its roots in the early space experiment success involving the growth of monodisperse latex. Sensitive, closely controlled polymerizations, in a solid-liquid matrix often are adversely affected by particle collisions due to sedimentation and stirring. Stirring, during ground-based polymerizations, is necessary in order to maintain suspensions. However, agitation from stirring can cause violent particle-particle collisions resulting in flocculation and coagulation. These phenomena are major obstacles during the seeded emulsion polymerization of polystyrene latex microspheres. It was shown by Vanderhoff through orbital flight experiments that populations of nearly monodisperse (less than 1% variation) large latex microspheres (up to 30-μm–size range) could be formed by low-gravity processing of smaller-size seed latexes.[2] The size distributions of the microspheres grown in microgravity were sufficiently monodisperse and well characterized for acceptance by the National Institute of Standards and Technology as 10-μm and 30-μm standard reference materials. Although this high degree of monodispersity for smaller-sized latex spheres is currently achievable by Earth-based processing, as sizes approach 100-μm diameter, required radius variation and degree of monodispersity are most accessible by microgravity processing. The space-grown microspheres are useful as practical calibration standards for electron microscopy and x-ray diffraction analysis. They are also useful for testing the efficacy of separation techniques such as electrophoresis and electro-osmosis.[3] These early experiments were not aimed at exposing the underlying scientific details of polymer microsphere formation in reduced gravity, but were more applied in their nature, and guided primarily by empirical developments. Since those early developments, however, proposed research in this area promises advancement in laser technology.

Spherical dye lasers depend on individual spherical resonant cavities up to 5 mm diameter, with a maximum radius variation of 0.002%. Electromagnetic-wave resonance in these cavities is analagous to whispering-gallery acoustics. Additionally, 40-60-μm diameter, relatively monodisperse, dye-in-solution liquid droplets have shown whispering-gallery-mode resonances. The frequency at which the lasing action of these spheres takes place is highly dependent on their radii.[4] The geometry of the spherical laser eliminates the need for the traditional external optical cavity. The laser beam is contained in the sphere and amplified by total internal reflections at the boundary of the sphere.[5] Ground-based feasibility studies on dye-in-polymer matrix spheres demonstrate that dyes that exhibit lasing action can be incorporated into the spheres by diffusion, entrapment during polymerization, or by covalent bonding. These types of lasers could find application in optical computing, point light sources for use in holography and spectroscopy, or laser gyroscopes.

Polymer thin films with fewer defects and more uniform thickness, which would provide superior optical devices, might be prepared by electrochemical polymerization in microgravity due to the elimination of solutal convection. This is indicated by the work of Owen[6] and Riley et al.[7] who used the laser shadowgraph/schlieren technique to observe the concentration gradients in a 1 molar $CoSO_4$ cell during electrodeposition experiments on a KC-135 aircraft in parabolic flight. At identical times into the electrodeposition experiments, comparisons were made of the ground-based and 10^{-2} g processes. Shadowgraphs showed the absence of "plumes" at the electrode surface in low gravity. The feasibility of using electrochemical polymerization to prepare third-order nonlinear optical (NLO) polymer thin films for use in devices was demonstrated by Dorsinville et al.[8] These researchers used this process to prepare films of polythiophene and a homologous series of thiophene-based polymers that had $\chi^{(3)}$ values that are among the largest and fastest for polymers. The maximum measured value for the series was 11×10^{-9} esu at 532 nm which is comparable to measured values obtained for polydiacetylenes.[9]

Organic thin films of phthalocyanines prepared by vapor deposition processes are excellent candidates for the development of nonlinear optical devices because these materials have two-dimensional planar π-conjugated system and excellent stability against heat, chemicals, and photo-irradiation. Ho et al.[10] grew thin films of chloro-gallium (GaPc-Cl) and fluoro-aluminum (AlPc-F) phthalocyanines by vapor deposition onto fused silica optical flats at 150 °C and 10^{-6} Torr. The thickness of the GaPc-Cl and AlPc-F were 1.2 and 0.8 microns and the values for $\chi^{(3)}$ were 5×10^{-11} and 2.5×10^{-11} esu, respectively.

The research of Debe et al.[11-13] indicates that better quality thin films for use in NLO devices might be obtained by closed cell physical vapor transport (PVT) in microgravity. In the PVT process, the source material is sublimed in an inert gas and allowed to convect or diffuse down a thermal gradient and to ultimately condense at a crystal or thin film growth interface.[11] The advantage of thin film growth in microgravity is that it provides the opportunity to eliminate buoyancy-driven convection. Debe reported the results of experiments in which copper phthalocyanine (CuPc) were epitaxially deposited onto highly oriented seed films of metal free phthalocyanine (H_2Pc) contained on a 1.4 cm diameter solid copper disc. Analysis involving the use of external reflection-absorption infrared (IR) spectroscopy, grazing incidence x-ray diffraction, and visible near IR reflection-absorption spectroscopy reveal that the microgravity-grown films are more highly uniaxially oriented than Earth-grown films, and consisted prominently of crystalline domains of a previously unknown polymorphic form of CuPc.[12] In addition, scanning electron microscopy analysis revealed that there was a distinctly different microstructure in the center of the space-grown films and that the circular perimeters of the microgravity-grown films had a microstructure much like that of the ground-control films.[13]

Polymeric materials show great potential for NLO applications because they offer unique flexibility in terms of their chemical, mechanical, and optical properties. One particularly interesting class of compounds is polydiacetylenes, which are both crystalline and polymeric.[14] Because of their highly conjugated electronic structures, polydiacetylenes are among the best nonlinear optical materials known. They also have the advantage of being readily formed as thin films, which is very useful for device fabrication. The optical quality (hence, performance in a device) of a polydiacetylene depends critically on the crystal quality and orientation of the monomer film from which it is obtained. Like the phthalocyanines, polydiacetylenes could benefit from microgravity deposition by physical vapor transport.

Solution crystal growth has been performed repeatedly in microgravity, particularly within the protein crystal growth program. Many organics, also good NLO materials, are amenable to solution growth and are ideal candidates for studies of the kinetics and fluid dynamics of solution growth processes. Knowledge of such processes can lead to significant improvement in crystals grown in space or on Earth. A ground-based investigation involving several tasks has been undertaken to grow bulk single crystals of important materials, such as, L-arginine phosphate (LAP) and several diacetylenes. This study will allow an assessment of the coupled effect of gravity-driven convective flows, supersaturation, and temperature on growth kinetics. An investigation is underway on solution growth of polydiacetylene thin films. Preliminary experiments indicate potential for producing thin films that could possess the required optical quality for NLO devices. There is certainly evidence that microgravity could play a role in this case. It has been demonstrated that in some cases microgravity has an effect on solution growth of macromolecular crystals, e.g., protein crystals, as well as on solution polymerization processes.

Organics have many features that make them desirable for use in optoelectronic devices such as high second and third order nonlinearities, flexibility of molecular design, and high damage resistance to optical radiation. However, their use in devices has been hindered by the fragility of organic single crystals which makes processing difficult. Azor et al.[15] improved the strength of organics by growing thin film composites of aligned crystals of m-nitroaniline (mNA) in poly(methyl methacrylate) (PMMA). The growth method was based on the temperature-gradient zone-melting (TGZM) method.[16,17] The apparatus consisted of two aluminum blocks separated by a 1 mm thermally insulating layer. One block was heated and the other cooled to create a sharp gradient. Meta-nitroaniline (mNA) crystals were aligned in the PMMA host by drawing the sample holder, which consisted of thin films of PMMA/mNA between two glass slides, slowly across the blocks at a predetermined rate. Bulk composites of aligned NLO organic crystals in low molecular weight transparent polymers having improved mechanical strength and fewer defects might be prepared by growing these composite materials in microgravity using a Bridgman apparatus.

Finally, fundamental studies ranging from determination of morphologies of particles of single polymer molecules, their interplay in amorphous and semicrystalline bulk polymers, and the effect of nonuniform stress distribution on extrusion of long structural components of a crystallizable polymer could benefit from studies in a microgravity environment. Normally, individual molecules feel little effect due to gravity. However, assuming a 10% density difference with the solvent, stratification begins to occur for particles or aggregates of molecular weight 10^8 amu or more in the absence of convection. Aggregates of this size are common in polymer processes and separations. In fact, a single polymer molecule can have a weight on this order. Microgravity, therefore, may be useful to reduce stratification in these processes to investigate both stratification effects and phenomena that are obscured by stratification. In fact, a low acceleration centrifuge on orbit could provide information on the effects of stratification at intermediate acceleration levels. Further, polymerization often results in the formation of a polymer which is insoluble in the reactant solution. This greatly hampers the possibilities of producing a polymer of high molecular weight. The near convectionless conditions in microgravity might allow the processing and study of such polymerizations since aggregation in this environment should be much slower.

This document is a collection of ideas and research relevant to microgravity processing of organic and polymeric materials by a cross section of scientists in the discipline. Contributions include an extended abstract by the authors and a transcription of their presentations to the Organic and Polymeric Materials Workshop convened in Huntsville, Alabama, on April 27, 1993.

Although Drs. Seth Marder and Joe Perry were involved in the initial planning of the workshop, they were unable to attend. However, they presented a seminar in Huntsville at the Marshall Space Flight Center within 2 weeks following the workshop. Thus, the format of their input deviates from the format of the other workshop contributors.

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D. O. Frazier
C. E. Moore
B. H. Cardelino

II. EXTENDED ABSTRACTS

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ORDERED ORGANIC THIN FILMS SELF-ASSEMBLED FROM THE VAPOR PHASE

M. K. Debe
Science Research Laboratory, 3M Company
201-2N-19, 3M Center
St. Paul, MN 55144

The physical and chemical properties of organic and polymeric thin films are quite possibly more dependent on a film's physical structure characteristics than bulk properties are on bulk structure. As with bulk properties, the dimensional scales over which variations in physical structure can be important span the range of Angstroms to tens of microns. However, the variety of microstructural forms obtainable in thin films exceeds those in bulk materials, and are very dependent on the processing methods and conditions. An obvious characteristic of a two-dimensional film is the extent to which its basic structural units are uniaxially ordered with respect to the film plane.

Organic films self-assembled from a liquid phase, as in Langmuir-Blodgett or adsorption from solution, have received much attention in the past decade as techniques to achieve highly oriented-ordered polymeric thin films. Many organic compounds including some of the same fatty acids, have been vapor deposited as well. However, organic pigments and dyes comprise a major class of important materials which have very low solubilities yet excellent thermal stabilities, making them ideally suited for film deposition from the vapor phase. Surprisingly, such molecular systems exhibit a significant propensity to self order, a high sensitivity to deposition parameters, and a range of microstructural forms that cannot be duplicated by the less energetic mechanisms associated with solution adsorption processes.

Molecular solids such as heterocyclic polynuclear aromatics are excellent candidates for film formation by vacuum deposition means. Over the past decade, our work and that of others investigating a wide variety of perylene and phthalocyanine derivatives have identified five deposition parameters that can significantly affect film morphology, physical microstructure, and type and extent of ordering developed in vacuum and vapor transport grown films. These parameters are substrate temperature, deposition rate, substrate chemistry and epitaxy, ambient gas convective flows, and post deposition annealing. In this presentation we present examples of how each of these conditions manifest themselves in the film structure and ordering, most frequently revealed by scanning electron microscopy, reflection absorption infrared spectroscopy (RAIR), and grazing incidence x-ray diffraction (GIX).[1]

As a first example, vapor deposited para-chlorophenylurea films as thick as one micron show GIX diffraction patterns indicative of the longest range ordering we have seen.[2] Films deposited on glass substrates display eight strong diffraction (001) orders (figure 1). RAIR spectra imply the degree of order varies with film thickness, maximizing at 300 Å with as much as 90% of the molecules oriented with the **c*** axis of the unit cell perpendicular to the substrate.

By far, most of the data on sensitivity of self ordering to deposition conditions has been acquired with perylene and phthalocyanine derived compounds. Considering substrate temperature

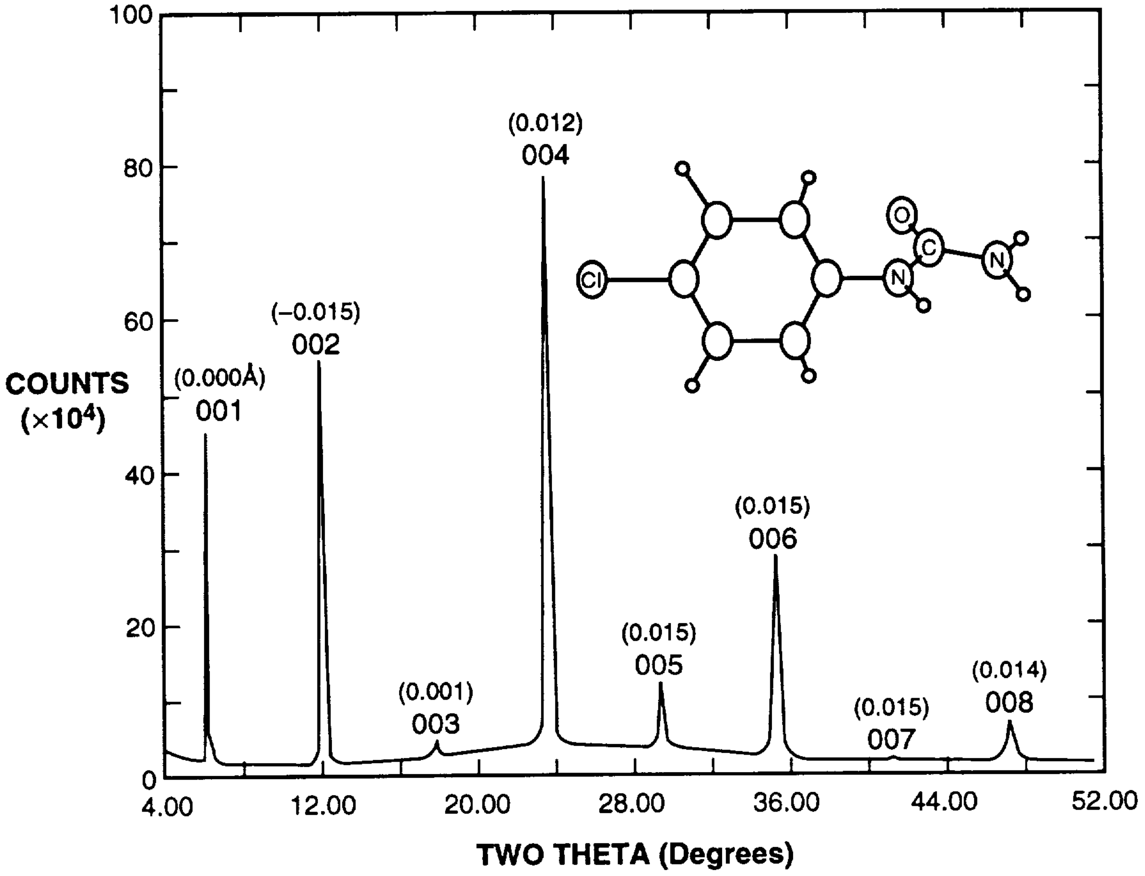

Figure 1.

effects first, two materials, phenethyl and 3,5,xylyl dicarboximide perylenes (RED), show a wide range of film morphologies over a relatively narrow substrate temperature range.[3,4] In addition, a critical temperature is indicated by variation of various optical properties. The existence of a critical substrate temperature is even more dramatically revealed in vacuum deposited films of metal free (H_2Pc).[5] Within a narrow few °C range about a substrate temperature of T_c = 5 °C, both of these molecules form smooth, highly (95%) uniaxially ordered films characterized by a molecular packing **b**-axis oriented 26.5° from the surface normal direction.

The effect of deposition rate on film ordering is clearly illustrated by the behavior of vanadyl phthalocyanine (VOPc). Both GIX and visible absorption spectra show a discontinuity in ordered film growth at a deposition rate between 1.7 and 2.4 μm/cm²-min. Even more striking is the combined effect of substrate temperature and rate on "reversing" the packing arrangement of CuPc and H_2Pc systems. At 70 °Cand rates ~500 Å/min, the **b**-axis is oriented parallel to the substrate instead of nearly normal to it as noted above occurs at $T_{sub} = T_c$.[6] The oppositely oriented films display significantly distinct optical constant spectra as revealed by variable angle spectroscopic ellipsometry.[7,8]

Substrate chemistry and epitaxial control of the ordering in subsequently deposited films has also been shown. The first few molecular layers of a perylene dicarboximide deposited on an oxide surface are highly oriented with the molecular planes perpendicular to the surface,[9] due presumably to hydrogen bonding between the RED molecules' carbonyls and surface oxide hydroxyls. The ordering decays as the film thickness increases. Even more interesting is the use of a first ordered seed layer of H_2Pc (deposited at T_c) to isoepitaxially control the orientation of a CuPc layer. The seed layer will force the CuPc to molecules to stack at the same temperature in a direction orthogonal to their usual direction when deposited on a noncrystalline substrate.[6]

An important part of any model attempting to understand these effects is that of high surface mobility of the top layer of adsorbed molecules during film deposition. This derives from weak molecule-molecule interactions characteristic of van der Waals solids, which also encourages a diversity of crystalline polymorphs with closely related packing structures and energies. Perhaps the most amazing evidence of high surface mobility is the unique film structure formed when a thin (~1000 Å) film of the RED perylene derivative, deposited at room temperature, is annealed in vacuum at temperatures over ~200 °C. An initially smooth film converts in minutes by growth about screw dislocations, to a dense array of discrete single crystalline whiskers oriented perpendicular to the surface, each uniform in size and shape, ~1 μ tall and ~500 Å in cross section.

The preceding examples of how deposition parameters influence the self-ordering of organic molecules have all been done in sufficient vacuum that no gas phase collisions occurred. Physical vapor transport (PVT) of RED and CuPc through low pressure (0.1-10 Torr) inert buffer gases has also been studied, both in the laboratory at 1 g and in the microgravity environment of the Space Shuttle Orbiter aboard flights STS–20 and STS–51.[10-12] The complex process of film growth now includes not only the direct effects of the ambient phase impinging directly on the film growth interface, but also the transport phenomena of diffusion and convection. The experiments show clearly that the type of "inert" buffer gas and pressure affect the film structure, and, in fact, a new polymorphic crystal form (the ninth known) of CuPc (M-CuPc) was discovered to result by PVT. More interesting, however, detailed comparison of the μg and unit-g results shows significant differences in film physical structure spanning seven orders of magnitude range of scale. CuPc films grown by PVT in the absence of buoyancy-driven convection are denser and smoother on a 1-10 μm scale. They show a higher fraction of molecules uniaxially oriented in a common direction and replicate the orientation of a seed film better than 1 g grown films. The μg-grown films consist primarily of the new M-CuPc polymorph, whereas the 1 g films are mixed.

In conclusion, organic molecules deposited from the vapor phase can form highly ordered thin films exhibiting a diversity of physical micro- and nano-structures having high sensitivity to deposition conditions (figure 2). These small scale physical structures strongly determine the film macroscopic properties. The not so subtle and surprising effects of buoyancy-driven convection on the physical structure of PVT deposited films, occurring even at the molecular packing level, is not understood.

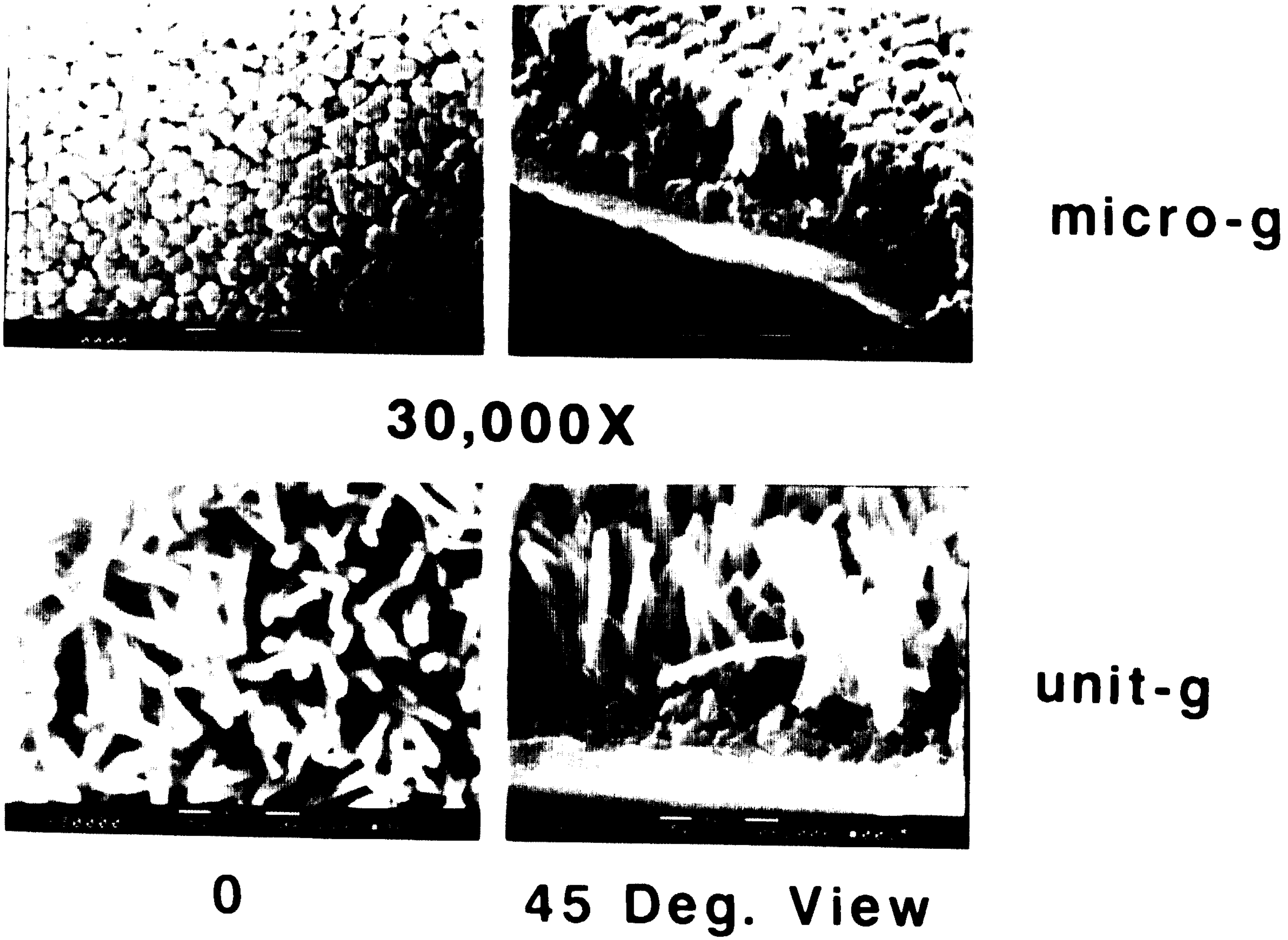

Figure 2. This figure compares scanning electron micrographs of 1-µm thick films of copper phthalocyanine deposited by physical vapor transport in the 3M PVTOS flight (STS–20) and ground control experiments. In microgravity the film's microstructure is very dense compared to that produced in unit gravity in the presence of convection. This difference in microstructure has a significant affect on the macroscopic film optical properties.

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Extended Abstract N94-24340

NUMERICAL MODELING OF PHYSICAL VAPOR TRANSPORT UNDER MICROGRAVITY CONDITIONS: EFFECT OF THERMAL CREEP AND STRESS

Daniel W. Mackowski and Roy W. Knight
Department of Mechanical Engineering
Auburn University, AL 36849

One of the most promising applications of microgravity (μg) environments is the manufacture of exotic and high-quality crystals in closed cylindrical ampoules using physical vapor transport (PVT) processes. The quality enhancements are believed to be due to the absence of buoyant convection in the weightless environment—resulting in diffusion-limited transport of the vapor. In a typical experiment, solid-phase sample material is initially contained at one end of the ampoule. The sample is made to sublime into the vapor phase and deposit onto the opposite end by maintaining the source at an elevated temperature with respect to the deposit.

Identification of the physical factors governing both the rates and uniformity of crystal growth, and the optimization of the μg technology, will require an accurate modeling of the vapor transport within the ampoule. Previous μg modeling efforts have approached the problem from a "classical" convective/diffusion formulation, in which convection is driven by the action of buoyancy on thermal and solutal density differences.[1-3] The general conclusion of these works have been that in low gravity environments the effect of buoyancy on vapor transport is negligible, and vapor transport occurs in a diffusion-limited mode. However, it has been recently recognized than in the non-isothermal (and often low total pressure) conditions encountered in ampoules, the commonly-assumed no-slip boundary condition to the differential equations governing fluid motion can be grossly unrepresentative of the actual situation.[4,5] Specifically, the temperature gradients can give rise to *thermal creep* flows at the ampoule side walls. In addition, temperature gradients in the vapor itself can, through the action of *thermal stress*, lead to bulk fluid convection.

Thermal creep is the slip-flow of gas over a surface induced by a temperature gradient in the gas tangential to the surface. The phenomenon can be explained from simple kinetic theory arguments.[6] The velocities of molecules striking the surface will be higher for molecules originating from the hotter regions of the gas than those originating from the cooler regions. The reflection of the molecules from the surface, on the other hand, will be diffuse (i.e., independent of direction) for practically all surface materials. As a consequence, there will be a net tangential momentum transfer to the surface from the molecules. To compensate for the uneven momentum transfer, the surface "pushes" against the gas, creating a slip flow over the surface directed toward the hotter gas. From the viewpoint of a continuum flow regime, the creep velocity can be phenomenologically related to the tangential temperature gradient of the wall by[6,7]

$$v_{TC} = \frac{c_s \nu}{T} \frac{\partial T_w}{\partial x}, \qquad (1)$$

where c_s is the coefficient of thermal slip (≈ 1.1 for diffusely-reflecting surfaces[7]), and ν is the kinematic viscosity of the gas. It should be emphasized that thermal creep, unlike the often-associated phenomena of temperature-jump and viscous-slip, is a continuum-flow phenomenon;

that is, it is not confined only to rarefied flow regimes or to length scales on the order of the mean-free-path of the gas molecules.

Thermal creep is well known to aerosol scientists as the driving force behind the small particle transport mechanisms of thermophoresis and photophoresis.[7,8] When length scales larger than the few μm associated with aerosol particles are considered, thermal creep has been justifiably neglected in comparison to the buoyancy-induced flow in analyses of heat and mass transfer. Indeed, Equation (1) indicates that the creep velocity does "creep" along—in that a considerable temperature gradient is required to set up a moderate velocity under standard temperature and pressure conditions (e.g., $\sim 10^3$ K/cm for $V_{TC} \sim 1$ cm/s in air).

However, in μg crystal growth processes a small convective flow could still have an appreciable effect on growth rates. From an order-of-magnitude analysis, the characteristic flow velocity arising from thermal creep in a closed ampoule will be[4,5]

$$V_{TC} \sim \frac{\nu}{L} \frac{\Delta T}{T}, \tag{2}$$

where L is the length of the ampoule, T is the average temperature, and ΔT is the temperature difference across the end faces. Rosner[4] reported that the temperature gradients and low pressures associated with copper phthalocyanine PVT experiments are sufficient to lead to creep-induced bulk flows on the order of centimeters per second—which is on the same order as the diffusion velocity of the vapor. His conclusions were supported by an analysis of combined thermal creep and free convection in the limit of vanishing gravity by Vedha-Nayagam and Mackowski.[9]

In a closed ampoule thermal creep would produce a recirculating flow, with vapor "pumped" along the side walls toward the source (hot) end, and returning to the crystal (cold) end along the center. In this sense, the phenomenon would be analogous to flows at gas-liquid interfaces produced by surface-tension gradients. As is the case with buoyancy-induced convection, the creep-induced convection would act to increase the mass transfer rate from the source to the crystal. In addition, the recirculating flow would result in radial concentration gradients at the crystal surface, and could thus lead to non-uniformity in the crystal growth rates—which would be analogous to the effects arising from carrier gas recirculation.[1]

An accurate modeling of vapor transport in the ampoule would require inclusion of the thermal creep effects in the boundary conditions of the differential equations for fluid motion. The modeling would also require a consistent level of accuracy in the formulation of the constituitive laws governing mass, momentum, and energy transfer. Here again, temperature gradients could play an important role in the transport of vapor species.

Under the high ΔT and low P conditions of certain ampoules, the accuracy of the fluid stress constituitive laws employed in the Navier-Stokes equations will require reexamination. Specifically, temperature gradients can result in a *thermal stress* in the gas and lead to a bulk convective motion. Thermal stress is a feature of the Burnett contributions to the stress tensor, which constitute the second-order approximation to the Boltzmann equation at small Knudsen number.[10] The total stress tensor appearing in the fluid momentum equation would be the sum of the thermal stress tensor and the familiar Newton-Stokes fluid stress-fluid deformation tensor. In a manner qualitatively similar to natural convection, thermal stress would result in a coupling of the momentum and energy equations.

In most "normal" flow situation (such as natural or forced convection), the contribution of thermal stress to the stress tensor is quite negligible compared to stress arising from fluid deformation. However, it has been shown by Kogan[11] and Napolitano et al.[5] that in slow-moving, non-isothermal flows in the continuum regime ($Kn \sim 0$), thermal stress can have a significant effect on the overall motion of the fluid. From an order-of-magnitude analysis, the convective velocity arising from thermal stress will be on the order of[5]

$$V_{TC} \sim \frac{\nu}{L}\left(\frac{\Delta T}{T}\right)^3 . \tag{3}$$

Although the thermal stress velocity is expected to be smaller than the thermal creep velocity for most µg PVT experiments, it can still be of sufficient magnitude to warrant the inclusion of thermal stress in the fluid momentum equations. Estimation of the effects of thermal stress upon the flow field within an ampoule is not as straightforward as is the case for thermal creep. However, numerical predictions of gas motion in closed, non-uniformly heated containers[11] suggest that thermal stress would produce a recirculating flow in a direction opposite to that produced by thermal creep—that is, flow would be driven from the hot to cold ends along the side walls, and return along the axis. The flow field within an ampoule under the combined effects of thermal creep and stress could thus be quite complicated.

It is not surprising that thermal creep and stress have not been considered, or even recognized, in detailed modeling of PVT in µg environments. Previous modeling efforts have been built upon the governing equations and boundary conditions applicable to "normal," Earth-bound conditions—for which thermal creep and stress are truly higher-order effects. Under buoyancy-free conditions, however, both of these effects could contribute significantly to the vapor transport process. Considering that the ostensible purpose of the µg environment in PVT is to obtain diffusion-limited transport, it is important that all sources of convection be represented in numerical modeling schemes.

To address the above issues, we are initiating a numerical investigation of vapor transport in cylindrical ampoules under µg, non-isothermal conditions. The goal of the research is to identify the effects of thermal creep and stress on the rates and uniformity of vapor transport. The investigation will adopt the steady-state, two-dimensional, binary PVT system that has been extensively investigated by Rosenberger and his co-workers[1-3] The model parameters used in the computation will be chosen to be representative of realistic substances and conditions encountered in ongoing experiments. In particular, calculations will be performed using sample/carrier systems of both comparable and highly disparate molecular weights, total pressures from a few torr to atmospheric, and $\Delta T/T$ values from 0.01 up to unity. Although the focus of the research is on µg environments, the effect of creep and stress on buoyancy-driven convection under normal gravity will also be examined. Due to the inclusion of thermal stress into the momentum equation, numerical solution of the equations cannot rely on Navier-Stokes based codes used in previous PVT diffusive-convective modeling.[1-3] Rather, the system of governing equations will be solved by adapting a finite difference method of the type used for simulating flows of variable density Newtonian fluids. Existing methods of this type include the explicit-implicit predictor-corrector algorithm of MacCormack.[12] The appearance of the thermal stress term in the stress tensor could result in a strong link between the momentum equations and energy equation, analogous to the linking seen in buoyancy-driven free-convection problems. This linking could result in a need for modification of the existing stability requirements for the chosen numerical method.

The numerical calculations will be designed to determine the relevant parameters (temperature differences, total pressures, ampoule aspect ratios, gravity levels, etc.) at which thermal creep and/or stress become of sufficient magnitude to compete with Fickian diffusion and buoyant convection vapor transport. For conditions where the thermal mechanisms are found to be significant, the resulting effects on overall mass transfer and mass flux uniformity at the deposit will be delineated. In addition, the feasibility of reducing creep-induced convective flows through manipulation of the side wall temperature will be investigated.

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Extended Abstract

ELECTRIC FIELD-MEDIATED PROCESSING OF POLYMER BLEND SOLUTIONS

G. E. Wnek and S. Krause
Department of Chemistry
Polymer Science and Engineering Program, Rensselaer Polytechnic Institute
Troy, NY 12180-3590

Multiphase polymer blends in which the minor phases are oriented in a desired direction may demonstrate unique optical, electrical and mechanical properties. While morphology development in shear fields has been studied extensively, little work has focused on effects of electric fields on phase structure. We have explored the use of electric fields for blend morphology modulation with particular attention given to solventcasting of blends in d.c. fields. Both homopolymer blends (average phase sizes of several microns) and diblock copolymer/homopolymer blends (average phase sizes of hundreds of Angstroms) have been investigated. Summarized here are important observations and conclusions.

Much of our work has focused on the system poly(ethylene oxide)/poly(styrene) or PEO/PS. The ability of PEO to dissolve salts is attractive because it offers the opportunity to modify the dielectric constant of the that phase relative to that of the matrix, although no salt was added to the PEO in the experiments described here. PEO/PS films (10 wt% PEO) were cast from cyclohexanone between evaporated metal film electrodes on glass (spacing ca. 2 mm) in applied fields ranging from 3 to 12 kV/cm. The polymer films exhibited several unique morphological arrangements depending upon the molecular weights of the blend components and the applied field strength.[1,2] For example, blends of PS with PEO of 10,000 g/mol showed a pearl-chain morphology (figure 1) when cast at 10 kV/cm where spherical PEO phases (~5-10 μm diameter) in a PS matrix were assembled into chains which were oriented in the direction of the applied electric field. At the same field and composition, blends with higher molecular weight PEO (100,000 g/mol) showed deformation of the PEO phases into columnar structures which were oriented in the field direction. Observation of the solutions containing the lower MW PEO under an optical microscope revealed that during solvent evaporation in an electric field, spherical PEO phases initially elongated and then broke up to form smaller spherical phases. Subsequently, these smaller spherical phases formed chains.[3] It may be that the elongated PEO domains break up due to a Rayleigh instability which becomes more important as the interfacial tension increases as solvent evaporates. We believe that the columnar structures observed with the higher MW PEO blends could be the result of kinetic stabilization of the columns toward breakup due to the higher viscosity of the PEO phases.

Similar morphologies, but with smaller phase sizes (~1-3 μm), were observed with samples containing up to about 2 wt% of a PEO-b-PS diblock copolymer.[3] Here the PEO MW was about 10,000 g/mol. However, samples containing about 5 wt% diblock copolymer exhibited elongated, column-like structures which were observed with their long axes in the field direction. We suggest that the diblock copolymer lowers the interfacial tension and keeps it low even as solvent evaporates. A composition of ca. 5 wt% diblock thus stabilizes the elongated PEO phases which would otherwise break up as the solvent evaporated.

In a different set of experiments, solution-cast films of binary blends of PS and PS-b-PEO produced microphase-separated spherical domains (~300 Å). Depending upon the applied field strength, these domains were observed to cluster (ca. 2 kV/cm), form islands elongated in the field direction (ca. 4 kV/cm) and finally form cylinders (8 kV/cm) in the field direction (figure 2). It is suggested that this apparent sphere-to-cylinder transition is driven by an increase in the local concentration of diblock copolymer caused by aggregation in the electric field.[4]

We note that several other polymer pairs exhibit interesting and novel morphologies when cast in an electric field.[5] These include poly(methyl-methacrylate)/PS, poly(vinyl acetate)/PS, and poly(otoluidine)/PS. In the case of poly(butadiene)/PS, where the dielectric constants are quite similar, no morphology differences were observed between samples cast in the presence and absence of an electric field. We are presently preparing polymers of relatively high dielectric constants (> ca. 8-10) to allow morphology manipultion in blends at significantly lower applied fields. The magnitudes of interfacial tensions are also important in determining the extent of phase shape modulation, and interfacial tensions are now being measured in our laboratory. We are working on the development of ion-containing, multiphase polymer systems[6] which are of emerging interest as transducers and "smart" polymers and where homogeneous dispersions of a minor phase in a matrix are very important. Microgravity may be useful in avoiding the formation of spatially heterogeneous blends which result from settling of the denser polymer phase. In addition, microgravity may prove to be important in delineating key issues of polymer phase separation which might be masked in normal gravity.

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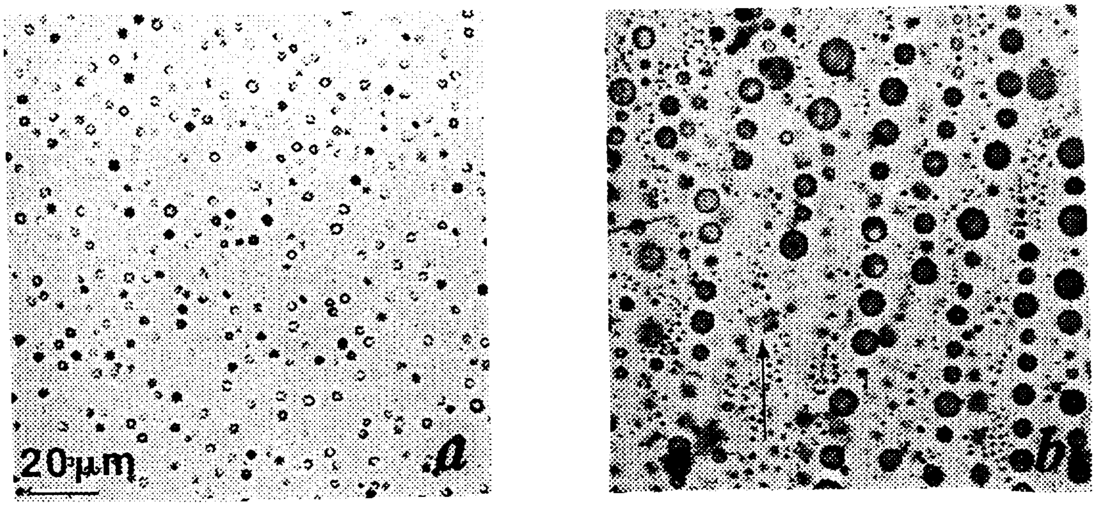


Figure 1. (a) PEO/PS blend cast from cyclohexanone in the absence of a field. (b) similar blend cast in a field of 3 kV/cm. Arrow indicates field direction.

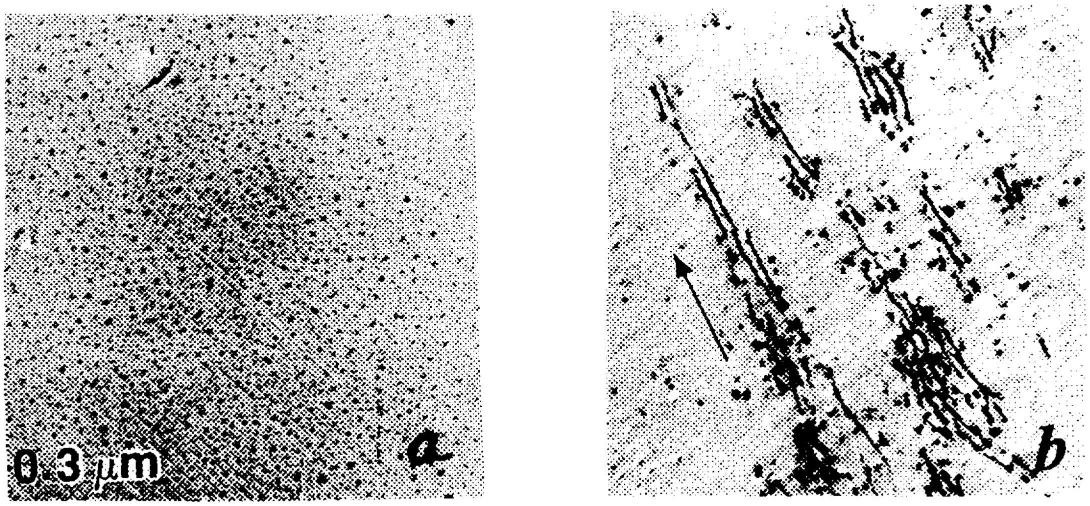


Figure 2. (a) PEO-PS diblock/PS homopolymer blend cast from 85% toluene, 10% THF, 5% methanol mixture in the absence of an electric field. A similar blend cast at 8 kV/cm. Arrow indicates field direction.

Extended Abstract

DEFECTS IN ELECTRO-OPTICALLY ACTIVE POLYMER SOLIDS

David C. Martin
Materials Science and Engineering
The University of Michigan
2022 H. H. Dow Building
Ann Arbor, MI 48109-2136

1. Introduction

There is considerable current interest in the application of organic and polymeric materials for electronic and photonic devices (Prasad and Williams, 1991). The rapid, non-linear optical (NLO) response of these materials makes them attractive candidates for waveguides, interferometers, and frequency doublers. In order to realize the full potential of these systems, it is necessary to develop processing schemes which can fabricate these molecules into ordered arrangements. There is enormous potential for introducing well-defined, local variations in microstructure to control the photonic properties of organic materials by rational "defect engineering." This effort may eventually become as technologically important as the manipulation of the electronic structure of solid-state silicon based devices is at present.

The success of this endeavor will require complimentary efforts in the synthesis, processing, and characterization of new materials. Detailed information about local microstructure will be necessary to understand the influence of symmetry breaking of the solid phases near point, line, and planar defects. In metallic and inorganic polycrystalline materials, defects play an important role in modifying macroscopic properties. To understand the influence of particular defects on the properties of materials, it has proven useful to isolate the defect by creating bicrystals between two-component single crystals. In this way the geometry of a grain boundary defect and its effect on macroscopic properties can be determined unambiguously. For example, the discovery of superconductivity at high temperatures in copper oxides has renewed interest in the effect of grain boundaries on transport behavior. Figure 1 shows a plot of the critical current Jc for a superconductive bicrystal of a 1-2-3 $YBa_2Cu_3O_7$ copper oxide compound as a function of the tilt or twist misorientation angle between the crystals (Dimos et a., 1990). Note that the value of the critical current drops markedly as the angle of misorientation between the crystals increases.

In crystalline polymers it would be valuable to establish a similar depth of understanding about the relationship between defect structure and macroscopic properties. Conventionally processed crystalline polymers have small crystallites (10-20 nm), which implies a large defect density in the solid state. Although this means that defects may play an important or even dominant role in crystalline or liquid crystalline polymer systems, it also makes it difficult to isolate the effect of a particular boundary on a macroscopically observed property. However, the development of solid-state and thin-film polymerization mechanisms have facilitated the synthesis of highly organized and ordered polymers. These systems provide a unique opportunity to isolate and investigate in detail the structure of covalently bonded solids near defects and the effect of these defects on the properties of the material. The study of defects in solid polymers has been the subject of a recent review (Martin, 1993).

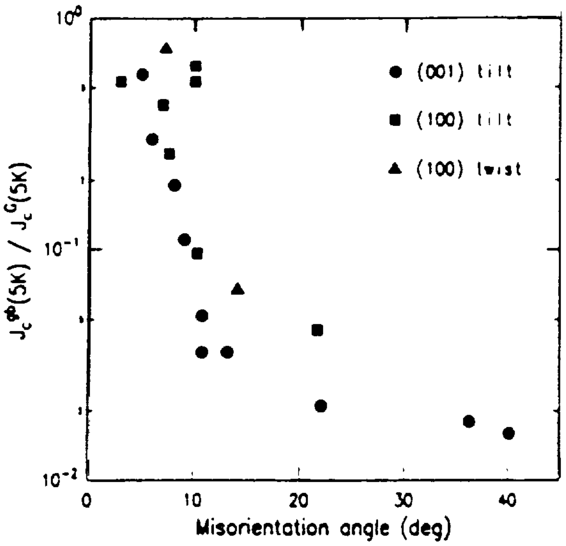


Figure 1. Critical current Jc as a function of misorientation angle between grain in bicrystals of the high temperature superconductor $YBa_2Cu_3O_7$ (Dimos et al., 1990). There is a dramatic drop in Jc as the amount of tilt or twist between the crystals increases.

A limitation with defect studies in polymers has been the difficulty in studying polymer microstructures at the high resolution normally acheived in inorganic materials systems (0.2-1.0 nm) However, the careful application of low dose procedures has made High Resolution Electron Microscopy (HREM) feasible for certain polymers (Martin and Thomas, 1987). These efforts are most successful when applied to electron beam resistant polymers which usually have highly conjugated or aromatic backbones. HREM studies have now made it possible to directly image defects such as dislocations and grain boundaries in polymer solids. Other studies include the local nature of deformation in rigid-rod polymers (Martin and Thomas, 1989), as well as the evolution of solid-state crystallization in thin films of poly(imides) (Martin et al., 1990).

In the following section (2) we briefly review the current understanding of the role of grain boundaries in determining the properties of solid polymers. Then, we discuss in section 3 important aspects of poly(diacetylenes) (PDAs), polymers which can be polymerized in the solid-state from crystals of the precursor monomer. PDAs can also be prepared in thin films using Langmuir-Blodgett techniques. In section 4 we discuss our experiments which consist of examining structure-property relationships in PDA thin films and crystals. We describe procedures for growing crystals of diacetylene monomers, joining these together to make a grain boundary, and then polymerizing through the grain boundary. With this approach it is possible to prepare "polymer bicrystals." We then describe the experimental protocol for measuring the photoconductive response of these bicrystals. We also outline experiments for structural characterization involving x-ray scattering and Transmission Electron Microscopy (TEM). In section 5 we present an analysis which illustrates how our studies will provide fresh insight about the details of grain boundary structure in these materials. In particular, we develop a theoretical model which predicts that measuring physical properties as a function of misorientation angle between the crystals should give information about the dislocation structure of the grain boundary.

2. Grain Boundaries in Polymers

Although the study of grain boundary structure and properties is well established in atomistic solids, a similar sophistication of understanding has yet to be realized for solid macromolecules. Recently, a geometrical scheme for categorizing grain boundaries in polymer solids in terms of the orientation of the molecules and the orientation of the grain boundary was presented (Martin and Thomas, 1990). This work was inspired by HREM studies of the rigid-rod polymers poly(paraphenylene benzobisthiazole) PBZT and poly(paraphenylene benzobisoxazole) (PBZO). Sutton and Balluffi (1989) have shown that geometrical considerations are of limited value in determining the energetics of grain boundaries in crystals of atoms and small molecules. However, the strongly anisotropic bonding in polymer crystals may make geometrical concerns more useful.

Based on the orientation of the chains and the grain boundary plane, it is possible to consider four unique classes of grain boundaries in polymers (figure 2). Martin and Thomas (1990) discussed the general features of the structure, energetics, and mobility of these different classes of boundaries in extended-chain polymers. Although these qualitative ideas about grain boundary geometry and energetics are useful, the influence of specific types of grain boundaries on the properties of the bulk polymer solid remain to be firmly established. Also, it would be useful to establish a more quantitative description of the grain boundary microstructure.

One of the problems in understanding the relationship between grain boundary structure and properties in polymers is that the typically small crystallite size (10-20 nm) means the global grain boundary concentration is so high it is not possible to isolate the effect of a particular boundary. Also, high resolution structural studies of defects in polymer solids have proven problematic because of the sensitivity of organic materials to the electron doses typically used in high resolution imaging. In order to isolate the characteristics of a single grain boundary, it is necessary to grow large, perfect polymer bicrystals, which would then have large, well-defined grain boundary structures. In this way, the specific influence of a particular grain boundary defect on the properties of the polymer solid can be isolated and unambiguously determined. It is also important to consider systems in which high resolution structural studies will be appropriate, so that structure-property relationships can be characterized in detail.

3. Poly(diacetylenes)

Poly(diacetylenes) (PDAs) can be synthesized by polymerization in the solid-state from crystals of the low molecular weight precusor monomer. The polymerization is catalyzed either thermally, mechanically, or by exposure to radiation (Wegner, 1979).

A model showing the general chemical structure of a diacetylene monomer and the mechanism of polymerization is shown in figure 3 (Wegner, 1979). The basic chemical formula consists of a four carbon backbone with acetylenic groups between the (1,2) and (3,4) carbons. There are two (perhaps different) side groups R and R' which are attached to the 1 and 4 carbons. During polymerization, a bond is formed between the 1 carbon and the 4 carbon on neighboring diacetylene monomer units within the crystal. This results in a polymer molecule with a fully conjugated backbone, giving PDAs strong photoconductive and non-linear optical properties. The

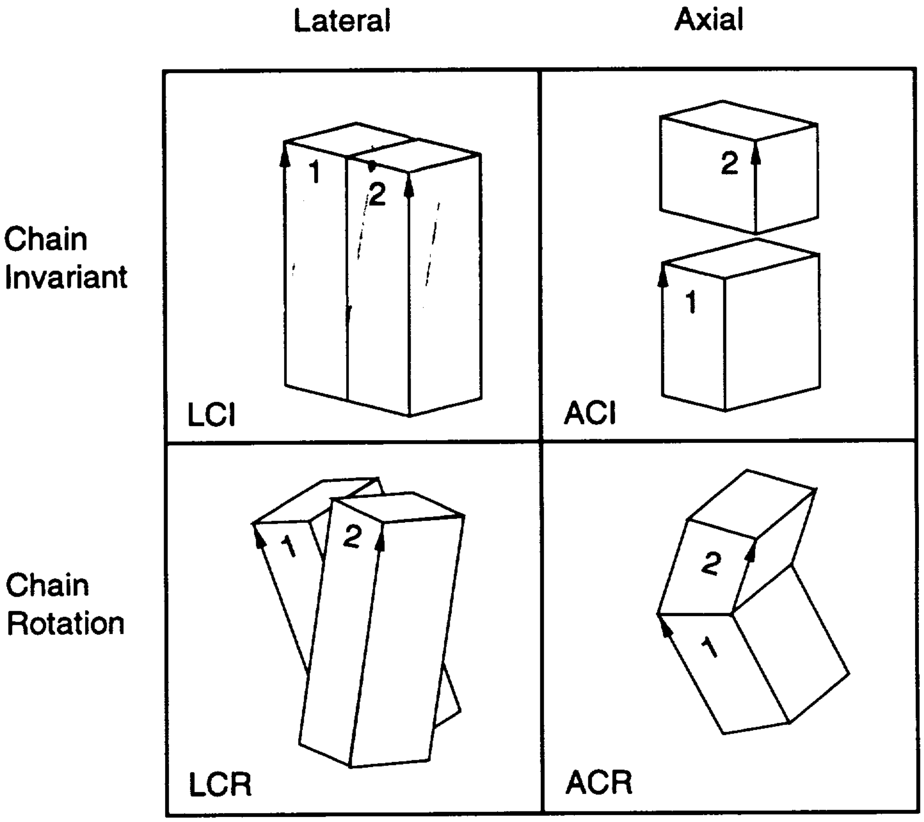


Figure 2. Categories for describing the different types of grain boundaries in polymer solids (Martin and Thomas, 1990). The scheme considers the relative orientation of the polymer chains in the two crystals (invariant or rotation) and the orientation of the grain boundary plane with respect to the chains (lateral or axial).

polymerization is characterized by a dramatic change in the appearance of the sample; the monomer crystals may be colorless; whereas, the polymers are strongly colored or even metallic in appearance (Wegner et al., 1975).

There are several types of PDAs available depending on the particular choice of the side groups R and R'. Amphiphilic diacetylenes in which one R group is hydrophobic and the other hydrophilic have been polymerized on water as Langmuir thin films. Their optical activity and ability to be organized into unique structures means PDAs are of particular interest for making molecular electronic devices.

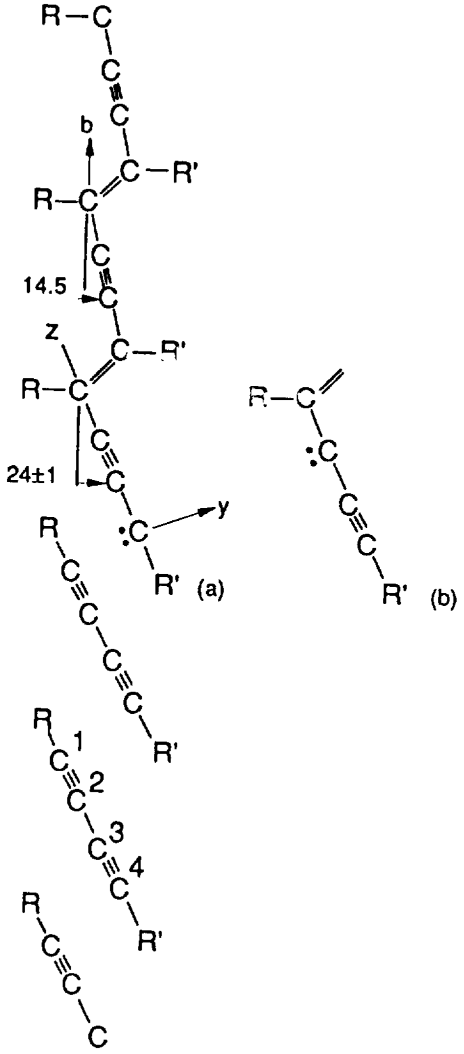


Figure 3. Model showing the chemical structure and mechanism of polymerization for diacetylenes (Wegner, 1979).

The solid-state polymerization proceeds without disrupting the crystalline order present in the original diacetylene monomer crystals. This means it is possible to make large PDA single crystals. This is markedly different from typical flexible polymers which crystallize from solution into lamellar crystals with a thickness on the order of 10 nm. Figure 4 shows a schematic of the polymerization in progress, and illustrates both heterogeneous growth in which local areas of polymer are nucleated and then grow, and homogeneous growth which results in a solid solution of polymer in the monomer matrix (Wegner, 1979).

Studies of PDA single crystals have provided new physical insight about the polymer solid-state. Spectroscopic techniques have been developed which have correlated Raman band shifts with local deformation (Batchelder and Bloor, 1979; Tashiro and Kobayashi, 1989), allowing PDA crystals to be used a local, sensitive "strain gages" for model composite studies (Galiotis, et al., 1984; Fan and Hsu, 1990).

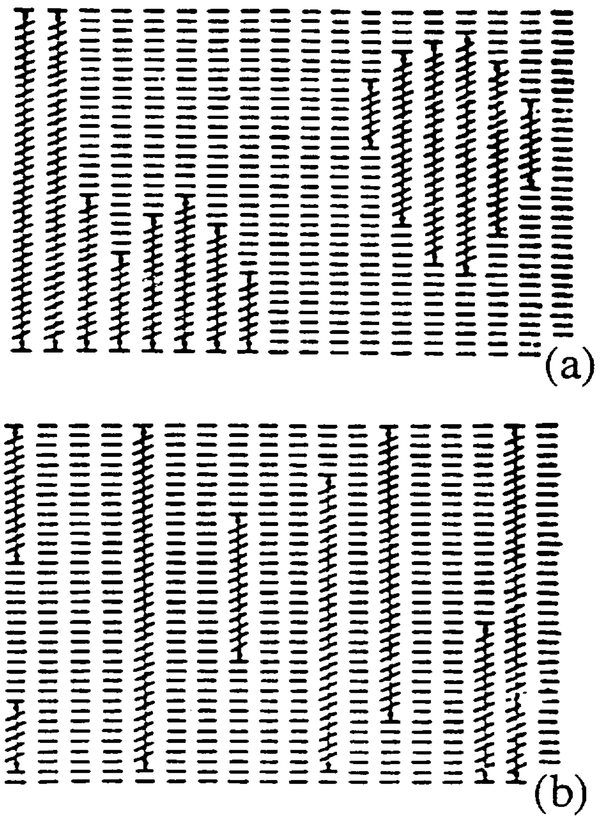
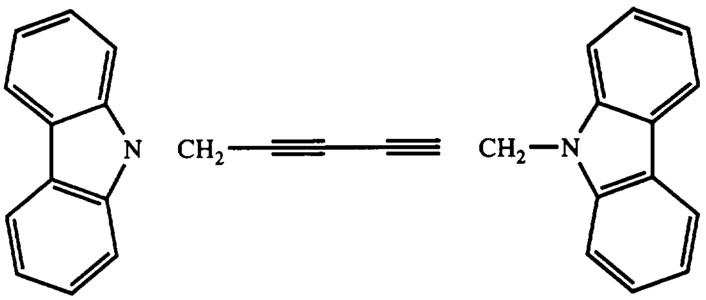


Figure 4. Model of the solid-state polymerization reaction in progress (Wegner, 1979). (a) hetergeneous nulceation, (b) homogeneous nucleation.

HREM studies of certain PDAs have already been successful (Read and Young, 1984; Young and Yeung, 1985; Yeung and Young, 1986). The PDA DCHD (figure 5) was found to be particularly resistant to the high energy electron beams used in TEM, with a critical dose for loss of crystalline scattering of approximately 20 C/cm^2 at 100 kV. HREM images showed that DCHD crystals are highly perfect, although there were some instances of the imaging of dislocation dipoles within DCHD crystals. Initial studies showed the DCHD crystals had a tendency to lie with their chains parallel to the carbon support film. Novel methods of sample preparation (heating in a vacuum oven at 100 °C) made it possible to grow abbreviated DCHD crystals oriented with their chains perpendicular to the carbon substrate. This facilitated images corresponding to direct projections of the DCHD polymer molecules down their chain axis.



DCHD: 1,6 di(n-carbazolyl)-2,4-hexadiyne

Figure 5.

The reactivity of different poly(diacetylenes) is known to vary widely. The reactivity is apparently influenced by the spatial relationship between polymerizable chemical moieties within the unit cell. It seems that the best results are obtained when the polymerization proceeds without severely distorting the crystal structure (Wegner, 1975). However, the deviations from an ideal arrangement which will still facilitate polymerization remain to be clearly established.

By attaching amphiphilic side groups it is possible to form polymerizable monolayers of diacetylenes using Langmuir-Blodgett techniques. Day and Lando (1980) found that when these polymerized PDA monolayers were deposited onto glass slides, they would often crack at the boundaries between domains of locally oriented polymer. These observations suggest that large angle grain boundaries between domains do not facilitate polymerization. However, the structure and properties of these boundaries have not yet been addressed in any detail.

4. Experimental Approach

While the crystallization and processing of inorganic materials and biopolymers has now been explored in some detail (Rosenberger, 1979), much less attention has been focused on similar phenomena in small molecule organic and synthetic polymer solids. Defect-mediated reorganization can be induced, for example, near surfaces and interfaces. By controlling the curvature of the surface it is possible to introduce variations in the local structure of the sample.

Our research has focused on the construction and characterization of defects in poly(diacetylene) systems. The long-range goal of our work is to isolate and examine the influence of specific grain boundary defects on the macroscopic electro-optic behavior of poly(diacetylene) systems. Recently, we found that there could be significant structural reorganization of diacetylenes during crystallization of thin droplets deposited on substrates (Wilson and Martin, 1992). Recent results confirm that the DCHD diacetylene polymerization occurs through a series of crystalline-intermediate states in a manner that is prescribed by the parent crystal (Liao and Martin, 1993).

PDAs are also of interest because of their photoconductive properties. The carriers responsible for charge transport have been proposed to move along the poly(diacetylene) chain by Solitary Wave Acoustic Polarons (SWAP) (Wilson, 1983). In this mechanism, the carrier is an electron which causes a local deformation of the poly(diacetylene) crystal lattice (Donovan et al., 1985). Recent work has indicated that the mobility of charge carriers in photoconductive poly(diacetylenes) undergoes an apparent transition from trap-limited motion at low fields to acoustic limited behavior as the electric field increases (Fisher, 1992; Fisher and Wilcox, 1992, 1993).

As organic materials become of more interest for use in molecular electronic devices, the effect of defects on the dissipation of these carriers is of particular concern. While only limited work has focused on these effects, some progress has been made. Donovan et al. (1985) have shown that physical "cuts" in the side of a pTS crystal can have a dramatic influence on the photoresponse of the material. They also found that it was possible to influence transport in DCHD by exposing the crystals to a series of lines written with an electron beam.

A typical photoconductivity experiment involves measuring the time-of-flight required for a charge transport across a sample under an applied voltage (Mort and Pai, 1976). During the experiment the sample is placed between electrodes, a voltage is applied, and the current is recorded during exposure to UV irradiation. The mobility of carriers m is determined from the relationship

$$\mu = L^2 / tV ,$$

where L is the sample size, V the applied voltage, and t the transit time. The transport mobilities of poly(diacetylenes) are on the order 1 cm^2/V sec (Chance et al., 1976; Donovan et al., 1989). This means for a typical sample with L = 0.1 cm and a voltage of 300 volts, it is necessary to have a laser pulse width and current detection system with a temporal resolution better than 10 μs. We are using a system with a 600 psec pulsed 337 nm UV nitrogen laser. A similar system has been used with success for measuring photoconductive properties of various polymers (Freilich and Gardner, 1989).

We are characterizing the transport mobility of carriers in poly(diacetylene) bicrystals as a function of the misorientation between the crystals. The misorientation between grains disturbs the molecular connectivity across the grain boundary and therefore disrupts the transport of carriers through the sample. This information is useful for understanding the particular mechanisms proposed for carrier generation and transport.

We use a variety of techniques including Optical Microscopy (OM), Wide Angle X-Ray Scattering (WAXS), Small Angle X-Ray Scattering (SAXS), Scanning Electron Microscopy (SEM), Bright Field (BF) and Dark Field (DF) Transmission Electron Microscopy, Selected Area Electron Diffraction (SAED), Atomic Force Microscopy (AFM), and High Resolution Electron Microscopy (HREM) to characterize the structure of the polymer bicrystals. This allows us to examine the optical anisotropy, crystal structure and orientation, surface structure, and details of the organization of PDA molecules near the defect. These facilities are presently available in the laboratories of the Materials Science and Engineering Department and the Electron Microbeam Analysis Laboratory at the University of Michigan. In particular, we have access to a JEOL 4000 EX Transmission Electron Microscope which has a 400 kV operating voltage and a point-to-point resolution of 0.17 nm. The microscope is equipped with a Minimum Dose System (MDS) for imaging samples which are sensitive to electron beam damage.

The study of the local structure near defects requires the careful application of HREM techniques at low incident doses (Martin and Thomas, 1987). However, the conjugated structure of poly(diacetylenes) makes them more resistant to beam damage than other, less thermally stable materials (Kumar and Adams, 1990).

5. Grain Boundaries in Poly(diacetylenes): Theoretical Analysis

The important question our research addresses is the nature of the solid-state polymerization of poly(diacetylene) through a grain boundary. By analogy with inorganic solids, we have found that certain physical properties of polymer bicrystals, such as transport behavior, are particularly sensitive to defect structure. While morphology is known to play a role in the electro-optic response of polymer materials (Freilich and Gardner, 1989), the typically high defect density of traditional materials makes interpretation of the data difficult.

The SWAP model for photoconductive carrier transport in poly(diacetylenes) involves motion of an electron along the backbone of the polymer (Wilson, 1983). If there is a grain boundary which disrupts the connectivity of the polymer molecules then it is reasonable to expect that this boundary will disturb the mobility of the SWAP. Furthermore, if it is possible to measure the decrease of carrier mobility across the boundary as a function of misorientation angle, then this will provide important information about the connectivity of the polymer molecules across the interface.

The following analysis is a theoretical development designed to illuminate the physical origin of this hypothesized influence of grain misorientation on the properties of the boundary. We first consider small angle boundaries which are approximately perpendicular to the molecular orientation. For illustrative purposes we consider the structure of the PDA DCHD (Read and Young, 1984; Young and Yeung, 1986). The crystal structure of DCHD is monoclinic, with a = 1.740 nm, b = 1.287 nm, c = 0.491 nm, and γ = 108.3°. A model illustrating a projection of the unit cell in the [001] direction down the chain axis is shown in figure 6. Also shown are two properly oriented cross-sections showing the shape of DCHD crystals.

Figure 7 shows a similar projection for two crystals of DCHD with a slight (3°) relative twist about the [001] axis. Note that there is coincidence between the chain axes for only one of the many pairs of monomers in the field of view. This emphasizes that even small misorientations may have profound effects on the structure and properties of the grain boundary.

The geometry of crystalline interfaces is described by the "0-lattice" theory developed by Bollman (1970). The geometry of a boundary is characterized by a 0-lattice which describes a network of sites on the interface where coincidences occur between points which belong to the same equivalence class. Equivalence classes are defined as those sites which have the same internal unit cell coordinates. The 0-lattice can be determined as long the transformation matrix A which relates crystal 1 to crystal 2 is known. For twist and tilt rotations the size of the 0-lattice varies smoothly with misorientation between the boundaries. The 0-lattice sites are widely separated at small misorientation angles and move closer together as the relative misorientation increases. Certain special 0-lattices may be coincident with actual lattice sites in the crystal, these special types of 0-lattice are called "coincident site lattices."

By definition, grain boundaries disrupt the crystalline ordering of the molecules in the system. If the crystalline structure is the most thermodynamically stable state, then disturbing it necessarily occurs at a cost in free energy. Often molecular relaxations can occur near the boundary

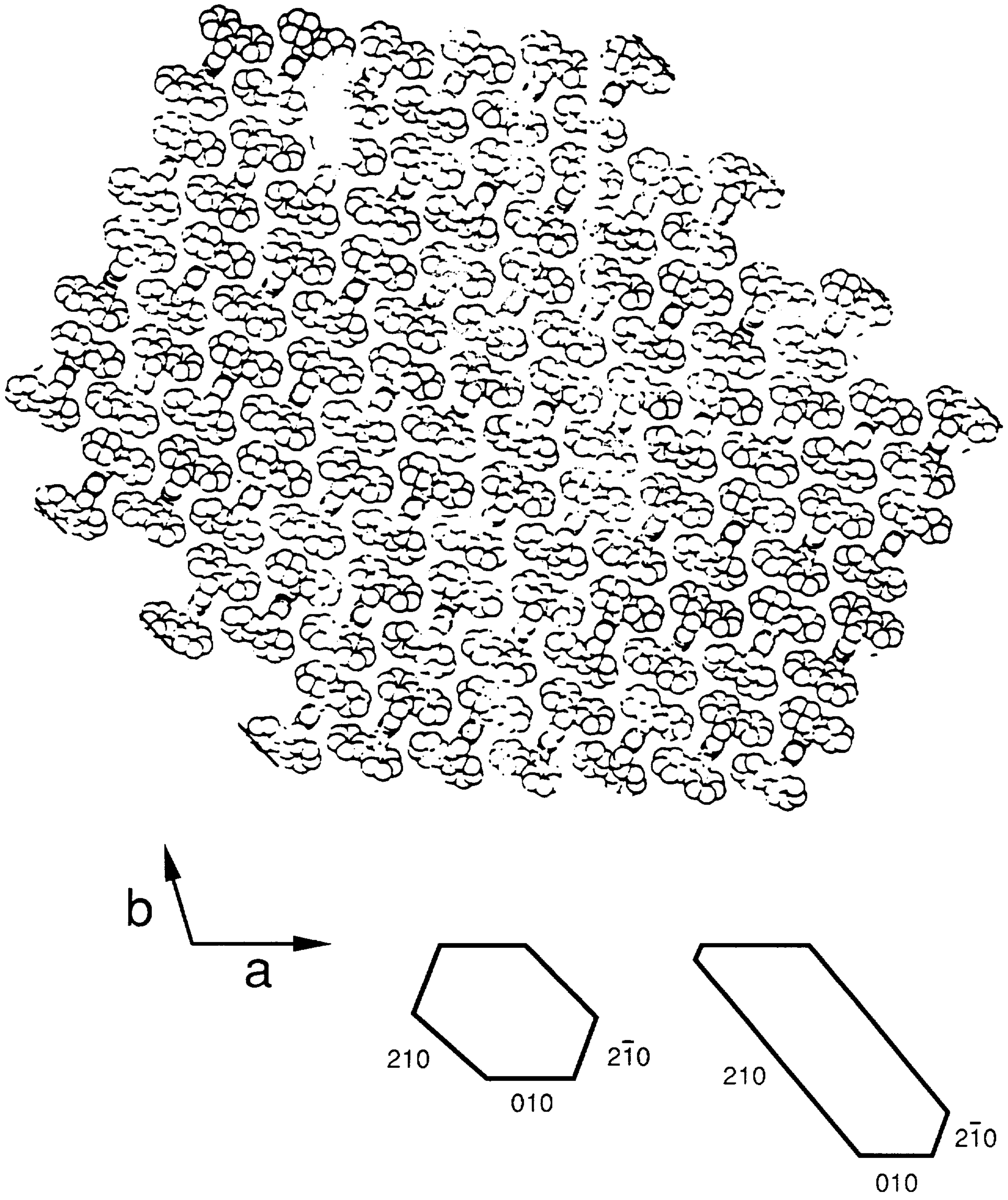


Figure 6. Schematic of the crystal structure of the diacetylene DCH viewed down the chain axis. Properly oriented cross-sections from the work of Galiotis et al. (1984) are also shown. The stable crystal faces are the (210), (010), and (210) planes.

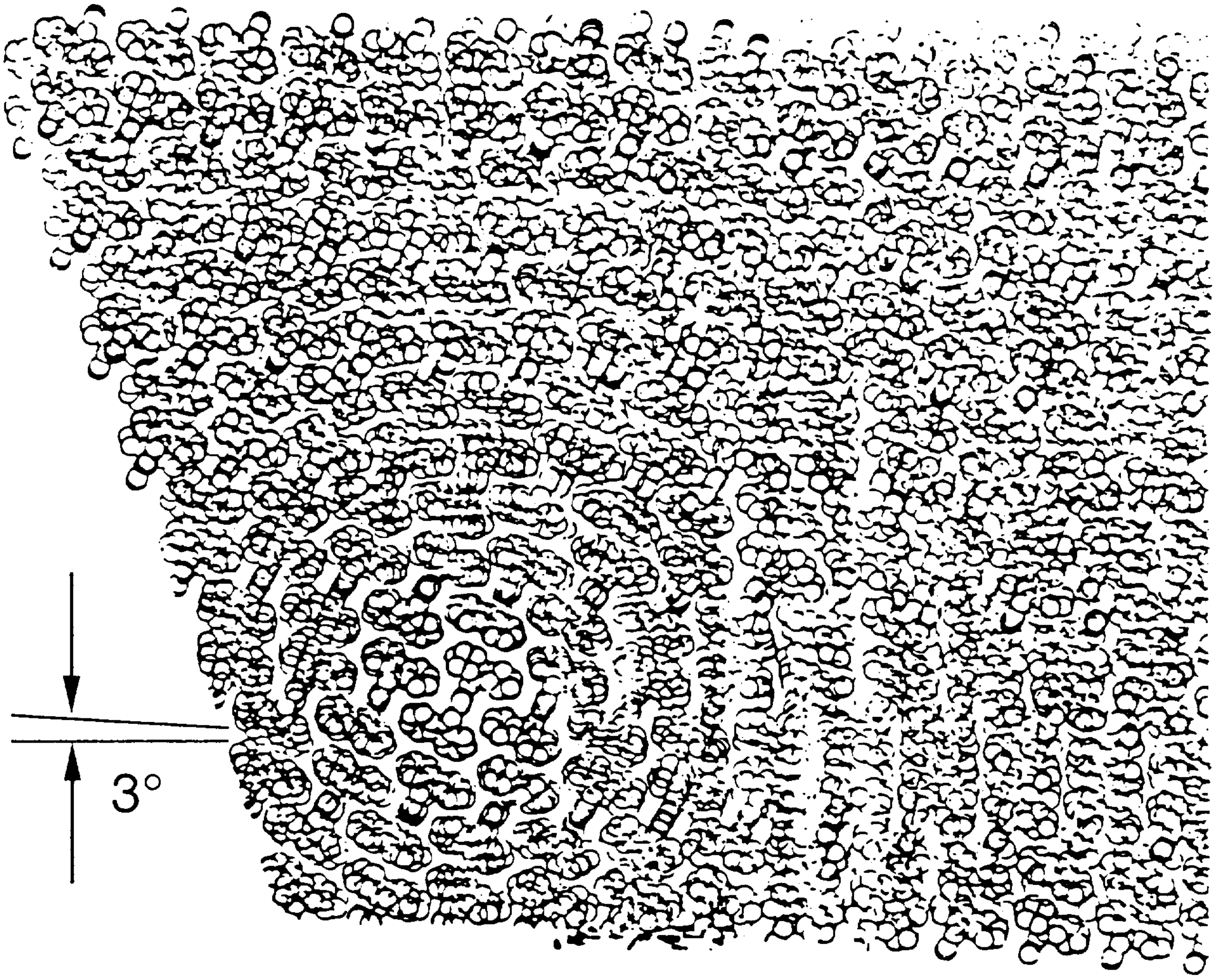


Figure 7. Superposition of two grains of DCH with a relative twist of 3 degrees about the (001) direction. There is only one position in the field of view where there is a direct superposition of the chain axes. In metallic and ceramic systems small angle grain boundaries such as these are known to localize deformation at the boundary into an array of dislocations. The relaxations and reorganization which might occur at similar boundaries in polymers are unknown.

to order to minimize the local energy penalties. In small angle grain boundaries of inorganic solids this usually happens by relaxations within the interior of each 0-lattice cell, forcing the deformation to localize into dislocation defects which connect the 0-lattice sites. The structure which results is a dislocation network. For tilt boundaries the local deformation is perpendicular to the direction of the defect and the dislocations are "edge" dislocations. For twist boundaries the local deformation is parallel to the direction of the defect and the dislocations are "screw" dislocations.

This analysis leads directly to our theory of the effect of misorientation angle on the properties of a grain boundary. We will assume that the property of interest depends on the ability of the material to relax near the boundary. The deformation required is assumed to be localized into defects with some characteristic width **b** which we assume to be a property of the material and therefore independent of misorientation angle. The problem which remains is simply to find out how the area of the grain boundary which is not disturbed by defects varies as a function of tilt and twist misorientation angle and the characteristic width **b** of the defect.

Essentially we propose that for a grain boundary the property of interest, which we will term μ, may often scale as

$$\mu = \mathbf{f}\, \mu_o$$

where μ_o is the corresponding property of the perfect crystal and **f** is the fraction of the grain boundary which is relaxed. In the case of poly(diacetylenes) bicrystals, **f** represents the number of chains which are "connected" across the boundary.

For simplicity, we first consider the problem in which both surfaces are described by similar two-dimensional square lattices. Now consider a uniform twist deformation about a perpendicular axis through the origin. In this case the transformation matrix is:

$$\begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix}$$

The unit cell vectors of the 0-lattice are given by (Bollman, 1970):

$$\mathbf{u}_1 = (1/2, -1/2 \text{ cotan } (\theta/2))$$
$$\mathbf{u}_2 = (1/2 \text{ cotan } (\theta/2), 1/2)$$

From these equations it is evident that as θ increases from zero the spacing between 0-lattice sites decreases. This behavior is illustrated in figure 8. The length of the side of one unit cell of the 0-lattice is given by

$$L = /u_1/ = /u_2/ = (1/2)^2 + (1/2 \text{ cotan}^2(\theta/2))^{1/2}$$

and the area is

$$A = u_1 \cdot u_2 = (1/2)^2 + (1/2 \text{ cotan}^2(\theta/2)) .$$

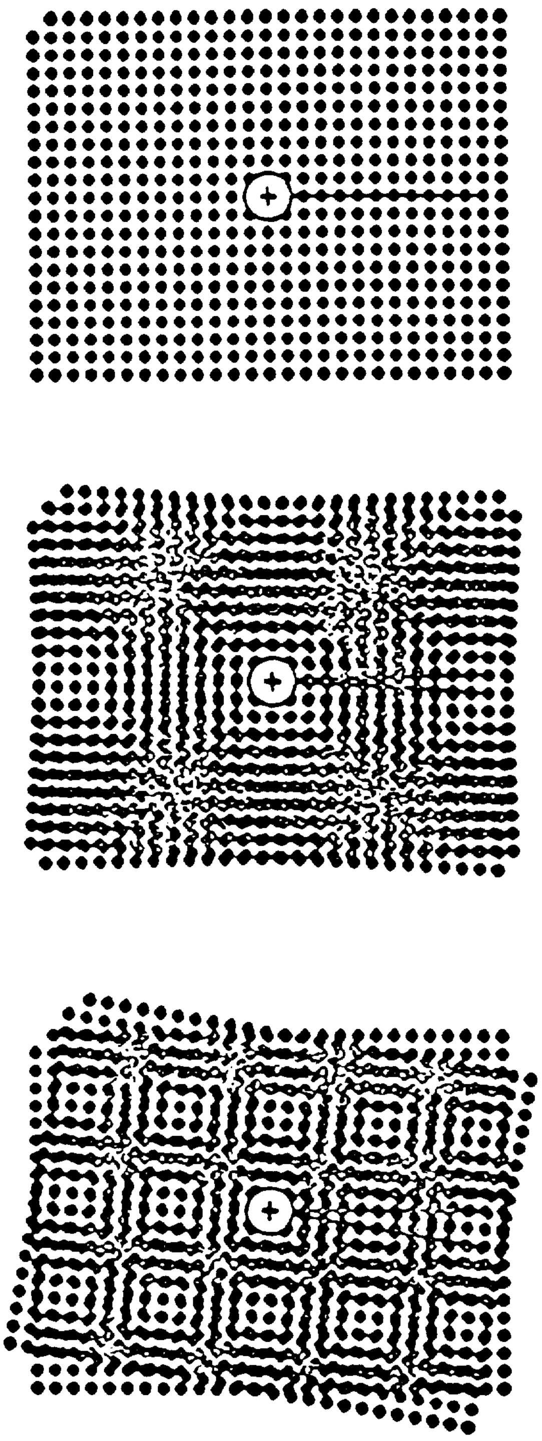


Figure 8. Projected structure of a grain boundary between two crystals as a function of twist angle about an axis normal to the boundary plane. The 0-lattice describes the interference pattern which is created by coincidences between sites belonging to the same internal coordinate equivalence class. The spacing between 0-lattice sites decreases as the misorientation increases.

If we assume that the width of the defects is **b,** that these defects correspond to the 0-lattice network, and the the rest of the interface (the interior of the 0-lattice cells) is able to relax back to the original configuration of the crystal, then the area of the surface which is NOT defects is given by

$$\mathbf{A_f = (L\text{-}b)^2}$$

Substituting from above and simplifying gives us the fraction of the interface which remains coherent as a function of the width of the defect **b** and the misorientation between the crystals θ:

$$\mathbf{f = (-b + (1/4 + 1/4\ \mathrm{cotan}^2(\theta/2) \,/\, (1/4 + 1/4\ \mathrm{cotan}^2 (\theta/2))}$$

Figure 9 shows **f** for a particular choice of **b** and **θ** as a black square. Figure 10 shows **f** as a function of **θ** for different choices for the size of the defect **b** (in units of **b/a** where **a** is the size of the underlying lattice). Notice that the larger the defect, the faster the area of relaxed molecules decrease as a function of misorientation. If we take the first derivative of the equation for **f** with respect to **θ** and take the limit as **θ** goes to zero, we obtain

$$\mathbf{\partial f/\partial\theta\ (\theta\text{->}\ 0) = -2\ b}$$

This equation shows that the change in **f** at small θ is directly related to the size of the defect **b**. For **b** large this analysis also shows that **f** will equal zero at some critical angle **θc**. This critical angle decreases with increasing **b**.

If the properties of the grain boundary are determined by the area between defects along the 0-lattice, then **f** can be directly related to the property of interest (such as the tensile strength or carrier mobility). Our analysis predicts that there should be a decrease in **f** which depends on the misorientation between the grains and the size of the defect. Measuring the actual variation in the property of bicrystals as a function of grain geometry therefore provides an interesting experimental test of these ideas.

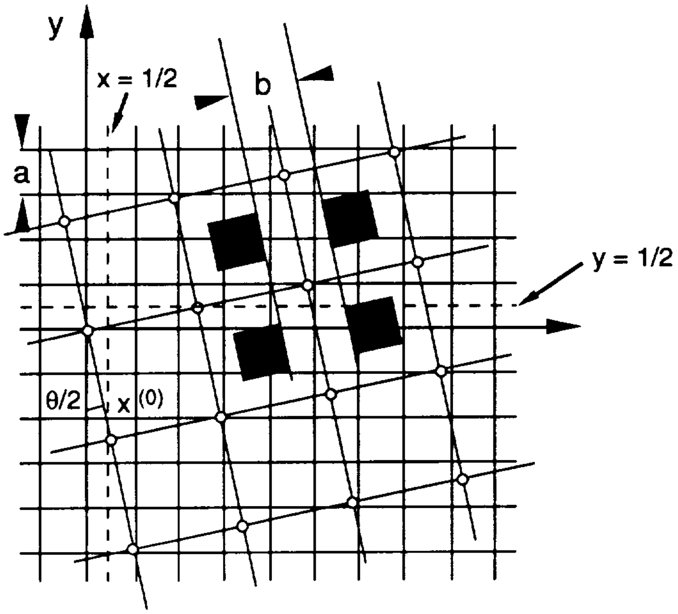


Figure 9. Model of the geometry of a twist boundary in a material with cubic symmetry (see text for details). The dark areas represent the area which is relaxed if the boundary is modeled by an array of dislocations along the 0-lattice having a width **b**. The amount of relaxed material is a function of both **b** and the angle of misorientation θ. Figure adapted from Bollman (1970).

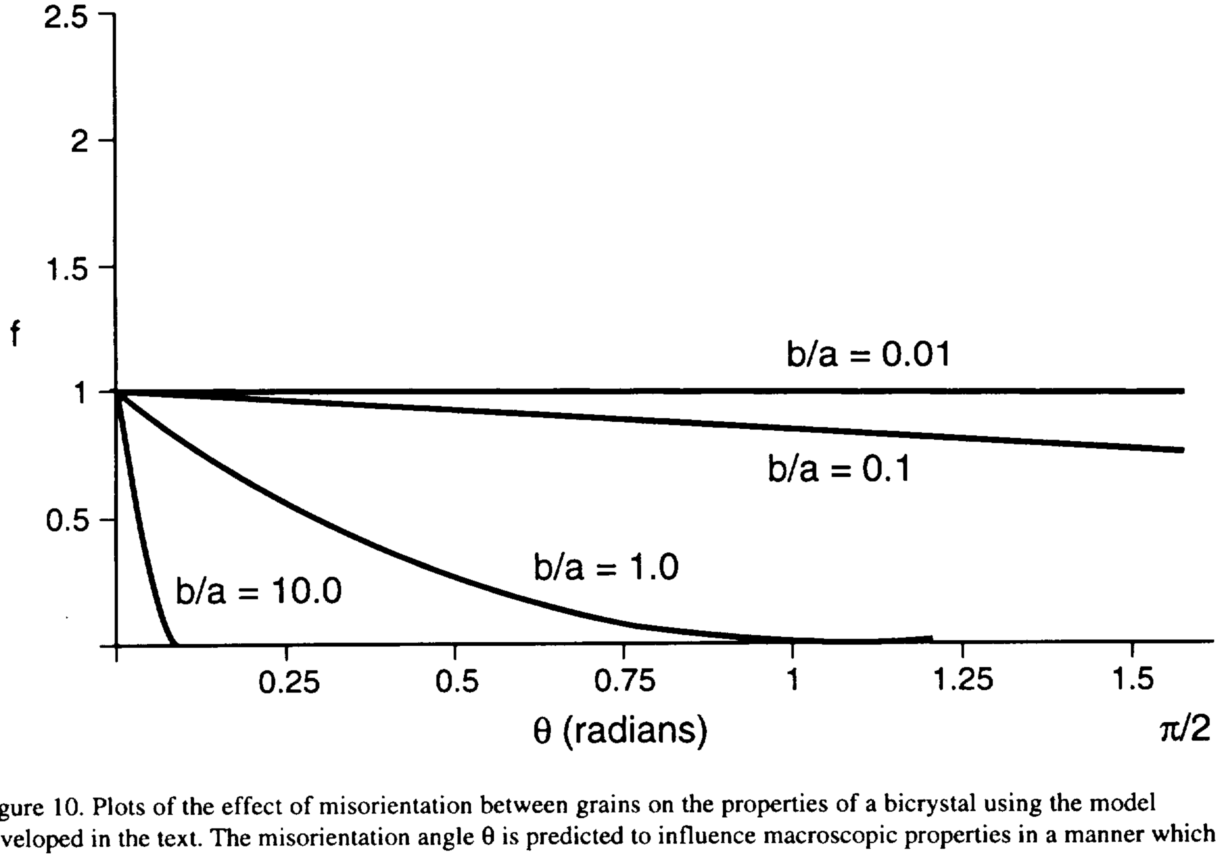


Figure 10. Plots of the effect of misorientation between grains on the properties of a bicrystal using the model developed in the text. The misorientation angle θ is predicted to influence macroscopic properties in a manner which reflecs on the ability of the material to localize deformation at the grain boundary into defects. The smaller the width of the defect **b**, the less the effect on θ on the properties of the boundary.

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Extended Abstract

PREDICTION OF NONLINEAR OPTICAL PROPERTIES OF ORGANIC MATERIALS

General Theoretical Considerations

B. Cardelino
Atlanta University Center

C. Moore
NASA-Marshall Space Flight Center
Huntsville, AL 35812

S. Zutaut
University of Alabama in Huntsville
Huntsville, AL 35899

The prediction of nonlinear optical properties of organic materials is geared to assist materials scientists in the selection of good candidate molecules. A brief summary of the quantum mechanical methods used for estimating hyperpolarizabilities will be presented. The advantages and limitations of each technique will be discussed.

Particular attention will be given to the finite-field method for calculating first and second-order hyperpolarizabilities, since this method is better suited for large molecules. Corrections for dynamic fields and bulk effects will be discussed in detail, focusing on solvent effects, conformational isomerization, core effects, dispersion, and hydrogen bonding. Several results will be compared with data obtained from third-harmonic-generation (THG) and dc-induced second-harmonic generation (EFISH) measurements. These comparisons will demonstrate the qualitative ability of the method to predict the relative strengths of hyperpolarizabilities of a class of compounds.

The future application of molecular mechanics, as well as other techniques, in the study of bulk properties and solid state defects will be addressed.

The relationship between large values for nonlinear optical properties and large conjugation lengths is well known, and is particularly important for third-order processes. For this reason, the materials with the largest observed nonresonant third-order properties are conjugated polymers. An example of this type of polymer is polydiacetylene.

One of the problems in dealing with polydiacetylene is that substituents which may enhance its nonlinear properties may ultimately prevent it from polymerizing. A model which attempts to predict the likelihood of solid-state polymerization is considered, along with the implications of the assumptions that are used.

Calculations of the third-order optical properties and their relationship to first-order properties and energy gaps will be discussed. The relationship between monomeric and polymeric third-order optical properties will also be considered.

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Moore, C. E., B. H. Cardelino, B. G. Penn, J. Bllard, M. Sanghara, and R. D. Clark, "Prediction of the static second-order polarizabilities of (2,4)-dinitro substituted benzenes," to be submitted for publication.

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Extended Abstract

TEMPERATURE DEPENDENCE OF PROTEIN SOLUBILITY–DETERMINATION, APPLICATION TO CRYSTALLIZATION, AND GROWTH KINETICS STUDIES

Franz Rosenberger
Center for Microgravity and Materials Research
University of Alabama in Huntsville
Huntsville, AL 35899

A scintillation method was developed for determinations of the temperature dependence of the solubility, and of nucleation induction times of proteins, in 50-100 $\mu\ell$ volumes of solution. Solubility data for lysozyme and horse serum albumin were obtained for various combinations of pH and precipitant concentrations. These data and the nucleation induction information were used for dynamic crystallization control, that is, for the controlled separation of nucleation and growth stages. Individual lysozyme and horse serum albumin crystals were grown in 15-20 $\mu\ell$ solution volumes contained in x-ray capillaries.

The morphology and kinetics of the growth and dissolution of lysozyme in aqueous solutions with 2.5% NaCl and at pH = 4.5 was studied in situ with a depth resolution of 300 Å (4 unit cells) by high resolution optical microscopy and digital image processing. The bulk super- or undersaturation, σ, of the solution inside a closed growth cell was controlled by temperature. The growth habit was bound by (110) and (101) faces that grew through layer spreading, although with different growth rate dependencies on supersaturation/temperature. At $\sigma < 10$ (obtained at higher temperatures) growth was purely kinetically controlled, with impurity effects (macrostep formation and kinetic hindrance) becoming significant for $\sigma < 2$. At $\sigma > 10$ (lower temperatures), anisotropies in the interfacial kinetics were more pronounced, with interfacial kinetics and bulk transport becoming equally important to the growth morphology. Growth rates were growth-history dependent. The formation of striations (layers of irregularly incorporated solution) was unambiguously correlated with growth temperature variations. Etching exposed dislocations and various high-index faces whose growth morphologies were studied during return to the steady-state growth form. Growth steps were observed to originate from two-dimensional nuclei or from outcrops of growth striations, and from dislocations that preferentially formed in growth sector boundaries.

References

This talk summarizes the following recent publications.

Rosenberger, F., S.B. Howard, J.W. Sowers and T.A. Nyce, Temperature dependence of protein solubility - determination and application to crystallization in x-ray capillaries, J. Crystal Growth **129** (1993) 1-12.

Monaco, Lisa A., and F. Rosenberger, Growth and etching kinetics of tetragonal lysozyme, J. Crystal Growth **129** (1993) 465-484.

Detailed reference lists for earlier work on the various topics treated can be found in these publications.

N94-24345

Extended Abstract

MODELING OF PCG FLUID DYNAMICS - SALIENT RESULTS

N. Ramachandran
Universities Space Research Association
NASA Marshall Space Flight Center
Huntsville, AL 35812

Materials processing in space-based laboratories has already yielded higher quality crystals during previous space flights, and opportunities for several fluids experiments are anticipated during the extended duration missions planned for the future. Crystal growth in space benefits not only from its reduced gravity environment but also from the absence of the hydrostatic pressure which assists certain crystal growth and refinement methods. Gravity-driven phenomena are thus reduced in strength, and a purely diffusive fluid's behavior can be attained. In addition, past materials science experiments have shown that microgravity can also help produce larger crystals. While gravity-related effects are definitely curtailed in space, they are nevertheless present to some degree due to the acceleration environment onboard the spacecraft. This residual acceleration level is comprised of quasi-steady, oscillatory, and transient components, and is caused by a variety of mechanisms. For example, gravity gradient forces produce low frequency disturbances, and the operation of machinery, control thrusters, solar panels, human activity, etc. contribute to higher frequency accelerations. These disturbances are collectively referred to as g-jitter, and they can be deleterious to certain experiments where the minimization of the acceleration level is important. Advanced vibration isolation techniques can be utilized to actively filter out some of the detrimental frequencies and help in obtaining optimum results. However, the successful application of this technology requires the detailed analysis of candidate fluids experiments to gauge their response to g-jitter and to determine their acceleration sensitivities.

Several crystal growth experiments in the Protein Crystal Growth (PCG) area, besides others, are expected to be carried out on future shuttle flights and on Space Station Freedom. The need for vibration isolation systems or components for microgravity science experiments can be expected to grow as experiments and available hardware becomes more complex. This technology will also find increased application as the science community develops an awareness of their specific needs relative to the environment available in manned space missions. Vibration isolation research strives to develop a microgravity environment requirement that defines tolerance limits on the allowable g-level, and provides the required technology to achieve it. This effort will assist in establishing the tolerable acceleration levels for specific fluids experiments. The primary effort is directed towards modeling PCG and the approach undertaken for this investigation is outlined in the following sections.

Objectives

1. To computationally determine vibration sensitivity of protein crystal growth experiments.
2. Determine if these experiments can benefit from vibration isolation techniques.
3. Provide realistic requirements for vibration isolation technology.

Convection Effects in PCG

Several proteins have been flown during past shuttle missions with the aim of growing bigger and better crystals. Protein crystal growth in microgravity benefits from the following advantages:

1. The free suspension of the protein in the growth medium (due to diminished gravity) promotes uniform crystal growth and eliminates container interface effects.

2. Convection effects are minimized and a diffusion-controlled crystal growth can be realized.

3. Internal stresses in the complex biological macromolecules are eliminated due to the reduced hydrostatic pressure environment. This helps in improved internal order of the grown crystal and prevents the collapse of the big complex molecules.

The data collected from past shuttle missions have all indicated that microgravity can be effectively utilized to obtain higher quality protein crystals. The space-grown crystals tend to be significantly better than the best Earth-grown samples and thus are ideal for protein crystallography. However, past experience has also shown that the microgravity environment on the space shuttle can sometimes yield unpredictable results in PCG. Poor crystal quality due to cracking, stunted crystal growth, multiple and sometimes showers of small crystals have been observed with certain PCG experiments. The causative factors for these effects have not all been completely understood. It is generally agreed however, that crew activity and g-jitter all play some role in this crystal degradation process.

In any PCG experiment, the solution transport within the growth medium and the crystal surface attachment kinetics play key roles in determining the crystal growth rate. With most small molecule crystals, the solution transport is the rate limiting step. In such situations, forced convection in the solution will increase the growth rate up to a certain point beyond which surface kinetics becomes the controlling factor. Experiments by Pusey et al.[1] using tetragonal lysozyme have shown that forced flow rates of 30-40 μm/s slow and eventually stop the growth of 10 μm crystals. Recent experiments by Pusey[2] suggest that this growth cessation is present even at lower flow rates but the growth declines over a much larger time than at the higher flow rates. In the experiments,[2] even very small velocities of the order of $\cong$2.5 μm/s were seen to irreversibly terminate the (110) face growth of tetragonal lysozyme crystals. Corroborating results have been reported by Nyce and Rosenberger,[3] who further showed that this growth cessation is not observed in the growth of orthorhombic lysozyme crystals. In their studies, Grant and Saville,[4] proposed and subsequently disproved based on theoretical analyses a host of mechanisms that may account for the growth cessation behavior. The inclusion of contaminants from solution was hypothesized as the probable cause of this behavior. However, as mentioned in,[2] this mechanism does not explain the absence of similar effects in the growth of orthorhombic lysozyme.[3] Thus for some crystals at least, even small convective flows are deleterious for growth of the crystal. The exact mechanism for this effect is as yet not fully understood.

In order to realize a fully diffusion-limited (D/L) crystal growth, the convective effects have to be eliminated. The tolerable microgravity levels to achieve D/L growth can be established by implementing a simple Order of Magnitude Analysis (OMA) of the equations describing the system. The analysis involves choosing appropriate scaling factors for length, velocity, concentration, and other variables of importance to the experiment, while determining the dominant terms in the governing equations describing the system. Estimates of fluid sensitivity as a function of acceleration amplitude and frequency are obtained, and these estimates can be used as a preliminary guide to more detailed computations. A representative OMA curve for proteins is shown in figure 1.[5] The analysis shows that the proposed Space Station Freedom microgravity environment would be conducive towards achieving this goal. PCG onboard other manned vehicles, on the other hand, would have to resort to other means to achieve the required acceleration environment. Vibration isolation technology can be used to filter harmful frequencies and thus minimize the resulting convective effects. Active vibration devices being developed at NASA Lewis Research Center can filter frequencies up to approximately 0.1 Hz and thus hold promise in this area. It should be pointed out that OMA estimates are based on a very crude model of the physical processes and probably over estimate the convective transport. The model is, however, expected to provide correct trends and perhaps quantitative information within an order of magnitude accuracy. This level of accuracy has, however, to be evaluated by detailed CFD modeling.

Fluids Modeling

The modeling and analysis of PCG experiments is being carried out in three concurrent steps:

1. A familiarization phase, where past PCG activities were reviewed with respect to the types of fluids/proteins used, flight hardware utilized, procedures followed, difficulties encountered, results obtained, and inferences drawn from the experiment. Fluid properties and hardware operating conditions like temperature, concentration, etc. were noted during these past experiments onboard the shuttle. This learning phase is a continuous effort and fairly long term in nature, since several different proteins are examined and as redesigned hardware is continuously monitored. From this ongoing effort, a candidate protein (lysozyme) has been chosen for analysis and modeling. Results from this modeling will be used for comparison purposes and as a benchmark for future analyses.

2. The code development phase consists of modifying the in-house 2-D code to model PCG. The modification includes the introduction of the species equation to model solutal diffusion and convection, the input of the PCG geometry description into the code, the addition of source terms to the Navier-Stokes momentum equations to account for solute-induced buoyancy forces, and steady and unsteady code verification by comparisons to bench mark solutions.

3. The detailed modeling phase involves the numerical solution of the governing equations and boundary conditions for PCG. Several g-jitter scenarios can be examined to provide detailed results of the fluid response to the imposed excitations. The results can be compared to OMA estimates to gauge the level of agreement between the two methods. While OMA allows only a single frequency input, the numerical model allows the flexibility of simulating multiple frequencies of different magnitudes acting on the system in different directions. G-tolerance levels can be established, and the results can be used to determine if the experiment will benefit from vibration isolation. Realistic requirements for VIT can also be established. The initial effort is focused on a single candidate protein and simplified boundary conditions, with the simulations performed for the worst case scenario with regard to the individual frequencies and their orientations. More realistic and complex boundary conditions, other flown proteins, and different g-jitter directions will be simulated in subsequent computations.

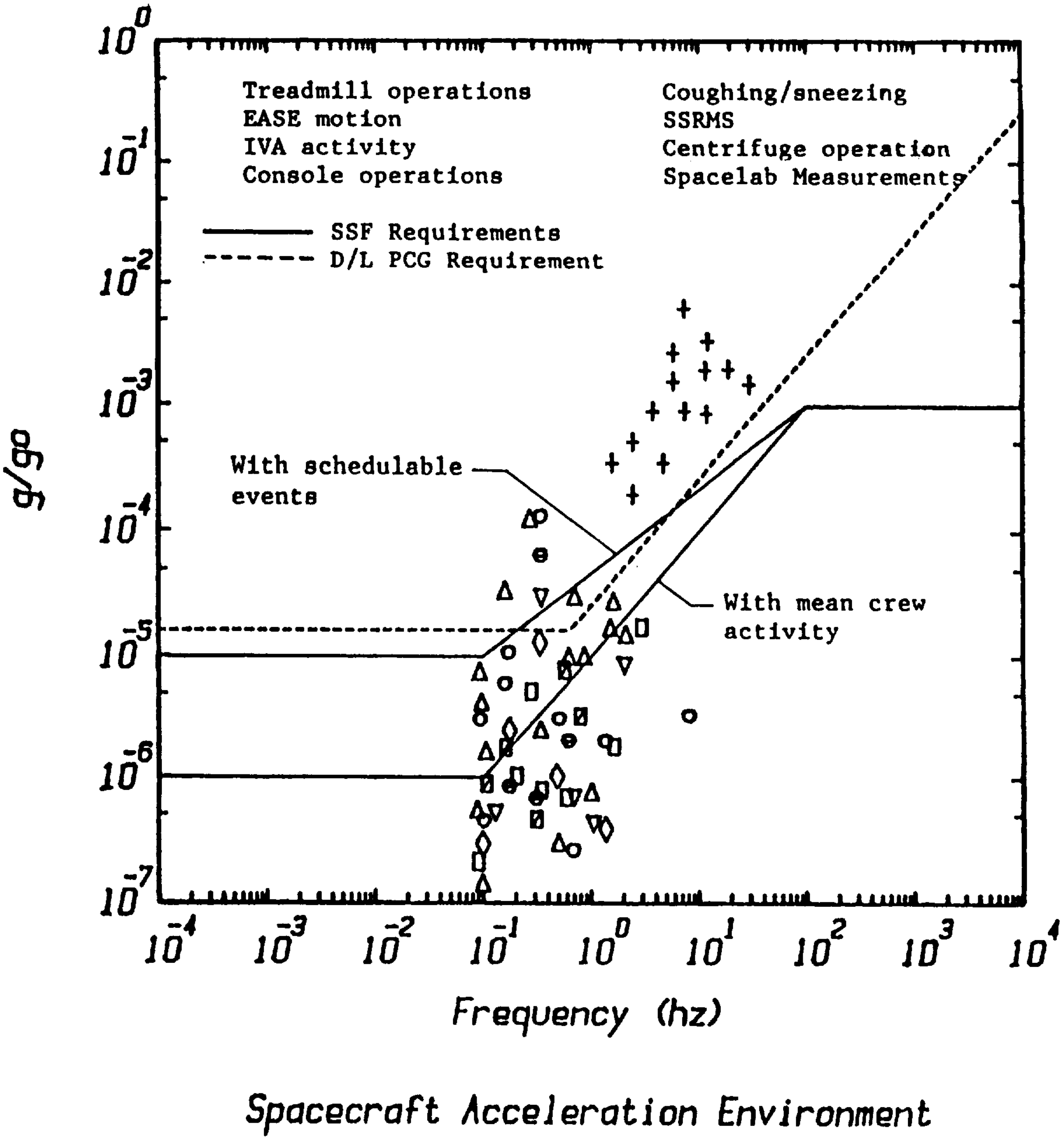


Figure 1. Representative order of magnitude analysis curve for protein crystal growth.

In the detailed numerical modeling phase, the response of the candidate protein to different g-jitter scenarios, will be determined. Simplified boundary conditions will be initially examined, followed by more realistic boundary conditions. The fluid response to the following g-scenarios are being investigated.

(i) Steady state g-levels, ranging from

$g = g_o$ (terrestrial gravity)

$g = 10^{-4}g_o$

Microgravity

$g = 10^{-5}g_o$

$g = 0$ (zero gravity)

(ii) Transient excitations: single and multiple step functions. These excitations model random impulse type disturbances that occur on a space-based laboratory. Different impulse strengths and durations will be investigated.

(iii) Periodic accelerations: Simulations will be carried out for low ($<10^{-3}$ Hz), intermediate (10^{-2} to 0.1 Hz) and high frequency (>1 Hz) disturbances. Different amplitudes will be examined. Comparisons will be made with OMA estimates.

(iv) Combined excitations: In this effort, realistic g-jitter will be simulated by combining transient, residual (low frequency), and oscillatory (intermediate and high frequency) disturbances. Fluid sensitivity will be determined, and tolerable g-levels will be established.

Numerical Modeling of Other Proteins

Among the 20 or so proteins that have flown on previous shuttle flights, several have failed to yield optimum results. Some of these proteins will be examined to see if they will benefit from vibration isolation.

Modeling Results (Preliminary)

The 2-D computational model is shown in figure 2. The crystal is modeled in planar two dimensions assuming an axis of symmetry (as opposed to an axisymmetric model). The actual crystal growth process is typically of the order of 1-2 mm/day and hence is treated as a quasi-steady phenomenon. This implies that even though time accurate calculations are carried out to record the fluid response to time varying disturbances, the actual growth of a crystal phase is not modeled. This is a reasonable assumption considering the disparity between the respective time scales. No slip boundary conditions are applied on the crystal walls and on the computational domain $x = L$ and $y = 0$.

The fluid response to terrestrial gravity (1 g_o) is shown in figure 3. A strong convective plume with maximum flow speed of 247 m/s is observed to rise from the crystal. Tangential fluid velocities of 3 m/s are calculated adjacent to the crystal face. It should be noted that zero velocities (tangential and normal) are prescribed on the crystal wall in the present calculations. If there is any slip flow in this region, the corresponding calculations will result in vastly different velocity values. However, the modeling of the velocity boundary condition is dependent on the attachment kinetics of the molecules to the growing crystal and in this instance this phenomenon is not completely understood.

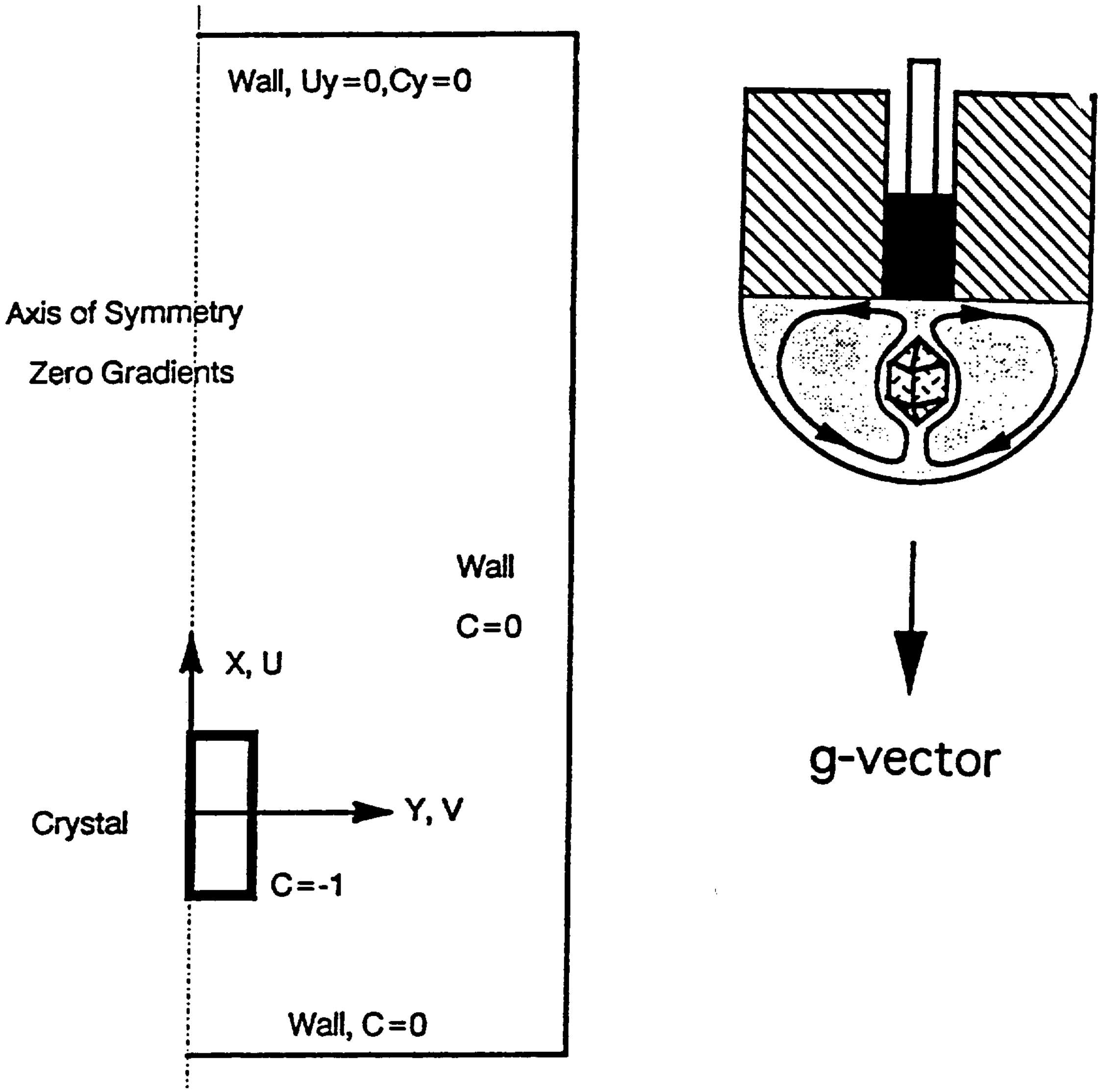
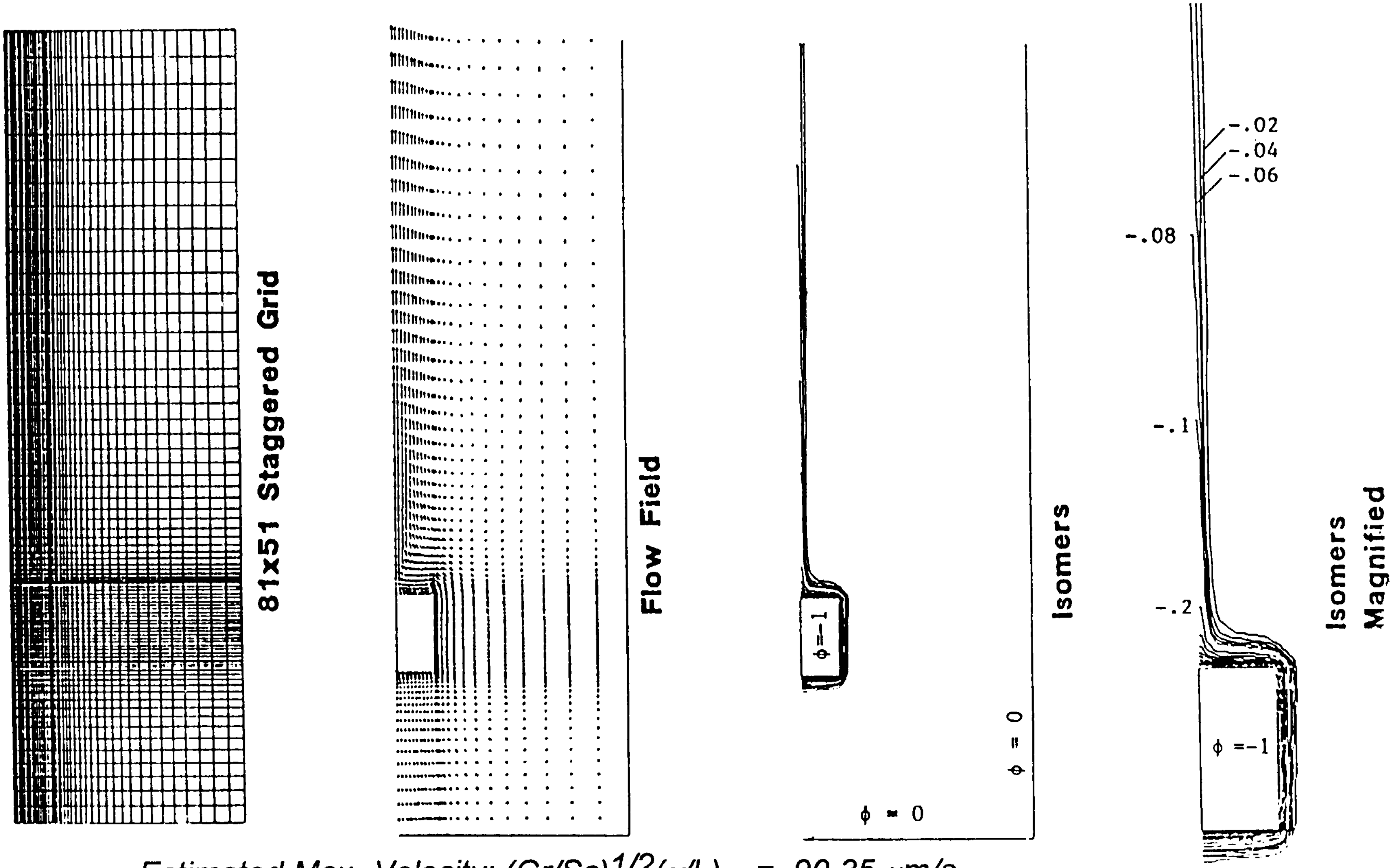


Figure 2. Two-dimensional PCG computational model.

The equi-concentration contours or isomers for this case are also shown in figure 3. The steep concentration gradients next to the crystal are apparent from the figure. The boundary layer thickness is 0.12 mm. The mass transfer into the crystal is characterized by the average Sherwood number. For the 1 g_o case, Sh = 16.4, compared to Sh = 1.0 for the pure diffusion case. The fluid response to a parametric variation of the g-level (10^{-2} g_o, 10^{-3} g_o, 10^{-4} g_o, 10^{-5} g_o, and 0 g_o) is plotted in figure 4 as isomer distributions. The maximum global velocities, their OMA estimates, the average Sherwood numbers, and the maximum velocities next to the crystal are also indicated on the figure. All of these values characterize the strength of convection within the cell and are seen to diminish as the gravity level is reduced. The gradual thickening of the solute/concentration boundary layer is clearly visible as the g-level is decreased. The pure diffusion case ($g = 0$) represents the ideal crystal growth conditions. The isomer distortions at $g = 10^{-5}$ g_o (typical of the residual gravity level in space) can also be discerned from the figure. Diffusion-limited crystal growth conditions are approached at this low-gravity level.

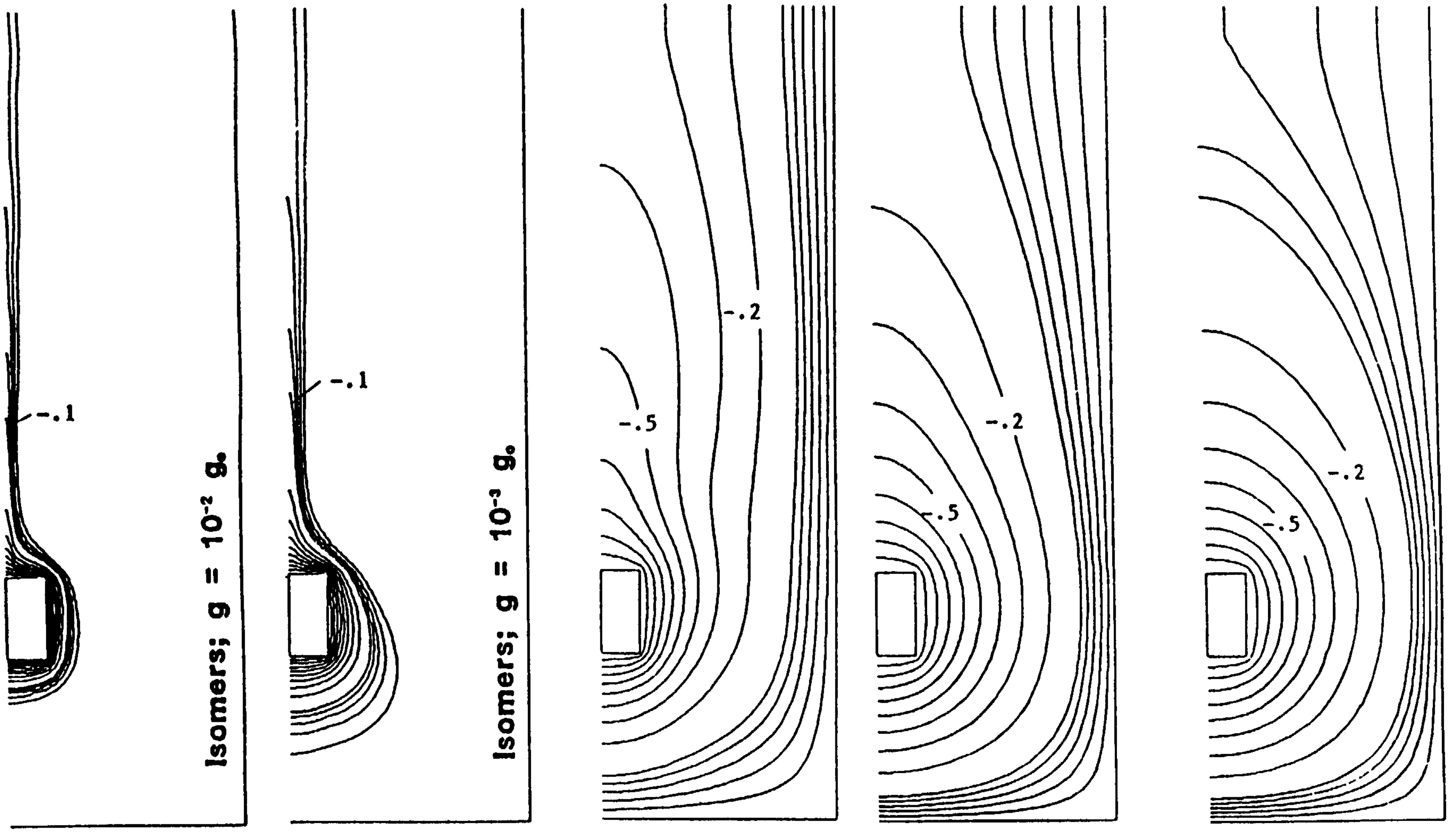
PCG Numerical Modeling ($g=1g_o$)



Estimated Max. Velocity: $(Gr/Sc)^{1/2}(\nu/L)$ = *90.35 µm/s*
Calculated Maximum velocity = *70 µm/s*
Average Sherwood Number = *16.4*

Figure 3. The fluid response to terrestrial gravity.

PCG Numerical Modeling (Residual Accelerations)



Velocities (µm/s)	10^{-2} go	10^{-3}go	10^{-4} go	10^{-5} go
Maximum	7.00	2.00	0.30	
Next to Crystal	0.247	0.090	0.004	0.0007
OMA Estimate	9.03	2.86	0.90	0.280
Sherwood Number	5.67	3.61	1.27	1.00

Figure 4. The fluid response to a parametric variation in g-level.

Impulse type disturbances:

Scenario

1. Ten seconds of no gravity; pure D/L conditions.
2. One second impulse of strength 10^{-3} g_o.
3. Calculations carried out for 600 s (10 min) after impulse with no gravity.

Figure 5 shows the isomers and stream function plots at different times in the calculations. The onset of the flow is immediate after the impulse and the flow development is complete 1 sec after the impulse. No disturbance effects are, however, evident in the concentration field at this time. Some isomer disturbances are evident 100 sec after the impulse disturbance and clearly noticeable variations are seen 10 min after impact. The flow field shows a gradual decaying trend subsequent to the impulse.

Oscillatory disturbances:

The system response characteristics to an oscillatory disturbance frequency of 3.183 Hz (20 rad/s) and amplitude of 10^{-3} g_o are shown in figure 6. This frequency is close to the 2.5 Hz noticed in the SAMS data during treadmill operations on the space shuttle. The figures show complete flow reversal during each cycle. Figure 6 shows the isomer and stream function plots during the 5th cycle of g-jitter and are representative of a periodic behavior attained within the PCG solution.

Conclusions

The salient results from the investigation are as follows:

1. G-jitter dominates the spacecraft acceleration environment. It is comprised of a myriad of frequencies and displays no preferred orientation. The g-jitter magnitudes can be as high as 1 milli-g (10^{-3} g_o).

2. Impulse-type disturbances are random in nature and hence unpredictable. The solutal field response to impulsive forces is especially long term and considerable. Impulse-type disturbances are also deleterious to PCG in other respects, e.g., drop dislodgment, multiple crystals, crystal cracks etc. It is, therefore, prudent to take remedial measures to safeguard against their pernicious effects on materials processing.

3. PCG observations and analyses indicate susceptibility to g-jitter.

4. Calculations show the PCG flow field to be susceptible to 1-10 Hz frequency range.

5. PCG is a PRIME candidate for vibration isolation. NASA LeRC developed active vibration isolation system filters up to 0.1 Hz; passive systems can also filter down to this frequency level.

6. Passive isolation system for PCG - A FIRST RECOMMENDATION.

IMPULSE DISTURBANCE

Impulse Strength = $10^{-3}g_o$; Duration = 1 second
Impulse at t = 1 second and Calculations carried out for t = 590 seconds

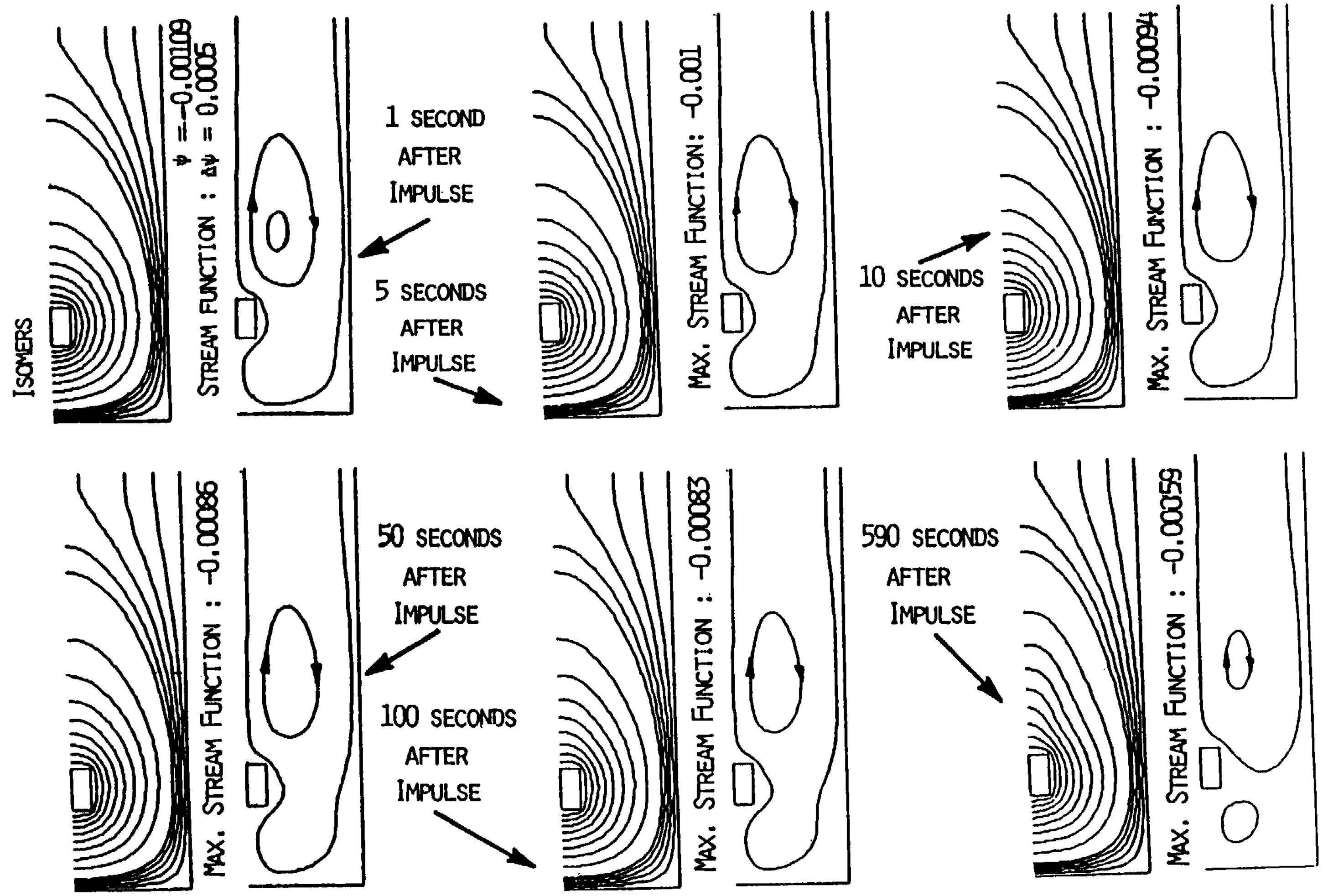


Figure 5. The system response to a 1-s impulse excitation of 10^{-8} g.

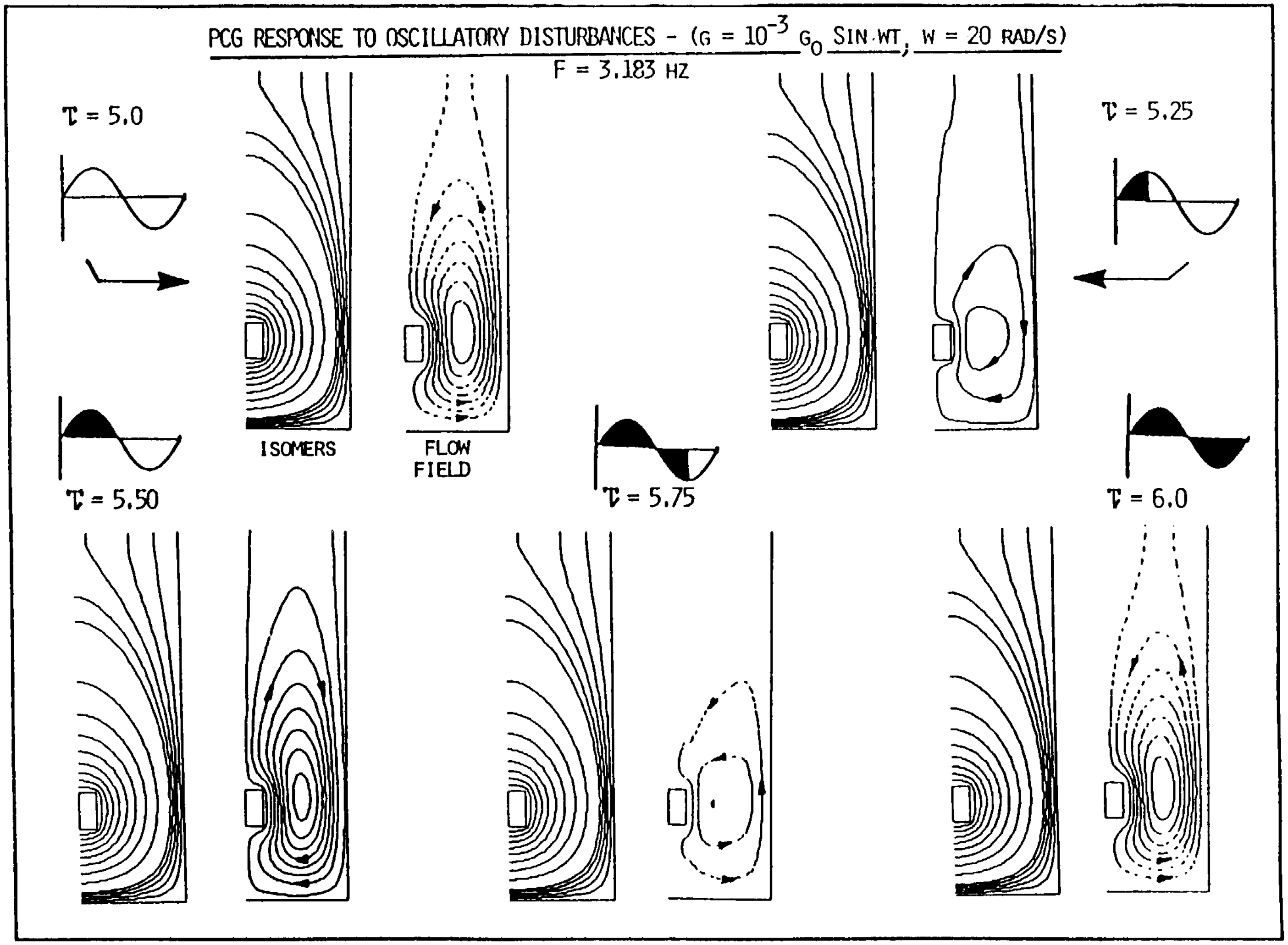


Figure 6. The system response characteristics to an oscillatory disturbance frequency of 3.183 Hz and amplitude, 10^{-3} g.

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Extended Abstract

LOW-GRAVITY ELECTRDESPOSITION AND GROWTH OF POLYMER THIN FILMS WITH LARGE THIRD-ORDER OPTICAL NONLINEARITIES BY ELECTROCHEMICAL PROCESSES FOR DEVICES: THIOPHENE-BASED POLYMERS

Benjamin G. Penn
Space Science Laboratory
NASA Marshall Space Flight Center
Huntsville, AL 35812

and

Clyde Riley
University of Alabama in Huntsville
Department of Chemistry/Materials Science
Huntsville, AL 35899

It has been proposed that NLO thin film properties may be improved by low-gravity processing. Strong candidates for NLO thin film applications are the polythiophenes. Polymeric thiophenes are attractive materials due to their ease of preparation, stability, and high $\chi^{(3)}$.[1-5] A simple and convenient method for preparation of polythiophenes is electrochemical oxidation. We will apply some of our experience and lessons learned in low-gravity metal, metal/cermet electrodeposition to improve the quality of polythiophene(s) thin films. In low gravity electrodeposition of Ni at a high rate on an Au substrate often results in the production of an x-ray nondiffracting surface. Cobalt metal deposition does not give this result nor does Ni when deposited similarly on a glassy carbon substrate.[6,7] Co/Ni alloy composition produced during electrodeposition is strongly dependent upon the amount of convection. Codeposition of neutral inert cermets with metals is influenced significantly by the presence of gravity and the size of the cermets. Tracks left in the 1-g surfaces by unsuccessful particle occlusion indicate suspension of the large particles is not the only reason for poor volume percentages of the larger particles in the deposits. All size particles are more homogeneously distributed in the deposits in low-gravity electrocodeposition than in 1-g. Low gravity gives larger volume percentages for the larger particles in the deposits, while 1-g gives larger volume percentages for the smaller particles. Intermediate size particles give mixed results. The experimental cells were constructed with flat electrode end plates such that 1-g bench reference electrodepositions could be carried out at various orientations with respect to gravity. A series of bench studies using similar designed cells are suggested so that convection modification can be applied to electrochemical thin film preparation. Convection effects can then be coupled with other parameter variations in current, temperature, concentration, solvent, electrolyte, and anode substrates to optimize the properties of NLO thin films before resorting to low-gravity processing.

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Extended Abstract

POLYDIACETYELENE THIN FILMS FOR NONLINEAR OPTICAL APPLICATIONS

Mark S. Paley, USRA
NASA Marshall Space Flight Center
Huntsville, AL 35812

One very promising class of organic compounds for nonlinear optical (NLO) applications are polydiacetylenes, which are novel in that they are highly conjugated polymers which can also be crystalline.[1] Polydiacetylenes offer several advantages over other organic materials: because of their highly conjugated electronic structures, they are capable of possessing large optical nonlinearities with fast response times; because they are crystalline, they can be highly ordered, which is essential for optimizing their NLO properties; and, last, because they are polymeric, they can be formed as thin films, which are useful for device fabrication. We have actively been carrying out ground-based research on several compounds of interest.

Polydiacetylenes are prepared by synthesizing diacetylene monomers, growing crystals or thin films of the monomers, and, then polymerizing these monomers, usually in the solid state, by exposure to UV light or g-radiation.[2] Because this can be a difficult and time consuming process, we have developed computational modeling methods to calculate the nonlinear optical properties of diacetylene monomers, and predict their ability to undergo polymerization in the solid state.[3] Using geometry optimized monomer pairs, semiempirical AM1 calculations were carried out to estimate the crystal packing parameters of several known monomers, and trends in these results were used to develop a predictive tool for solid state polymerizability. We tested this model by synthesizing and characterizing two previously unknown diacetylene derivatives of pyrrole, whose differing behavior was successfully predicted by the model. Such computational modeling is of great value for saving labor by screening potentially interesting compounds from others, and is essential for carrying out the search for new compounds in a pedagogical fashion.

We have also been investigating a polydiacetylene derivative of MNA, a well-known NLO material, for both second- and third-order NLO applications. Computations performed on this compound indicated that it should have large optical nonlinearities, and that it should polymerize in the solid state. We have synthesized this compound, and prepared thin crystalline films by vapor deposition growth that show good second-harmonic generation. Because epitaxial growth is often not possible for diacetylenes,[4] the effects of ordered polymer substrates such as teflon on the orientation and NLO properties of these films is being investigated.[5] Indeed, we have found that films grown onto oriented teflon exhibit greater ordering and 8 times greater SHG than those grown onto quartz glass under identical conditions.[6]

Additionally, we have developed a novel solution polymerization technique to prepare thin films with very high optical quality.[7] Such films turn out to exhibit outstanding third-order NLO behavior; for degenerate 4-wave mixing at 532 nm they give excellent phase conjugate reflectivities of 40% with $\chi^{(3)}$ values on the order of 10^{-4}. This result is very exciting; it demonstrates the tremendous potential of polydiacetylenes as NLO materials. We intend to develop this method further and attempt to use techniques such as electric field poling to induce orientation into the films.

Ultimately, once conditions have been optimized on the ground, we wish to study the effects of the microgravity environment on the growth of polydiacetylene thin films. It is known that gravitational effects, primarily buoyancy driven convection, can be detrimental to both crystallization and polymerization processes. Experimental results on physical vapor transport growth of phthalocyanins, another organic material of interest for NLO, have demonstated that microgravity growth yields films with improved ordering and differrent crystal morphologies than films grown in 1-g.[8] We intend to carry out similar flight experiments to understand the role of convection in both vapor and solution growth of polydiacetylene thin films.

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Extended Abstract N94-24348

CRYSTAL GROWTH OF ORGANICS FOR NONLINEAR OPTICAL APPLICATIONS

N. B. Singh and R. Mazelsky
Westinghouse Science & Technology Center
1310 Beulah Road
Pittsburgh, PA 15235

We have extensively studied[1-3] the crystal growth and characterization of organic and inorganic nonlinear optical materials. For example, inorganic crystals such as thallium arsenic selenide have been studied in our laboratory for several years and crystals in sizes over 2.5 cm in diameter are available. Organic crystals are suitable for the ultraviolet and near infrared region, but are relatively less developed than their inorganic counterparts. Very high values of the second-harmonic conversion efficiency and the electro-optic coefficient have been reported [4] for organic compounds. We have grown single crystals of a binary organic alloy based on m.NA and CNA and observed higher second harmonic conversion efficiency than the values reported for m.NA.

Crystals were grown in a sealed quartz ampoule in the Bridgman geometry. We used an 11-mm i.d. tube attached with a 4×4×12 mm rectangular seed tube as the ampoule. A two-zone glass furnace was designed employing silicone oil and ethylene glycol as heat transfer media. These liquids do not mix and maintain sharp phase boundaries. Silicone oil works as the hot zone, and ethylene glycol acts as the cold zone. The temperature was controlled within ±0.5 K. The translation rate of the ampoule was controlled with a motor attached to a reduction gear.

The transmission was studied at different locations along the crystal. We did not observe any difference in the transmission characteristics. This was confirmed by examining the bulk distortion in an 8 mm thick parallel polished slab with and without a grid also. This indicated that there was no gross compositional inhomogeneity in the crystal.

The second harmonic efficiency test result is summarized as follows: We used a beam of 1.5 mm diameter, 10 ns pulse length and wavelength at 1.06 μm. The input energy was 0.3 mJ, peak power density was 1.7 MW/cm^2 and the test crystal was 2 mm thick. Because the m.NA-CNA samples were fabricated with the polished surfaces parallel to the b-plane, only a limited range of orientations inside the crystal could be probed with the laser beam. To help overcome this problem, a fixture was designed. This permits the material to be suspended in an index-matching fluid. The fixture allows the sample to be rotated over a wide range of angles with respect to the incident laser beam.

The orientation of the crystal (b-plane) was chosen because the crystal has a natural tendency to cleave along this plane. For m.NA, type I phase matching can be achieved in the c-b plane at an angle of 54° to the c-axis. This angle for CNA is 43° for type I phase matching. The refractive index for the m.NA-CNA mixtures of different composition is not available in the literature, but the studies on pure m.NA and CNA show that the type I phase matching angle would be between 43° and 54° range from c-axis on the b-plane. As discussed earlier, the crystal was rotated over a wide range of angles with respect to the incident beam. Green light (0.53 μm) reflects in all the directions indicating substantial amounts of scattering due to defects in the crystal. In spite of large scattering, we were able to measure a phase matched output in a collimated output beam at 0.53 μm at approximately the expected phase matching angle. The output was 0.023 mJ at 0.53 μm for an input energy of 0.3 mJ (1.7 MW/cm^2) at 1.06 μm, corresponding to a conversion efficiency of 7.7% in a 2 mm thickness of crystal.

The effective nonlinear coefficient, d_{eff}, from the measured data was determined by the equation:

$$\eta = \tanh^2\left[\left(2\mu_o^{3/2}\varepsilon_o^{1/2}\frac{\omega^2}{n^3}d_{eff}^{\,2}L^2 I\right)^{1/2}\right] \quad (1)$$

where η is the efficiency, L is the crystal length, I is the pump beam intensity, ω is the angular frequency, and n is the refractive index. Using the values of experimental parameter, we calculated that d_{eff} was 14 pm/V. This value should be considered as a lower limit considering the amount of scattering in the crystal. In spite of large scattering in the crystal, this d_{eff} value is higher than the measured value for pure m.NA. Equation (1) takes into account the depletion of the pump beam. Inserting the modest pump intensity, 1.7 MW/cm^2, the value used in the present experiment, we see that 1 cm long crystal should be able to produce a conversin efficiency over 78%. For the laser damage studies, we exposed the crystals to 1.06 μm radiation at 1 mJ pulse (10 Hz repetition rate, 0.35 mm spot size, and 10-ns pulse) corresponding to 100 MW/cm^2 power density. For an exposure to 100 pulses, the crystal did show signs of deterioration.

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N94-24349

Extended Abstract

NONLINEAR OPTICAL THIN FILMS

Thomas M. Leslie
Chemistry Department
University of Alabama at Huntsville
Huntsville, AL 35899

This work presents a focused approach to development and evaluation of organic polymer films for use in optoelectronics. The issues and challenges that will be addressed include: (1) material synthesis, purification, and the tailoring of the material properties; (2) deposition of uniform thin films by a variety of methods; (3) characterization of material physical properties (thermal, electrical, optical, and electro-optical); and (4) device fabrication and testing. Photonic materials, devices, and systems have been identified as critical technology areas by the Department of Commerce and the Department of Defense. This approach offers strong integration of basic material issues through engineering applications by the development of materials that can be exploited as the active unit in a variety of polymeric thin film devices.

Improved materials have been developed with unprecedented purity and stability. We can tailor and control the absorptive properties to provide significant improvement in propagation losses and nonlinear performance. Furthermore, the materials have been incorporated into polymers that are highly compatible with fabrication and patterning processes for integrated optical devices and circuits. By simultaneously addressing the issues of materials development and characterization, keeping device design and fabrication in mind, we have overcome many obstacles to implementation of these polymeric materials and devices into systems. We intend to considerably improve the upper use temperature, poling stability, and compatibility with silicon-based devices. The principal device application that has been targeted is a linear electro-optic modulation etalon.

Organic polymers need to be properly designed and coupled with existing integrated circuit technology to create new photonic devices for optical communication, image processing, other laser applications such as harmonic generation, and eventually optical computing. The progression from microscopic sample to a suitable film-forming material in a working device is a complex, multifaceted endeavor. It requires close attention to maintaining the optical properties of the electro-optic active portion of the polymer while manipulating the polymer structure to obtain the desired secondary polymer properties.

This work represents a focused approach integrating: (1) material synthesis, purification, and tailoring of the optical properties of the active unit; (2) formation of polymers with secondary properties suitable for use in device processing; (3) characterization of material physical properties (film formation, thermal, electrical, optical, and electro-optical); and (4) device fabrication and testing in collaboration with the Electrical Engineering Department.

Complex film structures, such a waveguides (Mach-Zender interferometers) and interferometric cavities (etalons) could be used to provide switches and free-space optical interconnects among processors in advanced general purpose multiprocessor supercomputers. Fabricated on the surface of integrated circuits, such structures may find applications in areas such as optical communications and the optical interconnection of multiprocessor systems.[1,2] The ability to create thin-film optical modulators would allow for the conversion of electrically stored information to optical information which could be broadcast to receiving arrays. It is for this reason that a thin film interferometric etalon device has been chosen to first test the material properties.

The objective of this research is to synthesize materials that will allow us to build stable, thin-film based NLO devices. The first device we have chosen to fabricate is a tunable etalon. This will allow us to determine the electro-optic coefficients and processing characteristics of a polymer and crystalline materials of similar structure. This allows for the direct comparison of polymeric-based devices with existing organic NLO materials and their inorganic counterparts.

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Extended Abstract N94-24350

FEASIBILITY STUDY: MONODISPERSE POLYMER PARTICLES CONTAINING LASER-EXCITABLE DYES

John W. Vanderhoff and Jing-Hong Chen
Emulsion Polymers Institute and Department of Chemistry
Lehigh University
Bethlehem, PA 18015

OBJECTIVE

The objective of this work was to determine the feasibility of the preparation of monodisperse spherical poly(methyl methacrylate) and polystyrene particles that contain laser-excitable dyes in the size range 0.1 μm to 1 cm. Poly(methyl methacrylate) and polystyrene were chosen because of their excellent optical properties. The sphericity was required for uniformity of spectral output of re-irradiated light from the dye-containing particles. The monodispersity was required to give each particle the same optical properties when exposed to laser light.

INTRODUCTION

Preparation of Monodisperse Spherical Particles

Both poly(methyl methacrylate) and polystyrene are hard, brittle, rigid polymers with good optical clarity and T_g values of 100 °C. Earlier, we have prepared monodisperse particles of polystyrene or styrene derivatives of 0.1 μm to 1 cm size using the following types of polymerization:

1. Submicroscopic polystyrene particles of 0.1 to 2 μm size by successive seeded polymerization using conventional emulsifiers (e.g., aerosol MA).
2. Microscopic polystyrene particles of 2 to 200 μm size by successive seeded polymerization using the three-component emulsifier system developed for use in the MLR flight experiments.
3. Microscopic polystyrene particles of 1 to 10 μm size by a single-step dispersion polymerization and larger sizes up to 20 μm by successive seeded polymerization using these latexes as a seed.
4. Macroscopic polystyrene and poly(tert-butylstyrene) particles of size up to 1 cm by seeded suspension polymerization.

We have also prepared monodisperse poly(methyl methacrylate) particles using the following types of polymerization:

1. Submicroscopic particles of 0.1 to 2 μm size by successive seeded polymerization using conventional emulsifiers.
2. Microscopic particles of 2 to 10 μm size by successive seeded polymerization using the three-component emulsifier system developed for use in the MLR flight experiments.
3. Microscopic particles of 2 to 10 μm size by dispersion polymerization.

Conventional suspension polymerization of methyl methacrylate gives particles of 0.1 to 1 mm size. Larger sizes can be made by seeded suspension polymerization using the techniques developed earlier for tert-butylstyrene (i.e., swelling the suspension beads with monomer, followed by dispersion in water and polymerization).

Thus, several different techniques can be used to prepare monodisperse polystyrene and poly(methyl methacrylate) particles of 0.1 µm up to 1 cm size.

Incorporation of Dyes

Several methods have been developed to incorporate oil-soluble dyes into latex particles.

1. Physical occlusion in the particles, e.g., by swelling the particles with a solution of the dye in a water-immiscible solvent that is a good solvent for the polymer and removing the solvent by distillation or extraction, leaving the dye behind.
2. Copolymerization of a monomer containing the dye molecule, e.g., by covalent binding of the dye molecule to styrene or methyl methacrylate, followed by copolymerization.
3. Post-reaction to covalently bind the dye to functional groups on the latex particle, e.g., covalent binding of carboxyl groups in the dye molecule with carboxyl groups on the latex particle by water-soluble carbodiimides.

We have developed a method to incorporate dyes into latex particles by physical occlusion, as well as a method to covalently bind carboxyl-containing dyes to latex particles containing carboxyl groups by water-soluble carbodiimide and amine-containing dyes to latex particles containing aromatic amine groups by diazotization.

The following toluene-soluble laser-excitable dyes have been proposed for incorporation by physical occlusion or post-reaction with the polystyrene and poly(methyl methacrylate) particles:

1. PPO
2. bis-MsB
3. alpha-NPO

The following laser-excitable dyes have been proposed for incorporation by copolymerization of a monomer containing the dye molecule:

1. Coumarin 4
2. Coumarin 120
3. Coumarin 334
4. Rhodamine B

Experimental Approach

The following experimental approach was proposed for the feasibility study:

1. Selection of four different particle size ranges for this work:

   a. Submicroscopic particles of 0.1 to 0.3-µm size
   b. Small microscopic particles of 1 to 5 µm size

c. Larger microscopic particles of 10 to 100 μm size
d. Macroscopic particles of size up to 1 cm

2. Preparation of monodisperse poly(methyl methacrylate) and polystyrene particles in each of the four size ranges using the following apparatus:

a. Capped bottles
b. Stirred flasks
c. The rotating-cylinder reactor that was developed to obviate the effect of gravity

The degree of monodispersity required for the uniform irradiation from the particles containing laser-excitable dyes is not known precisely; however, the submicroscopic particles prepared thus far have coefficients of variation of 0.5-1.0%; the small microscopic particles, 2.0-2.5% (except for the particles made in space, which have coefficients of variation of 1.0% or less); the large microscopic particles, 2.0-2.5%; and the macroscopic particles, ca. 15% for those prepared by "limited coalescence" suspension polymerization.

3. Selection of three different dyes for incorporation into the particles by physical occlusion, according to the desired optical properties of the dye-containing particles, the solubilities of the dyes in toluene (or other water-immiscible good solvents for the polymer) and water.

4. Incorporation of these dyes into particles of the four different size ranges by physical occlusion, either by mixing a solution of the dye in a water-immiscible solvent for the polymer, swelling the particles with the dye solution and then removing the solvent by distillation or extraction, or dissolving the dye in the monomer before polymerization.

5. Incorporation of the dyes by copolymerization or post-reaction with functional groups of the latex particles will be assessed if the particles containing physically occluded dye are not suitable. One possible problem with both methods is that the spectral properties of the dye may be altered by its covalent binding.

6. Preparation of other laser-excitable dye-containing particles by copolymerization or post-reaction with functional groups of the latex particles, according to the results of the evaluation of the first series of dyed particles.

7. Assessment of the sphericity of the dye-containing particles. The intended application of the dyed particles requires that the re-irradiation excited by the laser light be uniform in all directions so the particles must be perfect spheres. Latex particles are considered to be perfect spheres; however, the 10 μm particles prepared in space were more perfect spheres than their ground-based controls. The sphericity of the particles results from the interfacial tension between the particles and the aqueous medium during polymerization; thus, it is expected to decrease with decreasing interfacial tension and increasing particle size. Therefore, the sphericity of the submicroscopic particles may be better than that of the macroscopic particles.

8. Improvement of the sphericity of the particles, if necessary, by heating the aqueous dispersion of the particles to 120 °C, well above T_g. The interfacial tension acts as a stretched elastic membrane to minimize the interfacial area and thus make the particles more perfect spheres. The interfacial tension should be maximized before heating by removal of the emulsifiers and stabilizers.

9. Submission of samples of the dye-containing particles to NASA for evaluation, correlation of the results, formation of conclusions, and submission of recommendations for future work to NASA in a final written report.

PREPARATION OF MONODISPERSE POLYMER PARTICLES

Thus far, we have prepared poly(methyl methacrylate) and polystyrene latexes with the requisite monodispersity and sphericity using emulsion polymerization, dispersion polymerization, and suspension polymerization.

Emulsion polymerization

Monodisperse polystyrene and poly(methyl methacrylate) latex particles with diameters of about 0.1 µm were prepared by a single emulsion polymerization using the polymerization recipe given in Table 1 (Dezelic et al., Macromolecular Syntheses **6** 85-89 (1977)).

Table 1. Emulsion Polymerization of Styrene

Ingredient	Parts by Weight
Styrene	20.00
Aerosol MA Emulsifier	0.750
Potassium Persulfate Initiator	0.100
Sodium Bicarbonate Buffer	0.125
Water	80.00

The reactants were charged to a bottle, which was capped and shaken for 30 min at room temperature to give the emulsion and then polymerized by rotating end-over-end at 32 rpm for 7 hours at 80 °C. Figure 1 shows a scanning electron micrograph of this latex that shows the narrow distribution of particle sizes. This type of emulsion polymerization was the simplest approach to prepare monodisperse latexes, and it was used to prepare polystyrene particles for the incorporation of laser-excitable dyes. The next step was to demonstrate the effect of emulsifier and temperature on the particle size distribution. Also, this latex was to be used as a seed latex for the successive seeding emulsion polymerizations.

Dispersion Polymerization

Polystyrene and poly(methyl methacrylate) particles of 2.5-8.0 µm size were prepared by a single dispersion polymerization using the recipe given in Table 2.

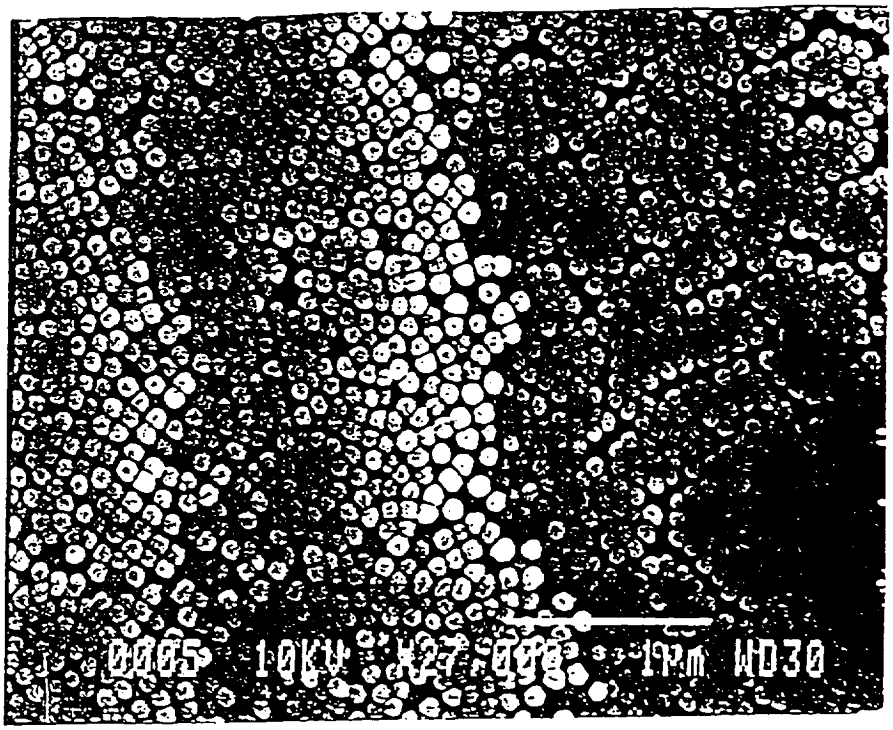


Figure 1. Scanning electron micrograph of polystyrene latex made using the recipe given in Table 1.

Table 2. Dispersion Polymerization of Styrene

Ingredient	Parts by Weight
Styrene	25.00
Ethanol	75.00
Poly-N-Vinyl Pyrrolidone (PVP K-30)	3.00
2,2'-Azobisisobutyronitrile	0.25

The polymerizations were carried out in capped bottles rotated end-over-end at 32 rpm for 24 hours at 70 °C. The particles were allowed to settle, and the ethanol supernatant layer was decanted and replaced with water. This sedimentation-decantation was repeated several times until the ethanol was replaced by water, to give a 20% dispersion of the polystyrene particles. The average particle size of the first polystyrene sample (PS01) was 5.7 μm by scanning electron microscopy. Figure 2 shows a scanning electron micrograph of this sample that shows the uniformity of the particle size distribution.

Another styrene polymerization (PS-2) was carried out using the same recipe except that the 2,2'-azobisisobutyronitrile was increased to 0.400 parts. The reaction conditions and post-

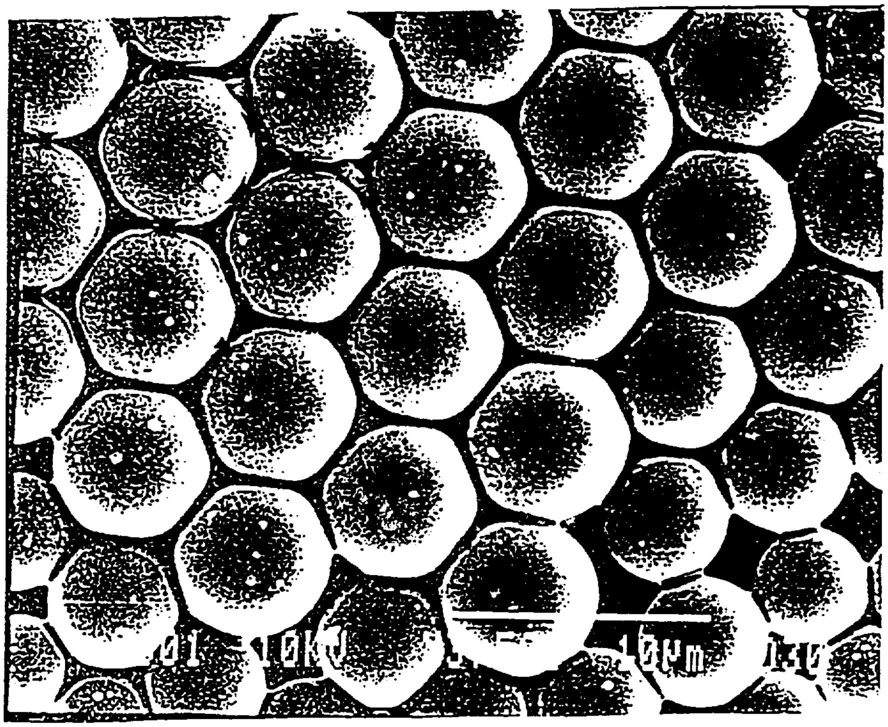


Figure 2. Scanning electron micrograph of polystyrene latex PS–1 made by dispersion polymerization.

polymerization recovery procedures were the same as with Run PS-1; the final percent solids was 50%, and the average particle size was 8.0 µm. Figure 3 shows a scanning electron micrograph of this sample that shows the uniformity of the particle size distribution.

A poly(methyl methacrylate) dispersion polymerization (MMA01) was also carried out using the polymerization recipe given in Table 3.

Table 3. Dispersion Polymerization of Methyl Methacrylate

Ingredient	Parts by Weight
Methyl Methacrylate	10.00
Methanol	85.90
Poly-N-Vinyl Pyrrolidone (PVP K-30)	4.00
2,2'-Azobisisobutyronitrile	0.10

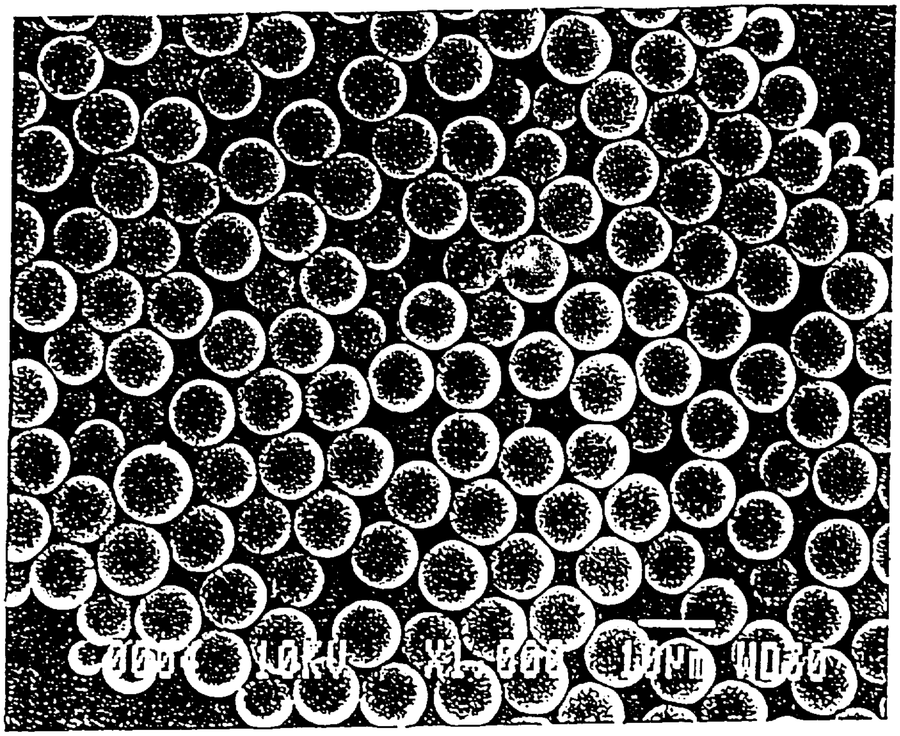


Figure 3. Scanning electron micrograph of polystyrene latex PS–2 made by dipersion polymerization.

The polymerization was carried out in a capped bottle, which was rotated end-over-end at 32 rpm for 48 hours at 55 °C. The particles were washed with water by repeated sedimentation-decantation to replace the methanol with water and give a 20% solids dispersion. The average particle size was 3.6 micrometers by scanning electron microscopy.

These experiments were repeated to prepare 120 g polystyrene particles and 80 g poly(methyl methacrylate) particles. These polymerizations gave not only microscopic particles of polystyrene and poly(methyl methacrylate), but also some particles which were smaller than the main distribution. These smaller particles were removed by the repeated sedimentation-decantation of the cleaning process. The poly(methyl methacrylate) particles were more difficult to clean in this way than the polystyrene particles.

Suspension Polymerization

Suspension polymerization is both an art and a science, a science in the sense that the polymerization follows the principles of radical chain polymerization, and an art in the sense that a recipe is used for the polymerization, and the skill of the practitioner can affect the outcome of the polymerization. A water-immiscible monomer is dispersed in water using a suspending agent and polymerized using an oil-soluble initiator. The function of the suspending agent is to stabilize the droplets during polymerization; if the droplets do not coalesce during polymerization, the final bead size distribution is essentially the same as that of the droplets. The droplet size distribution is determined by the choice of the suspending agent and the agitation conditions. The bead size distributions produced are generally broad; however, narrower size distributions can be prepared using "limited coalescence" suspension of polymerization or seeded suspension polymerization.

For systems where the monomer is a good solvent for the polymer (as is the case for styrene and methyl methacrylate), the critical stage of a suspension polymerization is the "sticky" stage, which occurs in the conversion range of 20-60% for styrene and methyl methacrylate. Below 20% conversion, droplets that coalesce can be redispersed by the mechanical shear; above 60% conversion, the collisions between the beads are elastic, and coalescence does not occur; between 20% and 60% conversion, however, the droplets are still fluid enough to coalesce, but their viscosity is too great for redispersion to a smaller size. The result is that coagulation of the beads is most likely to occur during this sticky stage.

There are two general types of suspending agents: (1) water-soluble polymers, such as methylcellulose, and (2) colloidal particles that have the proper hydrophilic/hydrophobic balance to adsorb in the oil/water interface, such as tricalcium phosphate. Actually, both types may be particulate in nature.

The first suspension polymerization of methyl methacrylate (MMA-S1) used the recipe given in Table 4 and was carried out in a capped bottle. The Methocel K4M hydroxylpropylmethylcellulose (Dow Chemical) suspending agent, anhydrous disodium phosphate buffer, and stearic acid lubricant were dissolved or dispersed in the water, and the methyl methacrylate containing the dissolved benzoyl peroxide initiator was added. The vapor space was flushed with nitrogen, and the bottle was capped and shaken to form the suspension. The capped bottle was then rotated end-over-end at 32 rpm for 6 hours at 80 °C. The beads were allowed to settle, and the supernatant layer was decanted and replaced with water. This sedimentation/decantation was repeated several times until the suspending agent was removed. The average bead size by scanning electron microscopy was 40 μm; the solids content was 20%.

Table 4. Suspension Polymerization of Methyl Methacrylate

Ingredient	Parts by Weight
Methyl Methacrylate	23.60
Methocel K4M Suspending Agent	0.300
Anhydrous Disodium Phosphate Buffer	0.440
Stearic Acid	0.488
Benzoyl Peroxide Initiator	0.600
Water	77.00

Another suspension polymerization (MMA-S2) used the same recipe except that the 0.150 parts Methocel K4M suspending agent was replaced by 0.150 parts Na Polyacrylate ND-445 (Rohm & Haas), and the 0.244 parts stearic acid, by 0.366 parts. The beads were bean-shaped (prolate spheroids), about 5 mm long and about 2 mm around. These bean-shaped beads are generally produced in polymerizations which have only marginal colloidal stability.

INCORPORATION OF DYES BY PHYSICAL OCCLUSION

The oil-soluble laser-excitable PPO, alpha-NPO, and bis-MSB dyes were incorporated into polystyrene and poly(methyl methacrylate) latex particles by physical occlusion. A solution of the dye in an organic solvent swelled the latex particles by physical occlusion. A solution of the dye in an organic solvent (cyclohexane, toluene, or dioxane) was added to the latex, and the mixture was stirred gently and then allowed to stand. The solvent swelled the latex particles, taking the dye along with it. The solvent was then removed by evaporation under vacuum at room temperature, leaving the dye behind in the latex particles. Table 5 gives the proportions used in these experiments and the dye concentrations in the particles.

Table 5. Physical Occlusion of Dyes in Polystyrene Latex Particles

Latex Sample	Dye Solution (solids, %)	D_n (μm)	Dye	Solvent	Concn. (g/g polym)	Water (%)
PSD-D1	10.6	2.6	bis-MSB	dioxane	6.2×10^{-3}	89.4
PSD-D2	10.6	2.6	bis-MSB	25% dioxane	6.2×10^{-3}	64.4
PSD-D3	20.0	5.7	PPO	dioxane	8.8×10^{-3}	80.0
PSD-T4	20.0	5.7	PPO	toluene	8.8×10^{-3}	80.0
PSD-C5	20.0	5.7	PPO	cyclohexane	8.8×10^{-3}	80.0

These preliminary results showed that the concentration of the laser-excitable dyes in the particles was too low, however. These dyes have no functional groups, and their solubilities in organic solvents such as dioxane and toluene are low. Our experimental results, however, showed that water-soluble dyes with ionic groups can be incorporated into polystyrene particles using this physical occlusion method.

In all of these experiments, the dropwise addition of the organic solvent solution of the laser-excitable dye to the latex gave a precipitate. A control experiment showed that the organic solvent solution of the dye precipitated upon addition to water. This indicated that the dye was precipitated by water from the mixture before it was absorbed by the latex particles, leaving only a low concentration in the particles. Therefore, the dyes were incorporated into the particles by addition to the monomer before polymerization.

EMULSION AND DISPERSION POLYMERIZATION OF STYRENE/DYE MIXTURES

An improved method to incorporate the laser-excitable dyes into polystyrene latex particles was by physical occlusion during polymerization. The PPO, bis-MSB, and alpha-NPO laser-excitable dyes were similar to styrene in that their structures contained benzene rings, and they were soluble in styrene. Moreover, our experiments showed that these dyes did not interfere with the polymerization of styrene by free radical initiators in emulsion or dispersion polymerization, so that the dyes were merely physically occluded in the particles.

The emulsion polymerization of styrene-containing dissolved laser-excitable PPO dye was carried out using the recipe given in Table I, except that 0.200 parts PPO dye were added, and 78.7 parts water were used instead of the 80.0 parts of Table I. The aerosol MA emulsifier and sodium bicarbonate suffer were dissolved in the water, and the styrene monomer containing the dissolved PPO dye was added with stirring. The resulting emulsion was stirred for 4 hours at room temperature, the potassium persulfate initiator was added, and the stirring was then resumed for another 4 hours at room temperature. The emulsion was then placed in a capped bottle and rotated end-over-end at 32 rpm for 7 hours at 70 °C. The latex contained about 20% coagulum, which was attributed to the precipitation of the dye during the polymerization. The latex was cleaned by serum replacement with distilled water. The average particle size by photon correlation spectroscopy (Nicomp) was 0.085 micrometers or 85 nm.

Other laser-excitable dyes were incorporated into polystyrene latex particles by dissolving the dyes in the monomer before polymerization. The polymerizations were carried out in capped bottles, which were tumbled end-over-end in a thermostated bath. Table 6 gives the recipes used and the results obtained.

Table 6. Emulsion Polymerization of Styrene/Dye Mixtures

Ingredient	PSD-E1	PSD-E2	PSD-E3
Styrene	20.0	20.0	20.0
Laser-Excitable Dye	0.200	0.100	0.100
	alpha-NPO	bis-MSB	PPO
Aerosol MA Emulsifier	0.750	0.750	0.750
Potassium Persulfate	0.100	0.100	0.750
Sodium Bicarbonate	0.125	0.125	0.125
Water	80.0	80.0	80.0
Polymerization Conditions			
Temperature (°C)	70	60	60
Time (hours)	7	24	24
Tumbler Speed (rpm)	32	16	16
Particle Size (Nicomp)			
Number Average (nm)	274	230	71
Coefficient of Variation (%)	18.5	20.9	25.4
g dye/g Latex, x 10^3*	1.587	0.989	0.989

*Sample PSD-E3 was cleaned by serum replacement with distilled-deionized water; after cleaning, the particles contained 1.587×10^{-3} g dye/g polymer as determined by ultraviolet spectrophotometry; samples PSD-E1 and PSD-E2 contained 0.989×10^{-3} g dye/g polymer based on the recipes.

The particles of Samples PSD-E1 and PSD-E2 were more uniform than was indicated by the measured coefficients of variation. Dried films of these latexes showed, respectively, the turquoise/gold and pink/green iridescent color combinations, as would be expected for monodisperse particles of the measured average particle diameters. Sample PSD-E3 showed no iridescent colors, as would be expected for its small particle size.

A dispersion polymerization of styrene containing dissolved laser-excitable PPO dye was carried out using the recipe given in Table 7. The polymerization was carried out in a capped bottle, which was rotated end-over-end at 32 rpm for 24 hours at 70 °C. The particles were washed with water by repeated sedimentation-decantation to replace the ethanol with water, to give a 20% solids dispersion. The average particle size was determined by scanning electron microscopy, and the presence of the dye was determined by ultraviolet spectrophotometry (see following section).

Table 7. Dispersion Polymerization of Styrene/Dye Mixtures

Ingredient	Parts by Weight
Styrene	25.00
PPO-Laser-Excitable Dye	0.250
Ethanol	75.00
Poly-N-Vinyl Pyrrolidone (PVP K-30)	3.00
2,2'-Azobisisobutyronitrile	0.250

SUSPENSION POLYMERIZATION OF METHYL METHACRYLATE/DYE MIXTURES

The laser-excitable dyes were incorporated into poly(methyl methacrylate) beads by dissolving the dye in the monomer before polymerization. Table 8 gives the recipes used for these suspension polymerizations. The use of Methocel K4M suspending agent in combination with stearic acid gave small beads, 30-50 µm in diameter. The combination of Methocel K4M/stearic acid mixture with the Na Polyacrylate ND-445 (and also with stearic acid) gave a tenfold larger size, 0.3-0.6 mm.

Optical microscopy of Sample PMMA-S1 showed that its bead size distribution was broad, in the 30-50 µm range. Similarly, Samples PMMA-S8 and PMMAD-S9 had broad bead size distributions, with diameters in the 0.3-0.6 mm range. Narrower fractions of 150-212 and 212-250 µm size range were separated from these samples by sieving. The incorporation of the laser-excitable dye had no effect on the polymerization. These sieved fractions were omitted from the samples of the suspension beads submitted to NASA because they became fused during drying.

Therefore, we decided to repeat the preparation of PMMAD-S9, but this time with the addition of a crosslinking monomer such as ethylene glycol dimethacrylate to the recipe. These crosslinked beads were to be separated into narrow size fractions by sieving, and these narrow fractions were to be swelled with monomer and polymerized, to give more uniform larger beads of up to 1-3 mm diameter.

Table 8. Suspension Polymerization of Methyl Methacrylate/Dye Mixtures

Ingredient	Parts by Weight PMMA-S1	 PMMA-S2	 PMMAD-S9
Methyl Methacrylate	23.6	23.6	23.6
Methocel K4M	0.300	0.200	0.200
Na Polyacrylate	---	0.200	0.200
Disodium Phosphate	0.440	0.440	0.440
Stearic Acid	0.488	0.488	0.488
Dye (Bis-MSB)	---	---	0.100
Benzoyl Peroxide	0.600	0.600	0.600
Water	77.00	77.00	77.00
Bead Size (μm)	30-50	---	---
Bead Size (mm)	---	0.3-0.6	0.3-0.6

SEEDED SUSPENSION POLYMERIZATION OF METHYL METHACRYLATE

Earlier Work With Tert-Butylstyrene

Our preparation of large beads by suspension polymerization was based on the seeded suspension polymerizations of tert-butylstyrene carried out by M.H.J. "Jimmy" Kang (Ph.D. dissertation, 1986), which has not yet been published; therefore, this work is recounted in some detail here. He prepared large poly(tert-butylstyrene) beads crosslinked with 0.05% divinylbenzene of 3–10 mm diameter. First, smaller beads were prepared by conventional suspension polymerization. These beads were cleaned and sieved into fractions of narrow size distribution. The swollen beads were filtered from the excess monomer, suspended in water, and polymerized to form the larger beads. The conversion of the absorbed monomer was quantitative. Two to three swelling/polymerization cycles were needed to prepare 3-5 mm diameter beads.

The tert-butylstyrene monomer (Dow Chemical) was washed with 10% sodium hydroxide solution and water, then dried over sodium sulfate. The Methocel K4M hydroxypropylmethylcellulose (Dow Chemical) and cellosize QP-100M hydroxyethylcellulose (Union Carbide) suspending agents were used as received. The sodium hydroxide, sodium sulfate, and sodium bicarbonate (Fisher Scientific) were used as received.

The solution of suspending agent was charged to the 2-liter stirred flask, which was equipped with a reflux condenser and a top-supported four-blade open anchor-type impeller. The impeller was driven by a GT21-18 Heavy-Duty Laboratory Stirrer (G. E. Heller). The loop-like anchor-type impeller was particularly effective for suspension polymerizations. The flask was heated with a heating mantle with a PL-112 Cordtrol Regulator (Glas-Col Apparatus). The temperature was controlled by a solid-state Thermocap Relay (Series 500; Niagara Electron Laboratories). The monomer was added to the flask with stirring to form the suspension. The polymerizations were carried out in a nitrogen atmosphere, except where noted.

The seed beads were swelled by charging them to a bottle, adding the monomer, and tumbling the bottle end-over-end at room temperature. The swollen beads were recovered by filtration, and the excess monomer was separated. The swollen beads were then rinsed with a solution of the suspending agent, suspended in water, and polymerized with stirring.

The seed beads were prepared by conventional suspension polymerization. The tert-butylstyrene monomer containing 0.050% divinylbenzene crosslinking monomer and 0.20% t-butylperoxy-2-ethylhexanoate initiator (half-life 10 hours at 73 °C in benzene, 77 °C in dodecane solution) was mixed with the suspending agent. The suspending agent was Methocel K4M, with or without Cellosize Qp-100M.

Table 9 gives the polymerization recipes and the size distribution of the beads. Run 2047 gave small, uniform beads; Run 3025 gave beads larger than 1 mm in diameter. Both samples were used as seed beads in this work. The 0.076% Cellosize QP-100M concentration was estimated from the manufacturer's technical bulletin to give a viscosity comparable to that of a 0.40% Methocel K4M solution, so that the viscosities of the water phases were about the same.

Table 9. Suspension Polymerization of Tert-Butylstyrene

Parameter	Experiment 2047	Experiment 3025
Monomer/Water Phase Ratio	50/50	10/90
Suspending Agent (% based on water)		
Methocel K4M	0.80	0.40
Cellosize QP-100M	---	0.076
Temperature-Time Schedule	4 hr at 70° + 2 hr at 90°	2 hr at 70° + 4 hr at 90°
Preheating of the Medium	no	yes
Nitrogen Atmosphere	no	yes
Bead Size Distribution (wt.%)	26	1.6
0.0-0.5 mm		
0.5-1.0 mm	74	45
1.0-2.0 mm	--	54

Table 10 gives the surface tension and viscosities of solutions of Methocel K4M hydroxypropylmethylcellulose and Cellosize QP-100M hydroxyethylcellulose. The stability obtained with the Methocel K4M was attributed to its high surface activity, and that obtained with the Cellosize QP-100M, to its thickening of the aqueous phase. Thus, useful suspending agents can be prepared from various combinations of these two suspending agents. The use of a nitrogen atmosphere and the preheating of the suspending agent solution before the monomer was added gave larger beads; this was attributed to the more rapid rise in viscosity of the dispersed phase due to the faster polymerization rate.

Table 10. Comparison of Aqueous Suspending Agent Solutions

Parameter	K4M*	QP-100M**
Surface Tension (1%) (dynes/cm)	44-56	63-69
Viscosity (2%) (cps)	4×10^3	10^5

*Methocel K4M
**Cellosize QP-100M

The crosslinked poly(tert-butylstyrene) seed beads were cleaned, dried, and, where necessary, sieved into fractions of narrow size distribution. Each fraction was swelled and polymerized individually using the same monomer composition as was used for the preparation of the seed beads. This procedure gave final large beads of uniform size. Different fractions were swelled and polymerized using different numbers of cycles to give the same predetermined final size of 3-5 mm. Thus, no seed beads were wasted.

A swelling time of 24 hours was used. Longer swelling times gave deformed beads in a few cases. On the other hand, it was necessary to swell the bead network sufficiently to eliminate the possibility of local stress buildup during polymerization, which would give chipped or cracked beads. The seeded suspension polymerizations were carried out using an organic/water phase ratio of 35/65 or smaller, to prevent overcrowding and to achieve effective heat transfer during polymerization. Typical swelling ratios were 16-18/1, according to the size of the seed beads. Table 11 gives the variation of bead size and size distribution from generation to generation.

SEEDED SUSPENSION POLYMERIZATION OF METHYL METHACRYLATE/DYE MIXTURES

We used the foregoing experiments with tert-butylstyrene as a guide for the seeded suspension polymerization of methyl methacrylate containing laser-excitable dyes. 0.050% Ethylene glycol dimethacrylate was used as the crosslinking monomer, and the Methocel K4M/stearic acid combination in disodium phosphate solution, as the suspending agent. Table 12 gives the recipes used in the seeded suspension polymerizations, and Table 13 gives the bead size distributions produced in these seeded suspension polymerizations. The Methocel K4M, Na Polyacrylate ND-445, disodium phosphate, and stearic acid were dissolved or dispersed in the water and charged to me bottles. The ethylene glycol dimethacrylate, laser-excitable dye, and benzoyl stirring, and the seed beads were added and allowed to swell for 8 hours at room temperature.

Samples S-13 and S-22 were used as the seed beads; these were sieved into narrow-size fractions and swelled in excess monomer; the swollen beads were recovered by filtration, washed with suspending agent solution, and charged to the aqueous phase in the bottles. The bottles were capped and tumbled end-over-end at 32 rpm for 4 hours at 80 °C. The polymerized beads were washed with deionized water and an alcohol/water mixture, and dried at room temperature. These experiments showed that the beads prepared thus far comprise as much as 91% in the 500-1000 µm range. The preparation of beads of 1-3 mm diameter using these as seed beads was started.

Table 11. Seeded Suspension Polymerization of Tert-Butylstyrene

Experiment Bead Diameter (mm)	2047(a)	3042(b)
	wt.% of beads in a given size range	
0.0-1.0	---	24
0.0-0.5	26	---
0.5-1.0	74	24
1.0-2.0	0	76

Experiment Bead Diameter (mm)	3025(a)	3074(c)
	wt.% of beads in a given size range	
0.0-2.8	---	57
0.0-0.5	2	---
0.5-1.0	45	---
1.0-2.0	54	---
2.0-2.8	0	---
2.8-4.8	0	43
>4.8	0	0

Experiment Bead Diameter (mm)	3074-2(d)	3079(e)
	wt.% of beads in a given size range	
2.0-2.8	100	0
2.8-4.8	0	37
>4.8	0	63

(a) Seed beads prepared by conventional suspension polymerization
(b) A second generation, using Sample 2047 as the seed beads
(c) A second generation, using Sample 3025 as the seed beads
(d) A fraction of Sample 3074
(e) A third generation, using Sample 3074-2 as the seed beads

Table 12. Seeded Suspension Polymerization of Methyl Methacrylate/Dye Mixtures

Ingredient	Parts By Weight							
	SW-1	SW-2	SW-3	SW-4	SW-5	SW-6	S-13	S-22
Methyl Methacrylate	23.6	23.6	13.0	11.8	23.6	23.6	23.6	23.6
Methocel K4M	0.20	0.20	0.20	0.20	0.20	0.12	0.20	0.20
Na Polyacrylate*	0.20	----	---	---	0.20	---	---	0.20
Disodium Phosphate	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44
Stearic Acid	0.48	----	---	---	0.48	---	0.48	0.48
EGDMA**	---	----	---	---	----	---	0.118	0.118
Laser-Excitable Dye‡	0.118	0.118	0.118	0.118	0.118	0.118	0.118	0.118
Benzoyl Peroxide‡‡	0.40	0.40	0.40	0.40	0.40	0.40	0.40	---
Water	77.0	77.0	77.0	77.0	77.0	77.0	77.0	77.0
Seed Beads	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00

*ND-445

**Ethylene Glycol Dimethacrylate

‡Alpha PPO SW-3, SW-4, S-13; Bis-MSB SW-1, SW-2, SW-5, SW-6, S-22

‡‡(70%)

Table 13. Size Distribution of Poly(Methyl Methacrylate) Beads

Bead Sizes (μm)	Percent							
	SW-1	SW-2	SW-3	SW-4	SW-5	SW-6	S-13	S-22
<150	2.3	0.6	12.7	1.4	0.3	1.2	27.7	14.4
150-212	2.2	1.4	38.3	1.3	1.2	0.3	21.7	27.7
212-250	1.6	1.7	43.9	0.9	0.5	0.4	8.0	21.1
250-300	3.3	3.3	4.3	1.3	0.6	2.1	14.4	18.2
300-500	27.5	62.4	0.8	37.0	1.4	0.2	18.0	18.4
500-1000	63.1	30.6	----	58.1	91.3	88.7	0.2	0.5
>1000	----	----	----	----	4.7	7.1	----	----
Seed Sizes	250/300	212/250	<106	212/250	300/500	300/500	----	----

DETERMINATION OF DYE CONCENTRATION IN THE PARTICLES

Dye Concentration in Polystyrene Latex and Dispersion Particles

A method to determine the dye content of the particles was developed to characterize the optical properties of the dye-containing particles. This section describes the experimental procedure and results of experiments on the particles made by emulsion and dispersion polymerization.

The latex or dispersion was cleaned by serum replacement with distilled-deionized water until the concentration of sulfonate emulsifier in the effluent stream was reduced to less than 5 ppm and the surface tension was increased to more than 68 dynes/cm. The dispersion was washed with distilled-deionized water until ethanol could no longer be detected in the effluent stream by gas chromatography, and the dispersing agent could no longer be detected by scanning electron microscopy.

Ultraviolet spectrophotometry was used to measure the characteristic absorption of the dye and to construct calibration curves to determine the concentration of the dye in the particles. A weighed amount of latex containing 0.5-1.0 g polystyrene particles was placed in a 150-ml separatory funnel, 50 ml distilled-deionized water was added, and the mixture was shaken with 15 ml chloroform for 5 min; the sample was then allowed to stand and separate into two layers, and the chloroform layer was separated. This operation was repeated three times. The combined chloroform extracts were diluted to 50 ml solution and filtered through cotton wool to remove the water, and the absorbance was determined by ultraviolet spectrophotometry.

The measurements were made at room temperature using chloroform as the reference standard. For the PPO laser-excitable dye, the wavelength of maximum absorption was 307 millimicrons. The calibration coefficients were: $K = 0.8064$; $B = 0.0629$.

The latexes prepared by emulsion and dispersion polymerization were measured using the foregoing method. The particles prepared by emulsion polymerization contained 5.869×10^{-3} g dye/g polymer solids, equivalent to 359 styrene units/mole PPO dye. The particles prepared by dispersion polymerization contained 1.5×10^{-3} g dye/g polymer solids, equivalent to 1362 styrene units/mole PPO dye.

From the recipes of the emulsion and dispersion polymerizations, the weight ratio of dye/styrene was about the same for both types, i.e., 1/100, but the amount of dye absorbed by the emulsion polymerization particles was about 4 times greater than that absorbed by the dispersion polymerization particles. This difference was attributed to the possibility that some of the dye dissolved in the ethanol medium of the dispersion polymerization and was washed out.

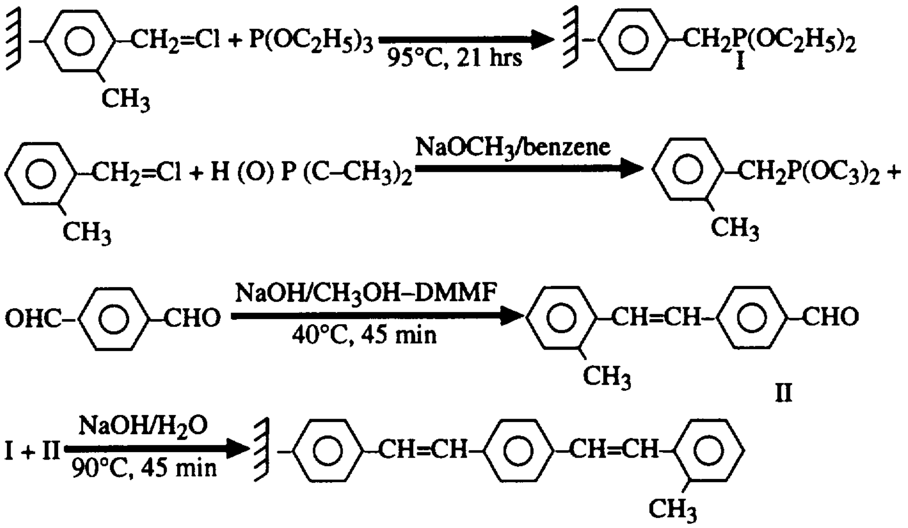
Dye Concentration in Poly(methyl Methacrylate) Suspension Beads

This method was also applied to determine the dye concentration in Poly(methyl methacrylate) suspension beads. A sample of beads was washed by stirring for 4 hours in an excess of ethanol at room temperature; this process was repeated four times and then the beads were washed with distilled-deionized water three times and dried. A 0.100 gm sample of these beads was dissolved in 25 ml chloroform, and the absorbance in the ultraviolet wavelength range was measured. For the bis-MSB laser-excitable dye, the wavelength of maximum absorption was 350 mμ. The calibration coefficients were: $K = 0.0339$; $B = 0.0002$.

The beads of Sample PMMAD-S9 contained 0.0742% by weight of the bis-MSB laser-excitable dye; the theoretical content was 0.4237% assuming that all of the dye remained in the beads. Obviously, some of the dye was lost, either because it was changed by exposure to radicals during polymerization or it was removed by the ethanol and water washing.

POST-REACTION TO COVALENTLY BIND DYES TO LATEX POLYMERS

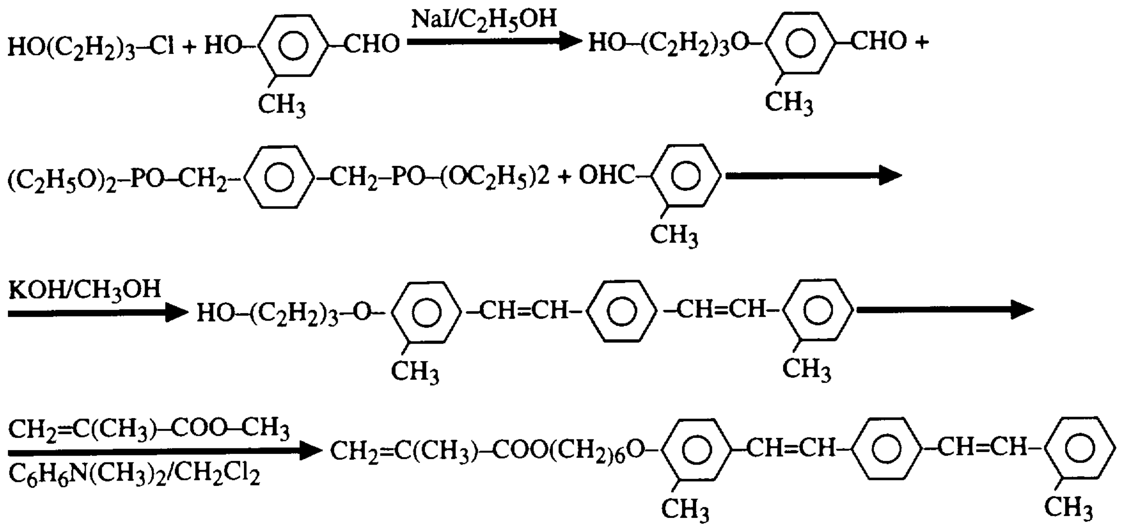
We have investigated the covalent binding of the dyes to the polymer backbone to increase the concentration of these laser-excitable dyes in the polystyrene and poly(methyl methacrylate) particles and to develop the best compromise with respect to the desired optical and mechanical properties. The following reactions have been worked out to covalently bind the laser-excitable dye bis-MSB to poly(styrene-co-vinyl benzyl chloride) particles. The vinylbenzyl chloride groups are incorporated by copolymerization of a shell containing this monomer around seed latex particles. Thus far, the polystyrene-co-vinyl benzyl chloride particles have been prepared, but the rest of this synthesis has not yet been carried out.

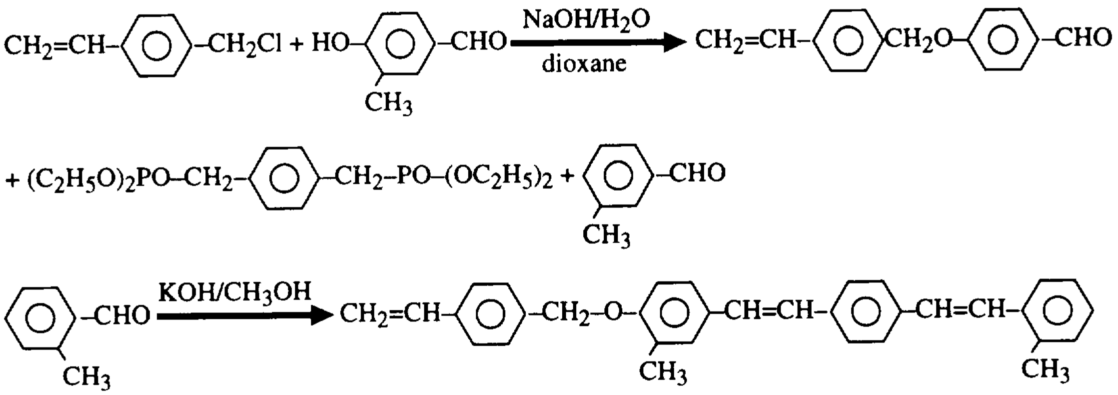


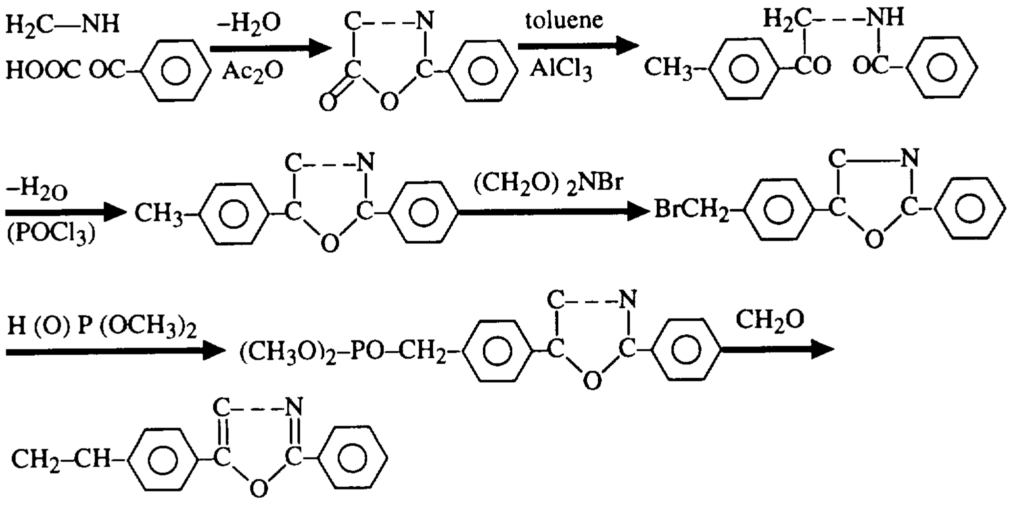
SYNTHESIS AND COPOLYMERIZATION OF MONOMERS CONTAINING DYES

Another approach is to incorporate the laser-excitable dye into a monomer and then covalently bind the dye to the particle by copolymerization. The following reaction schemes have been worked out to incorporate the chemical structures of the laser-excitable dyes PPO and bis-MSB into monomers that can be copolymerized to form the desired particles. The chemicals for these syntheses have been ordered, but the synthetic work has not yet been started.

Methyl Methacrylate/bis-MSB Adduct







All three of the methyl methacrylate/bis-MSB, styrene/bis-MSB, and vinyl derivative of PPO monomers can be polymerized by dispersion polymerization.

SUMMARY

1. The emulsion polymerization of styrene and methyl methacrylate has been demonstrated to give monodisperse spherical particles of about 0.1 μm diameter. These latexes were used as particles for the incorporation of dyes or as seed latexes for the successive seeded polymerizations to give larger particle sizes.

2. The dispersion polymerization of styrene and methyl methacrylate in ethanol and methanol solution has been demonstrated to give monodisperse spherical particles of 2.5–8.0 μm diameter. The ethanol or methanol media were replaced by water by repeated sedimentation and decantation.

3. The suspension polymerization of methyl methacrylate has been demonstrated to give spherical particles of about 40 μm diameter. The beads were used as seed beads to prepare larger sizes.

4. The laser-excitable dyes bis-MSB and PPO have been incorporated into polystyrene latex particles by physical occlusion, i.e., by adding a solution of the dye in an organic solvent, allowing the solvent to swell the particles, taking the dye along with it, and then removing the solvent by evaporation, leaving the dye in the particles.

5. The laser-excitable dye PPO has been incorporated into latex particles by both the emulsion and dispersion polymerization of styrene containing the dissolved dye. Apparently, the dye did not interfere with the polymerization.

6. A method has been developed to determine the concentration of the laser-excitable PPO bis-MSB dyes physically occluded in the particles, i.e., by extracting the dye from the particles with chloroform and measuring the concentration of dye in the chloroform solution by ultraviolet spectrophotometry. This method is also expected to be applicable to the other laser-excitable dyes.

7. A method has been worked out to covalently bind the laser-excitable dye bis-MSB to polystyrene or poly(methyl methacrylate) particles. This method requires the incorporation of reactive chlorine groups, e.g., by copolymerization of vinyl benzyl chloride in a shell around the particles. The vinyl benzyl chloride-containing particles have been prepared, but their use in this synthesis has not yet been demonstrated.

8. Three synthetic routes to incorporate the laser-excitable dye bis-MSB into styrene and methyl methacrylate monomers, and to prepare a vinyl derivative of the laser-excitable dye PPO, have been worked out so that the dye can be incorporated into the particles by copolymerization. The chemicals required for these syntheses have been assembled, but the synthesis has not yet been completed.

a-2

Extended Abstract N94-24351

PROCESSING OF SEMICRYSTALLINE POLYMERS

Peggy Cebe and Mark V. Brillhart
Department of Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139

Introduction

Our research group has been interested in the processing-structure-property relationships in semicrystalline polymers and blends for many years. We are using in situ real time x-ray scattering at elevated temperatures to monitor the development of structure. We have an ongoing collaboration with Dr. Malcolm Capel at the Brookhaven National Synchrotron Light Source to perform real time wide and small angle x-ray scattering to study the phase transformations in semicrystalline polymers. The first part of my presentation will be about our recent use of x-ray scattering to study blends of poly(ethylene terephthalate) with polyarylates. This work has been published recently.[1–4]

The purpose of the next portion of the presentation is to show how we may study effects of self-deformation of polymers during processing in the gravity environment, using real time x-ray scattering. In this way we learn how processing stresses alter the microstructure of semicrystalline polymers, and ultimately we hope to develop microgravity processing strategies that will result in more uniform morphology in these polymers.

A microgravity environment offers many opportunities for the processing of materials. High performance semicrystalline thermoplastic polymers such as nylons, polyesters (including PBT and PET) and polyolefins (such as polyethylene and polypropylene), and composites based on these materials could benefit from containerless processing and the fact that in a microgravity environment self-deformation due to a material's own weight is greatly reduced. Thus the problems encountered on Earth that pertain to self-deformation and contact with forming containers could be eliminated, resulting in the possibility of more uniform material microstructure and component geometry. Since many high performance applications require low safety factors, the properties of any material must be consistent throughout the component and geometric variances must be minimal. Additionally, many material processes in space could be employed to manufacture bulky components (such as struts and shells) from efficiently stored materials such as liquid resins and pellets of polymers.

Microgravity-induced effects on convection and the results of convection effects on crystal growth, dendrites, and alloy solidification have been examined.[5,6] Preliminary research on material shape behavior in a microgravity environment with emphasis on containerless processing, material positioning, and liquid and droplet studies has been reviewed.[5,6] Also, hydrostatic effects on liquid floating zones[5,7] and the effects of microgravity on sedimentation and buoyancy have been explored.[5] Additionally, the benefits of drawing glass clad crystal core fibers in a zero gravity environment by capitalizing on the fact that in space, molten glass will not sag under it's own weight have been discussed.[8] Although metals,[5,6] glasses,[8] and latex drop prepared from polymer solution have been explored,[5] there appears to be a need for the investigation of processing polymer components in a microgravity environment.

Objective

Extrusion is one of the most commonly used methods for the processing of polymers into pipes, tubes, and profiles (structural shapes).[9] One of the problems of extruding sections is that gravity tends to interfere with the process. If a structural component such as a tube is extruded from a horizontally oriented machine the product is passed through a fluid bath to prevent self-deformation due to the material's own weight. The material is pulled through the fluid bath via mechanical devices. Complex profiles (such as a "Z" cross section) tend to warp and deform upon contact with the fluid. Residual stresses are locked into any shape due to this quenching process. It is also difficult to move the material through the fluid without contacting the component surface. Finally, with semi-crystalline materials, the fluid dramatically affects the crystallinity of the material which, in turn, affects the material properties. These difficulties all arise due to the fact that gravity causes the material to self-deform.

If a vertically oriented machine is employed to extrude a section in the direction of the gravity field, a different set of problems arise. Gravity will cause a nonuniform stress to be distributed over the length of the section. If a section is assumed to be fixed at one end and hanging under its own weight, then the tensile stress in the material due to gravity as a function of distance from the free end can be expressed as:

$$\sigma(x) = \rho\, g\, x. \tag{1}$$

Where $\sigma(x)$ is the stress as a function of x, x is the distance from the free end, g is the gravitational constant, and ρ is density of the material. On the macroscopic scale, this stress distribution can cause the material to locally yield and ultimately fail at the fixed end where the stress is at a maximum. On the microscopic level, this gravity-induced stress distribution can cause variations in the material microstructure (which could be manifested as inhomogeneous material properties) along the length of the section. This effect could be quite large with semicrystalline materials as a nonuniform stress distribution could lead to nonuniform crystallinity. As crystallinity plays an important role in determining the properties of a crystallizable polymer, variations in crystallinity would lead to variations in material properties. From Equation (1) it can be seen that this stress field reduces linearly with a reduction in the gravitational force.

For both cases of extruder orientation it can be seen that gravity must be compensated for in the handling of the material. Microgravity environments would eliminate the need for gravity compensating devices and could possibly allow for the extrusion of very long structural components with more uniform microstructure. Thus the objective of our research project is to investigate the effects of a microgravity environment on the microstructure of semicrystalline polymers as they solidify under a nonuniform stress field imposed by the weight of the material.

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Extended Abstract

CONVECTIVE INSTABILITIES IN TRAVELING FRONTS OF ADDITION POLYMERIZATION

John A. Pojman, Chris E. Jones, and Akhtar M. Khan
Department of Chemistry and Biochemistry
University of Southern Mississippi
Hattiesburg, MS 39406-5043

An autocatalytic reaction in an unstirred vessel can support a constant velocity wavefront resulting from the coupling of diffusion to the chemical reaction. A flare front is a common example in which heat is the autocatalytic species that diffuses into unreacted regions, stimulating a reaction that produces more heat. Traveling fronts have been studied in synthetic polymerization reactions under high pressure by workers in the former USSR.[1–6] More recently, propagating fronts of methacrylic acid polymerization have been studied under ambient conditions, both with video techniques[7–9] and by NMR.[10]

If a solution of methacrylic acid and a thermal initiator, such as a peroxide or nitrile, is heated at the top while in a test tube, a solid front can be observed to propagate with a constant velocity (figure 1*a*). The velocity is a function of the initiator concentration (figure 1*b*).

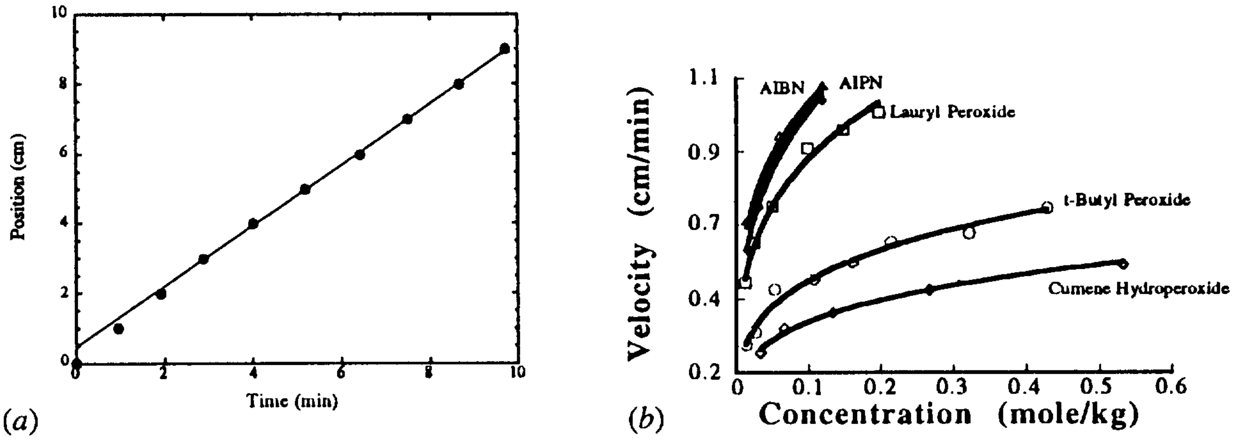

Figure 1(*a*). The front position versus time for methacrylic acid polymerization with 1 g benzoyl peroxide/100 ml monomer. (*b*) The velocity as a function of initiator concentration for methacrylic acid polymerization at 298 K.

Immediately under the descending front, vigorous fluid motion can be observed. Some of this is caused by bubble formation during the polymerization as the temperature reaches 195 °C,[7] exceeding the boiling point of methacrylic acid (163 °C). However, more interesting is the rolling motion of the low viscosity polymer. As monomer reacts, it rapidly heats up and increases its volume. Because of the solid mass of polymer above it, it can only swell and push down. At lower initiator concentrations, less fluid motion exists.

The effect of the tube orientation with respect to the gravitational field was investigated. If the tube in which a front is propagating downward is tilted 45° to the vertical, the reacting solution ascends along the solid front. This material quickly forms a solid front that was perpendicular to the gravitational vector, as shown in figure 2. If the tube is returned to its original orientation, the front levels off. The velocity of the front was not affected. If the tube is inverted so that the front would be propagating upward, vigorous antisymmetric convection of the unreacted solution ensues. The increased fluid motion removes sufficient heat to stop the reaction.

With higher concentrations of benzoyl peroxide (>0.5 g/100 ml), descending "fingers" of polymer are observed which break off to form drops of solid polymer raining down the tube. Figure 3 shows an image of fingering. The fingering is believed to be a result of a double-diffusive instability resulting from the competition between the large thermal expansion and the isothermal contraction occurring during reaction. There is a minimum and a maximum concentration necessary for fingering. The appearance of fingering is very sensitive to the temperature of the solution.

Pojman and Epstein[11] postulated that any exothermic traveling reaction front could cause conditions for double-diffusive (multicomponent) convection if the sum of the partial molar volumes of the products was less than the sum of the partial molar volumes of the reactants, i.e., the product solution is more dense than the reactant solution. Or, it may be thought of as having a thermal expansion ($\Delta\rho T < 0$) and an isothermal contraction[12-14] and occurs in a wide variety of physical systems, including ocean layer mixing, crystal growth,[15] and zone centrifugation.[16] The effect on traveling fronts in aqueous systems has recently been studied.[11,17-19] Free-radical polymerizations are very exothermic and form products that are more dense than the monomer. Thus, double-diffusive convection should occur in traveling fronts in a polymerization reaction.

We have taken samples of the fingers after they have settled on the bottom of the tube and analyzed their molecular weight distribution via gel permeation chromatography. The fingers have a substantially high molecular weight, with material extending above 10^6 g/mole as compared to 10^5 g/mole for the bulk polymer.

The temperature profile of the front at four different distances from the center of a 2.2 cm (i.d.) tube was measured. Near the center, the temperature is almost 50 °C higher than at the wall.

Pulsating Front

Under some conditions, periodic pulsations in front velocity coupled with vigorous convection under the front were observed. These appear as striations left in the polymer. The front accelerates and simultaneously vigorous turbulent fluid motion occurs directly under the front. A layer of bubbles is left in the solid polymer, most likely consisting of methacrylic acid vapor and CO_2. The front slows down while the fluid motion subsides. The cycle is repeated with a frequency of about 10 pulsations/minute.

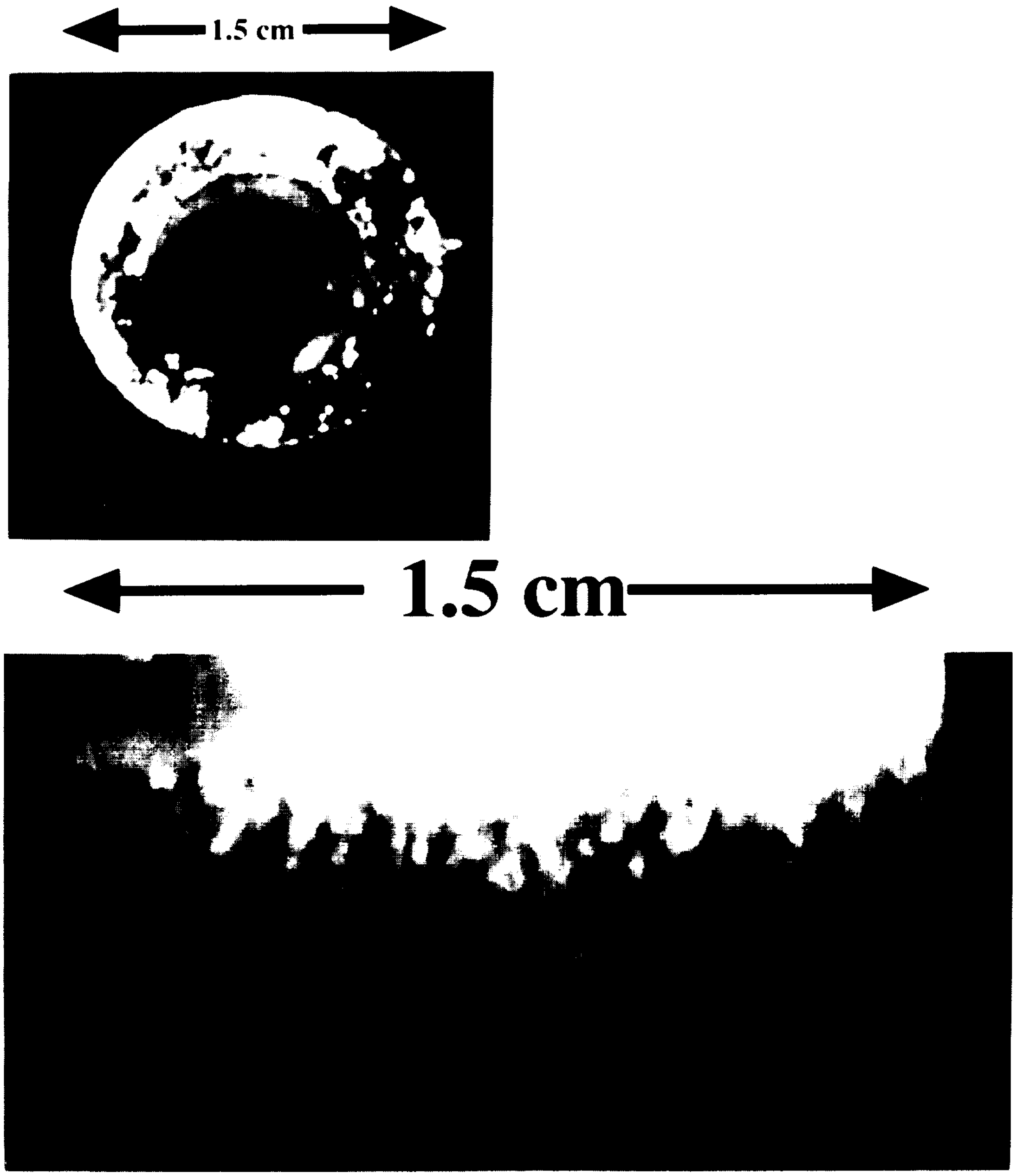

Figure 2. Fingering across the entire front of methacrylic acid polymerization with methyl ethyl ketone peroxide (8.0 ml/100 ml) as initiator with 1 drop cobalt naphthenate solution/20 ml in a 1.5 cm (i.d.) tube. The inset shows a cross section of the front and the hole formed by the fingering. Notice that the hole tapers from a diameter of 1 cm at the start of the fingering zone down to 0.4 cm at the end of this 4 cm long section.

Figure 3. "Fingers" of polymer in a solution of methacrylic acid and benzoyl peroxide. The experiment was performed in a 2.2 cm (i.d.) tube but only the central 1-cm wide region is shown. Ambient temperature was 26 °C. [Benzoyl peroxide] = 1.0 g/100 ml.

Matkowsky and Shivashinsky[20] calculated that adiabatic thermal front propagation is stable when

$$\alpha = \frac{E_a}{2RT_{\max}}\left(1-\frac{T_0}{T_{\max}}\right) < 2+\sqrt{5} \approx 4.2$$

where E_a is the activation energy of the front, T_0 is the temperature of the unreacted material, and $T_{\max}$ is the temperature of the reacted zone.

We estimated the upper limit of the E_a to be 136 kJ/mole. The stability parameter for T_0 = 298 K, $T_{\max}$ = 463 K, and E_a = 136 kJ/mol, $\alpha = 6.3$, is well above the stability limit. From these relatively crude measurements, we cannot rule out thermal pulsations that drive convection.

Acknowledgment

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N94-24353

Extended Abstract

POLYMER MORPHOLOGH

Bernhard Wunderlich
Department of Chemistry
University of Tennessee
Knoxville, TN 37996-1600

General Outline

All polymeric materials in their final application are aggregates of many molecules. For linear macromolecules, these aggregates are highly entangled and their macroscopic properties are affected in a little-known way by the interpenetration and entanglements of the molecules. We have done over the years occasional investigations of single molecule single crystals and found that there are many unsolved questions about their nucleation, growth, kinetically determined shape, and ultimate path to equilibrium morphology on annealing. This initial work could be extended by a study of the applicability of microgravity methods for the production and study of formation of single molecule particles.

The production of separated molecules of sufficient size to produce phase-like behavior would involve perhaps a spray of solutions containing single molecules, followed by evaporation of the volatiles, or precipitation out of dispersion droplets. Other methods may involve Langmuir films etc., as shown in our prior work. Microgravity environment should enhance the efficiency of any of these methods by avoiding the joining of growing particles by reduction of convection and settling due to density differences.

Once produced, the single molecule droplets are to be quenched into the glassy state and analyzed morphologically and thermally. Their shape alone can be used for molecular mass determination (an old problem that suffered from the need to estimate the shape of collapsed (flat) droplets on a surface). Next would be the study of changes of properties as a function of time, temperature and molecular mass (and distribution) on fusion to macroscopic single phases.

A synthetic effort envisioned in this research would involve the production of variously modified polymers with respect to stiffness, branching, blockyness, different chemical nature along the chain, side- or main-chain mesogens, etc.

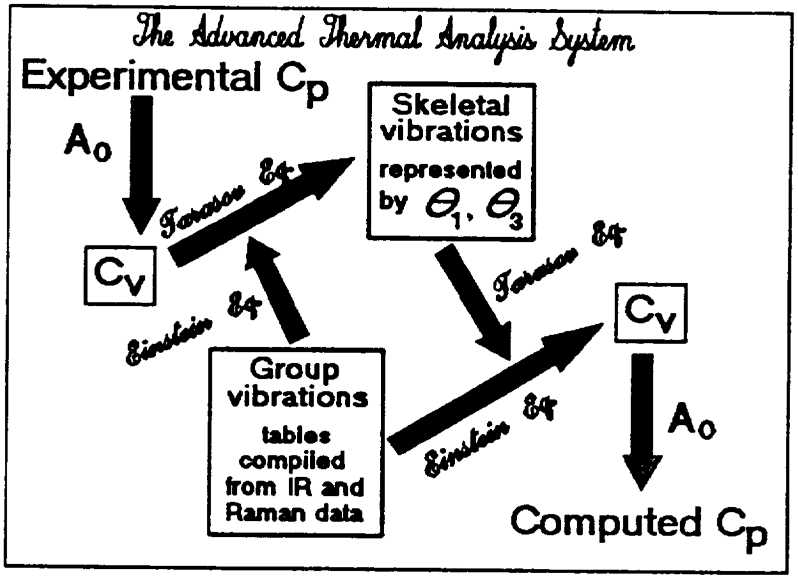
The different shapes in the glassy state could furthermore be analyzed with respect to their fluid dynamic behavior and packing density.

The research discussed in this summary is part of preliminary work considered by the polymer research group of the Chemistry Department of the University of Tennessee and may result in a full proposal to be offered for support to various agencies.

Thermal Analysis

Thermal analysis provides macroscopic information about the total energy involved in molecular motion and its change with temperature (via calorimetry through measurement of enthalpy, ΔH, and heat capacity, C_p). The theory of thermal analysis is well developed, consisting of thermodynamics, statistical thermodynamics, irreversible thermodynamics, and kinetics.[1] For the present proposal, use will be made of the *A*dvanced *TH*ermal *A*nalysis *S*ystem (ATHAS) summarized in the following paragraph.[2] As soon as samples of more than 1 mg are available, full thermal analysis of single molecule particles are possible. Immediate analyses can be undertaken on samples believed to contain separate single molecular domains. After display of the proposed thermal analysis, research on structure analysis is described that would involve electron and atomic force microscopy. Single molecules of an atomic mass of 10^6 daltons have a diameter of about 15 nm (assumed to form spherical particles with a density of 1.0 Mg/m^3), sufficient to be directly seen by electron or atomic force microscopy. This structure analysis is thus possible on a few single molecule particles (amorphous or crystalline).

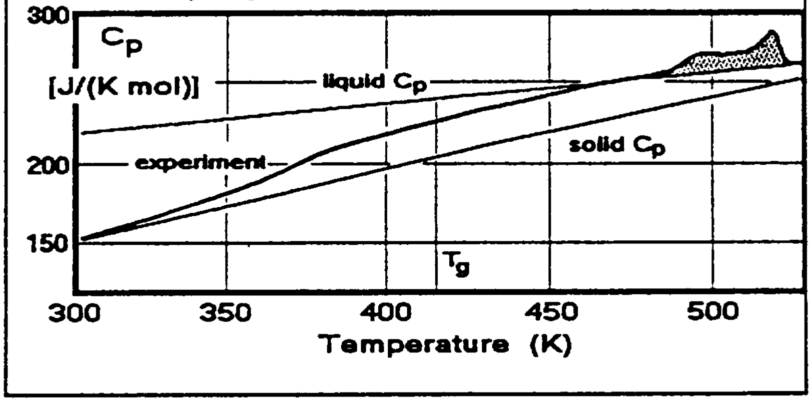
At lower temperatures, one finds good agreement of the heat capacity of solids with computed heat capacities under the assumption that vibrations are the only type of motion. The figure summarizes the method of deriving the pertinent information: The experimental heat capacity at constant pressure, C_p, is often only available over a limited temperature range. It is converted to constant volume, C_v, using the appropriatethermodynamic relationship, or (up to about 400 K) the established Nernst-Lindemann approximation,[3] using a universal constant A_o. At sufficiently low temperatures, below about 150 K, the difference between C_p and C_v becomes negligible and no conversion is necessary. Next, the vibrational spectrum of the solid is approximated. The whole spectrum is somewhat arbitrarily divided into group and skeletal vibrations. The group vibrations are then collected from analyses of infrared and Raman spectra using normal coordinate computations. Usually these vibrations are sufficiently narrow in frequency range to allow the calculation of their heat capacity contributions with Einstein functions or box distributions. Subtraction of the group-vibration contributions to the experimental heat capacity yields the skeletal contribution. For linear macromolecules the heat capacity contribution of the skeletal vibrations is approximated by a Tarasov function with an intramolecular part (characterized by an upper limiting frequency T_3) and an intermolecular part (characterized by the lower and upper frequencies T_3 and T_1). Once T_3 and T_1 are established, the heat capacity due to vibrations can be computed beyond the range of experimentation for the whole temperature range of interest. The detailed computations and computer codes are presented in the literature.[4] The only experimental input parameters necessary to compute vibrational heat capacities are thus T_3 and T_1. Analyses of over 100



polymers have given the empirical background to even guess at likely values T_3 and T_1. In case of homologous series, such as polyethers, polyesters, and polyamides, functional relationships between structure and the limiting vibration frequencies could be established. The heat capacity of liquids can also be linked to its vibrational, conformational, and external contributions,[5] but it was found easier to set up addition schemes from chain segments.[6]

Identification of a Broad Glass Transition and a Small Endotherm by the Baseline Method

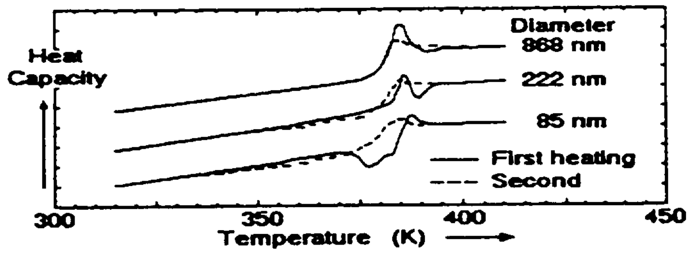
Poly(oxybenzoate-co-naphthoate) 58/42



With C_p, the basic function of thermal analysis, known to a precision of 1-3% for many polymers in the liquid and solid states, we set up the ATHAS data bank.[2] In its present form it contains information on the total body of experimental heat capacities, the group vibrational frequencies of interest to polymers, the computed heat capacities fitted to the experimental data, the integral functions: enthalpy, entropy, and Gibbs energy, and the separately measured transition parameters (extrapolated to equilibrium). A typical example of the application of the ATHAS is shown in the above figure. The broad glass transition of a modern composite can only be established with help of the computed "vibration-only" and the liquid heat capacities.[7] Note that normally glass transitions are only 5–10 K in width, but the figure permits the quantitative analysis of a 150 K wide transition. A similar analysis is proposed for the process expected on the fusion of isolated,glassy amorphous molecules. The segments of the molecule on the particle surface should have higher mobility and thus a lower glass transition temperature (T_g). In addition, one expects an exothermic response on fusion of the separate particles. Preliminary experiments of this type have been done a number of years ago[8] by analysis of various sizes of polystyrene spheres, originally produced for calibration of electron microscopes. The figure on the left illustrates the type of calorimetric results expected for the single molecules. Precision would be higher and the analysis could be more quantitative through the use of ATHAS, not fully developed at that time. Both glass transition and exotherm can be analyzed as a function of time, and with new modulated thermal analysis, the

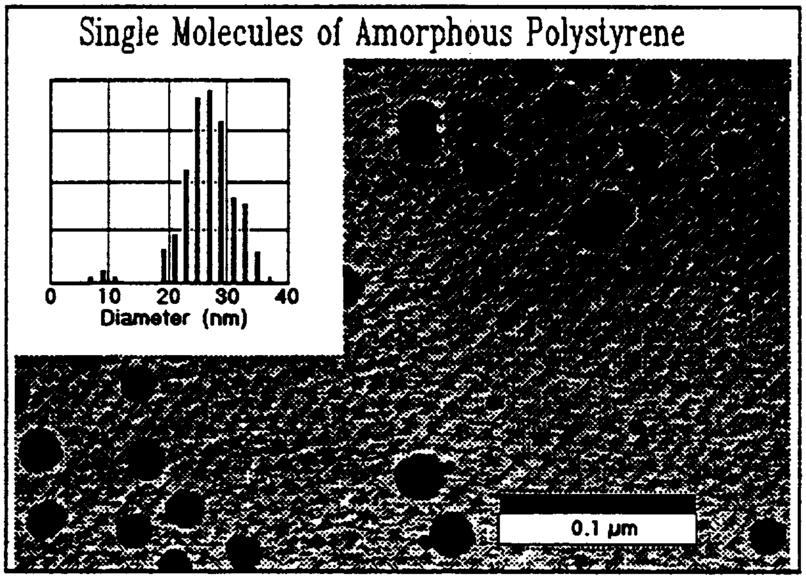
Analysis of polystyrene beads with surface strain

Polystyrene beads of the given diameter are analyzed. On the first heating, the glass transition starts earlier and there is heat released on coalescence. All second heating curves are approximately the same.



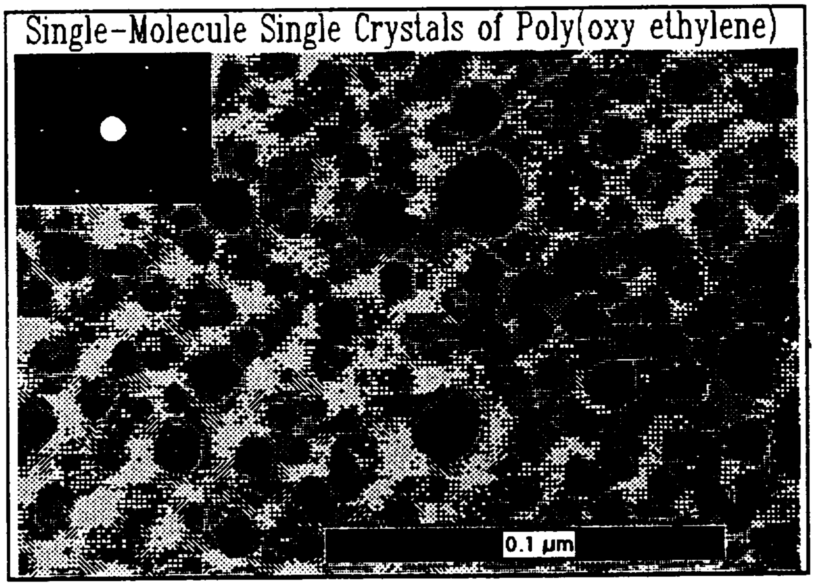
reversing parts of the heat capacity can be separated from the nonreversing parts. The thermal analysis of the coalescence of single molecules is to be compared with the changes in viscosity.

STRUCTURE AND ANALYSIS OF SINGLE MOLECULE SINGLE CRYSTALS


Single Molecules of Amorphous Polystyrene

As with coalescence of amorphous particles, it is expected that the fusion of single-molecule single crystals can be analyzed via change in melting temperature, effect on heat of fusion, and annealing processes on heating. Considerable experience exists in our laboratory to analyze melting and annealing as a function of particle size, macroconformation and morphology.[9] Note that the equilibrium surface area of the above assumed single molecule in single crystal form is at least 1.6×10^6 m^2/kg; i.e., there is a substantial surface free enthalpy to influence melting.[1] The annealing processes will receive especial attention, since it has been found earlier that poor polyethylene crystals, grown on quenching melts of broad molecular mass distribution, seem to anneal on heating to single-molecule single crystals without fusion to larger, higher melting multi-molecule crystals.[10] It is thus expected that the kinetics of the joining of separate crystals can be followed easily by thermal analysis and yield information of the difference of the annealing behavior within and between the molecules of a crystal.

The initial characterization of a single molecule particle involves electron and atomic force microscopy. Both techniques have sufficient resolution to serve as a tool to determine the molecular mass of a single molecule. The results can then be compared to time-of-flight mass spectrometry. The figure above shows an electron micrograph of amorphous polystyrene of molecular mass 1.3×10^6 (polydispersity 1.09).[10] Early work to attempt to utilize such pictures of close to hemispheres for the determination of molecular mass has been reported in the literature.[11] The density of the particles indicated the rapid thickness increase, characteristic of a sphere or hemisphere. It was found at that time, that crystallizing polymers could not be used for such analyses because of their irregular shapes. The figure on the next page shows the first example of a solution-grown single crystal of largely separate molecules of a flexible macromolecule, poly(oxy ethylene) (mass 6.7×10^5).[10] The single crystalline nature of the particles is clearly established by the enclosed electron diffraction diagram. It is obvious from the figure that even single molecules grow in this case of a flexible macromolecule as folded-chain lamellae with a lamellar thickness determined by the crystallization kinetics. Another example grown recently is that of an isotactic polystyrene.[10] In this case it was possible to also produce scanning tunneling micrographs.[10] The first (and only other) reported single-molecule single crystals consisted of molecules of cellulose tricarbanilate and resulted in rod-like particles with considerably larger foldlength.[12] The possible observation of the change in morphology from a meta-stable, thin, folded-chain crystal for a flexible molecule to a close-to-equilibrium morphology for a more rigid molecule on initial crystallization is of importance for the understanding of crystallization of linear macromolecules and should be followed by a quantitative study. Atomic force microscopy is a relatively new technique, available in our laboratory. It has been used for the study of block copolymer surface morphologies and could be proven to be able to resolve structures of the size proposed to be analyzed.[13] It may even be able on more regular crystal surfaces to reach atomic resolution.[14]


Single-Molecule Single Crystals of Poly(oxy ethylene)

Summary

Thermal analysis and determination of the morphology of particles of single molecules grown in microgravity should enable us to gather important information about the interplay of microphase-size molecules in amorphous and semicrystalline bulk polymers. The study of samples with increasing numbers of molecules may then permit a link of single molecule behavior with that of the bulk.

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III. ABSTRACT AND REPRINT

N94-24354

OPTIMIZATION OF MICROSCOPIC AND MACROSCOPIC SECOND ORDER OPTICAL NONLINEARITIES

Seth R. Marder
Jet Propulsion Laboratory, California Institute of Technology
4800 Oak Grove Drive
Pasadena, CA 91109 USA
and
Molecular Materials Resource Center, The Beckman Institute
139-74, California Institute of Technology
Pasadena, CA 91125 USA

Joseph W. Perry
Molecular Materials Resource Center, The Beckman Institute
139-74, California Institute of Technology
Pasadena, CA 91125 USA

Nonlinear optical materials (NLO) can be used to extend the useful frequency range of lasers. Frequency generation is important for laser-based remote sensing and optical data storage. Another NLO effect, the electro-optic effect, can be used to modulate the amplitude, phase, or polarization state of an optical beam. Applications of this effect in telecommunications and in integrated optics include, impression of information on an optical carrier signal or routing of optical signals between fiber optic channels.

In order to utilize these effects most effectively, it is necessary to synthesize materials which respond to applied fields very efficiently. In this talk, it will be shown how the development of a fundamental understanding of the science of nonlinear optics can lead to a rational approach to organic molecules and materials with optimized properties. In some cases, figures of merit for newly developed materials are more than an order of magnitude higher than those of currently employed materials. Some of these materials are being examined for phased-array radar and other electro-optic switching applications.

Introductory Concepts

In 1893, Pockels demonstrated that the polarization state of light passing through a crystal was modified by the application of a static electric field. In 1961, shortly after the invention of lasers, Franken observed that focusing a ruby laser beam into a quartz crystal produced a faint output at the second harmonic of the ruby laser frequency. These are two classic examples of nonlinear optical effects (NLO) whereby the phase or polarization state of light may be modulated, or where new optical frequencies may be generated. Second-harmonic generation (SHG) and the linear electro-optic or Pockels effect are two technologically important second-order NLO effects. SHG and other second-order optical mixing processes allow the extension of the useful frequency range of lasers. Such effects can be used for laser-based remote sensing and optical communication and storage. In optical disk devices, a four-fold enhancement in bit density could be achieved by halving the output wavelength of a 820 nm GaAs laser, used to write the bits to 410 nm, thereby reducing the diffraction-limited spot size to which the beam can be focused. The Pockels effect can be used to modulate the amplitude, phase, or polarization state of an optical beam. Applications of this effect in telecommunications and in integrated optics include impression of information on an optical carrier signal or routing of optical signals between fiber optic channels.

The origin of these NLO effects is related to the modification of the refractive indices of the material by applied electric fields and the modulation of light beams by the field-dependent indices. A materials refractive index is determined by the ability of its charges to be displaced by the electric field of the light, i.e., its polarizability. Under low intensity conditions, the induced polarization is proportional to the electric field strength. At high intensity, the material becomes sufficiently polarized that its polarizability itself changes, and thus, the induced polarization is a nonlinear function of the field strength. As an intense laser beam travels through a material, the index of refraction and therefore the propagation of the beam, may be modified, relative to a weak beam, e.g., it may be focused, defocused, or bent.

Since the advent of lasers, there has been an explosion of concepts for using light to carry and process information. The current push to exploit photonic technologies has created a need for high performance NLO materials whose properties are very sensitive to applied fields. Physicists and theoreticians have developed models to describe the origin of NLO effects that are often couched in complicated equations often involving the expression of the nonlinear polarizability (hyperpolarizability) tensors in terms of transition dipole moments and energy gaps between states. The role of the materials chemist is to translate these models into optimized molecules and then to incorporate these molecules into optimized materials.

When attempting to define "optimized," it is important to realize that the magnitude of the desired optical nonlinearity will be only one of many criteria that will ultimately dictate the material of choice. In addition to having high NLO activity, materials must also satisfy stringent requirements for optical absorption, scattering loss, fabricability, and mechanical, thermal, and environmental stability. Our current understanding of NLO materials suggests that these variables are frequently interrelated and that there is often no ideal NLO material. For a given application, the material of preference will typically be one that is the best compromise of several variables. Recently, organic molecules have received much attention for NLO applications because they are known to exhibit large nonlinearities and are amenable to optimization of their properties by rational modification of their structures. This article focuses on our research at the Jet Propulsion Laboratory and The Beckman Institute, California Institute of Technology, to understand, optimize, and ultimately utilize organic materials for second order NLO applications.

Optimizing Molecular Second-Order Optical Nonlinearities: Bond Length Alteration, Aromaticity, and First Electronic Hyperpolarizability

Our ability to build devices that exploit the NLO properties of organic materials relies on a fundamental understanding of relationships between chemical structure and molecular nonlinearities.[1] Large second-order optical nonlinearities are associated with structures that are very polarizable in an unsymmetric manner (i.e., the ease of polarization in one direction is different than in the opposite direction). The polarization is a *nonlinear* function of the applied field, and the efficacy of a molecule to be polarized in this nonlinear manner is called its first hyperpolarizability (β). Organic molecules with delocalized π-electron systems capped with endgroups of disparate electron affinities (electron donors and acceptors), to induce asymmetry, can fulfill the above requirements.[2] Thus, as the electrons interact with the oscillating electric field in light, they will show a preference to shift from donor toward acceptor and a reluctance to shift in the opposite direction. Two prototypical examples of NLO chromophores are p-nitroaniline (p-NA) and 4-

N,N'-dimethylamino-4'-nitrostilbene (DANS) (figure 1). In p-NA, there is the directional asymmetry in the polarizability; the benzene ring π-system provides the polarizable electrons and the amine acts as the donor and the nitro acts as the acceptor. In DANS, the two benzene rings and the double bond are conjugated, providing a longer π-system. In general, increased conjugation length leads to increased linear and nonlinear polarizabilities.

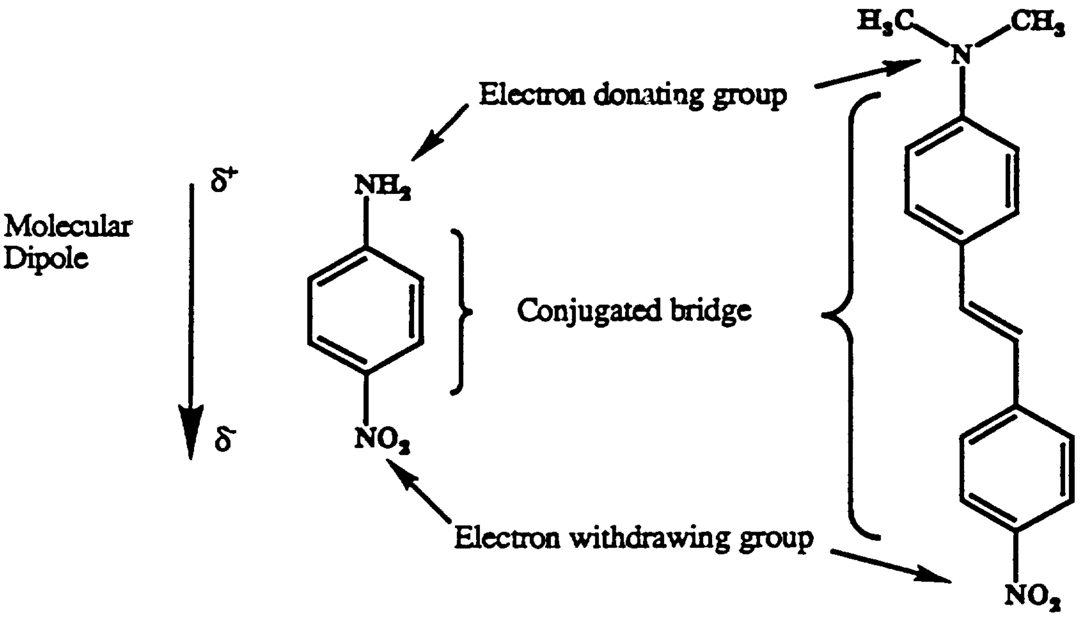


Figure 1. Typical π-electron conjugated organic chromophores; [left] p-nitroaniline (p-NA); [right] 4-N,N'-dimethylamino-4'-nitrostilbene (DANS).

From a quantum mechanical viewpoint, the nonlinear polarization arises from an electric field induced mixing of the ground state of a molecule with a charge transfer state wherein the electron density of the molecule has been preferentially shifted toward one end. Recently, we have shown that there is an optimal combination of donor and acceptor strengths that leads to the correct degree of mixing needed to maximize β.[3] We next sought to correlate hyperpolarizabilities with a molecular parameter that we believe can be tuned systematically—bond length alternation.[3,4] Bond length alternation refers to the difference in length between adjacent carbon-carbon bonds in a polyene chain. In polyenes there are alternating double (short, 1.34 Å) bonds and single (long, 1.45 Å) bonds and, thus, these molecules show a high degree of bond length alternation. In donor acceptor polyenes, this parameter is related to the degree of ground-state polarization in the molecule. To better understand this correlation, it is illustrative to discuss the ground-state structure in terms of a linear combination of two limiting charge transfer (CT) resonance structures. For polyenes with weak donors and acceptors, the neutral resonance form will dominate the ground-state wave function and the molecule will exhibit a high degree of bond length alternation.[4] As the donor and acceptor strengths increase, so will the contribution of the charge-separated resonance form to the ground-state wave function (figure 2A).

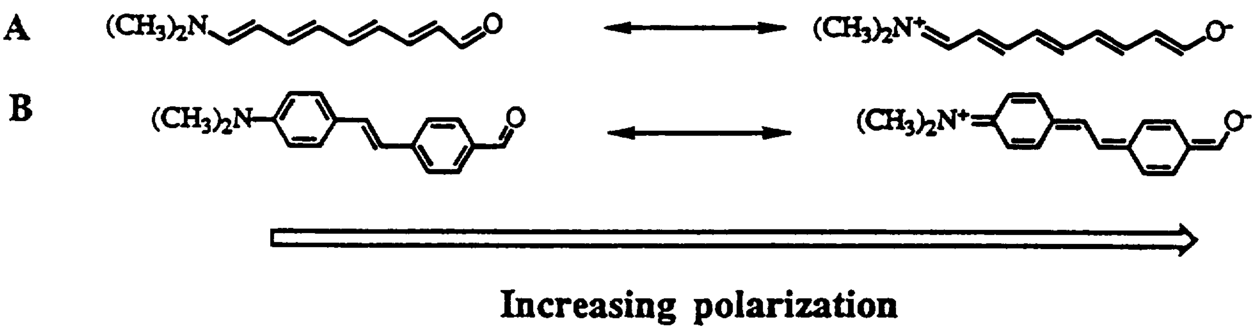


Figure 2. Neutral and charge transfer resonance forms: **A** - donor acceptor polyene, **B** - a donor acceptor stilbene (containing aromatic rings in the neutral form).

When the two resonance structures contribute equally, as is the case for a symmetrical cyanine (figure 3), the molecule will exhibit essentially no bond length alternation. It is even possible for the charge separated form to dominate the ground-state wave function. In this case, the molecule will exhibit bond length alternation, but it will have the opposite sense from that of the neutral donor/acceptor polyene (figure 2A, right). Molecules in which the neutral resonance form contains aromatic rings, such as six-membered benzene rings (figure 2B, left), will have a diminished contribution of the charge-separated form to the ground-state wave function. This is due to a large energetic price associated with the loss of aromaticity upon polarization (figure 2B, right). As a result, most molecules with aromatic ground-states will tend to be more bond alternated for a given donor and acceptor pair than a polyene of comparable length.[3]

Figure 3. Two resonance forms for a symmetric cyanine that results in essentially no bond length alternation.

Computational Studies on the Correlation of Hyperpolarizabilities and Bond Length Alternation

In order to study if and how β correlates with bond length alternation, we have used the semi-empirical AM1 Hamiltonian in the MOPAC package[5] to examine merocyanine $(CH_3)_2N\text{-}(CH = CH)_4\text{-}CHO$ (figure 2A) under the influence of an external perturbation designated to vary the ground-state polarization and geometry. This perturbation has two positive point charges (called Sparkles in the MOPAC program) placed above and below the acceptor and two negative point charges placed above and below the donor. The charges were moved in steps from 40 to 5 Å from the molecule and at each distance, the geometry was optimized, and β was calculated by a finite field subroutine in the MOPAC program. A bond length alternation parameter, defined here as the difference between the double bond and single bond lengths (Å) in the neutral canonical resonance structure, was calculated for each geometry optimized structure. A plot of β (figure 4) versus bond length alternation is consistent with that which we previously predicted based on a four-orbital calculation.[3]

As can be seen in figure 4, β peaks at a value of 0.04 Å of bond length alternation. *Thus, the peak is closer to the cyanine limit than to the bond length alternated polyene limit.* This optimal degree of bond length alternation had not been reached previously. Researchers had used molecules where the aromatic bridge itself strongly biased the molecule to resist charge transfer polarization and prevented sufficient ground state polarization from being achieved. For example, molecules such as, typically, stilbenes have greater than 0.10 Å bond length alternation and are, therefore, closer to the polyene limit than to the cyanine limit.

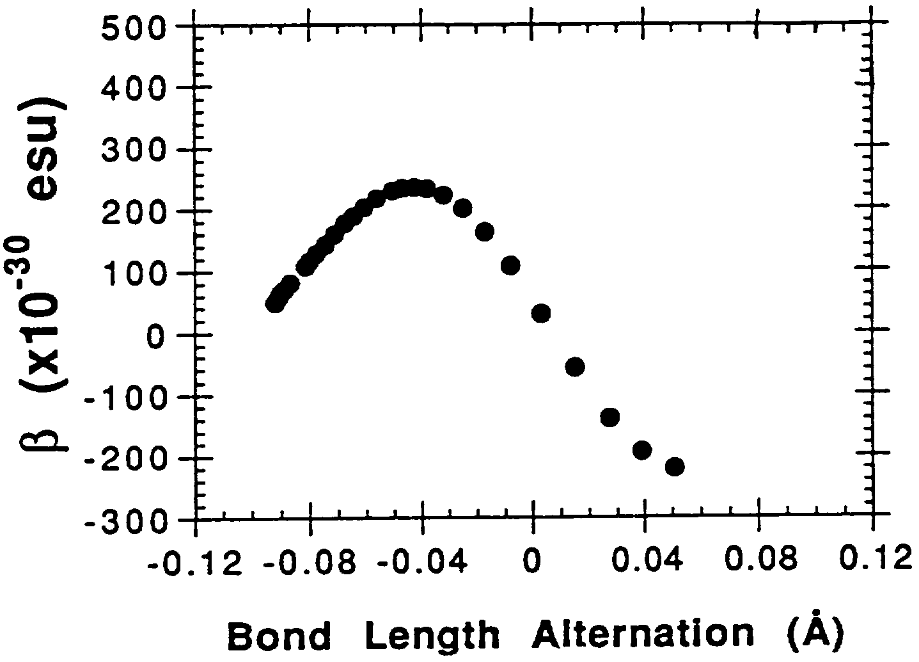


Figure 4. A plot of the first hyperpolarizability, β, as a function of bond length alternation for $(CH_3)_2N-(CH = CH)_4-CHO$ peaks at 0.04 Å

Experimental Efforts to Optimize β

To avoid paying the large energetic price of lasting aromatic bridge stabilization in the charge transfer form, we synthesized new donor substituted polyenes with *thiobarbituric acid acceptors*. In the neutral, ground-state form of these molecules, the donor ring is aromatic and the acceptor ring is somewhat quinoidal and in the charge transfer state these roles are effectively reversed; i.e., the guinoidal ring *gains* some aromaticity upon charge transfer. Thus the π-electron bridge no longer has a strong energetic bias for the neutral form; now the degree of polarization and bond length alternation is dictated by the electron affinities of the endgroups. We have shown that molecules containing thiobarbituric acid acceptors have greatly enhanced nonlinearities in comparison to conventional molecules of the same size.[6] For example, the thiobarbituric acid-containing chromophore (figure 5, bottom) that we have developed has an unprecedented molecular hyperpolarizability ($\beta = 1141 \times 10^{-30}$ esu) compared to the commonly used 4-N,N'-dimethylamino,4'-nitro stilbene DANS (figure 5, top) or 4-N,N'-dimethylamino,4'-formylstilbene (figure 5, middle). Note that each of these molecules has the same endgroup atoms. The key difference between the stilbenes and the thiobarbituric acid derivative is that the topology of the π-electron bridge in the former has been designed not to impede polarization. Following this logic, we have synthesized molecules with unprecedented nonlinearities, many times those of conventional chromophores. If these highly nonlinear molecules are sufficiently stable with respect to the processing and operating conditions required for specific device applications, they will be the active elements in the next generation of NLO materials.

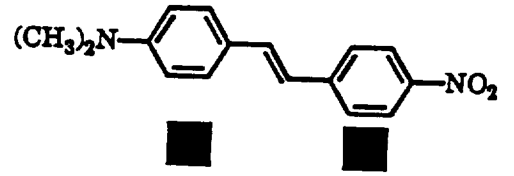
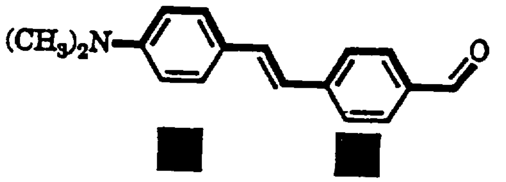
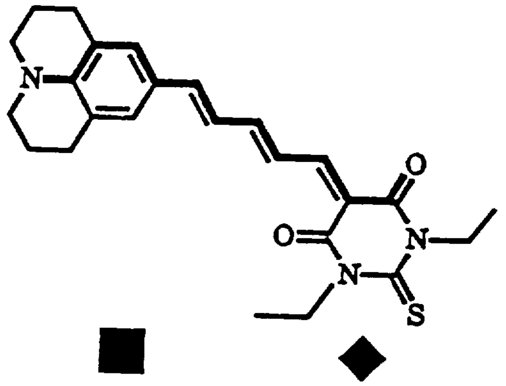
	$\mu \times 10^{-18}$ (*esu*)	$\beta \times 10^{-30}$ (*esu*)	$\mu\beta \times 10^{-48}$ (*esu*)
	6.3	74	466
	3.5	23	81
	6.3	1141	7152

Figure 5. Dipole moment (μ); β and their dot product, μβ (a useful figure of merit for polymer applications), for [top] DANS; [middle] dimethylaminoformyl stilbene and [bottom] a thiobarbituric acid derivative. The middle and bottom compounds have the same endgroups and number of atoms (this pathway is highlighted in bold). Rings that lose aromaticity upon polarization have a square below them—the one that gains aromaticity upon polarization has a diamond below it.

Optimization of Macroscopic Second-Order Optical Nonlinearities: Organic Salts

Since second-order NLO effects result from an unsymmetric polarization, they occur only in molecules lacking a center of symmetry. Likewise, a bulk material comprised of nonlinear molecules must also lack a center of symmetry if the molecular β is to lead to a macroscopic susceptibility, $\chi^{(2)}$.[1] Unfortunately, 75% of all known achiral, organic molecules crystallize in centrosymmetric space groups (containing a center of symmetry), and thus have no net $\chi^{(2)}$.[7] We have utilized an approach whereby cationic chromophores with relatively large β are crystallized with various anions with the exception that desirable noncentrosymmetric crystal packings would be obtained in some cases. We found that with a particular class of compounds, containing donor substituted 4'-N-methylstilbazolium cations, the "salt methodology" provides a higher probability of obtaining $\chi^{(2)}$ active crystals, as compared to crystals of conventional neutral dipolar organics.[8] Roughly half of the 70 4'-N-methylstilbazolium salts examined exhibited sizeable second-harmonic generation (SHG) efficiencies, indicative of a high incidence of noncentrosymmetric crystal packing. More significantly, for most of the nonlinear cations, an anion could be found that leads to very efficient SHG. One compound, 4-N,N'-dimethylamino-4'-N-methylstilbazolium tosylate (DAST, figure 6, left), has a powder SHG efficiency larger than any other material to date, some 20 times greater than lithium niobate, a commonly used inorganic material.

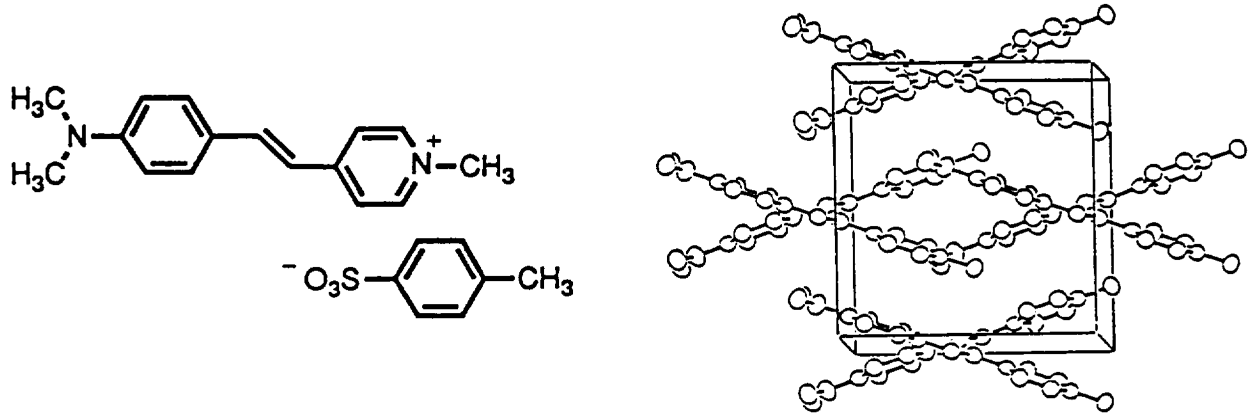


Figure 6. [left] Chemical structure of DAST. [right] Packing diagram for DAST viewed approximately along the c axis. Hydrogen atoms and tosylate anion are omitted for clarity.

For electro-optic applications, the largest nonlinear coefficients will occur when all of the molecules are aligned in the same direction. In DAST crystals the only deviation from a completely aligned system is the 20° angle between the long axis of the cations and the polar ***a*** axis of the crystal (figure 6, right).[9] We are currently trying to understand the intermolecular interactions that are responsible for the unusually high incidence of noncentrosymmetric packing in these salt crystals. With this knowledge, we hope to develop a rational strategy for optimizing β and optimizing crystal packing, thereby allowing us to synthesize a new generation of highly nonlinear crystals. We have observed a structural motif that is common to seven of the compounds that have been characterized by x-ray crystallography, wherein sheets of cationic chromophores are interleaved with anionic sheets. Within the anion sheets, the molecules are usually roughly perpendicular to the molecular planes of the cations. We believe that the formation of alternating cationic and anionic sheets can facilitate the formation of macroscopically polar structures.[9] Donor-acceptor, hydrogen bonding, and π-π stacking interactions often yield polar sheet structures. In neutral dipolar molecules there can be dipole-dipole or steric interactions (indicated by **+B**, figure 7, lower left) between neighboring sheets when they are aligned in parallel, and hence an antiparallel orientation often results (figure 7, lower right).[10] In several of the noncentrosymmetric salt crystals, polar cationic sheets are separated by sheets of anions that are roughly planar, or have approximate mirror symmetry with respect to the plane of the sheet. As a result, the interactions between the cationic sheets may be screened by the anion sheet. Since the anions can be polar, a combination of streric and polar interactions (indicated by **-A**, Figure 7, upper left) will define the most favorable orientation of the anions with respect to the cations. Due to the rough mirror symmetry of the counterion sheet, the interactions that define the preferred orientation between the anion sheet and the first cation sheet could provide a driving force to align the subsequent cation sheet roughly parallel to the first. Thus, the intermediate anion sheet could provide a driving force *favoring* a net polar alignment of cation sheets (figure 7, upper left) and *disfavoring antiparallel alignment* (figure 7, upper right). The concept proposed here is in some ways analogous to that involved in magnetic interactions in materials. Magnetic dipole-dipole interactions between spins favor antiferromagnetic rather than ferromagnetic alignment of spins. As a result, some groups that are attempting to synthesize materials with bulk magnetic moments have focused on *ferrimagnetic materials*, i.e., materials comprised of alternating *antiferromagnetically coupled* sets of two spin systems, wherein the alternating spins are of different magnitudes. We believe that the symmetry of pseudosymmetry of interactions in two-component polar, layered lattices could give rise to a higher incidence of *polar three-dimensional packing arrangements*, than for single component systems, despite the fact that all of the interactions may not necessarily be controlled.

The exceptional powder SHG efficiencies and the excellent alignment of the chromophores in the crystal led us to infer that crystals of DAST could have electro-optic properties that could enable the realization of new devices unattainable with state-of-the-art materials. Accordingly, we have grown good quality specimens of DAST from solution, with dimensions up to about 5×5×1 mm^3, such that the second-harmonic and electro-optic properties of DAST single crystals could be characterized. A large SHG nonlinear coefficient, d_{11}, 620±200 pm/V (roughly 20 times lithium niobate) was measured.[11] The electro-optic coefficient, r_{11}, of DAST is 400±150 pm/V for frequencies up to at least 100 kHz.[12] Modulator array devices, such as high-speed spatial light modulators, require large nonlinearity and low power consumption. Therefore, it is desirable for the NLO material to have a low dielectric constant, ε, to minimize the charge required per switching operation. A useful power figure of merit for an electro-optic modulator is n^3r_{11}/ε~800 pm/V, one of the highest power merit values for any material as compared to lithium niobate for which $n^3r_{11}/\varepsilon = 11$ pm/V. Additionally, thermal studies indicate that DAST is stable to temperatures in excess of 250 °C, suggesting that these salts could be compatible with silicon device fabrication technology.

The extremely large d and r coefficients measured for DAST, the high incidence of noncentrosymmetric crystal packing, demonstrate the tremendous potential of this material class for use in applications such as optical signal processing, communications, and interconnect applications requiring highly nonlinear, fast, thermally stable materials. Currently, our collaborators are attempting to develop DAST electro-optical modulators for magnetic resonance imaging and phased-array radar applications.

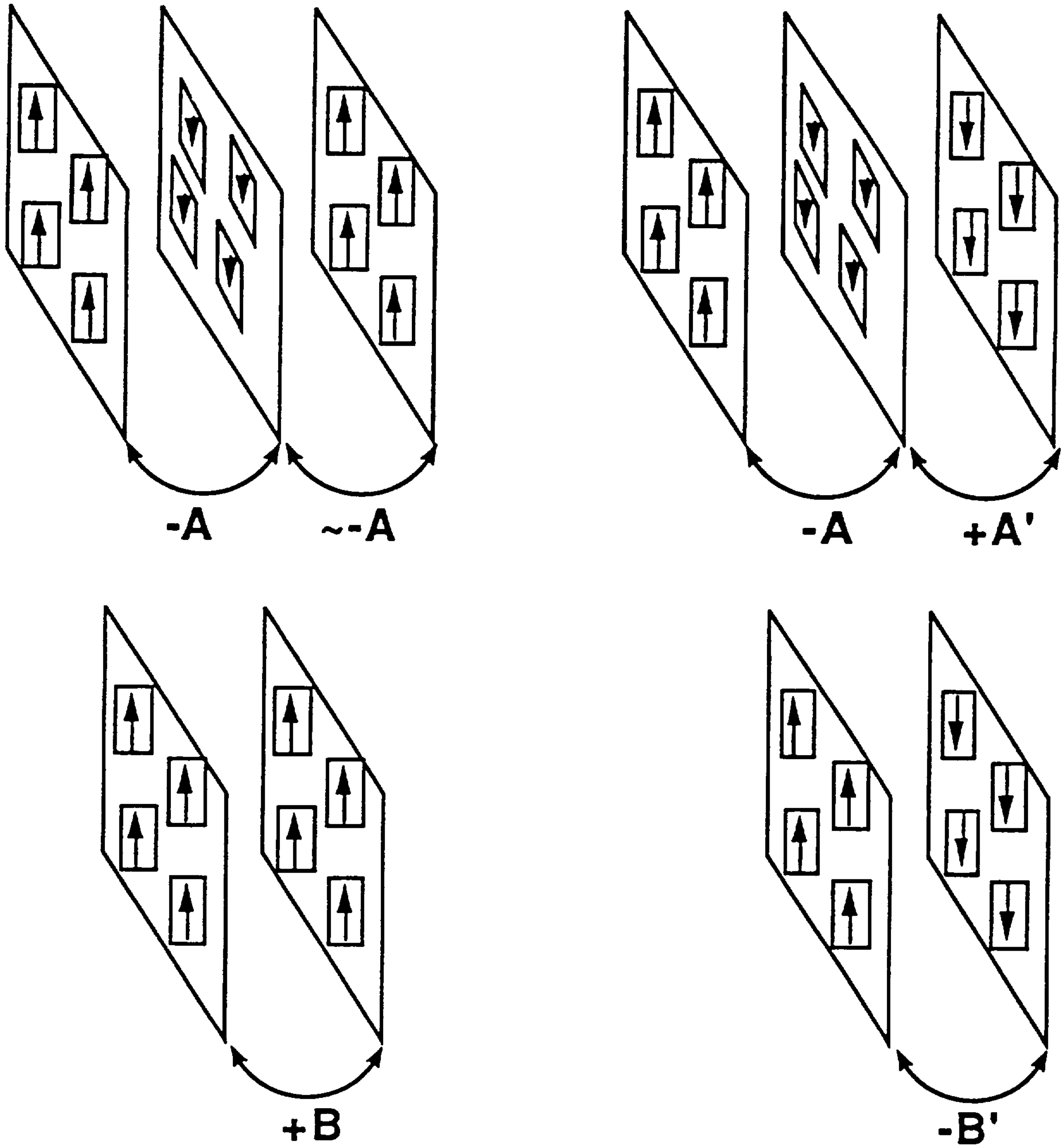


Figure 7. [upper left] Parallel arrangement of polar sheets for a salt; [upper right] anti-parallel arrangement of polar shjeets for a salt; [lower left] parallel arrangement of polar sheets for a neutral dipolar compound; [lower right] anti-parallel arrangement of polar sheets for a neutral dipolar compound. The letters **A, A', B, and B'** generically label a possible overall interaction energy between the adjacent sheets. The minus and plus signs indicate whether this interaction is net stabilizing or destabilizing, respectively.

Conclusions, Summary, and Outlook

We have shown that by control of topology of the π-electron system in organic donor acceptor molecules, large molecular hyperpolarizabilities can be achieved. We then demonstrate how variation of the counterions in organic salts can give rise to a nearly optimized crystal structure. It is interesting to note that although DAST has among the highest, if not the highest, electro-optical figure of merit for any known material, its molecular hyperpolarizability has been estimated to be only comparable to that of DANS. This suggests that the development of a new generation of organic salts with highly optimized chromophores and crystal structures could result in nonlinearities one or two orders of magnitude greater than DAST. The impact of such materials on optoelectronics would be revolutionary, if their secondary properties such as processability, stability, and transparency will allow them to be successfully incorporated into device architectures. In conclusion, the work described in this paper emphasizes how the development of a fundamental understanding of the science of nonlinear optics can lead to a rational approach to molecules and materials with optimized properties.

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IV. TRANSCRIPTS OF PRESENTATIONS

Transcript of Presentation

ORDERED ORGANIC THIN FILMS SELF-ASSEMBLED FROM THE VAPOR PHASE

Mark K. Debe

I appreciate the opportunity to talk about something close to my heart, and I hope that at least some of what I'm going to say today will help you meet the objectives you set for this workshop. The content will naturally fall into two parts. At first I'll talk about organic materials and, specifically, not polymers. Rather, organic types of molecules that have been formed into films by vacuum sublimation. It is necessary to understand how deposition parameters influence these films in order to go on to the second part, which deals with physical vapor transport in the experiments we flew on the shuttle (STS–20 and STS–26 in 1985 and 1988, respectively). So, when I talk about molecular self-assembly from the vapor phase, I'm talking about both vacuum deposition and vapor transport. We're going to start with vacuum deposition. Now this cartoon shows that we're talking about films that are roughly 1 μ or less in thickness. These molecules are arriving at the surface and participating in various types of film-forming processes, forming films that are very rich in their physical microstructure. As for bulk materials, structure determines properties; here, the physical microstructure determines the macroscopic properties. But as opposed to bulk materials in thin films, the influence of this structure on those properties are much, much larger, principally because the scale of the microstructures are on the same order of the film thickness. So the whole theme is understanding how to control the physical microstructure. "How" depends on the deposition parameters like substrate temperature, deposition rate, the influence of epitaxial effects on the substrate, in order to obtain the desired macroscopic structures. We're going to be going through this pretty quickly. As always, I have too much material. So, stop me if something is not clear, because there is an attempt to try to build from one concept to the next. So, what kind of organic materials are we talking about? Well, principally, ones that have a reasonable vapor pressure at a temperature insufficient to decompose them. This means materials that have fairly weak intermolecular interactions and strong intramolecular interactions; molecular solids, or Van der Waals solids, as they are called. A good example of this are pigments, which by definition of the word "pigment," means they are not soluble in organic solvents, for example. So if you want to form a film of these, they must be vapor-deposited. Pigments and dye materials like perylenes and phthalocyanine compounds are excellent candidates; they are very thermally stable. But, certainly, we can vapor deposit lots of materials: polyethylene, polypropylene—those types of things. Today, I'm going to be strictly talking about pigment materials, and as an example, talking about perylene compounds whereby these groups on the end can be changed by a host of ways. The phthalocyanines: you can have different materials here in the center of the molecule. You can have hydrogen, the original metal-free phthalocyanine; you can have vanadyl; you can have titanyl; you can have a whole host of substituents there, and different things attached on the outer rings. We are going to be pretty much talking about just the simpler phthalocyanines today with simple substituents in the center here. These are large, flat organic planar molecules, substantially planar, and when they form crystals, they tend to form herring-bone structures. I want to bring out the idea here of a b-axis (it's the stacking axis), because that's a good way to ask how these things are ordered. When you put them on a substrate, when you deposit these things from the vapor phase they have this enormous propensity to self-orient, to uniaxially orient, and I find that a very

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intriguing characteristic. One obvious question then to ask with respect to how they are ordered, is "what is the orientation of this stacking axis relative to the substrate normal direction?" Two simple, dramatically different cases are, where the b-axis is oriented parallel to the substrate, or the b-axis is oriented in a standing configuration, either at some angle or normal (...these represent an edge-on view of these planar molecules). Deciding the orientation of this b-axis in the crystalline components, and what fraction of the molecules are oriented in that way is the first question you can ask about these materials. Now we're still talking about, initially, vacuum deposition as a lead-in to the vapor transport. What are the important parameters that affect the film microstructure? Substrate temperature, deposition rate, epitaxial effects, and even post-deposition processing contributes to some really amazing structures. So, let's start with substrate temperature, and ask the question "how important this is as a parameter in controlling the degree to which the films are oriented, or how they are oriented." We're going to go back to the perylene red molecule (that's this one on the top here), and just look at some SEM micrographs. These films are deposited on susbstrates at different temperatures (minus 139 °C, 33 °C, 98 °C, and 226 °C). Notice the structure of the film (this is a 1-μ bar, 30,000, this is a 50,000 magnification of the 1-μ bar — these are all at 50,000, 1 μ). Look at the range in the scale of the physical microstructures. It far outweighs anything you can get with inorganic films, first of all. Secondly, in direct contrast to inorganic materials, which as you increase the substrate temperature, potentially any deposition process may get smoother, these films tend to get more crystalline. Because the crystals formed in these materials tend to be more needle-like, highly anisotropic crystalline forms, you get what appears to be significant roughening. But we can ask more delicate questions about how the molecules are oriented in these films. I have to make an aside here, because I've been using this technique, reflection-absorption infrared spectroscopy to answer that question. Infrared spectroscopy is very useful for these kinds of materials because they have very rich spectra. They have very well-defined symmetries for the various infrared band modes, and you can extract a lot of information from the film. You can determine the film thickness, the mass thickness, you can determine the orientation of the various molecules with respect to the surface; that is, whether the b-axis is oriented this way, or standing; the type of crystalline polymorph. You can even extract a number, like an order parameter, specifying to what degree the molecules have a particular orientation. Basically, you're just coming in at a glancing incidence on your film that has been depositied on a reflective metal substrate in a special attachment in the conventional infrared spectrometer. The important point is that the incident and the reflected beams couple in such a way, because of the boundary condition imposed by the metal substrate, that the p-waves, the p components, produce a standing electric field at the surface. If you have a molecule on the surface with a vibrational transition moment, in the vertical position, it will couple very strongly to this resultant electric field. If the transition moment is parallel to the substrate, you won't see it at all. Let me give you a dramatic example that also illustrates the effect of substrate temperature. Now, this is the infrared spectrum just over the range of 1600–600 wavenumbers from metal-free phthalocyanine. This bunch of bands is due to out-of-plane bending modes of the hydrogens around these aromatic rings here, whereas, these bands are due to transition moments in the plane of the molecule. We've got a nice tool, now, to try to determine the molecular orientation. Now this is a spectrum from a KBr pellet, so there is no orientation information in there. The top one was deposited at a substrate temperature in the 5–10 °C temperature range. The major thing is that the critical substrate temperature within which (the range is very narrow, within 5–10 °C) the films will be highly oriented (how highly oriented?). Well these are the out-of-plane bands, and these are the in-plane bands; same material. The point is this is extremely highly oriented so that this electric field which is normal to the surface is only coupling in with these transition moments that are essentially normal to the plane of the molecule. If you go to a temperature of 70 °C, it flips over the other way. Now the b-axis is oriented this way. Now you see the in-plane transition moments because they are sort of parallel to these little lines and they couple strongly to the resultant electric field; but not the transition moments that are normal to the plane. So it is a very good technique, but that is not the main point. The main point is that going from 5 to 70 °C, you completely flip the way in which these films want to order. The same thing is true for copper phthalocyanine, which may not be too surprising since they have very similar lattice structures. Again, this is the case for low temperature, 5 °C, and higher temperatures, 70 °C. Another good complimentary tool to use, and this is again is an aside, is grazing incidence x-ray diffraction, and I have to show this because we are going to be talking a lot about this in the vapor transport experiments as well. Again, you are coming in at low angles of incidence onto your film plane. It's a standard theta, 2-theta diffraction scan. But the point is again, you can sense diffraction peaks produced by lattice spacings in the direction normal to the film plane. So it's a good complimentary tool; it's telling you something about the long-range order of the crystallites that form the film. We have an example for those films I just showed. You can't really appreciate this until you have seen a bulk spectrum, and that will come later, from the copper phthalocyanine. But essentially there is just one peak, here, in the film that has been deposited at 70 °C, where the b-axis is parallel to the substrate. Now the spacing you see is between the columns, and that is about 12 Å. So you see that peak only. You don't see anything out here.

Now, I will go on to the second example of a deposition parameter: "how does the deposition rate influence the microstructure?" I'll just show one example. Not too much of how the microstructures change, but the influence on the macroscopic properties. This is a perylene compound; you remember the one I started with; it is not exactly that one, but is related to it. But the point is, look how significantly different the UV-visible absorption curve is depending on the deposition rate. Well, is it really different? This is 1800 Å/min, 25 °C ; this is 25 °C at 140 Å/min. Over a factor of 10 change in deposition rate and a little change, certainly, in the absorption spectrum. But it is much more significant if you go to a higher temperature, so, the upshot is, just to summarize, that the deposition rate is important. But how important it is depends on the substrate temperature, because the substrate temperature is what's important in the surface diffusion of these molecules. That is the key process that is going on and influencing all of this; the large amount of surface diffusion.

QUESTION: On the one hand, you are saying that this surface diffusion is controlling the molecules there based on the Gaussian curve, but on the other hand, the data you showed with the variation of the substrate temperature, it does not make sense.

ANSWER: OK, say it again? This last one you say doesn't make sense?

QUESTION: Yes. Because would it be possible that you could tell what is the controlling factor there. Is it kinetics, or is it thermodynamics?

ANSWER: Yes. Both are contributing there. I am only showing you just a tip of the data. The point is, and it is hard to extract this from here, we changed the deposition rate over a factor of 10 at room temperature, substrate temperature, and it has a little bit of aggregation. This is what is causing this shift down here. But if we go up to 104 °C, then only a factor of 3 change in deposition rate has made a much larger change in the degree of aggregation. So, I'm saying, substrate temperature has an influence. Here is deposition rate and we are just looking at a ratio in the absorption curve of two bands. We aren't trying to deconvolute them at all. At substrate temperatures of 100 and 200 °C, there is no influence. But at 25 °C there is a big influence. So you have this competing effect of these molecules arriving from the gas phase trying to find these low energy binding sites and if you've got a high substrate temperature, and lots of surface mobility, it is easier for them to find those sites, essentially the surface species, as opposed to the molecules arriving from the gas phase. So I don't think there is any conflict there between the results. It is just that the substrate temperature is a stronger factor in controlling the microstructure, than deposition rate.

QUESTION: This is transport limited?

ANSWER: Surface transport. I think it is an important point that most people don't think about, and that is a stronger phenomenon with these molecular solids than inorganic materials. That is maybe the key to bring out here; that surface diffusion is extremely important. I'll show you some more dramatic examples. It isn't always just a linear thing. Here are some vanadyl phthalocyanine films deposited at different deposition rates. Again, the x-ray diffraction, shows something very discontinuous happening at this deposition rate range; just as with that example of perylene, vanadyl phthalocyanine (this isn't our work, this is someone else's) shows exactly the same thing. Depending on the rate at which you deposit the films, the degree of aggregation is significant.

Now, going on to the third parameter: substrate effects, and specifically, epitaxial effects. I use that word "epitaxially" in a sense that may be appropriate for these organic materials; it is not the kind of epitaxy you would have in a III–V compound, for example. But still you can see the strong influence of the substrate. First, this is just the perylene red again, deposited on aluminum at different film thicknesses. Again, we have an infrared spectrum. These bands are due to out-of-plane modes, and these bands are due to in-plane modes, but notice how the relative intensity changes dramatically as you go down to the substrate. In fact these out-of-plane modes have almost completely disappeared. This is a 35-Å film, so it is only a couple of monolayers. The essence is, then, that at this surface of this oxide of aluminum, these perylene molecules are oriented either edge-on, or end-on, but not flat-on.

QUESTION: Excuse me. Do you know that by reflection, or what?

ANSWER: Yes. By reflection absorption infrared. What it is telling us is that the surface molecules are oriented this way and this way, but there are none oriented flat. We don't see any of the vibration modes for that. Now, what's next is particularly pertinent to the vapor transport experiments I will talk about later. This is the influence of the seed film on the way in which a subsequent film orders. Now on the top, this is again an x-ray diffraction scan from a film deposited on a copper substrate at a substrate temperature of 70 °C. Remember, we said that gave you the condition in which the film was oriented with the b-axis in this direction, parallel to the substrate. And so, we are only going to see the spacings between these channels, these columns, and that is on the order of 12 Å. That is why we get this large d-spacing down here. This is the typical spectrum from bulk powder. There are two things I want to point out, please remember, there are four peaks only in the 3.24 to 3.72 Å range from copper phthalocyanine and these are the d-spacings associated between the planes of molecules in the crystal structure, and these are the spacings between the actual columns of stacks. OK, so the experiment is, we know that at 70 °C the material wants to order with its b-axis parallel to the substrate. So we are going to put on, first of all, a metal-free phthalocyanine so we can distinguish it from the copper phthalocyanine; ordered on the substrate by depositing it at 4 °C. This means that the b-axis of the metal-free is going to be standing. Then we are going to heat it up to 70 °C and put the copper phthalocyanine on and ask will it order this way, or, will it follow the substrate. The answer is, that it follows the substrate, and very dramatically. At 70 °C, with that standing b axis metal-free phthalocyanine seed film, this is the copper contribution, not the metal-free. You see, there are only diffraction peaks due to d-spacings, so in this case the propensity to orient according to the seed film has been much stronger than the substrate. Temperature post-deposition effects have nothing to do with a microgravity experiment, but I want to point out, perhaps due to the question that was asked "how important is the substrate temperature?" If we vacuum deposit a film of this perylene, the one I started with, the long one (this is 100,000, this is 50,000 magnification). I just want you to see that it looks fairly common. I mean, you couldn't tell if this was a sputtered cobalt-chrome film from an SEM or if this were organic. It's just an ordinary looking kind of film. If we take this film, now and heat it in a vacuum, it forms just an amazing structure. This original film has now gone to form these 1-1.5 μm tall films of single crystalline fibrils, or whiskers. Each of these whiskers is single crystalline. There are 3–5 billion of them per cm^2. They have very high packing densities; they are substantially oriented perpendicular to the surface. This is a metal film substrate. This is a normal incidence view, and this is a 45° angular view. So, this is something that has been created strictly by surface diffusion. The belief is that what you have here are initial screw dislocation sites, and the surface molecules start moving around as you heat these up in the vacuum, and they find these screw dislocations and that is where the low energy binding sites are. They start filling up the screw dislocations just like shoe boxes on a spiral staircase, and the whisker just grows up on the substrate. All of the material is conserved. So there is no arrival from the vapor phase; this is a zero supersaturation rate process; it is strictly just surface diffusion. To conclude this section on vacuum deposition, people may know this, I don't know, but I find it quite striking. This is parachlorophenylurea's crystal structure, and may be of interest to the nonlinear optics people here. When we vacuum deposit a 1-μ film (it's a hydrogen-bonded kind of structure between the carbonyls and nitrogen containing moieties, not one of those van der Waals molecular solids - first let me show you the bulk x-ray powder diffraction for this material), it is extremely highly ordered. We can identify it because we know that the crystal structure is oriented with the 00L plane parallel to the surface. I find this really striking, that they are so sharp and well-resolved all the way out. For such a thick film, we can use the infrared spectroscopy to determine how much of the material is ordered like this; over 80%, and in fact, there is an optimum thickness as well. So this was just a quick summary to point out that, if you're going to self-assemble, or vapor deposit these things, you have to appreciate the importance of substrate temperature, and take into account deposition rates and surface epitaxy effects. In fact, the epitaxy effects can be a useful key to answering the question of how convection in a buffer gas might impact film growth.

So I'm going to switch, now, to the vapor transport experiments, and try to just "pop" from the proverbial "tips of the icebergs" describing results from a couple of our experiments in which we did physical vapor transport. There are many people here who know everything to know about vapor transport, I'm sure. Essentially, we're putting an organic material into one end of an ampoule, and heating it up with a buffer gas in this confined environment, imposing a temperature gradient so that it is hotter in this end than the substrate end, and allowing the material to evaporate and deposit and grow a film on this substrate. I'm referring to this as our platen. It's a copper platen that may or may not have a seed film on it. We measure the temperature of the platen. There's a heat pipe operating here. This whole thing is in a very fancy thermos bottle, so to speak. That's essentially the experiment. I won't put any more time on it except to say that there are nine of these kinds of cells and the ampoule is inside this confined environment. We measure the purity of the gasses before and after, and do our best to make controlled experiments comparing successive experiments done on the shuttle with those done in the ground-control experiments. There are many things to account for, as well as all those deposition parameters I talked about. But also, if you want to sort out the effects of convection, you have to account for the effects just due to the thermophysical properties of the buffer gas, and those induced by the oriented seed film, for example, and primarily to answer the question "does convection have any role in how these films are ordered?" I think we have some real surprises and there are some questions that have still not been answered. Again, just to review, I'll be showing you and talking about films that we deposited on these copper platen substrates in ampoules such as is schematically shown. The copper phthalocyanines are being deposited on the metal-free phthalocyanine, as a seed film, so the copper phthalocyanine in these experiments is what is being transported. This (metal-free phthalocyanine) was already deposited in preparation of the ampoule by strictly vacuum vapor deposition in the laboratory in two different orientations. We're going to explore, also, how the seed-film orientation has been maintained or influenced by the presence of convection. Just, again, to show you a picture, you're looking through the ampoule wall at the platen. There is a lot of parasitic wall deposition that depends on the types of gases you've got in there and the pressures, but the important point is that we are looking at and characterizing the thin film on this surface. One of the reasons for using the thin films in the first place, in this experiment, is because they are so amenable to a large variety of characterizational tools.

Now, first of all just focus on PVTOS-1, the first experiment. Ignoring the pinholes, you're looking straight down at the top of that copper platen that has the copper phthalocyanine deposited on it. Controlled experiments in unit gravity and the STS-20 flights (the microgravity result) is at 0° viewing angles and at 20° viewing angles. The first thing we saw is that there was this strange appearance in the microgravity deposited films. They looked very dark at normal incidence; tilt a little bit, and it was pink. You could swear you were looking right through the film with some interference phenomena. But why? The unit gravity film did not show that influence. We looked at them with a variety of tools in decreasing order of spatial resolution: ellipsometry with about 1 mm resolution across the film showed very dramatic differences; we looked at them with high resolution UV-visible absorption with about 0.1 mm resolution - very large distinct differences. We looked at them with phase-contrast interferometry which is a good tool for looking at the smoothness. I don't know if you can see the difference here, but the microgravity films were distinctly smoother in the centers than the ground-controlled films. This is looking in the 10–100 μ range. We looked at the differences with the scanning electron microscope, and there is where you really see where the microstructure is different. These are SEM micrographs. The films are on the order of 1-μ thick. Very distinct columnar structure; this is from the microgravity-grown films. They are very densely packed, close together, as opposed to the ground-control experiments which have a very open (looks like the perylene red whiskers, but it's not) structure. I think you can start to appreciate that there is a very distinct difference in density here with this film. The optical parameters are going to be very different. You can understand differences in those larger-scale phenomena, but primarily the thing that hits you is this very distinct difference in microstructure that presumably is just there due to differences in buoyancy- driven convection. You go on down to the x-ray diffraction, and you start to see that there are more subtle differences. The microgravity films consisted strictly of a new type of polymorph. There were eight known polymorphs for copper phthalocyanine claimed. We have patented a ninth form based on x-ray diffraction and IR spectra. There are two extra peaks. You may recall at the beginning, I showed you a bulk spectrum for the copper phthalocyanine. You should note that there are four peaks. There are two extra ones that had not been seen before. One of the ground-control films also showed some of this, but the point was that the microgravity samples consisted only of this type. Notice there is no absorption, no peaks down here associated with material that is oriented in a parallel b-axis configuration; only in the standing b-axis configuration. The ground-control samples showed primarily the opposite orientation. Infrared spectra were consistent with the x-ray diffraction suggesting there is a new polymorph here. I won't take the time to go through that (I think we're running out of time), except to say they are consistent. Over a large scale, a 10^7 dimensional range of scale, there are differences in the microgravity and the ground-controlled experiments. That led us, then, to pursue this in the PVTOS-2 experiments where, now instead of just having two sets of cells that were dedicated to the phthalocyanines, we have all nine. And now we have more flexibility in choice of buffer gas and the orientation of the seed film (as I said, we did it with both standing and parallel orientation). Again, similar types of photographs show lots of deposition. I'm going to show you a microgravity one and ground-control, and the only difference is that you can really see is that for the case of helium, a lot more material deposited in the microgravity case on the walls than in the ground-control. We are going to see that the same is true for the material that is deposited on the substrate.

QUESTION: Were all of the phthalocyanines deposited at the same substrate temperature?

ANSWER: You just led right into this. Are the substrate temperatures the same? Is that what you're asking? Essentially, yes. We measure the substrate, but there is a very distinct difference in what's happening on a small temperature scale. But first of all, this is the maximum substrate temperature observed. The squares are from, for example, the third ground-control experiment of the nine cells, rather eight cells for this one, and this is the PVTOS-2 experiment. There isn't any real consistent difference between circles and squares. What you're seeing here is actually He to nitrogen to CF_4 to xenon, so the substrate temperature we see varies definitely with the thermal conductivity of the buffer gas. But for any one buffer gas, there is no real difference between ground-control or microgravity in the maximum temperature reached. There are pressure differences that cause a bit of scatter here.

QUESTION: Isn't that something you control in the experiment, substrate temperature?

ANSWER: No, we control the hot end temperature to ±0.2°. The substrate temperature is pseudo-controlled by the heat pipe, but not actively controlled. So, for example, here are some of the temperature scans. The temperature is ramping up, and this is the hot-end temperature that is being controlled. If I showed you those curves, they are just step-functions for the hot-end temperature. The substrate temperature, as you can see, doesn't equilibrate. In some cases it takes, usually, several hours for it to really equilibrate. But there is still a wide variation in the substrate temperatures we observe. These are all the microgravity cases.

QUESTION: Is there any evidence that the growth rate is changing all the time?

ANSWER: Growth rate or arrival rate?

QUESTION: Whatever you want to call it.

ANSWER: It may well be. I can't say that it is not. There is a thickness difference in the material. So, if you want to say that the thickness is the growth rate divided by 4 hours, then yes, there will be a difference in the growth rate. But I think that it is not a large effect in this experiment because it is such a slow growth rate; it is so slow (it takes 4 hr to put down a 1-μ film), that it is probably below any threshold at these substrate temperatures that is important.

QUESTION: Why do you not want to control the substrate temperature directly? Is there some reason for not wanting to do that?

ANSWER: No. It is just that it would be very difficult, or experimentally more complex.

Let me go on here. Just note that there is some noise on these PVTOS-2 substrate temperature vs. time profiles, but no real periodic kinds of disturbances as opposed to the ground-control experiments which show some very distinct fluctuations. This was the first direct evidence we had in our ground-control experiments that we had convection present. If you scale up these fluctuations, there are some very interesting characteristics. The shape of the temperature fluctuations looks like a relaxation oscillator. The periodicity is changing with the type of gas as the most dominant thing. The amplitude is changing. Just to summarize, it was the first evidence that, yes, the ground-control experiments had these convective type of disturbances, as opposed to PVTOS-1 where we had no real direct evidence that there was convection. We suspected it. Here we seem to have some direct evidence of that.

QUESTION: On your ground-based things, is the cell oriented horizontal?

ANSWER: No. It's either all hot-end up or hot-end down. We're just trying to maximize the effects.

QUESTION: Did you see more convection in one orientation as opposed to the other?

ANSWER: Yes. Actually, only in PVTOS-1 were both sets of hot-end up and hot-end down orientations used; in PVTOS-2, they weren't.

Here's, maybe, an absolutely simple-minded cartoon of what could be going on, extrapolating from some ideas in Franz Rosenberger's earlier papers on convective flows. It perhaps might be something like this, a mode-hopping mechanism, where if you correlate these temperatures here, it builds up, then suddenly flips back, builds up and suddenly flips back, like a breathing mode in a relaxation oscillator. The amount of material that is deposited you can get from the infrared absorption spectra. It seems to correlate directly with the diffusivity, the binary diffusivity, which you can calculate for the copper phthalocyanine through the specific buffer gas. This is helium out here, sort of independent, as you might expect, of the seed film orientation. That was not necessarily the case with the ground-control experiments Remember I said that the helium deposited much more profusely in microgravity. With helium, copper phthalocyanine was deposited much thicker, then, on the side walls, in 1-g, than in the microgravity case. This shows that that was true on the substrate also.

It is a matter of great embarassment, but despite the fact that this experiment, PVTOS-2, was flown in 1988; and there are just realms of data, for reasons I won't go into now - I haven't been able to publish it. I haven't had the opportunity to publish it, but hopefully, that will be forthcoming.

One of the questions we asked was how the substrate epitaxy was influenced by the presence of convection. It's a probe. It's an angle to get at the influence of convection. We know how important epitaxy can be in the vacuum vapor deposition. Again, I'm summarizing a lot of data here. This is looking at, again, the infrared spectral band absorbances as a measure of how much material was deposited. Does the amount of material that deposits depend on what the substrate epitaxy is? You might say, yes, it does because it has one particular crystalline orientation on the surface. The sticking coefficient depends on that; so you might expect to see, yes, a dependence. If you look at the ground-control experiments, I may have to explain why there were no b-axis perpendicular oriented seed films; because we had to throw out one cell in order to make this pumping connection. So that one wasn't done on PVTOS-2, but there was no dramatic amount of difference in the amount of material that was observed. These are all the 3.5 Torr nitrogen, so everything else was the same. In microgravity, there seemed to be a very clear dependence of the amount of material deposited on the substrate orientation. That is a qualitative thing; can we see any difference in the way the material is oriented in microgravity versus ground-control? Remember I showed you on PVTOS-1, both phthalocyanine samples were definitely better oriented. In the PVTOS-2, all eight cells support this. These are all in the case where the seed film is oriented with the b-axis standing, so we would expect to see that this band is much larger than these bands. Only in the one case of xenon in unit-g is this true, as opposed to the microgravity cases, where indeed the seed film has maintained its ability to influence the growth direction of all the vapor transport deposited film. The infrared spectra and the x-ray diffraction all show consistently that the microgravity films are better oriented. They have maintained the seed film orientation. Let me show you this last example of the x-ray diffraction. This is an oriented metal-free phthalocyanine seed film. This is in the case where the b-axis is oriented parallel. This is what it looks like if it's perpendicular. The x-ray scattering is just a lot stronger from these stacked-up rows than it is from the plane, and that is why there is so much more intensity here than here. This is a very highly ordered film. This is what we are putting the copper phthalocyanine onto. Is there a difference in the copper phthalocyanine deposited on this versus the b-axis parallel oriented seed film? The infrared shows there was. Here is one example for the 10 Torr helium case. The b-axis of the seed film was perpendicular. In 1-g, it is just the opposite. In microgravity, it has maintained that orientation. So, it is consistent with the infrared results.

QUESTION: How was the seed film initially made?

ANSWER: That was initially made by vacuum vapor deposition at the critical substrate temperature of 4 °C. That was what we started with at the beginning today. That's why it was important.

The major conclusions are that the substrate temperature fluctuations provided a direct evidence of convection in the 1-g controls. The microgravity films replicate the seed-film orientation better than the 1-g controls. How could that be, just on the basis of slow-scale moving convection? The microgravity films are generally better ordered. These are the main points right here. Believe me, the controls we've tried to do to eliminate these other effects (the thermophysical properties of the gases, variations in the degree of perfection of the seed film, variations in substrate temperature) don't appear sufficient, by a long shot, to explain these differences that we are, therefore, ascribing to the presence of convection. I think there are some real fundamental issues lurking there as to why that should be. But these materials are good candidates for exploring this type of thing, because they are so amenable to being influenced. They are weakly bonded materials, they have many different polymorphs, and they are rich in their spectroscopies. There are lots of handles to get a hold of.

QUESTION: How reproducible would you say your results are?

ANSWER: In PVTOS-2 we had nine flight ampoules. We did three sets of ground-control experiments, for about 20 or 30 or, roughly 24 ampoules. Then there were even some preliminary preflight ground controls, and they were all usually self-supporting. There is a lot of variation...it's not like they were all done with the exact same set of parameters, because we tried to learn also the influence of, say, the thermophysical properties of the buffer gas and pressures. So, within any one set, like the nitrogen buffer gas ampoules, we had three flight and then six (I've got to be careful here) or four ground controls where the only difference was the presence of the seed film and its orientation. As I said, we meaured the gas composition after the flight by probing into the ampoules to use the mass spectrometer to determine the distribution of gases at total pressures. We tried to take all of that into account. Thank you.

COMMENT: I'd like to ask one more question of Mark. My background is in semiconductor crystal growth, but as a materials scientist, the one thing that I saw over and over again through my academic career is, inevitably, someone is going to draw me a triangle, and there is going to be structure at one corner, and processing and properties. I think we can't get away from that. In fact that's the real meat of what materials science is. It seems like when I take a look at the work that you've done, you're really strong in a couple of the corners, but it looks like the basic theoretical framework between structure and processing is still a little hazy. Is that fair to say?

ANSWER: Yes, absolutely. This whole field has not been pursued, even to a fraction of the extent that inorganic materials processing has been. The Japanese have had a few people working in it since the 1960s. Presently, there are two major people in the U.S.; Professor Neil Armstrong at the University of Arizona and Steve Forest who, just recently, I understand, went back to Princeton from the University of Southern California. They have been working at, primarily, vacuum deposited and molecular beam deposits of organic films for a good number of years now and learning a lot of fundamental things. Pryor, in England, is another person who has had a long history in this. But, vapor transport growth of thin films? We are the first ones to ever do that. Certainly, the first to ever do it in microgravity. Absolutely no way have we any kind of fundamental understanding of this because of the number of man years involved in this work. So, a lot of it is empirical. We're just finding it out for the first time. That's kind of where the serendipity and excitement of discovery is.

COMMENT: By way of general comment, that really matches the kind of position, I think, where materials science is in microgravity research. That is, we are in a phase of exploration and discovery. As we can gain better quantitative understanding of the various points of the triangle, I think the whole field gets richer. For example, we see that there is a potential impact of convection. We need to have a solid understanding of the atomistics of attachment kinetics, diffusion, all of these kinds of things. And those are really the areas where g is present. This is pretty exciting stuff. I wouldn't have guessed it. If you had told me up front what the result was, I would not have guessed it.

RESPONSE: Yes, the initial simple calculations show that there should be no convection in those kind of ampoules. Secondly, why should something like that, just a superimposed small velocity on this large scale diffusional velocity, influence the film microstructure over such a large dimensional scale?

QUESTION: When do you hope to publish PVTOS-2 results?

ANSWER: I've said this before, but by the end of the year.

QUESTION: If you want to, could you control the substrate temperature?

ANSWER: I suspect you could. But not with our present hardware as it exists, because there is no active heater in that portion; no active control mechanism associated with the heat pipe. No you couldn't without some modifications.

Transcript of Presentation

NUMERICAL MODELING OF PHYSICAL VAPOR TRANSPORT UNDER MICROGRAVITY CONDITIONS: EFFECT OF THERMAL CREEP AND STRESS

Daniel W. Mackowski and Roy W. Knight

I'm certainly not going to answer them all, but questions Mark raised in the previous talk are some of the issues involved in modeling of physical vapor transport under microgravity conditions. Specifically, there are vapor convection mechanisms that haven't been recognized in previous modeling attempts; thermal creep and thermal stress. We've just initiated this project, so we don't have any results. Furthermore, I want to say that I am coming here from a heat transfer and mass transfer background, not from a materials background. Please bear that in mind. Maybe this is a pretty strong statement, but it seems that physical vapor transport has demonstrated its potential for growing high-quality crystals in low-gravity environments. A simplified situation is where the sublimate, from a source at some higher temperature, deposits as a crystal at a lower temperature. Obviously, accurate modeling, of the transport processes is required to optimize this technology, especially in view of the considerable cost of running experiments in microgravity.

There has been a considerable amount of modeling, and most of it has been done with Rosenberger's group. These models have been based upon so-called classical Navier-Stokes formulation of convective-diffusive transport. The general conclusion of these modeling efforts has been that, at low-gravity levels, buoyancy-driven convection is negligible compared to diffusive transport. In fact, in a recent paper by Rosenberger, in 1992, they concluded that at gravity levels as high as 0.1-g, the influence of buoyancy on growth rates and on the uniformity of the growth doesn't appear to be that great. But under non-isothermal conditions which are characteristic of physical vapor transport processes, there can be additional convection mechanisms which hadn't been recognized in previous Navier-Stokes based formulations. These transport mechanisms fall into, basically, two categories. One is thermal creep, which is simply a slip-flow of gas over the side walls of the ampoule and is driven by a temperature difference in the gas tangential to the walls. Because of thermal creep, the usual no-slip boundary conditions at the wall do not hold.

QUESTION: Is it really fair to say that no-slip doesn't work? I mean this is still a certain distance from the walls.

ANSWER: No. This would be the slip right at the wall.

COMMENT: That, to me, is enhanced surface diffusion.

RESPONSE: This might be where we are speaking a different language. Usually, the traditional boundary conditions have zero velocity at the wall. If there is a temperature gradient at the surface, the velocity right at the wall will not be zero. As you will see, typically it is a small velocity, but under microgravity conditions, it can be significant.

QUESTION: Can that be physically seen?

ANSWER: Yes. It is the transport mechanism that results in thermophoresis of aerosol particles.

The second convection mechanism is thermal stress. This has to do with the constitutive modeling of the stress tensor, in the momentum equation. Traditionally, fluid stress is related to the fluid deformation by the Newton-Stokes stress tensor, but when you have a temperature gradient, you can also have a source of stress in the fluid directly from the temperature gradient. I also want to put some of this in a historical perspective. These effects were first identified by Rosner in 1989 when he was doing the modeling for Mark Debe. Additional work has been done by Napoliatano recently, and myself and Vedha-Nagegam, but Rosner really should get the credit for this. I'd like to discuss thermal creep and thermal stress in some detail. Thermal creep, again, is a slip-flow at the surface that is induced by a temperature gradient at the surface. It's fairly straightforward to explain from a kinetic point of view. It arises from uneven molecular transfer at the surface. Consider a temperature gradient in the fluid. Molecules coming from the high temperature direction transfer more momentum to the surface than molecules coming from the low temperature direction because of the higher molecular velocities. To balance the uneven momentum transfer to the surface, the surface essentially pushes against the fluid, and drives the slip-flow across the surface in the direction of the temperature gradient. A phenomenological relationship for the thermal creep velocity at the surface is given by the expression:

$$V_C = \frac{C_s}{T}(\nu)\frac{dT}{d_s}.$$

Here, C_S is a dimensionless constant of order unity, and d is the kinematic viscosity of the gas. I also want to note that this is not a rarefied flow phenomenon. This is a continuum flow phenomenon. It is not limited to the rarefied flow regimes as are the commonly associated phenomena of temperature-jump and velocity slips; that is, phenomena that are usually associated with higher Knudsen numbers.

QUESTION: Does that mean that it wouldn't be limited to gases?

ANSWER: Well, phenomena such as thermophoresis do occur in liquids. It is very difficult to predict; to come up with a simple constituitive relationship.

It is relatively straightforward to do an order of magnitude analysis to compare thermal creep to characteristic velocities based upon buoyancy and mass diffusion. This first ratio here represents the ratio of the creep velocity to the buoyant velocity:

$$\frac{V_c}{V_B} = \frac{\nu^2 \Delta T}{T(g)L^3}.$$

Here, we have a situation where there is an ampoule of length L, with a temperature difference ΔT imposed across it; g is gravitational acceleration; d is the kinematic viscosity. The ratio of the thermal creep velocity to the characteristic diffusive velocity, if we have both Lewis and Schmidt numbers around unity (which is typical of gases), would be the temperature difference divided by the mean temperature of the gas. These are some parameters for copper phthalocyanine physical vapor transport (PVT) which were identified in Rosner's physics of fluids paper. You see that in Earth gravity, the thermal creep velocity, compared to the buoyant velocity, is around 7% which is somewhat significant. At lower gravities, of course, it would be much higher. Also, the thermal creep velocity compared to the diffusive velocity is, again, quite significant. Typically, under most situations (Earth-bound situations), thermal creep is justifiably neglected as compared to buoyant convection. But in low pressure, non-isothermal conditions, thermal creep can result in velocities that are comparable to the characteristic, buoyant, and diffusive fluxes. It is interesting to note that strategies designed to minimize buoyant convection, such as low pressure which will reduce the Grashof number, small aspect ratio, or smaller L which will reduce the Grashof number again, actually act to increase the thermal creep effects relative to buoyant effects.

QUESTION: Is there an analagous thing, like solutal creep?

ANSWER: Yes, there is. You can have creep and stress induced by concentration gradients just as well as temperature gradients.

Just from a qualitative point of view, it seems like thermal creep will produce a recirculating flow in the ampoule. Creep would drive a slip-flow over the ampoule walls from cold to the hot which would recirculate back to the crystal. Perhaps this could adversely affect the uniformity of growth of the crystal. We don't know. It might be similar to carrier gas recirculation you get in a purely diffusive mode where the carrier has to recirculate around in the ampoule.

With thermal stress, again (when we have a slow moving nonisothermal flow) we have to reexamine the constituitive relationships that relate the stress in the fluid to the deformation of the fluid. Thermal sets is predicted from the Burnett contributions to the fluid stress tensor. These represent the second-order approximation in small Knudsen number to the Boltzmann equation. The Navier-Stokes approximation is the first order. Kogen showed that in slow-moving non-isothermal continuum flows, thermal stress terms can be comparable to the traditional fluid deformation stress. Napoliatano has performed an order of magnitude analysis to obtain a characteristic thermal stress convective velocity. Now we expect, for most microgravity conditions (and physical vapor transport conditions), the stress velocity to be somewhat smaller than the characteristic thermal creep velocity. But, Rosner has noted that for a consistent level of formulation, the thermal stress effects need to be included in the model, as well as the thermal creep effects.

QUESTION: This is independent of the gravity level?

ANSWER: Yes. This is a convective mechanism that arises from temperature differences, yet it has nothing to do with buoyancy.

The qualitative analyses indicate fairly strongly that under certain conditions, thermal creep and thermal stress can result in convective mechanisms under low gravity physical vapor transport processes. All of these qualitative analyses really can't tell us that much about what these convective mechanisms will do to the transport rates and the growth uniformity at the crystal surface. That is why a quantitative analysis is needed, which will require a numerical model which includes thermal creep and stress into a detailed analysis of physical vapor transport. What we are doing is, basically, adopting the work of Rosenberger and his colleagues. Our model will consist of a binary physical vapor transport system in a closed cylindrical ampoule, and we're going to look at a steady state axisymmetric formulation. Steady state, just from the previous talk, may not be a very realistic situation, but we might as well start there. The parameters in the model will include ampoule length, aspect ratio, transport properties of the carrier and the sample, total pressure, the equilibrium partial pressure of the sample at the interface, and the interface temperatures. We will choose the parameters to be representative of realistic conditions of ongoing and planned experiments.

QUESTION: How safe is the axisymmetric approximation?

ANSWER: For buoyant-driven flow, I don't think it is very safe because your first instability is not a symmetric roll. I believe, though, that for the thermal stress and thermal creep, this will be a symmetric problem, but it's hard to say where the instabilities might arise.

QUESTION: What will you use to vary your substrate temperature?

ANSWER: That is an interesting question, because of the previous talk. I had always assumed that the substrate temperature was simply fixed. We will approach the modeling, at first, as if that were the case. What we would really like to do is just march on from Rosenberger's work and include these additional transport mechanisms.

COMMENT: You are ultimately going to have to incorporate some property of the carrier gas.

ANSWER: That is correct.

QUESTION: Just out of curiosity, how many experiments are going on in this area?

ANSWER: Well, experiments have been going on in inorganic materials on vapor transport processes...Ludwig Vanderberg, Harry Weidemeier, Ching Hua Su... Yes, that is correct. This is certainly not pegged directly into organic and polymeric materials.

COMMENT: In fact, it looked like when you came up with the ratios of velocities, they didn't seem to be material specific as much as absolute temperature specific In fact, presence of the absolute temperatures is kind of surprising to me. Normally, in conventional fluid mechanics, you look at temperature differences more than absolute temperatures.

COMMENT: Let me say something in defense of his approach. He tries to demonstrate how important that effect is as compared to not taking it into account. That is the place to start. Now, let's go from there.

To conclude, we are in the process of putting together a code for examining thermal creep and thermal stress. Our first objective is to simply develop that code. The second objective is to determine the parameters in which thermal effects significantly alter vapor transport from diffusive and buoyant predictions. If there are regimes which correspond to ongoing experiments , we intend to identify the effects of thermal creep and stress on transfer rates and growth uniformity at the crystal surface. Furthermore, if we see a significant result, we would like to investigate the feasibility of reducing creep and stress induced flows through manipulation of the side wall temperature. That concludes my talk.

QUESTION: What is the magnitude of these effects?

ANSWER: As stated, about 60% in the absence of buoyancy effects.

Transcript of Presentation

ELECTRIC FIELD-MEDIATED PROCESSING OF POLYMER BLEND SOLUTIONS

Gary Wnek and Sonja Krause

Thanks, Don, very much for the opportunity to tell this audience, first of all, what we have been doing for the last few years in the area of electric field mediated processing of polymer blends as the title suggests. There is nothing to do with microgravity at this point, but there are some issues here that I would love to discuss and the ideas that may come from part of the audience. Let me tell you, first of all, who the players are and who the team is here. My key colleague is Sonja Krause in chemistry - she and I started this work back in 1989. Keith Nelson, who is in the Electrical Engineering Department, has been a quite a bit of help, in fact, in modeling the electric field profiles from some of our electrodes. Former graduate student Ganesh Venogopal is now a post-doc at AT&T Bell Labs. Joe Serpico is continuing the work in my group now. Joe is writing his thesis which is due in the graduate office on Wednesday; so he is virtually done, although he's got a couple of all-nighters to go I think. We have some colleagues in Xerox who I have to acknowledge who have been very, very helpful. We've had some nice productive collaboration with Drs. Tom Smith, Marty Abkowitz, and Keith Watson. Xerox has provided us with some support, in fact, for the last two summers. We have had one of our students go out there and spend the summer at the Webster Research Center. Also, NSF and DARPA have been quite generous in funding this activity. Our activity, specifically, has to do with polymer blends. Let me just say a couple of words about blends in general. If one tries to mix a pair of polymers at the molecular level, we frequently find that mixing does not occur to a great extent. More often than not, phase separation occurs. The general idea for "why" in a sort of zeroth order picture is illustrated here. If you take a two-dimensional lattice, and try to imagine something like carbon tetrachloride and benzene mixing, xs and os, like a checker board, you find that there are many permutations by which you can arrange the xs and os on the checker board. What this means, thermodynamically, is that the entropy of mixing can be quite high for small molecules. It turns out that when you've got polymers mixing, your checkerboard squares, which you might consider to be about the dimensions of the repeat unit, are filled, many of them with a single polymer chain and those multiple fillings restrict the number of sites that another polymer chain can fill into. What this translates to, in general, is that the entropy of mixing of a pair of polymers is frequently lower, sometimes substantially lower, in entropy of mixing than small molecule pairs. Phase separation is more often than not the case. Our work, as the title suggests, has been to look at the creation of polymer blend films from solution where initially the three components, the solvent and the polymer pair, are homogeneous; they are miscible. We're going to be doing film casting; letting the solvent evaporate and looking at the morphologies of the resultant polymers after evaporation. I'll just mention this: most polymer pairs are immiscible; hence, phase separation. Here is the key question. Consider a phase morphology which is frequently, and we will see photographs of these later, a dispersion of spherical droplets of polymer A in a sea of polymer B if polymer A is the minor phase. Can you modulate that morphology and generate anisotropic properties? We haven't come this far yet. We're starting to understand in some detail, at least, this issue, and that will be the main focus of what I have to say this morning. In terms of the anisotropic properties, we have some ideas there, but have not yet done anything in that direction. A little bit of polymer chemistry here in terms of systems we have been studying; my group has focused primarily on the combination of polystyrene and polyethylene oxide. We are interested in polyethylene oxide because it can dissolve large quantities of salts. It is a common polymer electrolyte used as a prototype for studies in high performance batteries. The fact that it can dissolve salts like lithium triflate is of interest to us because it allows us to, in principle, change the dielectric constant of this phase. I'll tell you, in just a few moments, some of these effects we are seeing have their origins, to a large degree, in the dielectric constant difference between the two phases. Sonja Krause's group has focused a lot on polystyrene/PMMA. I'll show you one photomicrograph of that system and they've also been looking at polystyrene and polyvinyl acetate. Polystyrene has been a common host in our studies here, where the minor phase has been other things. Another polymer system that my group has looked at, in collaboration with Tom Smith and his colleagues at Xerox, has been a block copolymer of styrene and ethylene oxide as the minor phase in a host of polystyrene. One other introductory bit about our systems (again, the polystyrene/PEO is the one we concentrated on the most), we're talking about phase sizes of several microns here. Again, the motivation of PEO phases is that we can change the dielectric constant, in principle, by addition of various quantities of salt. In this blend system, the diblock copolymer/homopolymer blend, we should have phase size, now, that are on the order of a few hundred Ångströms. It was of interest to us, once we started this work, and saw that we could indeed get some interesting morphological changes during film casting compared with casting outside an electric field, to see how far can we extend this in terms of small phase size. Does what we see break down at small phase sizes? These are some of the key variables, only a few of which we have studied in any kind of detail, or semi-detail at least. There is the molecular weight and the viscosity of the components, and the dielectric constant difference. We're doing solvent casting. How does the solvent partition between the two components during evaporation? There is an interfacial tension between these two incompatible components. We play with different electrode arrangements and ac vs dc fields. All I'm going to tell you about this morning are dc field experiments. We have only done a very few ac field experiments. We'll be doing more of those beginning this summer.

There are three effects I want to tell you about by way of introduction. Then we'll get to some of our data and experiments. This phenomenon of "pearl chain" formation has been known for many years. For example if you take spherical silica particles and disperse them in a fluid like silicone oil and apply a field, you can see in a microscope that the particles line in the field direction. This is a phenomenological model for what is happening here. The critical field which causes a pearl chain formation depends on the negative 3/2 power of the radius of the particles. There is this dielectric constant, this delta epsilon term in this part of the equation here that we think is important, and of course there is a temperature dependence. These are some of the assumptions that have gone into the development of this model back in the late 60's and early 70's. The first one breaks down, certainly for our materials. We don't have polarizable hard spheres. We've got viscoelastic, solvent swollen droplets coming out of solution at the onset of phase separation. It's not quite clear to what extent we can apply this equation directly. But we still think, regardless of that, this relationship holds, and perhaps the larger the dielectric constant difference, the easier it will be to see these sort of effects at lower applied electric fields.

The explanation for what is happening with pearl chaining, for example, is if you've got nonconducting particles in a matrix of something else, you get interfacial polarization, and, to a polymer chemist, you're essentially getting polymerization here. These little spheres are acting like difunctional monomers in the crude following sense. You get polarization within the spheres that generate positive charges at one surface and negatives at the other, and they attract each other and line up with the field. I know that is crude, but that is essentially what is happening here. The more formal explanation is that the electric field lines are coming closer together. The regions of highest field are at the interfaces of the particles themselves, and they attract each other. Because we have, not hard spheres but deformable droplets, there is another electric field phenomenon that must be considered that people have realized for a number of years, and that is deformation of liquid droplets in an electric field. There is also a theoretical development in this area which dates back to the mid-60's or so. And here is a relationship, again, with the field ratios. This axial ratio depends on the applied field, and the field at which you're going to get a spherical droplet elongated in the field direction depends on delta epsilon. Notice, here is an interfacial energy term, sigma, which is going to become important later. We have added diblock copolymer to some of these polymer blend samples in an attempt to lower the interfacial tension to see if this process can become easier at lower fields.

There is one last phenomenon I will talk about, and then we will get to our experiments. We can generate long cylindrical columns of liquid which eventually become unstable and frequently, they break up. What one notices....you probably can't read this in the back; let me just tell you what the caption says. "This is a thread of nylon 6,6 in a matrix of polystyrene that has been heated above the melting point of the nylon..." What you start seeing is that this thread of nylon starts to form these pinched-off regions reminiscent of what a physical chemist in this area would term a Rayleigh instability. Eventually the liquid columns break up into droplets. The larger droplets, here, have a somewhat smaller interfacial area, and that is the driving force for the break-up. In summary, there are at least three things that can happen. One can have spherical particles which can chain in the field direction. If those particles are fluid enough, they can elongate in the field direction. If they become too elongated above some critical ratio of length to diameter, depending on viscosity of the matrix, and a lot of other variables we haven't quantified yet , the highly elongated phases can breakup. Given that by way of introduction, let me try to summarize our experiments.

This is a typical electrode array that we use to do our experiments. These are parallel electrodes in an interdigitated fashion made by lithographic techniques. We received a mask from IBM to do this and these spots are actual samples of polymer which resulted from solvent evaporation. We drip on our three-component solution, two polymers and a solvent, e.g., polyethlene oxide, polystyrene, and cyclohexanone. We attach our voltage source to the ends of the array and let the solvent evaporate over certain periods of time. We put a petri dish, inverted, on top of this to try to limit the rate of solvent evaporation, and then examine in an optical microscope, in the case of the blends, exactly what we have done. In terms of what the field lines look like, this is a crude model, courtesy of Professor Nelson at RPI. This is our glass substrate on which these electrodes have been patterned. This is just air underneath. Right here are aluminum strips. Here is our droplet of solvent. We put in several parameters for the dielectric constant of the polymer, etc. The point is that there are field inhomogeneities within the droplet. These blends were typically 90% polystyrene and 10% PEO at two different molecular weights; 10,000 and 100,000. Other experiments, in collaboration with the group at Xerox, have been with this diblock copolymer which they have prepared having these characteristics (molecular weight of the polystyrene block of about 150,000; the PEO block of about 35,000). Since then, one of my students spent last summer at Xerox and made a whole series of these diblock copolymers. I'd like to go to the slide projector and the first thing I want to show you is a photograph from the literature that got us thinking about this whole thing. These are mouse myoloma cells which are chaining in an electric field. This is the kind of photograph that really got me thinking about polymer blends, for example. Imagine phase separation of droplets of polymer A in a sea of polymer B. If you can align cells in a field direction, can you align droplets of polymer? It is really a biological paper that started the whole thing going here. The first photograph is a sample of PEO 10,000 molecular weight in polystyrene host, about 10 wt.% PEO. You see the typical spherical morphology that one would expect. By the way, this is a kinetically trapped morphology. If you think about a thermodynamic result here, it should be like what happens with oil and water. PEO should form one continuous phase and polystyrene should form another separate phase. Because of the tremendously high viscosities of these polymers, especially toward the end of the casting when there is very little solvent left, you get these kinetically trapped spheres of the minor phase in a sea of polystyrene. This is in the absence of a field, by the way.

When we did this casting on one of these electrodes at 3 kV/cm applied field, we got pearl chains. We were quite excited to see this, because this was the sort of effect, based on the biological cell chain alignment in the field, that we were expecting. It is certainly possible to modulate the morphology of this particular blend system by casting in a field. Now here is a parallel experiment. In this case the molecular weight of the PEO is 100,000 Daltons, polystyrene is the same; this blend is also 10 wt.% PEO. This is in the absence of a field. The spheres are somewhat larger on average, than they were in the previous case, cast in the absence of a field. We think this is because there is a larger interfacial tension associated with the higher molecular weight PEO.

When we did the analagous experiment, casting this sample in the field, we got column-like structures. These are PEO columns that are on the order of approximately the same diameter as some of the spheres, 6 to 8 μ, on average. Some of these extend almost the gap of the electrodes, which is on the order of 2 mm. A somewhat better picture comes from our first paper, here. This is PEO, 10,000 molecular weight; this sample was cast, now, at 10.5 kV/cm. The PEO is 100,000 molecular weight. Notice there is a distinct molecular weight dependence. Everything is the same here in terms of composition and in terms of applied field during casting. The only variable that we attempted to control here is the molecular weight of the PEO. Notice these pinched-off regions of these column-like structures. This looks like a classical Rayleigh instability in fluids, and we think this is a sign that this particular column exceeded its critical length and began to break up, and was frozen there. These are final photographs, by the way. This is after all of the solvent is evaporated. So this is the final record of the morphology.

Let me go to the next slide. We decided to try to investigate some of the dynamics of this process rather than just look at the final morphology. Sonja Krause's group, now by the way, has an image analyzer connected to the optical microscope and we can start doing these experiments in a more sophisticated way. This series of photographs is an attempt to find out what happens to these droplets when you turn the field on. The first thing we notice, and this is when the sample is still very fluid (10,000 molecular weight PEO in polystyrene with cyclohexanone as the solvent) as soon as the field gets turned on, these sausage-like structures appear. We think that the first key process is elongation of droplets, and perhaps some fusion of droplets into larger droplets and then elongation into these sausage-like structures. What is curious, is that in some areas we start seeing already some of these pinched-off regions that are characteristic of a Rayleigh instability. After the solvent evaporates, the sample gets more viscous we start seeing what looks like clearly the Rayleigh instability and breakup of these sausage-like structures into these elliptical entities.

Finally, at the very end, we have pearl-chains. We think, from these kinds of studies, that pearl-chains are not being formed, at least in this particular sample, by droplets of PEO phase separating, and then aligning in the field direction. We think the droplets are coming from the generation of column-like structures which then break-up due to the instability in the field to generate what look like pearl chains. Why in the higher molecular weight PEO did we get column-like structures to the very end, we think might be due to a kinetic phenomenon where you've got a much more highly viscous PEO component because the molecular weight is higher. These columns are perhaps stabilized by the higher viscosity, although we are not quite sure about that.

QUESTION: Is this at room temperature?

ANSWER: Yes, this is all room temperature, by the way.

QUESTION: Is there any mutual solubility between the phases?

ANSWER: Very, very little. They are essentially incompatible.

COMMENT: These look very much similar to monotectic microstructures. I understand 30 years ago, someone in Bruce Chalmers laboratory did try to do the organic materials, cyclohexanone, and some other component and they got exactly a similar microstructure. Also, Don Frazier has published very extensively in the monotectic system and they align very dependent on the growth velocity, I should say solidification velocity, and very much with these kind of morphologies.

RESPONSE: Are these polymer samples?

COMMENT: Organic samples; and they are using similar solvents.

COMMENT: Succinonitrile/water samples have significant mutual solubility. Also, you get things like thermal migration going on since you've probably got thermal gradients, etc. It's different.

QUESTION: Gary, at what concentration do you get precipitation out of solution?

ANSWER: I just don't have those numbers, David. It depends on the molecular weight of the PEO. Sonja Krause's group has been interested in constructing phase diagrams which can quantify this. They, so far, have limited their studies to the PMMA/polystyrene system.

Let me just try to mention some of Sonja Krause's work. What we are seeing in the PEO/PS system is a fairly general phenomenon for various polymer pairs. This is a sample of poly(methyl methacrylate) as the minor phase in a sea of polystyrene, and we see these rather extended, elongated structures generated by casting. In the case of poly(vinyl acetate) in polystyrene, we see rather nice looking columns breaking up due to, apparently, a Rayleigh instability. The only case in which we have never seen an effect of the electric field changing the morphology of the final polymer is polybutadiene/polystyrene. There, we think the dielectric constants are so similar, there is just not enough contrast.

QUESTION : Gary, a lot of those columns that are in there are well in excess of the Rayleigh limit. Why are they still there, and appear to be unperturbed?

ANSWER: Well, I'm not sure. Let's move on to this equation very briefly. This predicts a growth rate for the generation of these Rayleigh instabilities. You've got, for example, an interfacial tension term here; you've got a viscosity ratio - this is the ratio of the viscosity of the column phase to the matrix. All I can say is, perhaps, due to solvent partitioning, in the case of the one I just showed, the viscosity of the column is growing faster than the viscosity of the matrix because the solvent is preferentially in the matrix and, therefore, it is retarding the growth rate. You can see that there are a whole host of areas there that we have to study. But in this equation is this interfacial tension term, and we thought perhaps we can stabilize these elongated structures by lowering interfacial tension deliberately. How can one do that? We've got a polyethylene oxide/polystyrene blend; what can one do to lower the interfacial tension? Add a diblock copolymer of styrene and ethylene oxide. And that is in fact what we did. In the deformation equation, the ease with which you can deform one of these fluid droplets depends on the interfacial tension.

COMMENT: Just by increasing temperature might be a way too.

Yes, we opted for a chemical method rather than that. But you are right, that would be another way to do it. We prepared a series of samples where we increased progressively the amount of diblock copolymer from zero up to about 4.6 wt.%. To make a long story short, what we are looking at is the case where there was 10,000 molecular weight PEO in polystyrene. We never saw anything but pearl-chains no matter how high a field we went to. If we add a little more diblock copolymer, nothing seems to happen, except that the phase sizes get a little smaller because we are lowering the interfacial tension. Finally, at 4.6% we see these elongated structures. This is only at 3 kV/cm, by the way. One of my earlier figures, was at 12.5 kV/cm, and all we saw were pearl-chains. So we think there might be some credence to the idea that we are stabilizing the break-up of the PEO elongated structures, or columns, in this particular case. I want to switch back to one overhead for a moment, then we will wrap up. Talking about block copolymers, block copolymers have thermodynamic morphologies rather than kinetic morphologies. We were interested in investigating how electric fields might modulate some of these morphologies which are at quite fine scale, by the way, in comparison with homopolymer blends. Here is the general idea in a nutshell. We decided to take a diblock copolymer polystyrene/PEO, where B is smaller than A, but B is such that you should form a cylindrical morphology of PEO in a sea of polystyrene. We decided to take that material and dissolve it in homopolystyrene. All you should get are micelles essentially. These are the PEO chains, and the blue chains dangling from the surface are the polystyrene tails of the diblock, and this blue background is a sea of polystyrene. What we are interested in is investigating what would happen if we cast films of these in the absence or presence of an electric field. Let me just show you what we get. This is the morphology after staining of PEO polystyrene diblock in a sea of polystyrene. These droplets are on the order of 200-300 Å in diameter, so they are very, very small. Now at 2 kV/cm in one of our array electrodes, we start seeing clustering. There is a tremendous depletion of the micelles and clustering into these regions. We think this is driven by local electric field inhomogeneities. This is TEM, by the way. It is a much more difficult kind of experiment, because you can't really see what you've got at the end of the experiments as we did with the blends. This is a transmission electromicrograph obtained after microtoming and staining with phosphotungstic acid to give us the contrast of the PEO regions. That only stains the PEO. So what we are seeing are the PEO micelles. At 4 kV/cm, we start seeing island-like structures. These structures are starting to elongate in the field direction. We have proven that this is the field direction by some control experiments. At 8 kV/cm, rather remarkable worm-like elongated structures are obtained which are apparently cylinders if you cut the sample this way and look down. What we think is happening is the following. Because of this field-induced clustering, the local concentration of diblock in the polystyrene is becoming quite high within these regions. Since this diblock copolymer wants to form cylindrical phases naturally, in short, what we think we are doing is driving a sphere to cylinder transition in these localized regions. We have no idea yet as how to control spatially where this occurs. But we are excited about the prospect because we are manipulating here phase sizes that are on the order of about 200-300 Å in diameter, and generating these column-like structures that are about the same diameter. We're modulating the morphology of polymers on a very, very fine scale.

ANSWER TO QUESTION ON WHETHER THEY ARE SKEWED:

No, these are not skewed. This happens to be the way they were photographed, but in this viewgraph I just showed you, the field direction is virtually parallel. Let me wrap up and tell you a couple of things about where we are going. One of the side advantages of this work has been the following. At Xerox, they have begun investigating the dielectric relaxation properties of some of these materials. We thought dielectric spectroscopy might be an interesting way to characterize what we have done in terms of morphology modulation. What they find is something very interesting. If you take PEO, and disperse it in polystyrene, and do a dielectric relaxation spectrum, you get the entire spectrum very cleanly, including the melting point. If you just take a sample of PEO and run the dielectric spectrum, because of the conductivity of PEO and traces of ions, you get a huge tan delta signal. But because you have dispersed the PEO droplets in an insulating matrix, so they are not connected (they're not talking to each other), one can go from sub T_g transitions all the way to T_m and get a very, very beautiful profile. We are writing up that work now. That is an interesting thing. In terms of where specifically our work is going, Sonja Krause's group is focusing more on the physical chemistry, measuring interfacial tensions. She has an apparatus now that will allow her to actually quantify some of these parameters in equations I showed you She is also looking at the phase diagrams and how electric fields affect phase diagrams. Our group is interested in, among other things, polymer synthesis. We are trying to make polymers with large dielectric constants, greater than at least 6 or 7 into the low- to mid-teens. For PEO and polystyrene, delta epsilon is quite small. Polystyrene is about 2.5, and PEO is about 3.4, so to get the effect we have seen here with such a low delta epsilon suggests that if we could make delta epsilon significantly larger, then we could see some of these effects at very, very low fields, for example, polymers like these with nitro, thio, phenoxy groups which we've been able to make have dielectric constants between 8 and 10. These are siloxane materials; we've come up with a way to cross-link these rather fluid materials so we're going to be doing some investigations with these. Lastly, we have prepared these monomers to make polyurethanes which are also of interest in nonlinear optics. We have made a whole series of these that we are investigating as monomers for polyurethanes for high permittivity polymers in these experiments. We are doing some vapor deposition, by the way, in relation to some of the things you have heard about earlier. Professor To Ming Lu in the Physics Department is codepositing, in the vapor, these diols with isocyanates to make polyurethanes onto various substrates. Thanks very much for listening, and I will be happy to take a question or two.

Comment regarding work to make waveguides has shown all of the structures described, e.g., metanitroaniline in polystyrene, etc.— optical quality is poor, but basically, poling, etc., is being done for optics—discussion follows.

More discussion on whether or not end groups are polar of these polymers.

Additional discussion regarding whether or not sedimentation could be an issue, here, for processing. Comments regarding the similarity of these systems with monotectics where processing in microgravity is required to prevent sedimentation. Are the density differences between phases large enough, and is viscosity low enough such that space processing would be beneficial?

The response is that there certainly could be an issue here.

Transcript of Presentation

DEFECTS IN ELECTRO-OPTICALLY ACTIVE POLYMER SOLIDS

David C. Martin

It certainly is a pleasure to be here and have a chance to discuss what we are doing in my group. I wanted to give just a little bit of an overview about the research that is going on in my research group in Materials Science and Macromolecular Science at the University of Michigan. We really have four different thrust areas. The area I'm going to talk about today, has been funded for the past 2 years by the National Science Foundation, and it involves defect physics in polymers and polymer crystals. What we have been doing is looking at polydiacetylene materials, isolating defects in those materials, and looking at how those defects control electronic and optical transport through those materials. Of course, that topic is central to the topic at hand, and I'm very anxious for the chance to get some good constructive criticism and feedback from what it is that we are doing and interested in.

One of the aspects that makes this problem particularly interesting is that there is a very nice phase transition from monomer to polymer in a polydiacetylene system. That has been something that we have focused considerable attention on just recently. The other areas of research that I have going on, which I will be happy to talk with you about later, if you are interested, is that we are looking at surface organization in polymer films, and how the presence of a free surface changes the organization of a polymer as it approaches a boundary. That is particularly important for adhesion and fracture initiation, and the polyimide system is what we have been focusing our attention on there, in work that has been sponsored by Dupont and General Motors. We also have work going on in making new structural fibers. High strength materials have a particularly insidious limitation in compression. They fail by forming "kink" bands. So what we have is a monomer that has an activated group on the side that will go through a thermally-induced, mass-conserving cross-linking reaction at elevated temperature that will allow you to introduce lateral organization, lateral cross-links, between materials. That monomer, and those of you who are chemists will know, can be incorporated into anything that has terephthalic acid in it, which includes Kevlar, PBO, PBT, PET, etc., a very large range of currently interesting high-performance polymers, so this is some very exciting stuff.

The other thing that we have going on is the synthesis of polypeptides by genetic engineering. My interest is in the self-organization of these materials and their processing. SLPF is a genetically engineered protein polymer that is similar to silk that has incorporated in its backbone the functionality that is specific to human fibronectin. The ability to create new materials by genetic engineering, I think, represents a new frontier in materials science that has considerable implications for the future. What I want to focus my talk and discussion on today is the central question that I think the people in this room should be interested in. That is, what are defects in organic and polymer crystals? What defects are, first of all, possible? How do we control those defects? How, through creative processing, do we put those defects in or take them out? What role does gravity play in changing what defects are there and how those defects arise? And, how are these defects different from those of crystals that we know so much about—the inorganic systems that have been the focus of attention for many, many years? How can we use that insight that exists to modify, and to guide and to really do the sort of defect physics that is appropriate? The polydiacetylene system is a nice system to study these questions, because it is possible to grow very large single crystals using the monomer precursors to the polydiacetylenes.

The electronic and photonic properties of these materials are quite interesting for optical applications because of the conjugation of the chain backbone. Therefore, the polydiacetylene system is very useful to study because of its possible role in optical properties. There is also this question of a solid state phase transition where we go from monomer to polymer and that is something that a materials scientist like me finds very interesting. The other thing that is met scientifically is that the polydiacetylene systems have a large body of knowledge that is available. Therefore, we can do good materials physics because if you want to do a new system you do not want to spend an inordinate amount of time on a system where you have got to completely reinvent the wheel. And so there is a whole host of information and other people interested in doing things that means that it is competitive. You have to make sure you are good to get good things done, but it also means that you can do those good things. What we are interested in is defect isolations. What we want to do is to take the usual frame of mind, and turn that around to our advantage. Ordinarily, when we are making crystals, we'd think "Oh, darnit, we've made defects, and those defects are going to destroy our properties." But what we are saying is, "OK, let's live with those defects, look at those defects, and understand the defects, and then we can know how those defects control and limit the properties of the materials we are interested in." We've got the possibility of zero-dimensional voids. We've got one-dimensional defects like dislocations. We've got two-dimensional defects which are surfaces and grain boundaries. Our approach is to find methodologies that allow us to put those defects in on purpose, and then isolate them, understand them, and know how they control the properties of our material. Now, I don't think it is hard to appreciate the rationalization for how important that approach can be. If you know anything about the semiconductor materials industry, you know that the control of defect processing and processes through doping, etching, and device manufacture has been the reason that we have had this incredible revolution in the control of electronics as what has happened in transistors. Where we stand right now, I believe, is on a similar forefront for seeing a similar revolution for using photonics, for using light, and using organic materials to do the same sorts of things. So we are really, I think, in perhaps the 1950's of the semiconductor industry looking toward the future of what could possibly happen. Now, maybe it's not going to be that big of a deal, but I think that is why we are all here and why we are all interested in this. That is what we have to find out. What can we do, and what can't we do?

What I want to talk about, today, is the work we are doing on defect characterization. If you are going to be interested in the defects in a material, you have to know everything about the material itself, because in order to describe the defect, you have to know the symmetry and properties of the parent phase. You need to have very high resolution techniques for characterizing microstructure. You also need to be able to compare those microstructural studies with some properties. So, I am going to allude to the fact that this is an area where we can make a much better match, and I'm hoping that we can talk about experiments that will be appropriate. We are looking at electronic measurements where we measure time-of-flight of electronic carriers through our materials. We are collaborating with people at Wright Patterson Air Force Base on looking at photonic properties and measuring χ^2 and χ^3. The polydiacetylene materials, as I have said, can be grown into large single crystals. Here are some crystals that we have grown in my laboratory. These are the monomer crystals, and you can grow these from solution which is the way we typically do it. What we are interested in is putting defects in these materials after we have grown the large, and ostensibly perfect crystals. Just to point out how important defects are before we go on, here is a view down the chain axis of a polydiacetylene crystal. We are looking at the individual chains, so I would ask you to imagine a case where we would have a single grain boundary; where we have taken one polydiacetylene crystal and superimposed another polydiacetylene crystal on top of that. The questions we are interested in, when we talk about electronic and photonic transport, relate to how many chains are connected across an interface of this sort. Because it is the chains that do all the electronic and photonic transport. The question is, as I start to misorient these crystals, what goes on at the interface? What you can see is that as the orientation gets smaller and smaller, there are regions (this is called the "O" lattice) where there is coincidence between similar sites and the lattice of crystal 1 and lattice of crystal 2. You can describe an interface like this in terms of an array of screw dislocations if you are twisting, or an array of edge dislocations if you are tilting. In fact, if you model what the interface looks like, the number of lattice sites that will remain connected, given a width of a defect, is related to the dimension of the lattice spacing itself. As the width of the defect is very small with respect to the lattice spacing, this property, the conductivity, is very insensitive to the defect. If the width of the defect is very big, then you only need a small amount of misorientation between the crystals, and your properties are shot. So, what we are interested in, is how do properties vary as a function of defect geometry? Let me talk a bit about some experiments that we have been doing.

This is a high-resolution transmission electron micrograph that is taken in a low-dose mode where we are operating only with the number of electrons that we absolutely need to take the image. This is a projection of the polydiacetylene DCHD that we have been studying in some detail; projection of the 100 direction. This is the projected electron potential. This is the theoretical image that you should see given the operating parameters of our electron microscope which is 400 kV. This is the experimental image. As you can see, we can reproduce things quite well. The lines, here, correspond to the individual stacks of the polydiacetylene molecules and they are 12 Å apart. One of the things you can also see, is that you can start to reveal the submolecular structure. You can interpret these images in terms of a local map of the orientation of the polymer molecule. In the images I will be showing you, we will be examining the nature of how these local lattice images change near those defects. Here is a thin film of the DCHD diacetylene deposited from solution onto a substrate. The crystallization conditions that we have used in this case are such that the chains are now oriented normal to the surface of the substrate, and if you look down at an individual crystal, you can actually see the a-axis and the b-axis, and the crystallographic angle of 108° between those axes. It's a monoclinic crystal structure. Its space group is P21 over c. And this is essentially, now, a map of what I showed you on the overhead where you can actually look down those molecules and imagine those packing together laterally.

The other experiment that we have been doing is to isolate the individual defects. When we deposit material onto a substrate, what we'll often see are individual droplets. The droplets all have cracks in one direction. What that corresponds to is the fact that the droplets have a uniform orientation of the chain axis. When you take an electron diffraction pattern, you can see that there is a single orientation of the polymer chain. The polymer chain is running in this direction, and a schematic of what is going on in the droplet is as follows. Now this droplet geometry makes it possible for us to isolate defects, and determine how the properties of those defects change. We can look at the ends of molecules here, and we can look at the sides of molecules here. If we look at the side of the droplet, what we see, in fact, is that at the edge of the droplet, the lattice lines will curve. So when it crystallizes in the presence of a free surface, the molecules are forced to curve in order to accommodate the presence of that free surface. We can imagine in a situation like this, where you've got the material trying to crystallize, but now it's crystallizing near a curving surface, because of that (and this is a tic-tac model; if you take some tic-tacs and put them in a circular container you'll see that they will do a similar thing - where they are frustrated by the local requirement to crystallize in a local need to follow the curvature of the free surface). If you look, in some detail, in that region outlined in the box, here is another case where you can see that the lines are curving like this. Now, it is possible actually to identify individual dislocations that are present that will allow you to accommodate that curvature. This is a well-known phenomenon in other actual systems.

QUESTION: (regarding possible clustering)

ANSWER: There is no clustering here at all. The stippling that you see is simply due to the shot noise of the electrons.

We are required to operate at doses that are less than 20 C/cm^2 which means that you use every electron you can send through. Every electron that goes through is doing something to your sample. As I will show later, we have been able to exploit this phenomenon. We can induce the polymerization from a monomer by using the electron beam. So you can actually use that to get some interesting physics. The image corresponding to the white lines represents traces of the individual molecules packed together laterally at 12 Å. It is not possible for us to unambiguously say that the white line is the molecule, and the black line is the space; or the black line is the molecule and the white line is the space. But we do know that it is one or the other. So we know where the dislocations are. It's unambiguous. What we are interested in is the reorganization near the dislocation core.

QUESTION: Normally when you have dislocations that are not of high density, and you start to get alignment, you might start producing a low-angle grain boundary. Do you see that there?

ANSWER: In fact, if you want to use a schematic diagram, this is a 5° low-angle grain boundary in which all of the dislocations are of like sum. Now, that is actually something that is interesting and relevant to polymers, because any grain boundary in a polymer system has a given flux of chains that is present at the interface. You either match that flux, or one crystal has more flux than the other. So the chain flux from each crystal is either the same or it is different. If it is different, then there is more coming from one side. If there is more coming from one side, that means all the extra chain ends are associated with that crystal. You've connected all the rest of them. That is exactly what we see here. All of the edge dislocations go with this upper chain where we are sort of moving it around until you've got extra polymer chains at the end, and they are coming in from this side where there is more flux of chains.

FOLLOW-UP QUESTION: So that was the growth direction, then?

ANSWER: Well, these are droplets, and it is crystallizing in the droplet. You've got the crystallization going on in the droplet geometry where we have deposited this monomer solution onto the substrate. Reorganization occurs as the solvent is leaving this droplet. These are edge dislocations actually running in different directions than the c-axis, which we have not yet resolved. There are also edge dislocations running this way.

One of the things that we became interested in was, we know that the polydiacetylene reaction is a topochemical reaction that involves a very specific local chemical change. The reactivity of the molecule is very much sensitive on the geometry. But the geometry near the defect, the symmetry, is different than it is of the bulk crystal. So, what we believed was that we could look at the dislocation core and get information about the extent of reactivity and the disorder necessary to induce changes in reaction by etching away, essentially, the unreacted material we felt should be present at the core of the dislocation. This is a scanning electron micrograph (this is in our stem). Here is a single grain boundary running through the bulk of the crystal. This is an etched droplet. You can see that there is etched material that has been taken away near the edges, and in certain regions in the interior. The next photo shows a view down at the other end of the droplet where you can see the molecules come nearly straight when they are perpendicular to the edge of the droplet. (Next slide) This is the model of how you introduce dislocations to cause curvature of a crystal lattice. (Next slide) This is the same micrograph I showed earlier. (Next slide) Here is the case where we now etch the droplet. What you can see is that we have evidence for the swelling of grain boundaries arranging themselves into layers that are normal to the chain direction consistent with the formation of this bending that is involved in these crystals. You can also see regions near the edge where we have removed material.

QUESTION: How big is the droplet?

ANSWER: The droplet itself is about 2 or 3 microns across.

QUESTION: How can you distinguish between a small angle boundary and a void?

ANSWER: We can distinguish that. Next slide. Apparently I don't have that figure with me, but we can distinguish between a small angle boundary and a void because the small angle boundary is composed of dislocations. The voids will be present inside the crystal. So, what we do is to look at a simultaneous TEM/stem image so we can get information from surface morphology and from the projected thickness. The TEM gives you information about how much projected electron potential there is in your direction, and it is not possible to distinguish between a void and a dislocation. But it is possible, if you can get simultaneous information about the surface, because the screw dislocations will all come up to the surface, and the voids you see internally. In fact, you can distinguish very nicely, in an image, what's a void, and what is a screw dislocation that has undergone etching.

Can we back up a minute? I can't say, in this case, which are voids and which are screw dislocations. But, here is where it is unambiguous about the dislocations. Here is an instance of a small-angle boundary. The other image where we see the layers of the voids is consistent with this image because the position of those defects is the same as we see when we do the high resolution. But this question of voids and defects is something we are interested in, and something we would like to learn more about. Here, the contrast is nearly linearly related to thickness. The question that is coming up here is, are these holes from voids, or are they from dislocations that have been etched? I cannot tell from just a TEM image, because you need to have both the surface information and the TEM image. So, I did not mean to imply that these necessarily are edge dislocations. What

I meant to imply was that the arrangement into layers is consistent with what we saw in experiments where we knew they were dislocations.

Let me talk now about the phase transition, because I think there are some interesting things there that are worth spending a little time on. (Next slide) What we want to know in the phase transition from monomer to polymer, is the nature of the transition. In other words, how heterogeneous or homogeneous is the distribution of monomer that is reacting inside the solid state material. So we start out with all monomer, and we go to polymer. The question is, do we nucleate new domains of polymer within a domain of monomer, or do we have a uniform distribution of material, or is it some combination, thereof? (Next slide) So what we did in this case, was to take a single crystal of our diacetylene, imbedded in an epoxy matrix. We then microtome in a direction perpendicular to what will become the polymer chain axis. We look at these thin sections, and view down the chain axis so we can watch this phase transformation. What we see is that there is a dramatic change in the crystallographic angle, gamma, from 94° to 108°, that you can use as a signature for how far along the reaction is. (Next slide) The critical step that made this experiment work, was that you can actually use the electron beam to initiate, or to derive, this phase transition. It turns out that the dose you need to do that, however, is extremely low. The dose to convert is on the order of 10^{-4} C/cm^2. That is five orders of magnitude lower than the dose that you would normally use to destroy the sample. Anyone who has ever looked at a polymer with TEM knows how low that is in the first place. My initial response to the graduate student who proposed to do this work was, "...that's going to be extremely difficult, I don't know if it'll work..." Well, I told him it wouldn't work, but he went ahead and did it anyway. The point is that this is something that is extremely limiting when you're trying to worry about getting these sorts of microstructures. So here is a view down the monomer chain axis. You can now see the individual monomer molecules. That is the orientation; here are the angles, 94°. (Next slide) And it goes to 108° when it is polymerized. So what we are going to do, is to watch this phase transformation, dynamically, in the electron microscope. (Next slide) Here is just another example of that change in the angle. (Next slide) Here is an electron diffraction pattern down an individual single crystal of monomer, and you can see that the angle is 94°, just like you would expect. As we turn on the video camera, and track this process, what we can do is watch all of the intermediate stages from the monomer to the polymer and record those. We can go back and forth to get information about what exactly happens now.

You can see already that the spot that's starting to broaden a little bit (next slide) as you can see here, has gotten a bit broader. What happens in the intermediate stages of transition, if you look in gory detail, there is streaking that occurs, certainly in characteristic directions, that is consistent with defects that form perpendicular to those streaks that gives information about how that reaction proceeds. If I go to the next slide to show you the summary of the data, what you see is that at the start of the phase transition, the angle is 94°. As you turn on the beam, you see the continuous change from the monomer crystallographic angle to the polymer. And, in fact, those spots will broaden and then come back, then sharpen at the end of the reaction. If I plotted the intensity of the streaking, there would be a maximum at the intermediate stage of the reaction. The next slide shows sort of a schematic of what happens. There are no composition fluctuations. It's all monomer. The polymer has no composition fluctuations either; it's all polymer. But half-way through, we have local fluctuations on the degree of conversion. Since there is a shape transformation, there is a local stress that arises due to the fact that one place is a little bit more converted than others. That leads to cracks that form in certain characteristic directions that are low shear strength planes in the material. (Next slide) This is just dark-field imaging to show that you can also watch this process in real space. What we are interested in now, is looking at the interaction of the reaction with the defects that I was describing earlier. If you look at the defects in the video tape (next slide), that's the electron diffraction pattern showing you the monomer diffraction pattern. (Next slide) These bend contours correspond to local fluctuations in the orientation of the polymer crystal. And as it turns to polymer, essentially all of the bend contours leave the crystal. Because, now, the polymer crystal is very much stiffer than the monomer crystal, and it doesn't bend nearly as much as the monomer. So what you see is essentially the bend contour sort of just leaving. But if you look at the next slide, you see it is still monomer; it's still a single crystal. We still maintain the integrity and the crystal perfection. (Next slide) This is just to show that we can also get the phase transition in real space. (Next slide) Here is the 12 Å spacing (I suppose it is difficult to see but they are there believe it or not). We've got the lattice energies now on video tape, so we can watch the reaction proceeding at the molecular length scale. (Next slide) They sort of move from the upper left down to the right during the exposure. The next slide shows the digital Fourier transform showing that, yes indeed, they actually are there. Let me just conclude with some statements about where we are going and what we would like to do.

The experiment that we're interested in doing to isolate defects involves creating bi-crystals where we have, now, bicrystalline polydiacetylene that has a single grain boundary. We put contacts on the surface, and we measure the time-of-flight and the number of electronic carriers that we activate by exposing the sample to a pulsed UV laser. What we are doing is measuring those electronic properties as a function of the defect geometry. So we take the two crystals, we match them together, we polymerize across the interface, and then we look at how that grain boundary limits the electronic or photonic properties. What we would like to do is find out more about the materials that you are interested in, and how we could approach them in the same way. This is just a schematic of what we are doing in terms of the electronics.

QUESTION: Is that time-of-flight, or is that a recombination time?

ANSWER: It is a time-of-flight. We generate carriers, and we measure how long it takes for those carriers to move from one end of the sample to the other. This is an experiment that has been done many times in the polydiacetylene system which is why we felt comfortable doing it. We weren't reinventing the wheel here. These experiments have been done over and over. What we were doing is simply introducing a systematic change in the morphology of our sample, and doing a first-order extension of what work was there. Of course, what I would like to do, is talk with you here about doing a similar set of experiments, but look at changes in χ^2, changes in χ^3 as you systematically introduce defects of known numbers and types through the process.

QUESTION: Are you doing any theoretical modeling to include defects?

ANSWER: I'm not doing any theoretical modeling, but there is a woman, C. Singh at UCSB, who we are talking to. We really need to work with people who are familiar with how that structural organization changes the electronic and optical properties of the materials.

There is a lot of work on x-ray topography. What the x-ray topography work said was that there was a discontinuous phase transition. What I'm saying is, that you can get information like this from x-ray topography, but there is no way that x-ray topography can give you information about the organization near the defect that the resolution I'm showing you is necessary to see. When you etch those dislocations, you see a 60 to 360 Å region near the core that can be etched away. There is no way that x-ray topography can give you that sort of information.

Therefore, what you need to do is have systems where you can introduce known numbers of defects where you know what those defects are and you know where they are. That is what we are doing. And we feel that this approach of structural characterization gives us information about relaxation and reorganization near the defects that you really can't get by other methods, and that sort of detail is important. I'm not saying that we shouldn't do certain things that people can do to corroborate our information; it is just that if you want to see the defects, then you better go look at it. That makes sense to me.

COMMENT: In the electronic materials industry, the crystal growers have really become defect engineers in that they control properties of materials through the control of defects. But I think you are right. You are probably back in the 1950's in that regard in that you don't know the impact those defects have on electronic properties. It is an exciting place to be.

ADDITIONAL COMMENT: Just to argue on that fact, I think even organics; if you look at the solidification literature even at the turn of the century, 1910, 1915, people had started from that time with organics and polymers.

ANSWER: People have understood that defects are there, and people have understood that they are interesting. But what people have not understood, is how those defects control macroscopic properties of the system, and how you can control processing to put those defects in there on purpose to get the property that you are interested in. That is why we are all in this room today, right? Because that is what, essentially, everything we do boils down to. It is not the perfect crystals that make the devices. I've heard it said once that crystals are like people; it is only the defects that make them interesting.

Transcript of Presentation

PREDICTION OF NONLINEAR OPTICAL PROPERTIES OF ORGANIC MATERIALS

C. Moore, B. Cardelino, S. Zutaut

I would like to present some work that Beatriz Cardelino and I have been working on the last several years. Most of our work has been on calculations of first- and second-order hyperpolarizabilities (beta and gamma). The calculations are, of course, single molecules in the gas phase, but we have addressed to some degree this oversimplification. We feel there is a great deal that can be done on the molecular level which can be used as a predictive tool.

We started work with Benjamin Penn, here at NASA, and Wayne Hyde, who was with the JOVE program, from Northwestern Louisiana State University, some years ago. They were interested in synthesis of nonlinear optical materials and we have developed a method for screening candidates. We try to focus on major trends so we can predict relative strengths of the molecular polarizabilities. The method is very easy to use.

First I would like to present some predictions on 2,4-dinitro substituted benzenes. This is work we did in conjunction with Ronald Clark, from New Mexico Highlands University, and Mohan Sanghadasa, from the Physics Department of the University of Alabama at Huntsville.

The table shows the second-order polarizabilities or beta for substituted dinitrobenzenes and for plain dinitrobenzene as a comparison. The first column shows our calculated values and the second column shows the EFISH measurements. The third column shows the EFISH measurements after we have done some corrections to account for dispersion and solvent effects. The thrust of this presentation is to explain how we go from the second column to the third column. You can compare our predictions with these corrected measurements and you see that they are within 25%. We will explain later, too, how we get the error estimates shown next to the predicted values.

You see from the table that it is not particularly straightforward to compare theoretical predictions with experimental data and that one has to be careful to get a sense of the accuracy and reproducibility in the theoretical results. We are going to present data concerning p-nitroaniline because it is well discussed in the literature.

The plot shows the values of beta for p-nitroaniline as a function of the incident radiation. The top curve corresponds to experimental values in dioxane solution. The bottom curve corresponds to calculations on single molecules. Extrapolation of the bottom curve to zero energy corresponds to the static property for p-nitroaniline. An extrapolation of the experimental values to zero field gives a measure of the solvent effect that dioxane has on the property. What we want to point out is that the two curves are not parallel; thus, the solvent effect has also a dispersion dependence.

There are two main approaches that can be used in calculating molecular polarizability. One is the sum-over-states method. If one is away from resonance, one can use perturbation theory. It has the advantage of giving the dynamic property, but it is somewhat limited in the size of the molecules that can be treated using this method. The second method is the finite-field method. Theoretically one places the molecule in static fields of different strengths and directions. One incorporates these fields in the Hamiltonian. One obtains an expression of polarization as a function of field. The second-order coefficient of these expansions corresponds to the beta values and the third-order coefficient to the gamma values. These coefficients are related to second- and third-harmonic generation.

With the finite-field approach we have to be concerned with numerical instabilities. Some theoretical chemists think that there is no good theoretical approach to estimate nonlinear optical properties. We believe that much of that skepticism is because of the numerical instabilities one is faced with. We have spent a lot of our time dealing with this problem. We think we have obtained a procedure that is reliable. The way we have been able to overcome this problem of numerical instabilities is by using a large number of calculations with different fields. At the present time, we are performing 253 field calculations for every molecule, for which we obtain data of polarization versus strength of the field. The fields are placed along the axes in both directions, positive and negative, and also in different quadrants. When we have two component fields, the magnitudes of the components are chosen to be the same, and their sign may be the same or opposite. This has allowed us to derive equations that give us all the tensor elements needed for the calculation of the properties. Another thing that we had to work with is the range of strengths of fields. We found that we had to go to fields as high as 0.7 V/A, which are about 20 times smaller than the internal fields. So we believe that we are still within the limits, that is, that the fields that we are using are sufficiently smaller than the internal fields.

Another way to evaluate the numerical instabilities of our calculations is by looking to these terms that are related through Kleinman symmetry. Kleinman symmetry stipulates that, under static field conditions, the tensor elements which have the same indices should have the same values. In the formula presented for beta, the first index refers to the direction of the polarization and the other indices refer to the direction of the fields. Our calculations cannot distinguish any permutations that involve only the second two indices. But we can check symmetry for permutations involving the first index. As an example, we show the values of a diacetylene molecule with a pyrryl group at one end and a p-aminophenyl group at the other end. This is work we did in conjunction with Steve Paley, working here at NASA.

The table shows values of the beta tensor elements as a function of polynomial expansion. These values are those related through Kleinman symmetry. I forgot to mention that another thing that we did was to perform those polynomial expansions of polarization versus field strengths for a range of degrees. We go from as low as 4 (because we need at least four terms to get third-order polarizabilities) to as high as 18. The table separates the terms that should be equal due to Kleinman symmetry as follows: the first line of these groups corresponds to the unique term, the second to those two terms we cannot distinguish which involve permutation of the field indices. You can see that, particularly from orders 6 to 18, the numbers look very close. The zeros in the table come from the mirror symmetry that the molecule has. The small components along the z direction are due to the fact that the amino group is out-of-plane.

QUESTION: How long does it take for these calculations to be completed?

ANSWER: Roughly about one-third of the time it takes for the geometry optimization routine.

An intrinsic problem we have derived from using a semi-empirical program that only includes valence electrons. There is a neglect of core electrons. Since core electrons are centrosymmetric there is no effect in the predictions of beta, but they come into play when one is dealing with gammas. So we have made an empirical correction for the core electrons in calculating gamma based on monosubstituted benzenes that we apply to other molecules.

The table shows six different monosubstituted benzenes. The first column shows our predicted values with no adjustments. The last column shows the values obtained from third-harmonic generation after correcting for dispersion. They look very different. But if you look at the values relative to benzene, the experimental and the predicted numbers don't look that different. That is what led us to believe that we were missing some other correction. We believe it is the core effect. Using the empirical data, we were able to get core corrections for all the atoms that we were working with. The comparison of our core corrected predictions with the third-harmonic generated values is quite good. In these examples, the core corrections are very large, but these are tiny molecules with relatively small third-order effects. When we go to other molecules with larger third-order effects, the core corrections become 10% to 20%. We have tested these corrections for other systems, in particular, doubly substituted benzenes, and they are transferable.

I would like to discuss some corrections for dispersion employing what we call the "close cousin approach." In calculating corrections for dispersion in beta, we make an empirical fit based on experimental data on a particular molecule. We then apply this correction to similar compounds. We have used p-nitroaniline to correct for dispersion of the beta values for m-nitroaniline, o-nitroaniline, and other compounds. The expression that we show is a function of wavelength in micrometers. For the third-order dispersion effects, since there is much less experimental data, we apply a theoretical expression based on the two-level approximation. One assumes that most of the perturbation comes from mixing with only the first excited state. The expression to correct for dispersion of gammas contains parameters for the incident radiation frequency and the resonance frequency. The application of the correction for beta was done twice because of the enhanced effect from the solvent on dispersion.

In dealing with many molecules, the primary consideration is how can one predict deformations based on the different environments of the molecules, as opposed to the molecule in the gas phase. Even using different Hamiltonians, we see differences on the relative stabilities of the conformations of a nitro group on a benzene ring. We see about two kilocalories difference between the perpendicular versus the planar conformations. So essentially, in the gas phase, the nitro group is close to free rotation. When we do calculations incorporating some charges to the molecules to mimic hydrogen bonding then we see increased stability in the planar structure. But rotation of the nitro group has an important effect on the magnitude of beta. We have also noticed important differences with the conformations of the amines like, for example, in dinitrobenzene, with a dimethylamine group. This work was done in conjunction with Ronald Clark.

The plot shows the values of beta as a function of dihedral angles of the dimethylamine.

The molecule has a linear structure along the x axis, which makes the beta x component to be the major contribution. The solid line shows the magnitude of the beta vector. The error bars show the variation that we obtained for the beta values when we performed the polynomial expansions between 4 and 18 terms. What is interesting is that there is a sharp reduction in the property when the dihedral angle reaches 45°. This is very important because, when the crystal is formed and the molecule interacts with other molecules, a change in dihedral angle can easily occur. We determined that this reduction in beta occurs because there is a change in the highest occupied molecular orbital. Up to 45°, the highest occupied molecular orbital is one of the delocalized molecular orbitals of the benzene ring. For larger angles, the highest occupied molecular orbital is the π orbital between the nitrogen of the dimethylamino and the carbon of the ring to which it is attached. The orbital of the ring is much more delocalized than the carbon-nitrogen orbital, even though both cases involve π electrons.

The second effect to be considered when dealing with multiple molecules, is crystal symmetry. You know that for second-order polarizabilities this is extremely important. If the crystal has central symmetry, one loses the property.

To deal with bulk corrections, we have also used the "close cousin approach" because this is the only thing we can do at this stage of our calculations. What we have done is to be able to predict the effect that different solvents have. We have used the example of p-nitroaniline to obtain two empirical fits that we can use, one based on the dielectric constants of the solvents and the other on the molecular refraction. We have transferred these empirical corrections to other molecules. The first table that we showed of the dinitro substituted molecules was obtained using these empirical corrections.

Future plans: we intend to go to these multiple molecular systems and we will have to use some classical approach, like Lennard-Jones potentials. At the present time we are working with molecular mechanics programs. Our final goal will be to predict the effect that defects in the crystals may have on the properties.

We want to acknowledge our sponsors: NASA (through an unsolicited grant and the faculty visiting fellowship program) and the NSF Center for Theoretical Studies of Physical Systems.

Steve Zutat left us some of his transparencies. He is in the final stages of finishing his degree. Please bear with me the fact that I am not too familiar with his work.

Steve worked in diacetylene polymerization. He studied the effect of having different substituents in the polymer and the length of the polymer. In the past, the color of crystals has been used as an indication of their gamma properties. He studied the value of the gamma xxxx term for various molecules with different substituents versus the magnitude of the gap between their highest occupied molecular orbital and their lowest unoccupied molecular orbital. The xxxx term is by far the largest component since these are linear molecules. This is very important because one wants to find systems in which the gamma is very large and usually that happens when the gap gets reduced (the color shifts toward the red). The problem then becomes that one may be too close to the resonance energy of the molecule. But, in effect, one may have a system with very large third-order polarizability which may also have the same HOMO-LUMO gap as others with lower gammas. Thus, this is an optimizable situation.

There have been studies in the literature on trying to predict the values of the third-order polarizability by looking at the first-order polarizability. These are the values that Steve has obtained, which show that in most of the cases this is true but not necessarily so. The first order is related to the refractive index.

This transparency is almost a summary. First, he determined that by looking at the monomer, one cannot predict the properties of the polymer. But, by looking at oligomers, which are small molecules within the computational capabilities, one can predict properties of the polymer. The reason why one cannot go from monomers to polymers is, mainly, because one cannot predict how the backbone is going to form. Furthermore, one cannot predict the orientation of the substituents. For example, if one is working with a substituent like phenyl, in order to have a large third-order property, it needs to be conjugated with the conjugated chain. Due to steric effects, it may twist and one may lose the phenyl-chain conjugation. One may not be able to predict correctly, if one has two different groups, how they are going to orient with respect to each other.

This transparency refers to the overall third-order polarizability with respect to the number of units in the polymer. You see at the beginning that all points are in the same curve but then they drop. Thus, monomers cannot be used to predict polymers but once one has an oligomer, one can predict the properties of the polymer.

These are the acknowledgements.

QUESTION: When you study multiple molecules, are you assuming a rigid structure?

ANSWER: We work the problem in various steps. The first step assumes a rigid structure and then we go to oligomers.

QUESTION: How did you determine the solvent effect correction of the beta for dispersion.

ANSWER: Dispersion is a result of how close your laser energy is to where the material absorbs. For nonlinear molecules, their absorbence spectra is very solvent dependent, especially second-order molecules, because they have huge dipole moments. So their resonance band, their absorbance band, shifts depending on the solvent. These calculations are for isolated molecules in the gas phase. Their absorbance will be different when you start putting them in solvents. They shift, but there are ways to calculate that. The closer you get to the absorption energy the better mixing you get with the excited states.

QUESTION: Can you propose derivatives of p-nitroaniline?

ANSWER: The trick is to preserve nonlinear molecular properties when you are going into bulk. For example, rotation of dimethylamine has a much larger effect on the second-order property than rotation of an amine.

Transcript of Presentation

TEMPERATURE DEPENDENCE OF PROTEIN SOLUBILITY—DETERMINATION, APPLICATION TO CRYSTALLIZATION, AND GROWTH KINETICS STUDIES

Franz Rosenberger

Thank you for this kind introduction. Let me emphasize that the work that I will present is the result of contributions of many players of a team. I am just the spokesman of the team. I can proudly say they are all hard working people. I will introduce the individuals and their contributions at the end of my presentation.

First let me give you some common grounds: protein crystals are needed because they provide the only means, via scattering, to get access to the structure of the molecules which are important to know for drug design. That is the rationale. It is a billion dollar industry out there anxiously waiting for structural data to do rational drug design.

The other fact is that about one-third of the protein crystals that grew under low-gravity conditions diffract to higher resolution than their counterparts of same size that have been grown on Earth. That is a matter of fact. There are still some hard-core people that dispute this fact. But I am convinced.

Now the question: Why is this? Now, read my lips: Nobody on this Earth knows really why it is that one-third of the crystals scatter better; that means to higher resolution reflecting higher order inside the crystal. This is what our research is aimed at: we try to contribute toward an understanding of the underlying mechanism.

First I will point out some peculiarities that distinguish protein systems or many other organic systems from inorganic systems. I come from the inorganic research world and I want to know to what extent what I know from the inorganic world can be applied to protein growth. What are the differences; some of these are not so obvious, that is why I am going to point them out. Then I will tell you about the current protein crystallization practices and compare them to how we do it in the inorganic world in order to get high structural quality. After that I will emphasize my pet topic: temperature as control parameter. I will show how the temperature dependence of solubility can be utilized to reproducible and reversibly grow protein crystals. For this you need to know solubility curves. How can one determine solubility curves: I am going to tell you about that. And if we apply this knowledge to the crystallization of crystals, we might as well try to get the final product in an x-ray capillary, so that you don't have any handling between crystal growth and structural studies. I will also show that temperature changes can be a very powerful research tool for studying crystal growth and etching kinetics. What goes on at the molecular level? We don't see molecules but we can deduce what goes on at the molecular level from the kinetics observations that we have. So that is the outline.

Now on to peculiarities of protein solutions. At a certain concentration, whether in protein or salt solutions, you can estimate an average distance between the particles in the solution.

However, if the particles are as huge as the protein molecules, then their interspacing becomes very small. In sodium chloride they are far apart. When you do a little scaling you find that the average intermolecular distance in concentrated protein solution is only 3 to 5 times larger than the distance of the molecules in the final product, in the crystal. That is very important, because we are talking about 20, 30, 40 Å. Solvated protein molecules, therefore, cannot be expected to simply go through independent, good old Brownian motions. In addition, we have complex interactions between the various components that one has to put in the solution in order to prevent proteins from denaturing and to control the solubility, which is typically done by adding salt. One wants to fix the pH; the pH also determines the charge on the protein molecule. This plays a role in the binding when the molecules approach to form the crystal.

Another thing is purity. For an organic system, purity has a completely different meaning. Semiconductor people can determine, in particular, metallic impurities, down to ppb levels. This is not possible with protein systems. Because purity or impurity can mean that on a molecule that consists of many hundred amino acids, just one amino acid may be different, or that there may be just a carboxyl end different. This we cannot resolve with current characterization techniques. No matter how hard you work, you cannot discern such "microheterogeneities" by electrophoresis. When you get a sharp band, that is the criterion used for purity. But that does not mean you may not have percents of the same protein with little birth defects, so to speak, which may play a role in the crystal growth because a certain amino acid, which participates in some manner in the bonding process, may be altered. In addition, of course, proteins are thermally not very stable.

The most widely used technique for protein crystallization involves a hanging or sitting drop in which water as the solvent contains salt plus a buffer plus the protein in question. And then you have a closed chamber, and a desiccant sitting somewhere which pulls out the water, thereby supersaturating the solution. What happens then is that you come to conditions that nucleation sets in and the supersaturation level is kept continuously at that high values throughout the whole process until, of course, due to the growth of the protein crystals, the concentration drops. That is very important to keep in mind.

Now, this is an approach which we could not even dream of taking in the inorganic world. Because in the inorganic world, one has realized since the 18 and 1900's that as soon as nucleation sets in a supersaturated solution, you better drop the supersaturation to a value where no further nucleation can take place and only growth is restricted to the existing nuclei. Otherwise you have concurrent growth and nucleation; you get a mumble jumble as you typically get in protein crystallization. People don't like me for saying that but it is just a plain physical chemistry truth. The only reason why we get by with doing protein crystallization in this uncontrolled fashion is that the kinetics is so sluggish.

Now, since we are stubborn people, we want to transplant what we know from inorganic growth to protein growth. How can we possibly reduce the supersaturation after we have found that nucleation has set in? Well, the most convenient way is to utilize the temperature dependence of solubility. All you have to do is, either by light scattering or by some other means, identify nuclei, and as soon as you see that there is nucleation in the solution, drop the temperature, or raise the temperature in the case of retrograde solubility. That is very easy because heat propagates two to three orders of magnitude more rapidly than the salt. We can, in principle, of course, also reduce the supersaturation by getting water back into the drop; sure we can do that, but this is just much slower than heat exchange.

The temperature control, if you have the solubility curve, is clearly advantageous over any other approach. It does not mean less work; some people have been greatly disappointed because they got our little apparatus (which I'll show you in a second) and it didn't work immediately. It is just as much work to determine at each of the parameters (salt, pH, and protein concentration) where you have significant temperature dependence of solubility, as it would be with the other approach, where you explore the consequences of changes in pH and protein or salt concentrations at a fixed temperature. But once you have determined that solubility curve, then you have derived completely reversible conditions.

We are certainly not the first ones to use temperature change to influence protein crystallization. One of the first ones was Dorothy Hopkins, who had a big 20-μl vat, and she just unplugged the power and let the water bath cool off for several days to obtain nice little crystals in capillaries. But this can hardly be called growth control. We are insisting on knowing where we are on the supersaturation curve and to be able to reverse the supersaturation.

What does the little gadget for solubility determinations look like? This is an exploded view. The heart is a tiny cuvette with optical windows; the total volume is 100 μl. We can get away with 50 μl if we fill it half. There is a little stir bar there. Many protein people say: How can you stir the protein solution if you want to get good crystals? No; we don't want to get any crystals in there of any value; we want to study the solubility (I'll explain that in a second). If one is doing crystal growth, one doesn't stir; but unless we stir the solution, the little crystallites that form will sediment out at 1 g.

To keep them floating you have to stir, to keep them afloat, such that the laser beam coming from this little Toshiba diode that crosses the cell produces a scattering signal. This is not fancy dynamic light scattering, just a scintillation of tiny crystals that form in there and flicker photons off into reflections. Then we have a photodiode here and we have a reference channel, because the incoming intensity may vary, so we have a ratio signal and then we can see if we have crystals or not.

When do we see that? Upon temperature lowering. There is a temperature bath out there, and we lower the temperature to reach supersaturation where nucleation sets in. Then our signal goes up. With this lysozyme solution, we lower the temperature. After an induction time of about one hour the signal rises. Look! This happens at twentyfold supersaturation, not 2% or 3% like in sodium chloride. The scintillation is due to tiny crystallites of submicron size that scatter enough photons to be seen by the photodiode.

Then we increase the temperature again. This is done by hand, and from then on the computer takes over and lowers the temperature in steps, preprogrammed steps which are guided by the slope of this curve. What is happening here, is that we have succeeded in increasing the temperature to the extent that part of the crystals is redissolved and a steady population forms. If you go higher, even more crystals would get dissolved and you would decrease the signal again, until we come back to background, and that is our equilibrium point. And we know this is the solubility. Because through UV absorption we know that is the solubility temperature for the concentration we have in there.

If we do this for a couple of weeks, then we get complete solubility curves for one pH value for different concentrations of salt. We see that this is a very well behaved system. The solubility increases with temperature, that is "normal" solubility. The interesting thing is the role of the sodium chloride: the more sodium chloride you put in there, the lower is the solubility. This one refers to as salting out behavior, which is understood, to some extent. Interestingly, when you go to some other protein, like horse serum albumin, one finds retrograde solubility, i.e., decreasing solubility with increasing temperature. This fooled us for several months! If you increase the temperature you get it out of solution. On top of that, look!, we have first a salting-out tendency, but then it salts in again.

So now we know we have a solubility curve; in addition we know how long we have to wait at a certain temperature, given an initial concentration, to obtain nucleation. Let's say, we use 50 mg of lysozyme per ml of solution. We have to go down from the saturation temperature of roughly 32 °C to, say, 12 °C. There we wait for about 60 min in our little crystallization gadget, which I will describe in a second, and then we increase the temperature. If we don't increase the temperature after the induction period, even though we don't see any crystals yet, then we will get later too many of them.

QUESTION: Are you running a laser all the time?

ANSWER: The laser beam is going through the solution all the time; the power is too low to heat up the solution.

QUESTION: What is the shape of the nucleates?

ANSWER: They are submicron; we can't see them, I'll talk about shape later.

You want to have the final product in an x-ray capillary. Let us grow crystals with temperature control in a capillary. We fill the solution into an x-ray capillary, about 15-20 µl; we seal it on both ends, then we put it into a thermostatic jacket. Here we create a cold spot with a mini Peltier heat pump. If we utilize the kinetic information from the scintillation cell and increase temperature at the right time, most of the times we get one, two, or, at most, three crystals, and they grow right at this spot. If you take something that has retrograde solubility where you have to increase the temperature to get it out of solution, then, of course, you have to heat. This is the a lysozyme crystal grown in this fashion. This was grown in 3 days. Of course, anybody can grow lysozyme. But to grow this horse serum albumin is not so trivial; this is the case where we have to heat.

Now let's apply temperature as control parameter for studying growth behavior. We want to know what happens on Earth under unavoidable solute convection conditions. After we understand the dynamics and kinetics of the process under buoyancy-driven convection, the next phase we want to start is to impose defined forced convection over the crystal seed to see to what extent the kinetics change. So let me go over the kinetics part of our work.

The idea is that we now have a road map or solubility curve, and let's say we would like to investigate the kinetics of lysozyme, we choose an initial concentration of 50 mg per ml and see that it is strictly saturated at 32 °C. So, if we have a crystal in our microscope cell, which I will describe in a second, and we now lower the temperature, it will start growing; if you raise the temperature it will start etching, which is very important for making defects visible. We know from inorganic growth that the energy required to remove a molecule around a defect is typically different from that in an unperturbed part of the lattice. Hence, etching rates around defects are different. This can be utilized for the visualization of defects.

Just to make you appreciate this once more, in order to get nucleation we have to get down to 12 °C. You cannot supersaturate a sodium chloride solution more than say 10% when it snows all over the place. In the protein solution at 10% supersaturation nothing happens for a 100 years. You have to go to 200% supersaturation.

How do we do this? Well, we really want to see as much as we can. We have to design a growth cell in which a differential interference contrast microscopy illuminator lens can be brought within a few millimeters to the crystals. What you see here is a closed space in which we have a liquid bridge of about 25 μl contained between two microscope slides which are sealed against a stainless steal part here, the temperature of which is controlled by four thermoelectric units.

This whole thing is put on the stage of a research microscope. We have a very high quality image processing system, with a 1000 x 1000 pixel camera; a studio quality tape recorder. The computer has a frame grabber of 1000 x 1000 pixels for image processing. The idea is to computationally narrow the width of interference fringes. Then you have to put away with the old thing we have been teaching that you can only resolve height differences within a quarter of a wavelength. You can resolve steps on a face that are as small as a 20th of a wavelength or 50th of a wavelength. Then you are down by optical means to resolutions in height changes of some hundred Ångströms, right in situ at the solution solid interface. This does not allow us to resolve monomolecular steps, but five-molecular steps we can resolve.

Concerning limitation of the growth rate by interface kinetics, one does not need this fancy equipment, a magnifying glass is enough. Let us assume that two lysozyme crystals grow side by side in close proximity. And they don't slow down until they touch. What is this telling you? That transport is not that important. The growth rate is not transport limited, but rather kinetics limited. Which is not to say, as we will see later on, that transport does not play a role. But the rate limiting step definitely is the kinetics.

In addition we find that at different supersaturations the crystals take on different habits. The structure, of course, is the same but the aspect ratio is not. Rather than referring to all the crystallographic indices, let me refer to this face as the coffin face, for obvious reasons, and these are the pyramid faces. At low supersaturation we get crystal growth fast in this direction; at high supersaturation the other one is faster.

Interesting for the connoisseurs is that we adjust changes in the supersaturation through changes in the temperature. And don't forget that there are significant changes in the temperature. We vary it by 15°, which is not small compared to the absolute temperature any more. In case there are some thermally activated steps here in the kinetics limit, they might change significantly with such a temperature change. Not like in sodium chloride where you change the temperature by half a degree or a degree and you cover the whole supersaturation range possible. Here we have to change it over many degrees. That is superimposed. We say we vary the supersaturation, but at the same time we do vary the temperature.

In the future, of course, we need to fix the temperature at different supersaturation, which takes much more material and takes lots and lots of time. But it needs to be done in order to distinguish temperature and supersaturation effects. So, what do we see with our current approach? We see that the pyramid faces eventually do not grow faster with increasing supersaturation, while the coffin faces keep increasing their growth rate. That is kind of interesting.

If you now make a very crude assumption that if this were done at constant temperature, this growth curve would be parallel to the other one, then we take this difference to be due to a slow down because we have a decrease in temperature and you get an activation energy of the order of 25 or 30 kJ per mole, which is not crazy; it is, for instance, rather characteristic of hydration energies of the ions involved. This is not to say that we know what is going on at a molecular level.

Another feature is quite interesting. It takes rather high supersaturation, unlike inorganic systems, to get growth going at all. You go to 200% supersaturation then finally the growth rate starts picking up. This has been observed, not with that wide range, but similar behavior in inorganic systems. Particularly, Russian workers in the School of Chernov and co-workers found out that impurities on the interfaces can poison growth steps. When this happens, typically macrosteps form. The monomolecular steps bunch into macrosteps. And that is exactly what we see; at lower supersaturation we see macrosteps of several hundred Ångströms high, jagged, which is another indication for impurity pinning of the growth steps. When we increase the supersaturation, these macrosteps disappear. This observation is very important, since it forms a phenomenological confirmation for the postulated impurity effect.

Further, very important information comes from Vekilov, a Bulgarian researcher and former graduate student of Alex Chernov, who has done beautiful work in Japan by interferometry. He not only measured the normal growth rate of the crystal face but the step velocity of the macrosteps. And he found significant differences in growth behavior using two different sources of lysozyme. He concentrated on this region down here. These points agree very well with what he gets down here. Again, you see this sort of dead zone where no growth occurs, until critical supersaturation which (mechanistically speaking) is the one that pushes growth hard enough to overcome the impurity blockage.

What are these impurities? We don't know. But if you take lysozyme from two different sources (this is sigma, that we use in this country, and then a Japanese lysozyme) at the same supersaturation, you get much higher growth rate. When this dead zone is overcome, it always comes back to the same curve. This is perfectly reproducible. Unfortunately, there are no analytic techniques to allow us to determine really what this impurity is. Very likely it is some little defect in the lysozyme itself rather than an extrinsic impurity.

Now we do some interferometry and see again that it is true that this is a perfectly kinetically limited process. At "low" supersaturations, the surface is perfectly flat within a submicron or a few hundred Ångströms, as reflected by the perfectly parallel and equidistant fringes. If we increase the supersaturation, then the steps start curving. Within these steps you see fine structure. If you analyze this carefully, and we have done that with the image processing, you can actually discern individual islands on that surface which result from two-dimension nucleation.

If we further increase supersaturation, it leads to a kind of salad bowl situation, with depression in the middle of the facet. That is not surprising. In general, when a polygon is fed by some diffusive-convective transport mechanism there is a higher rate of supply to the corners than to the middle of the facets. That tends to make the crystal grow faster here at the edges and corners. If you go up to even higher supersaturation then you find through image processing of the interferogram that what appears as a deep depression is only 3 μ as compared to 300 μ lateral crystal dimension. Macroscopically, this is still flat. This macroscopic shape stability is a great trick that nature uses.

This was predicted 25 years ago by Chernov. If you have better supplies at the corners, they cannot grow away because as soon as the little depression of a few lattice constants forms in the middle of the facet, there is a higher growth step density there. That means, that in the depression building blocks are better utilized. Sticking probability becomes higher in the middle than out there. There is some justice in nature. Although these fellows out there are fed better, they can't grow away because they are lazy—they don't utilize the nutrient as well.

Interesting enough, not all corners are equal. In particular, these four corners here are sources for growth steps, while the other two ones don't do much until you go up to very high supersaturation. And we wonder why this is so. We speculate that it has something to do with underlying defects. And this is the next part of my story.

First we found that temperature variations during growth can be disastrous. What you see here are very crude temperature changes of 1° or 2° during the growth leading to veilings, that means, optical non-uniformities in the crystal. There are, I think, twelve steps and twelve veils, a one-to-one correlation. These veils are, extrapolating from the inorganic world, likely planes of occluded, trapped solvent.

Protein crystals are tricky anyway. They have already on the average, even if they have no defects, 50% by volume of solvent in the channels between the big molecules. That is not what I am talking about. What I am talking about is irregular excessive trapping of solvent. To be really honest, all we know is that these are optical inhomogeneities. There is some structural inhomogeneity. That is what counts. The more serious one, the more dark one, has formed at the lowest temperatures. Again, not very surprising because we have seen that growth on one facet starts freezing out. Hence, at the lowest temperature (high supersaturation means lower temperature), more serious trapping occurs.

When you focus on the microscopic differences, then you see some amazing things; you find these lines. These are actually nothing but the traces of where the corners used to be while the crystal grew. You increase the temperature; thereby - as we have seen - the aspect ratio changes, and, therefore, the corners propagate on a curve path. This is the meeting point between growth sectors. These are the traces where the growth steps from different faces meet, as they scan over the surface. There is the highest probability for trapping the impurities and defects in the lattice. That is where we have the highest inhomogeneities.

If you look with a beautiful $50,000 microscope in reflection, you will not see these defects. Only in transmission differential interference microscopy do you see these features. What we see is the paths that these corners take as they grow off from the nucleus. This is called the growth sector boundary where the growth sectors come together. This is to indicate where the veiling trapping occurs.

Short of doing x-ray topography, how can we get some idea about the structure of these defects? I told you; we have reversible control to the extent we can make a crystal grow or etch. We increase the temperature to 32 °C, where undersaturation begins. Then the surface starts etching. What do we see? We see many details, bumps. They mostly occur in these growth sector boundaries again, where the growth steps come together. How can we find out if these are point defects, just maybe trapped dust particles, tiny particles that are in the solution, or if they are linear defects, that they propagate in a linear fashion in the lattice?

QUESTION: How do you know if this is not an artifact of the etching process?

ANSWER: We etch and we regrow several microns, we come back to do some image. None of these dots get lost, some stay exactly at the same spot, some of them get displaced. This is, with 99% probability, reflecting the fact that the vector of these linear dislocations is inclined with respect to the facet. Further proof would require double crystal topography. But we can't do that right now.

How do we know that these defects are really involved in the creation of growth steps. On the coffin face, there is some evidence that the growth steps comes from two-dimensional nucleation. How do we know if there is certain connection between these property and the (very likely) dislocation in the growth process? Well, we do the same thing again. This is an etched surface and we regrow it. All you do is to turn the potentiometer to change the temperature, to grow, etch, whatever, completely under control. Though this is a poor copy of the original photograph, there is a one-to-one correspondence of etching features and growth step sources. So, growth steps are induced by lattice defects, just like in inorganic crystals.

Now let me summarize:

A scintillation technique has been developed for the determination of solubility temperature dependence. Of course, if there is no temperature dependence in solubility, this whole thing is for the birds. I cannot emphasize this enough: you have to work hard. I have been to a Gordon Conference on protein crystallization; they are all excited about structure determination of protein crystals. These people don't really care about protein crystal growth. Temperature control is not an easy remedy to all crystallization problems. You still have to work in a matrix approach to determination the combination of pH, salt, and protein concentration that has a significant effect on the temperature dependence of solubility. But, once you have this resolved, you are in the driver's seat: you have things completely reversible and reproducible. That is what I want to sell you.

On the kinetics part, if you have reasonable temperature dependence then we can use this powerful control parameter for growth and etching kinetics studies. The growth kinetics studies on lysozyme have shown that the growth on the coffin face and pyramid face occurs through layer spreading. At lower supersaturation, sigma less than ten, growth on all faces is limited by interfacial kinetics and transport in solution has no influence whatsoever on the growth morphology. At sigma less than two, impurity effects are manifested by this dead zone in the kinetic curve and the macrostep formation, which then disperses when you go to higher supersaturation. At higher supersaturation, the bulk transport becomes of some influence on growth morphology. But nature stabilizes the facets by creating this little depression in the middle, with higher step density, thereby better utilizing the leaner nutrient supply in this area. We still have macroscopically flat faces in spite of the nonuniform nutrient supply. Furthermore, some crystal corners become more active growth centers, most likely due to increased defect formation in the growth sector boundaries. In lysozyme, growth variations result from temperature changes as small as a tenth of a degree. Other proteins may be more or less sensitive.

Overall one can say that, in spite of the higher complexity of protein crystallization, inorganic and protein crystals grow by similar mechanisms, nothing is new. The huge difference is that the protein kinetics is much much slower. It takes extreme supersaturations (by inorganic standards) to get anything going to start with. That's also a blessing; this insensitivity of the kinetics with respect to supersaturation fluctuations is the saving grace. Otherwise we would not get away with these little hanging drop approaches and room temperature fluctuations. But this is my credo: this work I think, strongly suggests that the concepts and techniques recognized as essential for the achievement of high structural and compositional uniformity in inorganic crystal growth are equally important for protein crystallization. However, the big open link is still: Do these defects influence x-ray diffraction? Nobody knows. That needs to be done and that will be done very soon. Now we know how things grow at 1-g solution convection conditions. Next we want to study under forced convection conditions. We will take some of the crystals for which we know the growth conditions and resulting defects and try to establish a correlation to their x-ray diffraction properties.

As I said, I am just a spokesperson. The work was done by a whole team of people and I am not showing this list just because I am here at Marshall; I show it at other places just as well. We have a truly interactive effort with the protein crew at Marshall headed by Marc Pusey. The preparation of proteins is very complicated; there in particular, we get help from Marc's group. A year ago we started working on ovostatin, which has been isolated and prepared by Marc Pusey, Felecia Ewing, and Liz Forsythe. At our campus, Sandra Howard is responsible for the dialysis and characterization of all these proteins. Unless you do careful sample preparation, you will never get reproducible results. The scintillation technique was developed by Tom Nyce, Mike Banish, and Sandra Howard. The growth kinetics studies that I showed you are mostly due to Lisa Monaco. Peter Vekilov joined us 2 months ago. His growth step velocity measurements were done in Japan; very significant work. The x-ray characterization effort is being carried by Lisa Monaco with help from Dan Carter and Joe Ho (who used to have a different name).

Thank you for your attention.

QUESTION: Am I correct in assuming that you are saying that, early on in protein crystal growth, the biologists did things in the refrigerator or in the open, and there was not enough attention to temperature control. Do you believe that they were maybe fortuitously correct in not paying that much attention?

ANSWER: Some of them have a very deep understanding of the physical chemical principles. Hodgkin's pulling the plug and having a 20 gallon bath that cooled a tenth of a degree per hour; that is the right approach. But that has been forgotten. In addition, our approach permits to establish reversible conditions. Temperature control is very elegant if we have the solubility curve.

QUESTION: Why in the world, for the last ten years, protein crystal growth was done by the vapor diffusion technique that allows for so little control?

ANSWER: Let's do justice to these people. We have the luxury of spending our time to understand the crystal growth process. They have no time for that. They have their interest in structure studies. And, until they had these high power x-ray generators, rotating anodes, and high-speed computers, it took them 5 years, 10 years to determine one structure. Now they are able to do this fantastic job in 3 months. It wasn't necessary to pay attention to optimizing crystallization.

Thanks again.

Transcript of Presentation

MODELING OF PCG FLUID DYNAMICS—SALIENT RESULTS

N. Ramachandran

I am going to talk about fluids modeling today, specifically the modeling of PCG. I come from a mechanical engineering heat and mass transfer background and am not an expert in protein crystal growth itself. I am associated with the Acceleration Characterization and Analysis Project, ACAP, where the primary objective is to look at the microgravity environment on the space shuttle. I am mainly involved in numerical modeling and the use of these acceleration data to look at the fluid mechanics associated with specific crystal growth processes. PCG happens to be one of them.

I have worked on this problem a year or so ago and now I am revisiting it.

Here is a slide that I think comes from one of the NASA brochures. The objective here is the need to grow protein crystals which have improved internal order to determine their structure. I use as an example this picture where it talks about (isocitrate lyase) crystals grown on Earth that have many jagged edges and compare them to those grown in space that are close to pristine crystals. The latter are very good and useful in determining the structure of the protein. The main attribute of a protein grown in microgravity is the improved internal order and not necessarily a larger size. For the same size, you can get better order which can help you determine the structure by improved diffraction resolution.

One of the things that the crystal might benefit in a microgravity environment would be that it would be in a free suspension environment. So it would not suffer from the sedimentation problems that you encounter on Earth. These crystals are made up of large molecules that can lead to their collapse on themselves. The internal stresses can easily build up with added wall interactions that lead to their collapse. That is one of the things that would benefit from free suspension, and furthermore the growing crystal is exposed to a more uniform growth environment where it is bathed uniformly by the nutrient (growth) fluid.

Another microgravity attribute is a reduced hydrostatic pressure that also alleviates the internal stress problem and reduced fluid convection. The question of the effect of fluid convection on protein crystal growth is complex and debatable. Some of the results I discuss here have been published by NASA/MSFC and by Rosenberger's group. It has been observed in certain lysozyme crystals (tetragonal) that if they are subjected to forced convection of even very small quantities, 5 μ/s up to 50 μ/s, the crystal will grow up to a certain point and then you see cessation of growth altogether. This is not, however, true for the orthorhombic lysozyme crystals. For certain crystals you observe this growth cessation phenomenon and nobody has yet answered adequately as to why this occurs.

Reduced convection in microgravity implies that you can probably get close to diffusion limiting (D/L) conditions, which, if you can extrapolate from inorganic crystals, gives you a more uniform growth and, therefore, gives you better crystal size and internal order.

In PCG modeling, my approach has been to try and predict the departure from D/L conditions. If I can predict how far we are from diffusion-limited conditions due to the imposed g-jitter (microgravity environment onboard a spacecraft), then we might seek to remedy the situation probably by vibration isolation.

The analysis geometry is the hanging drop PCG method with the analysis focusing on a very localized area, adjacent to one crystal surface. I am not modeling the whole droplet because the convective phenomenon adjacent to each crystal and not the bulk convective flow is what affects the crystal growth. This chart gives you some scales: if the bulk concentration is denoted by Cb, and the interface concentration is Ci, we can come up with a solute boundary layer definition as shown. Here delta, the solute boundary layer thickness, scales as the Schmidt number to the negative one-fourth power. And to give you an example, for lysozyme which is a benchmark crystal, delta is about 33 μ at 1-g (1 Earth gravity). The Schmidt number, which is a measure of solute diffusivity, is extremely large, meaning these protein crystals have very thin boundary layers on Earth.

As a first step in the analysis, we consider an order of magnitude analysis. This is a scaling analysis. You take the governing equations and simplify them by retaining only the most significant terms and in doing so you come up with a rule of thumb describing the phenomenon. Then you can go and look at more detailed modeling. The easiest numerical approach is to use a two-dimensional Cartesian system with a center plane of symmetry and then perhaps you can go to an axisymmetric model or three-dimensional calculations if you want to.

The scenarios we are going to look at are quasisteady, which would be residual gravity levels, and also the effect of g-jitter or oscillatory and impulse-type disturbances on crystal growth. These are some of the physical parameters involved in the analysis. The width of the crystal is 0.05 cm; the height is twice that, 0.1 cm. The estimated properties for lysozyme are also listed here. The Grashof number that dictates the buoyancy strength and is defined here turns out to be about 81 for Earth gravity. Now we look at the growth plumes associated with this particular crystal at different levels of residual gravity. This is the quasi-steady gravity level and is of the order of a micro-g on the space shuttle. The primary contributory causes to this g-level are gravity gradient, drag, and rotational effects.

For convective transport we have a definite boundary layer being established so delta is much smaller than in microgravity. You can estimate these quantities. For example, delta is about 33 μ for 1 g and about 105 μ at a reduced gravity level of 10^{-2} g. The time scales associated with convective transport are fairly small as shown here. However, if you go to diffusion limiting conditions, which is what you expect in a microgravity environment because convection is not a big factor (g is small), then you are looking at delta being larger than the radius of the crystal. In that particular instance, you are looking at time scales (T) on the order of 0.25 sec. That means that if you have g-jitter or disturbances of the order of 1/T, i.e., 3 or 4 Hz, then the crystal will see the effect of that vibration.

These frequencies are regularly measured on the space shuttle and are due to the structural modes of the orbiter. The above discussion is applicable as far as velocity transport is concerned. If you look at the solute transport, due to the low diffusivity of the solute [about 10^{-6}], you are looking at a very large time scale. Thus, even though the velocity field or the flow field can immediately respond to disturbances, the solute field can take a fairly long time to respond. Here is a calculation that I did based on Motakef's work that showed for a similar problem that when the bulk thermal transport Peclet number was less than unity, you would get close to the diffusion-limited conditions. You can draw an analogy and come up with a solutal Peclet number, PeM. The solutal Peclet numbers from calculations are tabulated as a function of the gravity level which range from 1 g down to 10^{-5} g. Here is a value where PeM is less than one. This implies that you should achieve close to diffusive conditions at 10^{-5} g; that is about 10 µg.

Here is an order of magnitude analysis for oscillatory disturbances and impulse type phenomenon based on a one-dimensional analysis. This again gives an estimate of what kind of frequencies will be detrimental to PCG. It shows that oscillatory disturbances about 25 µg at 1 Hz or 250 µg at 10 Hz is what PCG can tolerate. Anything higher than that will be a problem as far as departure from diffusion-limited conditions are concerned. A graph of that curve is shown here. Also shown is the Space Station Freedom microgravity requirements curve. I don't know where it stands now, but you have two of those curves with or without schedulable events. The PCG curve for diffusion conditions is this dotted line. You see the problem area right there, 0.1 to 10 Hz area.

This color chart is a sample of the acceleration environment onboard the shuttle, taken in early 1986 out of data from STS-61C. What we did here is take 10 sec of data, do a Fourier transform, and render it pictorially. The abcissa is the time during which the data were acquired, and the ordinate is the frequency content. Color denotes the magnitude of that particular frequency. For example, you see a 17 Hz peak running through the whole figure, which corresponds to the dither frequency of the KU band antenna. You can see it reaches about a milli-g in magnitude. The lower ones at 3, 5, and 7 Hz are the structural modes of the orbiter itself. So you can see measurable disturbances in the region where PCG is susceptible. These accelerations have a potential impact on the fluid mechanics associated with the growth process. You see these disturbances during crew sleep periods also, although they are diminished in magnitude. Here is another picture of similar measurements from STS-40. These data are during an exercise period by an astronaut; I think it was an ergometer. You can see the enhancing of the structural modes due to crew activity. We have a lot of information in this regard, if anybody is interested in using them.

This is the PCG model itself, a crystal hanging in a drop. The axis of symmetry and the boundary conditions are identified in the figure. In the calculations, the growth rate which is so small is treated as quasi-steady.

QUESTION: How do you get a concentration gradient?

ANSWER: The crystal is treated as a constant sink. In reality, the concentration field will vary according to growth rate. In the calculations, however, it is treated as a steady sink; this means that it is constantly absorbing the material. The gradient is due to the depletion of the solute adjacent to the crystal.

QUESTION: Is that a moving boundary?

ANSWER: No, it is not a moving boundary. It is a very slow process; about 2 mm/h and is treated as stationary in the calculations.

QUESTION: Do you assume some equilibrium concentration which is different than the bulk concentration?

ANSWER: I assume a delta rho (density difference) due to concentration variations.

Here are the calculations for 1 g which is Earth's gravity. The grid adequacy has been tested to make sure that it resolves the boundary layer adequately. This is what the concentration profiles look like and here is an expanded view of it. Maximum velocity based on scaling was about 90 μ/s; we calculated 70 μ/s. The Sherwood number defined here is like the Nusselt number; it quantifies mass transfer just like the Nusselt number represents the heat transfer. If it is pure conduction, you have that equal to one. However, in 1 g, you have a very strong growth plume and Sherwood number quite different from it. Here is the variation of concentration profiles over different g levels 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5} and the pure diffusion case. The scaling analysis indicates that at 10^{-5} g we approximate diffusion conditions pretty closely, depending on whether PeM is less than one. And if you calculate the solute Peclet number for this case, it is very close to one. So, as far as residual g is concerned, you can probably tolerate up to 10 μg. We have a paper coming out of this work.

Here is a chart showing the calculations done on an impulse type disturbance. A zero g level is imposed for some time (10 s) and then you suddenly spike it with an impulse of say 10^{-2} g for a period of 1 s. I have done calculations for smaller magnitudes than that. Then you bring it back to zero and you see what effect there is on the flow structure itself. The velocity results are illustrated on this chart. We start out with diffusion limiting conditions as initial conditions. This is 1 second after impulse; this is at t = 12. You already see a very strong velocity field (flow field), but nothing is happening in the solute field. When you carry your calculations further you start seeing some departures in the solute field. Here is 600 s after impulse, about 10 min after impulse. The flow has started to die down, approaching the initial conditions. But now you see the effect on the solute field. So, even though, you cannot see anything immediately, it takes a long time for it to respond to the flow field. The reason for this is the solute boundary layer has been swept away by the induced flow and the solute gradient re-establishes itself. You can do a double impulse excitation also. For example, you can push it one way and the thought process goes that if you push it the other way, the effects will be removed. However, this does not happen. What happens is that the solute field remembers the second impulse and it reacts to that. All these calculations are detailed in a forthcoming paper.

Here is a summary chart on oscillatory disturbances. A frequency of about 3.183 Hz (20 rad/s) is imposed on the system with an amplitude of 10^{-3} g. This is close to a frequency that you observe on STS data that I showed you in the color charts earlier. What I show you here are flow and solute fields after periodic conditions have been achieved in the calculations. The flow responds to the excitation by establishing clockwise and counter clockwise cells but the solute field shows no perceivable effects. You see this oscillatory effect three times a second which is the imposed frequency. So the molecules in the vicinity of the crystal would be subject to this kind of periodic jiggling so to speak. Obviously, we try to avoid this kind of oscillation because it might affect the absorption of the molecules into the crystal and hence affect the growth of the crystal itself. The calculations indicate that it is prudent to provide some kind of isolation against these frequencies. Present vibration isolation techniques both active and passive can effectively filter these frequencies. Thank you.

QUESTION: to Franz Rosenberger. It appears that crystal growth is kinetics limited rather than mass transport limited. What kind of impact do you think this can have, because we do not really have the connection between defect generation and residual flow?

ANSWER: We have done some experiments 4 or 5 years ago with Tom Noise and Marc Pusey, but I have no idea. It seems to be influenced by mass transport, but it is unclear exactly how.

QUESTION: Have there been many studies of the effect of impulses on fluids? There was a rolling motion on USML1 which gave rise to a rather high impulse every 5 minutes which could affect results.

ANSWER: There are a few. The 10^{-2} g impulse that I showed you was actually measured on D1. Individual disturbances can be easily modeled.

MODERATOR: There is experimental evidence from USML-1 where an impulse of a fraction of a second affected experimental results for about 20 min. Many people wrongly disregard short impulses.

Transcript of Presentation

LOW-GRAVITY ELECTRODEPOSITION AND GROWTH OF POLYMER THIN FILMS WITH LARGE THIRD-ORDER OPTICAL NONLINEARITIES BY ELECTROCHEMICAL PROCESSES FOR DEVICES: THIOPHENE-BASED POLYMERS

Benjamin G. Penn and Clyde Riley

This is a new project that we are initiating at NASA Marshall Space Flight Center in collaboration with researchers at the University of Alabama in Huntsville (UAH). The effort at UAH is directed by Dr. Boon Loo, who is in the Chemistry Department.

Our immediate goal is to determine the feasibility of using electrochemical processes to grow high quality thin films of third-order nonlinear optical (NLO) polymers that are suitable for device applications. Polythiophenes will be studied in the initial phase of this program. In the future, we plan to evaluate the prospect of growing films with better quality in microgravity. Tasks that will be performed during the ground-based stage of this project include the following:

1. Design and fabricate a thin film growth system and define the experimental parameters required for the growth of high quality polymer films.

2. Develop a theoretical method for predicting third-order optical nonlinearities of polymers. This will be used in screening candidates and in the molecular design of new materials. Drs. Craig Moore (NASA-MSFC) and Beatriz Cardelino (Spelman College), who have developed a method to predict the second-order optical nonlinearities of organic molecules, will perform this task.

3. Determine the suitability of these films for use in devices by determining their third-order optical nonlinearities ($\chi^{(3)}$), uniformity of thickness, optical clarity, and defect content.

Conjugated polymers are excellent candidates for applications in optical switching and optical computing devices because a variety of them have been shown to have high third-order nonlinear susceptibilities ($\chi^{(3)}$) and fast response times. These materials can also exhibit high-laser damage thresholds, good mechanical properties, and stability in corrosive and high temperature environments. Moreover, polymers can be chemically modified to incorporate properties required for optical devices. Desirable properties for polymer films suggested for use as waveguides are smooth surfaces, good optical quality, low spatial scattering, and high uniformity of thickness.

Electrochemical polymerization is a method that should be thoroughly investigated for use in fabricating thin film waveguides. The procedure is relatively straightforward and films can be fabricated using many commercially available materials. Another desirable feature is that NLO films might be prepared on the surface of various substrates during polymerization for the fabrication of devices. In addition, this method has been used to synthesize several polymers in addition to the polythiophenes such as polypyrrole, polyazulene, and polypyrrole.

Thin films will be grown on various substrates during this project. The essential components of the electroprocessing cell that will be used are the anode, cathode, and voltage source. To grow films by this process, the electrodes, which consist of the anode and cathode, are placed in an appropriate electrolyte containing monomer. Polymerization is initiated by the imposition of a potential. The preparation of thin films by electrochemical processes is illustrated by Hotta, et al. in the polymerization of 3-methyl thiophene using a two electrode cell containing tetra-n-butylammonium perchlorate dissolved in nitrobenzene. Indium-tin oxide and a platinum plate were used as the anode and cathode, respectively. A film with a thickness of 8 μm was obtained on the anode after 20 min at 15 V and a constant current density of 2 mA cm^{-2}. Processing parameters that affect the quality of electrochemical polymerized films are the solvent, concentration of reagents, temperature, cell geometry, nature and shape of electrodes, applied electrical conditions, and monomer substituents.

Polythiophenes have been chosen for the initial study because they have environmental stability and structural versality and there are a variety of substituted thiophenes commercially available. These materials have been extensively studied because of their electroconducting properties; therefore, numerous publications are available to serve as a solid foundation for NLO research. The large third-order nonlinearities that have been reported for these polymers also make them desirable for further investigation.

Dorsinville et al. measured the third-order NLO properties of thin films of polythiophene (pT), polythieno (3, 2-b), thiophene (pTT), polydieno (3, 2-b, 2', 3'-d), and thiophene (pDTT). The $\chi^{(3)}$ values at 532 nm for pT, pTT, and pDTT were 6.6×10^{-9} esu and 11.3×10^{-9} esu, respectively. Electropolymerization of the monomers was performed in a two-compartment cell with indium-tin oxide electrodes. Typical thickness of films were 0.5–2 μm. Logsdon et al. sustained a $\chi^{(3)}$ value of 10^{-9} esu for Langmuir-Blodgett (LB) films of poly(3-dodecylthiophene). The polymer was first prepared by electrochemical polymerization. This was then used to prepare LB films. The electrochemical process was carried out at 5 °C using nitrobenzene as the solvent, tetra-n-butylammonium hexaflurophosphate as the electrolyte, indium-tin oxide as the cathode, and a platinum coil as the cathode. Several other references reporting the NLO properties of polythiophenes are available in the scientific literature.

Growth of films in microgravity might result in films with better quality for use in NLO devices than those prepared by Earth-based processes. This is indicated by the research of Dr. C. Riley and co-workers who electrodeposited metals and metal/cermet composites in low gravity. Since convection should be limited in microgravity and diffusion is expected to be the dominant transport mechanism, thin films of polymers prepared in low gravity by electrochemical processes might have smoother surfaces, more uniform thickness, and less defects.

The electrochemical polymerization process seems to be a promising method for the preparation of polymer thin films that are suitable for the fabrication of NLO devices in Earth-based processes and the growth of films of superior quality in low-gravity. A thorough investigation of these prospects is the goal of our research program. However, the discussion session of this talk reveals that there are many factors to consider. The scientific literature needs to be reviewed and experiments performed to determine morphological features, molecular weight distributions, optical clarity, and other properties of electrodeposited films. In addition, methods need to be developed for the fabrication of oriented films for the optimization of third-order NLO properties.

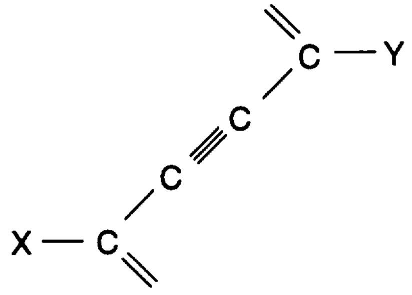
Transcript of Presentation

POLYDIACETYLENE THIN FILMS FOR NONLINEAR OPTICAL APPLICATIONS

Mark Steven Paley

This is research that I have been conducting at Marshall Space Flight Center for the past 2 or 3 years, working in the Space Science Laboratory, Microgravity Division, Chemistry and Polymeric Materials Branch (formerly Don's branch). The focus of my work has been on organic thin films for nonlinear optical (NLO) applications. In particular, I have been studying a class of compounds known as polydiacetylenes. Because there has already been some earlier discussion on polydiacetylenes, I am not going to get into a lot of background details.

Why are we interested in polydiacetylenes as NLO materials? First of all, polydiacetylenes are novel in that they are highly conjugated polymers which can also be crystalline. The basic zig-zag structure of the polydiacetylene repeat unit is shown here:



X and Y are the chemical functional groups which determine the chemical, mechanical, and optical properties of the polymer; by varying X and Y, one can alter the properties of the material.

There are three main advantages of polydiacetylenes over other organic NLO materials. The first advantage is their highly conjugated electronic structures; i.e., alternating single and double (or triple bonds). Conjugation means that the polymers have p-electrons which are delocalized; they are free to roam the entire backbone of the polymer instead of being confined to one localized bond. These electrons are quite mobile; and so they can respond very strongly and very rapidly to an applied external electric field. Because of this, polydiacetylenes can have very large NLO susceptibilities with fast response times.

The second advantage of polydiacetylenes is that, because they can be crystalline, they can be highly ordered, which is essential for optimizing their NLO properties in bulk form. It is one thing to produce a molecule with good optical nonlinearity, but preserving these properties in bulk materials can be quite challenging. Highly oriented materials are desired, and crystallinity is one means of achieving this.

The third advantage is that, because they polymeric, polydiacetylenes can be formed readily into thin films, which makes them useful for devices such as waveguides and integrated optics. There is of interest in both single crystals and thin films for NLO applications; however, in recent years emphasis has been increasing on thin films because they are advantageous for device fabrication. Based on their long zig-zag structures, polydiacetylenes are natural thin film formers.

How do we make polydiacetylenes? Obviously, one starts with a diacetylene monomer, which has the basic structure shown here:

$$X-C\equiv C-C\equiv C-Y$$

The name diacetylene comes from the fact that there are two acetylene units (triple bonds) joined together. As was mentioned in an earlier talk, diacetylenes have a very novel property; namely, that they can undergo polymerization in the solid-state. One can start with a crystalline diacetylene monomer, irradiate it with UV light or γ-rays, and obtain a crystalline polydiacetylene. This is quite uncommon among organic compounds; I am not aware of any other class of compounds which can undergo this type of solid-state polymerization.

COMMENT: There are dozens of compounds.

ANSWER: There may be many specific compounds, but I am not aware of any other classes of compounds which undergo this type of process. It is a very interesting reaction known as topochemical polymerization, and it was discussed in more detail earlier.

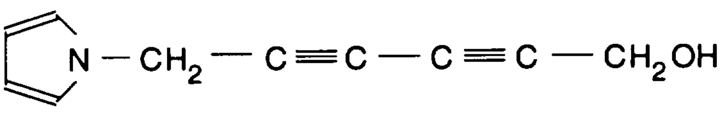
I should also point out that diacetylenes can be polymerized in solution, although very little previous work has been done in this area. However, we have found some extremely interesting results, just in the last couple of months, with polydiacetylene thin films obtained from solution that exhibit very good NLO properties. This is a entirely new area in which we are becoming very interested; again, little, if any, previous work has been done on solution polymerization of diacetylenes.

I now want to talk about some computational modeling work that was done the first year I was here at Marshall, in collaboration with Dr. Sam McManus' group at UAH. The synthesis of polydiacetylenes is not trivial. Preparing diacetylene monomers typically involves several steps that can be difficult and time consuming. Compounds are often quite reactive, and products may be obtained in low yields. Also, growing crystals and thin films possessing good quality is no trivial process. Furthermore, not all crystalline diacetylene monomers polymerize readily; and, even if a monomer does polymerize, there is no guarantee that the polymer will have useful properties. One could spend weeks or months in the laboratory synthesizing a compound and obtaining a decent crystal or thin film, only to discover that it won't polymerize or that the polymer is uninteresting.

For these reasons, we became interested in using computational modeling to try to predict the chemical and optical properties of diacetylenes and polydiacetylenes. In particular, we were interested in finding some means of determining which diacetylene monomers would be likely to polymerize readily in the solid state and which would not, as a means of screening potentially interesting compounds from others. We also wanted to calculate their nonlinear optical properties.

We chose several compounds which were previously known in the literature and carried out semi-empirical molecular orbital computations on these compounds using AM1. The calculations were performed by Steven Zutaut, who is a student of Dr. McManus at UAH. Computations were performed on single monomers and then on geometry optimized monomer pairs. The purpose of the monomer pair calculation was to simulate the crystal packing in an attempt to determine any trend between the packing parameters and the solid-state polymerizability of the diacetylene monomers. As it turns out, there is indeed a trend; when the calculated packing parameters are plotted against each other, we find that monomers which polymerize readily in the solid-state are grouped together in one area of the plot, while those that do not polymerize fall outside this area. This result is quite reasonable since one would expect that topochemical polymerization can only take place if neighboring monomers are sufficiently close together and are oriented suitably. So it appeared that we might have a predictive tool for solid-state polymerizability. In order to put the model to the test, we decided to select two previously unknown diacetylene monomers, perform computations, then synthesize the compounds and attempt to carry out solid-state polymerization to see how the computational model agrees with experimental results.

We chose as test compounds two diacetylene derivatives of pyrrole, which, despite having very similar structures, were predicted by the computational model to have different behavior in the solidstate.



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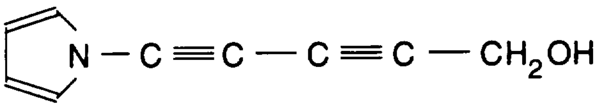

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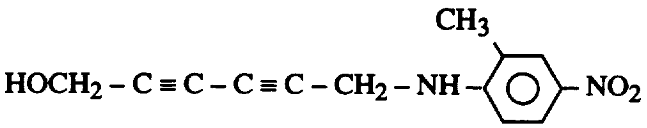
In particular, compound **1** was predicted to be unreactive for solid-state polymerization, whereas compound **2**, although it only differs by a CH_2 group, was predicted to be very reactive. I then synthesized compound **1**, grew a thin crystalline film of the monomer by vapor deposition in vacuum, and then attempted to polymerize it with UV radiation. I found that very severe conditions were required for polymerization, i.e., long-term exposure to high intensity UV light; and the polymer obtained was very poor quality.

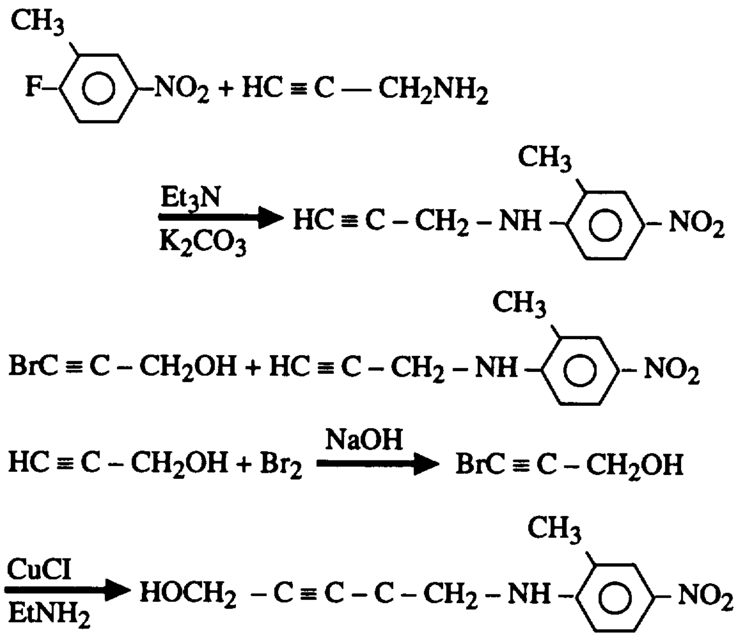
On the other hand, compound **2** was so reactive that, upon synthesis, the monomer spontaneously polymerized in the reaction mixture. I was unable to isolate any monomer, and used NMR spectroscopy to determine the presence of the polymer in the reaction mixture.

These results are perfectly consistent with our predictions based upon the computational model. That is very nice, because now we feel that we have a useful tool for screening potentially interesting diacetylenes from others without wasting a great deal of time carrying out difficult syntheses. This work has been published in the Journal of the American Chemical Society.

I next want to move on and talk about the compound that I have been working with most recently, which is a derivative of 2-methyl-4-nitroaniline, MNA, a very well-known organic NLO material. In fact, MNA is probably the most well-known organic NLO material, and so I thought it would be interesting to see how a polydiacetylene derivative of MNA might behave.



Just to give some idea of the synthetic steps involved in making a diacetylene, I have shown here the synthetic scheme for making the derivative of MNA, which we refer to as DAMNA. Compared to some other diacetylene monomers, DAMNA is relatively straightforward make. It is stable, not sensitive to air or water, and is not overly sensitive to light. Thus it is a more tractable compound to handle than, say, the derivatives of pyrrole I discussed earlier.



Now, I want to discuss the growth of thin films of these materials. There are three general methods that can be used to obtain polydiacetylene thin films. The first is to grow a crystalline thin film of the monomer from solution or melt onto a suitable substrate, and then polymerize the film in the solid state to obtain the polydiacetylene. The second method is vapor deposition of the crystalline monomer film onto the substrate, again followed by solid-state polymerization. And, finally, the third method is growth of the polymer film directly onto the substrate by solution-state polymerization of the monomer. By far, the first two techniques are the most well known. The third is a novel technique that we have discovered in our laboratory; to the best of my knowledge it has not been looked into to any extent previously. Most research on polydiacetylenes has dealt with solid-state polymerization because that is what makes them unique.

The advantage of the first two methods is that the polydiacetylene films obtained are crystalline; therefore, they are highly ordered. This is desirable for optimizing their optical nonlinearities in bulk form. However, the main disadvantge is that epitaxial growth of large-area single crystal thin films is generally not possible. This is because diacetylene monomers have such large crystal lattice parameters that it is difficult to find common, readily-available substrates which have lattice parameters to match them. So as a result, polydiacetylene films obtained are often polycrystalline in nature. Thus they appear translucent or opaque, which undermines their optical quality because of light scattering due to crystal grain boundaries and other defects. I should point out that epitaxial growth has been carried out for some diacetylenes, but, again, in general, it is not possible, especially for the larger molecules. So, while methods 1 and 2 have the advantage of forming ordered, crystalline polymers, the drawback is that it can be difficult to obtain films with large-area monocrystalline domains.

On the other hand, method 3 has the advantage of producing polydiacetylene films with excellent optical quality because there are no grain boundaries or other crystal defects to scatter light. The reason for this is that the films obtained by solution polymerization are not crystalline. And herein also lies the disadvantage of this method; the films obtained are, at present, amorphous and thus are not well-ordered. Since I have only recently grown films by this technique, and have not completely characterized them yet, I cannot conclude anything absolutely. However, based on the way they were grown, my strong feeling is that they are essentially amorphous. In any case, they definitely are not crystalline. Despite this, we have found that the films exhibit very good third-order NLO behavior.

QUESTION: How different from the single crystal are the solution-grown films? You mentioned earlier the benefits of single crystalline polymers for good NLO properties.

ANSWER: The advantage of crystalline polymers is that they are highly ordered, which enables one to optimize the NLO properties in the bulk material. The films obtained from solution are amorphous, and so are highly disordered. Nonetheless, they exhibit excellent third-order NLO properties. Since we don't yet have an ordered film grown from solution, we can't do a direct comparison between these films and the crystalline ones. One of our goals is to try to get oriented films from solution. The ultimate goal here is to obtain highly ordered films, whether it be from solid-state polymerization, solution-state polymerization, or any other technique, so that we can optimize the NLO properties at the bulk level. However, we also need to have good optical quality; we don't want grain boundaries or other crystal defects which can interfere and cause light scattering. Ideally, the best thing to have would be a large single crystal film. However, these are very difficult to obtain because epitaxial growth of these compounds is usually not possible. There are some alternative approaches we are using to try to get around this problem.

I want to talk briefly about the second-order NLO properties exhibited by this compound. MNA is a very good second-order NLO material, and so we expect that this polydiacetylene should also be good. Calculations carried out on DAMNA using our AM1 computational model indicated that it should have good NLO properties, and that it should polymerize in the solid state. I decided to grow thin films of this material by vapor deposition, which is the method I have generally been pursuing for growing thin crystalline films. They can be grown from solution, but, vapor deposition is usually preferable because there tend to be fewer defects. One doesn't have to worry as much about impurities because there are no solutions to deal with. Thus I grew thin crystalline films of DAMNA by vapor deposition in vacuum, and then polymerized these films by exposure to long-wave UV light to obtain the polydiacetylene (PDAMNA).

To characterize these materials, we did second-harmonic generation measurements at 1064 nm, a common frequency for these type of measurements, using a Nd-Yag laser. The first thing I wanted to do was to characterize the DAMNA monomer powder, to see what its inherent nonlinearity was compared to MNA itself. We found, using the Kurtz technique, which is the standard technique for determining second-harmonic generation powder efficiencies, that DAMNA is 62.5% as efficient as MNA for frequency doubling at 1064 nm. That is quite good; MNA is a good material, and so anything on that same order of magnitude is also good.

The next step was to characterize the polymer films to see what second-harmonic generation they exhibited. When this was carried out, we found that films grown onto quartz glass substrates showed slightly less second-harmonic generation than the monomer. The reason for this is that 532 nm lies in the edge of the absorption bands of the polymer, whereas the monomer's absorption bands are down in the UV. When the monomer is polymerized, the bandgap is shifted to longer wavelength, and as a result 532 nm winds up in the absorption edge. Thus some of the generated second-harmonic signal is being absorbed by the polymer. As a result, the polymer is about 70% as efficient as the monomer for frequency doubling at 1064 nm.

We are planning to carry out measurements at different wavelengths; however, we just don't have our characterization facilities set up for that yet. We have only gotten our equipment set up recently, and so, for the time being, we only have the capability to characterize at 1064 nm. There are two common laser wavelengths used to perform NLO measurements: 1064 nm and 1907 nm; we are currently in the process of obtaining the equipment necessary to do measurements at 1907 nm. Then the doubled frequency is at 950 nm, which is well outside the absorption bands of the polymer, thereby allowing a more true determination of the nonlinearity.

QUESTION: What is the quality of the film?

ANSWER: These films are crystalline, but, they are very highly polycrystalline. They are not of high optical quality because of their lack of transparency. If one examines them under a microscope, one sees a random distribution of needle-shaped crystalline grains. There is no orientation to the grains because we haven't been able to carry out epitaxial growth.

QUESTION: Have you tried to control the substrate temperature?

ANSWER: I have tried a couple of temperatures, but I really haven't done any serious experiments on that yet. I have been side-tracked recently by the solution-state polymerization work. Eventually temperature is something we will have to get into in more detail.

We next wanted to try to obtain and control orientation in these films by varying the substrate. It was just mentioned that temperature is one factor, but another factor that can affect the morpholgy of the films is to change the substrate. Some recent results in the literature have suggested that ordered polymer surfaces, particularly, teflon, have an excellent ability to induce orientation into crystals and thin films grown onto them. So we became very interested in the idea of growing polydiacetylene thin films onto ordered polymer substrates, as an alternative to epitaxial growth. Thus I decided to grow a thin film of PDAMNA onto an oriented teflon surface, under the same conditions used to grow films onto quartz. We found that the film obtained did indeed show better orientation, and, more importantly, better second-harmonic generation than the films grown onto quartz. Specifically, the second-harmonic generation was 8 times greater for the film grown onto teflon. The growth conditions were identical in terms of substrate temperature, source temperature, length of time, and film thickness; the only difference was the substrate.

QUESTION: How do you know the increased second-harmonic generation didn't come from the teflon itself?

ANSWER: We characterized a blank teflon substrate and saw no second-harmonic generation.

QUESTION: When you say 8 times greater, what are you measuring?

ANSWER: The intensity of the scattered second-harmonic signal generated by the film, using the Kurtz technique. These films are polycrystalline and do not give a coherent signal; thus one has to use the same technique that is used for measuring powders. Thus we determined the efficiency relative to a standard; in this case, we compared the DAMNA monomer powder to MNA, and then compared the PDAMNA films to an unpolymerized DAMNA film.

QUESTION: What is the particle size?

ANSWER: For the thin films, the grain size averaged about 15 μm.

QUESTION: How does the particle size of MNA compare with the size of these particles?

ANSWER: I'm not sure what the actual particle sizes were, but both the MNA and the DAMNA monomer powders were ground up thoroughly to approximately the same size before their second-harmonic generation efficiencies were determined.

Of course, it would be better if we could do measurements on single crystals; the best comparison would be between single crystals of the same size. Failing that, the next best thing is the Kurtz powder method. We didn't want to waste a lot of time growing nice single crystals, only to find out that they didn't show good second-harmonic generation. We felt that it made more sense to do the simpler experiments first, and then, if the initial results looked promising, go back and do more sophisticated ones.

We are just in the preliminary steps of this work, and our first results are looking promising. We are definitely seeing an effect with the teflon substrate. We still need to characterize the nature of that effect. Under a microscope, I did see a difference in the alignments of the grains in the teflon-grown film versus the quartz-grown film. There was a definitely a tendency toward alignment along a certain direction on the teflon substrate, whereas on the quartz substrate, the orientation was random. So the teflon certainly shows potential for obtaining ordered films. We now have to go back and optimize the growth conditions in order to obtain films with less polycrystallinity, and eventually see if we can get large-area single crystal thin films of PDAMNA. Then we can carry out more specific second-harmonic generation measurements to obtain $\chi^{(2)}$ values, and do phase-matching experiments.

I now want to talk about the third-order NLO properties of this compound, which is actually our most exciting result at the moment. These results were obtained with the PDAMNA thin films grown by solution-state polymerization. The second-order properties I have been talking about were all determined with films grown by vapor deposition and solid-state polymerization. One has to have an ordered, eccentric structure to observe second-order NLO effects; amorphous, random structures are incapable of exhibiting second-order NLO activity. Thus we expected that the films grown by solution-state polymerization would show no second-harmonic generation, and, in fact, when we tested one such film, there was no detectable second-harmonic signal. This certainly supports the notion that the films are amorphous.

Nonetheless, the films obtained by solution-state polymerization can exhibit third-order nonlinearity, so we decided to investigate that. We found some very exciting results. First of all, the films have excellent optical quality. Unlike the vapor-grown films, which are translucent because of their polycrystallinity, these films are transparent because they are glassy. Thus there are no grain boundaries or other apparent defects to scatter light. We plan to do a thorough surface characterization of these films, but haven't had a chance to yet because this result is less than a month old.

To determine the third-order NLO properties, we took a thin film of PDAMNA polymerized from solution onto a quartz substrate, and carried out degenerate 4-wave mixing experiments.

QUESTION: Have you done any third-harmonic generation?

ANSWER: Not yet. That is still down the road. Again, this result is less than a month old.

QUESTION: What is the thickness of these films?

ANSWER: These films are about 0.5 to 1 μm thick. The films grown by vapor deposition are about 1 to 2 μm thick. So the films grown from solution are definitely thinner.

The NLO properties exhibited by these films are excellent. For example, their third-order nonlinear susceptibilities ($\chi^{(3)}$ values), determined from 4-wave mixing experiments at 532 nm, are on the order of 10^{-7} esu, which is quite large. And these results are observed at very low laser pump power: 3.3 mJ per pulse; if one goes to higher power the films can become damaged. Typical $\chi^{(3)}$ values for polydiacetylene thin films are around 10^{-9}-10^{-10} esu. In fact, the largest reported non-resonant $\chi^{(3)}$ value is that for another polydiacetylene, PTS, which has a value around 10^{-9} esu. A direct comparison between this value and our value for PDAMNA is not proper, since our number is somewhat resonant enhanced. Recall that 532 nm is in the absorption edge of the polymer. As we go out to longer wavelengths, the value of $\chi^{(3)}$ will decrease because there will be less resonant enhancement. Nonetheless, it should still be quite large and, in fact, may be as good or better than that of PTS. We are very excited about these initial results, and are anxious to determine the nonlinearity at non-resonant wavelengths.

QUESTION: How large can $\chi^{(3)}$ values get?

ANSWER: Resonant values can be as large as 1. The further one moves into the absorption bands, the larger $\chi^{(3)}$ becomes because of resonant enhancement. The problem is that response times become slower because excited states become populated, and materials can become more easily damaged due to absorption heating. So resonant enhancement is not always a magic way to get large $\chi^{(3)}$ values; the number becomes large, but one sacrifices other things.

The large $\chi^{(3)}$ values we are observing with our PDAMNA films grown from solution are especially intriguing because the films are essentially amorphous. As I have mentioned previously, in order to optimize the NLO properties, ordered films are desired. Thus, in the future we intend to pursue techniques for inducing orientation into these films, which could increase the $\chi^{(3)}$ values by at least an order of magnitude.

Last, I want to, at least, briefly mention the microgravity relevance of this work. Again, this has been bantered about all day: why is there microgravity interest in this area? The point we have been trying to stress is that the NLO properties of polydiacetylenes, or, for that matter, any type of organic or polymeric thin film, depend critically upon the quality and orientation of the molecules in the film. In order to optimize nonlinearity, highly ordered structures are necessary, whether they be crystals or thin films. It is well established that gravitational effects, in particular, convection, can be detrimental to crystallization and polymerization processes. Convection can certainly be disruptive to the ordering on a thin film or crystal face. Again, referring to the work that Mark Debe talked about, we have seen that phthalocyanine films grown by vapor transport in microgravity definitely exhibited improved ordering and different crystal morphologies than those grown in 1-g. Even with our PDAMNA films grown by vapor deposition here on Earth there is some evidence of convection in that the thicknesses are not uniform. They consistently tend to be thicker around the edges than near the center. Some of that can be changed by varying the design of the growth apparatus, but it does indicate that there is some convection taking place in the vapor growth cell. And in the solution-state polymerization process there is certainly convection because there is a lot of heating taking place in the thin film growth chamber. Irradiation of the chamber through the quartz substrate window with UV generates heat unevenly across the solution, which leads to thermally driven convection. As stated before, eventually we want to attempt techniques for inducing orientation into the films, such as electric field poling to align the molecules. The presence of convection in the chamber will be disruptive to these techniques and could prevent their success. By going to the reduced-convection environment of microgravity, we should be able to obtain films with improved ordering over those obtained in 1-g.

I want to acknowledge my co-workers: here at NASA, Dr. Don Frazier, formerly head of the Chemistry and Polymeric Materials Branch, Dr. Hossin Abeledeyem, an NRC Fellow who has been doing our third-order NLO characterization work, Mr. David Donovan, who has been instrumental in the design and construction of the chambers for solution growth of thin films and will be involved with electric field poling experiments, Dr. Craig Moore, who has been doing calculations on the optical nonlinearities of our compounds; at UAH, Dr. Sam McManus, who has been active in polydiacetylene research for several years, Dr. Steven Zutaut, who carried out the computational modeling of the chemical and optical properties of these diacetylenes and polydiacetylenes, and, Dr. Mohan Sangahadasa, who has performed second-order NLO measurements on our materials.

Transcript of Presentation

CRYSTAL GROWTH OF ORGANICS FOR NONLINEAR OPTICAL APPLICATIONS

N. B. Singh and R. Mazelsky

Introduction

Dr. Cardelino and Dr. Moore gave a very good introduction for my talk. And just remember, organic crystals have been well known to the community for a long time. I am just publishing this work which was finished over a year ago.

Although the title of the talk is "Crystal growth of organics for NLO applications," I am going to talk about "Crystal growth of binary organics." Why did we do this work? What did we achieve? What I am going to present is: growth of meta-nitroaniline-chloronitroaniline (m.NA-CNA) systems, experimental results, and its suitability in real devices.

We have talked quite a bit about nonlinearity and electro-optical applications. Being responsible for SHG, and acousto-optics, I have to balance what work has to go where; otherwise, I would be spending lots of time on organics and getting nothing done. Just to give you an idea about the introduction of my talk, here is the second-order harmonic coefficient and here is the electro-optic coefficient being responsible for the linear effects. This curve simply shows values compared to the ammonium dihydrogen phosphate (ADP), potassium dihydrogen phosphate (KDP). Compounds 2-methyl, 4-nitroaniline (MNA), Cl-nitroaniline (CNA), and m-nitroaniline (m.NA) have d coefficients that are at least an order magnitude higher than the so-called inorganic materials, which are being produced and used by the different companies here.

While trying to grow CNA, we experienced a lot of problems with instability and decomposition. So, we tried m.NA and CNA binary mixtures and observed that the coefficients were very different, and indeed, we found them to be much higher. So the summary of my talk is: binaries are much better than single components. Another story that came out from the binaries is that they have higher damage thresholds.

QUESTION: What is the need for these materials?

ANSWER: Lasers are not available at every wavelength. There are two ways to convert the wavelengths. When you talk about a CO_2 laser, you take a 10-μm wavelength, you convert to 5, and then 3, 2, all those things. The reverse is you take a laser from 1 to 2 μm, 2 to 4 μm, and so on. The first approach is called harmonic conversion and the second is optical parametric oscillation.

I am showing you some inorganic crystals also to make my point more clearly. Here is a fabricated crystal of thallium arsenic selenide. This is on production scale right now. And here is d^2/n^3; n is the refractive index. And, as you know, m.NA, CNA, and MNA, all these have high d^2/n^3. But, for practical applications, we have grown thallium arsenic selenide (TAS) crystals of 50 mm diameter and 10 cm length, transmitting from 1.2 to 17 μm. As you know, for organics there are many absorption bands between 0.4 and 2 µm. So, for continuous tuning, like going from the visible up to 2 µm, we have problems due to absorption bands.

We did the experiments with binary-organic materials, CNA and m.NA, but we used that knowledge to improve our inorganic material, TAS. When we observed that binary components have a better damage threshold and better d coefficient, we took thallium arsenic selenite and mixed it with thallium arsenic sulfide and again observed damage thresholds and better d coefficient.

Transparent experiments can be designed with organic analogs because of low temperature and transparency here and, again, you can use that knowledge for inorganic materials. And, again, I want to just mention here that there are a lot of things which are scientifically very important, which you can do with these simple organic materials.

All the materials which have low heat of fusion, such as pyrrolic succinonitrile and carbon tetrabromide, solidify like metals. They show nonfacetting morphology. But all the nonlinear materials (I just showed a list; as I mentioned, each chemist and physicist has a long list) have very high heats of fusion and they try to solidify in the faceted form. For example, even for a material such as methyldinitrobenzene, you can see that these are dendrites, unlike the dendrites of pyrrolic acid and succinonitrile.

Experimental Method

We tried to purify, by multiple sublimation, CNA for our experiment. For m.NA, we distilled it and then directionally solidified the material. We combined m.NA and CNA for the present experiment. Typical of organic materials, both of these were listed as having 99% purity. Our approach, since we are very interested in bulk materials, was to use a two-zone Bridgman furnace. Also, since this is a binary system, we were concerned about solutal convection.

This is a sketch of the Bridgman furnace. For this kind of furnace, the temperature gradient was close to 8°/cm. We are talking about a material with a melting temperature close to 115 °C. The problem is that these materials start to decompose above 140 °C. If you go to higher temperatures to achieve the desired gradient, let us say you go to 150°, it will decompose. When you are trying to grow 3 to 4 days, materials will turn black. I could not achieve a high enough thermal gradient.

QUESTION: That assumes that your temperature gradient goes across the whole sample. In other words, that it is the same value along the first cavity.

ANSWER: Organics have low thermal conductivity and it takes much time to stabilize the gradient. These are very anisotropic materials; they crack the tube. In fact, I will show you a couple of examples.

We achieved a high gradient in the following manner. We took two liquids of two thermal conductivities: silicon which has a relatively high thermal conductivity, and glycerol or glycol, which has low thermal conducitivity. These are immiscible liquids. Then, we put them in a furnace, silicon in the upper portion and glycol in the lower portion. With the same setting of temperature, we got much higher thermal gradient, somewhere close to 21°/cm. Just because of two liquids having very different thermal conductivities. Then, we could achieve the desired growth conditions.

QUESTION: The two liquids have different thermal conductivities within the same setups?

ANSWER: These liquids are in the same glass furnace and provide a nice interface. Their conductivities were very different even in the same setups. We were able to keep a convex interface during the crystal growth.

The one other point that I wanted to mention here is that you can observe the interface; you can see what is going on in your experiment. That is the one beauty of organic materials.

Now, coming back to Mike's question, you think that organic materials are very soft, very fragile. Look at this; this is a quartz tube. When you grew the crystal, this is how it was. And when it cooled to room temperature, you see what it is: cracked along a cleavage plane. Right, this is in a quartz tube, and just because of the cooling, this came out. A cleavage plane is a b plane, which is cracking this way.

One of the tricks we have learned from the inorganic materials, selenite, if you want to grow the crystals, what you can do is turn this thing toward the open side. Put a seed such a way that it will expand toward the open part of the furnace, in the liquid. Then you can grow the crystal without cracks.

Results and Discussion

The wafers look like this one. But by turning the seed in the cleavage direction what we got looks like this, which is much improved in quality. When we turn the seed toward the cleavage, still you can see the cracks here, this way. Then the question came back as to how much you can lower the gradient so that thermal stress does not crack the crystal. By optimizing the growth conditions, we grew cm size crystals. Here, I can mention that again, this is not one of the best crystals. This, however, is the kind of crystal that came out. Most of the crystals had good transparency, good quality, something that looks like this one. This crystal did not show any bulk or growth defect. There is no striation, there is no crack. To give you an idea that we did fabricate better organic crystals and bigger crystals, we cut them with a string saw, and polished them on a pad, and I will show you a couple of transmission curves. Now, when you have even a little bit of impure material, you are in trouble. At least, two times distilled and zone refined material has to be used for crystal growth.

This transmission curve was for an 8 mm thick sample. One thing I have to mention here, since we talk a lot about NLO applications, is that we can use 1.06 μm wavelength and convert it to 0.53 μm with these crystals. But, for continuous tuning, there will be problems because of absorption bands. There are CH, CO, NH, and other characteristic frequency bands. So, I would say you cannot tune it from one end to another end but for selective frequency conversions, or wavelength conversions, organics are good systems. To give you some idea of the homogeneity of these several cm long crystals, I prepared m-dinitrobenzene, doped with CNA. You see there are three different slices, and we measured the transmission coefficient for these. We determined the slice we wanted to use which we thought was going to be even better than the last portion of the crystal. Let me give you some idea from the viewpoint of the users, from the optical-physicists

C-3

point of view. We did x-ray Laue pattern for orienting. In this case, we tried to do the transmission topograph. The only thing I can say is that they are nowhere close to the quality of inorganic crystals like thallium arsenic selenite. They are way behind right now.

What we now did is that we improved the crystal by reducing the gradient drastically and using higher purity material. How did the crystal look? Look at this. This was a great crystal. This is the intensity from a polished slice of the crystal.

Now let me give you the fun part of this result. Test conditions were: wavelength, 1.06 µm, response time, 10 ns, beam diameter was 1.5 mm, input energy, 0.3 mJ, sample thickness 2 mm. Obviously, SHG output of this one, with the 2 mm thick sample, was 7.7%. I did not show you the viewgraph which indicates that the output will be length squared, considering other factors. That means a 1 cm crystal, if I can grow the same quality which was tested, will show you an efficiency higher than 80%. No inorganic material can do it; in fact, our thallium arsenic selenite can only get close to 50% for a 5 cm long crystal. You can say binary organics came, at least, close to this efficiency which translates into 80%. At 1.06 µm, we could not damage the crystal up to 100 MW/cm^2 power, which was very impressive.

Once again, what I am trying to mention is that the binary materials (since we checked the single component and binary components in identical conditions) gave very high efficiencies compared to the single components.

QUESTION: Efficiency of the binary components in what respect?

ANSWER: The d coefficient is higher and output was also higher.

QUESTION: The quadratic length, ℓ squared, is that for a film or is that for bulk?

ANSWER: For the bulk, it increases with the length squared. I showed a d^2/n^3 curve which is defined as efficiency.

QUESTION: How about scattering? Between the binary and the single component.

ANSWER: It is a nightmare. Binary crystal growth is definitely much more difficult than the single.

QUESTION: Was there general scattering where you placed the laser beam?

ANSWER: Actually, in our case, at the end of the program we were pretty successful. We could achieve m.NA-CNA equivalent to quality of m.NA.

QUESTION: Since you had a 1 cm crystal, why didn't you just try it?

ANSWER: When you test these crystals, like in our case, you have to orient at 55° from the c axis. For a 1-cm long crystal, cutting, polishing, and testing was very time consuming. And at the same time, the customer said "I need half of that crystal, right away." So they wanted to check the same piece in their laser system. So we had close to 7 mm each. We did not have a chance to really orient the whole crystal. But one thing I can mention, that the crystal quality for 2 mm will not be the same for the 2 cm or even 1 cm crystals. I showed one of the viewgraphs of transmission. Homogeneity is still a problem for 3 or 4 cm long crystals.

QUESTION: Phasematch or non phasematch?

ANSWER: Yes, at 55°. If you orient the crystal at 55° from c on the b plane, that will be the optimum direction. That is where you can get the maximum power.

QUESTION: Can you use this class of material everywhere?

ANSWER: I like to insist that one material cannot do everything. When you are talking about materials that can transmit 0.2 μm or so, understand that some materials transmit, let's say, 1 μm. Each has its own range. This class might be good for, I would say, 0.45 to 2 μm. This will never be good to replace our thallium arsenic selenite or cadmium germanium phosphide, or any of those materials. Each has a different transparent region where it can be important. Yes, there are other materials in this region which might be high in d coefficient. The important thing that I got from this project is that binary is better than single, and we can use this concept in the inorganic systems also.

QUESTION: Can mercurous chloride be used for NLO? Are organics available from your lab?

ANSWER: Headquarters has supported mercurous chloride. It is one of the best AO materials for different applications. We are working on AOTF. You can get these crystals from us. The organic crystals are not available right now.

QUESTION: If binary is better than unitary, is ternary better than binary?

ANSWER: I don't know. I did experiments only on binary.

QUESTION: What about mechanical properties?

ANSWER: Damage threshold is a lot higher and was better, but the question still remains about stability. Some crystals that came from China, they put them in the box and they turned yellow.

QUESTION: In solution growth, do crystals seem to be more stable?

ANSWER: Solution grown crystals are little more stable. But, I believe if you want to give someone one to put in a system right away, everything will turn yellow after 6 months.

QUESTION: This efficiency that you mention of 7%, is it intensity dependent?

ANSWER: No. Both pure m.NA and m.NA-CNA were examined at the identical and other test conditions. Binary showed 7.7% efficiency and m.NA showed much lower efficiency. You have to compare bread with bread, not bread with rice. The information which I can get for a lower power, why would I want to go to a higher power? There is always a risk at higher power. Crystals operated up to this, without damage.

Transcript of Presentation

NONLINEAR OPTICAL THIN FILMS

T. M. Leslie

I'm going to talk about nonlinear optical thin films. The driving force behind this is actually a device. We are trying to make a material that can be worked into electro-optics. My faculty collaborators, the ones who give the talks are: Steven Kowel, Electrical Engineering Department, UAH, and André Knoesen, from UC Davis.

Normally, I talk about nonlinear optics and simple devices. I've been in this business for 8 years, so I believe in it, that we can bring it to fruition. I will give a little bit of theory; some of the molecular parameters that have been bantered about as to what makes a good material; polymer parameters, because the easiest way that industry has gone is to make a polymer to make the device; the device characteristics; I will throw out the synthesis section; and we try to go from there.

Along with my collaborators, this was the target: a polymeric multilayer electro-optic modulator, necessarily an etalon, is easy to make. So the objectives were to make a polymeric reflection-mode spatial-light modulator. We actually demonstrated feasibility, using a Fabry-Pérot modulator, and we got better than 10 picometers/V modulation at 5 V, with 1% optical modulation.

We still have a way to go. Why are we aiming at an etalon? One of the reasons to do this is parallel optical interconnects. As computer get bigger, more sophisticated, they generate more heat. I don't know if anybody has seen pictures of the new alpha chip but it has two big aluminum cooling fins that are larger than the chips itself because it just generates so much power. To make the large-scale integration chips talk to one another through wires, electrons move through the wires; it generates tons of heat. One of the ways we can eliminate so much heat is to integrate the pieces using beams of light instead. It's sort of the Cray approach, where we want to get things packed closely, talking to one another fast. Only, by using light, we don't generate heat. So that's the driving force behind this thing.

What is an etalon? It is a very simple structure. The support, which is glass, is not shown there. We have a slab of electro-optic material, and we have two electrodes. We have a beam, a laser beam, typically, that comes into this structure; we trap it at the Bragg angle, so that it bounces between these two metal mirrors. The two metal mirrors are used for three things when we make this: one of them can be a full reflector or a partial reflector if it is a transmission or a reflector etalon, and the other one must be a partial reflecting mirror because we have to make a cavity. We are making a Fabry-Pérot cavity. So we make them into mirrors. Then we have to pole this polymer, because we make an amorphous glassy polymer. Then we also use it as our modulating electrode once we have cooled the polymer below T_g.

The big thing about this is that we have a phase change modulation or an intensity modulation. What we can do with this thing is you can make an AM radio out of it, if you want to. This is a linear electro-optical device and it responds linearly with applied field.

Little bit of theory. I would have thrown this out but it appears that there are some clarifications that are necessary here. If you want to do this the brutal way, you can use Schrodinger's equation. If you want to do it the easy way, you can use Maxwell's equations. And I have not decorated any of these equations with the hats, the dots, and the tensors, and the arrows. The total polarization of any molecule can be expressed as a linear combination of power terms, where the first one is alpha, and is essentially the refractive index dispersion with wavelength, that is the linear part. The first nonlinear term to the 2nd, the second order, is the beta term, which you notice it goes with field square. This corresponds, for most people, to the electro-optic coefficient, or can be, if you are in a fast frequency domain, that which generates the second harmonic. The third term is the gamma term, and the $\chi^{(3)}$ effects come from there, and that can be motional, which is pseudo third order or all electronic.

Of course, what we normally do when we talk about theory is we get rid of these high order terms because, we say, they are small. So, our job is to make them big and make them useful.

Even without the hats and dots and arrows, it can be expressed in tensor form, because we do have to worry about directionality. So, the thing is that you can see as the fields go up, the effects get smaller. But, what is more important, is that if you look at the equation, this is a tensor equation, therefore, odd rank tensor require asymmetry, that is what everybody has been saying. You need to get the correct crystal form; you need a non-centric form. It comes from this basic equation, because it is a tensor quantity. The tensor of the electric field interacting with the molecule is what generates the effect. To be non-zero, even rank tensors can be symmetric, for example, $\chi^{(3)}$ materials; everything is a $\chi^{(3)}$ material, even the glass on the viewgraph, but small because four-rank tensors can be symmetric and non-zero.

Let's take a better look at this beta term. We have all our quantum mechanical junk in here. And we have a number of omegas; we have capital omegas and we have little omegas. Capital omega is the energy of lambda max of something that I call the NLO phore or the molecule. In other words, that is the prime tensor for the prime oscillator, if you come from an electronics or physics background. *f* is the oscillator strength, that just means how well it will couple with something. And delta mu is the difference between the ground state and the first excited state dipole moments in the NLOphore. In fact, believe it or not, it does not matter, if it is positive or negative; they come in both forms. And then, of course, we have to talk about this dispersion term that people have been talking about, how close you get to the oscillation of the molecule. So we have to worry about the pump laser frequency.

For the bulk, the $\chi^{(2)}$, $\chi^{(3)}$, we have been talking about, also it is an ensemble average, therefore the carets mean, average all the betas over all space, and the number average per unit density. That is all. And then, this is what some of the other people have been talking about, by talking about the "nearest cousins," this is a local field factor, because these molecules are interacting with one another, and they affect one another. In fact, you can get crystals of different colors, and it is actually due to the local field effects of one molecule on the others that give them different colors; you have different crystal forms.

So, not only do you have to have the molecule asymmetric, you have to have the crystal or the environment asymmetric to get the second order term, which is a third rank, or an odd-rank tensor. So, in other words, if we distill this down into a useful equation, beta is just a bunch of junk which comes from the quantum mechanics, some dispersion term, how close we are to the absorption, the oscillator strength and the change in dipole moment, and as you notice, I can even put absolute brackets around it. So, I don't care whether it is positive or negative. I just want it to be big.

Let's blow beta up. This you can't do through Maxwell's equations; you have to go to Schrodinger's equation to do this. Then we have quantum mechanical terms we always have: 3/2 in there, an *e* squared, an *h* bar squared, and mass of the electron at rest. That is just the quantum mechanical stuff you have to carry along. Capital omega is the energy of lambda max of the NLOphore. This is a dipole radiator or dipolar oscillator; it has a resonance frequency; that is all it means. *f* is the oscillator strength.

How good a dipole radiator or oscillator is it? It can be poor or bad, or it can be better or can be great. Delta mu is the difference between the ground state and the first excited state dipole moment, as an approximation. (We had a speaker yesterday who was adding in more and more terms to refine this but it gives us a fairly good look at how good it's going to be.) That's the HOMO/LUMO transition. That is normally where the first excited state comes from. It is the main transition to look at.

The oscillator strength is just how good can we move the charge around this system, nothing more than that. An little omega is the pump laser frequency, because we have to worry about dispersion; the fact that, the closer you get to the actual oscillation of the molecule, the better you couple. But, as has been said before, what happens is you get absorption effects and heating effects and all sorts of detrimental effects. You have to be careful about that.

For the bulk, we just take the betas and, remember, it is tensored, as in free space, we take an ensemble average, therefore, we have to put the carets around these things. So betas are over all space, *n* is the number of molecules per unit volume. The denser we can pack them per unit volume, the better the effect is going to be. Fairly straightforward. Big *f* is the local field factor, which, as other speaker said, the "closest cousin" effect; because these molecules are very close in space, they will interact with one another and they will see one another's field. That is why we get different color crystals when they pack differently, because the local field around them is different and they are solvatochromic. That perturbs the π system in organics.

So $\chi^{(2)}$ is nothing more than a tensor average per unit volume. But, since it is a tensor average per unit volume, not only do you have to have an asymmetric molecule, you have to put that asymmetric molecule in an asymmetric environment. You can have asymmetric molecules pointing exactly opposite of one another, and the effect goes to zero.

So, we get it down to this useful equation; beta is just these quantum mechanical constants, so you can actually calculate betas from first principles, as some of our speakers have shown you, some dispersion terms that you do have to worry about, the pump oscillation and the natural oscillation of the molecule you are interested in, the transition probability—how probable is it that you are going to get this thing to oscillate; some are good oscillators some are bad oscillators, and delta mu is the change in dipole moment.

It becomes fairly simple to design these molecules. You want to maximize these two things: you have control over the dispersion term and then you have these quantum mechanical things you have to worry about.

How do you get the transition probability? The easiest thing to look at is the extinction coefficient. How easy is to move electronic charge from one end of the molecule to another, or from the ground state to an excited state? And the change in dipole moment—I don't care which way it goes, it can be little and go to big or it can be big and go to little, and that is why sometimes we see negative betas in the literature, because the dipole goes from big to small if you get a negative beta; that's all it means.

But, as this cartoon shows, what we want is this sort of environment where we, organic chemists, say we want something that is a donor of electron density, some sort of conduit to move this electron density around, and an acceptor to take up the electron density. Not only that; at the molecular level, we want to arrange them so that all these little dipoles or all these little oscillators are oscillating in the same way. Otherwise we don't see the effect.

The cartoon that I use to show to a lot of people is this one. So, nonlinear optical molecules are nothing more than an arrow in its simplest form. What is that arrow? Is a molecule with and electron rich end coupled to an electron poor end. In fact, if you are interested in the mathematics, you can go into the derivation of ferromagnets or an antenna, which is nothing more than a dipolar oscillator, and the mathematics is the same.

What I did get through to some of the upper management on this when I was in industry, because my research director came back with this simple picture, that this is what a basic NLO molecule should look like. We have a donor end, some sort of conduit of electronic charge, and an acceptor. So we can just go into our books, and play Chinese menu, where we look at the donating capabilities of this, the transmission of electronic charge through some conduit, and the strength of acceptors on the other side.

Now, the thing is that we are going to be moving partial charge. One thing I did not do was to spread beta out so big, as to show you that to maximize the change in dipole, it is a partial charge times a length cubed term. So, in other words, the longer the molecule, and the more charge you move over a greater distance. It makes sense—you are going to get a bigger dipole change, and that is the way it works.

This is an old slide that is still fairly valid, It shows molecular structural control of beta in a series of molecules and beta as determined by solvatochromism.

P-nitroaniline is sort of the grand daddy of this field. The methyl version is similar to the chloro version, packed in an asymmetric crystal environment, and therefore can be used for these effects. However, the betas of the molecules are the same, because we have the same donor group, the same acceptor group, and the same length over which we are making the charge move. If we change the groups, we put alkyl groups on, as the theoretists suggested, and we flatten out this nitrogen lone pair with respect to the ring. With the stronger electron acceptor on the other side, we get a four-fold increase in beta. So it is 4 times as effective in moving electronic charge.

What we really want is to make sure that that lone pair of the amine donor group never gets out of conjugation; we just tie it down. So we can make an aliphatic ring, from the benzene around to the nitrogen, and tie it down so it can't rotate anymore, as our theory says that is bad. Leaving the same acceptor group on, we double beta.

Let's make the molecule a little longer. Something happened here. The short little molecule now is twice as good as the longer molecule. The thing that isn't here is it is in the biphenyl system the rings are normally twisted 40° with respect to one another. So we don't have good planarity on the system to move the charge. In fact, you can see that the ter-phenyl system is one benzene ring longer; even though the rings are skewed with respect to one another, beta does go up.

Now let's look at some planarity issues. This dimethylamino Schiff base compound is really pretty awful, as far as its beta. If you look into the literature, what you will find out is that in the Schiff base materials, the two phenyl rings like to be perpendicular to one another so the one ring doesn't know that the other ring is there. So we don't effectively move the charge the full length of the molecules that we possibly can. But we can fix that: if we put a 2-hydroxy group into one ring, we have a 1-2-3-4-5-6 membered ring, the hydrogen and the oxygen of the hydroxy group now hydrogen bonds to the nitrogen lone pair, and brings those two rings into coplanarity; the molecule can talk from end to end again, and we see this three-fold increase of beta. Then if we put all of these things together and we make a giant molecule, we can see we can get outrageous beta effects.

QUESTION: What is the reference at the bottom of the slide?

ANSWER: It is Buckley et al., Polymers and Materials Science and Engineering Proceedings, ACS Division of Polymeric Materials Science.

QUESTION: You are describing these physical problems where people are trying to increase the beta. But in your first slide you put your main objective which is to build an etalon filter. Are you trying to understand electro-optic etalon? Are you trying to increase beta here or coefficient.

ANSWER: The efficiency of beta. There are two things that are going to affect the $\chi^{(2)}$: beta; we need to maximize that and the ensemble average of the orientation of the molecules. We need to maximize both of those things.

QUESTION: What I am saying is, if I understood clearly your slide on your objective is to have a new etalon. Now the kind of design you describe, it needs to have a higher electro-optic coefficient. But you are describing the basic physics of the beta coefficient.

ANSWER: We will get to it shortly.

QUESTION: What is the name of the last compound.

ANSWER: I have no idea. It is a butadiene.

This is actually ancient history, this is 86. What I am trying to do is to develop a background that states that we know how to make these molecules. How do we make a device out of these molecules. That is what I am trying to get to.

QUESTION: Is it possible to have a symmetric molecule and still get an asymmetric packing that would give you a non-zero beta?

ANSWER: For example, if you have a diacetylene, with two of the same groups on either side, there is absolutely no way that you get beta out of that. It is absolutely linear and it is going to move charge either from the outside to the middle or from the middle to the outside. So you are going to have equal and opposite movement of charge. No way. If it is bent, then you can get a net dipole change in one direction. You have to have a dipole change.

We can make NLO molecules. We know how to do that. How do we get them to cooperate, because we need to get them to cooperate with one another to make a device. Do we take what we get or do we force them to cooperate? We have these big long toothpicks that are dipolar. How are they going to one to stack if they grow together in a crystal? Antisymmetric, right? So, what we can do is to force them to cooperate by poling them. So that is why we use polymers. The thing is, why should we use single crystals in thin crystalline films? Use polymers, and I will show you can we manipulate those.

There are some good reasons to do that. The molecular units are packed more densely together. We don't have this extra fuzz that ties the polymer together, which is just lost volume, lost space. Crystals, if you get the correct crystal packing, don't require poling to obtain $\chi^{(2)}$. And I'll show you what we have to do to pole these polymers. Crystals can, depending on the packing arrangement, give a better alignment of the NLO materials.

So, single crystals can have a higher inherent $\chi^{(2)}$. And the operating voltage of the device, therefore, should be lower. We want to stay with silicon TTL levels. This work was done by Dr. Seth Marder on a compound known as styrylpyridimium, or DAST. I expected that Seth Marder would talk about that, but he wasn't able to come.

This is one of the biggest beta and $\chi^{(2)}$ materials known. So, if we are going to grow crystals, we need these vapor pressure data. This is probably 2 weeks worth of work. You get this very nice curve because, first of all, we have to know at what temperature and pressure we can start to grow crystals. Do we see any degradation of this material? Yes. At very high temperatures, we see deviation whether going up in temperature or coming down, we get different vapor pressures which is an indication that we have some degradation of the material. But we still have very accessible vapor pressures and temperatures to try to grow crystals.

Unfortunately, even though it has an appropriate vapor pressure, it does not grow crystals by vapor. We tried, and tried, and tried, and we couldn't get it to do it. So we are going to try something different that we are going to steal from liquid crystals. Marc Debe's talk sort of alluded to this. We are building on some of those concepts. However, I don't want to call it epitaxy, what I want to do is I want to steal the aligning substrate concept from liquid crystals.

In the display of your calculator or watch device, there is a polyamide on glass. That polyimide has been scratched enough so that the chains are all lined up. These molecules, like liquid crystal molecules, are cigar shaped, elongated things. So you can kind of make this quantum leap. This is DAST; this is the styrylpyridimium compound that I was talking about. What shouldn't you be able to get the cigar shaped molecules to sit down on this polymer surface and line up.

And it so happens that since (Seth Marder has done the x-ray and other good stuff) we know the structure of DAST, we know that all molecules are pointing in the same way. So we have a molecule that can move a lot of charge from end to end, and all the molecules are pointing in the same way, so we have a $\chi^{(2)}$ material.

If that isn't the way we want them to work, we don't want them to lie down, we may want them to stand up. We can do that with liquid crystals as well. We take an appropriate polymer, my favorite is maleic anhydride alkyls, we stick it onto the surface, the anhydride groups grab on to the glass or the silicon, and these hydrocarbon tails stand up, just like the LB films, and we should be able to get the molecules to stand or their ends, instead.

So those are the ways that we can possibly do that. These are the reasons to make a polymers: they are transparent, they are tough. They have environmental resistance. We can lock in alignment after poling. They can be made into many different forms. The easy way out.

What does poling mean? When we make these polymers, I'll show you one of these things, we spincoat them, we dissolve them and we spincoat them, then we have random unpoled nonactive materials, $\chi^{(3)}$ materials. This is an etalon that we have made, you can see. We have partial gold reflectors, because you can see through this one. We have this very nice clean glassy, optically clear polymer. What we have to do is put an outrageous field on these molecules to get these little dipoles all to stand up. We have to make anelectret.

QUESTION: Corona poling?

ANSWER: André Knoesen does corona poling. Here, this is an actual etalon. This is not corona poled. You can see, this is the back plane and then there are these fingers that come over the top. We put about 140 V across the 1 μm thick film micrometer at the glass transition. And the molecules said, yes sir, I will stand up. That is a million and a half V/cm. That is an outrageous electric field.

QUESTION: The purity of the polymer?

ANSWER: It has to be really good. The students have to clean the polymer about six times before we do anything with it.

There are some people that can tell you horror stories about trying to work with nonlinear optical polymers. So, what I said to myself: what is one of the best coating polymers around? We sit on it; it is on our tables; it is on our floors; polyurethane, polyurethane varnish. Why not make a polyurethane; typically very good coatings come out of polyurethanes. They have high glass transitions, at least 140. They are mechanically tough. They are easy to synthesize. High electric resistance; we put 140 V across 1.1 μ at the glass transition, where the polymer is soft enough to flow. They don't pick up moisture. They are environmentally robust. We can regularly space the NLO chromophores. This becomes important because we are interested in waveguides. We can tailor the refractive index by changing units without changing the beta or the $\chi^{(2)}$.

We have all this background. This is the styryl-pyridinium dimethyl compound. Marder reported its $\chi^{(2)}$ first, and some other people have shown similar things. If we put those two hydroxy tails on, we get disperse Red 19 (I have to apologize, I saw this in a talk yesterday). This is what the polymer is going to look like if you are making polyurethane. Disperse Red 19 is an old azo dye; that is why it has a name like that. We take toluene di-isocyanate, we do the polymerization, and we get this polyurethane.

This co-monomer is aromatic. It has pi system to it, which means it has a higher density of electron charge per volume, which translates into a higher refractive index. The refractive index is directly related to the density of the electrons per unit volume. This is the one we have been working on the most.

This is our low index polyurethane. We take the same units. We take isophorone di-isocyanlo cyanate. It doesn't have a π system. So, for the same unit volume we take out the π cloud; we expect a lower index of refraction; we get the same T_g. So we have polyurethane, same T_g, so we have infinitely compatible polymers. So we can make layers of these things. Or we can mix them and get gradients of refractive index.

Is this really a polymer? Here, there is a DSC trace. Temperature is in Kelvin; midpoint is 140°; if you do the calculation in Kelvin, it really is a glassy polymer, no crystallinity. If we put it through our HPLC chromatograph, we have nice clean polymer. Monomer comes out here. In fact, it is not even that polydispersed. Polydispersity, for you polymer people, is about 1.5, which is good for this sort of condensation polymer. It is nice and clean.

So we make that etalon structure that I told you and we pole it. We put the temperature up to 140°, and we crank up the voltage; notice that we got up to 140 V. We are probably getting currents in the order of 10^{-8} nA. It is a good dielectric, a real good dielectric.

Have we really poled it? It is an easy way to turn out. We have an electret. So we cool it to room temperature and we heat it up again. Since these dipoles are all aligned, once we allowed it to relax, the glass transition is that transition in which the molecules can move around, we should get back the current. And sure enough, at 145°, approximately, 5° higher, the molecules start to relax and it gives back some charge. This is called thermally stimulated discharge or thermally induced current; we see it both ways in the literature.

We have all the pieces. That is what an etalon looks like. We take our laser and we take this slab here, so we rotate it with respect to the laser beam and that is what this angle down here means. When we reach the Bragg condition, we couple the light into the cavity. The cavity is very dependent on the metals that you choose for the cavity. That is a whole other mess that I won't discuss. But gold is better than aluminum; silver can create plasmas; it is a whole mess.

So we have a cavity and we couple light into this thing, into this etalon device. Then we put the current on. We put a voltage across this and we spoil the cavity.

QUESTION: What kind of voltage did you use?

ANSWER: 10 V.

So, we can go from that first picture to that. You notice: if we sit here, we have a linear electro-optic modulator. The thing is that the etalon device directly relates voltage to spoil in the cavity. Because the refractive index changes linearly with voltage, if you look into the Pockel's equation, as I said, you can make an AM radio out of this thing.

To conclude, this is what you are asking. The layer of the polymer is about 1.2 µ thick, between the gold mirrors or aluminum mirrors, the R33 is 12 picometers/V, that is what is often reported, this is the number from two methods, corona poling second-harmonic generation in picosecond regime, we want only the electronic transitions; that was done by André Knesen. It is interesting that it matches what we get from the device measured directly.

One of the other problems with these is relaxation when you pole it. This relaxes after a week to 11 picometers/V. It is an 8% change. Normally, these things change 30%. Poling voltage, we didn't want to fry it so we only did 70-50 V, the same 70 per 1.1 µ calculated out, 10 V peak-to-peak, and the modulation—that is a total laser intensity, not just the cavity, you notice that the cavity was like 90%—of the cavity but that is the total modulation. You can see the the gold better than the other one. And there are two ways of calculating this; these are the lower numbers, multiply that by 2, if you want.

The accomplishments: We have demonstrated the polymers. You notice that we even knocked that number down—there is a lot of people that overstate what they have been able to do—10 picometers /V, really 12, with 5 V you can get 1% optical modulation.

The collaborations: André Knesen, he is in Davis, he is originally the PI, he got the NSF grant before I came onboard; Steven Kowel; myself; Shu-Ping Wang, works with Steven Patrick Wang in the EE Department; he is building devices with Mark Friends; they got materials from there and I would like to acknowledge UAH Research Institute for a minigrant to help this work get started; CMDS, in collaboration with Maria Zugrav doing the vapor pressure work, started to do the growth of crystal on these template polymer films; Patrick Wang and Jennifer. Patrick is a graduate student working with me and Jennifer, another student and very talented (graduated in January), made the polymers. Thank you very much.

QUESTION: At what wavelengths were the measurements done?

ANSWER: That was with He-Ne, where there is no absorbing light. I did not bring the absorption curves, but it is at 633.

QUESTION: What do you think the oscillator strength would be if you poled it at 140 V?

ANSWER: These are for transmission etalons. The cavity for a transmission etalon isn't as good as for a reflection etalon. What we are currently making now is a reflection etalon with gold. André is poling this by corona and he has gotten up to 21 picometers/V. We have to corroborate that with a ruby light.

QUESTION: How does it compare with a lithium niobate etalon?

ANSWER: The magic number there is 38 picometers/V. That's the biggest Pockels coefficient, and that is what you have to get.

QUESTION: You talk about the nonlinear coefficient very high, and the kind of the design you try here seems to be that you electro-optic etalon, even.

ANSWER: No. Has to have a large $\chi^{(2)}$. Has to have a Packel's effect. Has to be a Pockel's material.

QUESTION: Is there another way you can change that n^2?

COMMENT: The polymer inside the etalon. I don't know what is here. There are so many ways to improve those things.

ANSWER: There is another problem with lithium niobate. First of all, say you want to build this on top of a silicon chip. You can't grow epitaxial lithium niobate on silicon, first of all. It is lossy and it is slower because, as I mentioned, they are ferroelectrics and you are actually moving ions in a cavity to get the charge change and the refractive index change. Here we are moving electrons and, with respect to an ion, it has no mass.

QUESTION: The ideal situation would be if somebody tries to grow an organic on gallium arsenide.

ANSWER: What we are proposing here is to use some of these tricks with other things. And Marc Debe's talk has actually inspired us.

QUESTION: How many microns is the film?

ANSWER: We have been working around a micron because it is for the etalon cavity. There is this set of equations and it is a good regime to work. If we go to three, then we have to worry about other problems. But we make them as thick as 3 μ, if you want to do waveguides applications.

QUESTION: You never have done them in the glass plate?

ANSWER: It is just a glass slide. It is a microscope slide that we cut; we evaporate gold; we spin the polymer; get rid of all the solvent and all that junk; and we evaporate the second layer.

QUESTION: How do you get then to pole?

ANSWER: From top to bottom, across that micron. We are putting a million volts per cm on these things. They do say: yes, I will stand up. They don't have a chance.

QUESTION: There are other materials doing the same kind of applications; devices using inorganic materials. Have you had a chance to compare them?

ANSWER: The comparisons we made are in the R33 or D33. Lithium niobate as I said, is 37 or 38 in the big direction. Being a ferroelectric, it actually has three different R coefficients. The biggest one is 37 or 38, depending on which number you believe. There are the Celanese people who that claim 38 picometer/V; no one else has been able to achieve that but them. The numbers I have heard from other people working with the same material is the same as ours. Everybody wants to get that R up.

Transcript of Presentation

FEASIBILITY STUDY: MONODISPERSE POLYMER PARTICLES CONTAINING LASER-EXCITABLE DYES

J. W. Vanderhoff AND J.-H. Chen

I would like to report on a 1-year feasibility study that is going to be continued. What we were asked to do was to prepare monodisperse or uniform particles of poly(methyl methacrylate) and polystyrene, and incorporate into these particles some laser-excitable dyes. The range of particle sizes of interest was from 0.1 μm all the way up to 1-cm diameter.

Poly(methyl methacrylate) and polystyrene were picked because they both have excellent optical properties. Of course, we wanted to have particles that were perfect spheres so that there would be a uniform output of re-irradiated light. So this was the general objective of what we were charged to do.

We categorized the particles sizes into four different size ranges: submicroscopic, small microscopic, large microscopic, and macroscopic particles. The reason was that we had to use different methods to make the different-size particles. To make uniform particles of about 0.1 μm diameter, you should use emulsion polymerization. To make uniform particles of, let's say, 1-5 μm diameter, you should use dispersion polymerization. To make large microscopic particles, you should use suspension polymerization. And, finally, to make macroscopic particles, you should use seeded suspension polymerization.

How do we put the dyes into the particles? The simplest way is to add the dye to the monomer before polymerization. Another way is to put the dye into the particles after polymerization by diffusion. In both cases, the dye would be merely physically occluded. To covalently bind the dye to the particles, the dye molecule could be incorporated into a monomer that could be incorporated into a monomer that could be copolymerized with the methyl methacrylate or styrene monomer. Or a post-reaction could be used to covalently bind the dye to the particles.

We picked three dyes to work with: PPO, bis-MSB, and alpha-NPO. And we prepared particles in the four different particle size ranges using, in the simplest case, capped bottles or stirred flasks. We had the intention, if we needed more perfect sphericity, to use the rotating cylinder reactor, which has been under development here at Marshall, to simulate microgravity. And, of course, in the ultimate, we could go into space to make these particles. The 10-μm diameter particles that we made for the National Institute of Science and Technology (formerly National Bureau of Standards) were the most perfectly spherical particles they had ever seen.

QUESTION: How did they measure particle size?

ANSWER: The Bureau measured the particles size by metrology transmission electron microscopy, optical microscopy of particle arrays, and resonance light scattering.

We planned to prepare these particles containing laser-excitable dyes and submit samples to

NASA for its evaluation. Let me point out that emulsion polymerization is both an art and a science. We all know that, in cooking, the skill of the cook plays an important role in what the outcome is going to be. This is the recipe that we used. It is not necessary to take notes on this materials; I have given Dr. Frazier an extended abstract which has all the material in it, and I presume that it will be circulated.

We used Aerosol MA as the emulsifier. This is the dihexyl ester of sulfosuccinic acid sodium salt. Persulfate ion was the initiator. Sodium bicarbonate was used as a buffer salt so that the pH did not drop too low. You put all of these ingredients in a capped bottle under a nitrogen atmosphere, rotate the bottle end-over-end at 70 °C, and you make particles. This scanning electron micrograph shows the uniformity of the particles that you get.

QUESTION: Complete uniformity?

ANSWER: That is our objective. These particles are not perfect, but they are quite uniform.

Dispersion polymerization. That is a little different. Dispersion polymerization is really precipitation polymerization in the presence of a stabilizer. If you dissolve styrene in ethanol and polymerize it, the polystyrene will precipitate as it is formed. But, if you have a stabilizer present to adsorb on the precipitating polystyrene, you make spherical particles. And, if you can couple the proper degree of stabilization with the proper rate of radical generation, these spherical particles will be uniform in size.

Here, again, we make these particles in capped bottles. Of course, the particles as prepared are dispersed in ethanol. To get them into water, we allow the particles to sediment, decant the supernatant layer, and replace it with water. This recipe would typically give a particle size of 5.7 μm. If we change the initiator concentration, we get a somewhat larger particle size. The scanning electron micrographs show some of the particles made in this way. You can see that they are far from perfect, but they are relatively uniform. This one, I think, is a slightly better than they other one.

We also carried out dispersion polymerizations of methyl methacrylate in a similar way. We used methanol as the medium here; it works better for methyl methacrylate, but otherwise the formulation is similar. This recipe gave a particle size of 2.6 μm.

QUESTION: What controls the particle size?

ANSWER: The concentrations of the monomer and the stabilizer, and the rat of radical generation, are the main variables that control the particle size in this type of polymerization.

QUESTION: What standard deviations did you observe in these particles?

ANSWER: We have not measured the distributions of these samples that critically, but I would hazard a guess that, in the better cases, the coefficient of variation (the standard deviation divided by the number-average diameter) would be in the order of 2%.

QUESTION: Are these charged particles?

ANSWER: Yes, almost certainly. Although, let met point out that the poly(N-vinyl pyrrolidone) stabilizer is not a charged polymer. And there is no charge imparted by the azobisisobutyronitrile initiator. So there is no ostensible charge from the polymerization recipe.

QUESTION: [On whether or not certain particles are charged]

ANSWER: They are charged. It would be difficult to pinpoint the source of the charge, but no particles of that size are without a charge.

Suspension polymerization: Here, you take a monomer that is immiscible with water and you disperse it in water using a suspending agent and polymerize it using an oil-soluble initiator. That is a little different from an emulsifier or a dispersing agent that is used in dispersion polymerization. We use an oil-soluble initiator that is dissolved in the monomer. And, in this case, the bead size distribution would be the same as the droplet size distribution. In emulsion polymerization, that is not the case. You start out with emulsion droplets, perhaps 10 μm in diameter; you wind up with particles that are one or two orders of magnitude smaller, so this obviously involves a nucleation process and a growth process. In dispersion polymerization, which is essentially a precipitation polymerization in the presence of stabilizer, we also have a nucleation process and a growth process. Suspension polymerization has no nucleation stage in that sense.

We try to maintain the same bead size distribution as the droplet size distribution with some techniques such as "limited coalescence" suspension polymerization, which gives a narrower size distribution. The main difficulty with suspension polymerization is that it must go through the "sticky stage" without the polymerizing droplets agglomerating and coalescing. For styrene, the sticky stage occurs in the 20-60% conversion range; in the beginning of the polymerization, the monomer droplets are broken down to a fine size, which is maintained in a dynamic state, with droplets continually coalescing and continually breaking down up agitation; at conversions lower than 20%, the droplets are fluid enough so that they can be broken down by agitation; at conversions higher than 60%, the droplets are so viscous that they're bound upon collision and therefore do not coalesce; at intermediate conversions, the droplets are too viscous to be broken down after coalescence yet are sticky enough so that they coalesce upon collision. This sticky stage lasts for several hours in the suspension polymerization of styrene. For crosslinked styrene/divinylbenzene copolymers, the sticky stage may be as short as 10-20 min, and the conversion range is much more narrow.

Generally, there are two types of suspending agents: water-soluble polymers and colloidal particles with the proper hydrophobic/hydrophilic balance. In our case, we used a water-soluble polymer, Methocel K4M (hydroxypropylmethyl cellulose) suspending agent, and benzoyl peroxide initiator. Again, we carried out these polymerizations in capped bottles. This recipe gave a particle size of about 40 μm.

Incorporating the dyes. Let's say that the particles are dispersed in water. To incorporate the dyes, in the simplest case, we dissolve the dye in an organic solvent that is immiscible in water and that is a good solvent for the polymer; we add the solution to the latex or dispersion; we have used benzene, toluene, or cyclohexane for this purpose; the solvent swells the particles, taking the dye along with it; then, the solvent is removed, usually by evacuation at reduced pressure, leaving the dye in the particles. Using this technique, we have incorporated such oil-soluble laser-excitable dyes PPO, bis-MSB, and alpha-NPO. If the concentration of dye in the particles is less than desired, we repeat this process. These results, however, are for a single cycle, and these small microscopic particles were made by dispersion polymerization. For at least two of the dyes, the amount incorporated was close to 10^{-2} g/g polymer.

That is all right, but it gets a bit messy some times. So the question arises: Why not add the dye during the polymerization? To our pleasant surprise, this worked for these three dyes. Often, dyes interfere with polymerization: they inhibit the polymerization or are themselves changed during the polymerization. But, apparently, these dyes do not interfere.

So we carried out emulsion polymerizations with all three of these dyes added to the monomer, using somewhat different recipes to make particle sizes of 274, 230, and 71 nm, respectively. These submicroscopic particle sizes were measured by photon correlation spectroscopy using the Coulter N4M. This instrument is what I call a "black box." We put the latex sample in it; we get out a number and we are not sure how it was derived. It's a question of the software. The 274 and 230 nm particles were quiet uniform as shown by the fact that both latexes showed brilliant iridescent colors.

The iridescent colors arise from the diffraction of visible light by ordered arrays of the uniform particles. The center-to-center distance was in the proper range to diffract visible light. The 274 nm particles showed the turquoise-gold combination of colors that would indicate a center-to-center distance of 260-280 nm. The 230 nm particles showed the pink and green combination that would be typical of 220-250 nm. The 71 nm particles showed no iridescent colors, as expected; particle sizes smaller than 170 nm do show these iridescent colors.

Dispersion polymerization. The PPO laser-excitable dye was added to styrene monomer, which was then polymerized without difficulty. The same dye was also added to methyl methacrylate, which was polymerized by suspension polymerization using hydroxypropylmethyl cellulose suspending agent. We also used sodium polyacrylate, which gave beads of 0.3-0.6 mm diameter.

If you want larger particles, the next step is to prepare suspension beads by incorporating a small amount of crosslinking monomer in the polymerization, so that the beads can be swelled, but not dissolved, with monomer. A narrow size fraction of these beads is separated by sieving; the beads are swelled to equilibrium with monomer, dispersed in water, and polymerized.

We had gone through this procedure earlier using tert-butyl styrene monomer and hydroxypropylmethyl cellulose or hydroxyethyl cellulose suspending agents. The polymerization schedules were similar, but with some differences in the details. A mixture of two suspending agents is often used in this field; each confers something to the system. The hydroxypropylmethyl cellulose lowers the surface tension of the water phase significantly; the hydroxyethyl cellulose lowers the surface tension hardly at all. The viscosity of a 2% aqueous solution of these two suspending agents was much greater for the hydroxyethyl cellulose than for the hydroxypropylmethyl cellulose. The combination of surface tension lowering with an increase in viscosity of the water phase is sometimes advantageous in suspension polymerization.

We started out by making crosslinked poly(tert-butyl styrene) seed beads; these were dried and sieved into narrow size fractions; then, each fraction was swelled separately with monomer, dispersed in water, and polymerized. In this way, we were able to make uniform beads up to about 5 mm in diameter. It took about 24 h to swell the beads, using an organic/water phase ratio of 35/65 or smaller. Typical monomer/polymer swelling ratios were 16-18/1. Poly(tert-butyl styrene) swells in its monomer to a greater extent than styrene or methyl methacrylate. The different-size fractions were each swelled with monomer and polymerized to a larger size, so that in the ultimate, we could grow all beads to about 5-mm diameter in separate reactions.

We repeated this same procedure using methyl methacrylate monomer. The crosslinked seed beads were sieved into narrow size fractions, swelled in excess monomer, washed with suspending agent solution, dispersed in water, and polymerized in capped bottles. This recipe was typical of those used. Generally, we used hydroxypropylmethyl cellulose as suspending agent, some cases, in mixture with sodium polyacrylate, another water-soluble polymer. Disodium phosphate was used as a buffer electrolyte and ethylene glycol dimethacrylate as the crosslinking monomer.

Some of the final distributions are shown here. These distributions were sieved further into fractions of narrower size distribution. Using seed beads of 250-300 µm diameter, we made beads with the largest proportion in the 500-1000 µm range. If we used seed beads of less than 100-µm diameter, the main fraction would be in the 212-250 µm range. We would sieve these beads again, then grow them to still larger sizes. And so on.

So much for the polymerizations. Now, I want to describe how we determined the dye concentration in the particles. We must measure this concentration to show that the dye was physically occluded in the particles. We started out by taking the latex or dispersion and subjecting it to what we call "serum replacement." In serum replacement, the latex or dispersion is confined in a cell with a semi-permeable membrane, and water is pumped through it. We like Nuclepore filtration membranes because they have a remarkably uniform pore size. We can retain the particles and pump water through the cell, in effect, replacing the serum with water. And, if we use pure water, we can clean the sample until there is less than 5 ppm of the solvent in the emulsifier in the effluent stream, and the surface tension of the effluent stream is greater than 68 dynes/cm. For the dispersion polymers, there was no detectable ethanol or methanol in the effluent stream. Then, we extracted the latex or dispersion with chloroform and measured the dye concentration in the chloroform spectrophotometrically. Several extractions and the combining of the extracts were required, and so forth.

We found that the concentration of the PPO dye could be measured at 370 mµ wavelength and that of the bis-MSB at 350 mµ. These concentrations showed that, when we incorporated the dye in the dispersion polymerizations, we inevitably lost some of it during the polymerization, perhaps because of its solubility in ethanol or methanol.

That is all very good. We can incorporate the dyes into the particles during or after polymerization, but these procedures may not be good enough; the dye may have to be incorporated by covalent binding. Therefore, we developed synthetic routes to incorporate the PPO, bis-MSB, and alpha-NPO dye structures into a monomer that can be polymerized into the particles. This is an outline of these synthetic routes. This work has not yet been carried out, but these synthetic routes are described in the extended abstract.

The other way to do it, of course, is to covalently bind the dye to the particles after they are made. We have done some work with this type of binding of dyes and proteins using diazotizatin or water-soluble carbodiimides. For the diazotization, we copolymerized vinylbenzyl chloride into the particles and then converted the chlorine to the corresponding primary amino group, which was active enough to work with the diazotization. For the carbodiimide, we incorporated carboxyl groups into the particles by copolymerization of acrylic or methacrylic acid, then covalently bound the dyes or proteins using water-soluble carbodiimides.

To summarize, we have carried out: emulsion polymerizations of styrene and methyl methacrylate to make uniform submicroscopic particles of about 0.1 μm diameter; dispersion polymerizations in ethanol or methanol solution to make uniform small microscopic particles (which we have subjected to sedimentation-decantation to replace the alcohol medium with water); and suspension polymerizations to make large microscopic particles of 40-μm diameter. We have incorporated laser-excitable dyes into the particles by physical occlusion, either after or during the polymerization; we have measured the dye concentrations in the particles by extraction with chloroform and ultraviolet spectrophotometry of the chloroform extracts. We have outlined methods to covalently bind the dyes to the particles.

Well, that was the first year's work. NASA is going to continue to support this work for a second year. And, of course, what we propose to do is to supply the dye-loaded particles for measurement to Alabama A&M, as well as to W. Witherow, Marshall Space Flight Center and M. Malcuit, Lehigh University, a young faculty member in the Department of Physics who received his Ph.D. from the Institute of Optics, Rochester.

May I take a few more minutes to speak in a philosophical vein? I was asked by Don to list possible areas for research on polymers in microgravity. After thinking about it, it seems to me that one should look for phenomena that involve an interplay between surface and bulk properties of materials. To illustrate this with particle systems, the behavior of particles of about 100-nm diameter would be determined principally by their surface properties; bulk properties would have virtually no effect. In contrast, the behavior of larger particles, perhaps 1.0 cm in diameter, would be determined principally by their bulk properties; surface properties would have little or no effect. Thus, the range of interest for experiments in microgravity would be an intermediate size range in which both the surface and the bulk properties would be important.

Now, high-molecular-weight polymer molecules in a randomly coiled form have diameters of 10-15 nanometers. That is really too small to see any effect of whether the molecules are in microgravity or not. So, I think that the most interest would be in systems where you have clusters or aggregates or assemblies of polymer molecules. For the particulate systems, let me cite our own experiments with the Monodisperse Latex Reactor, where we worked in microgravity to avoid the formation of coagulum in the emulsion polymerization of small and large microscopic particles. As we prepared latexes by successive seeded emulsion polymerization, each latex prepared would be used as the seed latex for the next polymerization. When you carry out these polymerizations on

Earth, you find that, when you get up to about 2 µm diameter and larger, the latexes show an increasing tendency to coagulate during polymerization. These particles swollen with monomer are soft and sticky, and, at 2-µm diameter, Brownian motion ceases, so you have to stir the latex to keep the particles in suspension. The bigger the particles, the faster you must stir them. But the faster you stir them, the more easily they collide, coalesce, and coagulate. So, the net result is that you form a lot of coagulum during the polymerization.

It was our rationale that, by going into space, we would form less coagulum. That was vindicated: the polymerizations in space formed little or no coagulum, whereas those on Earth formed increasing amounts of coagulum with increasing particle size. But, in addition, we found that the particles made in space were more uniform (or monodisperse) than those made on Earth. Typically, the coefficients of variation were about 1% for the space particles, as compared to 2.5-3.0% for the corresponding ground-based control particles; the coefficient of variation of the 10-µm particles accepted as a Standard Reference Material by the National Bureau of Standards (now NIST) was only 0.9%. Why should this be so? I don't know, but we have some speculations. We speculate that monomer can be transferred from one swollen particle to another by a collision between the two particles. In space, we need to stir the sample only well enough to get good heat transfer and mixing, so that we used very slow stirring rates and the number of particle-particle collisions was minimized. In contrast, on Earth, we had to stir the sample more vigorously to keep the particles in suspension, and thus the particles collided with one another more vigorously and thus transferred more monomer on collision, which broadened the particle size distribution slightly. Or, if the sample on Earth was stirred at the same rate used in space (as was done with the ground-based controls), the particles would not remain in suspension, but would sediment and press upon one another to give the same result as particle-particle collisions. But this is only speculation.

Let me say that the rate of polymerization for the samples polymerized in space was the same within experimental error as for the samples polymerized on Earth. The basic processes of radical initiation, propagation to form a long growing chain, and termination to complete this chain are not affected by the presence or absence of gravity. Polymer molecules are simply too small, and that supports what I said earlier.

Flocculation of colloidal suspensions would be a possible fruitful area for research. These flocculations are big business in industry today. All sorts of stable colloidal suspensions from sewage treatment plants to ore processing plants, and the like, are flocculated by polymers such as polyacrylamide. That is a premium price polymer, yet we use it to flocculate a colloidal suspension from a sewage treatment plant. The reason that polyacrylamide is used is that it gives excellent flocculations at concentrations of only 0.1–1.0 lb polyacrylamide/ton suspended solids. Now, what is the mechanism of this flocculation? Well, one of the most commonly accepted mechanisms is "bridging": one polymer molecule adsorbs on more than one particle, and the whole system then flocculates. I have been trying to develop a polymer network theory where you form, by association in solution, a network, which, by one means or another, traps the colloidal particles; the whole network then subsides as a fishnet with weights, sweeping the particles along with it. This polymer network theory would explain the fact that polyacrylamide gives, not only flocculation in low concentrations, but also a remarkably clear supernatant layer, and it gives big flocs that settle rapidly, are easily filtered, and are easily washed. I don't think too many people have joined me in support of this polymer network theory, but now, in the literature, we are beginning to see a few cases where people are interpreting their results according to this theory.

COMMENT: I think it is interesting that you bring that up, John. I believe the USML-2 mission has a glovebox experiment that studies flocculation to make that decision between bridging and networking as you just described it.

ANSWER: Is that so? That would be very nice.

COMMENT: Mike, is that true?

WARGO: That is right. It should fly in 1995.

Let's hope it flies. If bridging is the mechanism, the system should flocculate in microgravity; if the polymer network theory is the mechanism, the system should not flocculate. We expect that some practical systems would flocculate by the bridging mechanism, others by the polymer network mechanism. We could distinguish between these mechanisms by a simple experiment in microgravity and then set the direction of the ground-based research, i.e., adsorption of polymer molecules on the particles for bridging, the association of polymer molecules in solution for the polymer network, etc.

Crystallization: Although other people have talked about crystallization of polymers, let me mention latex particle crystallites—uniform particle size latexes form ordered arrays. We want to study the nonlinear optical properties of particles loaded with dyes, both in the form of ordered arrays and as single particles. But going a bit further, all of the general phenomena of polymer crystallization can be mimicked by these latex particles, and the nice thing about it is that you can see visually whether they crystallize by simply looking at them. The ordered arrays diffract visible light and have different iridescent colors; you can look at the samples and determine the center-to-center distance between the particles in the ordered arrays. You don't even have to measure the parameters of the ordered arrays; you can tell them from the iridescent colors.

Phase separation: In growing particles to larger size by successive seeded polymerization, we ran into an interesting phenomenon where, instead of getting spherical particles, we got doublets—uniform doublets. We investigated this systematically and we found that we could make asymmetric or symmetric doublets. We could make eggs. We could make ellipsoids and even "ice-cream cones." There is a balance between the thermodynamic monomer/polymer mixing force, the retractile force of the crosslinked network, and the interfacial force between the polymer and water phases. To make these particles, we had to add a little crosslinking monomer to the polymerization; then we swell these particles with monomer containing a little crosslinking monomer. So, we are forming a lightly crosslinked network inside a lightly crosslinked network. With a certain combination of polymerization parameters, the retractile force of the crosslinked network, along with the interfacial tension force between the particles and the water and the thermodynamic monomer/polymer mixing force, interacts in such a way that the spherical monomer-swollen particles, upon heating from room temperature to the polymerization temperature, 70 °C, undergo phase separation to form a node or bulge on one side of the particle, which eventually grows to form a separate phase and gives a doublet. Since all of the particles were the same size, the resulting nonspherical particles were also uniform. This phenomenon, of course, is a strong measure of the thermodynamics of polymer swelling, and it would be interesting to carry out these experiments in microgravity to see if they worked in the same way.

QUESTION AND COMMENTS ON PARTICLE SWELLING TECHNIQUE:

Four parameters are important to determine whether or not you get uniform nonspherical particles: the particle size, the concentration of divinylbenzene in the swelling monomer, the monomer/polymer swelling ratio of the particles, and the temperature. The initiator concentration was not a critical factor. This phenomenon occurs in the small microscopic particle size range where both the surface properties and bulk properties are important. You can make it happen with submicroscopic sizes, but this would require a high concentration of the crosslinking monomer. We ran across it by accident and tried to avoid it, but we did investigate it systematically.

There are other possibilities here—high-impact polystyrene. This product has been produced on a large scale for many years, yet the process is not well understood. You dissolve rubber in styrene monomer and polymerize it; at a certain critical conversion, the system separates into rubber particles swollen with styrene and polystyrene dissolved in styrene. The agitation at this point of separation is critical in determining the rubber particle size. You continue to polymerize it, and the polystyrene formed in the rubber particles separates to form inclusions of rubber particles dispersed in polystyrene. This process is worthy of study in microgravity to investigate the phase separation, similarly, with rubber-reinforced poly(methyl methacrylate).

Someone mentioned foaming yesterday. It would be worthwhile to study the foaming of polystyrene beads, such as those that form this foam cup. Here, fine beads of polystyrene containing n-pentane are heated with steam at 100 °C; the n-pentane either diffuses out of the beads or it vaporizes. 100 °C is the apparent second-order transition temperature of polystyrene, so the polymer softens so that the vaporizing n-pentane forms small non-interconnecting cells. This process would be interesting to investigate in microgravity.

I have some other subjects here, but I have pretty well used up my time. I'm going to stop at this point. If there are any questions, I'll entertain them later. Thank you very much for listening.

QUESTION ON QUIESCENT POLYMERIZATIONS:

We have not carried out quiescent polymerizations in these studies, but quiescent polymerizations have been developed in industry. One of my colleagues in industry developed quiescent suspension polymerization processes for the production of poly(vinyl chloride). They worked very well. The problem you have to cope with, of course, is that the viscosity of the aqueous phase must be high enough to prevent separation of the monomer droplets or beads, which give problems with heat transfer. The polymerization is exothermic, and the heat of reaction must be removed if the polymerization is to be controlled under isothermal conditions.

COMMENT: I was going to say that I think there were some results of the work that Dr. Vanderhoff just described with respect to observing morphology-dependent resonances. This study was done by Dr. Venkateswarlu and his associates with particles made by Dr.Vanderhoff. Maybe you want to comment on this work. Just a short comment, please.

Dr. Venkateswarlu: We know that micro-drop lasers have been known for some time. The idea from Dr. Frazier and Dr. Penn was to develop these microsphere lasers. So, Dr. Vanderhoff, as described, has come up with a preliminary look at the microspheres, and we examined the first fluorescence by using an excimer laser, and the people involved were Chang, a graduate student, Dr. He, Dr. Sharma, and myself. What we found was, from three different samples, that the most interesting calibration was the 2.6-μm diameter polystyrene particles containing bis-MSB dye which gives the lasing action. In other words, how would you distinguish between the lasing action and the fluoresence? Fluorescence is a broad peak with a maximum and spans about 100 Å units or so. Now, once it begins to lase, the lasing action gets superimposed over the fluorescence, and we found that, in a sample of 2.6 μm particle diameter, a beautiful structure develops because these spheres act as resonators through reflection inside the spheres. So, from the equidistant structures, Dr. Sharma calculated that the diameter of the spheres was exactly 2.6 μm, the same as Dr. Vanderhoff had indicated. Obviously, more work is needed, but this lasing structure depends upon the concentration of the dye and the particle size of the sample; if it is too small, it won't work, and if it is too big, it won't work. So we are hoping that, in the second year, we will find out what samples give this lasing action. Now the question in coming to microgravity is that, evidently, the particle size relative to the wavelength of the incident light is important and a certain wavelength gives you this kind of structure; therefore, the uniformity and sphericity of the spheres are also important, and microgravity can clearly give better spheres and therefore better lasing action.

Thank you.

Transcript of Presentation

PROCESSING OF SEMICRYSTALLINE POLYMERS

Peggy Cebe and Mark V. Brillhart

Thank you very much for inviting me to give this presentation. I am going to show a listing of the research projects that have been going on in my research group in polymer physics. One includes electrical properties prior to relaxation in TSDC, which you will hear a little about this morning, and another in liquid crystal polymers; one I will talk about today which is in structure and properties of semicrystalline blends; one on optical properties of polyimides used for electronic packaging; and, a new project, starting in 9/93, which is real-time studies of processing of semicrystalline polymers. That's the most directly related to this workshop. A NASA Fellowship was awarded to my student, Mark Brillhart, for this research, but it is not starting until 9/93, so I have to talk about something I have already done. Therefore, I'll talk about the blend work. Also, a little bit of an introduction about what we would like to do on the way in which gravity can play a role in processing semicrystalline materials. Now, in the blend research, we are looking at two commercially important materials: poly(butylene terephthalate) (PBT) which has this chemical structure. It's glass transition is around room temperature. It crystallizes extremely rapidly. It is almost impossible to quench it in the amorphous state. It has a melting point of 230 °C. It forms a blending partner with polyarylate (PAR), which has some very similar portions in chemical structure. Polyarylate consists of 50/50 isophthalic and terephthalic units and it has a rather high T_g of 180 °C.

Now, in the molten state, these materials are miscible, but the one component will phase separate out. For those of you who are not polymer morphologists, I'm going to show some very simple schemes of morphologies that develop in materials. Here is the homopolymer, PBT, and generally when polymers are crystallized from the melt, or from the rubbery amorphous state, they form units of structure that are called spherulites. This picture shows four spherulites which nucleate at these four points. They nucleated simultaneously; that is why the boundaries between them are straight-sided. This unit of spherulite diameter could be as large as 2 to 40 μ. But the substructure is also of interest, and in the homopolymer, the substructure consists of crystal phase of poly(butyltene terephthalate), plus an amorphous phase that is in between the crystals. These crystals are in the form of lamellar crystals. My next slide shows a cartoon of lamellar crystals in which we have some portion of the crystal over which the unit cell concept is translationally invariant. And then we have an amorphous phase in which the chains approach the random coil configuration. There is an intermediate amorphous layer which we call an interface which is located adjacent to the crystals and contains the fold surface. As the chain stems are coming from the crystals, that flux has to be dissipated at the surface in order to go to the amorphous state which has a reduced density. Therefore, this interface region is deemed that region over which the flux is dissipated as the chains exit from the crystal surface.

The binary blends of PBT and PAR, as I mentioned, are miscible in the molten state, but on cooling, the PBT crystallizes. The polyarylate component is completely noncrystalline, so it has no possibility to participate in the crystallization. Therefore, the morphology of these materials will be quite complicated. If you try to think of the general superstructures that I showed, then one question we are trying to address is simply, "where does the polyarylate go?" When you have this phase separation, the materials are immiscible in the molten state, but following the phase separation of the PBT phase, the polyarylate is going to be excluded from the crystals, and it could be in one of those three locations: either interlamellar, interfibrillar, or interspherulitic. Here are three cartoons again that show, first of all, an interspherulitic placement of the polyarylate. It might be possible that the spherulites that form would nucleate and somehow push ahead of them all of the polyarylate completely excluding them from the spherulitic region. Based on this morphology, we would expect that we would have two glass transition temperatures because we now have two clearly identified amorphous phases. One of the glass transition temperatures would be that of the homopolymer, PBT, and it should be located near the glass transition of PBT. The other would be from this stuff, the polyarylate, so we would have another T_g that would be close to the homopolymer of polyarylate. That is a rather extreme picture of the way in which polyarylate can be excluded.

Here is an intermediate case where the PBT crystal phase forms bundles of closely spaced lamellar objects and then between fibrillar bundles, we would have stranded some of the polyarylate. This we would call, interfibrillar structure. Here, we would also expect also to see two T_g, one coming from the fibril bundle, from amorphous phase of PBT, and another from homopolymer, PAR. So, these two models could not be distinguished based on the observation of two glass transition temperatures. Finally, the last possible placement for the polyarylate is that it would actually intercalate itself completely in between the lamellar arms. So, now we would have the lamellar crystals of PBT and in between, we would have two amorphous materials. One would be the completely amorphous PAR, and the other would be that portion of the PBT that was not able to participate in the crystals. Here, we could get either one or two T_g. It would depend upon the homogeneous nature of that region. If we see one T_g, then we would assume that all of the amorphous PBT, and all of the polyarylate are completely mixed with one another. And, on the other hand, we might see the possibility of two T_g where there would be a layer near the crystal lamellae where amorphous PBT would reside. The polyarylate would be stuck with some residual PBT in the intermediate regions. By careful testing alone, or by DSC, in terms of determining where the location is for the polyarylate, we find that we would have trouble to interpret this because we always have the possibility of two glass transitions.

Another way to examine the structure, and what we are doing to look at structure, is to do x-ray diffraction. We use the Brookhaven National Synchrotron source. This shows some data taken at the synchrotron. We were able to do this at elevated temperatures, but for the purpose of this study, we are interested in room temperature morphology. This slide happened to come from a study we did on thermal expansion coefficient for PBT. We were studying the shift of the lattice as a function of temperature. The room temperature peaks, which are the dashed ones, can be used to determine both the degree of crystallinity from the area under the curve, and also by analysis of the full-width-at-half-maximum of these peaks, we can get an idea, roughly, of the coherence length, using the Scherrer equation to determine the size of crystals in certain directions. The PBT crystal is a triclinic crystal and the disposition of the crystal is not known with respect to the lamellar surfaces. So, we cannot say directly that the a*, b*, c* lengths may be translated into real lengths.

Nonetheless, we may make an assumption that the c* axis would be close to that of the c axis in the crystal. And, we see the length as a function of composition. Here, the first number represents the PBT composition and the second is the polyarylate. So, polyarylate is increasing in this direction. We see that as a function of the increase in polyarylate, that we do increase the dimensions of the crystal, roughly, in the a* and b* dimensions. That is rather puzzling, because that means the crystals are becoming more perfect as they are becoming larger. And the question we might ask, is "why do we get more perfect crystals in a system now that has a higher proportion of amorphous phase polymer?" The reason is that the crystallization kinetics is affected so dramatically, that the PBT is crystallizing now more slowly and the crystals that are formed are much more perfect. When PBT crystals form from homopolymer, they crystallize so rapidly that you get a large population of junk crystals. Those crystals have much smaller dimension. The effect of the polyarylate is to reduce the crystallization kinetics and make the actual crystals much more perfect. But there isn't much effect in the c* direction, and therefore, we say there is not much effect on the thickness of the crystals as a function of blend composition. The melt crystallized samples also have as a large coherence length as the cold crystallized samples (which I won't show). The trends are the same, but of course, the melt crystallized samples tend to be a bit more perfect.

The composition of the blend seems to affect the lateral dimensions of the crystals, but not the crystal thickness. If the polyarylate is going into an interlamellar morphology (interlamellar means in between the lamellar crystals), then we would expect it to wedge those crystals farther apart as we try to push more and more polyarylate in between. Therefore, the distance between any two adjacent lamellae should increase as a function of the increase in polyarylate if it is going into that location. The long-period trend versus composition alone cannot be used to determine whether the morphology is interlamellar, although many people have tried to use this. One key point that was missing from previous studies is that long period is controlled by the degree of undercooling of these materials. Prior to our work, it was believed that these materials had an interaction parameter that was zero, and in that case they could only be treated as having the same infinite crystal melting point, and no depression of the melting point. But our work showed that the blend composition does exhibit depression of the melting point. That means that there is a difference in the undercooling. Blends prepared at one constant temperature cannot be compared to one another because they are all being grown at different degrees of undercooling from their infinite crystal melting points. So that kind of comparison is unfair.

However, we can use long-period to determine how closely polyarylate is coming to an interlamellar morphology. The long period we calculated from this expression where lc, the crystal thickness, was obtained from the previous results of wide-angle scattering of the full-width-at-half-maximum. This is the volume fraction of crystallinity. By comparing the actually measured long periods to that calculated according to this simple model, you can see whether it is possible for the polyarylate to be going into an interlamellar position. This shows the results for both melt and cold crystallized samples as a function of blend composition. Here is the measured long period from small angle x-ray scattering done at Brookhaven and that calculated from an interlamellar placement. Of course, they had better agree for the homopolymer. They nearly agree, in both cases, for the 80/20 blend. But the departure now between the measured and calculated values become greater as the proportion of polyarylate increases. That means that if you assume, to make this calculation, that all of the polyarylate is going into the interlamellar places, then the long period should become huge. The fact that it is not huge as measured means that the polyarylate is residing in either interfibrillar or in interspherulitic placements.

The next slide shows a plot of the data I just showed for the melt crystallized sample where the green triangle represents the measured long period for melt crystallized samples and the red circle is that calculated. We see here that for the trend of composition, it is not fair to compare one to another, because although these are compared at the same temperature, they are not at the same degree of undercooling, so the kinetics is different. Nonetheless, we can compare the green triangle to the red circle, and we see that the departure is becoming greater and greater as the mass fraction of polyarylate is increased. The red dot, here, will be way off scale for the blend of highest polyarylate composition. The nature of our morphology study is to examine where polyarylate is going and how the material phase separates. The fact that L does not increase as a function of PAR composition means that the additional PAR must be going into one of these two regions. With dynamic mechanical studies, we know that the lower glass transition shifts upward as polyarylate composition increases. This means that there is phase heterogeneity in the amorphous phase. Amorphous PBT and PAR may be becoming more interpenetrated at higher loadings of PAR.

Phase separation in these materials is quite complicated. These materials form a very important class of materials that is being used today. One of the blends of Poly(butylene terephthalate), as well as a variety of other polymers (e.g., with polycarbonate), is being used as automobile bumper material. So, these materials are commercially important, and we want to understand what their morphology is and develop a general picture about the class of polymers that can form blends with PBT. Also, what is the role of crystallization kinetics in determining the ultimate morphology? PBT and its blend partner with polyarylate and polycarbonate will also form the subject of the study that we are going to be doing for NASA in microgravity. So now I would like to switch gears a little bit and go away from my own research, and talk about what we are going to plan to do with the microgravity research.

The goal of our project is to first study the effects of processing induced deformation on structure, orientation, and morphology of semicrystalline polymers. I should say also with blends as well. Second, to develop processing models that incorporate self-deformation which is the effect of gravity on Earth with respect to processing technology. And finally, to develop processing technologies for forming large profiles in the microgravity environment. Mike Wargo mentioned, yesterday, the triangle. I have to tell him that now we have a tetrahedron in terms of the materials scientist's view of our field. The four corners of the tetrahedron include processing which also has as its components: synthesis, analysis of structure, properties measurements, and the fourth corner is performance of material. Our research is going to go along the line of the red arrows. First we are going to process materials in the molten state under the influence of gravity. Of course, that is the way all processing is done on Earth. Gravity causes the material to deform. Every processing strategy involves gravity compensation. We are so used to working with it, we automatically compensate for its effects in the way we do the material handling. Gravity is going to cause deformation of the material, and that changes the microstructure. The result of this is a nonuniformity of the material properties across the piece, especially if the piece is a very long section, e.g., a tube or a strut. These materials are usually handled by pulling them from the extruder directly into a quenching bath. This nonuniformity is going to affect the material property. Particularly for a strut, it would affect the mechanical property, but also it could be possible to affect electrical properties of wires that might be formed. This ultimately is going to affect the performance characteristics of these parts.

I am not a processing person—I am a structure person. But I want to show you the way processing is done on Earth. Here is an example of a plastics extruder. Our previous speaker had extrusion and injection molding down on the last part of his slide, so that is a good lead-in for this. Here is a polymer tube that is coming out. At this end, the polymer is molten, therefore, there are stresses that are developing at this end. If you don't support this material, it is going to fall on the floor. So, what happens with this material is that it is immediately grabbed and pulled. It is dragged through some kind of support structure to allow it to quench and cool quickly. Why do we have to cool quickly? Because if we don't cool quickly, the material self-deforms. We wouldn't have that problem in outer space because the material isn't going to self-deform. Here are three examples of the kinds of materials that we could form in terms of the shape of this die. We could form films or tubes. If the dies are not rotating we would get a tube. If we form thin sections, we could make a biaxially oriented film. We have a slot dye so we could form bars. Finally, this filament dye shows that we could make McDonald's extruded french fries.

Here is a normal cartoon of a horizontally oriented extrusion process in an Earth-based environment. As the red polymer tip comes out of the end, the gravity starts to act on the molten material, and the tube has to be gripped and pulled through a fluid bath. That is shown here. The tube has to be gripped and supported while it is cooled. That gripping and support would not be necessary in the micro-g environment. As soon as the material enters the fluid bath, it starts to warp, because you are taking away the heat, and also it is being driven through in this direction. Gravity is still acting in the fluid bath, so it is going to start to warp. That means that in this rapid quenching process, residual stress is being locked into the material.

QUESTION: Wouldn't it work better if you turned the whole thing 90°?

ANSWER: Oh, yes. A lot of times we do turn sideways for vertically oriented extrusion. Now we have a material that is going to deform under its own weight. The stress that is developed from the free end, which is this end, is a function of x from the free end, and goes as rho times (x) times g. So here we have g pulling on this section and this section here has all of this weight pulling down on it. Now that is not a tremendous amount of weight. It is only about a tenth of a megapascal for a 10^2 cm profile, but don't forget this material is molten. So that kind of force, when the material modulus is so low, is going to affect the microstructure. The microstructure at this end isn't going to be the same as the microstructure down here which had no weight that had to be supported. As soon as this material enters the fluid bath, it has to be reeled up. If it is hose, or flexible tube, it is immediately reeled. That introduces stresses in the material that are not the same on both sides of the material. So, for the vertical extrusion profiles, again, warp upon contact with the fluid. The profiles have to be reeled up if they are hose. This little picture shows here that you are going to have one side under compression, another side under tension when you start doing the reeling. When you want to use the material, you have to unreel it. When you do that, you still have the residual stress locked into the material that is affecting the microstructure. The microstructure over here is not going to be the same as that over here. Gravity causes a nonuniform stress distribution over the length of the section. Over here on this hanging section, hanging under its own weight, stress at point 3 is going to include all of the weight of the material that came after it. So it is much greater than that at point 4. Because of that, the stress distribution is going to cause a nonuniform morphology. Finally, we can even in a very extreme case, observe local yield or nipoff where the piece would just fall off, which could occur at the fixed end.

QUESTION: This is starting to remind me of pulling Czochralski crystals in the other direction. Can they be controllably supported either by gravity coming down, or actually pulling them in the other direction; pulling them and unloading the system?

ANSWER: Yes, that's right. Everything we would do with that kind of processing is designed to minimize the effect of gravity. So, yes, every one of those methods is used for gravity compensation including fluid of neutral buoancy, so that the material, as it enters, would be self-supported.

Now what are some advantages of doing this kind of processing that would be available in the microgravity environment? First of all, the material won't sag at the exit dye. During solidification we wouldn't have the necessity for quenching it. We could let the material cool gradually and ease out some of those stresses, because it is not going to be creeping during solidification. We wouldn't necessarily need the same level of mechanical support at the exit dye. Fluid support is not required, so we are not going to have to extrude in a fluid medium, and the material can be easily formed into films, fibers, sheets, and tubes.

Now, I am specifically interested in thermoplastics, and semicrystalline thermoplastics, so I would like to mention a couple of advantages of extrusion processing of thermoplastics over the epoxy-based system. First of all, pellets and powder are stored under ambient conditions, whereas epoxy usually has to be stored in subambient, in order to minimize chemical reaction, or stored in two-component fluids which are then mixed at a later time. Semicrystalline thermoplastics are tougher; they are more radiation resistant; and they are nonvolatile, because they are being handled in the solid state rather than as fluids. Thermoplastic polymers can be repaired in situ by annealing. So, if you have an element in outer space that gets hit by a micrometeorite, an astronaut with a small laser can go out there and anneal that section. You are not going to be able to do that with an epoxy-based thermoplastic. Finally, the manufacturing of thermosets is very complex. Suppose you were processing a thermoset in your extruder, and you've got the two components mixing. You are going to do something akin to injection molding. You have got these components mixed, and all of a sudden you have a power failure. Now you have this stuff that is setting up around the extruder. On Earth, we would handle that problem for epoxy by taking the whole device, putting it into an oven, and burning it off. That is how we have to clean our extruder. However, oxygen is going to be at a premium. We are not going to want to burn off in an oxygen environment in outer space. So, in the case of a power failure, we would be much better if we were dealing with a thermoplastic. When the power comes back on, we just heat the system up again to the melting temperature, and we wouldn't have to run into the problem of burn-off.

Now what would be the advantages to a space mission of processing in microgravity? First of all, in carrying materials to outer space, pellets and powder could be easily stored. They could be used as insulation in the walls. They could accommodate to the shapes of whatever the available space. We would not have to transport large profiles. If we are going to be building elements in outer space, for example, Space Station Freedom, or constructing on Mars or on the Moon, are we going to be carrying up 40-ft timbers of composite materials? That is what we have to do if we do not have any processing in outer space. We are going to have to carry all of those things up in the shuttle bay. There are only so many ways you can orient 40-ft pieces to stack them together. So there would be some advantage in space requirements in not having to transport profiles. Another advantage would be that the kind of profile you would need for a certain job could be processed in situ to the exact length you would need. You could also get very large profiles because you wouldn't have the necessity for holding up a large amount of material. Large profile could be made to be homogeneous over this very great distance.

Our role in this is not to study the extrusion process necessarily. We are going to investigate thermoplastics whose microstructure has been varied by the application of stress, since the effect of gravity is to create stress in the material. Our processing variables are going to be stress and temperature. The microstructural studies are going to determine the degree of crystallinity in these materials, crystallite size, crystallite orientation, and nucleation density to determine how the application of stress affects those variables. Our approach will be to use real-time, wide and small-angle x-ray scattering performed at elevated temperature during the deformation process. So these are going to be in situ studies of deformation effects on polymer structure. The studies are done at the Brookhaven National Laboratory using their x-ray synchrotron light source. Another component of the project will include molecular modeling of the polymer crystal structure and orientation as a function of tensile deformation. Many polymers have solid-solid state phase transformations that occur when you apply stress. PBT is one of them. Finally, we will characterize the microstructure after processing.

How are we going to process? Well, we have one device called a zone annealer which is a small heater. The heater moves by a stepping motor that drags the heater in this direction, V. The polymer is shown in blue, gripped between two green grips. The small heating zone moves across the polymer, and the dead weight applies the tension force. This stretches the polymer and immediately as the polymer is exiting from the small slot, it becomes cooled and a new fresh amount of material enters the heating zone. This zone heater produces a material of extremely uniform cross section. It does not form a highly necked sample as you would find if you did this in an environmental chamber on an Instron. So you get a very nice sample; highly oriented, uniform orientation across the sample. This scheme can form a sample for study at room temperature. We also hope to develop a device like this which would have a heater on it (that is not shown) in which the synchrotron beam would pass through a tensile stage mounted in the beam perpendicularly. Here is our polymer sample. We have now a 10 cm^2 real-time detector. We are able to take spectra at the synchrotron on the time scale of 3 seconds and get resolved peaks that look like this. We can do very fast resolution of kinetics. Generally, at 3 seconds, we may average more than one scan, but that is just to give you an idea of the time scale kinetics that can be studied using this kind of a device.

This is my summary slide. We are going to take material that is isotropic and amorphous either cold-crystallized or from the molten state, and introduce either orientation or, as shown here, planar orientation in the amorphous state. Depending on the nature of the material we may see higher levels of order such as smectic-like layering, or semicrystalline order. All of these material characteristics of order are affected by stress, therefore, they will be affected by the gravity environment. This work that I talked about at the beginning is being supported by the U.S. Army, and the work that is upcoming is a NASA-sponsored fellowship as I mentioned before. I thank you for your attention.

QUESTION: If I understood clearly, you mentioned you did some DSC work?

ANSWER: Yes.

QUESTION: What kind of heat of transformation was involved at the glass transition temperature?

ANSWER: Generally, it is pretty small for the melting. For PBT homopolymer infinite crystal, the perfect crystal has a heat of fusion about 130 J/g.

QUESTION: The reason I ask it is that it is very much similar to the large organic molecules; that is where you get a spherulitic microstructure. For you it might be small, but if you compare with metals and alloys, the entropy of fusion is very high. One of the things that enters the picture is that, by any means, if those values could be lowered by, for example, doping or any other way, then they can be very well controlled. The spherulitic structure, interlamellar, etc., can be controlled if somehow that heat of fusion can be reduced. There is quite a bit of work on modification of structure.

COMMENT: I believe this is completely different. You see, one big difference here with polymers is that they are enormously undercooled. That means that all of the sugguestions which you may have to modify the structure by changing the heat flow do not work in the polymers too well.

RESPONSE: Selenium gives, most of the time, the same kind of microstructure which you described (mostly spherulitic), I understand. It depends on kinetics, and polymers have very sluggish kinetics.

ANSWER: That's right. And you may consider the polyarylate to be a form of dopant in the sense of reducing kinetics.

QUESTION: Suppose you have a very low temperature gradient, and very slowly you are decreasing the temperature. Is there any way one can nucleate even at the smaller ΔT?

ANSWER: You can seed the material by leaving residual crystals of the same polymer in it.

QUESTION: Does it change the morphology?

ANSWER: It changes the gross morphology in the sense of leaving a larger or smaller number of nucleation sites which changes the ultimate spheroid sites.

RESPONSE: That says that you can do it, I guess by different techniques.

COMMENT: In that regard, to try to connect between polymer science, semiconductor crystal growth, and metal systems, the heat of fusion enters into the choice of processing elements in a number of important ways. When people look at deep undercoolings of melts, one of the things they are trying to achieve is to try to get their undercooling so deep that, on recalescence, the heat that is released is not enough to take it back to the melting point, so you preserve your fine structure. In the semiconductor area, as you are growing crystals, say, for example, by the Bridgman technique, the faster you grow, the more latent heat you release. Then it couples to the heat transfer in the system, and it modifies the interface morphology, the shape of the crystals, and all of the other things. What is the role of the heat of fusion and undercooling in polymers? Is it in a similar vein? It appears that you have very deep undercoolings, and as a result is that an important issue in being able to control or influence the process?

ANSWER: Polymer crystal growth is dominated by nucleation kinetics. So the number of nucleation events is going to affect your ultimate morphology. That is going to be a strong function of undercooling. You can change the rate of crystallization by adding a large number of nucleation sites. One thing that processors do is to put in agents that serve as nucleation sites for the polymer.

RESPONSE: Well if you wanted to do single crystal growth of polymers, you wouldn't want to do that.

ANSWER: It would be very difficult to grow single crystals from the melts. Melt is very highly entangled and almost all single crystal growth would be done from solution.

Polymer Morphology
The Analysis of Single Molecules

A Discussion by Bernhard Wunderlich at the Organic and Polymeric Materials Workshop at the Marshall Space Flight Center, April 27-28, 1993

The Advanced THermal Analysis System Laboratory
The University of Tennessee and Oak Ridge National Laboratory

RESEARCH PROJECTS
IN
POLYMER PHYSICS

- Electrical Properties (dielectric relaxation and TSDC)

- Liquid Crystal Polymers

- Structure of Semicrystalline Blends

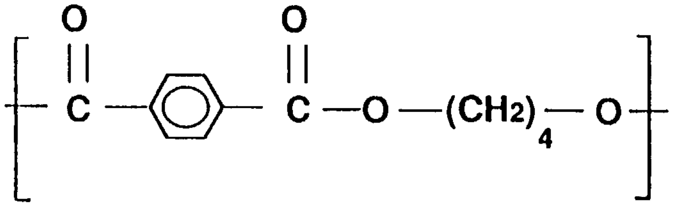
- Optical Properties of Polyimides for Electronic Packaging

- Real-Time Studies of Processing Semicrystalline Polymers

  (NASA Fellowship Award to Mark Brillhart for $\mu\vec{g}$ Research – 9/93)

CHEMICAL STRUCTURES

Poly(butylene terephthalate)

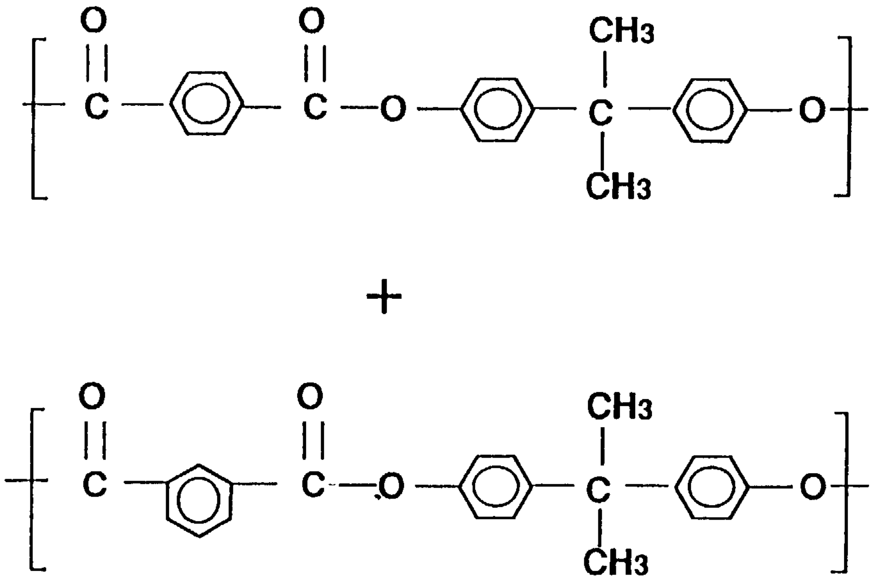


Tg = 30 °C

Tm = 230 °C

Polyarylate

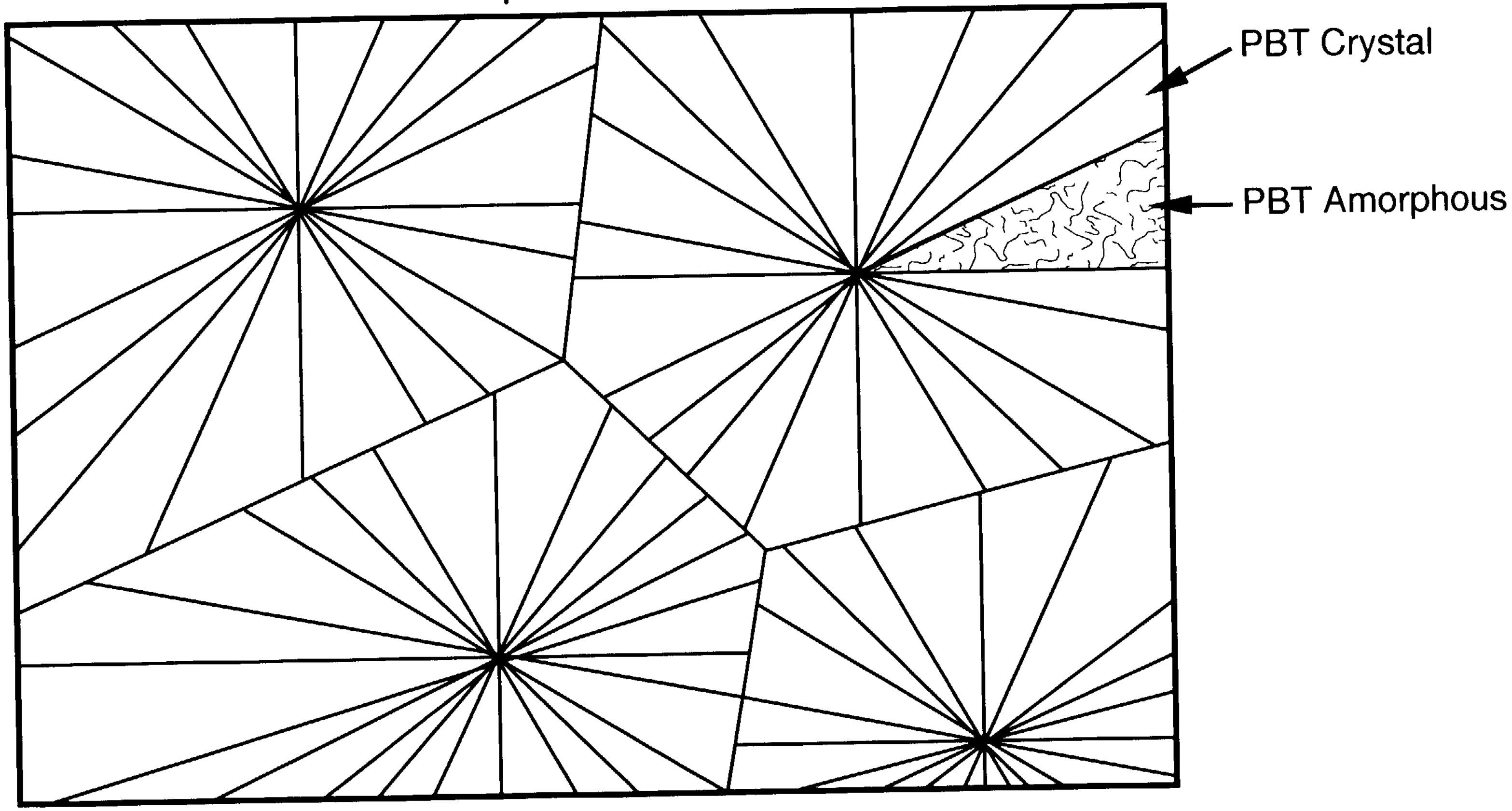
50:50



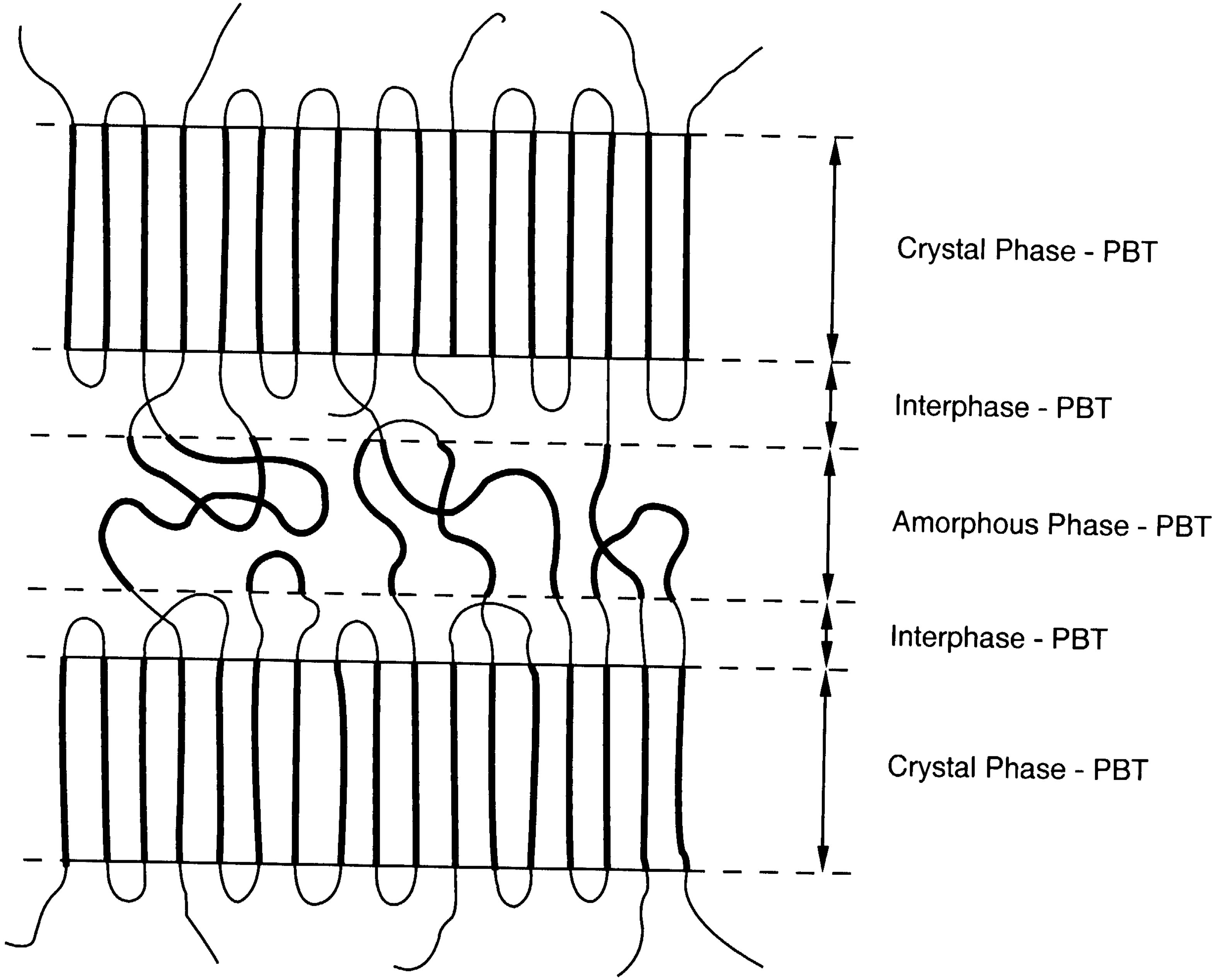
Tg = 180 °C

Poly(Butylene Terephthalate) Homopolymer

Spherulites



Lamellar Crystals



5-20888

Binary blends of PBT and PAr have been studied

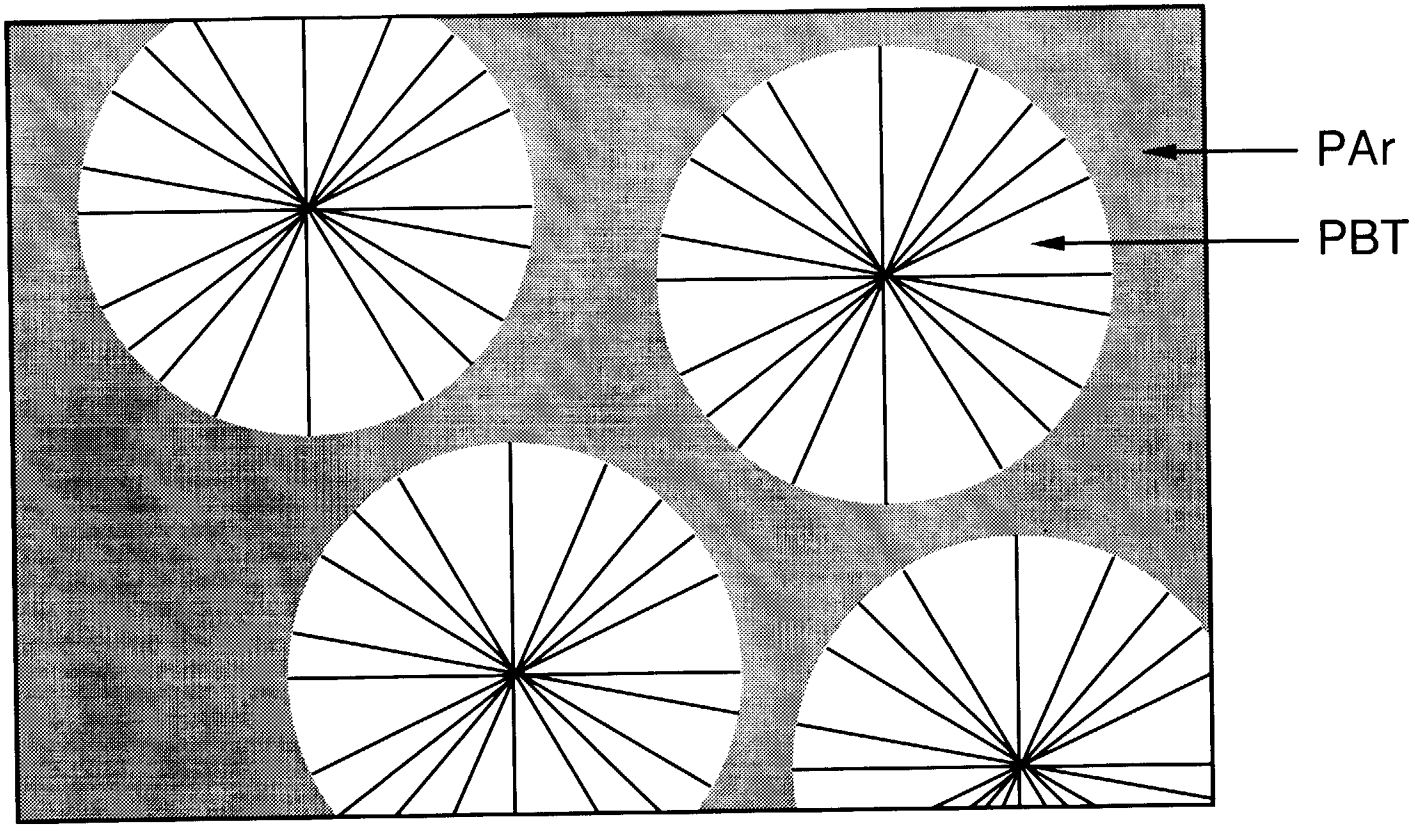
- PAr – non-crystalline
- PBT – semicrystalline

Blends are miscible in the molten state, but upon cooling PBT crystallizes.

Where is the PAr located?

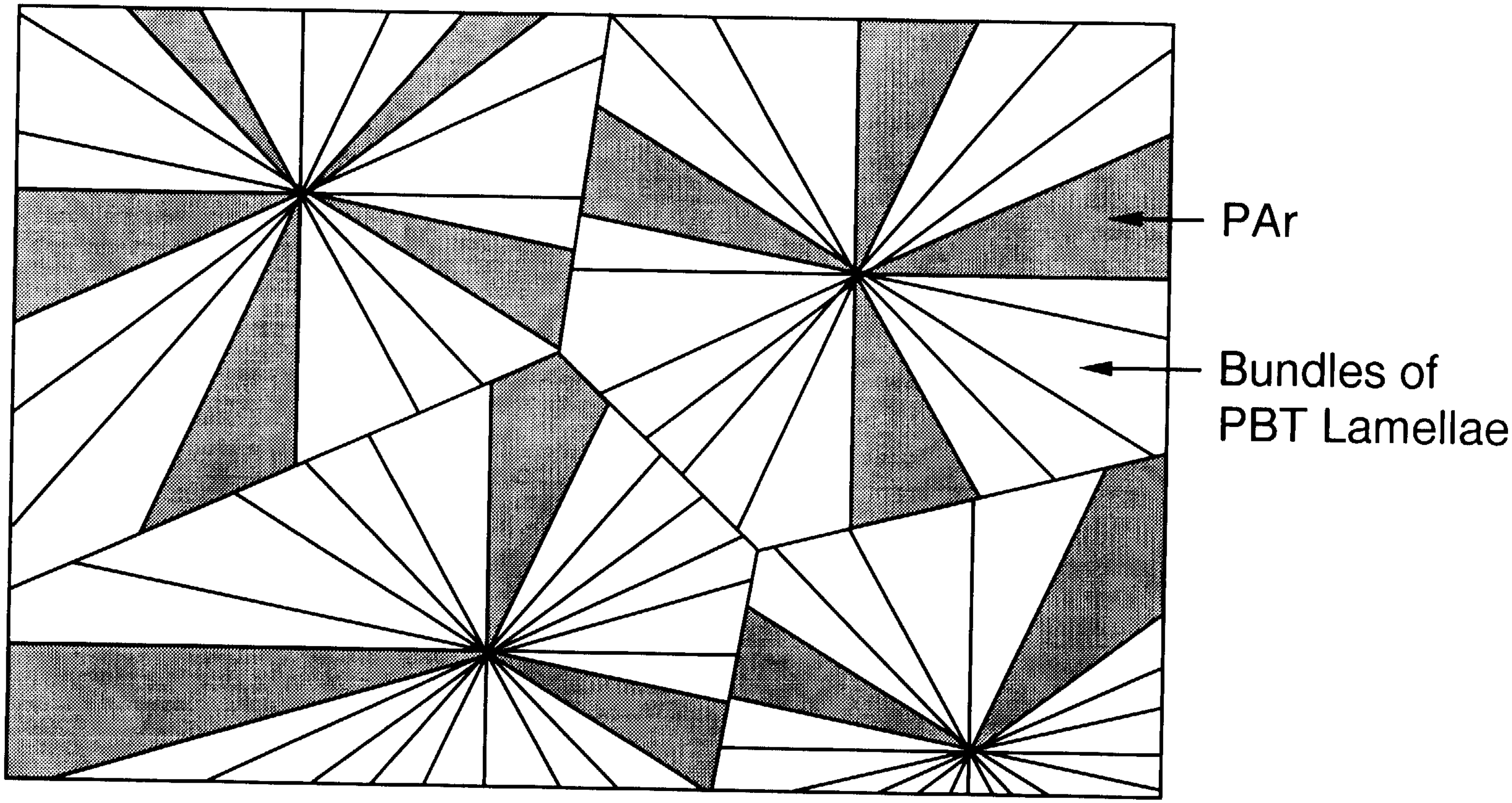
1. Interlamellar?
2. Interfibrillar?
3. Interspherulitic?

Interspherulitic Polyarylate



We would expect 2 Tg's,
one at Tg(PBT); one at Tg(PAr)

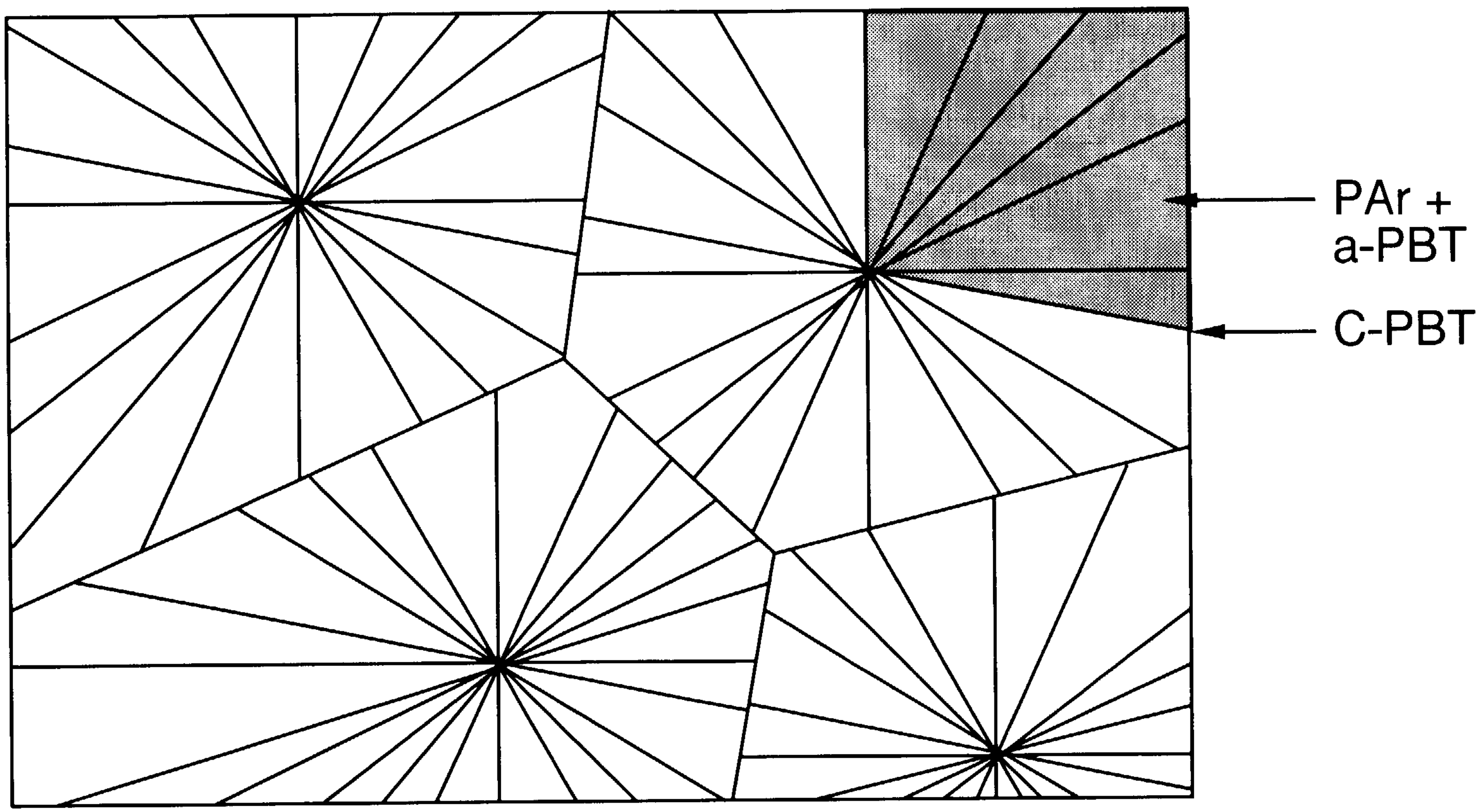
Interfibrillar Polyarylate



We expect 2 Tg's, one at
Tg(PBT); one at Tg(PAr)

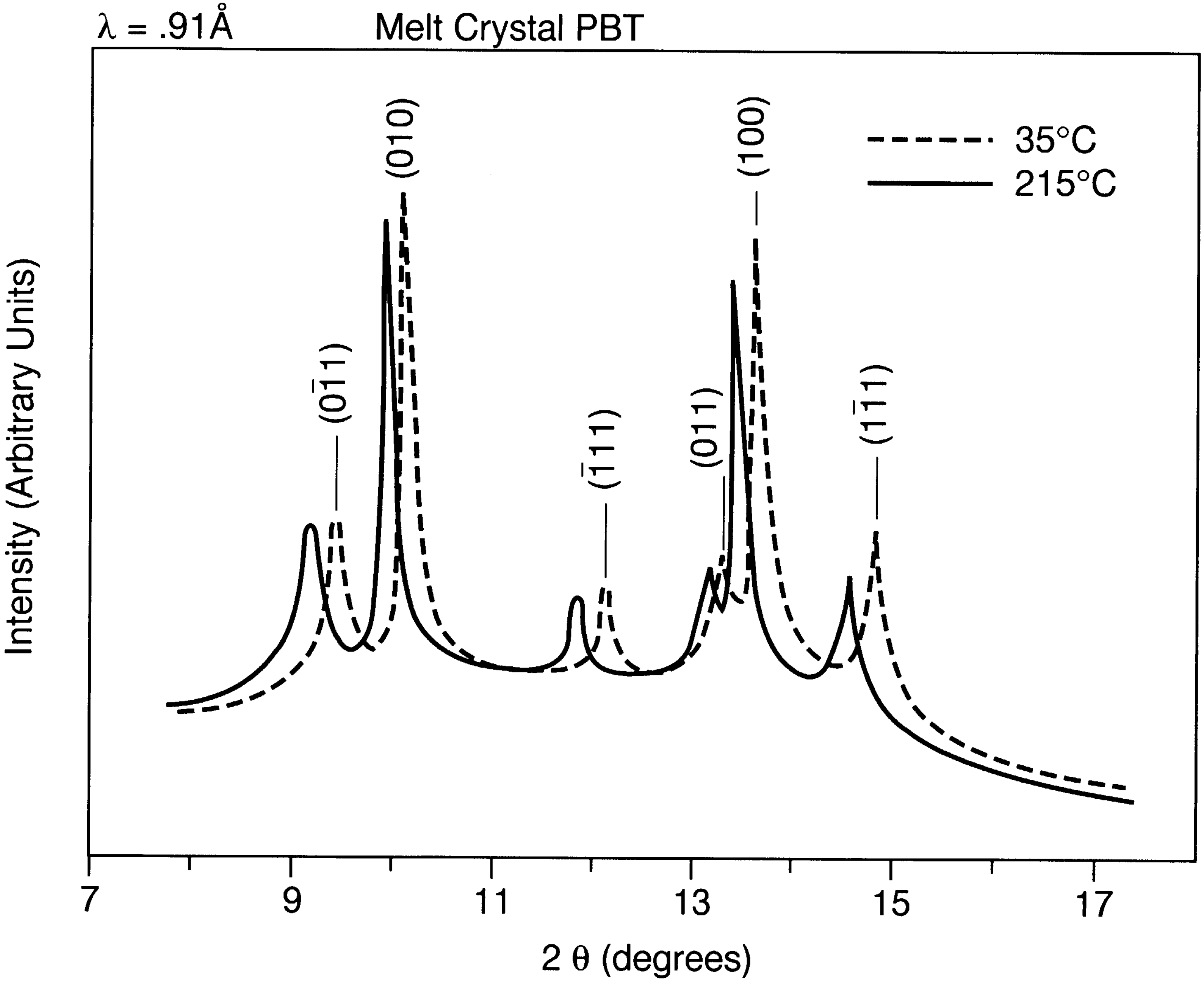
5-20890

Interlamellar Polyarylate



We expect one or two Tg's.
If two, the lower may be PBT interphase;
the upper may be PBT + PAr.

5-20891


λ = .91Å
Melt Crystal PBT
35°C
215°C
(0$\bar{1}$1)
(010)
($\bar{1}$11)
(011)
(100)
(1$\bar{1}$1)
Intensity (Arbitrary Units)
7
9
11
13
15
17
2 θ (degrees)

5-20900

PBT Estimated Coherence Length (Å)

(Melt Crystallized at 200 °C)

Sample	a*(±5Å)	b*(±5Å)	c*(±5Å)
100/0	100	160	50
80/20	120	180	50
60/40	150	200	50
40/60	200	190	50

- Melt crystal samples have larger coherence lengths than cold crystal samples.
- Composition of blend affects a*, b*, but not c*.

? INTERLAMELLAR MORPHOLOGY ?

- Long period trend vs. composition can not be used to determine whether morphology is interlamellar. Long period is controlled by undercooling.

- Long period for each blend was found from the SAXS peak position.

- Long period was calculated from the lamellar thickness and total volume fraction crystallinity found from:

$$L = l_c \, / \, v_c\,(t)$$

$$\frac{1}{v_c(t)} = 1 + \left(\frac{1-w_c(p)}{w_c(p)}\right)\left(\frac{\rho_1}{\rho_2}\right) + \left(\frac{x}{1-x}\right)\left(\frac{\rho_1}{\rho_3}\right)\left(\frac{1}{w_c(p)}\right)$$

- where p and t are the partial and total fractions, ρ_i is the density of the ith component (i=1, c-PBT; i=2, a-PBT; i=3, PAr); x is mass fraction of PAr.

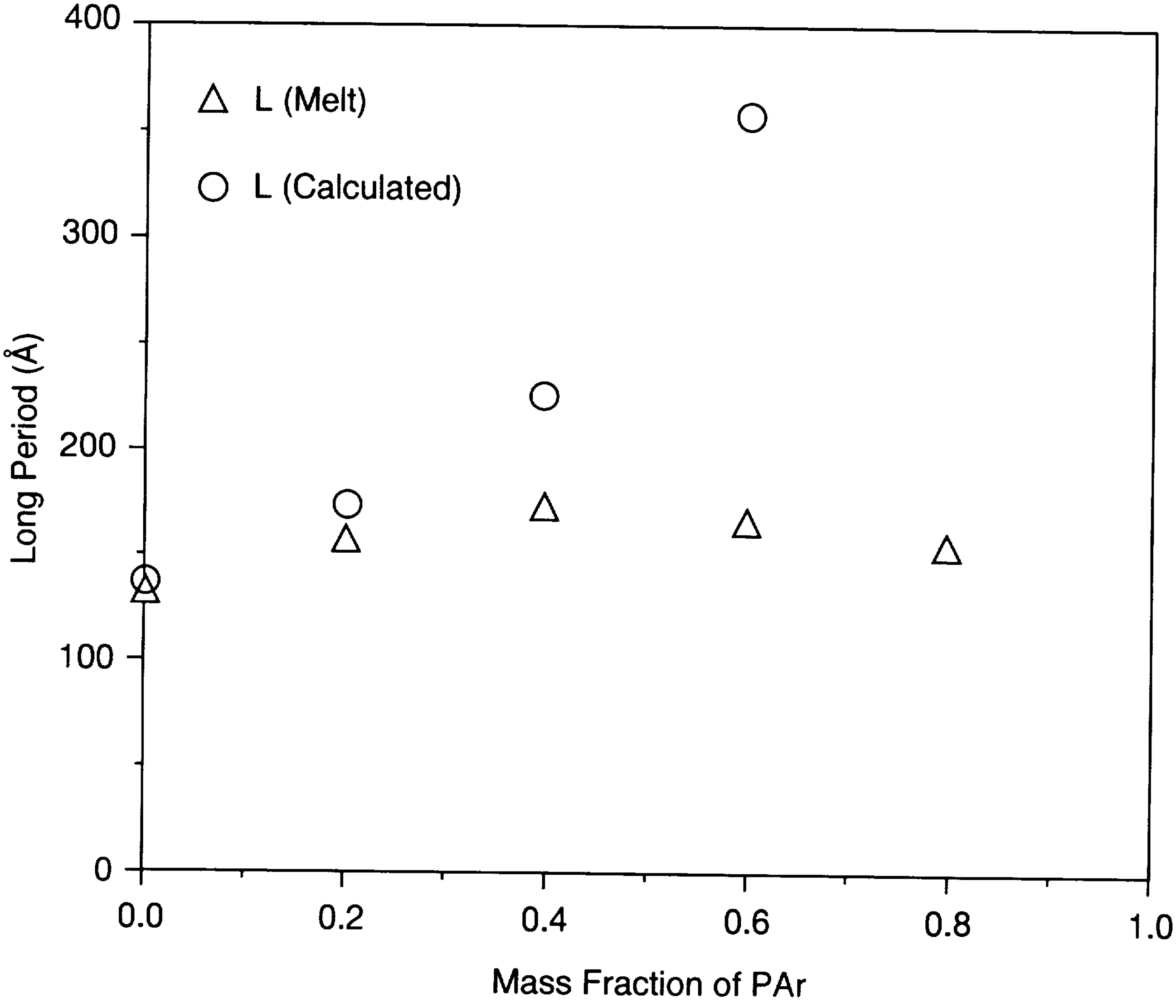
Long Period (Å)

1. Melt Crystallized

	(measured)	(calculated)
100/0	140	140
80/20	160	180
60/40	180	230
40/60	170	360
20/80	160	5000

2. Cold Crystallized

	(measured)	(calculated)
100/0	100	100
80/20	120	120
60/40	150	180
40/60	140	300
20/80	130	940


400
300
200
100
0
Long Period (Å)
△ L (Melt)
○ L (Calculated)
0.0
0.2
0.4
0.6
0.8
1.0
Mass Fraction of PAr

1. L does not increase as PAr composition increases.

   Additional PAr must be inter-fibrillar or spherulitic.

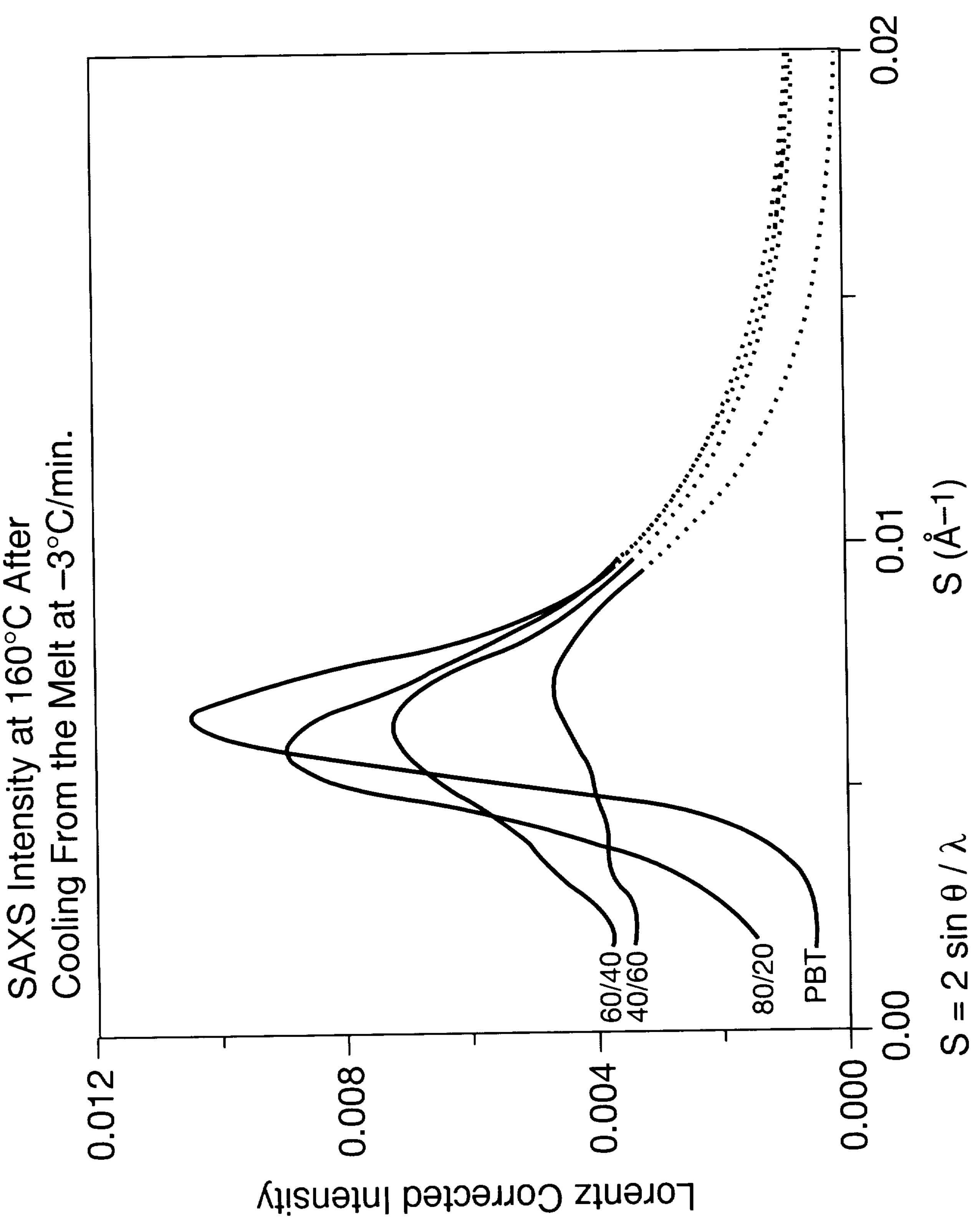
2. Lower Tg shifts upward as PAr composition increases.

   A-PBT and PAr may become more interpenetrated at higher loadings of PAr.

- If PAr were located in interlamellar regions, we would expect SAXS intensity to increase.
  - Lower density PAr would increase the electron density contrast.

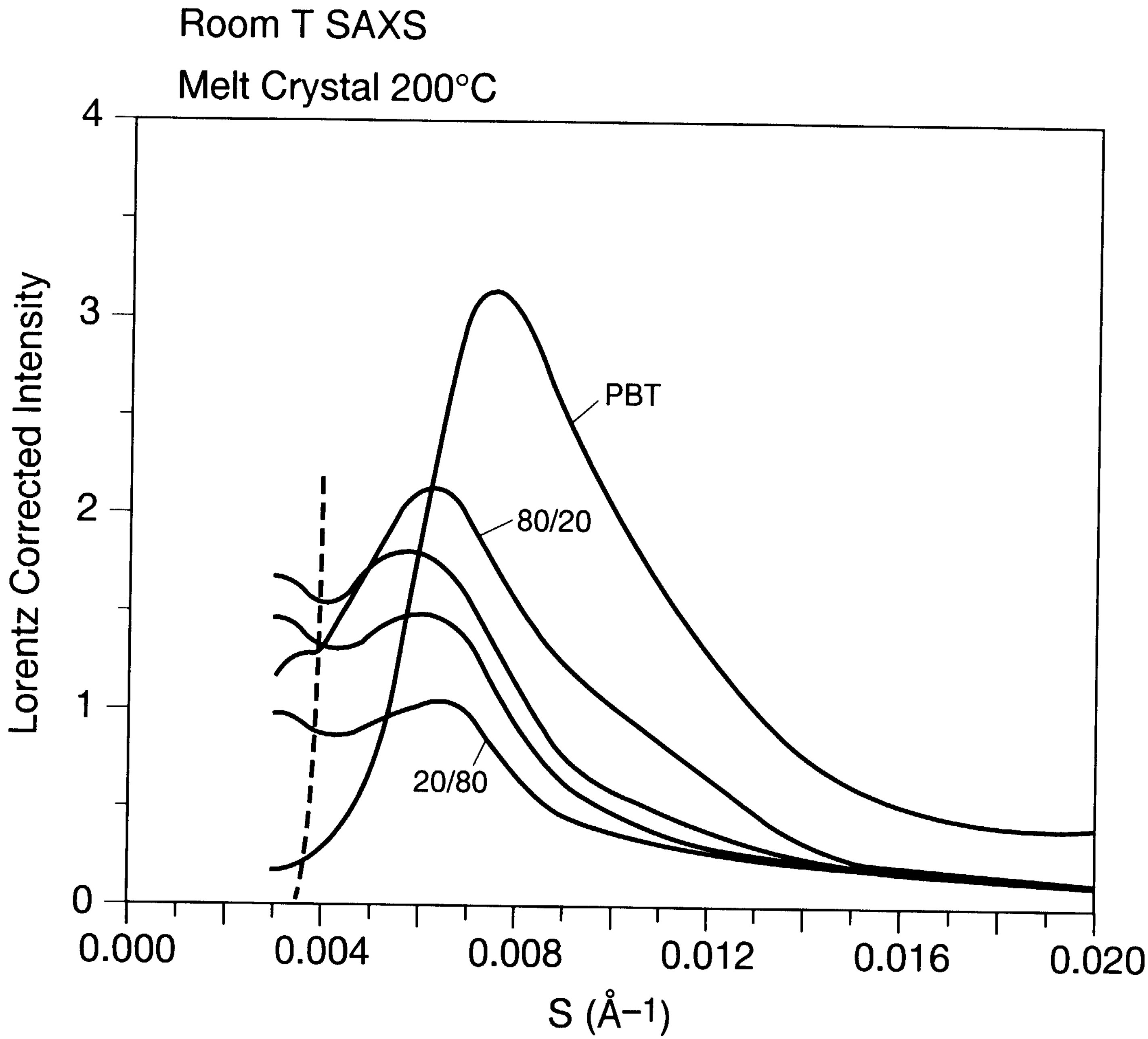
- SAXS intensity from periodic structures decreases as PAr composition increases.

- SAXS scattering at low angles (S→0) increases in both melt and cold crystallized blends.
  - There is strong interference from large scale structures.



SAXS Intensity at 160°C After Cooling From the Melt at –3°C/min.

5-20898

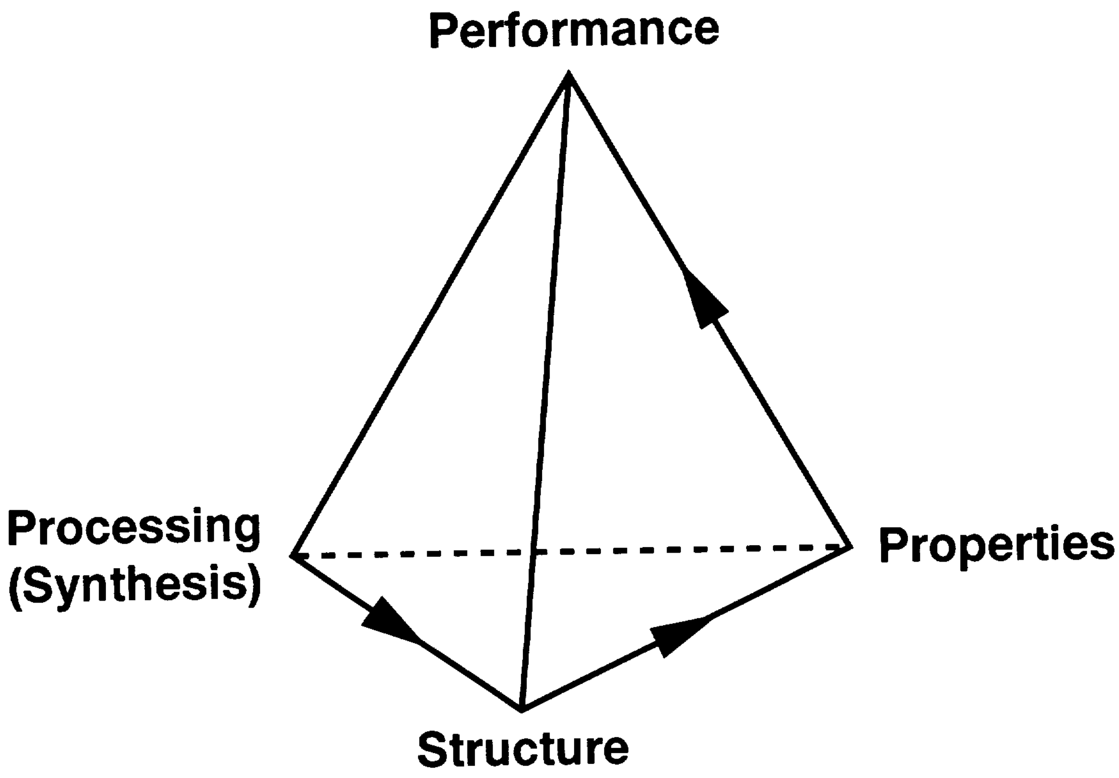

Room T SAXS
Melt Crystal 200°C
Lorentz Corrected Intensity
0
1
2
3
4
0.000
0.004
0.008
0.012
0.016
0.020
S (Å−1)
PBT
80/20
20/80

5-20897

PROPOSED MICROGRAVITY-RELATED RESEARCH

GOALS

- To study the effects of processing-induced deformation on the structure, orientation, and morphology of semicrystalline polymers
- To develop processing models that incorporate self-deformation caused by gravitational effects
- To develop processing technologies for forming large profiles in the microgravity environment



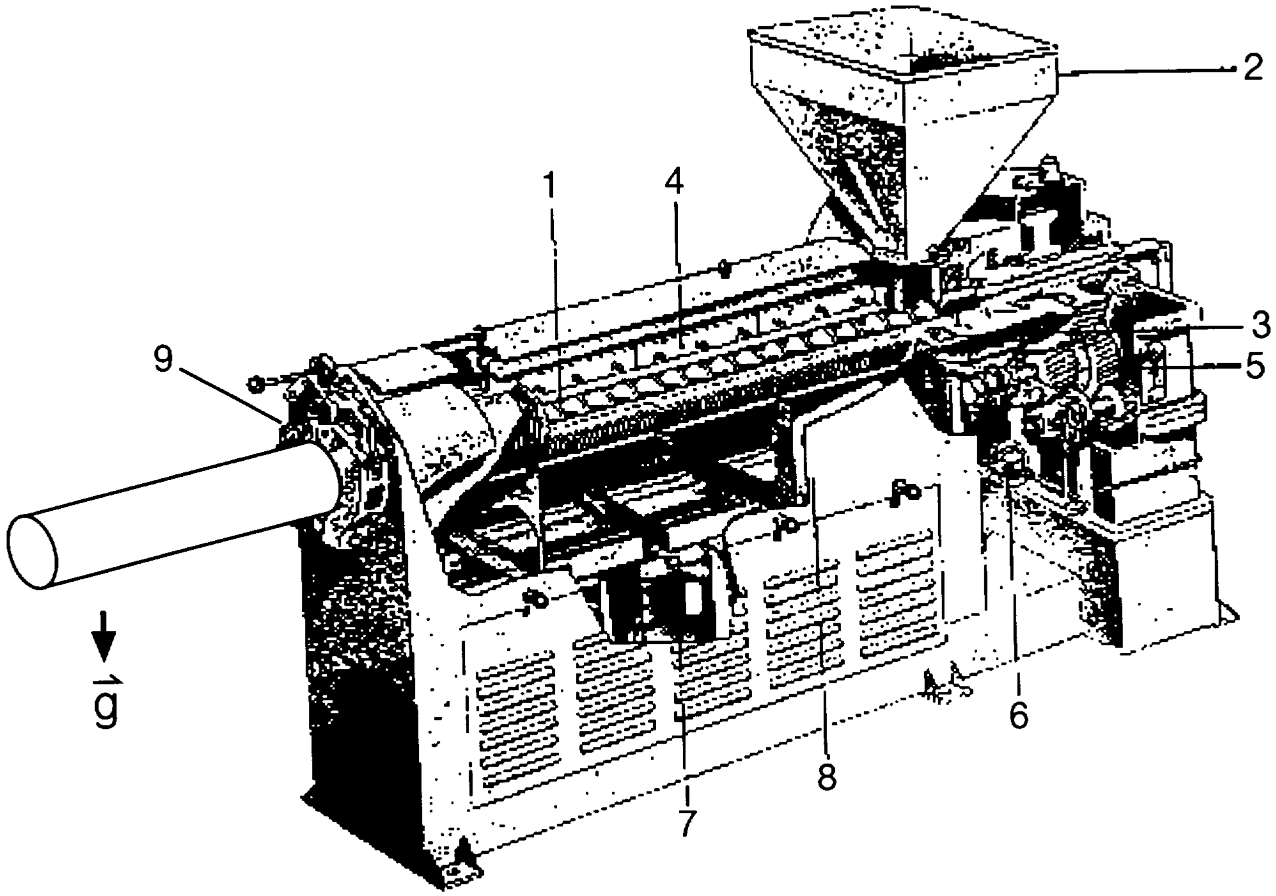
1. Processing in molton state in $\vec{g}$
2. Gravity causes material to deform, changing its microstructure.
3. Result is non-uniformity in the material properties;
4. This ultimately affects the performance characteristics.

PROCESSING SEMICRYSTALLINE POLYMERS IN A MICROGRAVITY ENVIRONMENT

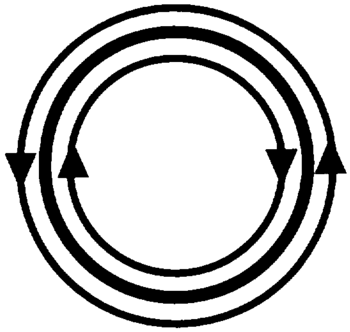
- Containerless Processing
  - Surface nucleation effects
  - Texture transfer effects

- Extrusion Processing
  - Self-deformation effects
  - Support structure requirements

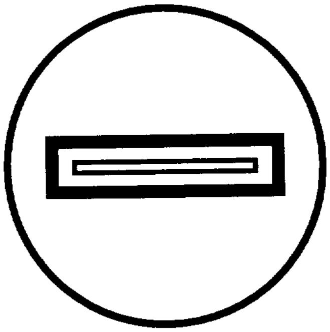
All Earth-based processing requires gravity compensation.



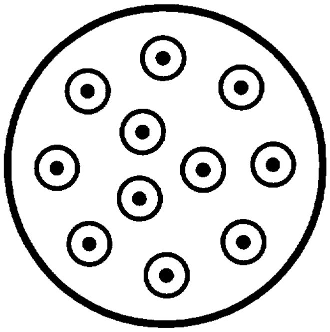
Sectional view of a single screw plastics extruder. 1, screw; 2, hopper; 3, feed section; 4, barrel heaters; 5, gear box; 6, lubrication system; 7, air blowers to control barrel heating and cooling temperatures; 8, double walled hood for balanced air flow; 9, die clamp assembly. (Courtesy of Francis Shaw & Co., Ltd., Manchester, England.)



Counter-Rotating Die

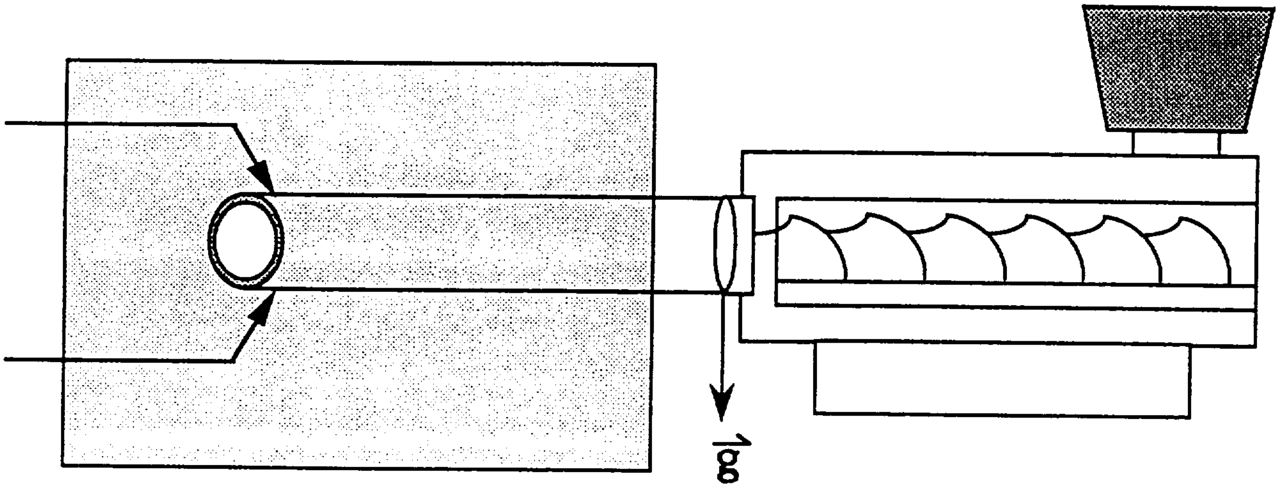


Slot Die



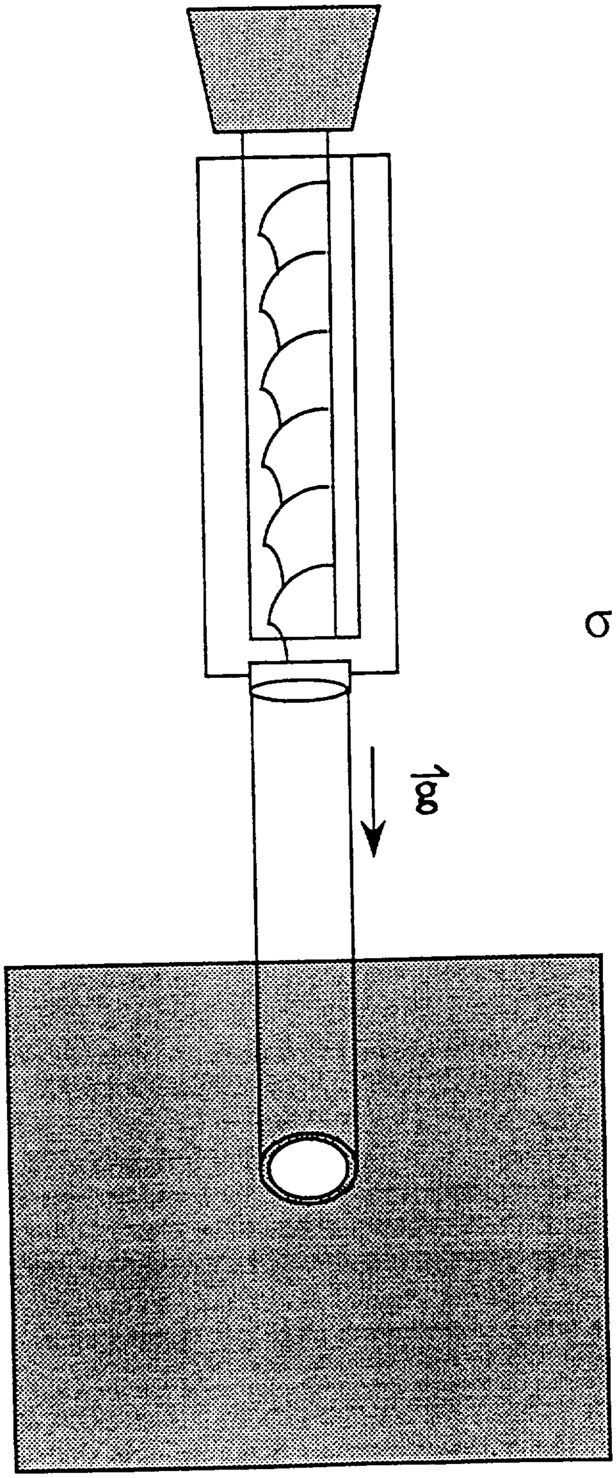
Filament Die

HORIZONTALLY ORIENTED EXTRUSION



- Tube must be gripped and pulled through a fluid bath, or
- Tube must be gripped and supported
- Pieces warp upon contact with the fluid
- Residual stress is locked in during quenching

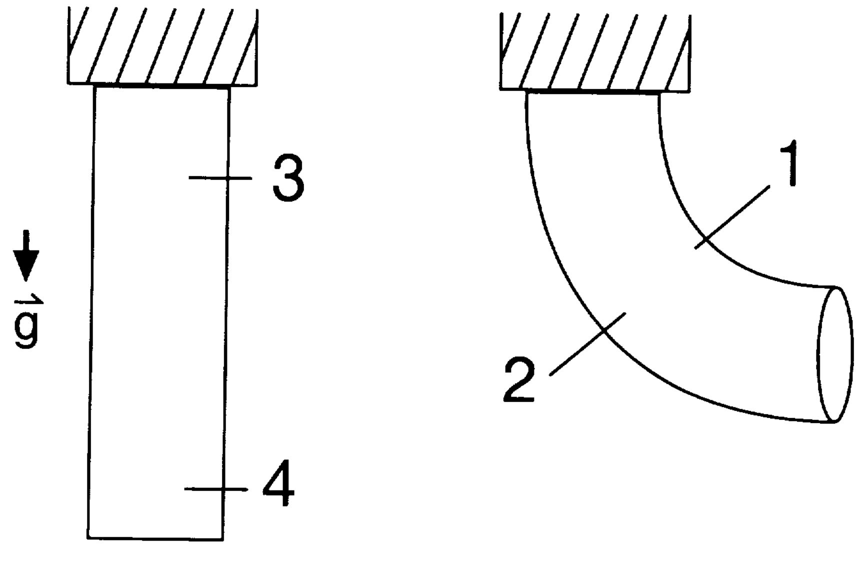
VERTICALLY ORIENTED EXTRUSION



$$\sigma(x) = \rho\, x\, g$$

Vertical Extrusion

- Profiles warp upon contact with the fluid
- Profiles must be reeled up $\sigma(1) \neq \sigma(2)$
- Gravity causes a non-uniform stress distribution over the length of the section $\sigma(3) > \sigma(4)$
- Stress distribution causes non-uniform morphology
- Local yield, including nip-off, may occur at the fixed end



EXTRUSION PROCESSING ADVANTAGES AVAILABLE IN MICROGRAVITY ENVIRONMENT

- Material will not sag at the exit die
- Material will not creep during solidification
- Mechanical support is not required at the exit die
- Fluid support is not required at the exit die
- Material can be easily formed into films, fibers, sheets and tubes

ADVANTAGES OF EXTRUSION PROCESSING OF THERMOPLASTIC POLYMERS OVER EPOXY-BASED SYSTEMS

- Pellets and powder are stored at ambient conditions
- Semicrystalline thermoplastic polymers are tougher, more radiation resistant, and non-volatile
- Thermoplastic polymers can be repaired in-situ by annealing
- Manufacturing of thermosets is more complex.

SPACE MISSION ADVANTAGES OF PROCESSING IN MICROGRAVITY ENVIRONMENT

- Pellets and powder are easily stored
- Profiles need not be transported
- Profiles can be formed to size in-situ
- Very large profiles can be formed

We will investigate thermoplastics whose microstructure has been varied by application of stress.

- Processing variables are stress and temperature.

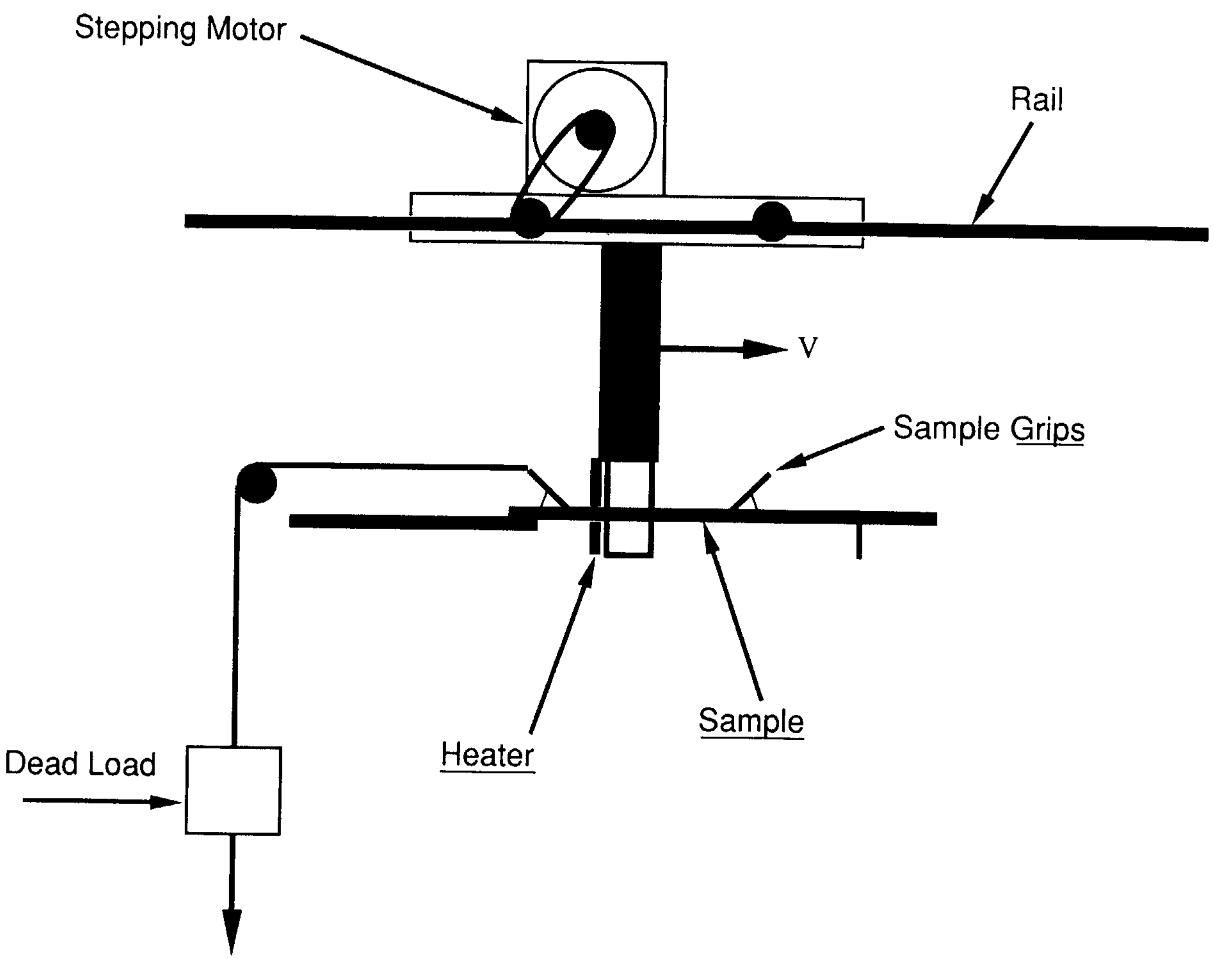
- Microstructural studies will determine:

  - degree of crystallinity
  - crystallite size
  - crystallite orientation
  - nucleation density

APPROACHES

- Real time wide and small angle x-ray scattering, performed at elevated temperatures during deformation
    - Studies done at Brookhaven National Lab, Using the Synchrotron Light Source
- Molecular modeling of polymer crystal structure and orientation after tensile deformation
- Characterization of microstructure after processing

Zone Annealer



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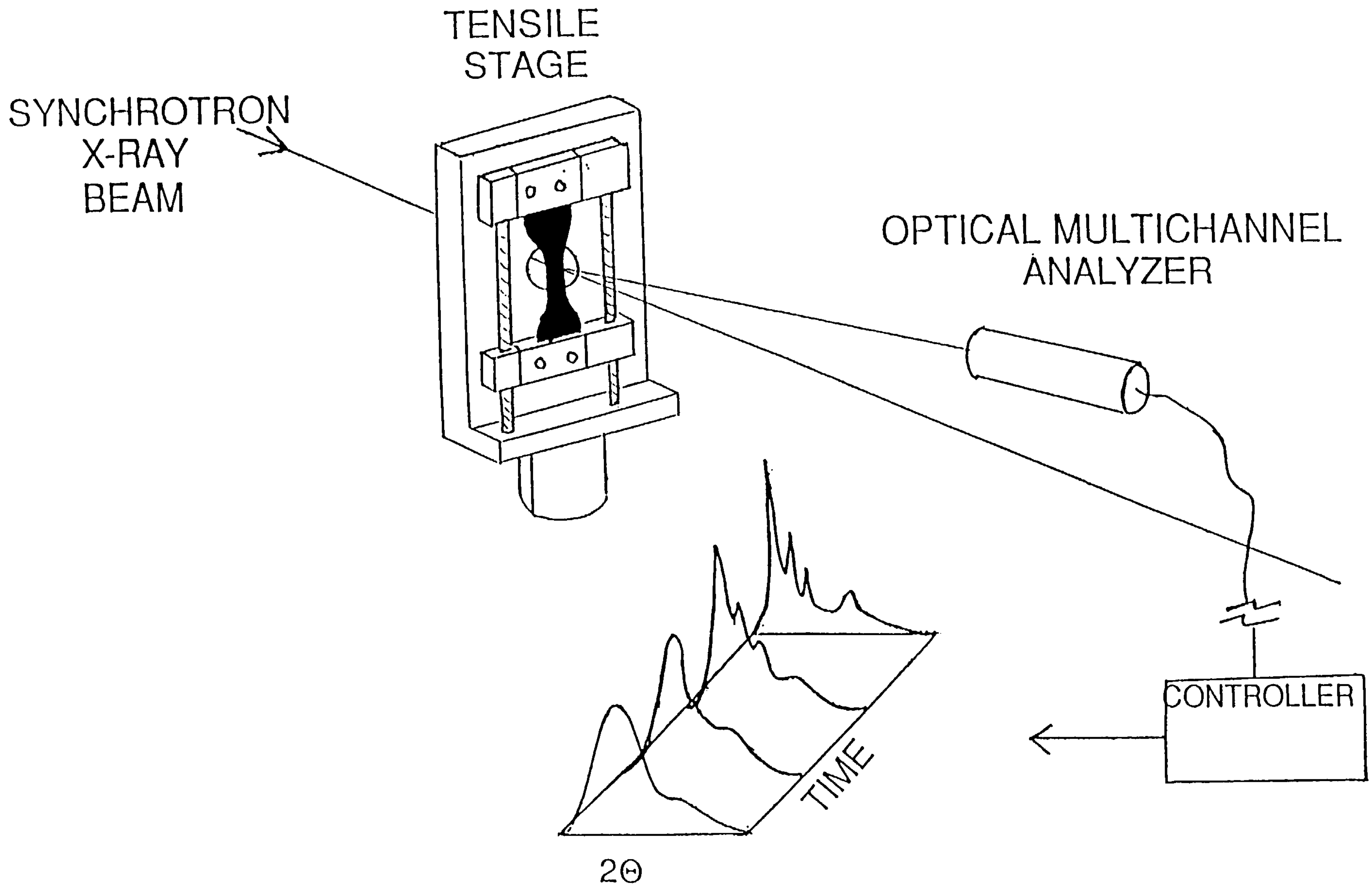
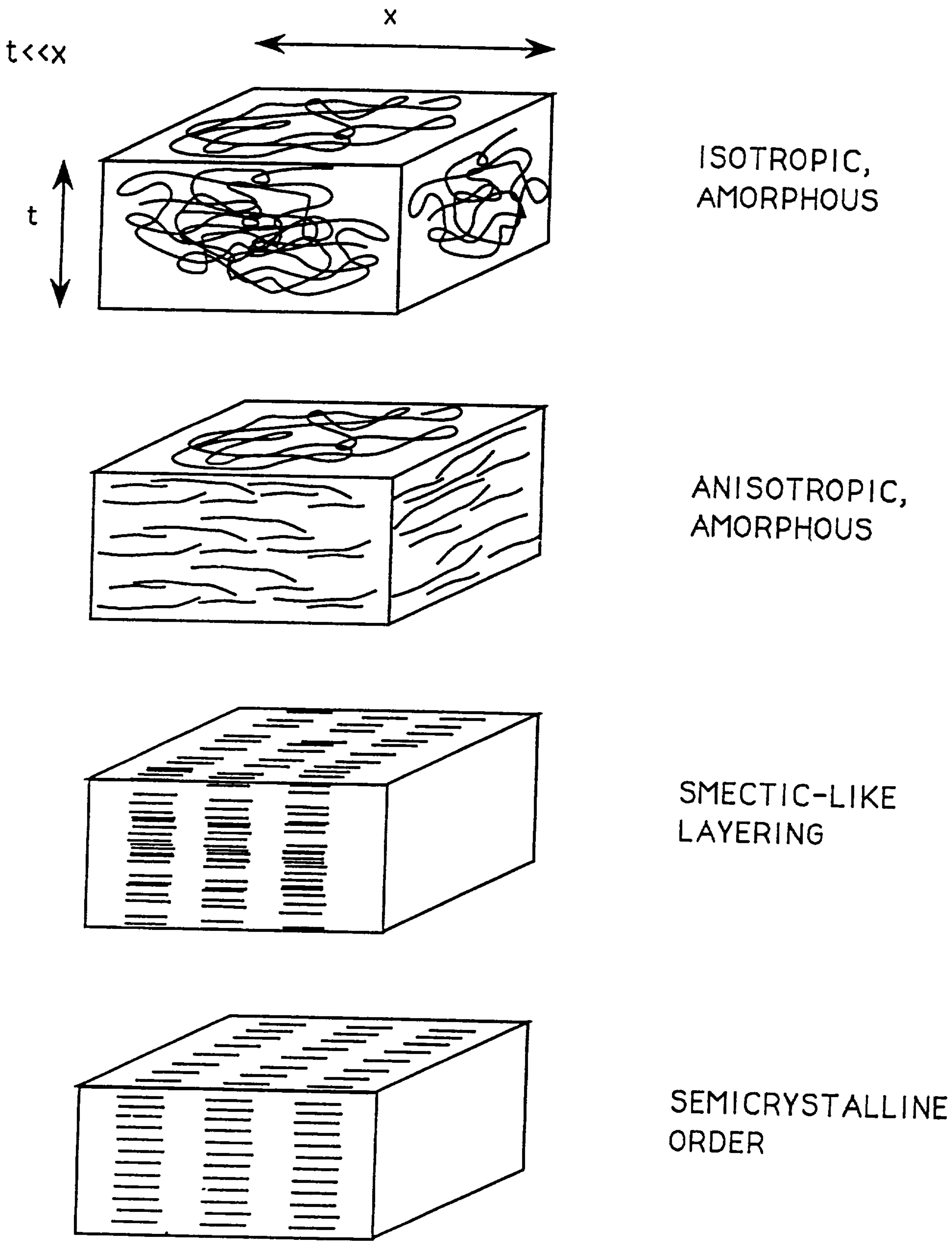
TIME RESOLVED X-RAY SCATTERING



LEVELS OF ORDER



Transcript of Presentation

CONVECTIVE INSTABILITIES IN TRAVELING FRONTS OF ADDITION POLYMERIZATION

John A. Pojman, Chris E. Jones, and Akhtar M. Khan

An autocatalytic reaction in an unstirred solution can often support a propagating front of chemical reaction. A simple example is a burning cigarette. Autocatalysis in polymer reactions can be found with DNA and RNA. A group in Germany has demonstrated propagating fronts of RNA replication. Another type of autocatalysis is the "gel effect," in which changes in the viscosity during a reaction decrease termination steps in causing a net increase in the rate of polymerization. Because it does not involve an autocatalytic species, diffusion cannot couple with this mechanism to provide a propagating front.

Now we can use, though, the Arrhenius nature of the kinetics of a free radical polymerization, or actually, any polymerization process. The reactions give off a lot of heat, and if we have a thermal initiator, whose kinetics depend, in this fashion, exponentially, we should be able to get a propagating front. The reaction would give off heat. The heat would diffuse and initiate the reaction and, in principle, we should be able to get a propagating front. So we decided to use some materials, methacrylic acid, that are cheap, available pure in large quantities, and have a very high boiling point so we don't have a problem boiling off our monomer before it polymerizes. We also used benzoyl peroxide and, since then, many other initiators. What we do is to put the solution in methacrylic acid and benzoyl peroxide in a large test tube. And we can heat the top of the reaction, or the top of solution, or chemically initiate it. But the net result is we get a very hot region. This is actually solid polymer. Below this is unreacted monomer and initiator. We have a very sharp interface here. This is about 25 °C here, and here it is about 200 °C. It is a very sharp thermal gradient. This will actually propagate this solid front at a constant velocity, if you just observe the position, whose slope, then, is the velocity of propagation. These are propagating on the order of centimeters per minute. That velocity is, of course, a function of the initiator. You increase the amount of initiator, and you increase the velocity. This can be done for a wide range of initiators.

Why do we want to study these problems? Well, one, our background is in nonlinear dynamics and we are interested in any sort of propagating front to look at instabilities that can arise. Also, the possibility of creating new materials whose properties will vary spatially—the possibility of new composite formation. We have since learned, after starting our work, that this technique is being developed, for commercialization, in Russia at the Institute of Chemical Physics. In fact, the technique has been used for making very large-sized composite materials at that institute. Another thing, primarily of interest, is also to test theories of nonlinear propagation. I am going to show you a video tape later that will illustrate all of the different types of instabilities that can arise. I am going to talk primarily here about the convective instabilities that can arise. To show that you can definitely get spatial variation, if you take your polymer and section it radially, and look at the molecular weight distribution, there are very large molecular weight gradients. This is probably on the order of hundred of thousands and the order of millions, here, of molecular weight, and they are polystyrene standards, and this is varying over a few millimeters. So there are very large molecular weight gradients that occur radially, not along the direction of propagation. That can happen because there are large thermal gradients.

Now, I said that there are large thermal gradients along the direction of propagation, but there is also a large gradient radially. This is a 50° temperature difference between the center of the reaction and the edge, radially; that's 50°/cm, because the system is not adiabatic. We'll talk a little bit about why that affects molecular weight. Our primary focus here, since we are looking at microgravity research, is the role of convection which has a very large effect. You can look at this two ways. Either it is a problem, if you want to make things and you have convection, or it is an interesting way to study convective phenomena. Presumably, any sort of polymerization process is going to have large temperature gradients, and you should be able to have similar sort of convective instabilities. This is a very nice, well-posed problem you can study. There are two types of convection. One we normally think of as simple convection, buoyancy. With simple buoyancy wherein hot air rises, hot solution will tend to rise under the influence of gravity. Indeed, we do see that, and we will name a more complicated form in a minute. Now, if we take our reaction tube (again, this is 2 cm and, originally, the front was propagating along this direction), and we tilted the tube with respect to gravity, the front, because this is a very hot reactive solution, tends to float up. The front will become flat and eventually will remain perpendicular to gravity and propagate at the same velocity down the tube. The bottom line is that you cannot have an ascending front. If you turn the tube over, there is so much antisymmetric convection that the front is cooled and killed. So it will only work in a descending mode unless you use materials with much higher viscosities which we will demonstrate later.

QUESTION: When you say the "same velocity," it is the same velocity along the direction of the tube?

ANSWER: That is correct.

The other type of instability that can arise is what we call the double diffusive instability. This one is a little more puzzling. We have a solution here which is about, probably, about 100-150 °C right underneath this zone. It consists of monomer solution and polymerizing material. Isothermally, it is more dense than the unreacted solution, however, it is extremely hot and as we saw, it tends to rise up. So we wouldn't expect to see any convection in the downward direction. But in fact, as you see here, this is the evolution of what we call "fingering." It becomes extremely extensive, looking sort of like a jellyfish, and with benzoyl peroxide, it occurs only in the center of the tube. The question we have here is, why do we have a convective instability that can occur even though we have an extremely large thermal gradient which, we would think, would tend to oppose this? Why would it only occur in the center? How is it a function of initiator concentration and temperature, and what effect does it have on the polymer that's formed? Well, the effect on the polymer is that it leaves a big hole in it. This polymer didn't have "fingering," but this does have "fingering," so it leaves this hole. There is a lot of relatively low molecular weight material here. This is solid, but it is actually maleable. You can poke it. So, there is already a difference in molecular weight. You can quantitate that. It is extremely sensitive to initial conditions. In fact, when we first discovered this phenomenon it would never work during the day; only at night. Because the air conditioner in Mississippi did not work very well during the day and it was a few degrees warmer during the day, when we did a more systematic study, we found a difference of a degree or two could change the appearance. There is an initial temperature threshhold below which we don't see fingering, and above which we don't with high benzoyl peroxide initiator composition. Here, a difference of 1° makes a difference between seeing fingering and not seeing fingering. So it is extremely sensitive to initial conditions.

QUESTION: How many data points do you rely on to get the 1° difference, and how statistically significant is it?

ANSWER: Probably not significantly valid, but upper and lower boundaries certainly are, but they may be an artifact.

This theory of what we call double diffusive convection, which I will go into briefly, is ubiquitous because it actually comes out of oceanography and "ocean layer mixing." I will explain that, but I want to show you a reverse phenomenon which we propose as the same mechanism and explain why. This is an aqueous reaction with chlorate and bisulfite and the front is propagating in this direction—it's a pH front. Acid is the autocatalyst. And you have a 40 °C temperature gradient here and, again, an isothermal density change. But you see this sort of fingering, but now it's only going up. The fingering in the polymer system is only going down, and I'm going to claim it is from the same mechanism.

This is the analysis of the oceanographers, and it goes back into the 50's, for "ocean layer mixing." I'm going to contend that we have an analagous system and we can replace it with this simple model of hot salty water overlying cold fresh water. The heat will tend to make this rise. It's stabilized. But the presence of salt will tend to make it more dense, so if there weren't a temperature gradient, this would sink. So you could balance it out exactly. In fact, if you have it exactly balanced, it turns out to be the most unstable. Let's see why. What is observed is that actually you see tendrils, or fingers, going up and down. It's certainly analagous to what I showed you before, but they go up and down. This is very easy to see. Turner has done a lot of work on this and it turns out to be pretty important in layer mixing near Gibralter. There are big effects on the mass transport across the interface. What can happen? Well, we need to distinguish between a static stability and a dynamic stability. If I can get this pointer to set there flat on the table, it will stay, and any fluctuations aren't going to move it away from its equilibrium position. But if I can get it to balance, I can actually reach a point where it will be statically stable, but a very small fluctuation could knock it over. This, however, is actually dynamically unstable, and let's see why.

If you have a perturbation on a molecular level (this is supposed to be a cartoon of a molecular sized perturbation), and this fluctuation across the interface occurs, this little parcel is salty and hot. The heat will diffuse out, and so will the salt. But the salt will diffuse out about a 100 times slower than the heat. That is why it is called a double diffusive instability. The result is that you now have a parcel of fluid which is salty and cool. Now it is more dense than the surrounding region and sinks. As it sinks, it loses heat and contracts. The surface area to volume ratio increases, accelerating this effect. So this parcel, then, is unstable with respect to fluctuations. The same thing can happen in the other direction where heat will diffuse in faster, leaving a fresh water which is hot and less dense than its neighboring region, and the water will tend to rise. That is why you get these alternating ascending and descending fingers.

QUESTION: The salt finger coming out of Gibralter has been stable for a few 100 years. Isn't that true?

ANSWER: I mean fingering onto the layers. You have hot, salty Mediterranean water overlying cold, fresher water. It is believed that salt fingering occurs at the interface of these ocean layers and facilitates the mixing, on an ocean scale. This is small scale.

Now what is different in a polymer system, and what is the same? One thing, we don't have a system where you can have fingering in both directions. Clearly, this is solid. But we do have this hot polymer solution. Now heat is the same as in the hot, salty water. And we say, let's replace the salt with polymer molecules. We know that polymethylacrylic acid is about 15% more dense than the monomer. So this is a big effect. In fact, one of the reasons why we looked at polymer fronts is because we thought these effects would be so large. You have very large isothermal density changes and very large thermal density changes. Now we know that it is more than hot enough to compensate; however, under some conditions (and we don't know why some fronts give the fingering and others do not), a fluctuation can occur. The heat is going to diffuse out much faster than a polymer molecule. The polymer is going to diffuse very slowly, more than 100 times different. This finger can go down, and that is what we are claiming are small fingers. As they go down, they actually have to force some sort of fluid motion. One of our original theories was the reason we only see it in the center of tubes (and we never saw it in 1.5 cm diameter tubes) was that perhaps there was a critical size necessary for this recirculation. That turns out not to be the case. If you change the initiator, as we will show on the video, to another peroxide (t-butyl peroxide), you will see fingering all the way across the front. There is something about the benzoyl peroxide initiated polymerization that is different.

Well, what is the molecular weight of the fingers? Does it have an impact? You can collect those fingers, and look at the material by gel permeation chromatography, and the fingers have a much higher molecular weight. You can see again, there is a very large gradient in what we call the anulus (that region I showed you in the photograph) right around where the fingers are coming from. There is a lot of low molecular weight material there; this is actually an oligomeric region here—it is unreacted monomer. We now know from quantitative studies that we are only getting about 90% overall conversion at the front, even though we're using a gram per 100 ml of initiator. We are somehow burning up this initator before it initiates polymerization. Why do the fingers have a higher molecular weight? Why is there any gradient at all? This is probably related to temperature. Why are the fingers sinking? Well, because they are losing heat, which means they are cooler. The viscosity of that little droplet is much higher than the material left behind at the front, which means the termination reactions are going to be much slower. The termination of two polymer chains is going to be diffusion limited. When the viscosity goes up, that will slow down. Presumably, these fingers are essentially, or the polymers there, are just growing and growing. Monomer can diffuse in, the temperature is low, and we are not initiating any more polymerization. That is why fingers have a molecular weight about 10 times as great as the material left behind. We think that is related to the gel effect. Perhaps it is also related to the mode of termination. At lower temperature, presumably, a combination reaction would occur more frequently than a disproportionate reaction which would mean you would get a higher molecular weight.

I want to show you a video that will demonstrate all of this. I want to spend most of my time just showing you a film, because it is the easiest way to see a transient phenomenon. To relate another motivation for this is that these convective instabilities occur, and I think they are interesting in their own right. Clearly, gravity is going to have a large effect there. One question we have is when we eliminate, or significantly reduce, gravity, are we going to eliminate double diffusive convection? Yes, we will. The question is: are there other types of convection that can occur? We have large thermal expansions. Can we see interfacial effects? Because we have two different layers and very large temperature gradients, is it possible to see other ones? If you want to look at this fingering phenomenon, why don't you do it in a centrifuge? Why do you need to go to microgravity? That is a good argument. We always say there is no way on Earth we can do these experiments. But we could see the double diffusive effect under a centrifuge to increase the gravity. But unless we eliminate the buoyancy-induced convection, we aren't going to see the other types of convection that can occur which presumably will be important in any sort of polymer processing. I'm thinking particularly of something on the order of a Marangoni type instability. So that is the kind of question I am posing here, for insight to what other types of modes could we look for that could arise with large thermal and solutal gradients.

QUESTION: Where is the free surface for the Marangoni-driven flow again?

ANSWER: There is an interface between two liquids of different solubilities. I am also thinking that at the solid polymer there is also a polymer melt. We haven't looked at it closely, but that is a question I am asking.

The other reason that this is interesting is solid state combustion, where you actually have a thermite reaction—a gasless oxidation reaction that occurs with niobium, and all sorts of bizarre alloys that form this way. This has been studied extensively at Chernogolovka, Russia, because it sort of came out of their rocket development program. Rajanov has done a lot of work on that and has developed this into a lot of studies because instabilities occur. The front will actually go through a period doubling route to chaos as you change, say, the external temperature. The front will pulsate, and it has never been determined definitively that it will actually propagate chaotically. So that is one of our motivations. We like to use these fronts as a very inexpensive way to look for instabilities in propagating problems. Not only can these convections interfere with the front, they probably couple to it in a way that can introduce new types of thermal instabilities. So I'm distinguishing here, now, a convective instability, and it has nothing to do with the fact the front is propagating. It only occurs because there are temperature and solutal gradients as opposed to the fact that the propagating front itself is unstable. I'll show you the film where the front is pulsating. One reason to go to a different gravitational condition is to eliminate the convection, or change it, and see if we still see the same sorts of instabilities. An example of that, and I'll show you this on the film as well, is that under some conditions the front will pulsate: accelerate and slow down, accelerate and slow down. What we get is an actual striated pattern of about ten to a centimeter. The question we have is, what is the source of this instability? Is it convection, or pure thermal instability?

Part of the future work to do more of this is to look at the temperature dependence of the front. This is the log of the front velocity versus the reciprocal temperature. We can get an effective energy of activation and use this in various theories of stability to predict when the front should become unstable. One thing you might note is that the energy of activation is actually concentration dependent. So, we don't have steady state polymerization, which isn't surprising given the huge temperature jumps.

Okay, I can have the video now. We'll just look at just regular propagation, the onset of the convective instabilities, the pulsations in fronts without convection to show that if we simply change the viscosity of our medium, we can eliminate convection. We use actually a different model. We use methacrylic acid with benzoyl peroxide. The field of view will be about 1 cm and will be in real time.

One of the problems you will notice, is that there is a lot of very vigorous fluid motion, partly caused by gas production from the initiator. Actually, the pressure builds up to about 2.5 atmospheres, and so there is concern that you do this carefully because the tubes can explode. This is 1-cm wide, so, it's about 20 °C here and 25 °C here, and this front is propagating toward the bottom of the test tube. The jets are caused, maybe, by boiling monomer, or just by gas produced from the initiator. Thermal initiators give off a great deal of carbon dioxide; i.e., benzoyl peroxide does. Other initiators give off volatile products.

QUESTION: (regarding the curvature of the solid-liquid interface)

ANSWER: It actually has the opposite effect. It stabilizes it. The reason is that we have a large temperature gradient. But you don't have it until the polymer solidifies. This fluid motion tends to keep the temperature homogeneous, and that is why the front is not curved.

QUESTION: What is ejecting so violently?

ANSWER: Probably carbon dixoide.

QUESTION: And where does it go? If those are bubbles, you don't see any effect after their development.

ANSWER: Polymers have lots of bubbles in them, and that is one of the problems we are having.

Now this an example, again, of benzoyl peroxide under different conditions. This is fingering occurring, again, in real time. Once again, 1 cm wide, it started near an edge slowly migrated toward the center of the tube and remained there. Notice, as it pushes down, the little mushrooms.

QUESTION: You don't get carbon dioxide evolution?

ANSWER: This is a lower initiator concentration. You get it but it gets stuck in the polymer—there is less of it.

QUESTION: The motion toward the center is the return flow causing that?

ANSWER: No. I'm not absolutely positive why. But there is a big temperature gradient, and I'm assuming that this has a lower viscosity, and that is why the fingers can form here. But I don't think it is related to the return flow. But, you will see, that there is an antisymmetric flow in this direction. In the next sequence, I'll show you fingering all the way across the front with a different initiator.

QUESTION: And g is vertically down?

ANSWER: Yes. This is not a normal Mississippi gravitation.

QUESTION: Is it my imagination, though, where it seemed like it started near the edge, and it walked toward the center?

ANSWER: Not your imagination, but I don't have an explanation for it. That will always occur. If it does occur somewhere, it will always end up in the center.

Now, this is with methethyl ketone peroxide, another initiator, used to make fiberglass. This is a much wider field (1.5 cm). This is fingering, now, all the way across; again, methacrylic acid polymerization. This is never observed in benzoyl peroxide. The front is actually still propagating along this direction. This zone itself is actually moving down and reacting. This is a continuous reaction.

QUESTION: Can that be run so that it is solutally stable and thermally unstable—in other words, upside down?

ANSWER: No. Not with this monomer. Because the hot monomer would simply rise up, turn itself over, and cool itself, and die—it would quench it.

QUESTION: Did you say there is no effect from the diameter of the tube?

ANSWER: There is an effect. There is an effect on the velocity as well as convection.

This is very high benzoyl peroxide concentration. This is the reacting zone. You can see there are periodic striations, or stripes that form. These are probably carbon dioxide bubbles forming. The front is actually going to accelerate, slow down, accelerate, and slow down. I'll show you a fast forward sequence in a moment. We can see that a little better, and we'll illustrate it with another example later. This is slow motion.

The question we have with this instability is this: Is it caused by convection, periodically occurring which periodically cools the front and slows it down, or is the front periodically accelerating, heating up, and causing convection? Is it being driven by the inherent instability in the front, or is it the convective instability causing the instability in the front, or is it a combination of both?

QUESTION: Did you ever try putting a small amount of reflecting particles in there?

ANSWER: No we haven't.

This is a little more precisely controlled condition. You will notice that this front is not propagating smoothly. It actually has different sorts of waves propagating through it. This is, again, 2 cm wide. This has laminar flow around in a constant temperature gas. We are controlling the conditions, and it is certainly not adiabatic. This is with a different initiator. This is AIPN. If you'll notice, this front is not stable. There will be periodic production of fluid motion underneath. This front is actually wobbling from side to side. I am going to show a fast forward sequence, and keep that in mind because the wobbling can be important. I am sorry these are a little out of sequence; it is hard to edit them easily. But I want to show you now what happens if you build convection: very little. This is triethylene glycol dimethacrylate. It is a viscous monomer which is at the diethylate, so it can cross link. This is propagating. Notice now the front is slightly curved because I had said there is a 50 °C temperature gradient. Why doesn't it propagate faster in the center? There is so much convection with methacrylic acid, it keeps it flat. But, if I use this more viscous monomer, it can curve ever so slightly, but there is still fluid motion underneath.

QUESTION: Is that a bubble down there that keeps moving down the same distance ahead of that wave front?

ANSWER: Never noticed it.

This demonstrates that in fact the convection is keeping the front flat under nonadiabatic conditions. Here there is less convection, so the front can curve slightly. We'll eliminate convection completely, and we will see a very sharply curved front. We would expect that the front velocity would be proportional to the front temperature. And notice these regions here. Those are actually carbon dioxide bubbles that form. They don't form uniformly throughout this polymer—this is a crosslinked polymer.

QUESTION: So the only reason there is no convection here is although the driving forces are the same, you have a very high viscosity?

ANSWER: That's right. And there is still some convection. Because at 200-250 °C, the viscosity of the monomer goes down, but it is not as dramatic. You certainly would never see fingering in this case.

QUESTION: You say you expect a curved interface? Doesn't the thermal conductivity of your container play a role?

ANSWER: Yes, it does. I'll show you in a moment.

Even though there is less convection, when you turn the tube sideways, the front will flatten itself out. That will show you the orientation effect of simple convection. If you turn the tube over, there is enough convection to kill the front. So you can't even get a horizontally propagated front, let alone an ascending front even in small tubes. The temperature difference is 180 °C here and 25 °C here.

QUESTION: What is the magnification here?

ANSWER: This tube is 2 cm.

QUESTION: How fast is that front propagating?

ANSWER: About 1 cm per minute. One-half to 2 cm/min is the range.

QUESTION: What do you do, change viscosities somehow?

ANSWER: This is a different material. But we can change viscosity tremendously by adding ultrafine silica gel. We can systematically change viscosity. The other way is that we pre gel this material. We let it react a little bit. So now it forms a gel. Now actually this is a gel of triethylene glycol dimethacrylate, so it is partially polymerized, and it has an infinite viscosity. It is a solid material, and the front is extremely sharp. It is also curved slightly. I should just point out that this metal ruler is actually extracting heat and keeping the side cool. There is no convection whatsoever, and there are no bubbles. This is rather interesting. Presumably, it is so viscous that the carbon dioxide bubbles cannot aggregate and nucleate. That is my guess. We have the same benzoyl peroxide, but you don't see any trails of bubbles here. You see the front is curved more here, just because of heat loss to the ruler. We let it propagate under a water bath and you can see a very sharp curvature at the front. So convection plays a crucial role in keeping the front flat when the system has a low viscosity. Here, you can see this is 1 cm (you're watching it propagate). Now we reverse the tube in cold water.

QUESTION: In conventional crystal growth, getting rid of heat actually increases the rate of crystal growth. In this case, getting rid of heat actually slows down your growth?

ANSWER: That's right. It's just like cooling a flame.

Here the front is curving very sharply now. This tube is immersed in ice water at 0 °C. Now this gel material is very easy to handle. You can actually touch one end of this with a soldering iron. If it doesn't explode, it's a nice material, and no problem to deal with. This material is very easy to handle. It is very easy to initiate fronts.

QUESTION: Why doesn't the front curve in the other direction? If you are getting colder, it seems as though the solid should curve in the opposite direction.

ANSWER: Well, it is hotter here, so it propagates faster over here. The better you take the heat out, the faster it is going to grow.

This is very powerful not for studying convection, obviously, but for looking at the nonlinear dynamics, because we can make two- and three-dimensional fronts. If we are going to be investigating the stability of the front as it passes, because the rates of curvature changes, you see an instability set in, which has been predicted by some mathematicians at Northwestern. As the curvature changes, you should see instabilities arise because of the curvature, so we can study that better in three dimensions.

Now, in the next viewgraph you're going to see in a moment, the front is going to propagate up to show you when you increase viscosity, you can have an ascending front, and it propagates at the same velocity. Finally, I'll show you one more case of a pulsating front which we believe is a terribly unstable mode coupling with convection.

QUESTION: Is that reaction endothermic or exothermic?

ANSWER: Exothermic.

This last couple of minutes is going to show, with methacrylic acid again, that initiation is very rough. You initiate by adding a mixture of methacrylic acid, benzoyl peroxide, and dimethyl aniline, which is used as "bondo" on your car. It is a promoter; it will initiate polymerization at room temperature.

QUESTION: How do you determine the bath temperature?

ANSWER: OK. This is actually in a glass reactor where there is air flowing up. This whole thing is inside a water bath, but the tube itself is not in contact with the water. The air is blowing up, and you're passing through a heat exchanger, so the monomer solution is at the same temperature as the bath. We can control that to within a hundreth of a degree. But we are also observing a nonadiabatic system. The advantage is that we can control the rate of heat loss by increasing the flow rate. That will be important. If you will notice, here, this front is not propagating flat. What is going to happen (if you look, there is vigorous fluid motion underneath) is that it will periodically stop and then restart. The front will actually wobble. I will fast forward so I can show it a little easier. Now, that front is sinusoidal. This sort of instability that can arise—"multiple heads" can react, meaning there is actually a hot reaction zone which is propagating around so the front is going down. So, there is a reaction region spiraling on the outside, and from the side, it would appear to be wobbling. In fact, there may be multiple spinning heads involved—now very little convection, and the convection will pick back up. Now, we would like to know for sure how much of this convection is causing the instability and how much the instability is causing the convection, or, are they mixed.

QUESTION: Is that indicative of some type of azimuthal flow into the fluid flow?

ANSWER: I don't believe so. It should occur if we have this system without any convection. It should be a pure thermal instability. That has been seen with thermite reactions, where in fact a very hot and incandescent region will propagate around and around as this thermite reaction goes. So, that sort of instability is known, and it has been observed for anionic polyermizations in Russia. They have done an analysis of it.

QUESTION: What is the driving force for that?

ANSWER: An interplay between energies of activation, the initial temperature, and the rate of reaction. Basically, you get pulsations when the energy of activation is so high that the front sort of reacts faster than the heat can diffuse into the neighboring regions. So you have very sharp oscillations. Now, what we would like to do is to vary these conditions and get to a point where it propagates chaotically, and demonstrate definitively that we have the first real, well-characterized chaotically propagating front. If the role of convection is apparent, we need to be able to understand its interaction. In fact, it may be inherently coupling with the instability, and that is one of the goals.

QUESTION: Is the color of that really green?

ANSWER: No, it is clear. That is just an artifact of the video.

I would like to acknowledge some of the financial support we have had, and also our colleagues Lon Mathias and Bob Lochhead with whom we are collaborating. Our project really consists of three facets: one is propagating fronts and the others are copolymerization reactions and the effect of gravity on emulsions.

Thank you very much.

Transcript of Presentation

POLYMER MORPHOLOGY

B. Wunderlich

The Analysis of Single Molecules

What I would like to talk about is polymer crystal morphology, but not the morphology of crystals of many molecules. If you are interested in this, there is a book of over 400 pages that deals with all the aspects of polymer morphology.[1] I wanted to pick the things that may be of interest and have not been treated before. This work has not been supported by anyone. So, this is what was needed to be done—a little bit here, a little bit there, and a little bit by every co-worker so that the work has been growing over the years. I am at the University of Tennessee, and also at Oak Ridge National Laboratory. Otherwise, our work deals with almost all aspects of structure and morphology of the solid state. We do thermal analyses, solid state NMR, atomic force microscopy, electron microscopy, optical microscopy, and large-scale simulations of crystals. The biggest crystals that we can simulate are polyethylene up to 30,000 atoms, and over the last 5 years we have used a total of 8000 hours on the Cray computer at Oak Ridge. That is about 1 year, morning until evening for these computations. They are quite interesting, and if anyone is interested, I have a few of our reports available.

Description of a Single Molecule

But let's turn to polymers in general, and I understand we are a relatively small group of the experts in the polymer field in this room. Let's take a page out of my introductory lecture of polymer science, just to give you a feeling of what a polymer molecule is. Especially, what is the shape of a polymer molecule? Think of the polymer molecule starting here, polymerizing, let's say, by one step after another. You add, let's say, one CH_2 group at a time to our growing polymer molecule. Mathematically, this is very easy to treat. It is nothing else but the random flight problem. That means you change to a random, new direction every time you have gone one step. And, if you want to know what is the end-to-end distance, all you have to do is a vector addition of all the steps. I will talk from time to time about my standard molecule, which consists of 20,000 CH_2 groups. That molecule, then, would have 20,000 terms in the sum and you need to know, obviously, all the angles and lengths to get to the end-to-end distance. Fortunately, we are usually not interested in the shape exactly. We are only interested in the magnitude of the end-to-end distance, and even not the magnitude of the end-to-end distance, but only the mean-square end-to-end distance. What we can do then is just to form the dot product of this summation. Since we take the average of this dot product, we have the advantage that all the terms are just as often on the negative side of the cosine as on the positive side, so all the terms drop out except the ones that duplicate themselves. That means only if the two vectors are equal, then we get an answer, and the sum can be summed up almost without any mathematics. The mean-square end-to-end distance is $x\ell^2$. This random walk leads, if one takes 1.54 Å for the carbon-carbon distance, to 21.8 nm for the end-to-end distance. Now, you know this is not a good model. You have to have a bond angle restriction, and one has to have the possibility of hindered rotation. At least not all rotations angles around the bond are permitted; only three of them are. The rotational isomer model comes in here. If you make those two corrections, you have two additional terms here. But you see it isn't really important; it gives you a factor of 2, or something like that. A more difficult question, which I will not really treat here, is the excluded volume. Some of the spaces are already filled with a molecule. It is not a random flight where you can get back to any space, but this restriction, again, increases the volume by a little bit, and experimentally, one can avoid it by working at the theta temperature. You see that the calculation and the experiment, by light scattering, agree very well. So, you know the approximate size of the molecule. Now, if I take this molecule and assume 50 nm as a good average, I may ask the question, how much space does such a molecule invade? I know its length normally would be 20,000 CH_2 groups. That is over 25,000 Å, 2500 nm, but how much does the volume involve? If I use the simplest assumption that mean-square end-to-end distance is the radius of the space invaded, I find that the space invaded is this size shown in the slide. But the molecule itself, the CH_2 group, has about 16 Å cubed van der Waals volume. If I multiply that with 20,000 you see it is only one thousandths of it. So what I would like you to learn from this little exercise is that only one per mil of the volume invaded by a polymer molecule is filled with matter. You know another example of that is a gas at atmospheric pressure. The density of a gas is about 1 gram per liter. The density of water in the condensed phase is about 1 gram of water per cm^2. That is, again, a factor of a 1,000 in there. So, if you talk about a polymer molecule, it invades an enormous amount of space just like a gas. If you talk about a polymer melt, that empty space is filled with other molecules. That means there must be an enormous amount of entanglement. That entanglement we need to study somehow. Some of the ways entanglements have been treated is by saying: "Let's look at the polymer melt, and let's make the polymer chain longer." Z is the number of units. I make the chain longer, and measure the viscosity. The viscosity normally increases almost linearly, then somewhere, at about 600 to 1000 of these units, I shoot up with a much higher slope. That, we say, is the entanglement point. We can have a picture drawn like this. There are more modern ways of representing it, e.g., to take all that is entangled around the chain and make a tube around it, because the mobility is actually a little more than you would have by tying sharp knots. So, you can maybe slide out of these tubes by reptatorial motion. The important thing is that these polymers are somehow entangled, and these entanglements need to be understood. So, let me stop with this for a moment and tell you what we otherwise do. I'll get back to these entanglements in a minute.

Thermal Analysis as a Tool to Analyze Polymers

We normally like to characterize our samples by characterizing the total amount of thermal motion. The total amount of thermal motion can be determined by thermal analysis, mainly by heat capacity measurement. In a solid, a single crystal at very low temperature, all you have are vibrations, and each vibration gives you a given contribution to the heat capacity. If I know the vibrational spectrum, I can calculate the heat capacity. And, in fact, very recently we got some samples of C_{60} and C_{70}, and, since they are so simple, we calculated the frequency spectrum, and then we measured the heat capacity, and I don't think you are surprised that the two agreed absolutely perfectly. So, we tried to do this with polymers. We have a data bank established. About one-third of the measurements are our own, and the other two-thirds have all come from all places in the world. For heat capacity measurements, in order to make an assessment of the thermal energy, you have to have them from zero Kelvin all the way to the temperature of interest. Normally, you don't make measurements over all the temperature. So, what we do is, we take the limited experimental data, and we recalculate from C_p to C_v (that's the only thing which theoretically makes sense) and fit it to an approximate vibrational spectrum. The group vibrations we know from infrared and other analyses, and what we do not know, usually, we can fit to what's called a Tarasov equation, and that takes care of the skeletal vibrations. We usually have only two parameters in this equation, theta-one and theta-three. So, if we have two points in the right temperature range, we can derive those two parameters. Once we have those two parameters derived, we can take the group vibrations again and the skeletal vibrations, and now calculate the heat capacity over the whole temperature range. So, with only two measurements, we can get the heat capacity from zero Kelvin to practically infinity. Now what do we have, then, over this enormous range of temperature? We have the heat capacity of the material that vibrates only. If there is anything else happening; if the molecules start also to rotate around the backbone bond; if they become mobile, then there is an additional contribution, usually an entropic contribution from the disorder, if it is a crystal, or from the added expansion of the crystal if it is an amorphous material. We can now take our computed heat capacity and compare it to the experimental heat capacity. I have many, many examples and I could give you hours of lectures for all sorts of materials, including things like the poly(butylene terephthalate). We have in our data bank now, as I have mentioned, 150 samples analyzed, and everyone has something different of interest to be discussed. Even if the polymer has been in commercial use for 20 or 30 years, you can find enormous quantities of new information. One application I brought, just as an example, is a model-polymer, a high-tech polymer supposedly; you use it as a matrix for carbon composites. One of the questions was that the early literature said that this material had no glass transition. No glass transition means that it never goes into the liquid state. Since you have to shape this material, (and it can be shaped) was from the beginning very suspicious to us. So we looked at it, and this is more or less the DSC curve which you get. You see there is no glass transition that you can easily see. This changes when considering those two lines of the solid and liquid heat capacities. This is the computed line, from heat capacity measurements at low temperature, and this is the liquid heat capacity which you can also obtain very easily. Then you see that the material starts it's glass transition at 300 K, room temperature, and it slowly increases to the liquid heat capacity. In addition to the glass transition, there is a small endotherm, perhaps, compared to polyethylene, 1% crystallinity that could also be analyzed in detail. So, by knowing the vibration-only heat capacity, I can make statements about glass transitions, even if they are as broad as a few hundred Kelvins.

Single Molecule Droplets

Now, let's get back to our polymer molecules and let's look at small beads. We buy these beads for calibration of electron micrographs. Obviously, I would love to have them a little bit more uniform and smaller. This is where we want to go now. Imagine the difference in material when you have a polymer molecule that is in a melt, or in a bead, where, let's say, 100 or 1000 atoms or molecules are nicely entangled and so on, and imagine that you have beads which consist of only one molecule. The latter must be completely different. We would love to put our hands on this material. We would love to measure, for example, the viscosity of this material. As long as the beads are separate, before they fuse together, they should have a viscosity which follows a linear increase. As soon as the molecules entangle, as time goes on, they should go up in viscosity by a factor of 1000 or more, depending on the molecular mass. This we would like to study, and you can also do thermal analyses on these, as shown, for example, polystyrene beads. These are the high viscosity, multiple molecule beads from 800 down to 85 nm. Let's look at the glass transition. The first heating has the beads separate and you can see there is a little hysteresis peak, and then at higher temperature, they are liquid. The second heating is supposedly just about the same for all of these materials. What one observes is, for the large bead, a little exotherm, that is the energetics when the beads lose their surface area. You can see if the beads get smaller and smaller, the exotherm gets bigger and moves to lower temperature. That means, when we look, now, at single molecules, we could first look at the surface diffusion of the material. We could see the broadening of the glass transition even with 85 nm; we would like to go down to 10 or 5 nm, then you would probably go to very low temperatures. So, it means, that is a material that would be very nice to study. The question is: Is it at all possible to make this material? The answer is, oh yes, we can do that, but unfortunately, only in ones and twos and tens and twenties and fifties, and not in a half-gram quantity. So, how can we make larger amounts? The single molecules were made by floating polystyrene patches on a Langmuir-Blodgett apparatus, capturing them, and by beginning to look at them under the electron microscope. This slide shows an analysis of the molecular weight distribution.

QUESTION: Are you sure that it is a single molecule?

ANSWER: Because the molecular mass distribution corresponds exactly to the molecular mass distribution done by gel permeation we are sure each is a single molecule.

Now we still have a little problem here, because we assume the cross-sections are half-circles. You know, it is not quite clear whether that shape is a half-circle or not. I don't know. So, there is a whole host of questions left. This method was developed, also about 20 or 30 years ago, as a method of determining very high molecular masses. When you get into the 10, or 20, or 50 million molecular mass, it is difficult to determine the molecular mass, so they were sprayed against a cold surface, and then, these type of pictures were developed and people made estimates of what the shape should be, that it should be half of a sphere. If it is half of a sphere, you can take the diameter and you can make an image analysis and you can determine the molecular weight. So, what we would love to do is get these particles in large quantities, which initially means 10 mg, 15 mg—hopefully, then, a gram so that one can make viscosity measurements. That's amorphous material. I hope I have shown you that amorphous material can be interesting in the form of single molecule particles. We can learn a lot about behavior of our bulk polymeric material by having these coalesce and by studying the coalescing of the particles of one, two, three, five, controlled numbers of molecules and look at their properties.

Crystal Habits

When we go to crystals, in the beginning slide of my little textbook, we can have various crystal habits. You know what the polymer molecule is: it is long—25,000 nm in length. But if we find out what habit do the molecules normally take, they should actually take a fibrillar habit. They don't; they take a lamellar habit. Our standard molecule of 20,000 CH_2 groups, for example, would form a crystal like this; that is not bigger than 10 nm. That means it has hundreds of folds at the top, or chains, that come out of the crystal and then return later on—a very surprising habit. When we describe crystal morphology, it is not enough just to say, "I have a single crystal of this shape, these are the surfaces, and so on." I have to also say what we like to call this the molecular macroconformation. That means we need to talk about two shapes: the shape of the crystal and the shape of the molecule. And since we can't say "the crystal morphology" nor the "molecular morphology," I think it is better to call the molecular slope the "macroconformation." Why "macro"? The word conformation is already taken for the shape about one, two, or three backbone bonds. So we want to know the conformation of the whole molecule. Making it simple, we have something like three limiting macroconformations. The one we just talked about was the amorphous macroconformation; the crystalline could be either folded, and that is most frequently found, or it could be extended. Now if you just have a standard melt crystallization, you have a little bit of everything. You have amorphous areas left, you have some folding left, you have some extension left, and everything is interconnected. This was proposed for colloidal structures by Herman and others in 1930, and we still call it the fringe micelle structure. The folded chain structures were studied greatly in 1953, although they were already described in 1938 in chewing gum preparations. The extended chain structure was actually at the root of proving that polymers are macromolecules. At the time of Marks at the BASF, and Sauter, the x-ray expert, together with Staudinger, they could show that crystals should contain long sequences of chain molecules. The important issue was that the crystal unit cell for polymers is a unit cell of subunits, and not the whole molecule. The molecule not only can reach beyond the unit cell, it can also reach beyond the crystal. So, our point, now, is if I take the normal, well-crystallized polyethylene from solution, it looks beautiful and very nicely arranged and identified with what all the surfaces are like. But if you take this size crystal, 1–5 μm or so, it is something on the order of 5 million nm^3, or something like 167,000 molecules our standard size. We have the conformation of the morphology of the crystal, but the macroconformation is folded, and, in addition to that, we have an enormous mosaic structure and we have to ask: "What space is invaded by what molecule?"

By the way, when we speak of higher temperature, it means getting closer to the dissolution temperature. One can get to within about 10 K within the dissolution temperature. If you go to lower temperature, then these single crystals do not show up. If you go another 10° lower, or so, you get dendritic growth instead of crystals which have the single crystal structure.

Crystal Growth, Melting, and Deformation

An important topic in polymer science is the deformation of the polymer crystal. But what we cannot simulate by molecular dynamics calculation, but would like to know more about, is what happens when one of these molecules stops; this must have an enormous influence on the mechanism of deformation. Everything which we wear, all the fibers, all the textiles, are all drawn into a fibrous shape and we don't understand the problem. It is all an empirical process. So, it would be of interest is to know what a single molecule is doing within a crystal. We know a little bit about what a single molecule is doing during crystallization. That goes back to some of our earlier discussion. Why don't we manipulate the heat of fusion and the temperature, and so on, to grow better crystals? Polymers are uniquely different from other materials. This is a poly(ethylene oxide). This is a melting and crystallization rate plot. Not too many people do such measurements. What you see is—let's pick the 6000 molecular mass—still relatively low but that crystals grow large enough so that you can do optical microscopy. It almost behaves like a low molecular weight material. What you find is that this is the melting temperature; beyond it you have a certain kinetics of melting. That means these materials melt more slowly than you can add the heat of fusion and means that you can superheat the crystals. But if you go through the melting point, and you cool the sample, then what you find is there is a temperature range where there is no crystallization. The crystals do not grow, despite the fact that they are nucleated. They will grow only with a supercooling of something like 10-12 K. The question is, "why?" It cannot be a nucleation problem, because there are plenty of nuclei. And what we see is the higher the molecular mass, the wider is the region where there is a metastable melt. Remember the freshman experiment? We bring in a bowl of supersaturated sodium sulfate. You add a little nucleus, and the solution explosively crystallizes. We can do the same experiment with polyethylene. You drop a little seed, and nothing happens. Months later, the seed swims in the supercooled melt, and doesn't melt and crystals do not grow. Something quite surprising. This experiment tied up, once, for several months our DSC. We had made very large, perfect crystals and thought they would be perfect seeds. They are no seeds. External seeding helps reduce the area of metastability only little. If you extrapolate the area of metastability with molecular lengths, one comes to a length of about one monomer when the crystallization does not have much of a break anymore. Melting and crystallization is continuous for small molecules, as it is expected to be.

For macromolecules, reversibility applies only for one molecule; i.e., one can have a half-crystallized molecule on the surface and by lowering the temperature, it can crystallize completely. But since we do our experiments on cooling with very many molecules, all the half crystallized molecules will crystallize on cooling. The ones which are floating in the surrounding material will not crystallize. They will do nothing! They must be nucleated on the surface; a nucleation which we have called for something like 15 years now: "molecular nucleation." That means if you have a perfect crystal in the melt, one needs a certain size patch of each molecule nucleated in order to fully move the uncrystallized portions to crystallize. Through the melting point, crystallization is discontinuous. If you crystallize the first unit of a macromolecule, the entropy of the whole molecule is reduced. The molecule, then, cannot move anymore. You can only go on crystallizing by finding the proper neighbors. You cannot crystallize any other material, just the neighbor that is already pre-polymerized. This again needs to be followed up by studying what we like to call single molecule, single crystals. So, sometime ago I told one of my students: "Make some single molecule, single crystals." Take some large molecules. Dissolve them. Polyethylene is always the standard for any polymer work; make the solution very dilute, crystallize it, and then look at the crystals. We went to very dilute and extremely dilute solutions until we found nothing anymore except the dirt which is always in the solvent. The best we could do was this. There are always aggregates formed. The problem is if you have these little molecules crystallizing, and I'll show you some when we get to the last slide or so, what happens is the crystals will float, they will settle, and they will come together. As soon as they come together, they fuse to aggregates. Only those little blobs you see here at a, b, and c are approximately the size of the molecules.

QUESTION: What exactly do you mean by "single molecules, single crystals"?

ANSWER: These are crystals which have only one lattice and consist of only one molecule.

QUESTION: One molecule in the unit cell?

ANSWER: Yes, but the unit cell is also the full crystal.

The size, which you would expect with reasonable molecular masses, is that of the order of magnitude of 100 nm or so. So these are not difficult to see with atomic force microscopy or scanning electron microscopy. If you have a single molecule, a single molecule should be very much more mobile in the crystal. If this wants to reorganize, it has to fold several hundred times within the crystal. We know the mechanism. If you want to thicken, if you want to anneal (and you can anneal crystals like polyethylene) to double the size, you have to shrink the whole crystal sideways, obviously. If one polymer chain wants to thicken, you have to pull its tail; that means a couple of hundred folds, all through the crystal. We know the mechanism—we have simulated it by molecular dynamics calculations and we have measured it; we know these processes should go at picosecond speed. What we would now like to know is how to go from small crystals to large ones and see how much the domains around single molecules are of importance. When these crystals thicken, it has been observed that they develop holes. These holes have little walls around them. They seem to be of the right size of being just one molecule. That means if a hole develops, it seems easy to get one molecule out. When you take a polymer and anneal, if the molecular masses are very high, it seems to anneal to single molecule, single crystals because the melting end of a well-annealed poorly crystallized sample seems to follow always the melting point of an equilibrium-shape single molecule, single crystal. How did we grow these single molecule single crystals? Polyoxyethylene, again, was on a Langmuir-Blodgett balance, put in patches on the surface, and then heated and crystallized. These are now of the right size. These little patches, here—the actual electron micrograph looks a bit nicer—are the first crystals which we have. These were done by a postdoctoral fellow Professor Bu from Fudan University who went back to Fudan University after being with me for 2 years and having initial successes with some of the polystyrene droplets. This work and instrumentation is supported through a World Bank grant. The first things you should see are, again, relatively thin lamellae. The thickness is not really very much different from the thickness of a polymolecule, single crystal. That means kinetics determines the thickness of the crystal. And what we would love to do is, again, have larger quantities of these, via solution crystallization, and if we can do that without convection, without the problem of having these get together or coagulate into larger groups, then we can hopefully make larger amounts of crystals to study their annealing behaviors, go to concentrations where they average two or three molecules per crystal, and study their annealing and deformation behavior by optical, electron or atomic force microscopy, and, hopefully, in this way understand our polymers somewhat better. That's about all I wanted to tell you. Thank you.

QUESTION: Is polyoxyethylene similar to paraformaldehyde?

ANSWER: Almost. It is paraformaldehyde with an extra CH_2 group per repeating unit It is more stable than paraformaldehyde.

QUESTION: In the quest for large molecules, individual, isolated spheres of, say, polystyrene, I guess I don't understand what the problem would be as long as you have sufficiently dilute solution; sufficiently enough time.

ANSWER: We have not been successful with dilute solutions, ever. Because the particles still move too much, and they get together, and if the solution is too dilute, as known from the protein research, then all the polymer disappears onto the walls and doesn't come off anymore. As long as they have just source separation, then they will, every few seconds or microseconds, collide with each other and immediately coalesce. The molecules do not stay separated.

COMMENT: Can I comment on that for a moment? I am sure I am misinterpreting what you said, but people have taken very dilute solutions of polystyrene, atomized them into the air, and collected them on electron specimen electron microscope grids.

ANSWER: That is what I was suggesting, and that is what we have done. But this does not give you a gram of material. And, also, what you do when you collect them, you usually flatten them. What we would love to do is have these sprayed into a vacuum, evaporate the solvent, and cool them by taking away the heat of evaporation so that the relatively slow polymer particle will be left behind to form the perfect sphere. After that is done, we can collect them. This would have to be done, somehow, in a continuous way so that we get large enough quantities.

COMMENT: So, you want a large quantity of single polystyrene molecules in a spherical form.

ANSWER: Yes, something like 500,000 or one million of them so that I can make a few milligrams.

COMMENT: If I recall, the electron microscopic work was done with solvents such as methylethylketone, in which case the polystyrene molecules will tend to ball up into a near spherical form and they clump them and then shatter them and use the calibration particles to establish a shadow angle, and calculate molecular weights. This is what has been done with these monodisperse polystyrenes.

ANSWER: But this was mainly done with amorphous material, and this was done, mainly, by Schultz and co-workers in Mainz. There is a series of about seven or eight papers on these which we had looked at and that's how we tried to rig those experiments, but you get only electron micrograph quantities. The amorphous materials are, at present, not of major interest to us. Of interest to us, and the whole idea came out from reading these papers, was (and these people will tell you) that as soon as there is crystallization, the molecular mass distribution didn't work. And so, we said immediately, "This is a one-molecule crystal. Let's look at the crystals—that is much more interesting." Then, we wanted to do the same with the crystals, and they seemed even worse than polystyrene particles. If you make the molecules a little stiffer—if you take a cellulose that is substituted—then you may be able to do very dilute solution precipitation. Also, this was something that was done in the 1970's at the University of Freiburg. There, they could get not lamellar particles, but elongated particles that have approximately the mass of one molecule per particle. So, this is another route one can follow; going from the more flexible molecules, then sticking to more rigid molecules that can still fold occasionally. If you once had a relatively stable particle formed, to get another one added to it seems to be difficult.

You see this whole area of how these molecules get together—how one molecule adds to a crystal of another—is not well understood. In fact, it is not researched in any laboratory, because we always say: "Ah, let's do it like the low molecular weight people do." I can tell you that whatever we have taken over from the low molecular weight people, the metallurgist, and so on, is all wrong for polymers. Polymers do not deform by dislocations, or anything of this sort. We could find the dislocations, but they don't move. The polymer chains are just internally mobile, and move completely different. Crystallization is not nucleation controlled from the point of view of having a primary or a secondary nucleus. It is controlled by having a molecular nucleus. That is something which is, I think, of interest also for the proteins, because if they grow globular protein molecules, they are the model for small molecules. But they slow down, and what they do need is some time to reorient themselves properly on the surface. But if you have a flexible molecule, that flexible molecule must first form a nucleus on the surface, and that nucleus isn't known. Hopefully, by making single molecules crystallize, maybe, we can find out more. It is not a research project where I can forecast "expected progress," because I don't know what the progress is. Maybe I get no progress.

QUESTION: Could you use vinylidene chloride, in this case? It's a polymer that in the amorphous form has a very low T_g; it crystallizes very readily, perhaps too readily, but you could do that experiment with that I would think.

ANSWER: Yes, in principle. It also falls under the very flexible polymers and I see no preference for one polymer over the other, except that you would like to have a relatively narrow, high molecular weight fraction, so you don't have too many small particles floating around which you cannot identify.

COMMENT: You could make polyvinylidene chloride in high molecular weights. The speed of crystallization may give you some problems.

ANSWER: Nothing crystallizes faster than polyethylene.

COMMENT: Well, I don't know about rates of crystallization, but polyvinylidene chloride crystallizes fairly rapidly.

QUESTION: In relationship to the applicability of microgravity as a tool, microgravity comes in a number of forms, depending on how you create it. It is all created from free fall. Being in orbit gives us continuous free fall, but if the time sequences are such that they can be very short, could this be done in a drop tower in a few seconds, or in parabolic arcs in, say, 10 or 20 s? I am trying to get a sense of time scale here.

ANSWER: Let me explain research plans at UT. The whole group of polymer chemist at the University of Tennessee has gotten together, and we spent last year once a month, an hour or two discussion, and we came up with a plan which we would like to do jointly. Some of these experiments have been done already and some experiments can be tried very easily. You don't have to immediately say that this research is only possible if done in microgravity. Maybe we don't need microgravity at all.

COMMENT: I was just going to say, it is not the presence or absence of a body force called "g"—it is really the containerless processing aspect of this. There are a number of ways to be able to process things containerlessly.

ANSWER: Yes, containerless processing is one thing; avoiding convection - this might be a help from microgravity, and so on. So there are a number of these things which would fit very nicely into such experimentation. Certainly, one would want to start with having larger volume spray techniques under 1-g. You can always spray in a downward direction, and so on, and see whether you can really reach spherical-shaped, glassy particles. We have to have both things. You have to get the solvent out, and the sample must be cooled to below the glass transition temperature. The glass transition temperature for polystyrene, for example, is 100 °C . And, yes, this may be done in seconds, and it may be a free-fall experiment which one can try. One might find that one doesn't need it at all. The same is true for solution growth of these single molecules, single crystals.

1. B. Wunderlich, Macromolecular Physics, Vol. 1, Academic Press, New York, 1973.

V. GENERAL DISCUSSION SESSION

COMMENT: Before we get started, can you enlighten us a little bit as to what NASA's interests are in terms of science and technology transfer versus basic research?

MIKE WARGO: If you take a look at the name of the division that would sponsor this kind of research, it is the Microgravity Science and Applications Division. We cover, from the most esoteric of pure science to, say, cutting edge technology, as part of that program. If you ask me what you consider to be, for example, a minimum size sample for growing crystals, I'd say: "That is going to depend on the investigator," because if you can imagine the full spectrum from pure scientific investigation to manufacturing, if you will (and I would like to make a comment in a minute about manufacturing), there is a whole spectrum of sample sizes that make sense for each one of those things from pure science to pure technology. I think that kind of spectrum is what we are dealing with here. The interesting concept of "single molecule, single crystals" to the kind of work that Peggy was talking about where you are forming structures on orbit for the purpose of building things. Right there, we have almost defined the edges of that spectrum.

I would ask you to look at microgravity as a tool. What can we do with microgravity that we cannot currently do without it? What can we elucidate, in the presence of microgravity, that we cannot now, being influenced by gravity? Use that as a basic guide.

QUESTION: My question would be, what kind of things is Headquarters looking for when it comes to funding proposals? Are they interested in fundamental science without applications? We are are looking for support on all of our work. What are they looking to fund?

MIKE: I think it is the wrong question to ask. I will tell you why. Because those proposals are not reviewed by Headquarters. Those proposals are reviewed by peer review panels of experts in the field. And we ask them to provide us with their best estimates of the quality of the science in the investigation. Fully recognizing that that spectrum exists, they make recommendations to the science branch. That recommendation goes through the Discipline Scientist for Materials Science (that is me) and through the Chief Scientist for the division (that is Roger Crouch). He makes the recommendations to the division director, Bob Rhome. There are certain programmatic issues that occur after the recommendations from the review panels. I think what we should concern ourselves with here is the highest quality scientific investigation that we can.

I am a visiting senior scientist not of the "NASA ilk" from the bureacracy side. I have been doing my own research for a long time, and have written a number of proposals. I know when I write a good proposal, and when I don't. To me high quality means, i.e., the things you want to see in a good proposal, are things like a focused investigation, with a solid motivation, with solid basic principals behind you, with a laboratory environment that supports that, the infrastructure that you need, with the "warm body" talent that you need. You have the right people to do the right job. In our case, there is something extra that you will not have in an investigation, for example, for the National Science Foundation. That is a clear need for microgravity—microgravity relevance. That is placed at a very high priority for the decision maker or, let's say, for the recommendations that are made by the peer review panel. If you think about writing the best proposal that you can for a scientific investigation and there is a clear motivation for the need for microgravity as a tool, that's a good proposal.

COMMENT: That's kind of where my question is leading. Do they consider something that has commercial application, or is it only fundamental science that is worth doing in microgravity, because I get conflicting readings on that. Are they interested in fundamental science things, and that is what they really want to look at, and other times it's got to be something that already's got commercial interest in microgravity.

MIKE: If you take a look at the investigations that were conducted over the past year (and the year of 1992 was the year of microgravity), we conducted more microgravity research in 1992 than the whole time since Skylab. In fact on one mission, the First Microgravity Laboratory this summer, we conducted more material science microgravity research than all the time since Skylab. The kinds of investigations go from studying critical point phenomena in liquid helium, which is a pure science investigation with the Nobel Laureate kind of testing going on for group theory—you're taken from that kind of purity in science all the way to the kind of things that are investigated in the Space Science Laboratory, where they are looking at technologically important electronic materials. Protein Crystal Growth: clear applications to technology and formation of tailored pharmaceuticals. So the whole spectrum is there.

DON: I guess that question has come up because there have been instances where in the past people have indicated that we don't want to do anything that is just "value added"—semiconductors have come up to some criticism, because you really want to go up to understand something fundamental about a process.

MIKE: I think that is an important point. I don't think your're going to see a minus five on the proposal because you have applications. To the contrary, having applications is a fundamentally good thing. On the other hand, if we aim this at "the best crystal ever grown...," to me, that is not a scientific investigation. To me, that is getting very close to predicting manufacturing in space, and I don't think we are there yet. Currently, we see ourselves in a phase of exploration and discovery—finding out what the potential of microgravity is. Looking at, for example, does the direction of the residual acceleration vector have an impact on the investigation that you are doing? Some people say it is real important; some people say it doesn't matter at all. We don't have the investigative proof, right now, to support the effect one way or the other. We have good models, but we haven't verified those models. That, to me, defines the quality of the investigation. To say that we are going to grow the best crystal in the room, to me, is not a scientific investigation.

MARCUS: I think primarily, if I understand the whole philosophy of microgravity science, is not only do we want to look at a material or several materials; that is beside the point. We want to look at processes. What goes on and how microgravity acts on processes—not necessarily the material. The material you use, to me, is just a model material. You have to use something to prove your point, but once you have the model material, the purpose of the material itself is not so great. You want to look at the process itself and determine what goes on and answer why microgravity or the "g" vector has an effect on processes. The fluid or vapor phases are probably the only phases that microgravity has some effect on. What is the subprocess that can take place? Is it because of convective flows? Or, in fact, sedimentation? Or is it some other effect that is causing the process to go one way or the other? I think that is what we want to be looking at, rather than just saying "I want to go up in space and I want to take this material up there, and maybe by some miracle, it is going to be the best thing that we have." I don't think that is the way to do it.

DON: That is another issue, I think. That is not quite as subtle as saying "I am going to do the best possible crystal." There is a "value-added" aspect to actually going up and accomplishing that.

MIKE: There are good reasons to have "bench-mark" materials.

DON: Right. But what you are saying is that that is not a sufficient reason. For example, in the protein crystal growth area, you make the best possible Reverse Transcriptase, and come down. You are then able to do something of technological importance from a health standpoint. That is kind of a lower level, it seems, of the "ideal" investigation. It seems to be a common Headquarters' perspective.

PATTON: As long as we are talking about processes, Dr. Wunderlich brought up something about globular proteins which would resemble in some ways the type of material he is looking for—the single crystal, single molecule polymer. You take a field like protein crystal growth, which gives very nice characterizable crystals, but if you ask them why, they really don't have a good idea. If you try to explain why you got something with a particular protein, then it is not of a lot of use because if it is unique to that protein, you haven't learned much. If you can look at polymers in orbit and understand their crystallization properties, maybe you can explain something about protein crystal growth in general. I think that has been an overlooked possibility in this field.

MIKE: In fact, you are voicing an opinion that I have been voicing for a long time. That is, if you look at materials of production on a national, international scale, it is typically conducted, uniquely, in an empirical manner. The science base is missing. If I take a look at semiconductors, for example, everything we learned on the advancement of technology in silicon crystal growth, and it has been terrific. It is proprietary, and it is empirical. The basic science is missing. So, if you want to transfer that silicon technology to gallium arsenide or indium phosphide, you go through the same iterative steps again and see there was very little that was learned the first time around that you could transfer to the other technology.

COMMENT: That was what I thought was the real advantage of Rosenberger's approach. He is trying to understand the processes going on in space, as well as on the ground.

MIKE: I agree. I don't want this to turn into a discussion of bureacracy, but I would like to take advantage of the wealth of experience we have here at this table to look at the potential for microgravity in conducting these kinds of investigations, where we know more when we come back than we did before we left. There are some examples, and if I were a crass individual I might say protein crystal growth might be one of those, for reasons that were just indicated by Patton and Don, that there is a question of how much we know after coming back that we didn't know before we flew. There are some real important issues that have to be tackled. It is those kinds of issues that I'd like to find out more about from you guys.

QUESTION: Could we discuss that more, as a model for what kind of research should go on? It might be valuable. I don't have a good feel for this, which raises another question I have. Why isn't there more dissemination of information on these experiments? What I'm asking is: Rosenberger has some real interesting theoretical arguments; there has been a lot of protein crystallization done in space; how do those two come together? Is he developing experiments that are tested during crystallization processes in space? Can you do that?

COMMENT: I don't know. Someone in this meeting suggested doing some macromolecule type of testing to see. I don't remember who said it, but we are at the point where something ought to be done. There has been a lot of protein crystal growth in space, but it seems to have all been driven by commercial interests. They do get better crystals at times, and perhaps have been able to design better drugs.

MIKE: It's a reasonable goal. If you look at the potential for the social impact of the results of those high quality, high resolution protein crystals, it's fantastic. There is a laudable goal, but I think we should be able to conduct solid, scientific investigations in that regard. That is in support of what you are saying.

COMMENT: Especially in the case of NLO materials where that goal is not nearly as clear to people as with the protein crystals.

MIKE: But, I'm not really sure what you're question is.

RESPONSE: It seems to me that in the protein crystal growth area, they know exactly what is of interest, but it still misses the mark of what you say your interest is.

MIKE: We don't have to live within that. In fact, I fully expect you not to live within that.

DON: We're getting on the right foot. We are a new group, basically, in the field, as far as microgravity processing is concerned. I don't think there has been any significant amount of organic and polymeric materials research in microgravity. This is the first workshop, which was pointed out initially. You would be the group, and your friends if you don't mind competing with your friends, as ambassadors, discussion participants, or whatever. We would like this community to grow and be an influence and have an impact. I believe that the world is significantly made up of organics and polymers, and I think NASA is missing the boat on, potentially, a lot of good research.

The work that Dr. Vanderhoff and Dale Kornfeld have done is another area that needs exploiting besides protein crystal growth. Although the monodisperse latex reactor (MLR) laudably produced the first manufactured product in space, in the context of this discussion, it is important to focus on the mechanisms, and to learn something that can be applied to ground-based activities. In other words, it is important to come back with new knowledge, and I believe that happened. But nevertheless, you, the MLR researchers, are people with experience who can expand on that activity. Out of this group, there are probably other ideas and it would help if we began with a fundamental perspective in my opinion.

MIKE: It has to be a look at those kind of investigations, that, if you were conducting them in your laboratory, and you had an extra switch in there, an extra knob, and you could turn down the influence of gravity: what could you learn that you couldn't learn without doing that? That is the kind of investigation of interest.

QUESTION: What about the kind of investigation where you turn it up, such as a centrifuge?

COMMENT: I was at a meeting where gravity was the key discussion. The attitude that was expressed by NASA people was that you should not propose doing microgravity unless you simultaneously proposed to do macrogravity.

COMMENT IN RESPONSE: Lewis has a lot of big training centrifuges, I think.

MIKE: There are a number of funding agencies that work from 1-g and up. The only funding agency you can go to that can provide you 1-g and down is NASA. That is our charge—to conduct microgravity research—and I think that is where we should aim.

ROGER: One of the reasons for that, possibly, were that the Russians and a few other people, saw some isolated cases where they got some very high quality crystals in a centrifuge. It is a real controversial kind of thing. Apparently, it's not even linear, but there are certain g levels, certain resonance levels. There is a lot of controversy. Some people believe in it with blind faith, and other people believe there is very little merit.

MIKE: It is centrifuge specific, and they even speak of magic numbers. It is a brand new field. There is no doubt about it. There may be things that we can learn from that. But NASA's charge is 1-g and less.

COMMENT: And the big thing is to find out how is it different than the 1-g environment. So you have to have a good basis in 1-g, so that when you get results, you have valid comparisons, and then you try to determine what the differences are. Historically, we have had, in NASA, ups and downs where while we were pushing applications rather than basic science, and then reversed it to push basic science; we've gone through cycles like that, which in the long run were very productive, but I suppose understandable. It is always a question when people submit proposals: What is NASA's attitude, basic science or applications?

MIKE: The answer is yes. What I mean by that is what is really important is that we conduct the highest quality investigations that we can. If they have applications, that is great. We have, however, conducted some very esoteric pure science through the Microgravity Science and Applications Division, and it, no doubt, is world-class work. It has been funded, and it has been supported. Now, the new Administration, and I certainly can't speak for them, is very interested in technology transfer. If you have something in your investigation that lends itself toward that, that is positive. But, to say "we are only going to do pure science, and any application that I have, I am going to leave out," should be avoided.

DON: I am glad you brought that up, because with the new emphasis on conversion, down-sizing of the military, dual-use, etc., when one proposes, does it make sense for someone to propose from an applications standpoint and emphasize some aspect of that through NASA? Is it in the purview of NASA to recognize that the direction of the current administriation is to move toward technology transfer?

MIKE: I think of it as just being pragmatic. If I were proposing to any agency, I would clearly indicate what applications they have. They are interested in that. Some of my research, funded by DARPA, was clearly applications specific. That is the only stuff they will do. The National Science Foundation is looking toward the future, but they also recognize that in the future there will be applications, not in the near term, but in the far term. I don't see any reason whatsoever not to do it, and it can clearly be adapted. But that does not say that going absolutely pure science is something that is fundamentally bad.

QUESTION: Is it fair to say that a proposal can be applications oriented, but you should know fundamentally more about the process when you come back than you did before flight?

MIKE: Yes, if it is a technological process that you are proposing, and there is not good science in there, it will not be funded, because it won't make it through the peer review process. That is the way in which we invoke the peer review process, based on the quality of the scientific investigation. I want to be very careful about this. It is necessary that it is a high-quality scientific investigation. Applications are terrific; it is part of our name: Microgravity Science and Applications Division. We have funded both, and we have been successful with both.

HOSSIN: I am just wondering about objectives of this type of research—microgravity research. My thing is that you are supposed to have both types of research in a way that basic research will help to understand microgravity itself. As was just mentioned, we are in the "baby" stage of understanding the microgravity aspect of this type of research. At the same time, a future objective is to aim toward the application. I was wondering about your statement regarding someone wanting to grow the best possible crystal in a microgravity environment, and you will not support it: Why? Why not try it and see? If part of our objective is to achieve, why not?

MIKE: If you don't understand it, what have you learned? The best you can say is that you have a standard material; that you have a bench-mark material. If you look at the cost for conducting microgravity experiments in low-Earth orbit, they are quite large. If you compare the cost of designing, constructing, and making sure that this is safe for space flight, it far exceeds anything that you spend in your laboratory on the ground.

MARCUS: I can tell you that per flight, it is something like 2 million dollars for 12 or 13 experiments.

COMMENT: Plus, there is no guarantee that by going into microgravity it will benefit you. It is just a shot in the dark.

MIKE: In fact, my own experience with microgravity is exactly that way. We had a reasonable understanding of the basics of crystal growth before we left, but not the relative sensitivities. We were made fully aware of that upon the return of the crystals. That allowed us to go back and look at terrestrial processing in a way that we had never thought of before. Not to say that we would have never thought of it. But it was a clear way to have us look at some things that were fundamental in heat, mass, and momentum transfer that we had not been aware of before. As a result, industrial processing of materials is better now than before we conducted those experiments. That, to me, is a success story. The crystals themselves, were actually pretty lousy. We got stuck in that many aspects of the Earth-grown crystals were better, by some characteristic, but we learned more. We must have learning as part of the research experience.

HOSSIN: Of course, this is basic research. What I am talking about is that the observation of this crystal has to be conducted after the research has been done. If someone is assuming, "I can grow a very good crystal...," of course, he is basing this assumption on earlier work that has been done, yours or sombody else's.

MIKE: I didn't tacitly assume that when you said that, because there have been examples where that wasn't done. Others here are sensitive to this, but we have to be careful that we don't go through that again—that we use the taxpayer's money in a meaningful way, that we can walk up to anybody on the street and say "this is what we spent your money on, and this is what we know now that we didn't know." Rather than "We tried this...thought it was going to work, but it didn't." I don't want to stand in front of an irate taxpayer, like me, and say that. But, again, I have been doing way too much talking. I would love to hear from you folks about what you think of that "knob" in your laboratory.

QUESTION: Can I throw out a question? Maybe some of the people here can answer it. How do you expect, in terms of thin films as opposed to bulk materials, that the gravitational interaction would be different, and so forth. It is easy for me to see where I have a bulk container, and I have buoyancy forces, and either density, temperature, or concentration differences. When the films are thin enough, I have more difficulty in seeing that.

COMMENT: Those same things may be happening right at the interface of a thin film. I am no expert on thin film growth, but I see no reason why similar factors that affect crystal growth wouldn't be important, if you have concentration gradients extending from the film out into the bulk (or vapor). In some cases, you could have chemical reactions occurring. In my case, I get convection not only from the concentration gradient, but I also have uneven heating in my cell due to the polymerization process occurring on my substrate. That is going to cause a large amount of convection in that cell.

DON: You saw Mark Debe's talk, the first talk?

RESPONSE: Yes. The question to ask there is, how do we get better films? The question is: How can we do the experiment in space that will tell us more about how to control the process?

ROGER: One of the difficulties you have, when you do the experiment in space, is that it would be very nice if you could take the same apparatus, and do it here on the table, then do it in space. Generally speaking, you can't do that, because in order to build a space apparatus, you have to arrange it in such a fashion that it doesn't work very well on the ground. That comparison isn't always that direct, but it is terribly important.

TOM: We have been working on the organic nonlinear optical crystal thin films, and we have had a lot of problems trying to get nonlinear optical crystals out of organics. It is difficult by vapor, by solution, by melt, any of those.

The work that Debe has started, essentially, has made him a pioneer in, I would say, middle-sized molecules. Realize the molecular weight of these organics is about 500. We're not macromolecules, but we are not small molecules either; we are middle range, and we are seeing all sorts of interesting effects. Obviously, Debe is getting much better ordering, but he is seeing these thermal gradient efffects, carrier gas dependence, and all sorts of interesting effects. So, unfortunately, we are in infancy, but we are trying to duplicate when we have the money. In our case, we did duplicate a nonflight apparatus that matches what is of value.

MIKE: The microgravity office recognizes that. These are all important issues. In fact, there is a continuing program for looking at reducing the amount of time it takes to get to flight, because these designs are both costly and time consuming.

I would like to go back and focus more on the science right now. I will leave it up to our highly qualified NASA engineers to solve that other problem. It will get solved.

DON: I want to point out one other thing relevant to an earlier statement regarding the drop tower. There is an option with the organic and polymeric people that is not so clear with the inorganic people, and that is that we can work under more ambient conditions, we can work with smaller equipment. So there is the middeck. With the middeck, there are more flight opportunities on space shuttle for small experiments in which you don't need a lot of heat and avionics. These are relatively simple experiments. I know that Roger is involved in the development of the middeck glovebox, and here is the point I want to make. In order to get into the glovebox in general, you've got to be in the program. You must have an approved proposal. I just want to point out that once you are in the program, you wouldn't have to wait, necessarily, for a particular carrier; you can perhaps get onboard on the middeck to perform these relatively benign experiments with greater frequency.

QUESTION: Will you send out descriptions, or any information on that?

MIKE: Those are typically part of the NASA research announcements for the full discipline. We'll make a list and make sure we get the information to you.

QUESTION: To get back to the basic question, then, is what you would want us to do is say: "Here is a physical or chemical principal which should be investigated in space..." Right?

MIKE: No, microgravity doesn't mean space. It doesn't have to. It is just one example. But, again, what we want to know is what you could learn that you are limited in learning now.

QUESTION: This NRA announcement that was on the table, which I think almost everybody got a copy of, the way I've always been told this works is, basically, you ask for a little money to say "I've got a system that I am going to develop, characterize, or whatever, and have all the ground-based work in place to show that I am prepared to utilize the microgravity idea that I've got." Then you put in another proposal when you have reached that point.

MIKE: You can think of this annual NRA as being seed money for looking at proof of concept kinds of things until the next discipline, major NRA. There is material science, fluids, combustion, and biotechnology. Those will go through cycles of, I think it is currently, 3 years.

DON: The next discipline for materials is '94, right?

MIKE: We are 1 year ahead. Actually, I am not sure that has been nailed down yet.

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MARCUS: In this vein, I would like to say we have available a KC-135 flight furnace that will enable you to process materials for about 20-second periods over about 20 different parabolas. In other words, 20 periods of 20 seconds of low gravity, 10^{-3} g or so. This furnace can be adapted to any temperature range that you wish. You can go from 25° to 1000° if you like. It has the ability to record video of the process as it is actually happening. So, if any one of you thinks he has a process that can fit into this apparatus and fly on the KC-135, you should let me know. It is something that you should think about. You should be able to get a lot more turnaround on the KC-135 than you can get on Spacelab. We have a lot simpler experiments to deal with, and we have fewer constraints, so it should be a lot easier to do these simple experiments without complexities.

QUESTION: What is the time of the drop tube?

ANSWER: About 3.5 or 4 seconds.

MIKE: We have one at Lewis that will take you up to about 5 seconds. What I would like to do is get a little more specific and say that there are influences by gravity and lack of it, and we have probably named three or four, right in a row. Buoyancy-driven convection has an impact on the kind of processing. I asked Gary a pointed question yesterday having to do with sedimentation. If you have separate phases of unequal density, are the circumstances such that that has an impact? If you could eliminate, or reduce drastically, the tendency toward sedimenation, can you learn something else? Another one, and Peggy alluded to it a little bit earlier, was the weight of something itself influencing the experiment, and, in fact, hydrostatic heads, if you will. These are just examples where gravity can have an influence on the process. Are there any things either within your research no, or do you, say, get the little light bulb over your head and say: "Yes, if I didn't have this, I could really look very closely at this." I am really intrigued about the single molecules, single crystals. It seems like that could be a container-related problem. In fact, a little bit earlier, John, I think you indicated also that contact with the container presents a difficulty. Now, there is more than one way to skin a cat in this regard. Microgravity can provide you that as a freebie. There are other ways, of course, to do containerless processing. There are electrostatic levitators, there are acoustic levitators, and any number of ways.

BERNHARD: All of the things we are talking about is controlling phase separation: either crystallization, or others. Many, many things we have talked about is controlling the structure of phases when they separate. That is mainly how I see it. In the area of polymer blends, this could be a big future—not just for crystalline polymers, but for amorphous polymers. Polymers don't like to mix. If we could control the demixing of polymers, we might be able to get new properties.

Getting back to the protein crystal idea, they suspect, for example, the stresses enforced by gravity give rise to microdomain information. They have changed that name to microphase structure. Going into the experiment we don't know. But, maybe by going up there we could grow a perfect domain structure and learn a lot about it. There are two ways of looking at it. One thing is to learn what within the discipline is worth striving for. The other thing is that you could contribute to continuing science. For example, uniform molecular weight in polymers is something we strove for for a long time, and when we got it, we found that the mechanical properties we got from it were not worth a damn. Even in striding for these things, I find that there is something in that microphase separation that we've been striving for for a long time that we might be able to get in a microgravity environment once and for all. But that's walking into the dark.

DON: But that's a great point you have made. Because I think that is, to a great extent, a no-no the way I hear it. Saying only in a proposal that "maybe we will do better if you go out in space and do it because of hydrostatic pressure" will get you shot down. But what I think you need to do is to have some proof or some, at least, theoretical foundation laid out that indeed it is probably the case. I have seen that happen.

MIKE: Don't get me wrong. If someone walks up to me and it happens to be my graduate student, I will say "why are you going to conduct this experiment?" And they say "I want to show that this is true." Bad experiment; you have blown it right at the beginning. What you want to say is that you will investigate this phenomenon without saying whether it is good or bad. You should have a basic idea from your basic understanding of the process which way you might expect it to go. Don't prejudge it. And so I think that if you propose an investigation where, in your theoretical treatment, there was a g in there somewhere and you said this was a driving force for something that is known to have an influence on the process and as a result we can investigate in new regimes and learn new things. Not being able to predict what the result is, I don't see any problem with that. That means we know we are looking to understand, not to manufacture. That could be a benefit where we get a new class of material.

COMMENT: I think Bernhard's pointing out that it may be worth finding out not just how to get a new material but maybe that it is not worth getting so we don't spend a lot of time trying to develop the process that is a Holy Grail.

MIKE: And I think semiconductors are a real good example of that. People have been looking for the perfect crystal for a long time without recognizing that the defects give you the properties. And that's why when I call myself a defect engineer now, it gets people to listen because they think I said a "defective" engineer. But I don't think you have to have investigations that you formally prejudge. Because if that's the case,why then are we doing it if we don't need answers?

PATTON: One thing that they talked about in the last conference that we have not touched on is they considered spinodal decomposition of polymers to be an excellent thing to study in microgravity. I would agree with that. Maybe one reason that a lot was not going on in that area was the equipment is not easy to put together. But, I believe at Lewis they are developing some very good light scattering equipment. I think the whole thing is going to be important with the separation of polymer phases, e.g., flocculation and aggregation. The whole work is wide open. I think some good research will come out of this once the equipment is ready which should be coming within the next few years.

DON: Just to reiterate, I thought all those things were good. The first item on the list was tensile stress to measure elongation viscosity. That's a containerless process. By doing so in microgravity, you know, you avoid drainage. Whatever happened to that proposal? I think it must have fallen through the cracks. The second thing was copolymerization, polymer morphology is very important. And convective mixing will have some effects on the kinetics—whether "a" or "b" will have a limiting role—that sort of thing. The other suggested studies, as mentioned, were spinodal decomposition and foaming. I don't think anything as yet has come out of those possibilities.

COMMENT: Another thing that I think that we are not doing is capitalizing on the funding that we already have.

DON: One of the things that Ben Penn is doing is to set up a continuation of the 3M work which 3M got out of because they changed CEO's and a lot of things happened, but that work was an interesting development.

There are other applications like vapor phase polymerization processes or vapor deposition of monomer by which you might be able to take advantage of that same preferential orientation.

STEVE: Vapor deposition is important for the diacetylenes.

MIKE: Where is gravity in that?

RESPONSE: We used two different temperatures and got two different orientations in microgravity which on Earth we did not. This is an application. We had the basic idea that microgravity was going to affect basic transport. And that makes sense, and we did not know how, so it was a very fundamental investigation. The goal was not easily perceived, and we did not have a demonstration project. It was a real experiment to see what the effect of g on the process was, and we found something.

COMMENT: One of the other things was that when we looked at the films we found them to be fairly good. On Earth they weren't very flat. There was more material on the edges than in the middle. In microgravity, they were of fairly uniform thickness all the way across.

DON: You noticed that on the edges of the film grown in microgravity they still had some disorder on the platen on which the film was grown some distance from the side. So I think they are thinking there were some convective currents between the sides of the cell and the platen. Although there was some convective in space, there was not nearly as much as in the sample grown at 1-g. The microgravity films were much better in the middle.

COMMENT: The thing that bothered me most about that project is that they were not looking at the experiments during the process. How can you get the really basic understanding of what the vapor is doing after the fact. You are trying to infer something that has happened with the results you have. That's very difficult.

MIKE: Mark mentioned that there was a deficiency in the theory in the framework between the relationship of processing and the structure that was missing. And I think that if we keep those kinds of things in mind that when you submit a proposal, that proposal should be balanced and should contain all the elements of that triangle. That includes characterization, and that includes theoretical framework—everything that you would like to do a complete job. Included in that, and you brought up Lewis just a little bit earlier (really top flight work in light scattering), is that if there is a critical type of technology that is either missing or that is deficient, then let us know that in your proposal. If you have ways to attack that, then propose that also, because that is integral to accomplishing the task.

MARCUS: Also, we want to keep in mind that we have to establish a protocol for your experiment. If you do not have a protocol then you really cannot draw any kind of conclusions from the results that you get. Earlier people were making totally false conclusions because there was no protocol.

MIKE: I realize that the devil is in the details, but I think we need to stay focussed on a much higher level than that. We need to focus on what are the basic areas that are considered to be important scientifically and technologically, and where can microgravity play, potentially, a very important role. I just asked our disciplinery working group in material science to attack those kinds of questions. There were general areas, for example, pattern formation, in material systems that are considered technologically important and scientifically challenging problems that they still do not know how to handle. Again, they saw microgravity as being of importance there. It's those kinds of high level kinds of issues that we are talking about. Phase separation sounds like it could go on that list, or there are other things that could go on that list.

COMMENT: I am curious, if there is something about copolymers that we were talking about. One of our interests is an assumption that the only problem is buoyancy. And one example is that of the Rayleigh-Bernard problem where everyone assumes that the only problem is buoyancy but not surface tension. What types of effects can occur in processing that are not simply buoyancy driven. Certainly, thermal creep in the gas state has been an eye opener.

MIKE: Dan Mackowski really changed the way I have to think about what I know about fluid mechanics. It may be a semantic difference at this point, but it is still that there is flow that can occur near walls that is driven by physics that we hadn't considered before. We can get deeper insight into that phenomenon because gravity can mask the situation. That's an area where microgravity can play an important role. That's why Dan was funded in this last NRA. There are those kinds of things in polymer science and organic materials that have that same kind of need for microgravity to lift the veil.

COMMENT: I am curious with you asking the question about surface tension. I don't know enough about it. I just know that the issue comes when you have a little thermal gradient and interfaces how important can that be?

DON: According to an experiment on USML-1, surface tension-driven convection by Dr. Simon Ostrach; it is very important when you have free surfaces.

MIKE: If it turns out that if you have two fluid surfaces or if you have polymerizing material and a monomer, can you have surface tension-driven convection?

DON: If that were the case I think that any process that we perform on the ground that requires a container could conceivably have convection at the wall.

PATTON: According to Mackowski, it does; it's just not that big.

MIKE: Well that's why I ask, since that's a continuing problem, does that include liquids. And there's a little hesitancy to stating it, but he says it is clear in gases.

QUESTION: What about monomers and polymers?

STEVE: Experimental work could be done on vapor deposition.

MIKE: We have this kind of work in place right now, and I expect that Ching Hua Su will work with those guys.

STEVE: We should try organics as well.

MIKE: And I think that's an example of where you have the real connection between gravity and fluid flows that can have an effect on the process. If you don't have a sense for where the balance is, if you can knowingly reduce one effect up to six orders of magnitude, does that give you the capability to reveal the other more subtle effects? That's a good example of where microgravity can play a role.

DON: Mike you just mentioned Ching Hua working with vapor transport but Steve is doing it too with organics. So is Ben doing it with phalocyanines and the work of Rosner at Yale that supports Debe's work. I think Mackowski takes some of his information from that work. So, we would like to get some of the organic and polymer talk into the microgravity lexicon so we are not ignored.

MIKE: Sure, take advantage of the tools that are out there that may not look exactly the way you expect them to look but they are still good tools.

BERNHARD: I hadn't given this much mention before, but selenium is a good polymer and you can grow it beautifully from the gas phase by polymerization and crystallization. We have done that a few years ago but I am sure there are many problems which have shown up that have not been resolved.

MIKE: Now, what have you learned in selenium? I am a great believer in model materials having worked in germanium and indium antiminide for a number of years. Because they are so much easier to deal with you can get so much insight into that simpler system compared to others. The insight that you would gain from using selenium as a model material: would it be applicable to other systems that are potentially more complex or technologically important?

BERNHARD: Yes, it is. I mean, from what we have done before, if you remember the graph of melting rate and crystallization rate, if you crystallize selenium from the melt, with ring-chain equilibrium, you find out that only the chains crystallize. They fold, and they have that gap of metastability. If you crystallize selenium from the gas phase by polymerization and crystallization, there is continuity of the crystallization and melting rate. So that is one of the nice examples. Another thing that you can see very easily by vapor transport is that you milk the vapor off Se_2 molecules. All the rings that are in equilibrium in the vapor just stay around and they don't do anything. They then, by chemical reaction, have to react back to the reduction in dimer concentration until they can crystallize. So selenium is a very interesting material for a polymer and it forms a chain folded material. If you have two layers of chain folded material, they open up the folds because the fold is half a ring. The ring can have a ring-chain equilibrium so they open up the ring on the other side and the top side also opens up, and they interconnect. It is one of those polymers that is half a polymer and half a mineral.

MIKE: And, of course, that's terribly appropriate. We were talking about technologically important materials. If they are complicated enough, is there a model material that will prove a microgravity investigation would give you insight into some of the more complex systems and other issues? I can say personally that I believe in models; model systems have been very good to me. They have given us a lot of insight. We fully recognize what their limits are too—at least we should.

BERNHARD: At least if they don't turn out well, you have not lost anything. Overall, it looks like there are not many things that happen in polymers where the knob, microgravity, is a big thing which you will stumble into immediately.

MIKE: That's the sense that I get; otherwise, I would not have done all the talking.

BERNHARD: The problem is that polymers are metastable not in equilibrium, and so the driving forces toward where they want to go are strong in every other thing but a little bit of gravity. Sedimentation is not fast, phase separation is not fast which is usually driven by the enormous supercooling.

MIKE: So there tend to be more kinetic effects rather than mass transport effects.

BERNHARD: The first influence on polymer crystallization is that these things chain fold into a metastability. The melting point is reduced by 10°, 15°, or 20° from equilibrium.

COMMENT: Heat transfer of molten polymers is not clear. Polymerization rates should be primarly influenced by what happens at the surface of the crystals.

BERNHARD: Yes, but this was polymerization together with solidification. Then the heat is very much involved.

PATTON: If you are talking about an already manufactured polymer, I would agree with you, but when you are talking about actually growing something and you have to have transport to your surface, convection again becomes a major player.

STEVE: We know that convection plays a very big role in deposition of polymeric materials so we know that can disrupt the ordering.

MIKE: And from as little as we can know from the interpretation of results from the 3M work it appears that transport is an issue in their results. The jury is still out.

GARY: In the case of NLO films there have been some reports that as one goes down the wish list of key properties, high beta of the chromophores, etc., finally you get a material that you think is of device quality, but you find that it is quite glossy. In terms of attenuation we were trying to understand why that is. It is particularly true of these networked crosslinked copolymers where you might have local concentrations of high crosslinked density versus low crosslinked density. Can those perhaps be minimized in low gravity? All are the result of density fluctuations which are a result of convection, and in the end I think this requires serious attention.

TOM: The largest loss in many of these is that these crystals or films do not absorb light—they scatter it because of their defects. These can be controlled. They can be cleaned by going through six dissolve-filter-precipitate cycles. Then they are filtered through to the order of microns.

GARY: That seems to be a reaction issue, but there seems to be these "scattered" defects.

TOM: The mass balance or the CHNO type compositions are perfect. So there's something in the microstructure for which you do not see any evidence in the DSC. If you start waveguiding and you run into anything about the size of the wavelength of light it scatters, it becomes very glossy at this point. We do not really understand where these things come from. These differences in crosslink densities could give rise to microstructures of differing diffractive indices that cause scattering. It has to be on the order of the wavelength if it is just half or smaller it just sees an average of the effect. If it is one-tenth the size, it does not see it. It appears that convection could play a role here.

COMMENT: There are also many problems in processing some materials due to uneven heating. A microgravity environment could minimize this difficulty.

DON: Organometalics might be able to help that situation somehow by improving on efficiency of heat removal.

DON: Tom, you are from industry: what is industry's interest in organics relating to chi 2 and 3.

TOM: chi 2 one is the most commonly used frequency doubler p to pp star dideuterated pthalate. The material for frequency conversion is very clear. Solution growth on Earth gives large crystals. You can cut them, polish them; they are nice inorganics; however, the efficiency is very low. It works on a vibrating ion on a lattice mechanism, not an electronic transition so they are somewhat slower; that's why they do not have as good an efficiency.

If we can make a good thin film of high chi 2 materials then we can start to think about taking, for example, putting these first of all .. does not spread the beam if you have a weak second beam you can put it through a centimeter of material you spread it out to 15-17 picoseconds. So there is a temporal spread. Think of your portable CD player. The laser in there is an 830 nm laser. They are cheap. It has a high enough efficiency that you can put a thin chunk in front of there and double the frequency to 415 nm. What that means is that you get 4 times the amount of recording time per area. Because half the wavelength means you have half the spot, so you can double it in the x and y directions. The Japanese are going into crystals for that in a big way. You know about their real big drop tube. But then there is the laboratory which is frequency doubling in the pico and femptosecond ranges where you do not want any temporal spreading of that. Then there is the fast electrooptic Mach-Zender switch. The way your network for fiberoptic phone calls works it today, you have semiconductor lasers at 1 micron, and they turn it off as fast as they possibly can. It lessens the lifetime and creates a problem of chirping where the frequency moves around and you get these sidebands on the main 1.3 micron band frequency. One of the ways they multiplex is they put four different wavelengths down that wavepipe. So you get four characters down the fiber. Now think of the switch. Mach-Zender is a digital electrooptic switch which you turn on real fast. If you leave your laser on, you do not have chirping. Your switch allows the signal or does not allow it to go through. So your laser lasts longer: you have no chirping and you have more clarity. So those are the two major industrial chi 2 applications.

DON: Are they happy with the inorganics or will they go to the organics.

TOM: Let me put it this way, they are still turning the laser on and off. Even though they are building the gallium arsenide quantum well and lithium niobate, they are still turning them on and off.

Chi 3 sensor protection is the big one. There are a couple of ways they can do that. Frequency conversion to the third harmonic is mainly sensor protection. Chi 3 materials will change their index of refraction with an intense light beam itself. They don't require an assist from an external electric field. That means that you can build, for example, a corner prism out of this magic material and when the laser intensity gets too high, it steers it away from a sensitive sensor; or, you can switch. There is parametric mixing links they do chi 3 if you have an intense laser beam in one direction and a weak one in the other. As soon as the weak one goes over some threshold, the power gets shunted to the other beam. Also because of the nonlinear electrooptic gates, there are a number of reasons to use them.

DON: I know they use phase conjugation already for tracking and other purposes. Do they want to go to another generation of organics or are they happy with the inorganics?

TOM: The big draw for organics is that they are using ferroelectric systems like lithium niobate, etc. They do not respond efficiently in the picosecond range. They do not see the femptosecond range.

DON: From what I understand IBM and 3M have gotten out of this. Why aren't these people putting their resources into this?

TOM: It's tough. Actually nonlinear optics has been known for a long time. The theory has been out there and we have had q switching .. lasers of inorganic materials. The organics came along and they were a lot faster and industries thought that they could just convert over. But there were problems that they just did not anticipate. Long term research in my career in industry was 3 to 5 years. And if you look at most of these programs, that is how long they lasted: there was no bottom line; they did not see a profit coming shortly. Now I believe these problems will be solved—I do not believe they will be solved in 3 to 5 years. So it's just the invested time and money for the expected return and it just was not coming back. Notice the Japanese, who are looking at 15 years, are continuing. American industry dropped organic crystals very quickly where the Japanese have continued. It just was not as easy as they had expected.

GARY: In relation to this issue that Tom has been talking about, there is going to be a symposium at the Spring ACS meeting at San Diego organized by Frances at 3M. The title of the symposium is something like "Organic NLO Materials: Industrial Opportunity or Academic Curiosity?" Trying to critically explore what are the real opportunities—I think that it will be interesting.

COMMENT: There is one other area that I think is probably catching on and that is electroactive materials. I am not sure what you call them—materials that respond to environmental effects and acclimate. They don't just resist transformations, they use them. These things are being invested in heavily. The smart concept, smart scan, smart strut, and smart sensors have a lot of applications here using combinations of electrooptical materials in combination with all the different forms of energy that you can imagine. Measurable feedback from an external strut for airplane wings and electrical charges for temperature controls. There is a lot of work going on in computer-controlled systems and self-correcting phenomena.

MIKE: What are the principles involved here?

COMMENT: A lot of those are very similar to NLO materials. You have very highly ordered materials polymers and piezoelectric polymers and high degrees of orientation of dipoles and growth of crystals. Mike: you said it much better than I could. Orientation of structures should go on the list also.

LON: A couple of very general comments on this. This is very tough to do, and the reason that it is tough to do is that if one is going to do a reaction, one brings an empirical subconscious background to the problem. And what we are trying to do here is to really focus in a very conscious way.

ROGER: It is easy to mix things in a lab but one cannot just do that in space. You must rethink how you are going to transfer or mix something. And very often that becomes a real problem and you have to have a different mind set.

PATTON: One problem is that polymers are such good surfactants, and we saw that again and again in USML 1's glovebox. You start mixing solution with surfactant, and it foams, and you have to wait for diffusion, and it does not happen readily.

LON: One thing that occurs to me that would be a very good exercise is to try lab experiments that we conceive of: work through them in our minds on a molecular level and a mechanical level.

STEVE: One of the proposals we had that got shot down which I think was a real good proposal was the suppression of unwanted bubble formation. This is a real problem in microgravity with transferring material with syringes. It can inhibit crystal growth.

MIKE: And again it's those real basic things that we need on the list. If we start getting too much into the details now, we find ourselves designing flight experiments and moving liquids around. We have to stay higher than that now. And it's basically said sitting around a gedanken experiment and saying I never really thought about this before: what would happen if we didn't have the influence of gravity, or if we didn't have to deal with a container? If you have the specifics it means you have already thought about the general.

LON: It's the unconscious part, thinking of the difference in a microgravity environment, that is difficult.

PATTON: There are project scientists that should bring up the "what ifs" to assist.

LON: Yes, but by then it's too late. We need to do this while planning the experiments at the thought stage.

MIKE: But what that brings up in my mind is that at each one of the corners of the triangle, there is characterization, there is experiment, and there is theoretical framework. It seems there are deficiencies and very solid approaches at each of these events for different types of materials research. There are some areas you have down pat but some areas you do not know. For ground-based research that is also appropriate for proposing, because these deficiencies limit our understanding. If we have a sense of seeing the effect of gravity, a theoretical framework is important to us. We fund a lot of modeling research and it does not have to be digital simulations. Anything that will help us to understand it from the perspective of microgravity is important to us. So maybe that is an area that we might want to focus on that there is a limit in the theoretical frameworks available for us to interpret microgravity results even if we have them. Is that fair to say? That is the sense I got from the 3M work, that we didn't have the theoretical framework by which to judge them. Yes, they were interesting and different but we did not have a tool available to start attacking what those results were.

STEVE: Mackowski's work could be a framework for some of the experimental work on vapor deposition.

DON: Maybe we should have an annual conference.

MIKE: Heading home, if we could jot down our thoughts and give them to Don for redistribution to the panel for comments.

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