Crystalline Colloidal Arrays in Polymer Matrices

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Introduction

Crystalline Colloidal Arrays (CCA, also known as colloidal crystals), compose of aqueous or nonaqueous dispersions of self-assembled nanosized polymer colloidal spheres, are emerging toward the development of advanced optical devices for technological applications. The spontaneous self assembly of polymer spheres in a dielectric medium results from the electrostatic repulsive interaction between particles of uniform size and charge distribution. In a way similar to atomic crystals that diffract X-rays, CCA dispersions in thin quartz cells selectively and efficiently Bragg diffract the incident visible light. The reason for this diffraction is because the lattice (body or face centered cubic) spacing is on the order of the wavelength of visible light. Unlike the atomic crystals that diffract a fixed wavelength, colloidal crystals in principle, depending on the panicle size, particle number and charge density, can diffract W, Vis or IR light. Therefore, the CCA dispersions can be used as laser filters. Besides, the diffraction intensity depends on the refractive index mismatch between polymer spheres and dielectric medium; therefore, it is possible to modulate incident light intensities by manipulating the index of either the spheres or the medium.

Our interest in CCA is in the fabrication of all-optical devices such as optical switches, limiters, and spatial light modulators for optical signal processing. The two major requirements from a materials standpoint are the incorporation of suitable nonlinear optical materials (NLO) into polymer spheres which will allow us to alter the refractive index of the spheres by intense laser radiation, and preparation of solid CCA filters which can resist laser damage. The fabrication of solid composite filters not only has the advantage that the films are easier to handle, but also the arrays in solid films are more robust than in liquid media. In this paper, we report the photopolymerization process used to trap CCA in polymer matrices, the factors which affect the optical diffraction qualities of resulting polymer films, and methods to improve the efficiencies of solid optical filters. Before this, we also present the experimental demonstration, of controlling the optical diffraction intensities from aqueous CCA dispersions by varying the temperature, which establishes the feasibility of fabricating all-optical switching devices with nonlinear periodic array Structures.

Temperature Switchable Optical Filters

Figure 1 shows the dramatic optical diffraction responses of aqueous CCA of poly(N-isopropy lacrylamide) microgel (PNIPAM) spheres as a function of temperature. [1,2] The CCA barely diffracted the incident light at IO 'C, but diffracted the light very effectively at 40 'C, and thus, this CCA dispersion acts as an optical switch. The optical responses of CCA with temperature are highly reversible, and no hysteresis was noticed even after several rapid heating and cooling cycles of the samples.

The PNIPAM gel is an interesting thermosensitive polymer which exhibits a reversible volume change in aqueous medium at 32 'C, causing many of its physico-chemical properties to change concurrently. Below the phase transition temperature, the low cross linked microgel spheres are highly swollen and have a refractive index value that is close to water. Above this temperature, the spheres are collapsed and have a refractive index close to the polymer. The decrease in particle size and increase in the refractive index of the spheres with increase in temperature have opposite effects on the particle scattering intensity. The observed increase in diffraction intensity indicates that the contribution from the changes in the refractive index dominates more than the particle size change in altering the optical properties.
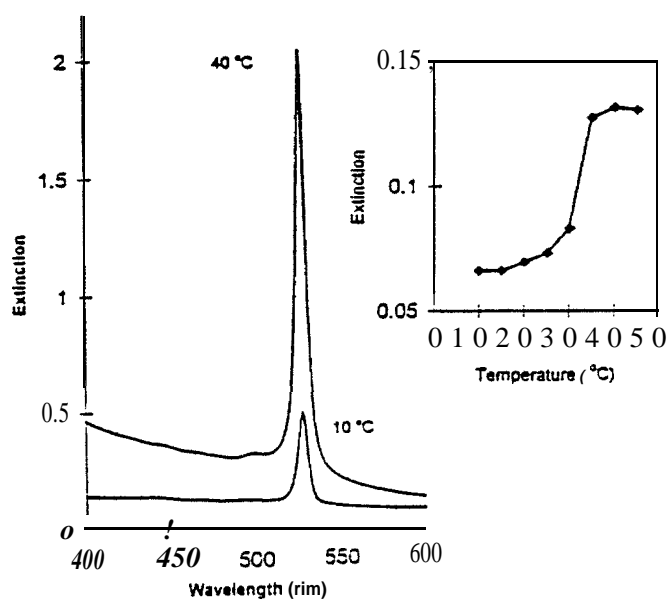

Figure 1. Optical diffraction intensity (left) from aqueous ordered dispersion of 3% crosslinked poly(N-isopropy lacrylamide) hydrogel spheres as a function of temperature. Light scattering from disordered dispersion of very low concentration of spheres as a function of temperature (right).

The scattering intensity from a very dilute colloidal dispersion (0.01 wt% solids) as a function of temperature is shown in the inset of Figure 1. Between the two extreme temperatures studied, the scattering intensity increased only by a factor of 2, however, the diffract ion intensity increased by a factor of 6. These experiments indicate that it is possible to create a laser induced optical switch or limiter with CCA incorporated with NLO materials.

Colloidal crystals suspended in liquid media are very sensitive to ionic impurities and, as well, to any external weak forces such as shear[3], heat, gravity[4,5] and electric fields that can melt these crystals. The fragility of the crystallites is due to their low bulk and shear moduli. Therefore, it is essential to convert these delicate structures into robust systems in order to use them in optical device applications. The recently developed photopolymerization methodology of traping the macroscopic ordered structures in solid polymer matrices is very successful in overcoming the aforementioned problems. [6-13] However, at the present time, the development of these polymer nanocomposite filters is not fully matured yet, and suffers from a lack of reproducibility of optical diffraction properties either from one polymerized film to another or from the prepolymerized fluid film to its corresponding polymerized film. The following section analyzes the method of preparation of solid filters and their optical properties to understand the dynamics of crystallite during the photoinitiated polymerization processes.

Crystalline Colloidal Arrays in *Acrylic* Polymer Matrices

To manufacture solid nanocomposite laser filters from liquid CCA dispersions, we initially modified the surface of colloidal silica spheres by treating them with the silane coupling agent, 3-(trimethoxy)silyl-propyl methacrylate (TPM). Transferred the TPM coated silica spheres into either methyl acrylate (MA) or methyl methacrylate (MMA) monomer, and allowed the spheres to self assemble before irradiating the monomeric dispersions.[6-10] The photo-polymerization experiments were conducted at ambient temperature for 4 h using a medium pressure mercury arc lamp. Figure 2 shows the optical diffraction from liquid and solid crystalline colloidal dispersions. A very large shift of the Bragg diffraction peak and a much wider bandwidth is obvious for the polymerized film. The diffracted wavelength shifted from 554 to 490 nm which corresponds to a 15°/0 decrease in *d* spacing or a 45°/0 compression of the original lattice. The peak bandwidth increased from 4 nm to about 15-20 nm in the polymerized film. The lattice compression in the polymerized film has been attributed mostly to the volume shrinkage of the host matrix. Based on the observation that only the thickness (but not length and width) of the polymerized film decreased, it has been proposed that the crystalline structure transforms from a face centered cube to a rhombohedral during the photopolymeri-zation process.[9-11]
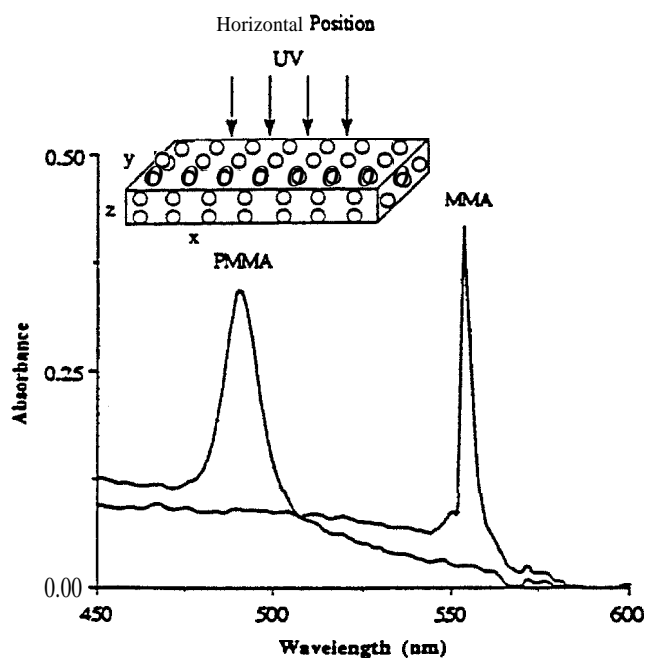

Figure 2. Bragg diffraction from arrays of silica spheres (35 wI'??) in methyl methacrylate before and after photopolymerization. The photocell (length = 70mm, width = 20mm, and thickness " 0.264 mm) was placed horizontally on a lab jack.

This model raises the following questions: why does the volume of the monomeric dispersion decrease only in thickness during polymerization? For example, the volume fraction of MMA used in the dispersion is 0.805 and hence a 17% decrease in volume (21% for neat MMA) can be expected after the solidification process. The decrease in volume is due to the loss of the bulky π electron cloud which is perpendicular to the carbon-carbon double bond. Since the volume change of the monomer matrix occurs at the molecular level, the volume should shrink uniformly in all three dimensions with a 5.6% decrease in each dimension. However, the host volume in the polymerized film decreased profoundly in one dimension, that is in thickness, by about 14%.[9] Secondly it is not clear how the microscopic volume changes during polymerization affects the lattice dimensions and the lattice structure during polymerization. On the other hand, the effect of macroscopic volume shrinkage of the host polymer network on crystal compression, when a temperature sensitive poly(N-isopropyl acrylamide) hydrogel network embedded with arrays of polystyrene latex spheres is exposed to heat, has been examined. The volume of the gel network shrunk isotropically with increase in temperature, and the network compressed the crystal lattice uniformly. [1] Thirdly, this model does not take into account the dynamics of colloidal crystals. It is well known that the spheres in a lattice vibrate continuously from their equilibrium positions, and colloidal crystals dynamically respond to external radiation stimulus.[14-16]

Dynamics of Colloidal Crystals

During the photopolymerization of silica-MMA dispersions, the dynamics of colloidal crystals changes dramatically, not because of the stress of volume shrinkage, but due to the changes in the dielectric properties of the host matrix. As the monomer converts to polymer, the dielectric property of the medium changes for two reasons. Firstly, the polarizability of vinyl monomer is greater than the monomer unit in the corresponding polymer and secondly the heat liberated during reaction decreases the dielectric constant. The dielectric constant of PMMA (2.60 at 1 MHz) is less than MMA (6.32 at 1 MHz) by a factor of 2.4. This decrease in dielectric constant of the host decreases the electrostatic repulsive interaction between the spheres as a result of counter-ion association. This causes the colloidal crystals to shrink during polymerization. The interparticle interaction potential (U) between two spheres of radius a at a distance r is a strong function of the dielectric constant (ε) of the medium, and is shown in Eq (1)[1]5

$$U(r) \;=\; \frac{(Ze)^2}{\varepsilon}\left(\frac{\exp(ka)}{1 + ka}\right)^2 \;\frac{\exp(-kr)}{r} \qquad (1)$$

where Ze is the particle charge, and the inverse Debye screening length k is given by

$$k^2 \;=\; \_ \left(n_p Z + n_i\right) \qquad (2)$$

where n_p is the particle concentration, n_i is the ionic impurity concentration, k_B is the Boltzmann constant and T is the temperature.

The effect of polarizability of dielectric medium on colloidal crystals of TPM silica has been demonstrated by Philipse and Vrij.[17] The number of charges on a TPM silica sphere decreased from -500 to 90 as the dielectric constant of the medium was changed from a pure ethanol (ε=25) to a mixture of toluene/ethanol, 70/30 v/v (ε=10). This led to a decrease in inverse Debye length from 100 nm to about 50 nm. The effect of local heating of colloidal crystals using a laser beam on lattice compression has been investigated by Asher et al.[15?]6 The localized compression of the dyed colloidal crystals has been attributed to reduced electrostatic interaction between the spheres which results from the temperature dependent dielectric constant of the medium. These experiments clearly support our assumption that the change in dielectric constant of the matrix is responsible for the lattice shrinkage during polymerization. The accompanied shrinkage in volume of the host minimizes the disorganization of sphere arrays.

The broader bandwidths resulting from a decrease in the degree of orderness of spheres, heterogeneities of optical diffraction properties within a polymerized film and the decrease in film thickness are ascribed to the effect of gravity induced convection and sedimentation. Before arguing the effect of convection on organized colloidal spheres in monomer matrix during polymerization processes, we discuss the origins of convection in silica-MMA dispersion, and the factors which influence the convective flows most.

Convective Instabilities

It is well known that gravity induced convective flows arise in an unstirred system whenever density gradients exist.[18] There may be several variations that can create density gradients: the presence of more than one phase, material phase transitions from one state to another, and differences in either temperature or concentration.

All of the variations mentioned above which can produce density differences do exist when a colloidal dispersion is subjected to irradiation. As UV radiation penetrates into the methyl methacrylate dispersion in which the arrays of submicron silica spheres are suspended, the light attenuates gradually in the direction of propagation because of the absorption of light by the photoinitiator and monomer molecules present in the dispersion. Further, the light attenuates due to scattering by the colloidal spheres which are in the of 100-150 nm diameter range and occupy about 20°/0 of the total volume. In contrast to the absorption of light by the photoinitiator and MMA molecules, the photon scattering by the colloidal particles produce no heat in the dispersion. The intensity losses due to absorption and scattering result in an intensity gradient along the direction of light propagation in the dispersion. Because of this intensity gradient in the dispersion, the polymerization rate, which is intensity dependent, varies in the dispersion. Hence, the reaction rate at the dispersion layers where the light enters would be higher and decreases gradually in the medium. Since the addition polymerization reaction is exothermic (the heat of polymerization of MMA is 13.0 kcal/mole), the liberated heat causes an added thermal gradient in the dispersion due to lack of thermodynamic equilibrium. Additionally, the glass/quartz cell containers used to fill the colloidal array dispersions also absorb the UV radiation and cause thermal gradients in the dispersion. These thermal gradients in

the dispersion generate density gradients ($\Delta\rho_{thermal}$ is negative), and the density gradients under the influence of **gravity** induces convective fluid motions.

Furthermore, a large decrease in the **partial** molar volume of the matrix and concentration changes of the monomer during polymerization induce density gradients ($\Delta\rho_{monomer}$ is positive) in the dispersion.[19] In addition to density gradients created by the matrix monomer during the reaction, density gradients exist even before the reaction starts due to the presence of denser colloidal silica spheres (1 .79 g/cm^3) dispersed in the lighter **MMA** (0.94 g/cm^3). As mentioned, the sphere concentration also changes due to reduced **interparticle** interactions, and heterogeneities in the reaction rate across the dispersion due to intensity gradients cause density gradients ($\Delta\rho_{spheres}$ is positive). Therefore, a net density change ($\Delta\rho$) during the polymerization of monomeric dispersion is

$$\Delta\rho = \Delta\rho_{thermal} + \Delta\rho_{monomer} + \Delta\rho_{spheres} \qquad (3)$$

Since the **photopolymerization** experiments are conducted at ambient temperatures, we presume that the density gradients which arise from the thermal effect is smaller than the density gradients resulting from concentration changes of monomer and spheres **(solutal** convection), and the volume changes of the monomer matrix (double **diffusive** convection). The reacted top layers in the horizontally held dispersion become denser because of the positive $\Delta\rho$ and are positioned above the less dense **unreacted** fluid layers. Therefore, under the influence of gravity, these dense layers sink to the bottom and a decrease in film thickness results after polymerization. This decrease in fluid film thickness during polymerization can create free surfaces and, consequently **Marangoni** convection may develop in addition to buoyancy effects due to the presence of density gradients in these **systems.**[20] The magnitude of fluid motions may be small due to small cell container dimensions, but large enough to deform the de **licate** crystalline structures. The following experimental observations also indicate that the gravity driven heat and mass transport **play** a crucial roles in the **photopolymerization** of monomeric dispersions in thin ceils.

The **silica-MMA** dispersion polymerized in the horizontal configuration **(Fig.2)** showed optical **diffraction** whereas the dispersion polymerized in the vertical configuration did not. Since no other experimental parameters are changed except the orientation of the cell, which can affect neither the heat of polymerization nor the volume shrinkage of the **host,** the observed phenomenon has to be gravity related. The disappearance of Bragg diffraction from the solidified films is a result of either complete **destruction** of ordered arrays of spheres or disorientation of the lattice planes of the crystallite. **Crandall** and **Williams,**[4] and **Kesavamoorthy** and **Arora**[5] have reported that the gravitational force significantly affects the interacting colloidal polystyrene spheres (100 **nm** in diameter and density of $1.05g/cm^3$)) dispersed in aqueous medium and compresses the lattice. Therefore, we initially thought that the disappearance of the **Bragg diffraction** peak from the **silica-PMMA** dispersion, which was kept in the vertical position just before polymerization, is due to the gravitational sedimentation of the colloidal crystals. The **crystallites** of silica spheres, which were grown for a few days with the **cell** container **in** the horizontal position, are in gravitational equilibrium because the rate of sedimentation equilibrium is **faster** than the rate of crystallization. Upon tilting the position of the ceil container **to vertical** orientation, these crystallite, under the influence of gravity, tend to reach a new sedimentation equilibrium, and can deform. However, the Bragg diffraction peak was not destroyed in the unpolymerized dispersion, although the peak position and shape change, when the fluid sample was held verticality **in** a **spectrophotometer** for 3-4 h, the duration of the **photopolymerization** process. These experimental results suggest that the absence of diffraction from the vertically held polymerized **sample** is not simply due to sedimentation of **crystallites** under the influence of gravity.

It appears that the polymerization process makes the fluid more unstable in a vertically oriented photocell than in one horizontally orientated. In the vertical configuration, as mentioned above, the gravitational force acts on colloidal crystals. In addition to this, density gradients in the dispersion, created by the intensity dependent reaction, induce convect **ive** flows. Considering the fact that the reaction liberates heat, the density of dispersion layers which are close to the radiation source become lower and gravity, therefore, induces movement of these layers. On the other hand, these layers become denser if the effect of **solutal** and **double diffusive** convection dominate thermal convection. Again, in this case, gravity drives the motion of the fluid layers. In any case, the fluid in the vertical configuration is unstable and the gravitational force can randomize the sphere arrays during polymerization. However in the case of the horizontal configuration, the fluid layers which are close to the radiation source are on top, and these become less dense due to positive AT. Since these layers stay over the dense bottom layers, gravity may not induce convection, and thus the dispersion in this configuration is stably stratified. The top layers become denser due to positive $\Delta\rho$ as mentioned above, and sink to the bottom by the acceleration due to gravity. The sedimentation of dense layers may not randomize the sphere packing, but lattice dimensions certainly change. That is why the polymerized film obtained in the horizontal position diffracted the incident light (Figure 2).

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In another experiment, in spite of keeping the photochemical cell in the vertical position, the Bragg diffraction has been observed from the solidified poly(MMA-*co*-HEMA) film (Figure 3).[8] As stated earlier, the vertical configuration is highly unstable because of buoyancy induced fluid fluctuations. Such motions in general are opposed by viscous drag forces. The HEMA (2-hydroxyethyl methacrylate) is more viscous and denser than MMA. Therefore the bulk viscosity of the monomer mixture (MMA/HEMA; 65/35 wt%) is higher than neat MMA and hence the high viscous matrix stabilizes the dispersion against convection and thereby minimizes the mass transport as observed with silica-PMMA film. As a result, the periodic arrays of silica spheres are not disturbed completely after polymerization. However, the crystalline lattice is still compressed during the reaction and this is because of reduced interparticle interactions as stated earlier. The attempts to self-assemble the colloidal silica spheres in neat HEMA are not successful because of the high viscous matrix which reduces the rate of crystal growth.
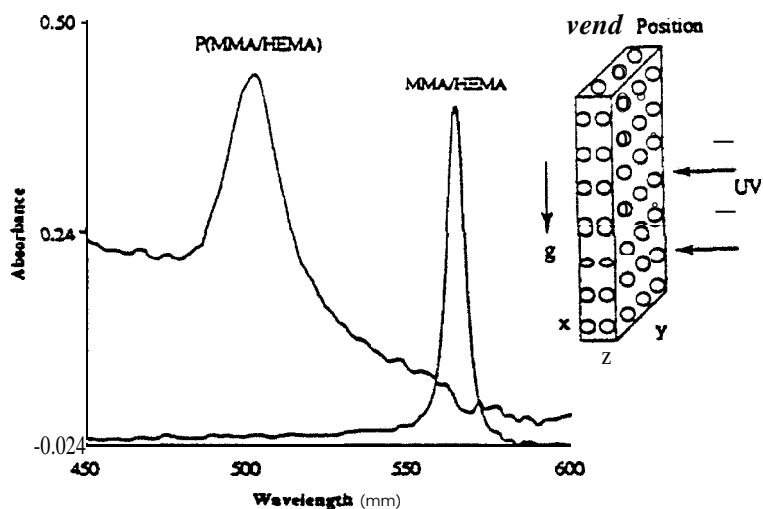

Figure 3. Bragg diffraction from silica-(MMA-co-HEMA) dispersion before and after polymerization. The photocell was placed vertically just before polymerization.

One of the major components in the dispersion which could lead to large convective instabilities during the polymerization process is the photoinitiator. if both initiator concentration&d its extinction coefficient are high in the dispersion, intensity gradients can produce large scale buoyant forces. The self-screening effect by the photoinitiator molecules can not be eliminated but maybe reduced by carefully choosing an optimum concentration of photoinitiator for a given thickness of the dispersion.[21] The initial concentration of the photoinitiator, 2,2-dimethoxy-2-phenyl acetophenone, employed in a 0.26 mm thick dispersion is I wt%. However, later investigations study the effect of varying this photoinitiator concentration (from 0.2 to 5.0 wt%) on optical diffraction properties of polymethyl acrylate composite films.[9] The diffraction peak bandwidths are narrower at 0.2 wt% which suggest that the periodic arrays are less disturbed at these levels. These results are not surprising because the lower the photoinitiator concentration, the smaller the intensity gradients in the dispersion, which thus minimizes the density gradients. The low initiator concentrations favor minimal convection at the expense of slow reaction rates.

Conclusion

We have identified several factors which influence the dynamics of colloidal crystals during the photoinitiated bulk polymerization process. To design better nonocomposite laser filters, the lattice compression, volume shrinkage of the monomer matrix, and the gravity induced convection and sedimentation have to be minimized. Further, understanding the effect of gravity on colloidal crystals during polymerization is essential. Microgravity provides a unique convection-free and sedimentation-tie environment. Processing of materials in such an environment could lead to a better understanding of the effect of gravity on these processes.

References

(1) Weissman, J. M.; Sunkara, H. B.; Tse, A. S.; Asher, S. A. *Science 1996, 274 (Nov. 8)*.
(2) Sunkara, H. B.; Weissman, J. M.; Penn, B. G.; Frazier, D. O.; Asher, S. A. *ACS Polym. Preprint 1996, 37, 453*.
(3) Imhof, A.; van Blaaderen, A.; Dhont, J. K. G. *Langmuir 1994, 10, 3477*.
(4) Crandall, R. S.; Williams, R. *Science 1977, 198, 293*.
(5) Kesavamoorthy, R.; Arora A. K. *J. Phys. A 1985, 18, 3389*.
(6) Sunkara, H. B.; Jethmalani, J. M.; Ford, W. T. *Chem. Mater. 1994, 6, 362*.
(7) Sunkara, H. B.; Jethmalani, J. M.; Ford, W. T. *ACS Polym. Mater. Sci. Eng. Preprint 1994, 70, 274*.
(8) Sunkara, H. B.; Jethmalani, J. M.; Ford, W. T. in *Hybrid Organic-Inorganic Composites,* Eds. Mark, J. E.; Lee, C. Y-C.; Bianconi, P. A. *ACS Symp. Ser. 1995, 585, 181*.
(9) Jethmalani, J. M.; Ford, W. T. *Chem. Mater.1996, 8, 2138*.
(10) Jethmalani, J. M.; Sunkara, H. B.; Ford, W. T.; Willoughby, S. L.; Ackerson, B. A. (submitted [o Langmuir).

(11) Jethmalani, J. M.; Ford, W. T.; Beaucage, G. (submitted to Langmuir).

(12) Panzer, H. P. ; Magliocco, L. G.; Cohen, M. L.; Yen, W. S. US Patent 5338492, 1994.

(13) Asher, S. A.; Holtz, J.; Liu, L.; Wu, Z. *J. Am. Chem. Sot.* **1994**, *116*, *4997*.

(14) Malcuit, M. S.; Herbert, C. J. *Acts Physics Polonica* *.4,1994,86*, *127*.

(15) Rundquist, P. A.; Kesavamoorthy, R.; Jagannathan, S.; Asher, S. A. *J. Chem. Phys.* 1991,95,8546.

(16) Rundquist, P. A.; Jagannathan, S. ; Kesavamoorthy, R.; Brnardic, C.; Xu, S.; Asher, S. A. *J. Chem. Phys.* 1991, 94, 711.

(17) Philipse, A. P.; Vrij, A. *J. Chem. Phys.* *1988*, *88,6459*.

(18) Turner, J. S. Buoyancy *Effects in Fluids*, Cambridge University Press, Cambridge, 1973.

(19) Pojman, J. A.; Epstein, I. R. *J. Phys. Chem.* 1990,94,4966.

(20) Winters, K. H.; '1%. Plesser, Cliffe, K. A. *Physics 1988, 29D, 387.*

(21) Bush, R. W.; Ketley, A. D.; Morgan, C. R.; Whitt, D. G. *J. Radiat. Curing 1980,7,20.*