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NASA FINAL REPORT

"Polyaryl Ethers and Related Polysiloxane Copolymer Molecular Coatings Preparation and Radiation Degradation"

NASA Research Cooperative Agreement NCC1-63

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FORWARD

The objective of this work was to synthesize polyarylether materials and related siloxane copolymers. A second investigation was to characterize their structure, mechanical behavior and to initiate radiation degradation studies by both particulate radiation as well as UV radiation. The technical approach was to utilize aromatic nucleophilic displacement reactions to produce highly aromatic polysulfones and related structures. Functional oligomers were also utilized to prepared well-defined siloxane copolymers. The grant number for this research was NASA Research Cooperative Agreement NCC1-63. The grant duration was 12 months. In addition to the principal investigator, other research scientists involved on this project; Mr. J. L. Hedrick, Mr. D. C. Webster, Mr. B. C. Johnson, Dr. D. K. Mohanty, and Dr. I. Yilgor. The NASA technical monitor for this program is Dr. George Sykes.

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SUMMARY

Wholly aromatic random copolymers of hydroquinone and biphenol with 4,4'-dichlorodiphenyl sulfone were synthesized via aromatic nucleophilic displacement. Their structures were characterized and mechanical behavior studied. These tough, ductile copolymers show excellent radiation resistance to electron beam treatment and and retain much of their mechanical properties up to at least 700 Mrads under argon.

In addition, perfectly alternating block copolymers of polysulfone and poly(dimethylsiloxane) (PSF/PSX) were synthesized by the silyl amine-hydroxyl reaction of the respective oligomers. Some basic structure-property relationships of these copolymers were examined. The addition of small amounts of these PSF/PSX copolymers to the homopolysulfone dramatically improved the impact and fracture toughness properties as expected. Moreover, surface modification in solution cast blends resulting from the migration of the siloxane to the air interface was achieved, as judged by ESCA measurements. Such phenomena may be important in toughness retention as a function of aging, UV stability of suitably pigmented coatings, and possibly in environmental stress cracking resistance (ESCR). Thus far, the ESCR critical measurements indicate that time to failure is increased with PSX modification, but that the critical strain to rupture itself is not enhanced.

Recently, we have also synthesized new macromolecular structures in the following classes; poly(arylene ether sulfones), poly(arylene ether ketones), and poly(arylene ether nitriles) and imide containing copolymers. Each of these materials are amorphous, but some have the potential for solvent induced crystallization. These wholly aromatic systems should prove to be also radiation resistant.

Other important structures presently under investigation include the polyimide-polysiloxane copolymers and polysulfone-polyimide copolymers. Degradation studies via UV and particulate radiation have been initiated.

Additional characterization of the materials described in this report is planned. The areas will include supplementary e-beam degradation studies (especially under vacuum), Co^{60} treatment, gas yield analyses, ESCA and STEM studies with melt blends, and extended critical strain measurements.

Finally, during this grant period, approximately 35 samples have been submitted to NASA Langley for further characterization by interested NASA personnel. Some of the sample submitted will also be sent up on the space shuttle for further realistic evaluation of their degradation behavior.

INTRODUCTION

Poly(arylene ether sulfones) comprise a class of materials known as engineering thermoplastics (1) which have a variety of important applications. These polymers are tough, rigid materials with good mechanical properties over a wide temperature range, and they may be processed by conventional methods into products typically having excellent hydrolytic, thermal, oxidative and dimensional stability.

Poly(arylene ether sulfones) and related structures are presently under investigation for aerospace applications (2,3,4). Specifically, these polymeric materials may be utilized as castable amorphous matrix resins for graphite reinforced composites because of their dimensional stability, low coefficient of thermal expansion, retention of modulus at high temperatures and radiation resistance. Unfortunately, these high performance materials cannot be used for certain aerospace composite structures because of solvent sensitivity.

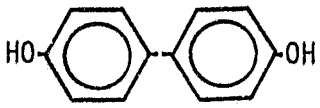
Previous studies by J. H. O'Donnell and coworkers (5,6,7) have shown that aromatic polysulfones exhibit excellent radiation stability, with retention of mechanical properties up to 50 megarads in air.

The aromatic character in these structures is the primary contributor to their radiation stability. However, the aliphatic character associated with Bisphenol-A polysulfone may thus be a prime source for the generation of free radicals which could then lead to subsequent degradation.

Recently, we (8) have synthesized a series of random copolymers derived from hydroquinone and biphenol together with 4,4'-dichlorodiphenylsulfone as shown in Scheme 1. In order to produce these polymers in high molecular weight, modified techniques were developed which utilized potassium carbonate as a weak base and NMP as a aprotic dipolar solvent.

Scheme I

SYNTHESIS OF BIPHENOL-HYDROQUINONE COPOLYARYL ETHER SULFONES
VIA N-METHYL-PYRROLIDONE/TOLUENE/K_2CO_3 ROUTE



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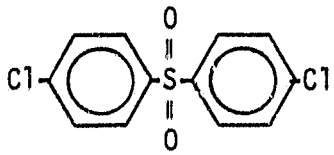
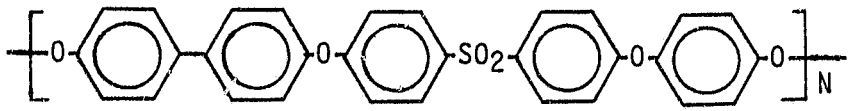


VARIABLE COMPOSITION

$-H_2O$
$-KCl$

N-METHYL PYRROLIDONE
TOLUENE, K_2CO_3



In a preliminary investigation, Bisphenol-A PSF and Hydroquinone/Biphenol PSF copolymers (Hq/Bp PSF) were exposed to electron radiation from a van de Graaf generator. The Hq/Bp PSF showed superior radiation resistance to that of the Bis-A PSF. In fact, the Hq/Bp PSF copolymers retained their mechanical integrity and showed no appreciable molecular weight changes up to 700 Mrads. We believe that the absence of aliphatic character in these structures is responsible for their improved radiation resistance.

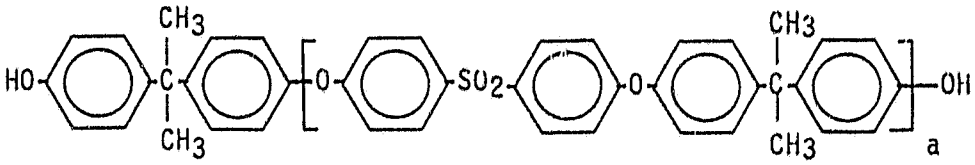
Most poly(arylene ether sulfones) and related structures are amorphous and therefore do suffer from several limitations. For example, it is a fact that many of them are somewhat notch sensitive in their mechanical response. That is, if one naturally or artifically induces a small notch into their final fabricated part the impact strength decreases significantly. Another problem which perhaps is more serious is that of environmental stress cracking. The materials may indeed fail catastrophically in the presence of certain organic liquids, even under moderate stresses or low strains.

The approach to improving the impact strength problem frequently entails the addition of a rubbery material to the glassy matrix as was suggested by McGarry and others (9). Usually the best results are obtained when the rubbery component phase separates from the glassy matrix xo that a dispersion of rubbery particles or rubbery domains in a glassy matrix is produced. A variety of these systems have been discussed, many of which are included in an important book by Bucknall (10).

An important example of the utilization of block copolymers to modify engineering polymers was discussed in a series of papers by Noshay and coworkers (12-16). They demonstrated that the preparation of perfectly alternating block copolymers of polydimethylsiloxane and polysulfones produced according to Scheme II were of wide application for the modification of this

Scheme II

SYNTHESIS OF POLYSULFONE-POLY(DIMETHYLSILOXANE) BLOCK COPOLYMERS (3)



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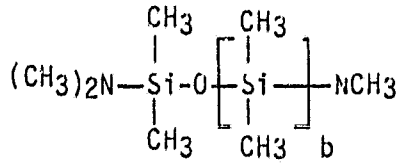
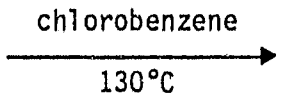
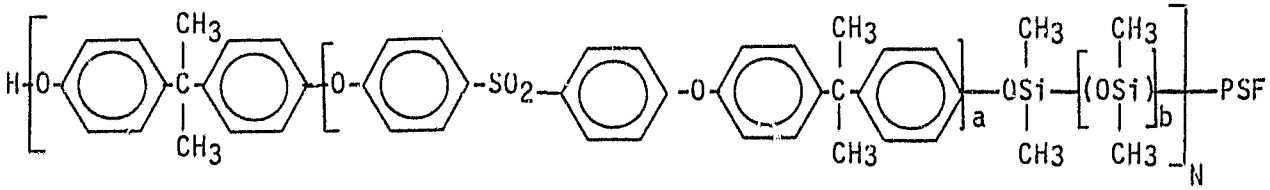






+ $(CH_3)_2NH$

particular engineering polymer. They showed that the notched Izod impact strength of polysulfone could be improved substantially (16).

Polydimethylsiloxane segments are known to be very useful for a number of reasons, which include properties such as a low glass transition temperature, good thermal stability and low surface energy. Other investigators such as Kambour and coworkers (17) have shown that the notched Izod impact strength of polycarbonates can also be significantly improved with the incorporation of polydimethylsiloxane block segments. In addition, they reported that the incorporation of this segment also lowered the ductile to brittle transition from -15°C to as low as -110°C.

Siloxane modification of engineering polymers may also play an important role in the alteration of environmental stress cracking resistance (ESCR). Some of our qualitative observations on the polycarbonate siloxane systems indicate that the ESCR improves markedly with the addition of the polydimethylsiloxane blocks. The reasons for these observations are unclear at the moment, however, we felt that the combinations of properties noted so far were of great interest. This led us to continue some of the earlier results reported in the literature in the hopes of obtaining a better understanding of these systems and indeed to also perhaps develop new and improved materials based on these engineering polymers. Morever, we also hoped to exploit their use as high performance matrix resins in radiation resistant carbon fiber composites.

An additional reason for investigating these systems was our finding (along with others) several years ago that the surface concentration of polydimethylsiloxane is much higher than that in the bulk (18). This means that it might also be possible to alter the surface properties of a matrix resin in a composite system. This in turn could affect wear resistance as we

have already identified in epoxy modified systems (19) and weathering resistance might also be enhanced in some of these siloxane-modified systems. In addition, the UV radiation resistance may be enhanced (especially in pigmented systems) by the presence of the siloxane on the surface.

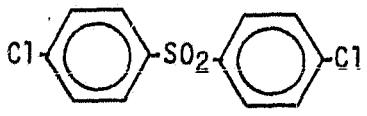
For our first system of study, we have chosen to utilize the sulfone siloxane modified systems, which were earlier reported by Noshay et al., to investigate fracture toughness measurements, surface analyses, and the critical strain phenomenon associated with environmental stress cracking. Other work in progress will report analogous behavior of engineering polymers such as the aromatic polyesters and polyamides.

EXPERIMENTAL

SYNTHESIS OF HYDROQUINONE AND BIPHENOL POLYSULFONE HOMOPOLYMERS AND BIPHENOL-HYDROQUINONE POLYSULFONE COPOLYMERS

Random copolymers of hydroquinone (HQ) and biphenol (BP) were synthesized by varying the molar ratios of the two bisphenols. The other monomer utilized was 4,4'-dichlorodiphenylsulfone. Before proceeding to the actual synthesis of the polymers, monomer and solvent purification will be presented.

Indeed, as in all condensation or step-growth polymerization reactions, monomer and solvent purification is essential in order to obtain polymers of high molecular weight. The 4,4'-dichlorodiphenyl sulfone (DCDPS) was obtained from Union Carbide and was



recrystallized prior to polymerization by the following procedure. A 200 ml conical flask with a large magnetic stirrer was placed on a Corning magnetic hot plate. To this flask were added 800-900 mls of toluene and 500 gms of DCDPS and the mixture was allowed to stir while gently heating. The DCDPS dissolved as the temperature reached 110°C. Next, approximately 2 gms of charcoal were added and the mixture was boiled for several minutes. Toluene (50 ml) was heated in another 2 liter conical flask which contained a large Buchner funnel fitted with filter paper and packed celite. The DCDPS solution was then filtered through the celite, yielding a clear solution. The flask was then placed on a hot plate and was stirred and heated to concentrated the solution volume to about 500 mls. Then the solution was cooled in a cold water bath while still being stirred until the DCDPS crystallized. This solution was filtered and the DCDPS crystals were dried in the vacuum oven at about 1 torr a 80°C until it was used.

The hydroquinone (Hq) was obtained from Eastman Kodak and must be recrystallized under nitrogen. A three neck, 2 liter, round bottom flask was utilized which was equipped with a nitrogen inlet, drying tube and a stopper which permitted inert atmosphere of this air sensitive bisphenol. About 200 gms of Hq was added to the flask together with approximately 500 mls of acetone. The mixture was heated with a mantle until the monomer dissolved. During this procedure an inert atmosphere must be maintained. Accordingly, nitrogen or argon was bubbled directly into the solution. The solution is next filtered through fluted filter paper and allowed to cool. The inert atmosphere was maintained until the crystallization process was complete; usually this took several hours. The mixture containing the crystals was filtered through a Buchner funnel via a water aspirator vacuum. The filtrate was next washed with 75 mls of cold deoxygenated water and dried under vacuum at room temperature for several (2-3) days. Finally, the Hq was stored in a desicator until used in a polymerization.

The biphenol monomer was obtained from Buffalo Color Co. and was pure enough to use as received without further purification.

The solvent utilized was N methyl-2-pyrrolidone (GAF) which was vacuum distilled over P_2O_5 and stored over molecular sieves and a nitrogen atmosphere until use.

The polymerization reaction was typically conducted in a 500 ml 4-neck round bottom flask which was equipped with stirrer, thermometer, Dean Stark trap and condenser. An argon dispersion tube, oil bath and hot plate were also utilized. The reaction assembly is shown on the following page. The synthesis of the homopolymers were carried out in the same fashion as the copolymers.

A detailed synthesis procedure is now shown for a hydroquinone

50% biphenol/50% polysulfone "random" copolymer. First, the reaction assembly must be purged with argon prior to the addition of the monomers or solvents. Next, 9.3 gms or 0.05 mole of 4,4' dihydroxybiphenol was accurately weighed into teflon coated aluminum pans. The monomer was delivered into the flask through a funnel and the delivery pan was washed several times with distilled NMP. In a similar fashion, 5.5 gms or 0.05 mole of hydroquinone were accurately weighed out and placed in the flask. Finally, the 4,4'dichlorodiphenyl sulfone was weighed out and added (28.7 gms or 0.1 mole). Each of the monomers were carefully washed down into the flask with distilled NMP. The final volume should be approximately 200 mls. To this solution, approximately 100 ml of toluene was added as an azeotroping solvent. Finally the base was added, approximately 18 gms or 0.135 mole of K_2CO_3. Note that K_2CO_3 was used in 30 to 40 percent excess. This reaction mixture was then heated until the toluene began to reflux. An optimum reflux temperature range appears to be about 140-150°C. The Dean Stark trap should be calibrated to hold approximately 40 mls of fluid. The initial distillate collected in the Dean Stark trap will be very cloudy. This is due to the water azeotroped from the system, as well as that released during phenoxide formation. The actual amount of water collected is related to the moles of phenol groups. After 1-2 hours the liquid in the Dean Stark trap will separate into two layers, the top layer is relatively pure toluene and the bottom layer is the azeotrope mixture. Refluxing must proceed until no more water is observed; this may take 4-6 hours. During this period the joints around the thermometer, gas inlet and mechanical stirrer must be kept fairly dry. This can be accomplished by utilizing a heat gun and heating the joints until the toluene and water particles coalesce and collect back into the solution; this is a key step in the dehydration. During this stage of the

reaction the solution may undergo several color changes. For example, during the initial formation of the phenolate, a yellow-brown color can be observed. As the reluxing proceeds, the color changes to a dark brown, and the solution may possibly have a dark green tint.

Once the water has been removed, the temperature is increased slowly. This may be accomplished by removing toluene through the Dean Stark trap. The temperature should increase to 180°C after removing toluene for about one hour. The Dean Stark trap must remain full and also a small amount of toluene should be left in the reaction vessel. This serves two purposes; (i) any water that is formed will be removed by the slowly refluxing toluene, (ii) the refluxing serves as an excellent method for temperature control. These reactions vary in time from 1.5 to 4 hours; completion or near completion may be estimated by the point the viscosity increases drastically; the polymer may even appear to come out of solution. At this point more toluene is removed and reaction temperature is increased to 190-195°C. The reaction is allowed to continue for an additional one hour.

The high molecular weight product is then filtered hot through a 2 liter course filter using a water aspirator. The solution must be diluted with an additional 200 ml of NMP. This will aid in filtration and in the cleanliness of the final product. The filtered solution is cooled and acetic acid should be added to neutralize the phenate. Acetic acid is added until the color changes from a dark green-brown to a transparent brownish color.

The polymer solution is added to a one liter separatory funnel and allowed to drip slowly into a stirred blender containing about 10x volume of methanol. The coagulated polymer is filtered and boiled in water for one hour to extract any trapped salts. Once again the polymer is filtered and dried under vacuum and 80°C to a constant weight. The final product should be a white, fibrous appearing polymer.

Synthesis of the PSF/PSX Segmented Copolymers

The perfectly alternating block copolymers were synthesized in solution using the silylamine-hydroxyl condensation reaction (12-16). The reaction was conducted in a 1-liter four necked round bottomed flask fitted with a mechanical stirrer, a Dean Stark trap, condenser, thermometer, inert gas inlet, and addition funnel. A typical reaction utilized to produce a polysulfone-polydimethylsiloxane block copolymer employs 22.3 g of a 4900 Dalton hydroxyl-terminated polysulfone oligomer placed into the flask with 500 ml of chlorobenzene. With stirring, the oligomer dissolves within an hour. Next, the temperature was raised until the chlorobenzene began to reflux (132°C). Approximately 100 ml of solvent was removed from the Dean-Stark trap to dehydrate the system. Separately, the 4400 dalton siloxane oligomer (20.0 g) was placed into the dry addition funnel under argon. Half of the oligomer was slowly added to the solution and allowed to react until the evolution of amine (as detected by pH paper) had significantly decreased. At this point, the rest of the siloxane oligomer was added slowly in increments. A noticeable increase in viscosity was observed, as the stoichiometric point was approached. The reaction was allowed to proceed at reflux temperature for another hour. It was then cooled and the product was precipitated in a ten-fold excess of methanol/isopropanol mixture. The fibrous product was dried in a vacuum oven at 60°C overnight, then was dissolved in chloroform, filtered, and precipitated in filtered methanol/isopropanol mixture. After drying again for 24 hours under vacuum at 70°C, the yield was 95 percent and the intrinsic viscosity in chloroform at 25°C was 0.6 dl/g.

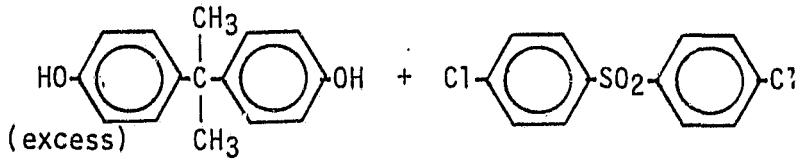
Synthesis of Dimethylamino Terminated Polydimethylsiloxane Oligomers

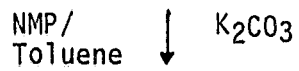
The dimethylamino-terminated polydimethylsiloxane oligomers are prepared by the anionic bulk equilibration of a low molecular weight oligomer with the cyclic tetramer, D-4. The precursor oligomer was obtained either from Union

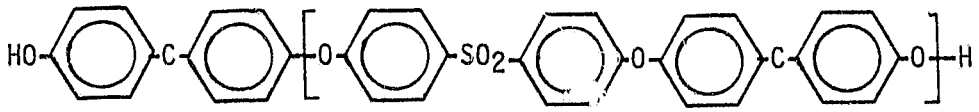
Carbide Corporation or Petrarch Chemical company. Its molecular weight was determined by titration with HCl in isopropanol. The reaction was carried out in a 3-necked round bottomed flask equipped with a mechanical stirrer, inert gas inlet, thermometer, condenser, and drying tube. In a typical reaction to produce a 5000 Dalton oligomer, 23.75 g of a 570 Dalton oligomer along with 226.25 g of D-4 were introduced into the reaction flask. Using a silicone oil bath and a hot plate as a heating source, the temperature was raised to 80°C with stirring and 1.5 g of dry tetramethylammonium siloxanolate catalyst is added. The reaction maintained at 80°C for 48 hours to ensure complete equilibration. The temperature of the reaction is then raised to 150°C to decompose the catalyst. After cooling, the reaction product is transferred to a vacuum distillation apparatus and the cyclic by-products are removed. The titrated molecular weight was 4410 Daltons.

Synthesis of Bis-A PSF Oligomer

Oligomers of Bis-A PSF were successfully synthesized by the NMP/K_2CO_3 route (20) Bis-A (Dow Chemical) and 4,4'-dichlorodiphenyl sulfone (Union Carbide) were coupled together in a stochiometric imbalance determined by the Carothers equation to give the appropriate molecular weight.







Characterization. The oligomers for this synthesis were characterized by non-aqueous potentiometric titration of the end groups either by using HCl in

the siloxane case or tetramethyl ammonium hydroxide in the case of the hydroxyl terminated polysulfone oligomer. The intrinsic viscosities of the copolymers were determined in chloroform at 25°C using a Cannon-Ubbelhode type dilution viscometer. Films were prepared by casting on clean glass plates from a filtered 20% chloroform solution.

Blend Preparation. Blends of polysulfone homopolymer and the siloxane copolymer were prepared as follows. The appropriate copolymer and the homopolymer were weighed into a 1-liter flask. Chloroform was added until a 10% polymer solution by weight was achieved. This required stirring of the mixture until all the polymer was dissolved, which usually took 8-10 hours. The solution was filtered to remove any impurities and coagulated in a 10-fold excess of filtered methanol. The blend was dried for at least 24 hours at 70° under vacuum. The dry fibrous material was then extruded at 300°C using a Custom Scientific Instruments (CSI) Mixing Extruder. The extrudate thus obtained was also dried overnight under vacuum before compression molding. Compression molding was carried out at 290-300°C in a hydraulic press.

Environmental stress cracking. Samples for environmental stress cracking were compression molded between ferro-type plates and cut into strips approximately 3.3mm thick, and 20mm wide, 15cm long. Strips were clamped in place along a Dow Elliptical bending form and a filter paper wick which was 10mm wide was placed in the middle of the polymer strip. Solvent was added to the wick and the specimen was examined periodically for stress-cracks or crazes (21,22). When cracking was stopped (i.e. no more cracks or crazes were observed to develop) the distance along the axis of the elipse to the last crack and the thickness of the sample were measured to determine the critical strain. A minimum of three tests were performed for each polymer-solvent combination.

Fracture Toughness. Standard three-point bend test specimens (23) were compression molded and milled to their appropriate dimensions. The precracks were introduced with a razor and broken at a crosshead speed of 0.5 mm/minute and 20 mm/minute.

Scanning Electron Microscopy. Scanning electron micrographs were obtained with an ISI instrument on samples that had been fractured either at room temperature or under liquid nitrogen conditions.

ESCA. Preliminary XPS spectra of the pure block copolymer and its blends with polysulfone were collected on a KRATOS XSAM-800 x-ray photoelectron spectrometer with a $Mg_{K\ 1,2}$ source operating at 15 kV and 30 ma, courtesy of Prof. D. W. Dwight. Samples with varying composition were prepared by casting directly on the XPS probe from dilute chloroform solutions. High resolution spectra were collected for C_{1s}, O_{1s}, S_{2s} core levels at three different photoemission exit angles. The analyser of the spectrometer was operated in the Fixed Retarding Ratio (FRR) mode where the sensitivity of a peak is directly proportional to its kinetic energy. Peak areas obtained with a planimeter, were normalized to consider this sensitivity by dividing them by their respective kinetic energies. The normalized peak areas were then used to calculate relative atom percentages from first principles using published values of subshell photoionization cross-sections (24) and inelastic mean free paths (25).

E-Beam Radiation Degradation Studies

Radiation (26). Samples in the form of 0.1 mm sheet and thin films for the FTIR measurements were exposed to electron radiation from a van de Graaff generator operated at 2.0 MeV. The procedure was as follows: up to eight films were stacked one on top of another and placed in a polyethylene bag fitted with an air-tight tubing connection. The bag was flushed repeatedly

with nitrogen gas, then connected to a mechanical vacuum pump. Aluminum foil of 0.025 cm thickness was placed over the bag in an attempt to provide a uniform distribution of secondary electrons. This entire assembly was attached to a water-cooled heat sink; a fine thermocouple interleaved among the samples registered a maximum temperature during irradiation of 60°C. The dose rate, determined by cellulose triacetate film dosimetry, was $1x10^5$ roentgens/sec.. Total irradiation times ranged up to two hours.

FTIR. A Nicolet MX-1 was used to measure an FTIR spectra from 4000-500 cm^{-1}. To obtain spectra, films less than a mil in thickness were cast from dilute solutions of chloroform.

^{13}C-NMR. A Jeol FX200 MH_z was used to obtain a spectra. Deuterated Chloroform was used as the solvent with TMS as the reference.

Thermal Analysis. Differential Scanning Calorimetry was obtained using a Perkin Elmer DSC-2 at a heating rate of 10°/min. and a sensitivity of 5 cal/min.

Thermogravimetric analysis was obtained with a Perkin-Elmer TGS-2 equipped with the System 4 microprocessor controller. Nitrogen atmospheres were used with a heating rate of 10°/min.

RESULTS AND DISCUSSION

Poly(arylene ether sulfones) have been previously synthesized by either potassium carbonate/dimethyl acetamide (20) or by aqueous caustic/DMSO techniques (27). Although these methods are very useful for bisphenol-A based systems, they are not directly applicable for the synthesis of high molecular weight copolymers such as hydroquinone/biphenol polysulfone (Hq/Bp PSF). The Hq/Bp PSF copolymers produce a high glass temperature material due to the presence of the wholly aromatic structure. These bisphenates are unfortunately insoluble in DMSO. Since DMAC has a relatively low boiling point, the copolymers could thus only be made at atmospheric pressure at relatively low solution concentrations. Therefore, to achieve high molecular weight and to prevent premature precipitation of the polymer, high reaction temperatures in alternative solvents must be used.

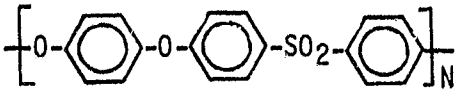
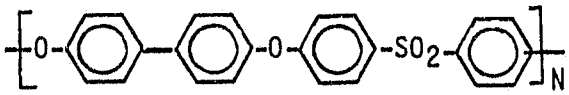
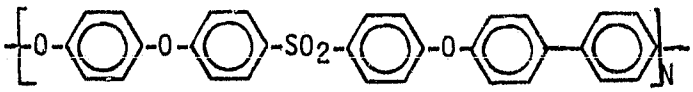
Recently, we (8) have synthesized poly(arylene ether sulfones) and related structures by an N-methyl-2-pyrrolidone/potassium carbonate synthesis route. This technique allows reaction temperatures up to the boiling point of NMP (202°C), which is higher than the DMSO or DMAC synthesis techniques. Hydrolytic side reactions typical of strong bases (28) can be minimized, thus allowing the synthesis of high molecular weight hydroquinone/Bp PSF copolymers.

Table 1 illustrates the various homo- and copolymers of Hq/Bp synthesized by the NMP/K_2CO_3 route. High molecular weight polymers were obtained for all by varying mole percents of the two bisphenols used. This is indicated by the intrinsic viscosity shown in Table 1. Utilization of NMP as a reaction medium permits these high intrinsic viscosities since it can prevent premature precipitation and be conducted at 190-200°C.

These polymers exhibit high glass transition temperatures as indicated in Table 1. The glass transition temperatures of these copolymers vary between

Table 1

HOMO- AND COPOLYMERS OF HYDROQUINONE AND/OR BISPHENOL POLYSULFONES

	Structure	$[\eta]$ (a)	Tg°C (b)
(1)	Hydroquinone Polysulfone	1.40	217
			
(2)	Biphenol PSF	1.00	232
			
(3)	Biphenol 10%/Hydroquinone 90% Polysulfone Copolymer	1.00	215
			
(4)	Biphenol 25%/Hydroquinone 75% Polysulfone Copolymer	0.72	212
(5)	Biphenol 25%/Hydroquinone 75% Polysulfone Copolymer	1.45	220
(6)	Biphenol 40%/Hydroquinone 60% Polysulfone Copolymer	1.37	227
(7)	Biphenol 50%/Hydroquinone 50% Polysulfone Copolymer	0.71	217
(8)	Biphenol 50%/Hydroquinone 50% Polysulfone Copolymer	0.85	217
(9)	Biphenol 60%/Hydroquinone 40% Polysulfone Copolymer	1.43	227
(10)	Biphenol 75%/Hydroquinone 25% Polysulfone Copolymer	0.67	220
(11)	Biphenol 90%/Hydroquinone 10% Polysulfone Copolymer	0.79	227

(a) 10 NMP at 25°C
(b) DSC, 10°/minute

the two extreme homopolymers as expected with most random copolymers. The high glass transition temperatures are attributed to the wholly aromatic structures which are para linked to either a sulfone or ether group.

In addition to higher glass transition temperatures, the Hq/Bp PSF copolymers show superior thermal properties relative to the Bis-A PSF. This is illustrated by the thermogravimetric traces for the Hq/Bp PSF copolymers shown in Figure 1. Rapid weight loss occurred for these structures between 580-650°C under a nitrogen atmosphere. In contrast, the commercially available Bis-A polysulfone UDEL, shows appreciable weight loss between 500-550°C (27). As the mole percent of biphenol was increased relative to hydroquinone both the thermal stability and char yield increased as well. The latter characteristic is believed to be important for flammability considerations.

Both FTIR and ^{13}C NMR were used to confirm the structure of each of the copolymers. An FTIR spectrum for the Hq 50%/Bp 50% PSF copolymer is shown in Figure 2. In all spectra these polymers showed a series of peaks at 3078, 3052 and 3042 cm^{-1} characteristic of the aromatic C-H stretching. Also, at 1245 cm^{-1} a band characteristic of -C-O-C- stretching of the aryl ether group is common to all of these structures. Finally, doublets in the region of 1280-1320 resulting from asymmetric O=S=O vibrations were observed.

A C-13 NMR spectrum is illustrated in Figure 3 for a Hq 50%/Bp 50% PSF copolymer. The assigned structure is also contained on the spectrum whose peaks are assigned to the corresponding carbons in the structure.

Mechanical Properties of Hq/Bp PSF Copolymers

Poly(arylene ether sulfones) are tough, ductile materials which exhibit a number of good properties over a wide temperature use range. Furthermore, these thermoplastics may be molded and extruded by conventional techniques.

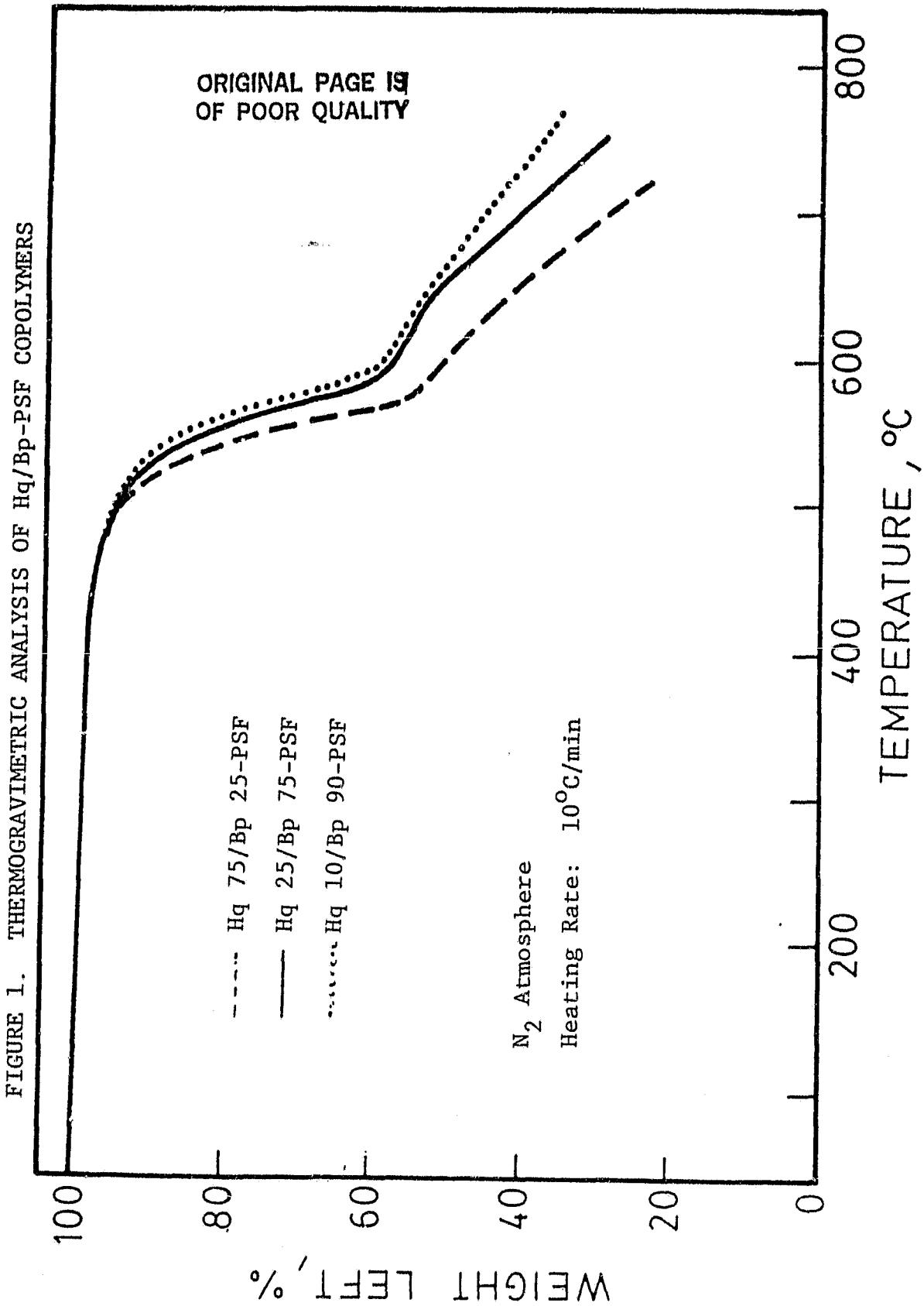
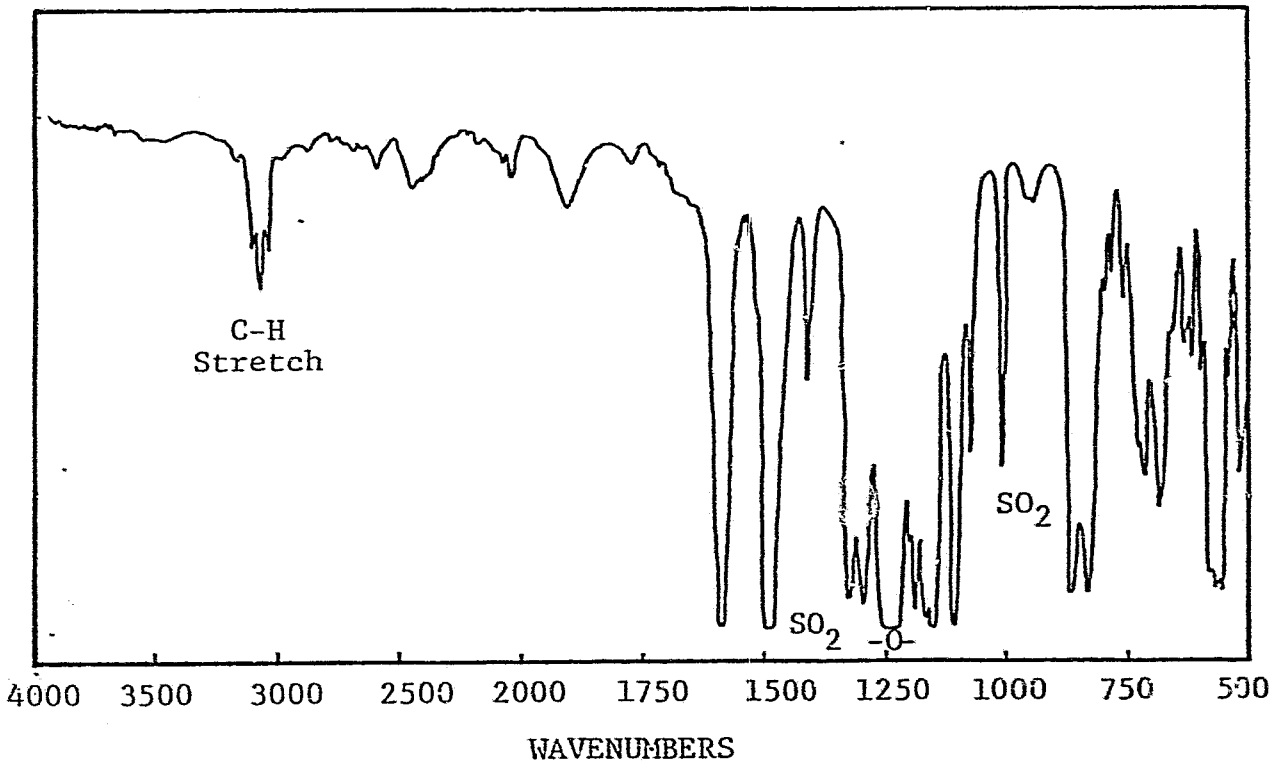


FIGURE 1. THERMOGRAVIMETRIC ANALYSIS OF Hq/Bp-PSF COPOLYMERS

FIGURE 2



I. R. Spectrum of Hydroquinone-Biphenol (50/50) Copolyaryl ether Sulfone.

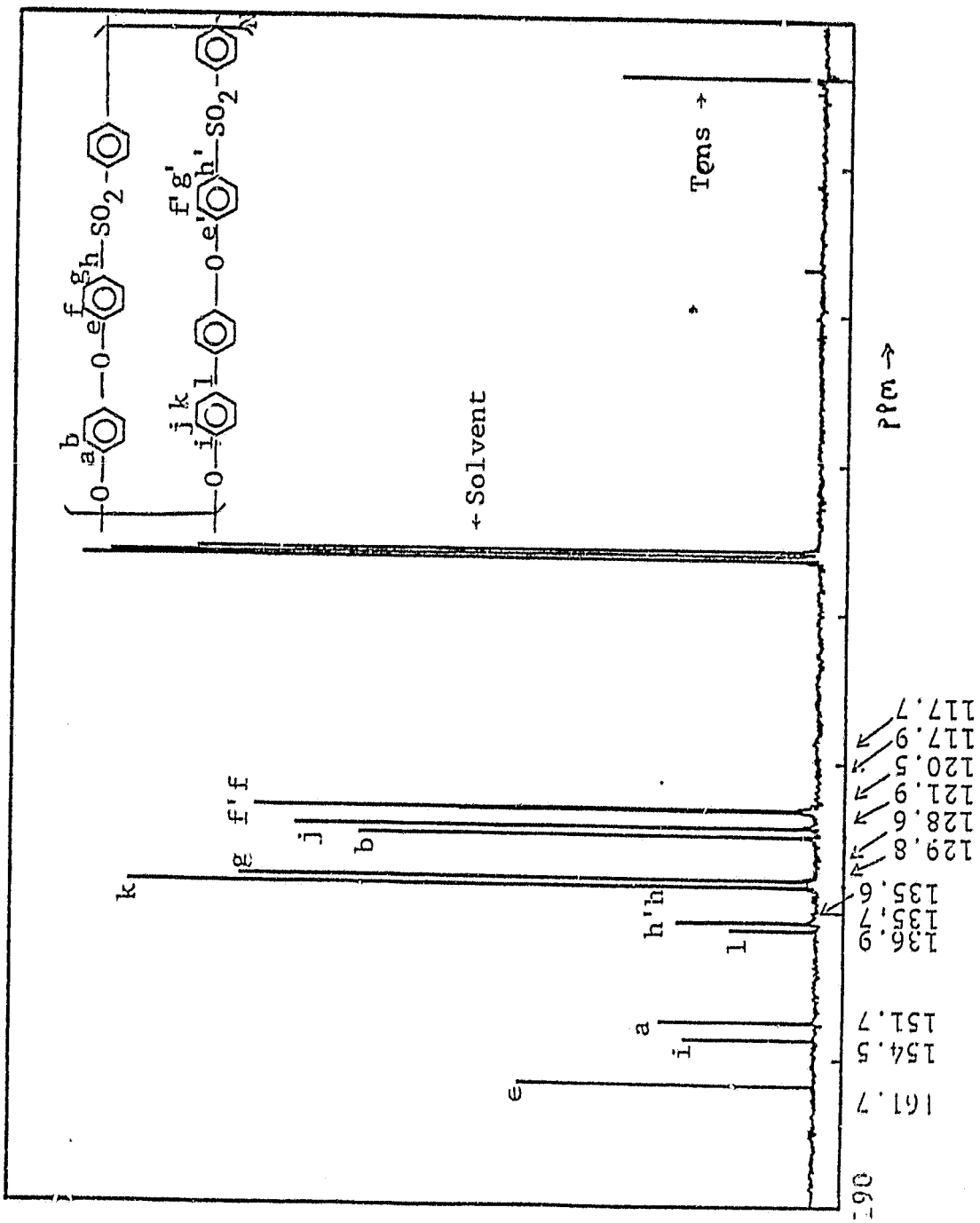


FIGURE 3

Tensile testing results obtained from an Instron are shown in Table 2. The wholly aromatic Hq/Bp PSF copolymers exhibit enhanced tensile yield stress behavior relative to that of the Bis-A PSF.

The dynamic mechanical properties of these copolymers were also investigated on both a Dupont DMA and a Torsional Braid Analyzer (29). DMA and TBA plots for the Hq 50%/Bp 50% PSF copolymer are shown in Figures 4 and 5. The glass transition temperatures obtained are fairly consistent with the DSC studies. The low temperature mechanical properties of the copolymers show a broad β-loss-modulus maximum occurring around -90°C, in a similar fashion to the Bis-A PSF (30). This β peak has been attributed to (i) relaxations involving motion in the aryl ether bond (ii); relaxations involving the sulfone-water complex (30). Good impact strength and ductile mechanical properties have been attributed to this β relaxation. As indicated by the plots, the copolymers retain their mechanical properties at high temperatures.

Another important material parameter commonly used to describe a material's resistance to crack propagation is the stress intensity factor, K. Basically, in linear elastic fracture mechanics (LEFM), the value K is a sufficient quantity to relate the intensity of the elastic stress-strain field near the crack tip to the loading and geometry of the specimen. The value K_{IC}, fracture toughness, indicates the critical stress intensity for a load which will cause catastrophic failure in mode I testing or tension. The value of K_{IC} varies with temperature, strain rate and chemical environment. The most common specimen geometries are the three point bend and the compact tension specimen given in Figure 6. The equation for K_{IC} for a three point bend specimen are given below (31).

Table 2

Stress Strain Yield and Fracture Behavior of Compression Molded Biphenyl/Hydroquinone Arylene Ether Sulfone Random Copolymers

Sample (mole % Hq)	Yield Stress (MPa)	Elongation at Yield (%)	Tensile Stress (MPa)	Elongation to Break (%)
0	73	7	68	76
10%	69	9	63	66
25%	69	8	70	76
50%	77	10	68	61
75%	78	8	69	65
(Bis A PSF)	67	7	57	86

* Instron data obtained at 25°C and 10 mm/min

FIGURE 4

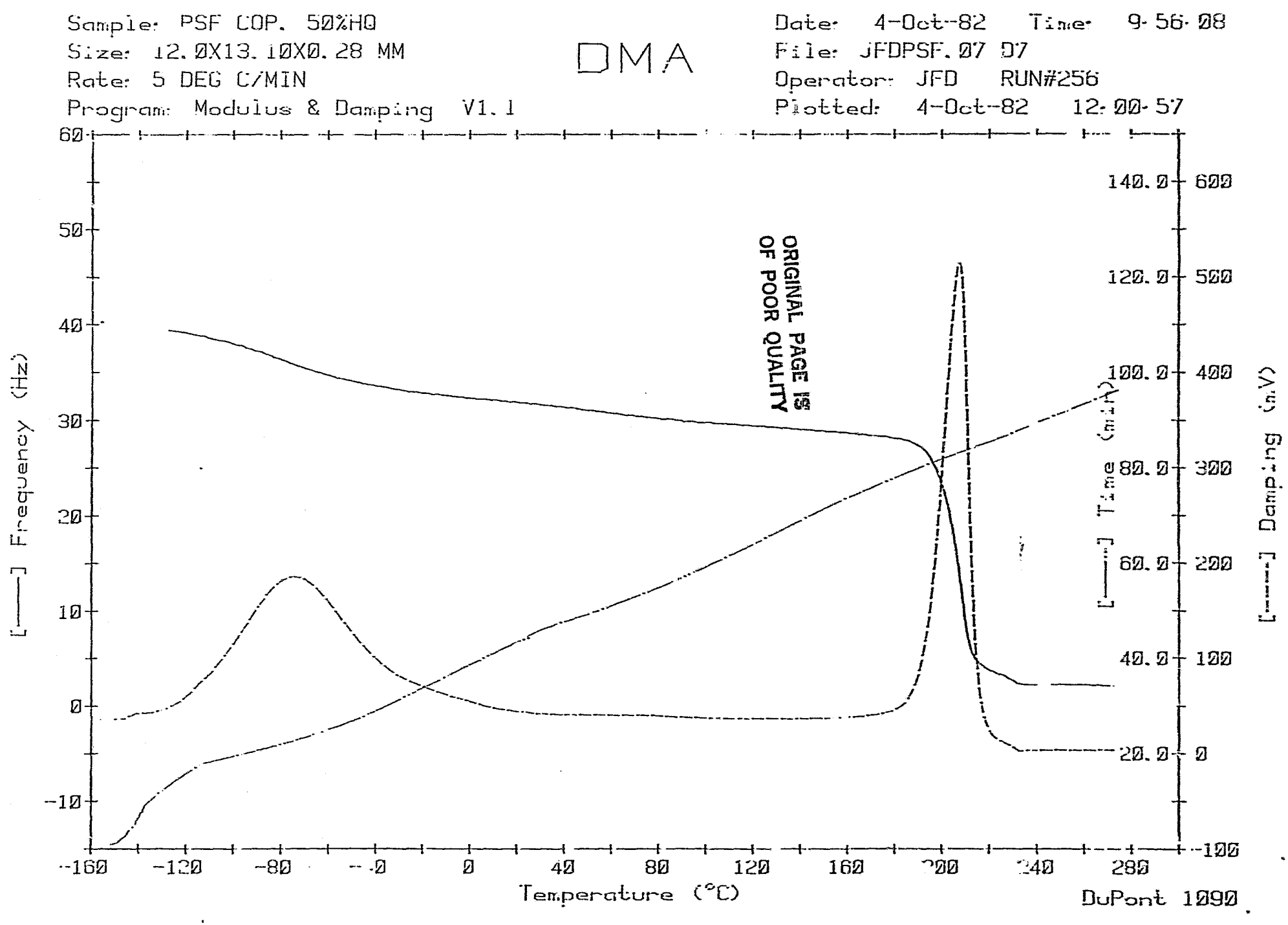
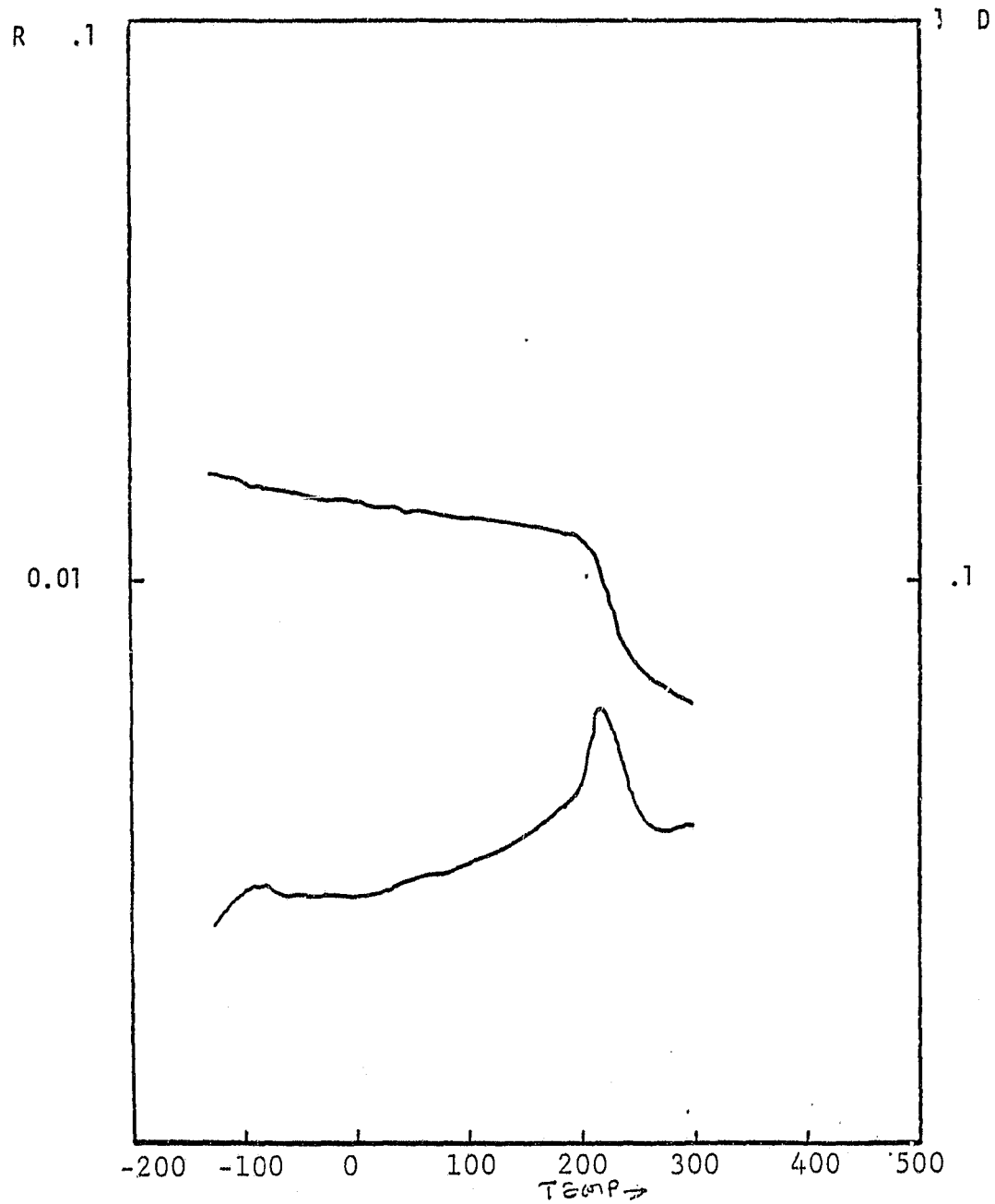
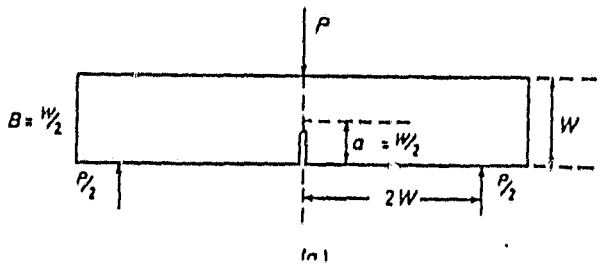

Sample: PSF COP. 50%HQ
Size: 12.0X13.10X0.28 MM
Rate: 5 DEG C/MIN
Program: Modulus & Damping V1.1
DMA
Date: 4-Oct-82 Time: 9:56:08
File: JFDPSF.07 D7
Operator: JFD RUN#256
Plotted: 4-Oct-82 12:00:57
ORIGINAL PAGE IS OF POOR QUALITY
[——] Frequency (Hz)
[——] Time (min)
[- - -] Damping (mV)
Temperature (°C)
DuPont 1090

FIGURE 5

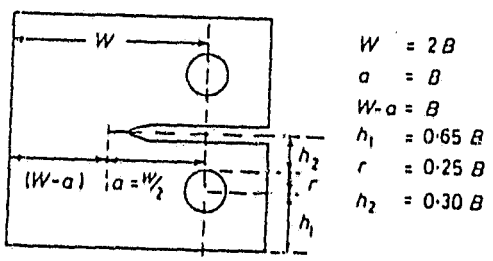


TBA of Hq 50%/Bp 50% PSF Copolymer

SPECIMEN GEOMETRY FOR
FRACTURE TOUGHNESS MEASUREMENTS (31)



(A) Single edge crack three point bend test piece



(B) Compact tension test piece

$$K_{IC} = \frac{3PLa^{1/2}\,Y}{Bw^2} \qquad (1)$$

P - load

L - 2w

B - thickness

w - width

a- crack length

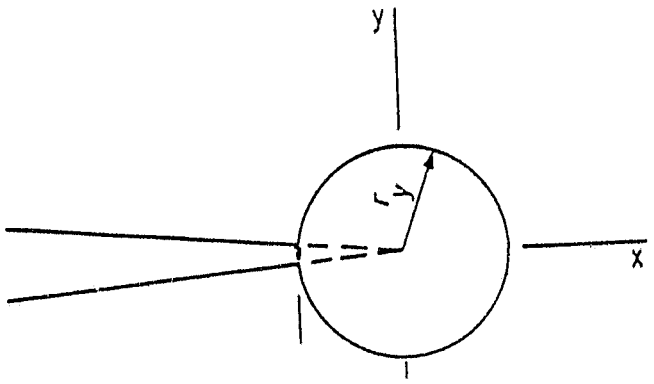
Y - geometric factor given by

$$Y = 29.6 - 186\,(a/w) + 656\,(a/w)^2 - 1017\,(a/w)^3 + 639\,(a/w)^4$$

Equation (1) indicates that the value of K_{IC} is directly proportional to the applied load which accounts for the specimen geometry and crack length. The fracture toughness number is valid provided that the load vs. crosshead displacement plot is linear. Any deviation from linearity is indicative of plastic deformation which means that LEFM no longer will produce a meaningful number. In such cases, utilization of J-integral analysis is appropriate (32).

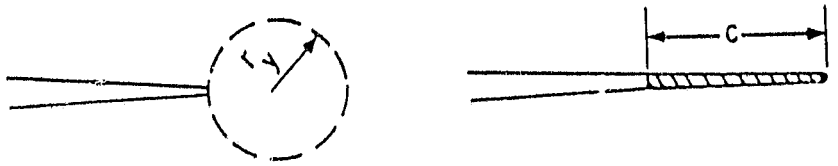
The infinitely sharp crack serves to increase the yield strength of the material by reducing the shear stresses which increases the constraint on the material. Moreover, it provides a site for stress concentration. In fact, the stresses at the tip of the crack front would approach infinity if the sample didn't yield at this point. This yielding gives rise to a plastic zone with a radius r as shown below in Figure 7 (33).

Figure 7



The value of r is dependent on the toughness and the yield strength of the material. The two most important models for predicting crack tip deformations are the Irwin and Dugdale models. The Irwin model predicts a yielding or plastic zone r and the Dugdale model predicts a craze zone with length C as shown in Figure 8 (24).

Figure 8



$$2r_y = \frac{1}{\Pi}\left(\frac{K}{\sigma_0}\right)^2$$

IRWIN MODEL

$$c = \frac{\Pi}{8}\left(\frac{K}{\sigma_0}\right)^2$$

DUGDALE MODEL

In each model as the yield strength decreases or the fracture toughness, K_{IC}, of the material increases, the deformation at the crack tip increases. In order to obtain valid K_{IC} values, the size of the deformation at the crack tip must be small relative to the crack length, a, the thickness of the sample, B, and the remaining ligament w-a, as shown below (33)

$$a > 40\ r_y$$

$$B > 40\ r_y$$

$$w-a > 40\ r_y$$

If the size of the plastic zone is too large, LEFM may no longer be used because the fracture mode will shift from plane strain to plain stress.

A SEM micrograph of the fracture surface of the Hq/Bp PSF (shown in Figure 9) indicates that fracture has indeed occured in a brittle manner in the plane strain mode, with only negligable plastic deformation. Therefore, K_{IC} values for these structures may be easily obtained for these systems.

The fracture toughness values for the Hq/Bp 50% PSF copolymer and the Bis-A PSF are given in Table 3. The fracture toughness of the Hq/Bp PSF is superior to that of Bis-A PSF. In fact, in comparison to fracture toughness values obtained by Ting (34) on commercial polysulfones, the Hq/Bp PSF exhibits comparable values to Union Carbide's Radel and is superior to both Union Carbide's UDEL and ICI's polyether sulfone.

END OF PRENOTCHED CRACK →

BRITTLE FRACTURE UPON INITIAL CRACK PROPAGATION →

AS CRACK PROPAGATES, SMALL AMOUNT OF PLASTIC DEFORMATION OCCURS →

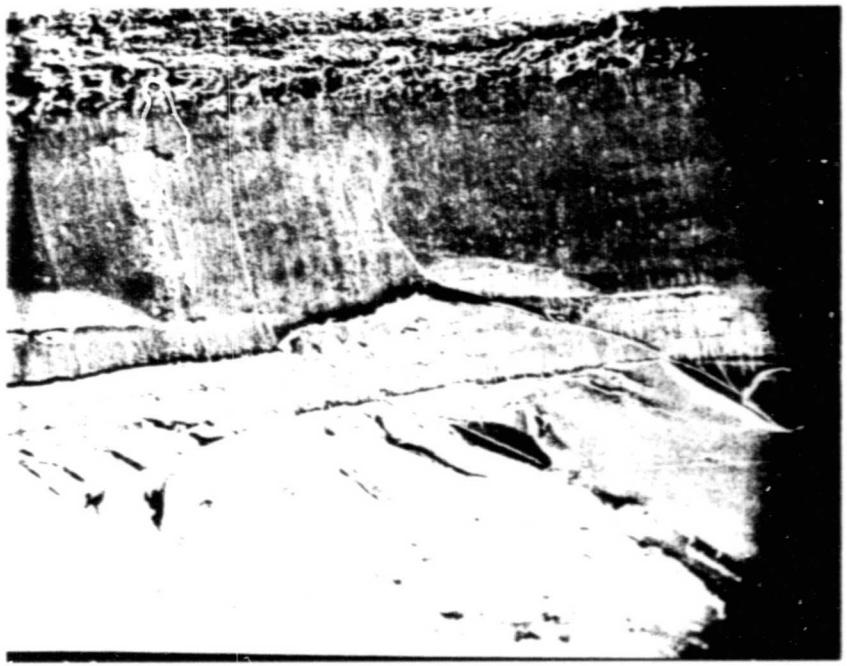


FIGURE 9

CONCLUSIONS:

- BRITTLE FRACTURE OCCURS IN THE PLANE STRAIN MODE
- K_{IC} MAY BE EASILY OBTAINED

Table 3

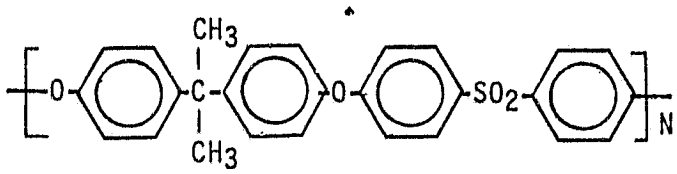
Fracture Toughness*, K_{IC}, Values for Two Poly(arylene ether sulfones)

	K_{IC} (psi $\sqrt{in}$)
Bis-A PSF	2300
Hq/Bp 50% PSF Copolymer	3100

* Crosshead speed 5.0mm/min.

II. Effect of Polysulfone Structure on Radiation Degradation by Electron Beam Sources

J. H. O'Donnell and coworkers (5-7) have shown that polyarylene ether sulfones are the most radiation resistant organic thermoplastic materials studied to date. In fact, these structures retain their mechanical integrity and show only small changes in molecular weight at low radiation doses. The two structures previously investigated were those commercially available namely Union Carbide's UDEL (Bis-A PSF) and ICI's polyether sulfone (Bis-S PSF).



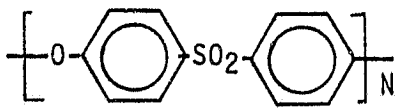
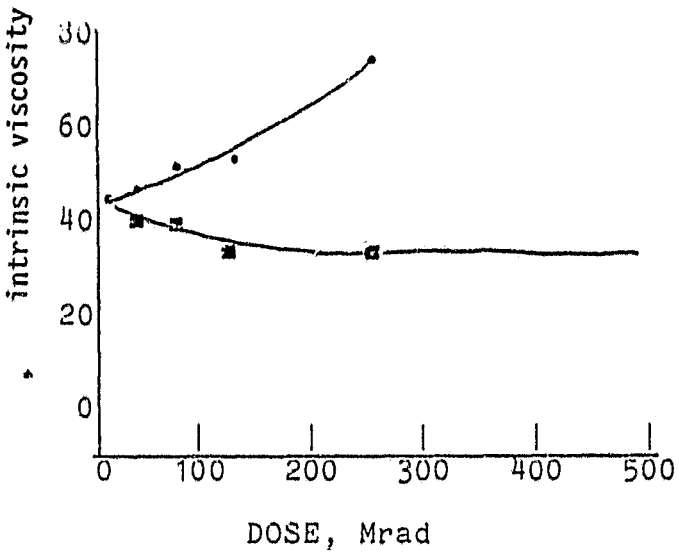


Figure 10 (5-7) shows an intrinsic viscosity plot as a function of radiation dose. When the Bis-A PSF is irradiated under a vacuum,gelation occurs at 250 Mrads. This is a consequence of the prolonged lifetime of the radical which leads to crosslinking as the major mode of degradation. In contrast, the Bis-S PSF remains soluble up to 575 Mrads in a vacuum. The difference in the behavior in these two structures was attributed to the presence of aliphatic character (isopropylidene linkage) associated with the Bis-A PSF.

The Hq/Bp PSF copolymer is a wholly aromatic structure which shows excellent radiation resistance and moreover these structures have mechanical properties similar to both commercial samples.

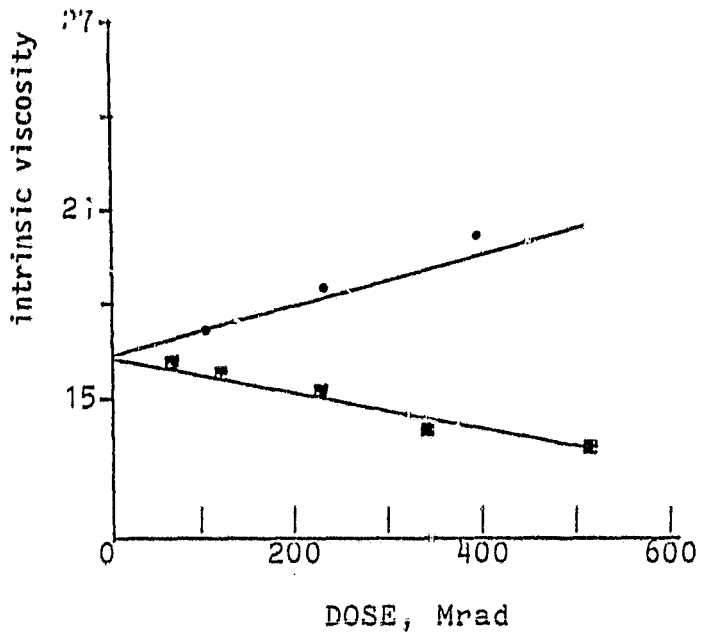
FIGURE 10

PREVIOUS RADIATION STUDIES ON COMMERCIAL POLYSULFONES



Limiting viscosity number, [η], versus dose for irradiation: (□) in air and (○) in vacuum

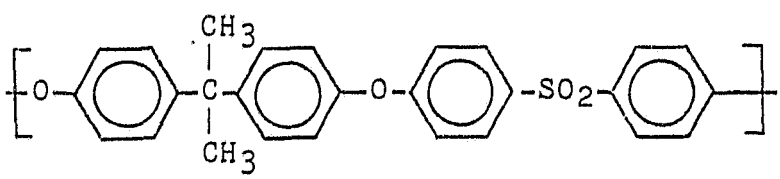
BIS A PSF:



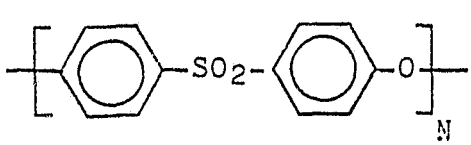
Limiting viscosity number, [η], versus does for irradiation of polysulfone II: (□) in air; (○)under vacuum.

BIS S PSF

BIS-A PSF:



BIS-S PSF:



Both Hq/Bp 50% PSF copolymer and the Bis-A PSF were exposed to electron radiation from a van de Graaf generator at doses of 120, 360 and 690 Mrads. Upon exposure, the samples darkened to a deep yellow brown which O'Donnell (35) had earlier attributed to trapped electrons, free radicals and a variety of complex intermediates, as well as variation in structures.

The tensile properties, before and after the irradiation for both structures, were determined and are shown in Tables 4 and 5. The Bis-A PSF retains much of its mechanical integrity after 120 Mrads. However, at the higher doses, the ductile properties of the Bis-A PSF are lost and the samples become very brittle.

In contrast the Hq/Bp PSF were observed to retain their mechanical properties even at the highest radiation doses studied. The modulus remains unchanged, although the yield strength decreases only slightly, and the ultimate strength and tensile strength remain unchanged at all radiation doses. The changes in the mechanical properties, especially in the Bis-A PSF are indicative of a decrease in molecular weight.

Thermal analysis including DSC and TGA, was performed on each of the structures at the various radiation doses. Both the Bis-A PSF and Hq/Bp PSF copolymer show a continuous decrease in the glass transition temperature as the radiation dose is increased, as illustrated in Tables 6 and 7. The decrease in the glass transition temperature is indicative of a decrease in molecular weight.

Table 4

Tensile Properties of Bis-A PSF as a Function of Electron Beam Dose

Dose (Mrad)	Tensile Modulus (MPa)	Yield Stress (MPa)	Elongation at Yield (%)	Tensile Stress (MPa)	Elongation to Break (%)
0	?	67	7	57	86
120	1424	63	6.0	54.3	65
360	1193	62	5.2	--	--
690	Too Brittle to Test		--	--	--

Table 5

Tensile Properties of Hq/Bp PSF as a Function of Electron Beam Dose

Dose (Mrad)	Tensile Modulus (MPa)	Tensile Yield (MPa)	Yield Elongation %	Tensile Stress at Fracture (MPa)	Elongation at Fracture %
0	1486	78	8.2	76	75
120	1368	70	8.2	70	79
360	1397	69	7.6	70	75
690	1436	66	7.5	65	70

Table 6

Thermal Analysis of the Glass Temperature (DSC) of Bis-A PSF as a Function of Electron Beam Radiation Dose

Dose (Mrads)	Tg(°C)
0	188
120	186
360	182
690	178

Table 7

Thermal Analysis of the Glass Temperature (DSC) of Hq/Bp PSF as a Function of Electron Beam Radiation Dose

Dose (Mrads)	Tg(°C)
0	217
120	216
360	213
690	208

The thermogravimetric traces show no change in thermal stability (as judged by weight loss) for either of the polymers as a function of dose. These data are shown in Figures 11 and 12.

Under the test conditions previously described in this current study both the Hq/Bp PSF and the Bis-A PSF remained soluble, even at the highest radiation dose, therefore, GPC was possible for each sample. The Bis-A PSF showed a strong shift to higher elution volumes which is indicative of the presence of lower molecular weight species. Furthermore, the breadth of the peaks increased as well. The GPC results for the Bis-A PSF are provided in Figure 13. The Hq/Bp PSF showed only a relatively minor shift to higher elution values as shown in Figure 14. However, there was a broadening on the low molecular weight end of the peak. It is apparent that chain scission is the predominate mode of degradation in these experiments from the mechanical, thermal and molecular weight analysis.

O'Donnell, et al (5-7) have investigated the mechanism of degradation in several polysulfone samples. From ESR and gaseous products studies one of the weakest links in these structures is the sulfur of the sulfone group and the aromatic carbon bond. This is apparent in Figure 15 (5) that sulfur dioxide is the major gaseous product constituent.

From these results we decided to follow the absorbance of the sulfone group as a function of radiation dose using an FTIR. FTIR was not sufficiently sensitive to monitor the small changes in these structures induced by irradiation. Moreover, ^{13}C NMR was also insensitive to these small changes in the structure. However, Sykes, et al (4) was able to detect changes in the IR spectra but only after very high dosage (1000 Mrads).

From this preliminary study we believe that small amounts of oxygen were probably present during these current radiation studies. As indicated by

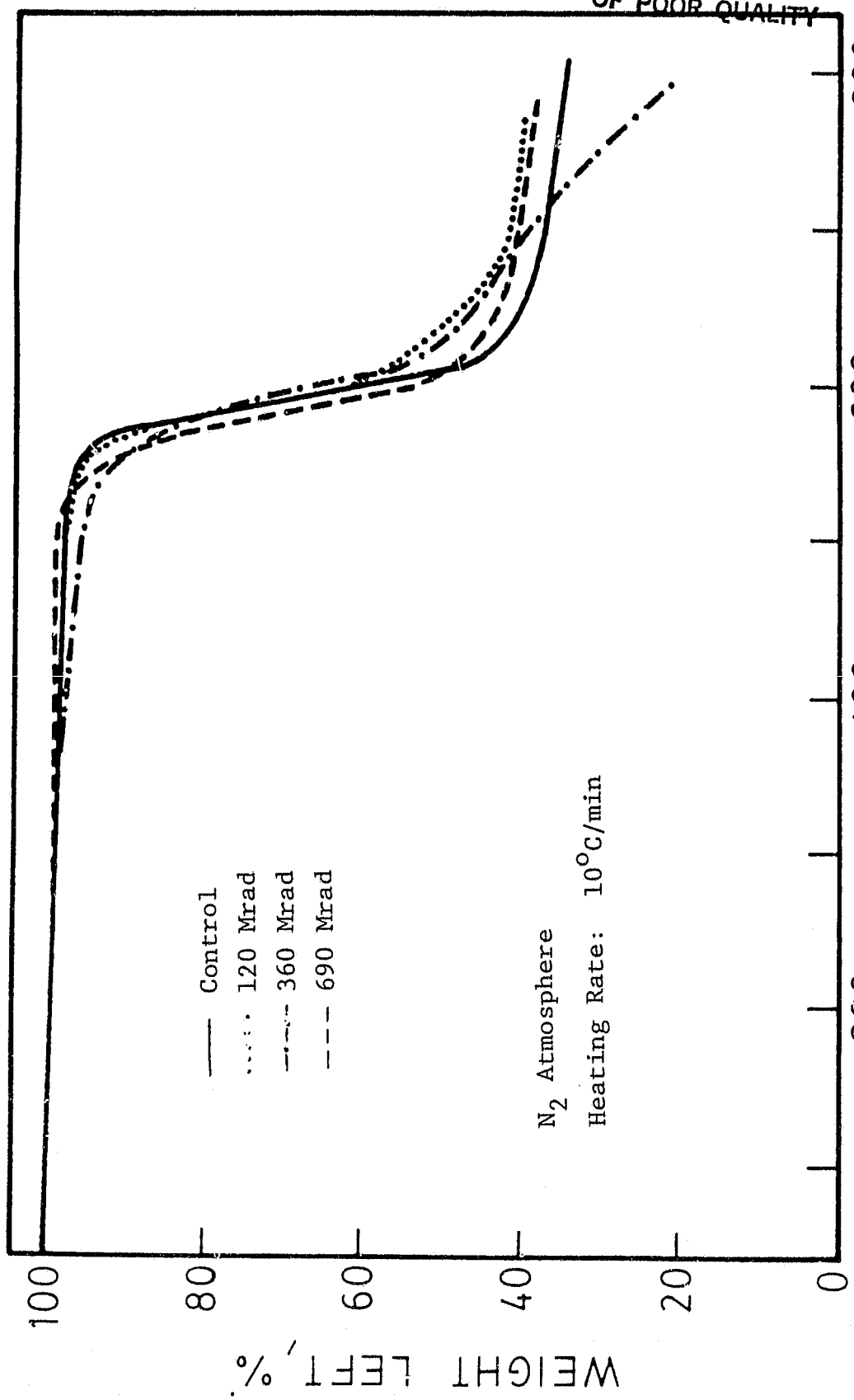


FIGURE 11. THERMOGRAVIMETRIC ANALYSIS OF BIS A/PSF COPOLYMERS AS A FUNCTION OF ELECTRON BEAM RADIATION DOSE

FIGURE 12. THERMOGRAVIMETRIC ANALYSIS OF Hq/Bp-PSF COPOLYMERS AS A FUNCTION OF ELECTRON BEAM RADIATION DOSE

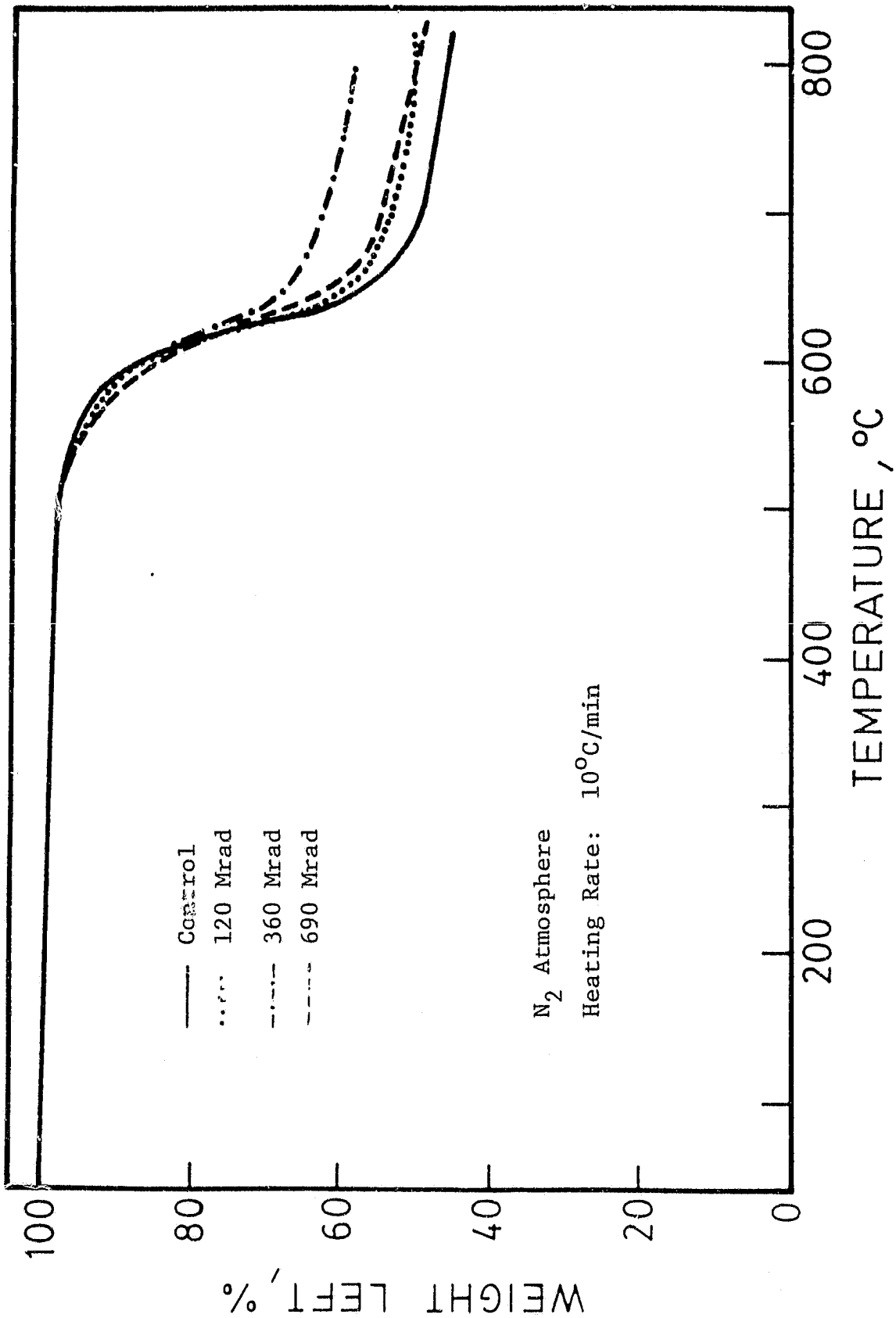


FIGURE 13. GPC CHROMATOGRAMS FOR BIS A-PSF COPOLYMERS AS A FUNCTION OF ELECTRON BEAM RADIATION DOSE

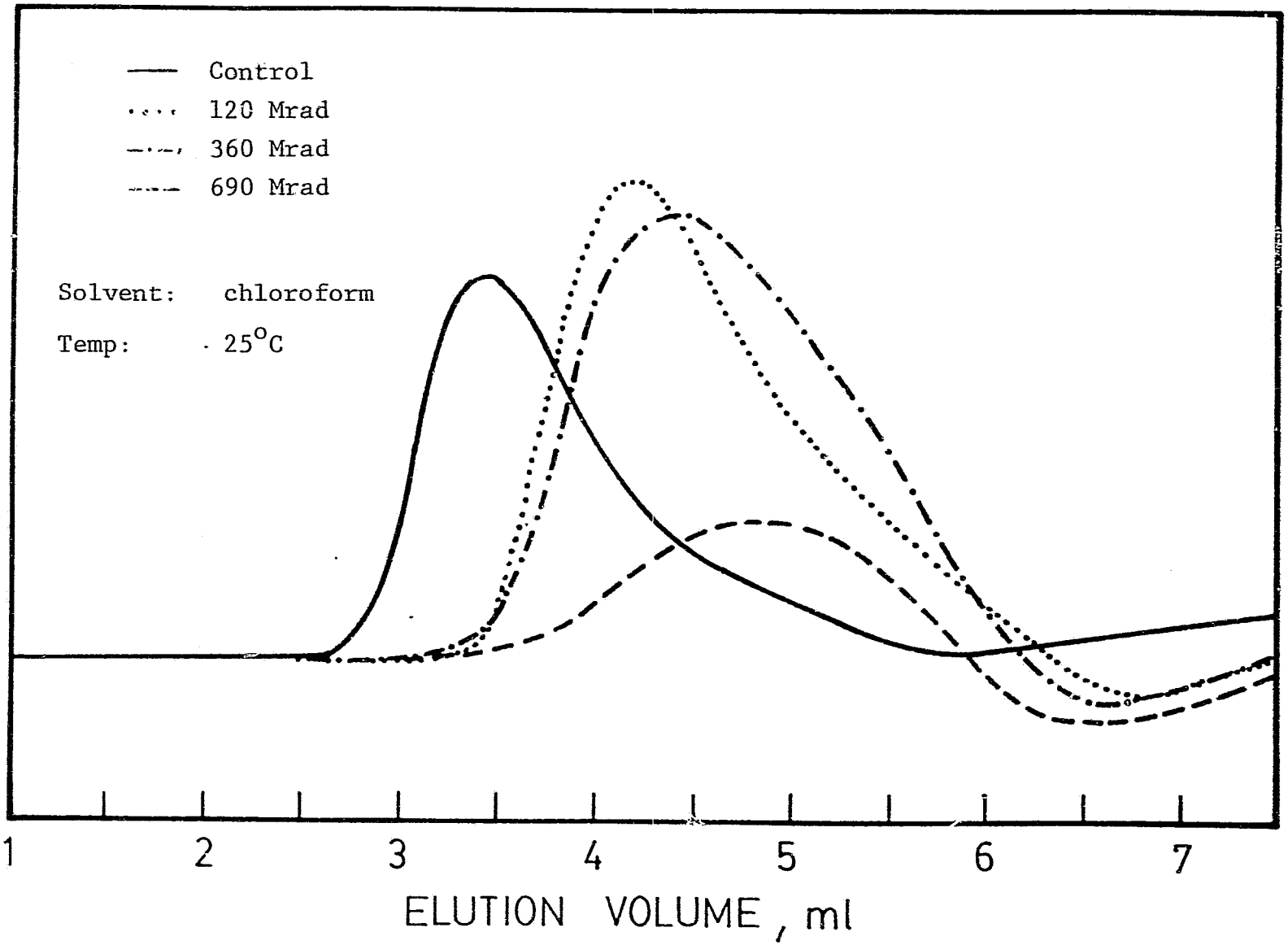


FIGURE 14. GPC CHROMATOGRAMS OF Hq/Bp-PSF COPOLYMERS AS A FUNCTION OF ELECTRON BEAM RADIATION DOSE

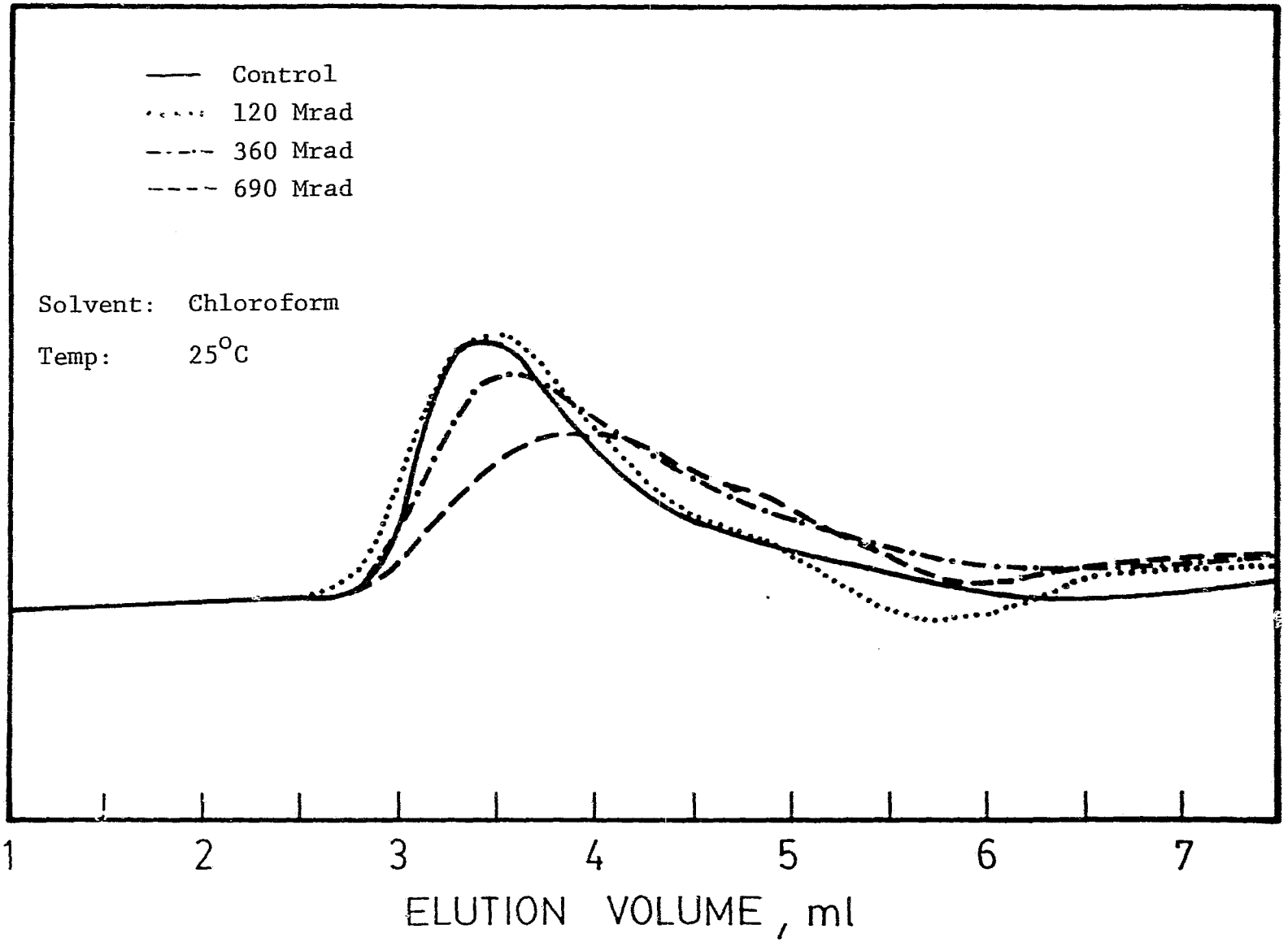


FIGURE 15. A REVIEW OF THE GASEOUS PRODUCTS OBSERVED DURING PREVIOUS RADIATION DEGRADATION STUDIES OF AROMATIC POLYSULFONES (5)

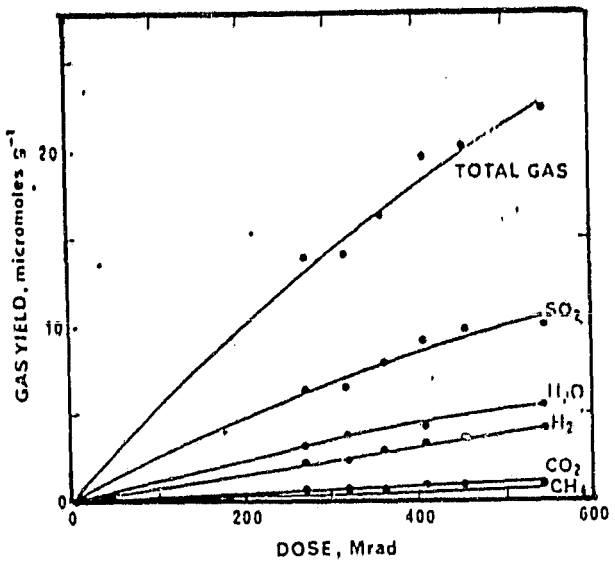


Fig. 3. Volatile product yields vs. dose for irradiation of polysulfone I at 30°C under vacuum.

BIS-A PSF

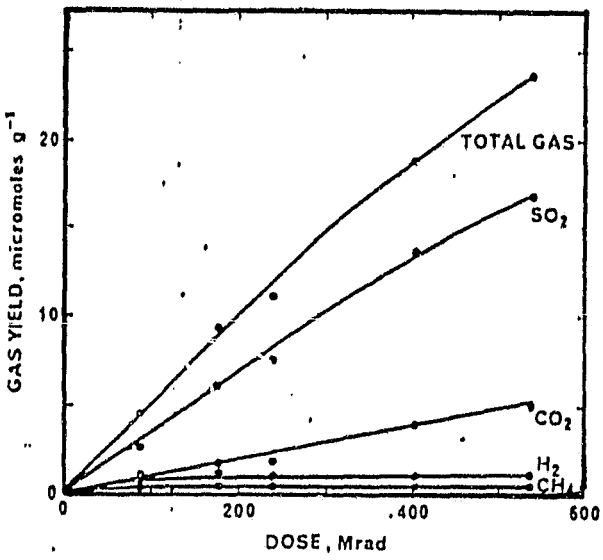


Fig. 4. Volatile product yields vs. dose for irradiation of polysulfone II at 30°C under vacuum.

BIS-S PSF

previous studies illustrated in Figure 10, the Bis-A PSF remains soluble and chain scission is the most important mode of degradation when oxygen is present. Therefore, under these conditions in this preliminary investigation, the Hq/Bp PSF shows superior radiation resistance to the Bis-A PSF. In fact, these copolymers retain most of their mechanical integrity and show only small changes in molecular weight.

III. Synthesis and Characterization of Polysulfone/ Poly(dimethyl siloxane) Segmented Copolymers

We have recently synthesized segmented or block copolymers of polysulfone and poly(dimethyl siloxane). These copolymers were synthesized by the interaction of dihydroxyl-terminated polysulfone oligomers and bis(dimethylamine)-terminated poly(dimethyl siloxane) oligomers in chlorobenzene at relux temperatures as illustrated earlier in Scheme II. This step-growth or condensation reaction evolves gaseous dimethylamine as the sole by-product and leaves an essentially pure solution of block copolymer.

The structure of these block copolymers is well defined because each of the oligomers can only react with each other. Thus the reaction yields a perfectly alternating block copolymer of the $-(A\text{-}B)_n$-type. The end blocks are designed to be polysulfone (the hard segment) so as to minimize the presence of hydrolytically unstable silyl-amine end groups.

A variety of copolymers were successfully synthesized by this technique as illustrated in Table 8. The molecular weight of the oligomers ranged from 4000-20,000 g/mol^{-1}. The lower molecular weight oligomers were the most straight forward to synthesize due to the abundance of reactive end groups. High molecular weights were also obtained in each of these structures as indicated by the intrinsic viscosity values, also included in Table 8.

An important feature involved in the synthesis of these structures is the necessity of minimizing homopolymer contamination. It is very difficult to remove any unreacted polysulfone. Furthermore, homopolymer contamination typically yields both a cloudy solution and cast film effects. The mechanical properties are no doubt effected as well. GPC was utilized to indicate the distribution of species in the copolymer. Figure 16 shows the GPC traces for several of the copolymers. It is important to note that in each case a

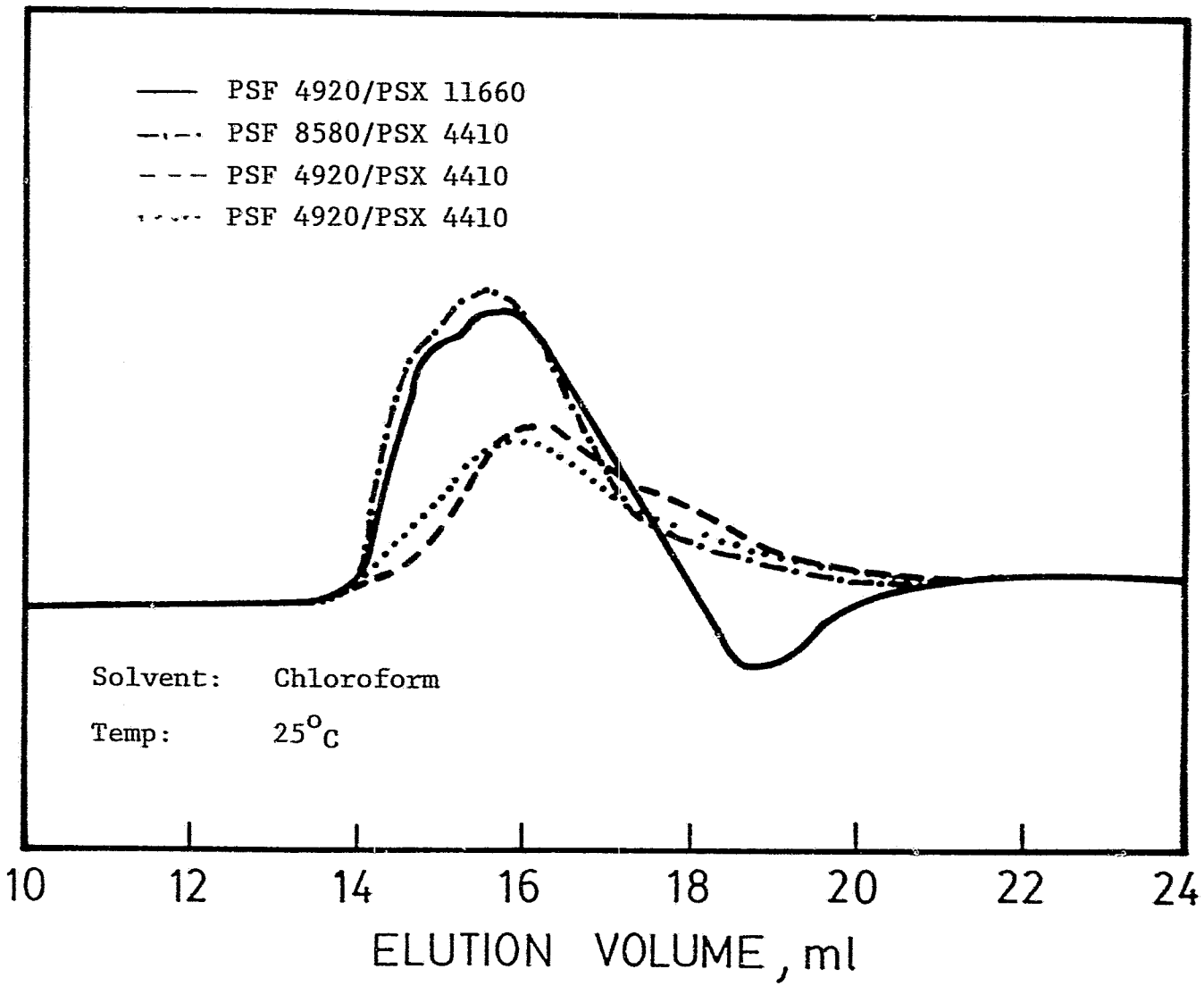
Table 8

Characterization of PSF/PSX Block Copolymers

Molecular Weight of Oligomer PSF / PSX	$[\eta]_{25°C}^{CHCl_3}$	Low Temperature Transitions Tg	Tc	Tm	High Temperature Transition Tg
4919 / 4409	0.67	-127	-	-	147
4919 / 4409	0.60	-125	-	-	139
8575 / 4409	0.67	-128	-99	-51	189
4919 / 12,800	0.55	-126	-99	(-62,-50)	120
9700 / 12,800	1.27	-124	-86	-47	143
13,441 / 12,800	1.14	-127	--	(-62,-48)	*
17,054 / 4409	1.03	*	*	-44	187
17,054 / 12,800	1.00	-130	-90	-43	189

* Very weak transition

FIGURE 16. GPC CHROMATOGRAMS OF PSF/PSX COPOLYMERS



unimodal molecular distribution is obtained.

Another way to evaluate the extent of the reaction is by proton NMR. By integrating the area from the isopropylidene linkage of the polysulfone block and comparing on a weighted basis to that of the methyl groups of the poly(dimethyl siloxane) block, the amount of siloxane incorporated in the copolymer may be calculated and compared to the amount actually charged. The following chart illustrates some of these results.

Characterization: Percent* Siloxane Incorporated in PSF-PSX Block Copolymers

Sample PSF	/ PSX	AMT PSX Charged Wt. Percent	AMT PSX Incorporated Wt. Percent
4919	4409	47.3	46
4919	4409	47.3	50.7
13,000	11,700**	46.4	37.7

* Determined by ^{1}H NMR.
** Contained significant amounts of homopolymer.

Both the polysulfone and the poly(dimethyl siloxane) homopolymers show excellent thermal and oxidative stability. Therefore, it is not surprising that the copolymers show these properties as well. Thermogravimetric analysis measurement under nitrogen shows the onset of weight loss at 400°C as indicated in Figure 17.

Furthermore, these copolymers show excellent hydrolytic stability, primarily due to the hydrophobic nature of the siloxane blocks, the two phase system and the low concentration of the water susceptible carbon-oxygen-silicon linkages (36).

The morphology of these PSF/PSX block copolymers can be influenced by

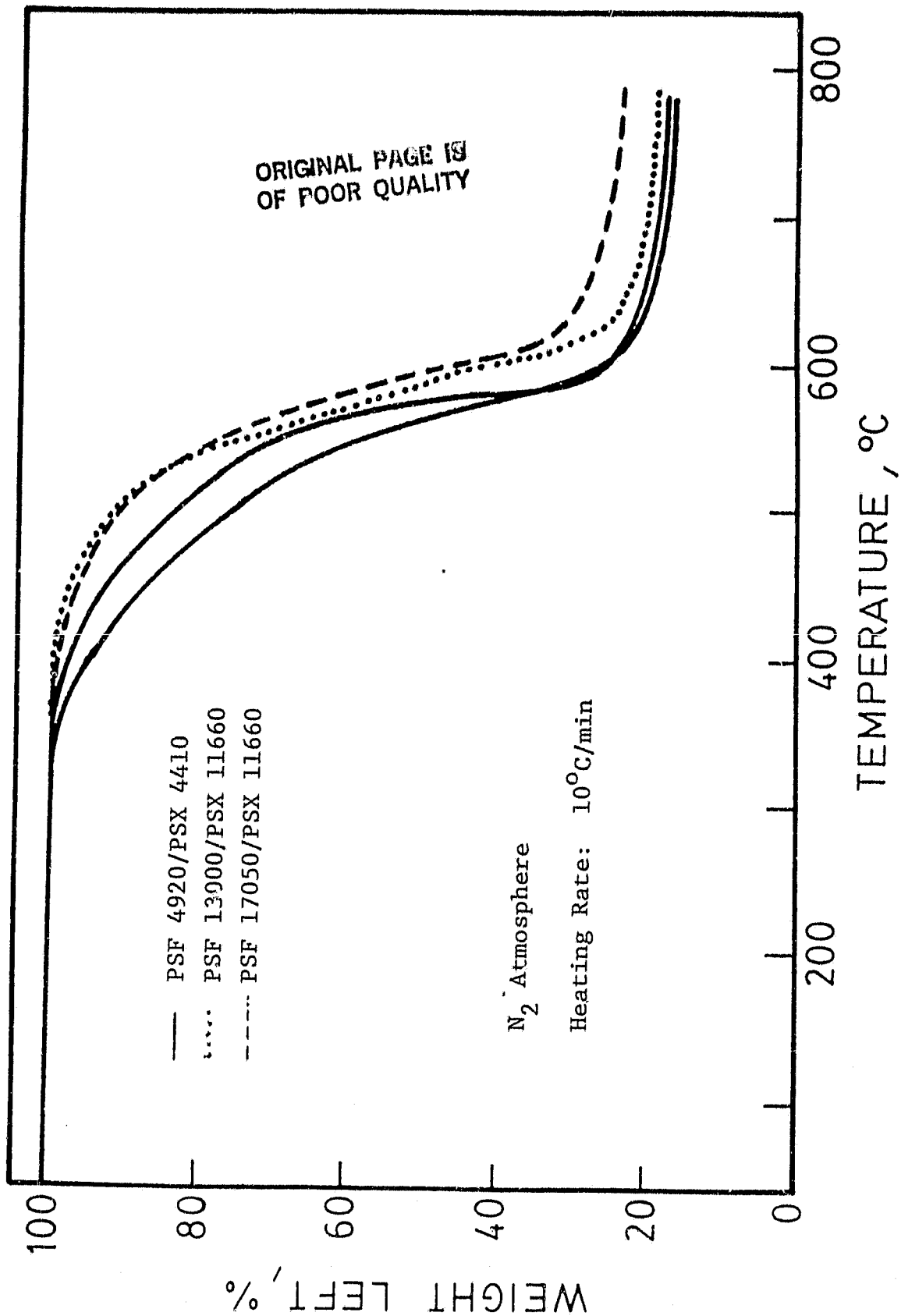


FIGURE 17. THERMOGRAVIMETRIC ANALYSIS OF PSF/PSF COPOLYMERS

varying the molecular weight of the oligomers. Oligomers of low molecular weight reported (36) gave single phase block or segmented copolymers, while blocks > 4000 $\langle\bar{M}_N\rangle$ produced two microphase systems due to the domain formation. The latter copolymers showed two glass transition temperatures: one at -120 due to the polydimethylsiloxane phase and another at 145-160°C resulting from the polysulfone phase as indicated in Table 8. For siloxane blocks of molecular weight > 11,000 $\langle\bar{M}_N\rangle$, a crystallization exotherm and two melting endotherms are typically observed. The extensive phase separation in these systems is attributed primarily to the incompatability of the polysulfone with the poly(dimethylsiloxane) (Solubility parameters equal 10.6 and 7.3, respectively) (36).

In addition to thermal analysis, STEM micrographs (39) were also used to confirm the morphology of these copolymers. The films were prepared by conventional microtoning techniques. The micrographs in Figure 18 illustrate the two phase morphology of the PSF/PSX 4900/4400 block copolymer. The EDAX analysis shows that the continuous phase is primarily the polysulfone component, while the discrete phase is primarily but not exclusively the siloxane block.

The mechanical properties of these segmented systems vary depending on the oligomer molecular weight ratio. These materials can vary from stiff and rigid to one that is flexible, and shows high elongation as indicated in Figure 19. The copolymers of high siloxane content show no plastic deformation and behave in a linearly elastic fashion up to 280% elongation where they break. This is a result of their two phase morphology where the polysulfone acts as an "anchor" site producing a physically crosslinked system (36). In contrast, those copolymers with a high polysulfone content are rigid polymers with a high modulus and undergo yielding.

STEM Micrographs of PSF/PSX 4900/4400 Copolymer

(a) 6350x
(b) 10,500x
(c) 2300x
(d) 49,000x

Fig. 18 p. 1

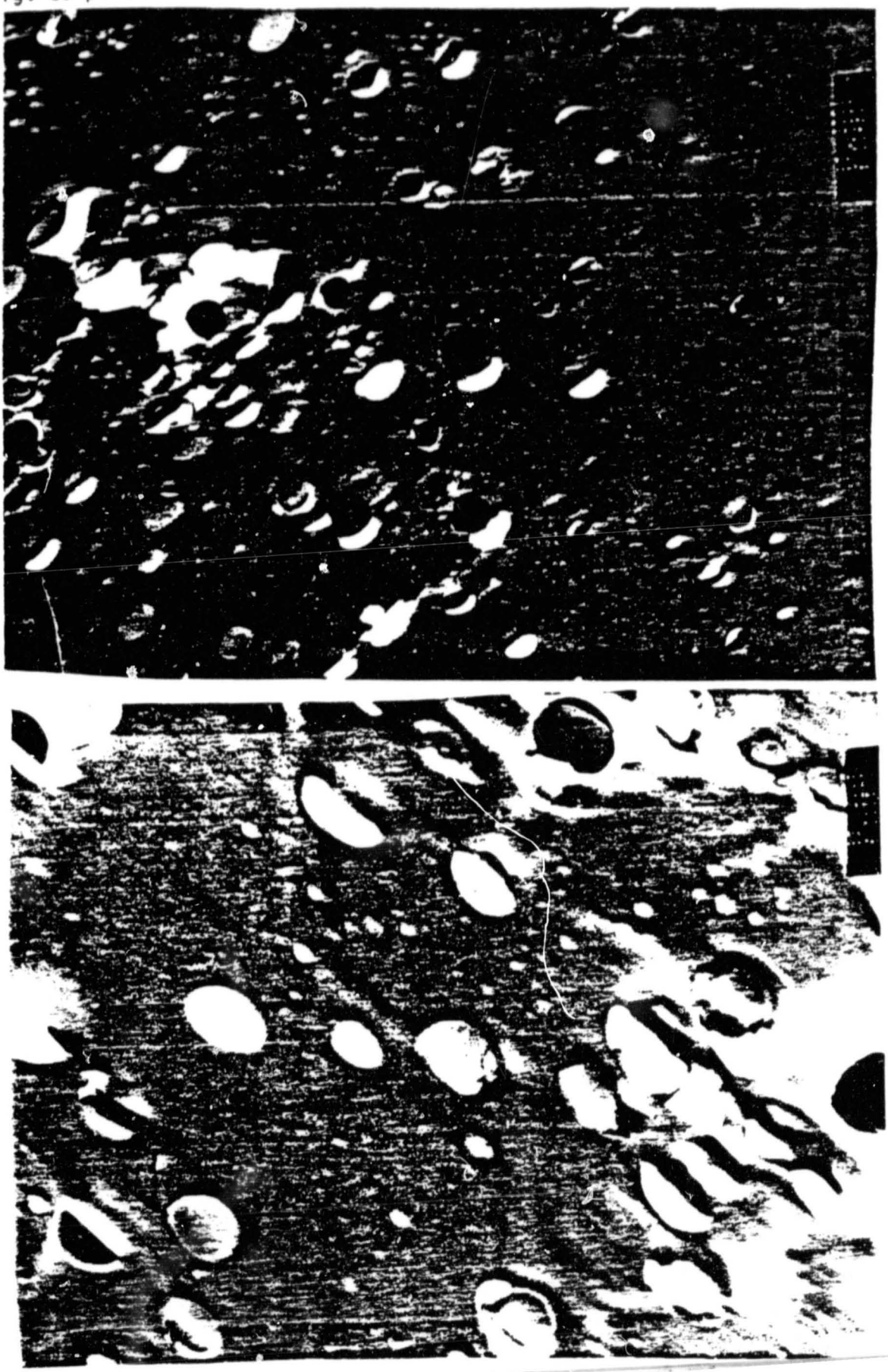


Fig. 18 p. 2

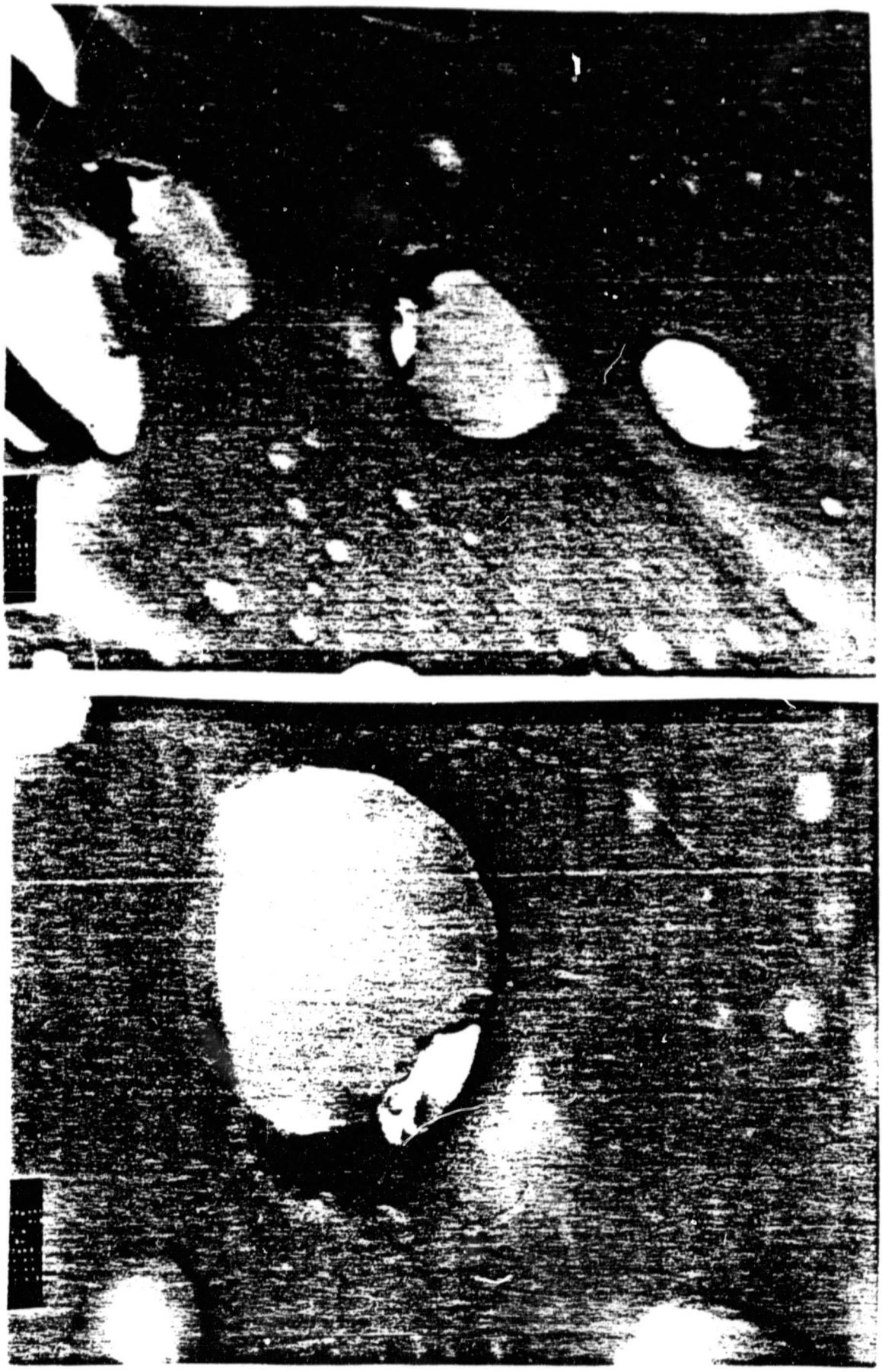
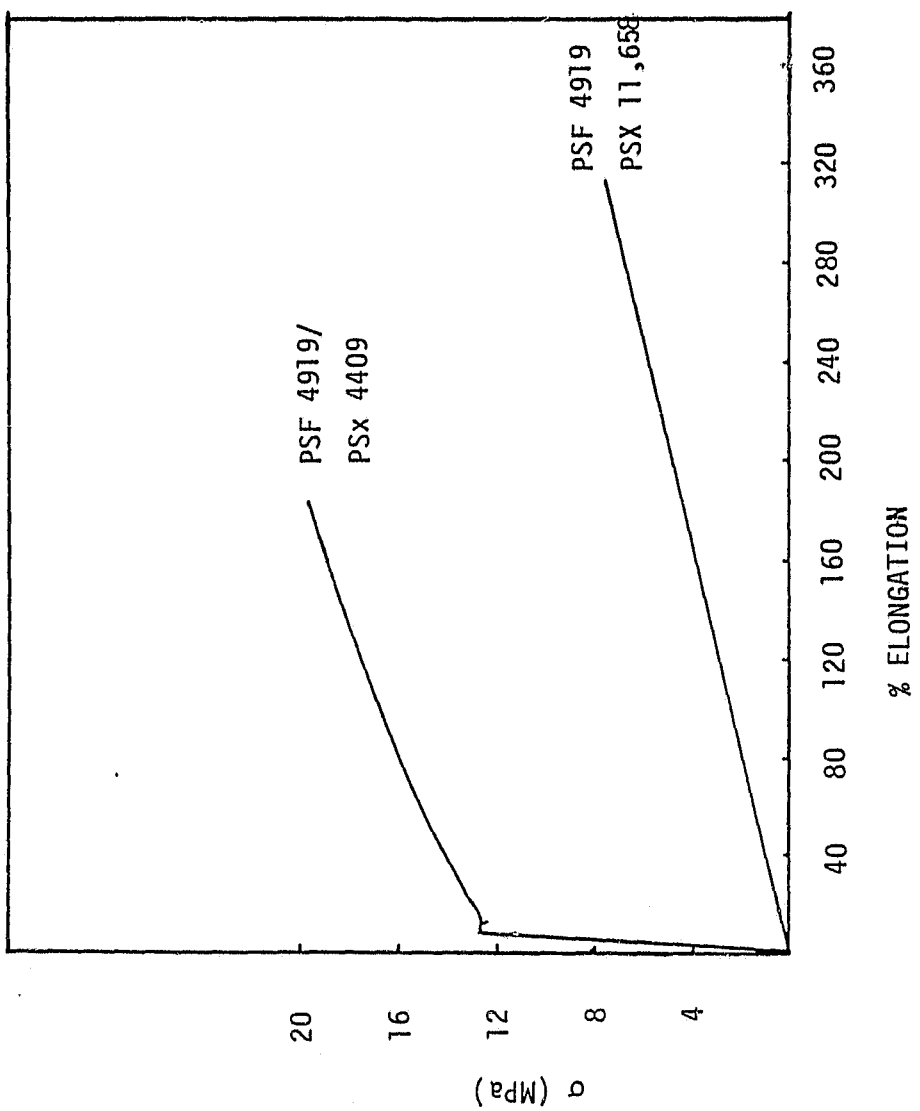


FIGURE 19. STRESS-STRAIN BEHAVIOR OF POLYSULFONE-POLYDIMETHYL SILOXANE BLOCK COPOLYMERS



Unfortunately, these PSF/PSX copolymers show poor melt processability due to their incompatibility even in the melt. Because these structures retain their 2-phase morphology in the melt, they typically show very high melt viscosity and melt fracture upon extrusion. Most thermoplastic elastomers which may be thermally processed, such as SBS (36), have a difference in solubility parameter of about 1.0. However, Matzner (37,38) has attributed the poor melt processability of PSF/PSX segmented copolymers to their vast difference in solubility parameters.

IV. PSF/PSX BLENDS WITH HOMOPOLYSULFONE

Results and Discussion

Most of the results to date were obtained by blending a copolymer that had segment molecular weights of about 4400 and 4900 grams per mole for the siloxane and polyarylether, respectively. The intrinsic viscosity of the copolymer was 0.6 dl/gram. The blends are listed in Table 9 with the composition shown in terms of both weight percent polydimethylsiloxane and weight percent of the entire block copolymer.

The environmental stress-cracking results are shown in Table 10 for cyclohexanone. As can be readily seen, the values are lower for the blends than for the homopolymer. One point not obvious from this table is the qualitative observation that although the final critical strain for the blends was lower, the time needed to reach these values was much longer. In other words, it appears that we may have changed the kinetics of stress cracking by the incorporation of siloxane into the polysulfone. We are attempting to observe the kinetics of the process in a more quantitative way.

The PSF/PSX copolymer contained in the blends segregates from the matrix of the homopolysulfone forming small particles ranging in size from 0.5 to 5.0 μ. The size and frequency of these particles increases with increasing copolymer concentration. The SEM photographs of the fracture surfaces in Figures 20 illustrate this phenomenon. The dark spots correspond to holes and the white spots are believed to be the copolymer particles.

The improved fracture toughness of these materials is attributed to the presence of these particles. The K_{IC} values for the homopolysulfone and two are tabulated in Table 11. These particles act as rubber-like modifiers, blunting the growing crack front providing a tougher material. By blunting the crack, the stress in this region is no longer concentrated, and

Table 9

Polydimethyl-Siloxane Block Copolymer (4400/4900) Blends with Polysulfone (a)

Blend	Wt. % PSX	Wt. % Copolymer
1	0.5	1.0
2	1.0	2.1
3	2.0	4.3
4	5.0	10.6

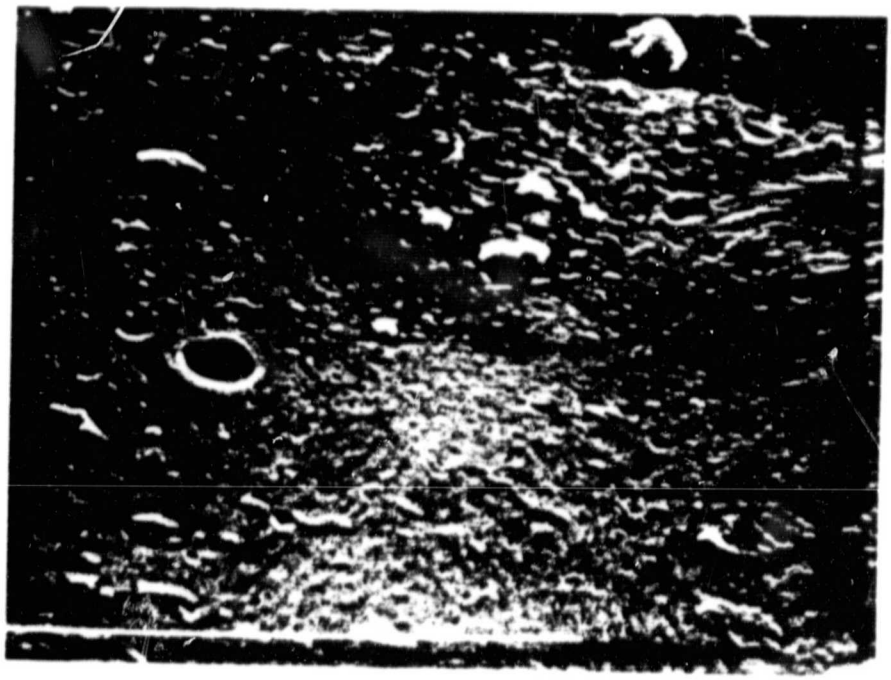
Table 10

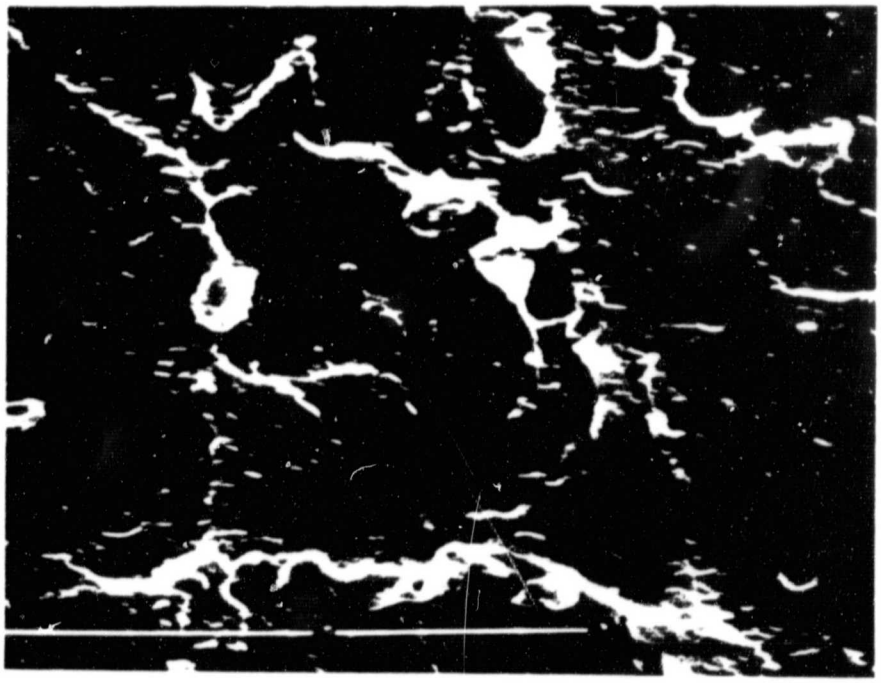
Environmental Stress Cracking Results for Sulfone-PSX/PSF Blends in Cyclohexanone

Wt. % PSX	ε_c(%)	Std. Dev., ±
0	0.174	0.002
0.5	0.156	0.004
1.0	0.156	0.004
2.0	0.154	0.003

Figure 20. SEM Micrographs of cold snap fracture surfaces of PSF 4919/ PSX 4401 copolymer blend with monopolysulfone.

(A) 0.5% PSX Blend
(B) 1.0% PSX Blend
(C) 2.0% PSX Blend





(Figure 20, cont.)

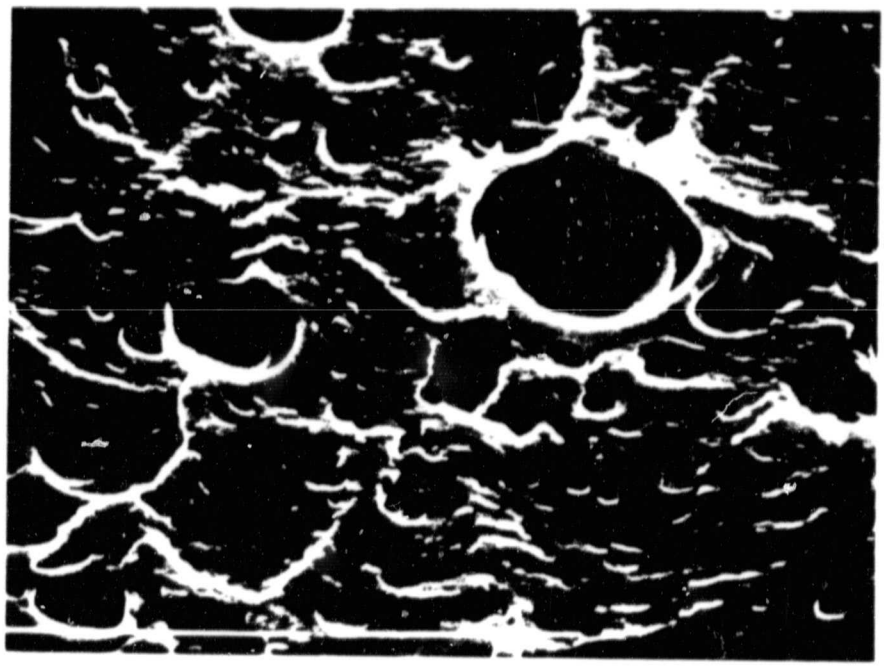


Table 11

Fracture Toughness of PSF/PSX Modified Blends

	% PSX Continued in Blend	K_{IC} ($N/m^{3/2}$)
PSF/PSX (4900-4400)		
	0	2.05×10^6
	0.5	3.56×10^6
	1.0	3.30×10^6
	2.0	*
	5.0	*
PSF/PSX (9700/12,800)		
	0.5	3.61×10^6
	1.0	4.04×10^6
	2.0	*
	5.0	*
PSF/PSX (4910/12,800)		
	0.5	3.30×10^6
	1.0	3.71
	2.0	*
	5.0	*

* Too tough to fracture in plane strain

consequently it requires more energy to propagate the crack through or around these particles suspended in the matrix. By the introduction of just a small amount of copolymer (1%) in the homopolysulfone, the fracture toughness increases by about 70% over that of the homopolysulfone. As the amount of copolymer in the matrix of the homopolymer increases the fracture toughness increases to such an extent that plane strain conditions are no longer satisfied. In fact, K_{IC} values can no longer be obtained. The J-integral analysis (32) must be utilized to obtain a J_{IC} value, the stress required to initiate stable crack growth. These values will not be reported since they cannot be directly compared to the K_{IC} values.

The tensile properties of two of the blends were measured with an Instron tensile tester as shown in Tables 12 and 13. The modulus and yield strengths increase slightly, while the yield strain decreases. The siloxane, being of lower surface tension, migrates to the surface providing a smooth surface. This conceivably accounts for the improvement in the modulus and the yield strength. However, the siloxane has a lower tearing strength than the polysulfone, thus decreasing in the yield strain.

The results of the quantitative treatment of the XPS data are summarized in Figure 21, where the weight % siloxane on the surface (calculated from C_{1s}/Si_{2s} peak areas) is plotted as a function of weight % siloxane in the bulk (calculated from blend composition and stoichiometry of the block copolymer). The siloxane on the surface remains constant below about 0.5% siloxane in the bulk and then increases by a factor of 2-3 before approaching the value exhibited by the pure block copolymer at about 10% siloxane in the bulk. Also since the XPS analysis depth is proportional to the cosine of the photoemission emission angle, it is evident that there is a rapid increase in siloxane concentration within the topmost molecular layer. The result is

Table 12

Tensile Properties of PSX 4410/PSF 4919 Blends with Homopolysulfone

Wt % PSX	E(MPa)	σ_y(MPa)	Elongation to Yield (%)
0	1450	67	7
0.5	1550	74	6
1.0	1470	64	6
2.0	1470	64	6
5.0	1550	64	5

* Instron

** Crosshead speed, 10 mm/min

Table 13

Tensile* Properties of PSF 4919/PSX 12,800 Blends with Homopolysulfone

Wt % PSX	E(MPa)	σ_y(MPa)	Elongation to Yield (%)
0.5	1620	77	5.8
1.0	1550	71	5.8
2.0	1460	68	5.8

* Instron

** Crosshead speed, 10 mm/min

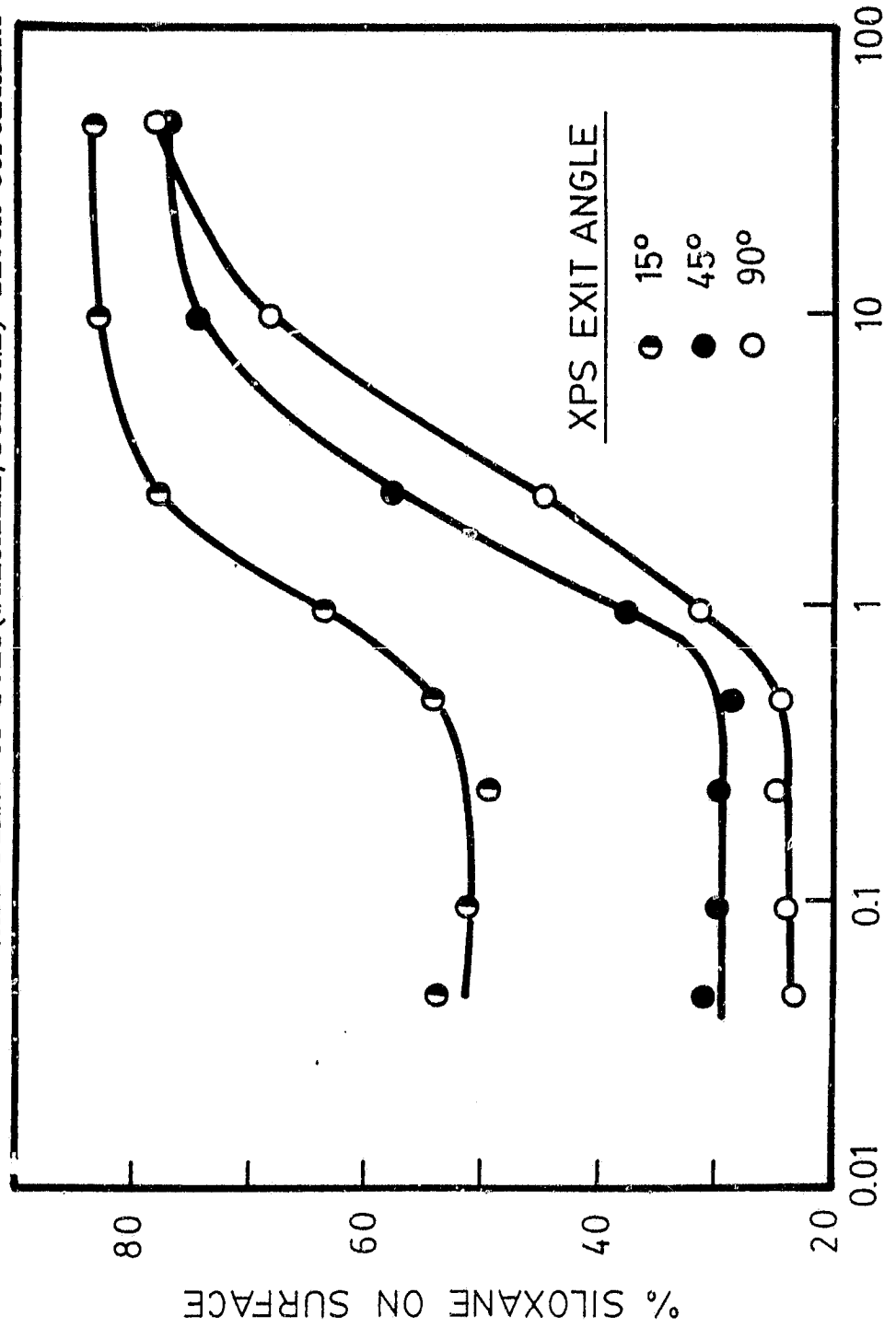


FIGURE 21. XPS INVESTIGATION OF SURFACE SEGREGATION IN CAST FILMS OF POLY(SILOXANE/SULFONE) BLOCK COPOLYMERS*

*Courtesy of Professor D. W. Dwight and Mr. N. Patel

qualitatively similar to those obtained in systems with siloxane blocks in combination with carbonate (18) and urethane (40).

A recent Scanning Transmission Electron Micrograph (STEM) (Figure 22) for the 0.5% PSX blend dramatically indicates a patchy surface in which the siloxane forms small domains of about 40μ. As the amount of PSX in the blends is increased the surface becomes totally covered with a continuous siloxane layer as indicated by the XPS results in Figure 21.

CONCLUSIONS

Wholly aromatic random copolymers of hydroquinone and biphenol with 4,4'-dichlorodiphenyl sulfone were synthesized via aromatic nucleophilic displacement. Their structures were characterized and mechanical behavior studied. These tough, ductile copolymers show excellent radiation resistance to electron beam treatment and and retain much of their mechanical properties up to at least 700 Mrads under argon.

In addition, perfectly alternating block copolymers of polysulfone and poly(dimethylsiloxane) (PSF/PSX) were synthesized by the silyl amine-hydroxyl reaction of the respective oligomers. Some basic structure-property relationships of these copolymers were examined. The addition of small amounts of these PSF/PSX copolymers to the homopolysulfone dramatically improved the impact and fracture toughness properties as expected. Moreover, surface modification in solution cast blends resulting from the migration of the siloxane to the air interface was achieved, as judged by ESCA measurements. Such phenomena may be important in toughness retention as a function of aging, UV stability of suitably pigmented coatings, and possibly in environmental stress cracking resistance (ESCR). Thus far, the ESCR critical measurements indicate that time to failure is increased with PSX modification, but that the critical strain to rupture itself is not enhanced.

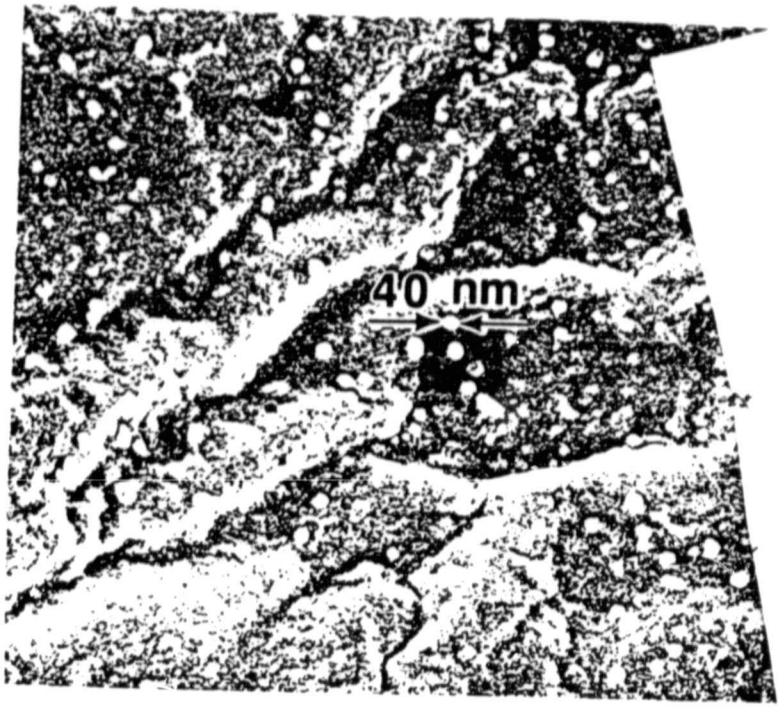


FIGURE 22. STEM Micrograph of the Surface of PSF/PSX 4900/4400 Blend at 0.5% PSX by Weight.

FUTURE WORK

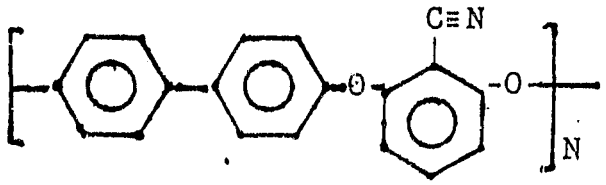
Recently, we have also synthesized new macromolecular structures in the following classes; poly(arylene ether sulfones), poly(arylene ether ketones), and poly(arylene ether nitriles) and imide containing copolymers. These are shown in Figure 23. Each of these materials are amorphous, but some have the potential for solvent induced crystallization. These wholly aromatic systems should prove to be also radiation resistant.

Other important structures presently under investigation include the polyimide-polysiloxane copolymers and polysulfone-polyimide copolymers shown in Figures 24 and 25, respectively. Degradation studies via UV and particulate radiation have been initiated.

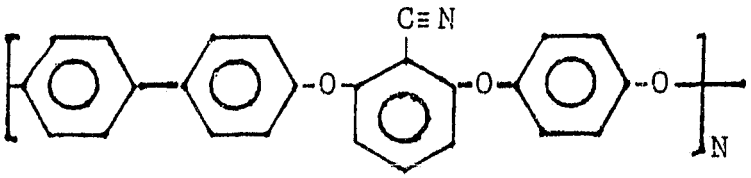
Additional characterization of the materials described in this report is planned. The areas will include supplementary e-beam degradation studies (especially under vacuum), Co^{60} treatement, gas yield analyses, ESCA and STEM studies with melt blends, and extended critical strain measurements.

FIGURE 23

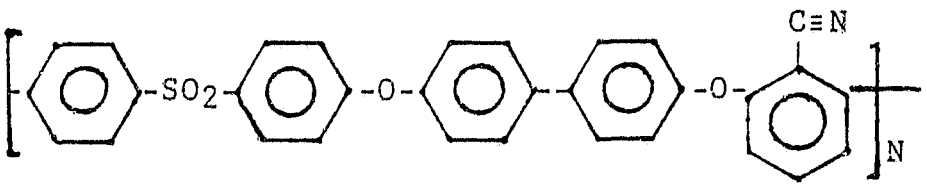
BIPHENOL POLYNITRILE



HYDROQUINONE/BIPHENOL POLYNITRILE



BIPHENOL POLYSULFONE/POLYNITRILE



BIPHENOL POLYKETONE/POLYNITRILE

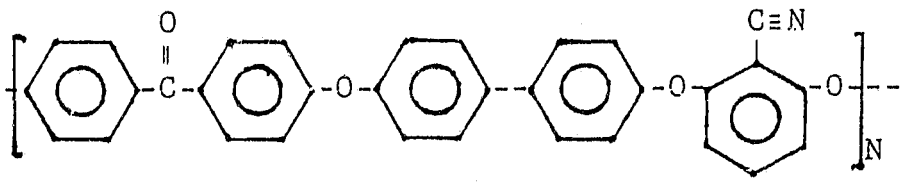
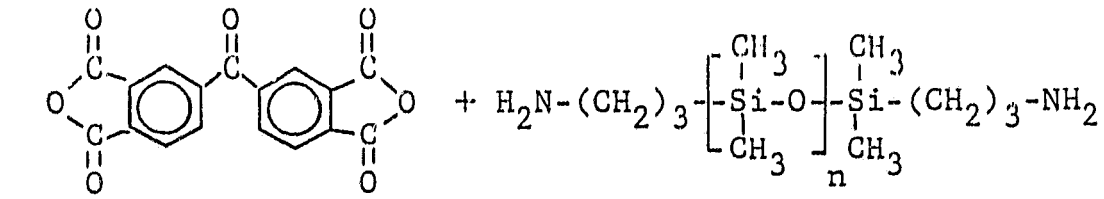


FIGURE 24

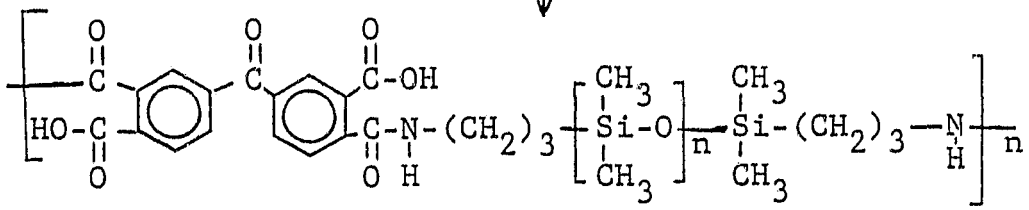
POLYIMIDE-POLYSILOXANE COPOLYMERS

REACTION:

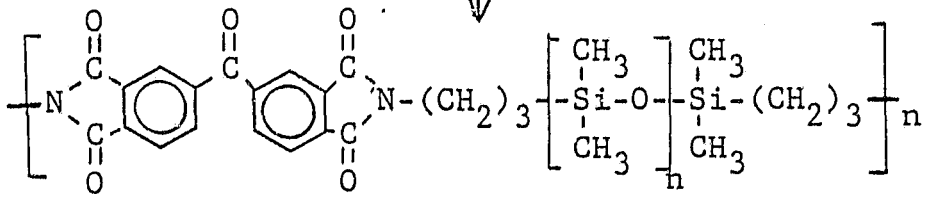


BTDA + POLYSILOXANE OLIGOMER

THF
ROOM TEMP



POLY(AMIC-ACID)

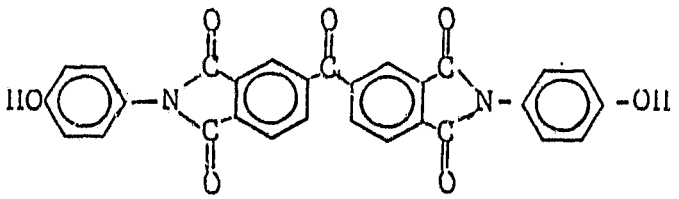


POLYIMIDE-POLYSILOXANE

FIGURE 25

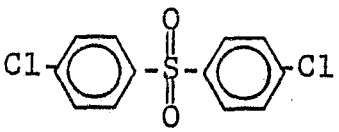
POLYIMIDE-POLYSULFONE COPOLYMERS

1)

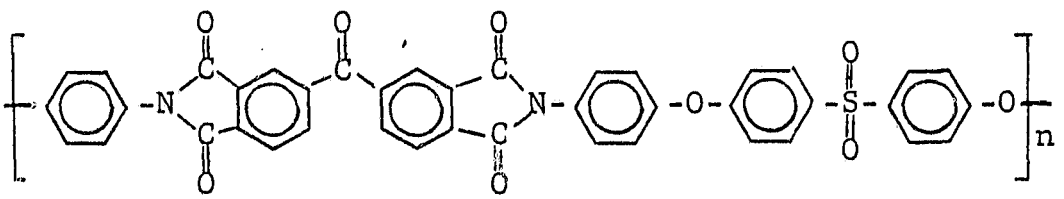


DIIMIDE BISPHENOL

+



NMP, K_2CO_3
150-190 C
TOLUENE
3-10 HRS



2) POLYIMIDE OLIGOMER (Mw = 2,000 to 10,000) OH TERMINATED REACTED WITH A Cl TERMINATED POLYSULFONE OLIGOMER (Mw = 2,000 to 10,000).

REFERENCES

(1) R. N. Johnson, Encyclopedia of Polymer Science and Technology, 11, p. 447 (1969).

(2) D. R. Tenney, G. F. Sykes, and D. E. Bowles, presented at AGARD Environmental Effects on Materials for Space Applications, Toronto, Canada, Sept. 22-24, 1982.

(3) R. M. Karland, J. F. Thomasson, and W. C. Beggs, Radiation Testing of Composite Materials, In Situ Versus Ex Situ Effects, NASA Contractor Report 3475, 1981.

(4) B. Santos and George F. Sykes, presented at the 13th National SAMPE Technical Conference, Mt. Pocono, Pennsylvania, Oc. 13-15, 1981.

(5) J. R. Brown and J. H. O'Donnell, Polymer Letters, 8, 121 (1970).

(6) J. R. Brown and J. H. O'Donnell, J. of Appl. Polym. Sci., 19, 405, (1975).

(7) J. R. Brown and J. H. O'Donnell, J. of Appl. Polym. Sci., 23, 2763, (1979).

(8) J. L. Hedrick, D. K. Mohanty, B. C. Johnson, R. Viswanathan, and J. E. McGrath, Polymer Preprints, 23(2), 164 (1982).

(9) S. Matsuoka, "Thermodynamic Aspects of Brittleness in Glassy Polymers", ACS Symposium Series No. 154, R. D. Deanin and A. M. Crugnola, Editors, p. 3 (1976).

(10) C. Bucknell, "Toughened Thermoplastics", Wiley (1977).

(11) A. Noshay, M. Matzner, and C. N. Merriam, J. Polym. Sci., Part A-1, 9, 3147 (1971).

(12) A. Noshay, M. Matzner, and T. C. Williams, Ind. Eng. Chem. Prod. Res. Develop., 12(4), 268 (1973).

(13) L. M. Robeson, A. Noshay, M. Matzner, and C. N. Merriam, Angew. Makromol. Chem., 29/30, 47 (1973).

(14) M. Matzner, A. Noshay, L. M. Robeson, C. N. Merriam, R. Barclay Jr., and J. E. McGrath, Appl. Polym. Symp., 22, 143 (1973).

(15) M. Matzner, A. Noshay, and J. E. McGrath, Amer. Chem. Soc. Div. Polym. Chem., Preprints, 14(1), 68 (1973);
Trans. Soc. Rheol., 21/22, 109 (1977).

(16) A. Noshay, M. Matzner, B. P. Barth, and R. K. Walton, in Toughness and Brittleness of Plastics (R. D. Deanim and A. M. Crusnola, eds). ACS Symp. Ser. 154, 302-311 (1976).

(17) R. P. Kambour, D. Faulkner, E. E. Kampf, S. Miller, G. E. Niznik, and A. R. Schultz, in Toughness and Brittleness of Plastics (R. D. Deanim and A. M. Crusnola, eds), ACS Symp. Ser. 154, 312-325 (1976).

(18) D. W. Dwight, J. E. McGrath, A. R. Beck, and J. S. Riffle, Polym. Prepr., 20(1), 702 (1979).

(19) N. Eiss, et al., Polymer Preprints, 24(2), 000 (1983).

(20) R. Viswanathan, Ph.D. Thesis, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, June, 1981; R. Viswanathan, B. C. Johnson, T. C. Ward, and J. E. McGrath, NASA Langley Final Report, Research Grant NSG 1599, May 1981; J. E. McGrath et al., Polymer (London), in preparation (1983).

(21) E. E. Ziegler and W. E. Brown, Plastics Technology, July 1955, 344-345.

(22) E. E. Ziegler and W. E. Brown, Plastics Technology, Aug. 1955, 409-415.

(23) ASTM E399, "Plane Strain Fracture Toughness of Metal Materials".

(24) J. H. Scofield, J. Electr. Spect. Rel. Phen., 8, 129-137 (1976).

(25) C. D. Wagner, et al., "Handbook of X-ray Photoelectron Spectroscopy", Perkin Elmer Corporation, Eden Praire, Minnesota, p. 5, (1979).

(26) Work done in conjunction with Drs. Jeffrey Hinkely and Frank Cambell at the Naval Research Laboratory; subsequent publications will be coauthored.

(27) W. A. Hale, A. G. Farnham, R. N. Johnson and R. A. Clendinning, J. Polym. Sci.: Part A-1, 5, 2399 (1967).

(28) R. N. Johnson and A. G. Farnham, J. Poly. Sci.: Part A-1, 5, 2415 (1967).

(29) Thanks to NASA for the use of DuPont DMA and the Torsion Braid Analyzer.

(30) L. Robeson, A. Farnham and J. E. McGrath, in "Molecular Relaxations in Polymers", D. J. Meier, Editor, MMI Press (1978).

(31) J. F. Knott, "Fundamentals of Fracture Mechanics", Wiley (1973).

(32) ASTM E 813-81, J_{IC}, "A Measure for Fracture Toughness".

(33) F. Hickerson, "Elements of Experimental Fracture Mechanics".

(34) R. Y. Ting, Journ. of Mat. Sci., 16, 3059 (1981).

(35) T. Browmer, J. H. O'Donnell and P. Winzor, J. of Polym. Sci.: Polym. Chem. Ed., 17, 1167 (1981).

(37) M. Matzner, A. Noshay, and J. E. McGrath, Polym. Prepr., Am. Chem. Sco., Div. Polym. Chem., 14(1), 68 (1973); Trans. Soc. Rheo. 21/22, 109 (1977).

(38) M. Matzner, and A. Noshay, private communication.

(39) Thanks to Prof. D. W. Dwight for STEM and ESCA micrographs; subsequent coauthored publications will be forthcoming.

(40) A. Sha'aban, et. al., Polymer Preprints, 24(2), 000 (1983).