

AD-A218 871

COPY

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

②

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Research, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

| | | | | | |
|---|--|---|--|--|--|
| 1. AGENCY USE ONLY (Leave blank) | | 2. REPORT DATE 1/22/90 | | 3. REPORT TYPE AND DATES COVERED Final 5/1/86 - 4/30/89 | |
| 4. TITLE AND SUBTITLE Synthesis and Characterization of Aromatic Polyester and Polysiloxane Containing Block Copolymers; Multiphase Transparent Atomic Oxygen Resistant Damping Materials, Liquid Crystal Films, and Touchscreen... | | | | 5. FUNDING NUMBERS 61102F 2203/A3 | |
| AUTHOR(S) James E. McGrath | | | | | |
| PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Virginia Polytechnic Institute and State University Blacksburg, Virginia 24061-0212 | | | | 8. PERFORMING ORGANIZATION REPORT NUMBER AFOSR-TTR-90-0085 | |
| SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NC Bolling AFB Washington DC 20332-6448 | | | | 10. SPONSORING/MONITORING AGENCY REPORT NUMBER AFOSR-86-0133 | |
| 11. SUPPLEMENTARY NOTES | | | | | |
| 12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for Public Release: Distribution is Unlimited | | | | 12b. DISTRIBUTION CODE | |
| 13. ABSTRACT (Maximum 200 words) AFOSR sponsored research on multifunctional polymers which has been conducted in our laboratories over the past three years covers three main areas. Each of the three areas is summarized below and described more completely in some depth in the three sections of this report. The first area includes the synthesis of siloxane modified silicate ceramics produced by sol-gel chemistry followed by ultrastructure processing. Using techniques such as acid free hydrolysis condensation reaction systems, it has been possible to incorporate at least 30% of siloxane oligomers via cohydrolysis of suitably terminated materials in the presence of TMOS. In different but somewhat related work based upon polyimides, extensive studies have been conducted with linear thermoplastic polyimide siloxane copolymers. The polyimide siloxane copolymers prepared to date have been based largely upon aliphatic terminated polydimethylsiloxanes which have adequate thermal stability for most purposes. The third area of investigation on multifunctional polymers was the synthesis and characterization of isotropic polyarylene sulfone, anisotropic aromatic polyester liquid crystal copolymers. We have demonstrated that with as little as 10 or 15 weight % of the liquid crystal segment, organic solvents which would easily dissolve or stress crack the amorphous engineering homopolymers like polysulfones, are no longer able to do so. | | | | | |
| 14. SUBJECT TERMS Multifunctional polymers; Sol-gel; Polysiloxane modified silicates; Polyimide-siloxane copolymers; Isotropic-anisotropic copolymers | | | | 15. NUMBER OF PAGES 39 | |
| | | | | 16. PRICE CODE | |
| 17. SECURITY CLASSIFICATION OF REPORT unclassified | 18. SECURITY CLASSIFICATION OF THIS PAGE unclassified | 19. SECURITY CLASSIFICATION OF ABSTRACT unclassified | | 20. LIMITATION OF ABSTRACT unlimited | |

Synthesis and Characterization of Aromatic Polyester and Polysiloxane
Containing Block Copolymers: Multiphase Transparent Atomic
Oxygen Resistant Damping Materials, Liquid Crystal Films,
and Toughening Components of Sol/Gel Glasses

A Final Project Summary

Contract Number AFOSR-86-0133

to

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFOSR)

Attn: Dr. Don Ulrich
AFOSR/NC
Building 410
Duncan Avenue
Bolling AFB
Washington, DC 20332-6448

| | |
|--------------------|-------------------------------------|
| Accession For | |
| NTIS GRA&I | <input checked="" type="checkbox"/> |
| DTIC TAB | <input checked="" type="checkbox"/> |
| Unannounced | <input type="checkbox"/> |
| Justification | |
| By | |
| Distribution/ | |
| Availability Codes | |
| Dist | Avail and/or Special |
| A-1 | . |

Prepared by:

James E. McGrath
Chemistry Department
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061
703-231-5976
FAX: 703-231- 8517

May 1, 1988 to April 30, 1989

Approved for public release;
distribution unlimited. ✓

Table of Contents

| | Page |
|--|------|
| I. EXECUTIVE SUMMARY | ii |
| II. POLYDIMETHYLSILOXANE MODIFIED SILICATES VIA SOL/GEL CHEMISTRY AND ULTRASTRUCTURE PROCESSING | 1 |
| III. SEGMENTED POLYIMIDE POLYDIMETHYLSILOXANE COPOLYMERS | 12 |
| IV. POLYIMIDE-SILICATE POLYMER-CERAMIC NETWORKS VIA SOL/GEL PROCESSES; REACTION SCHEME AND PRELIMINARY RESULTS | 20 |
| V. ANISOTROPIC-ISOTROPIC SEGMENTED COPOLYMERS | 22 |

I. EXECUTIVE SUMMARY

Multifunctional polymers could be defined as materials that may be capable of functioning in two or more applications. As advances in polymeric materials science have been made, it is clear that macromolecules from the same or somewhat similar chemical repeat units might provide both structural uses and possibly also function as, for example, an electronic material. Indeed, the options are further enhanced by the use of well designed multiphase block, graft, segmented and ion-containing copolymers. Further possibilities are developed through the use of inorganic-organic hybrid systems, sometimes referred to as polymer-ceramic materials.

This concept provides a focal point for interpreting our AFOSR sponsored research which has been conducted over the past three years in the area of silicone modified silicate ceramics. These materials were produced by sol/gel chemistry followed by ultrastructure processing. Silicone modified segmented polyimides which have utility in aerospace, electronic materials and structural engineering polymer applications are a second important example. The third area is termed anisotropic-isotropic block copolymer materials. Each of the three areas is summarized below and described more completely in some depth in the three sections of this report.

During the past three years, techniques have been developed for the controlled hydrolysis and condensation of tetralkylorthosilicates such as TEOS and TMOS. The tetramethoxy material (TMOS) has one significant advantage relative to other members of the silicate family, in that it does not require an acid catalyst to promote the hydrolysis-condensation reactions. Thus, it is particularly amenable for the incorporation of semi-organic polydimethylsiloxane oligomers which would otherwise be degradatively rearranged at elevated temperatures by the usual strong acids or strong bases that are conventionally applied. Using techniques such as the acid free hydrolysis condensation reaction systems, it has been possible to incorporate at least 30% of siloxane oligomers via cohydrolysis of suitably terminated materials in the presence of TMOS. A further advantage realized throughout this research was the utilization of a very mild pressure during the hydrolysis condensation which appears to be quite important in the generation of crack free monolithic transparent materials. The mechanisms of how the mild pressure decreases the tendency of cracking are not understood, but may relate to decreasing capillary forces which are very sensitive to the loss of solvents during the period of time in which the material is obviously shrinking very significantly. In any event, the materials are quite crack resistant and can then be further cured by taking the reaction temperature to higher values such as 300, 400, or even 500°C. An influence of curing temperature on water resistance has been noted and is believed to be connected with the ability to drive the condensation reaction to much higher extents. Preliminary estimates of % conversion have been obtained from NMR measurements and it is proposed to further expand these studies during the renewal period. Recently, the university has been able to order a greatly improved solid state NMR instrument which would simplify the proposed new studies.

In different, but somewhat related, work based upon polyimides, extensive studies have been conducted with linear soluble thermoplastic polyimide siloxane copolymers. These materials again are multifunctional since they are of interest in aerospace as strong, tough engineering materials which provide atomic oxygen resistance and as electronic materials which can possibly serve as good dielectric materials and even photoresists if they contain the right functional groups. Such materials may also be of interest in the general area of nonlinear optical properties and this is also true for the above mentioned siloxane modified silicates. The polyimide siloxane copolymers prepared to date have been based largely upon aliphatic terminated polydimethylsiloxanes which have adequate thermal stability for most purposes.

The third area of investigation in the multifunctional category was the synthesis and characterization of isotropic polyarylene sulfone, anisotropic aromatic polyester liquid crystal copolymers. The chemistry has now been quite well worked out over the past two years. The benefits that could be expected from the proposed systems fall into two broad categories. At low liquid crystal concentrations, it is possible to alter the solvent resistance of otherwise attractive amorphous engineering homopolymers such as the polysulfones. Thus, we have demonstrated that with as little as 10 or 15 weight % of the liquid crystal segment, that organic solvents which would easily dissolve or stress crack the amorphous materials are no longer able to do so. Data supporting this statement are provided in the enclosed main body. Secondly, a major well known problem for liquid crystal copolymers is there lack of transverse mechanical properties which essentially, among other things, translates into very low compressive strengths. The ability to incorporate a ductile isotropic segment may be of great interest here for compositions that are predominately liquid crystal like in nature. We have already made samples as high as 60% of liquid crystal polymer and are indeed able to mold such materials without any evidence of fibrillation that accompany the pure homopolymer.

II. POLYDIMETHYLSILOXANE MODIFIED SILICATES VIA SOL/GEL CHEMISTRY AND ULTRASTRUCTURE PROCESSING

ABSTRACT

The low temperature sol-gel process opens a number of new materials possibilities for generation of glasses with predetermined properties by the incorporation of organic modifiers into the network. Polysiloxanes are potentially interesting organic modifiers for toughening and possibly surface modifying the silicate networks. Some fundamental studies of the hydrolysis and condensation processes in a tetramethylorthosilicate (TMOS) system, in the absence of added catalyst, have been conducted using ^1H and ^{29}Si NMR. The effects of some of the reaction parameters and processing conditions for the subsequent conversion of the gel to monolithic dried gels by heat treatment have been investigated by techniques such as thermal analysis and mass spectroscopy. Procedures which employ mild pressures have been established that permit the generation of monolithic products which show greatly reduced cracking tendencies. Finally, methoxy functionalized poly(dimethylsiloxane) oligomers that can react into the sol-gel network have been prepared. The intermediates are commercially accessible and the process is scaleable. Utilization of catalyst free system eliminates the tendency of the siloxane modifier to undergo undesired rearrangements that are known to occur in the presence of strong acids or bases.

INTRODUCTION

"Sol-gel" technology refers to a relatively low temperature technique for the preparation of single-component or multicomponent oxide glasses. During this process hydrolyses and subsequent condensation of organic or inorganic alkoxides leads to the formation of a three dimensional glass network. Hydrolytic polycondensation reactions of tetraalkoxysilanes generate an oxide network similar to that of quartz, thus suggesting a possible way to form glass and ceramic materials by chemical polymerization [1]. Chemical reactions open new possibilities for the incorporation of organic modifiers into the network and therefore generation of glasses with predetermined properties. Polysiloxanes are potentially interesting modifiers which are capable of microphase separation and which could provide some toughening of the otherwise brittle glasses.

The most commonly used silicon alkoxide that has been studied is tetraethylorthosilicate (TEOS). Some aspects of the hydrolysis and condensation polymerization reactions of TEOS have been investigated in our own laboratories [2]. However, the strong acids typically utilized to hydrolyze TEOS would probably also cause undesirable degradation of the polysiloxane chains used as network modifiers. Thus, a relatively neutral reaction environment is required for the polysiloxanes to fully exhibit their potential bulk and surface modifying capability. Literature data suggest that tetramethylorthosilicate (TMOS) could hydrolyze in the absence of added catalyst. It has been shown that the rate of hydrolysis in the alkoxysilane series decreases and the gelation time increases with increasing size of the alkoxyl group [3,4]. It is also known that TMOS is environmentally more difficult to work with and hence well ventilated hoods and good safety practices are required.

The effects of the reaction conditions on the hydrolysis and condensation rate in a TMOS system, in the absence of added catalyst, using both ^1H and ^{29}Si NMR were investigated. The effect of the processing parameters on the subsequent conversion of the gel to monolithic dried gels by heat treatment was also investigated. Among other variations in processing, the utilization of mild pressures during drying of the gels seems to play a critical role in producing crack free specimens. Finally, the synthesis of a functionalized polysiloxane oligomer modifier, capable of reacting into the sol-gel network, is described and demonstrated.

EXPERIMENTAL

Materials

Chemical grade (99%) tetramethylorthosilicate (TMOS) from Petrarch, and HPLC grade water and solvents (methanol and tetrahydrofuran) from Aldrich, were used without further purification. Octamethylcyclotetrasiloxane (D_4) was purchased from Union Carbide and distilled from calcium hydride before use. Methyldimethoxysilane and 1,3-divinyltetramethyldisiloxane from Petrarch, were used as received. Hydrogen hexachloroplatinate (IV) hydrate catalyst was obtained from Aldrich and stored under inert atmosphere.

Sol-gel reactions

The general scheme for the preparation of silicate networks via sol-gel processes is outlined in Figure 1. The sol-gel reactions (up to the gelation) were carried out at room temperature (RT), under stirring. A one-necked flask was charged with the reactants in the order TMOS, CH_3OH and H_2O , at the desired molar ratios (deuterated methanol was used for the NMR studies). The flask was then closed using a fitted stopper and allowed to stir at room temperature. At desired time intervals, NMR samples were removed as a function of reaction time. Most of the compositions investigated generated homogeneous reaction mixtures. For a few compositions, however, the initial reaction mixtures were heterogeneous, but they became homogeneous as the water coreactant was consumed and more methanol was generated in hydrolysis reactions. Prior to gelation, the reaction mixture was poured into glass vials which were equipped with relatively tightly fitting caps and was allowed to gel at room temperature ($\sim 20^\circ\text{C}$). Further drying of the gels was carried out under controlled conditions to generate (for most cases) monolithic dried gels. In the present study, the drying of the gels was carried out in sealed glass vials or in a pressure reactor using a maximum pressure of 50 psig. A stepwise temperature profile (of 65°C , 100°C and 150°C) was used (see Figure 1), the heating rate between the steps being ca $0.5^\circ\text{C}/\text{min}$. In some cases, higher reaction temperatures (up to 500°C) were investigated, as discussed later.

Polysiloxane synthesis

Synthesis of methoxy functionalized polydimethylsiloxane oligomers was achieved in a two-step reaction. In the first reaction step, a vinyl terminated poly(dimethylsiloxane) oligomer was synthesized by a base-catalyzed redistribution reaction of the cyclic siloxane tetramer (D_4) and 1,3-divinyltetramethyldisiloxane as the chain transfer agent or end capper, as shown in Figure 2. The number average molecular weights (M_n) were controlled

by the appropriate ratio of the end-blocker to the cyclic tetramer (D_4). A transient silanolate catalyst was used and the reaction was carried out in bulk, at 80°C . The silanolate catalyst synthesis and the typical conditions for siloxane equilibration reactions have been extensively studied in our laboratory and are described elsewhere [5-7]. In the second step, Figure 3, the terminal vinyl groups were converted to methoxy end groups using methyldimethoxysilane as the hydrosilylation agent. The reaction was carried out in bulk, at $40-50^\circ\text{C}$, using H_2PtCl_6 as the hydrosilylation catalyst (ca. 5×10^{-5} moles catalyst/mole vinyl group). The resulting product is then capable of co-reacting efficiently with TMOS in the hydrolysis/condensation sol-gel process.

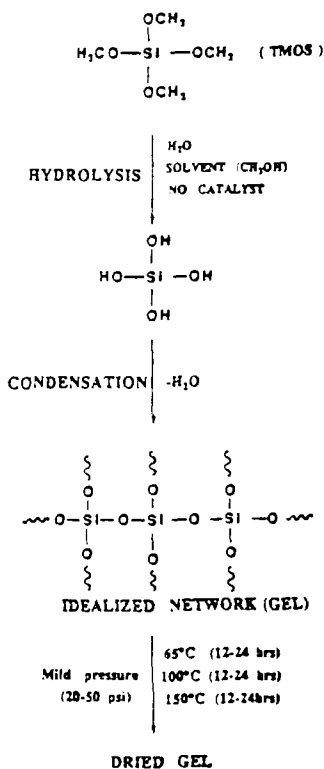


Figure 1. Generalized Reaction Scheme for the Preparation of Silicate Networks via Sol-Gel Processes

1. EQUILIBRATION REACTION

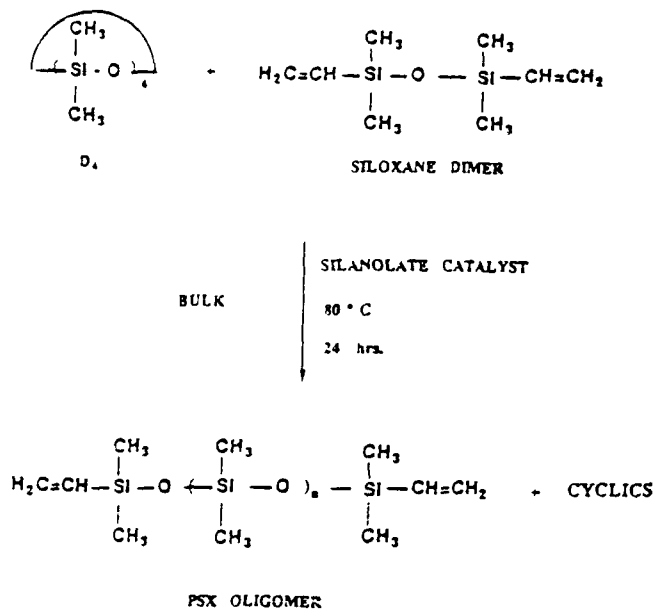


Figure 2. General Scheme for the Synthesis of Poly(Dimethylsiloxane) Oligomers with Vinyl Functional Groups

2. HYDROSILYLATION

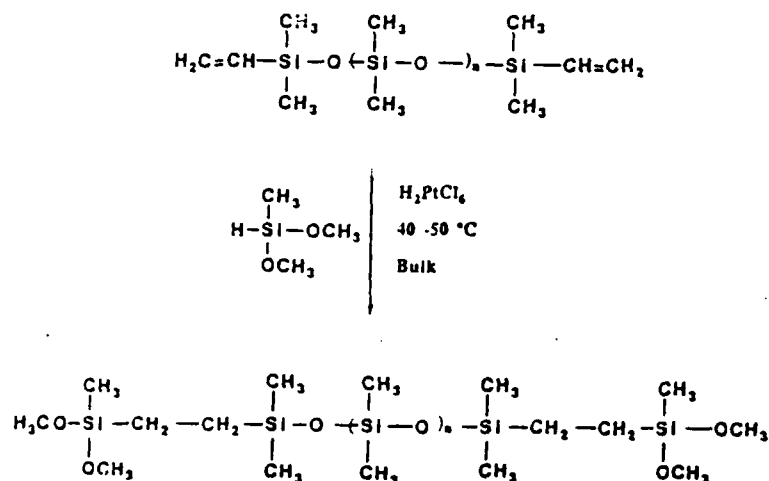


Figure 3. General Scheme for the Synthesis of Poly(Dimethylsiloxane) Oligomers with Methoxy Functional Groups

Analytical techniques

Spectral analysis: ^1H NMR data were acquired at RT on a Bruker WP 270 spectrometer operating at 270 MHz. CD_3OD , used as the reaction solvent, provided the deuterium lock signal and all resonances were referred to tetramethylsilane (TMS). ^{29}Si NMR spectra were acquired at RT on a Bruker WP 200 spectrometer operating at 39.759 MHz. The spectra were obtained with

inverse-gated decoupling; the decoupler was on during acquisition and off during the delay, to suppress any negative nuclear Overhauser effect (NOE). Chromium acetylacetonate $[\text{Cr}(\text{acac})_3]$ was added at $\sim 0.4\text{M}$ concentration to reduce the ^{29}Si spin lattice relaxation times. A pulse repetition rate of 6s was used and line broadening of 2.0 Hz was applied. Again, the deuterium lock of the instrument was provided by CD_3OD , the reaction solvent. For each ^{29}Si NMR sample, 600 scans were accumulated in order to obtain a high signal/noise ratio. The reported times of the spectra are the midpoints of data acquisition. In order to eliminate the interference of the ceramic and quartz components (from the probe and NMR tube), a subtraction technique was used. An example of a ^{29}Si NMR spectra before and after subtraction is shown in Figure 4 along with the assignments of each resonance frequency according to previous literature data [8]. ^{13}C CP/MAS NMR spectra were acquired at room temperature on a Bruker spectrometer operating at 22.53 MHz, with a ChemMagetics double-bearing CP/MAS probe. Samples were spun at the magic angle at ~ 2.2 kHz.

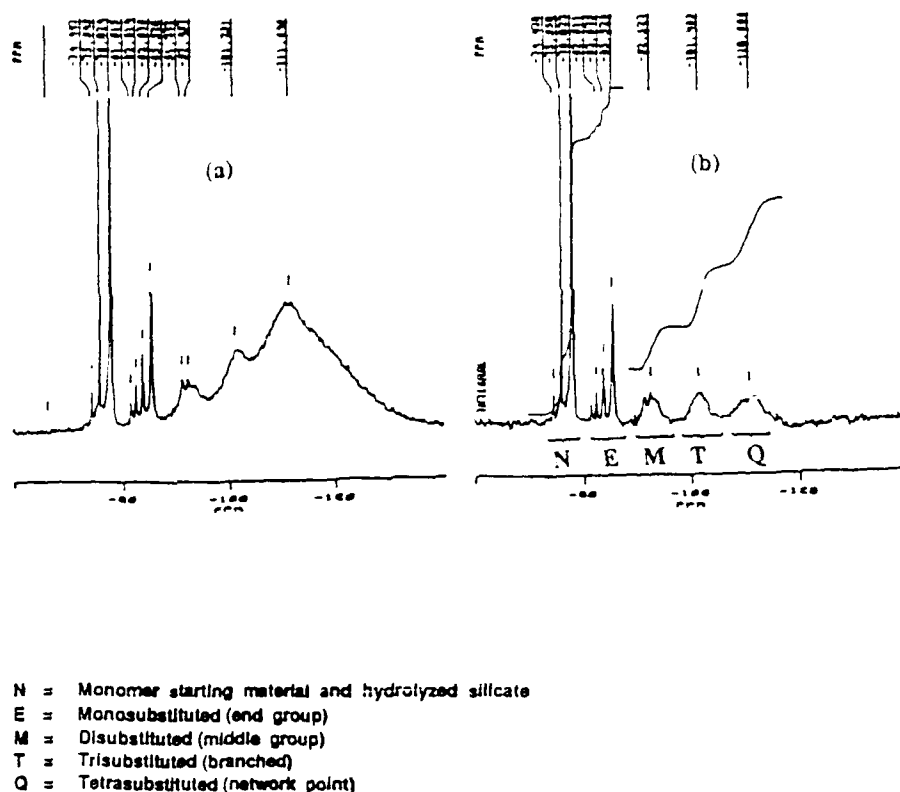


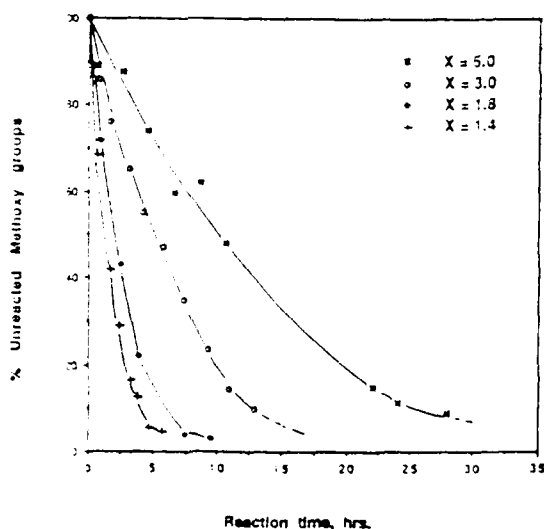
Figure 4. ^{29}Si NMR Spectrum of a TMOS Reaction, Before (a) and after (b) subtraction of the glass peak. Assignments are shown according to ref. 8.

Thermal analysis: Thermogravimetric analyses of the dried gels were obtained using a Perkin-Elmer thermogravimetric analyzer (model TGS-2). The volatile products were conveyed to a mass selective detector (Hewlett-Packard 5970 series MSD) via a two meter long, 10 μ m ID, deactivated capillary column. This capillary also serves to restrict the flow between the TGA experiment performed at ambient pressure (in a self generated atmosphere, with no sample purge) and the MS experiment performed in vacuum ($\sim 2 \times 10^{-5}$ torr). The sample was heated from 30°C to 300°C at a heating rate of 20 deg./min. To determine if any component of interest was actually released, selected ion chromatograms were obtained at the mass to charge ratio for the base peak of each component (ex: $m/e=18$, water; $m/e=31$, methanol).

RESULTS AND DISCUSSION

Effect of reaction parameters on the sol-gel reaction rate

Effects of silicon alkoxide content: Four different TMOS concentrations were investigated, corresponding to the CH₃OH/TMOS molar ratios of 1.4, 1.8, 3.0, and 5.0. The rate of hydrolysis reactions was followed by ¹H NMR. An increase in the alcohol content (decrease in the concentration of silicon alkoxide) resulted in a reduction of the overall reaction rate and longer gelation times. Figure 5 summarizes the results for such an experimental series.



Catalyst free system; RT reaction; Stirring;

Figure 5. Concentration Effect on the Reaction Rate in a TMOS System
(TMOS : H₂O : CH₃OH = 1.0 : 4.0 : X)

Effects of $H_2O/Si(OCH_3)_4$ ratio: The present work describes the investigation on the hydrolysis/condensation reactions for TMOS solutions having water content of 2.5 and 4.0 [$(H_2O)/(TMOS)$]. The rate of hydrolysis was followed by 1H NMR and the results are summarized in Figures 6a and 6b. In the absence of any added catalyst, it was observed that the rate of hydrolysis was increased with increasing water content from 2.5 to 4.0 and the gelation time was reduced accordingly.

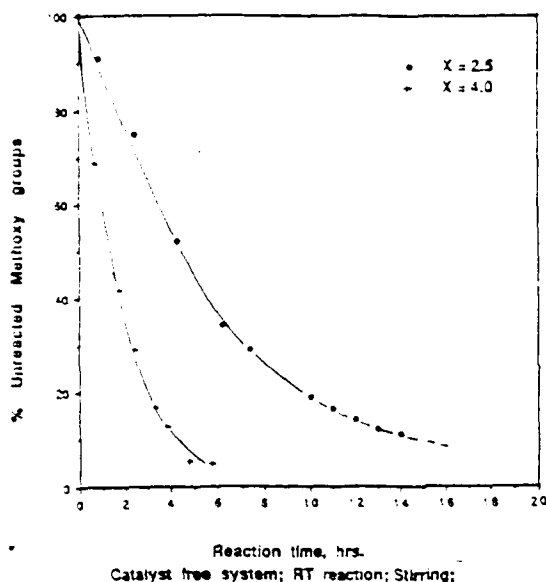


Figure 6a. Effect of the Water Level on the Reaction Rate in a TMOS System
(TMOS:CH₃OH:H₂O=1.0:1.4:X)

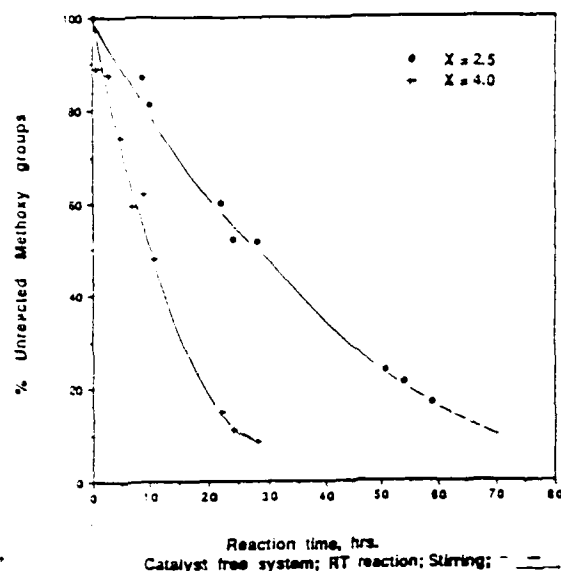


Figure 6b. Effect of the Water Level on the Reaction Rate in a TMOS System
(TMOS:CH₃OH:H₂O=1.0:5.0:X)

Preliminary results on the drying of the gels indicated that monolithic dried gels were produced with much higher frequency from the reaction compositions containing 4.0 moles of water than from the corresponding reactions in which only 2.5 moles of water were used. It was therefore of interest to determine if higher water contents resulted in a change in the polymerization mechanism. The evolution of the reaction species as a function of reaction time was followed by ^{29}Si NMR and the results for the two compositions investigated are shown in Figure 7. A reduced time scale was used for the normalization of the data for the two reactions [8]. Here τ represents the ratio between the time of scanning (t) and the gelation time (t_g). The sample was considered to have gelled when the solution would no longer flow.

The first observation is that the time evolution of the reaction species is similar under the two reaction conditions investigated, suggesting no mechanistic difference. However, even though this is not obvious from the figure, the integration indicated that the reaction containing 4.0 moles of water (7A) reached higher conversions when the gelation was approached ($\tau = 0.93$) than the reaction containing 2.5 moles of water (7B). Higher conversions resulted in higher contents of polymeric species and correspondingly lower levels of starting materials. This is also in agreement with higher hydrolysis rate of the reaction containing 4.0 moles of water, according to the 1H NMR data.

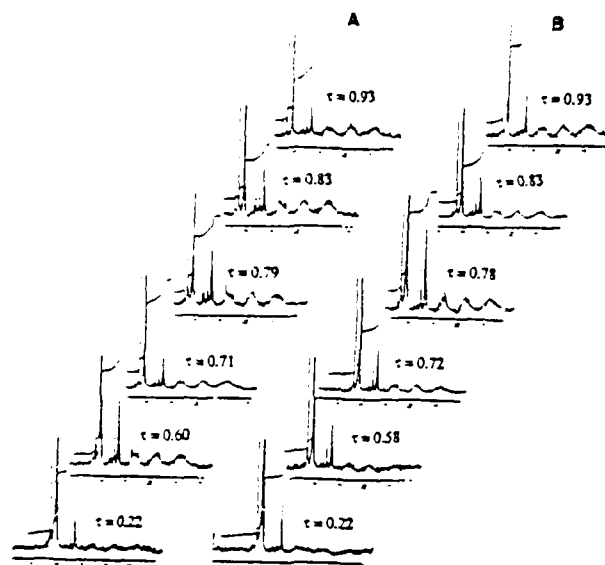


Fig. 7. ^{29}Si NMR Spectra as a Function of Reaction Time for Sol-Gel Reactions
 (A) TMOS : H_2O : CH_3OH = 1.0 : 4.0 : 1.4; t_g = 7.5 hrs
 (B) TMOS : H_2O : CH_3OH = 1.0 : 2.5 : 1.4; t_g = 19 hrs

A second observation was that hydrolysis and condensation are concurrent reactions, occurring simultaneously in both systems investigated. The presence of condensation species at low reaction conversions ($\tau = 0.22$) indicated that condensation reactions began long before hydrolysis was completed. On the other hand, the presence of unreacted starting materials at long reaction time ($\tau = 0.93$) indicated that the hydrolysis was not completed when the gelation occurred.

Effect of processing parameters on the dried gels

The most promising route to obtain glasses from gels through the sol-gel method is to first prepare monolithic dried gels. However, due to the expected very high compression forces inside the pores during the drying of the gels (when a liquid-gas curved interface is formed within the pores), the material, most often loses its integrity [10].

According to the theory of drying gels introduced by Scherer [11], the stress developed in a plate during drying is dependent upon the evaporation rate of the solvent and the mechanical properties of the gel. When drying is slow, the stress is independent of the mechanical properties of the gel [11]. This is probably the reason of some success in generating monolithic gels by very slow drying at room temperature [12]. However, when the relaxation time of the materials becomes much greater than the drying time, the stress developed will also depend on the mechanical properties of the gel, therefore, the stronger the network becomes, one expects it will better withstand the stresses developed during drying.

With this understanding of the factors involved during drying of the gels, we believed that the use of relatively high temperatures and mild pressures during the drying process would allow us to approach the following

conditions: (a) low evaporation rates due to low vapor pressure of the solvent at high external pressures; (b) decreased compressive forces in the capillaries of the gels, as a result of decreased solvent surface tension at higher temperatures; (c) increased overall conversion of the reaction with increasing temperature, resulting in a stronger network, which is capable of withstanding the stresses during drying. Following these procedures, monolithic dried gels could be obtained in most of the experiments that were conducted.

Thermogravimetric analysis was used for the characterization of the dried gels. As previously documented in the literature [13], the weight loss below 150-200°C is due to desorption of physically adsorbed water and alcohol. The weight loss that occurs above 200°C can be attributed, at least partially, to the removal of by-products of the step-growth or polycondensation reactions that can take place in the incompletely reacted network. If, as seems reasonable, the weight loss above 200°C is related to the extent of conversion, it follows that both the reaction composition and the drying parameters will affect the extent of conversion of the network system as shown in Figure 8 and Figure 9, respectively.

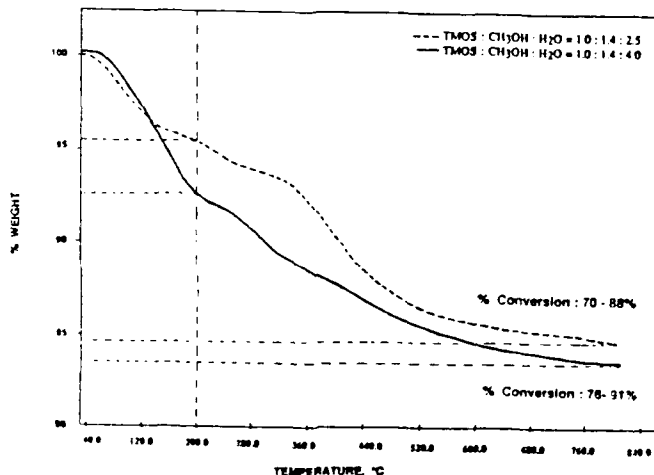


Figure 8. TGA - Effect of the Initial Reaction Composition on the Weight Loss in a SiO_2 System

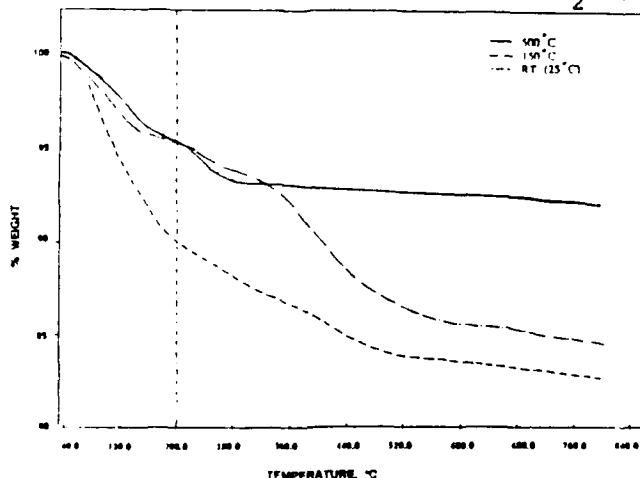


Figure 9. TGA - Effect of the Post-Gelation Treatment on the Weight Loss in a SiO_2 System

Using TGA-MS, ion chromatograms for methanol and water (possible by-products of condensation reactions) have been constructed and typical chromatograms are shown in Figure 10 and Figure 11. Both ion chromatograms show two peaks, one below 200°C and corresponding to the adsorbed water and methanol and the other above 200°C which can be attributed to further condensation reactions of the type:

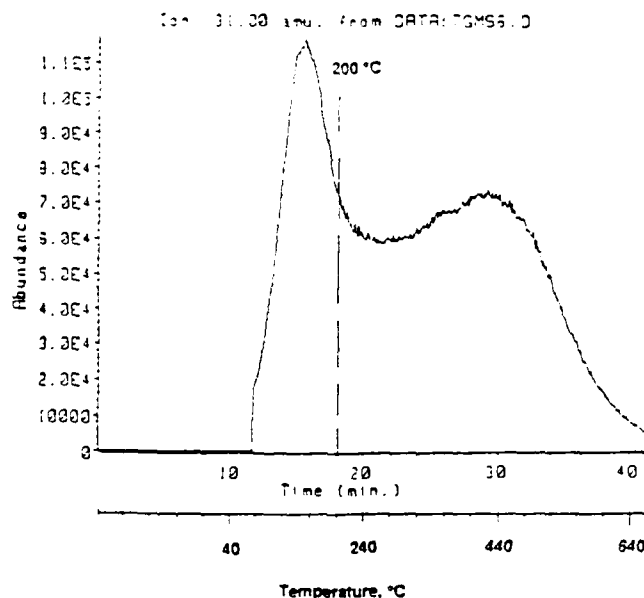
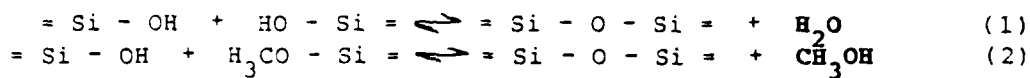


Figure 10. TGA - MS for a Dried SiO_2 Gel (max. drying temp: 150°C). Ion Chromatogram for CH_3OH Evolution During Heating (Heating Rate: 20.00 deg/min)

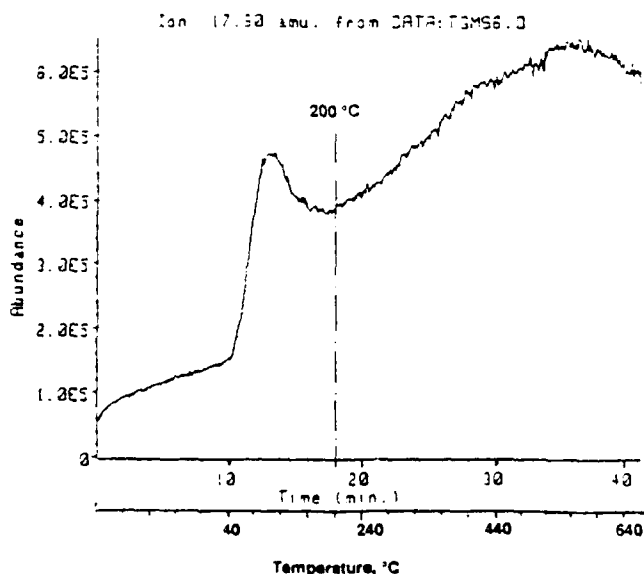


Figure 11. TGA - MS for a Dried SiO_2 Gel (max. drying temp: 150°C). Ion Chromatogram for H_2O Evolution During Heating (Heating Rate: 20.00 deg/min)

Polysiloxane modifiers

Three different molecular weight methoxy functionalized poly(dimethylsiloxane) oligomers were synthesized, as indicated below:

Table I

Theoretical vs Experimental Molecular Weights for Polysiloxane Oligomers

| No. | Number Average Molecular Weight $\langle M_n \rangle$, [g/mole] | |
|-----|--|-----------|
| | Theoretical | From GPC* |
| 1 | 2,000 | 2,500 |
| 2 | 5,000 | 6,300 |
| 3 | 10,000 | 12,500 |

* According to poly(dimethylsiloxane) standards prepared in our laboratory

The functionalized polysiloxanes can react into the sol-gel network and preliminary experiments did indicate that it is possible to incorporate up to 10-20 weight percent of the siloxane oligomer without significant loss of transparency.

CONCLUSIONS

The current study has shown that TMOS can be efficiently hydrolyzed and subsequently condensed in the absence of added catalyst to produce monolithic dried gels, under controlled reaction and processing conditions. Using ^{29}Si NMR and subtraction techniques to eliminate the quartz interference with the ceramic resonances, the evolution of species during the sol-gel process could be closely monitored up to the gelation point. New information on the type of condensation reactions that occur at higher processing temperatures was obtained using a TGA-MS techniques and solid state NMR. Controlled molecular weight methoxy functionalized poly(dimethylsiloxane) oligomers that can be reacted into the sol-gel network were synthesized.

REFERENCES

1. B. E. Yoldas, J. Mat. Sci., 12, 1203, (1977); 14, 1843 (1979).
2. J. E. McGrath, J. P. Pullockaren, J. S. Riffle, S. Kilic, and C. S. Elsbernd, Ultrastructure Processing of Advanced Ceramics, edited by J. D. Mackenzie and D. R. Ulrich (John Wiley & Sons, New York, 1988) p 55.
3. R. Aelion, A. Loebel, and E. Erich, J. Am. Chem. Soc., 72, 5705 (1950).
4. K. C. Chen, T. Tsuchiya, and J. D. Mackenzie, J. Non-Cryst. Solids, 81, 227, (1986).

5. J. E. McGrath, P. M. Sormani, C. S. Elsbernd, and S. Kilic, *Makromol. Chem., Makrom. Symp.*, 6, 67, (1986).
6. C. S. Elsbernd, P. M. Sormani, S. Kilic, and J. E. McGrath, *Polymer Preprints*, 27(2), 152 (1986); I. Yilgor and J. E. McGrath, *Adv. in Polymer Sci.*, 86, 1 (1988).
7. C. S. Elsbernd, M. Spinu, S. Kilic, and J. E. McGrath, *Polymer Preprints*, 29(1), 355, (1986).
8. L. W. Kelts, N. J. Effinger, and S. M. Melpolder, *J. Non-Cryst. Solids*, 83, 353, (1986).
9. I. Artaki, S. Sinha, A. D. Irwin, and J. Jonas, *J. Non-Cryst. Solids*, 72, 391, (1985).
10. M. Prassas, J. Phalippou, J. Zarzycki, *J. Mater. Sci.*, 19, 1656, (1984).
11. G. W. Scherer, *J. Non-Cryst. Solids*, 89, 217, (1987).
12. M. Yamane, S. Aso, and T. Sakaino, *J. Mater. Sci.*, 13, 865, (1978).
13. J. Zarzycki, *J. Non-Cryst. Solids*, 48, 105, (1982).

III. SEGMENTED POLYIMIDE POLYDIMETHYLSILOXANE COPOLYMERS

INTRODUCTION

Polyimides synthesized from aromatic monomers are of great interest for high performance applications due to their excellent thermal and mechanical properties. Unless carefully designed, however, these polymers are often insoluble and intractable in their fully imidized form. Incorporation of flexible siloxane segments into the polyimide backbone has been one effective means of achieving enhanced solubility and processability while maintaining excellent high performance properties of the copolymer systems [1].

In addition to enhanced solubility, incorporation of polysiloxane blocks yields additional benefits of particular importance for aerospace applications. The hydrophobic nature of siloxanes, for instance, results in reduced water sorption and enhanced adhesive bond durability in hot/wet environments [2]. Polysiloxane containing copolymers have shown potential for passive damping and reduced temperature sensitivity as a means to circumvent the creep and thermal cycling problems of space structures [3]. Most importantly, the great difference in solubility parameters of the siloxane and imide segments is a driving force for microphase separation. Because the polysiloxanes possess relatively low surface energies, they will migrate to the air or vacuum interface, yielding a surface dominated by the siloxane component.

In aggressive oxygen environments, such as the low earth orbit (LEO) atmosphere experienced on space shuttle flights, the siloxane segments convert to a ceramic-like silicate (SiO_2) which provides a protective outercoat to the bulk material (Figure 1). The conversion of the polysiloxane with oxygen plasma to silicon dioxide has, in fact, been well documented in the electronics industry literature. More direct evidence for the stability of siloxanes to the LEO environment was obtained from the results of the 1983 Space Shuttle flight (STS-8) experiment [4,5]. Of the materials evaluated, only the siloxanes, in the form of crosslinked polydimethylsiloxanes and poly(siloxane imide) segmented copolymers from our laboratories, such as 1, were stable to the test conditions.

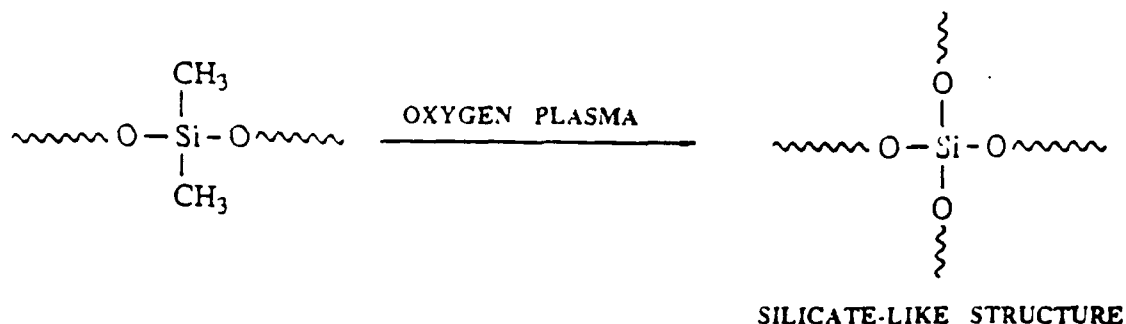


Figure 1. Proposed Siloxane to Silicate Transformation Upon Exposure to Oxygen Plasma

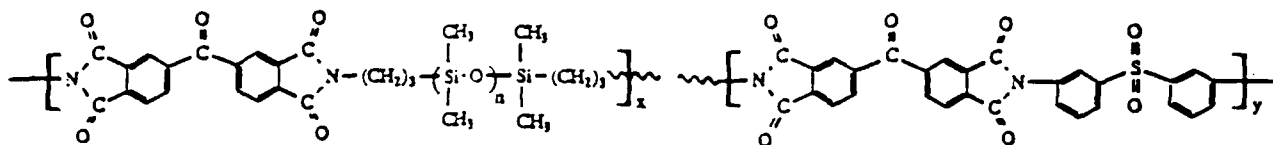
Ground-state, neutral atomic oxygen is the predominant species encountered in the LEO. Due to the orbital velocity (8 km/sec) of the spacecraft, oxygen atoms strike the satellite's surfaces with an average collision energy of 5 eV. These conditions, along with high-vacuum, present a gas-surface chemistry which has been the subject of very little laboratory investigation due to the inherent difficulty in reproducing the impact velocity and relatively high flux rate (10^{15} - 10^{16} O-atoms per sq. cm-sec) of oxygen atoms needed to reproduce the spacecraft environment. Oxygen plasma has been used in order to simulate the LEO atmosphere, however, the variables governing degradation in oxygen plasma and the LEO are quite different. One facility, Physical Sciences, Inc., has been identified which can provide high flux beams of oxygen atoms for material degradation studies. We have utilized these facilities to determine the stability in the LEO of a series of high temperature homopolymers, poly(siloxane imide) segmented copolymers and miscible polyblends of these components with polybenzimidazole (PBI), 2.

The objective of our research was to develop potential high temperature, processable composite matrix resins, structural adhesives and specialty coatings suitable for aerospace applications. Other researchers, notably MacKnight, Karasz, and coworkers [6], have demonstrated the miscibility of blends of PBI and commercial polyimides. We hypothesized that it would be possible to capitalize on the significant, pertinent advantages offered by the polysiloxanes by utilizing poly(siloxane imide) segmented copolymers as blend components with PBI, along with novel polyimide homopolymers synthesized in our laboratories.

EXPERIMENTAL

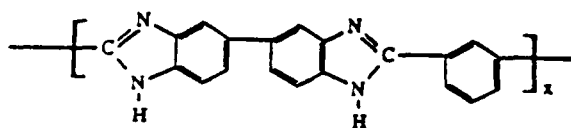
High molecular weight, soluble polyimide homopolymers (PI) and polydimethylsiloxane modified polyimide segmented copolymers (PI-SX) were prepared by a solution imidization procedure as previously described by Summers, et al [7]. The solution imidization procedure was effectively monitored by FTIR to ensure quantitative imidization had been achieved. The homopolymers were based upon 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 3,3'-diaminodiphenylsulfone; the copolymers included either 10

or 40 weight percent aminopropyl terminated polydimethylsiloxane oligomers of ~950 g/mole molecular weight. Unless otherwise stated, all references to the poly(siloxane imide) copolymers refer to the 40 weight percent siloxane composition. Figure 2 illustrates the polymers used in the blending study.



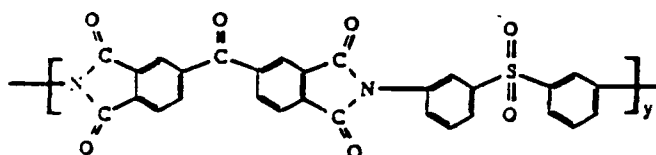
BTDA-DDS BASED POLY (SILOXANE IMIDE) COPOLYMER (PI-SX)

1



POLYBENZIMIDAZOLE (PBI)

2



BTDA-DDS BASED POLYIMIDE HOMOPOLYMER (PI)

3

Figure 2. Representative Structures of Polymers Used in Blending Study

Blending of dry PBI powder with the polyimide homo- and copolymers was accomplished by combining individual solutions of the components, each at a concentration of ~10 to 15 weight percent in dimethylacetamide, in a blender with vigorous stirring. Films were solution cast unto a glass plate and dried at 65°C under moderate vacuum for 2 days in order to remove most of the solvent. Further staging under vacuum at 120°C for 2 days and 300°C for 3 days yielded solvent-free films, as determined by dynamic mechanical thermal measurements (DMTA) and thermogravimetric analysis (TGA).

A Polymer Laboratories DMTA was utilized to obtain glass transition values of the homopolymers, copolymers and blends at a constant frequency of 1 Hz and scanning rate of 3°C per minute.

Water sorption studies were conducted by immersing film samples in distilled water at room temperature and removing the samples at periodic intervals, blotting dry and weighing to determine water uptake.

Atomic oxygen stability studies were conducted at Physical Sciences, Inc. of Andover, Mass. Their facilities employ a high power pulsed CO₂ laser to generate high flux, high velocity pulses of oxygen atoms to bombard the specimens in a 20 cm diameter vacuum test chamber. The exposure time for the eight specimens of this study was chosen to correspond to one week in the LEO environment. The test conditions are outlined in Table I; a detailed description of the Physical Sciences facilities is given in reference 8.

Table I
ATOMIC OXYGEN STABILITY STUDY
Test Conditions*

| | |
|--|--|
| Chamber Base Pressure | 2×10^{-5} Torr |
| Nozzle Pulse Repetition Rate | 1.4 Hz |
| Average Velocity | 8 km per sec |
| Distance from Throat to Sample | 40 cm |
| Area of Beam at Sample | 300 cm ² |
| Nominal Area Exposed on Target | 6.4 cm ² (-10%) |
| Number of Pulses | 54360 |
| Number of O-atoms per Pulse (Theory) | 2×10^{19} atoms |
| Number of O-atoms per Pulse (Kapton) | 5×10^{17} atoms |
| Average Pulse Fluence on Target (Theory) | 6.7×10^{16} atoms/cm ² |
| Average Pulse Fluence on Target (Kapton) | 6.7×10^{16} atoms/cm ² |
| Total Integrated Flux (Theory) | 3.6×10^{20} atoms/cm ² |
| Total Integrated Flux (Kapton) | 3.6×10^{20} atoms/cm ² |

*as per Dr. R. H. Krech, Physical Sciences, Inc., Andover, Mass.

RESULTS AND DISCUSSION

Miscibility of the blends of polyimide homopolymers and poly(siloxane imide) copolymers with PBI was ascertained by a number of different techniques over a wide compositional range. The formation of clear transparent films was the first evidence that these systems might be miscible and homogeneous. Scanning electron micrographs (SEMs) at 6600 X magnification (Figure 4) do not indicate any macrophase separation of the blend components. From DMTA, single, well-defined tan δ relaxation peaks associated with the glass transition were observed in every case (Figure 3).

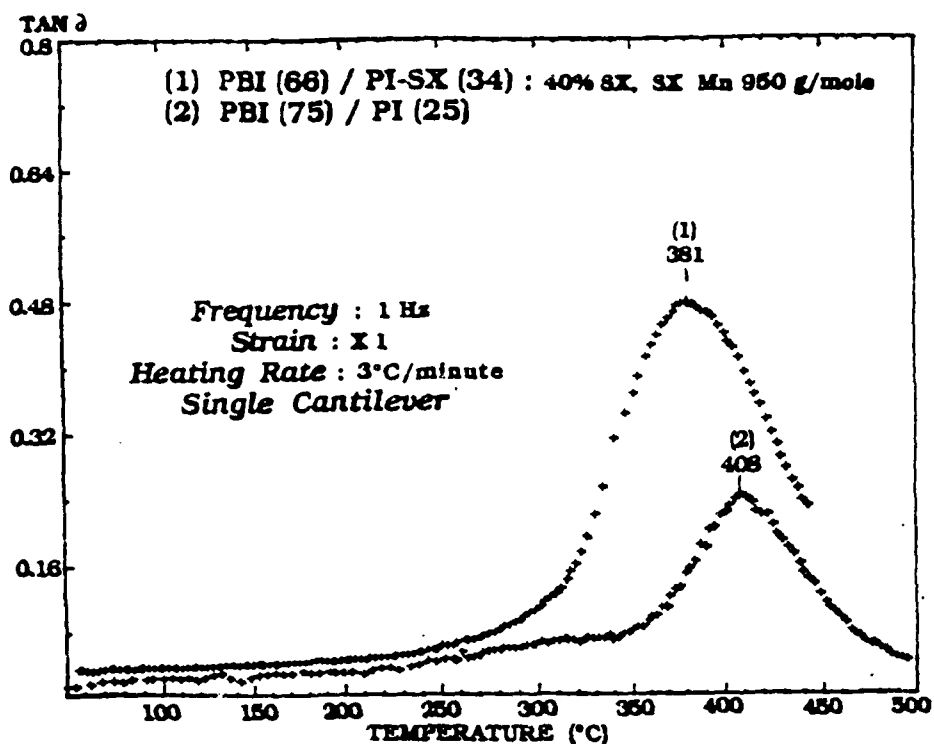


Figure 3. Dynamic Mechanical Thermal Analysis

The variation in the glass transition values as a function of the percent of PBI in the blends was found to positively deviate from the values expected from the simple Fox equation rule of mixtures. Thus, the glass transitions of the blends varied between 430°C, the T_g for PBI, and 275°C for the PI blend series and 185°C for the PI-SX blend series. Even with 34 percent PI-SX, for instance, the T_g of the blend with PBI was still remarkably high, at 381°C. Part of the complexity is related to the observation that the 40 weight percent 950 Mn polysiloxane segment is only a partially microphase separated system.

The hydrophobic nature of the siloxane component accounts for the significantly reduced levels of water sorption with increasing amounts of PI-SX in the blends with PBI. Specifically in the case of PBI, which is exceptionally hydrophilic, the water uptake was reduced from the equilibrium value of 16 weight percent to approximately 2 percent by incorporating 60 percent of the copolymer, or 24 percent siloxane overall.

Eight different samples were subjected to the one week equivalent LEO environment at Physical Sciences, Inc. and initially evaluated for weight loss and degradation of surface morphology. Additionally, all of the samples which were subjected to the atomic oxygen environment lost optical clarity. The siloxane containing samples, however, maintained a greater degree of optical clarity and spectroscopic methods are currently being utilized to quantitatively evaluate this. The weight loss data for these specimens are presented in Table II. Consistently, homopolymers lost more weight than

siloxane containing systems. Although the minor weight gains for the siloxane systems may not be real, the trend is consistent in that the greater amounts of siloxane correspond to greater weight gains. This result might be attributable to the nature of the proposed siloxane to silicate transformation. It is also noted that even an angstrom level coating of the soluble, transparent poly(siloxane imide) copolymer onto Kapton remarkably enhances the stability of Kapton to the aggressive oxygen environment. SEMs reveal that the coating was somewhat nonuniform, suggesting that even greater stability, comparable to that of the copolymer itself, may be obtained with improved coating techniques. The coating technique, therefore, offers a method of easily retrofitting existing spacecraft materials in order to avoid the surface erosion which is common to organic materials in the LEO environment.

Table II

ATOMIC OXYGEN STABILITY STUDY
Weight Loss Test Results*

| <u>Sample</u> | <u>Wt Loss X 10⁴ (gm)</u> |
|--|--------------------------------------|
| PBI | 23.13 |
| Polyimide Homopolymer | 14.01 |
| Poly(10% PSX Imide) Copolymer | 4.54 |
| Poly(40% PSX Imide) Copolymer | +3.10 (gain) |
| Blend of 40% PBI and 60% Poly (40% PSX Imide) Copolymer (24% Overall PSX Content of Blend) | +2.30 (gain) |
| Blend of 25% PBI and 75% Poly (40% PSX Imide) Copolymer (30% Overall PSX Content of Blend) | +2.95 (gain) |
| Kapton | 22.93 |
| Kapton coated with ~1500Å Poly (40% PSX Imide) Copolymer | 5.96 |

*Sample size: 1 square inch; Siloxane segment Mn was 950 g/mole

The SEMs in Figure 4 depict the enhanced stability to atomic oxygen of the poly(siloxane imide) copolymer and a blend of the copolymer with PBI relative to PBI and Kapton. PBI is found to undergo the most severe surface degradation and weight loss, comparable to Kapton, whereas the copolymer remains relatively stable to the aggressive oxygen environment. The blend system qualitatively undergoes surface degradation intermediate to its two components. The surface active nature of the siloxane component, however ensures that the protective silicate structure dominates the surface in the oxygen environment, preventing further degradation of the bulk morphology.

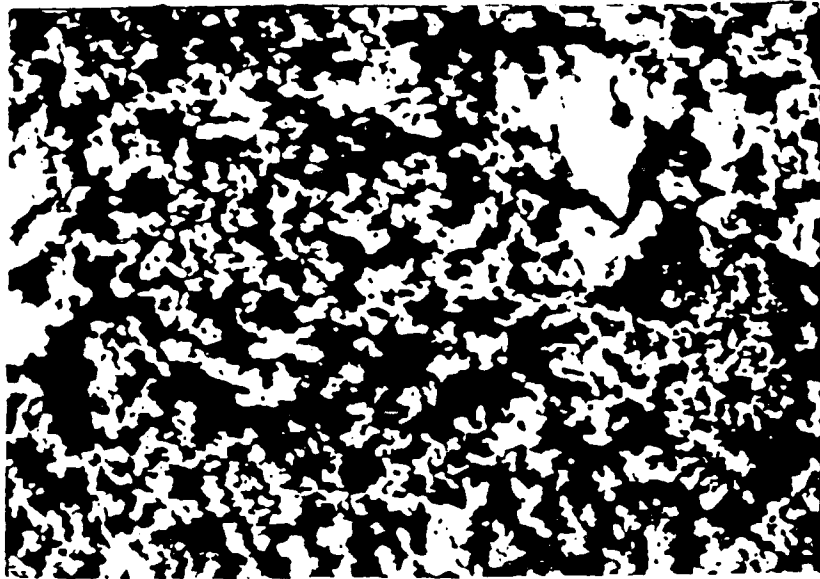
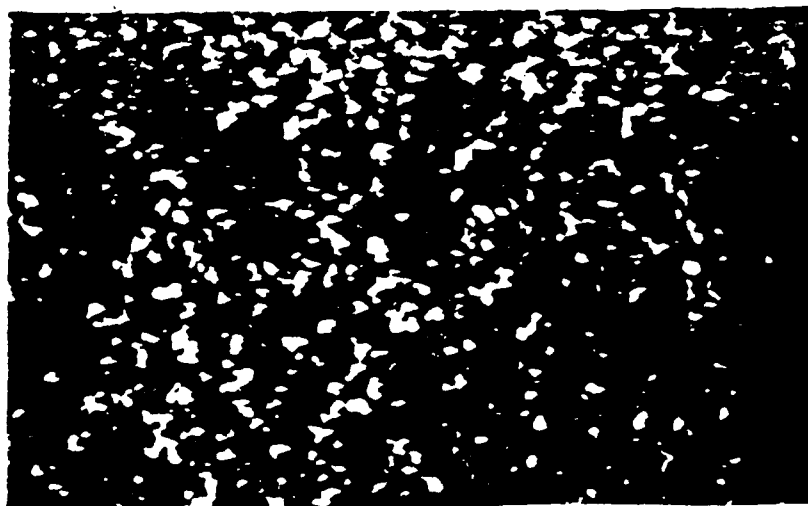
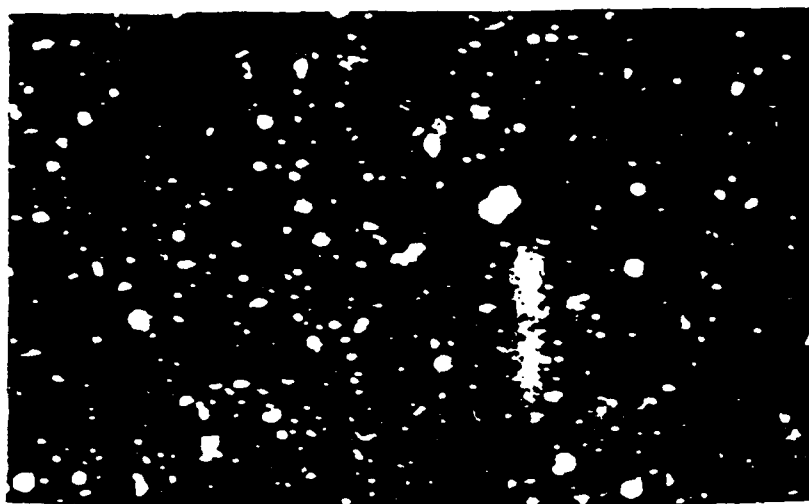


Figure 4 (A): Kapton After Exposure to Atomic Oxygen, 6600X Magnification

(B)



(C)



(D)

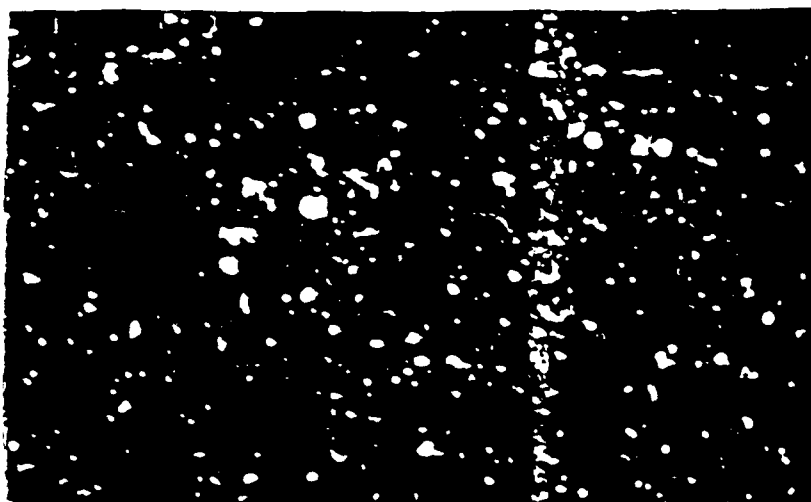


Figure 4: After Exposure to Atomic Oxygen, 6600X Magnification

(B) PBI;

(C) Poly(Siloxane Imide) Segmented Copolymer, 40% SX, SX Mn 950 g/mole;

(D) Blend of 25% PBI and 75% PI-SX (C, above)

CONCLUSIONS

A novel series of miscible polyblends of polybenzimidazole (PBI) and either polyimide homopolymers or poly(siloxane imide) segmented copolymers has been prepared. Incorporation of the polysiloxane blocks offers significant benefits (e.g. reduction in water sorption) for aerospace applications while still maintaining the excellent thermal and mechanical properties of the PBI and imide components. The most unique advantage of siloxane incorporation exploits the transformation of the siloxane segments to a silicate-like structure in the presence of oxygen plasma. Whereas most organic materials undergo serious degradation in aggressive oxygen environments such as the low earth orbit (LEO) atmosphere experienced on space shuttle flights, siloxane-containing systems are quite stable due to this transformation reaction. Materials degradation studies were conducted in an atomic oxygen environment and both weight loss data and surface morphology studies confirm the stability of the siloxane-containing systems. Siloxane concentrations of 20 weight percent or less can be employed, which allows the basic rigidity of the PI/PBI system to be essentially retained. We have demonstrated that crystalline PEEK resins are also blendable with the imide siloxane systems. Future studies will focus on these materials.

REFERENCES

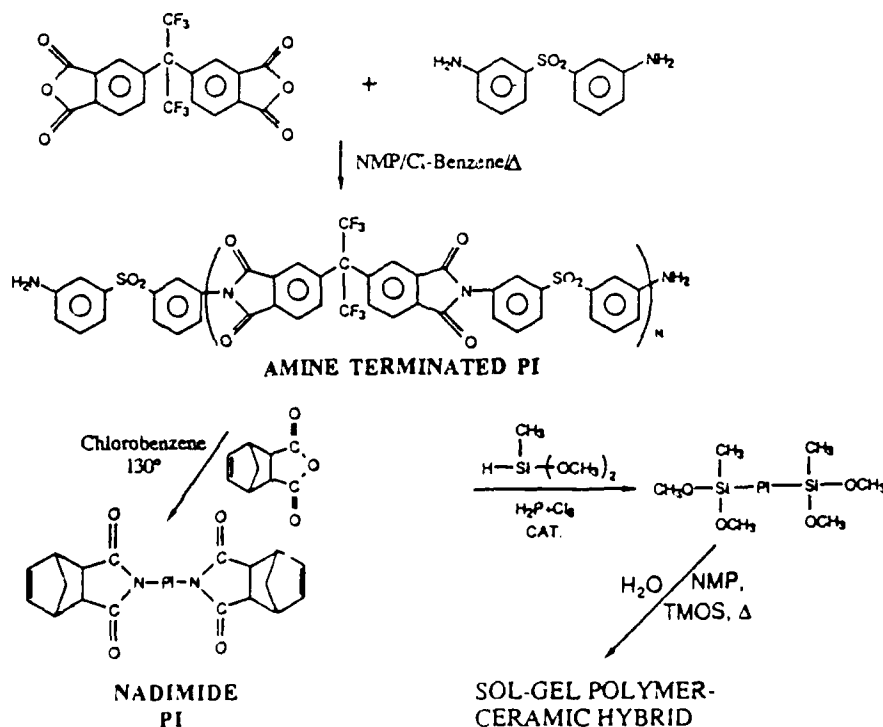
1. Arnold, C. A., Summers, J. D., Bott, R. H., Taylor, L. T., Ward, T. C., and McGrath, J. E., SAMPE Symposium No. 32, (1987) p. 586.
2. Bott, R. H., Summers, J. D., Arnold, C. A., Taylor, L. T., Ward, T. C., and McGrath, J. E., J. Adh. (1987) Vol. 23, p. 67.
3. Andolino-Brandt, P. J., Ph.D. Dissertation, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, 24061 (1986).
4. Slemp, W. S., Santos-Mason, B., Sykes, G. F., and Witte, W. G., Jr., AIAA-85-0421, AIAA 23rd Aerospace Meeting, January, 1985.
5. Visentine, J. T., Lejer, L. J., Kuminecz, J. F., and Spiker, I. K., AIAA-85-0415, AIAA 23rd Aerospace Meeting, January, 1985.
6. Stankovic, S., Guerra, G., Williams, D. J., Karasz, F. E., and MacKnight, W. J., Polymer Comm. (1988) Vol. 29, p. 14.
7. Summers, J. D., Arnold, C. A., Bott, R. H., Taylor, L. T., Ward, T. C., and McGrath, J. E., SAMPE Symposium No. 32 (1987) p. 613.
8. Caledonia, G. E. and Krech, R. H., AIAA-87-0105, AIAA 25th Aerospace Sciences Meeting, January 1987.

IV. POLYIMIDE-SILICATE POLYMER-CERAMIC NETWORKS VIA SOL/GEL PROCESSES; REACTION SCHEME AND PRELIMINARY RESULTS

The section described below outlines a new extension of the research in the general area of polymer-ceramic hybrids. It is of considerable interest to generate thermally stable polymers that might be suitable in all forms for at least brief utilization at 400°C or perhaps even higher without loss of significant molecular structure. The polyimides are certainly one of the first organic based materials that one would think about for such a new multifunctional application. The chemistry has been devised and, indeed, demonstrated but not optimized for the required materials. In the scheme shown below, we have outlined the synthesized route for a functionalized soluble thermoplastic polyimide which can be transformed into a thermosetting network either by simple hydrolysis or by cohydrolysis with a tetraalkyl-

orthosilicate. Our first experiments have utilized the 6F dianhydride in combination with the 3,3'-DDS under conditions using an aprotic dipolar solvent such as NMP and an azeotroping cosolvent such as chlorobenzene. We have, in fact, been able to demonstrate that amine functional fully imidized polyimide oligomers of controlled molecular weight from 5 to 20,000 or higher can be generated. The amine end groups were, indeed, titratable and agreed well with the predicted molecular weights as determined by the Carother's equation. Experiments have been conducted to derivatize the amine terminal fully imidized polyimides to either maleimides or nadimides. Shown in the scheme is the reaction which converts the amine terminal material to the nadimide functional system. The nadimide material is amenable to hydrosilation using chloroplatinic acid catalysis as indicated. One may either use the dimethoxymethylsilane or very recently, we have also demonstrated the trimethoxysilane is amenable to these hydrosilation catalysts. Thus, the functionality at the end of the chain can either be $F = 4$ or $F = 6$ in terms of the SiOCH_3 reactivity. The system shown is soluble in NMP; with less polar diamine it is possible to even get THF soluble polyimides which may be somewhat easier to work with. NMR has verified that the structures shown can be generated although indeed significant amounts of optimization remain. The ability to generate stable linkages between polyimides and silicates is a relatively new possibility.

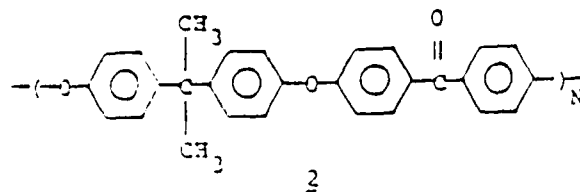
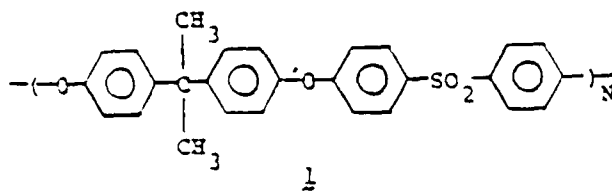
Synthesis of Functionalized Soluble Thermoplastic or Thermosetting Polyimides (PI)

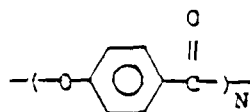


V. ANISOTROPIC-ISOTROPIC SEGMENTED COPOLYMERS

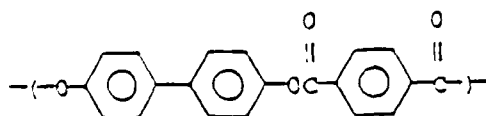
INTRODUCTION

Lyotropic and thermotropic high strength liquid crystal polymer systems have become an important area of research and development in polymeric materials (1-14). In general, these materials have afforded excellent high temperature stability and high strength in the oriented direction, but not in the transverse direction. Poor compressive strength in fibers and fibrillar fracture is one manifestation of this phenomena. Thus, "balancing" the properties in the longitudinal and transverse directions is an important research frontier. One approach to this objective is to introduce glassy isotropic microphase separated segments in order to obtain isotropic-anisotropic segmented copolymers. The isotropic phase is based upon a ductile poly(arylene ether) sulfone (1) or a poly(arylene ether ketone) (2), while the anisotropic segment is based on a rigid polyester moiety such as 3 or 4. The polyester is chemically connected to the polysulfone endgroups via ester linkages. Poly(oxy benzoate) was chosen as the polyester moiety due to the observation that the homopolymer and many copolymers incorporating this structure are known to be highly crystalline and liquid crystalline (4-10). In addition, biphenol terephthalate has also been investigated. The poly(arylene ether) sulfones were synthesized such that they had hydroxyl or carboxyl functional group termination (16). The functional groups included phenolic hydroxyl (16,17), acetate (15) or carboxyl groups (16,17). Ester forming monomers were subsequently reacted with the functional endgroups of the polysulfone via a high temperature melt acidolysis procedure to form the segmented copolymers. Significant improvements in this process were achieved via the initial use of chlorobenzene as a homogenizing solvent. Characterization of these polymers has included differential scanning calorimetry, FT-IR, hot stage optical microscopy and wide-angle x-ray scattering. Mechanically tough and chemically resistant structural adhesive studies were also initiated and initial results are presented. The physical properties of the resulting segmented multiphase materials may also be of interest as stress-crack resistant low coefficient of expansion (CTE) matrix resins for aerospace materials, high performance specialty films and as melt processible non-linear optical (NLO) materials.





3



4

EXPERIMENTAL

Materials: 4,4'-dichlorodiphenyl sulfone (DCDPS), 4,4'-difluorobenzophenone, p-hydroxybenzoic acid, hydroquinone, bisphenol A, biphenol, t-butylisophthalic acid, terephthalic acid and n-methylpyrrolidone (NMP) were obtained from commercial sources and purified according to earlier published procedures (15). Dimethyl sulfoxide (DMSO) NMP, DMAC and chlorobenzene were dried over calcium hydride and vacuum distilled before use. Acetic anhydride was dried over magnesium and distilled before use. The p-acetoxybenzoic acid was donated by Amoco and was used without further purification.

Preparation of Hydroxyl, Acetate and Carboxyl Terminated Polysulfones and Polyketones: Some/Major features of the synthesis of phenolic hydroxyl, acetate, and carboxyl functionally controlled molecular weight poly(arylene ether) sulfones or ketones based upon the bisphenols hydroquinone, biphenol and bisphenol A have been reported previously (15). In particular, the carboxy functional oligomers were prepared with calculated amounts of "monofunctional", p-hydroxy benzoic acid. There was no evidence of decarboxylation at the -170°C reaction temperature. There is some advantage to using chlorobenzene as the azeotroping solvent, since it maintains telechelic oligomer homogeneity, even at room temperatures. A detailed procedure for a 5000 Mn carboxy functional amorphous poly(arylene ether ketone) follows.

Carboxyl terminated Poly(Arylene Ether Ketone) PEK oligomers (e.g. <Mn> 5000): A four necked, one liter round bottom flask was equipped with a thermometer, a nitrogen gas inlet adaptor, a mechanical stirrer, Dean Stark trap with a condenser and oil bath. Bisphenol A (12.621 g, 0.0606 moles) 4,4'-difluorobenzophenone (13.093 g, 0.0554 moles) p-hydroxybenzoic acid (1.349 g, 0.0098 moles) dimethylsulfoxide and N,N dimethyl acetamide in a volume ratio of 2:1 (200 ml), toluene (80 ml) and anhydrous K_2CO_3 (30 g) were charged into the flask. The system was continuously purged with dry nitrogen, heated to $130-140^{\circ}\text{C}$ and maintained at this temperature for 3 hours until the water expected stoichiometrically was collected. The temperature was then raised to $165-170^{\circ}\text{C}$ by removing toluene from the reaction mixture which was allowed to proceed for about 10 hours. The mixture was cooled down to 120°C , separated from the solid salts, neutralized with concentrated hydrochloric

acid and then precipitated in methanol/water. The product was redissolved in chloroform, precipitated in methanol/water and dried overnight in a vacuum oven at 100°C to afford a light tan product.

Preparation of Poly(arylene ether) Sulfone-Poly(oxybenzoate) Segmented Copolymers: The aromatic poly(arylene ether) sulfone-poly(oxybenzoate) segmented copolymers were prepared using a one pot melt acidolysis procedure. The preformed hydroxyl terminated polysulfone was charged into a 1000 ml wide mouth cylindrical resin kettle. A stoichiometric amount of terephthalic acid was added to the vessel to offset the number of moles of polysulfone. This correction of course becomes less significant at higher oligomer molecular weights. The p-acetoxybenzoic acid was then added at various mole or weight percentages. Acetic anhydride, equal to the number of moles of polysulfone used, and a catalytic amount of sodium acetate were then added to the vessel. Chlorobenzene, 50% (w/v), was then added to the vessel to enhance mixing of the polysulfone oligomer and monomers. The top portion of the reactor, fitted with a high torque anchor mechanical agitator, teflon seal, mechanical stirrer and N₂ inlet, was then attached to the bottom of the reactor. The mixture was carefully purged with nitrogen, stirred, and heated to the reflux temperature (132°C) of chlorobenzene. After 1 hour, the homogeneous solution was raised to 300°C and the chlorobenzene was completely distilled off, leaving an apparently homogeneous melt. Acetic acid rapidly began to evolve from the mixture and the viscosity was observed to increase. As the rate of acetic acid evolution diminished, a vacuum was carefully applied to the system over a period of about a 1/2 hour, until reduced pressures approaching 50 mill. torr were obtained. At this point, the molten melt rapidly increased in viscosity to the point where it was barely stirrable by the high torque anchor stirrer. Note that no weight control agents were employed. Generally, the reaction was stopped after about 2 hours under vacuum and slowly cooled to room temperature under a nitrogen bleed. The polymer was removed from the resin kettle, ground and vacuum dried at 140°C for 24 hours. The aromatic polysulfone-poly(oxybenzoate) segmented copolymer based on carboxyl terminated polysulfones were prepared similarly, except that a stoichiometric amount of naphthalene 2,6-diacetate, instead of terephthalic acid, was used to offset the number of moles of polysulfone oligomer.

Preparation of Segmented Poly(Arylene Ether Ketone)-Poly(Oxy Benzoate) (PEK-POB) Copolymers (e.g. 25% by weight of POB): The polymerization was carried out via melt acidolysis. A 500 ml reaction kettle was equipped with a high torque overhead stirrer, nitrogen gas inlet and outlet adaptors and a heating mantle. Carboxyl terminated PEK oligomer (10.000 g), 4,4' biphenol diacetate (0.474 g), p-acetoxybenzoic acid (5.043 g), and in some cases, catalysts such as calcium acetate (0.0003 g), antimony trioxide (0.0003 g) and acetic anhydride (10 ml) were charged into the reaction kettle all at once. The kettle was heated to 200°C over a period of 1 hour. The reaction was run at 200°C for 2 hours and 250°C for 3 hours. The reaction was continued at 290-320°C, nitrogen flow was stopped, and a vacuum of 2 torr- 20 millitorr was applied until the reaction mixture became too viscous to stir. The product was recovered by cooling, swelling in chloroform, and dried. The dried product was then (in some cases) subjected to an additional "solid state polymerization" step at 270°C under high vacuum of 20 millitorr for 20 hours to further increase molecular weight.

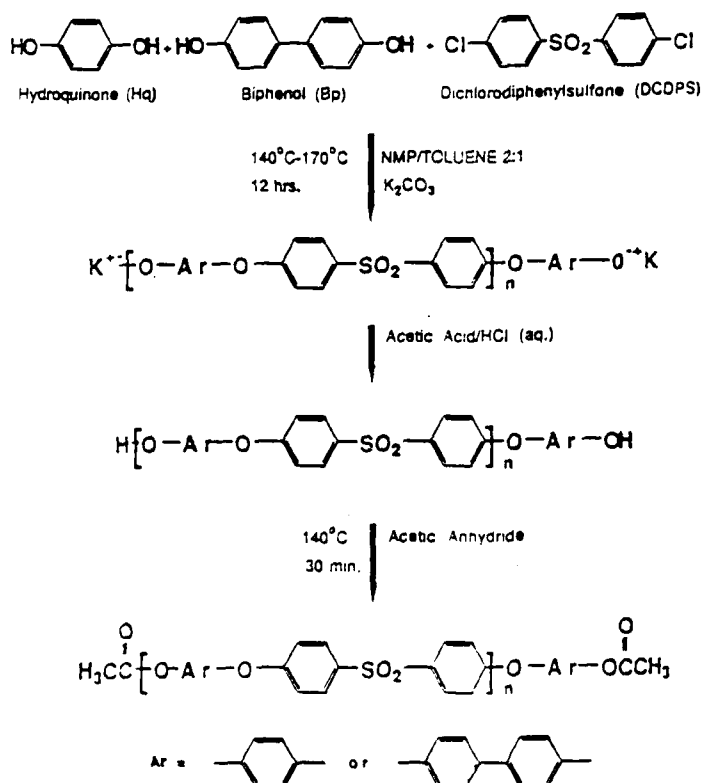
CHARACTERIZATION

The number average molecular weights (\bar{M}_n) of the phenolic and carboxyl terminated oligomers were determined by titration using a Fisher Titrimeter II^R automatic titration system as reported earlier in our laboratory. (18) The oligomers were dissolved in N-methyl-2-pyrrolidone (NMP) and titrated with a 0.1 N tetramethyl ammonium hydroxide in methanol. Intrinsic viscosity measurements were done in chloroform at or NMP 25°C using a Cannon-Ubbelohde viscometer. Differential scanning calorimeter (DSC) and thermal gravimetric analysis (TGA) were run at 10°C/min, N₂ atmosphere using a Perkin-Elmer Model DSC-2. Several heating experiments were conducted and generally little change was observed after the first heat. Dynamic mechanical thermal analysis (DMTA) measurements were conducted using a Polymer Laboratories (DMTA) instrument at 5°C/minute heating rate and multiple frequencies. The data were generally analyzed only at 1 Hertz. Wide-angle x-ray scattering (WAXS) was performed on the polysulfone oligomers and copolymers using a table top Philips generator equipped with a Worhus camera. Optical micrographs of polysulfone oligomers and copolymers were taken using a polarizing microscope equipped with a Mettler hot stage.

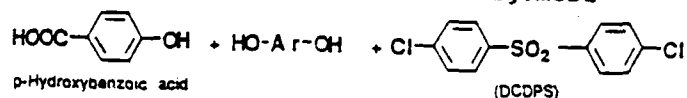
RESULTS AND DISCUSSION

The synthesis of functionalized poly(arylene sulfones) and poly(arylene ether ketones) is described in Schemes 1-3. Characteristics of representative oligomers prepared are shown in Tables 1 and 2. In general, intrinsic viscosities measured in and glass transition temperatures are in the expected range based on considerable research in these laboratories utilizing analogous systems (15,16,17). The agreement with expected \bar{M}_n values was good.

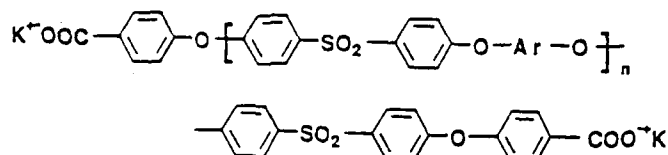
Scheme 1. Synthesis of Poly(arylene ether) Sulfone Hydroxyl and Acetate Functionally Terminated Oligomers



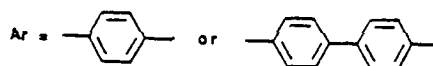
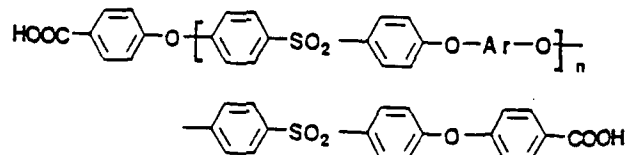
Scheme 2. Synthesis of Poly(arylene ether) Sulfone Carboxyl Functionally Terminated Oligomers



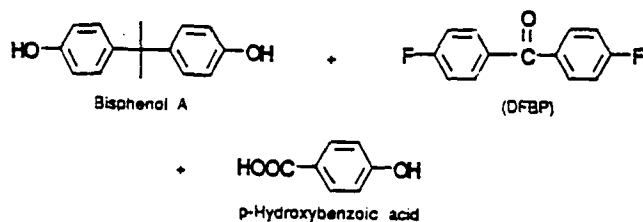
140°C-160°C
12hrs. DMSO/TOLUENE 2:1
K₂CO₃



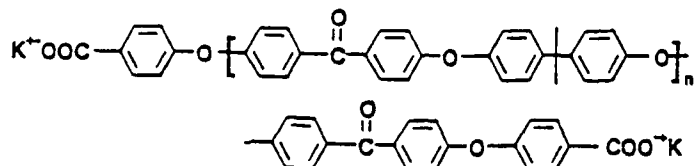
Acetic Acid/HCl (aq.)



Scheme 3. Synthesis of Poly(arylene ether ketone) Carboxyl Functionally Terminated Oligomers



140°C-160°C
12hrs. DMSO/DMAC/TOLUENE 2:1:1
K₂CO₃



Acetic Acid/HCl (aq.)

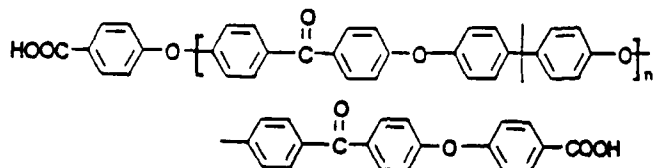


Table 1. Characterization of Acetate and Carboxyl Functionally Terminated Poly(arylene ether) Sulfone Oligomers

| <u>POLYSULFONE</u> | <u>\bar{M}_n gm/mol</u> | | <u>DSC(2)</u> | |
|----------------------|--------------------------------------|-----------------|----------------------------------|--------------------------|
| | <u>THEORETICAL</u> | <u>TITRATED</u> | <u>$[\eta]^{(1)}$</u> | <u>T_g(°C)</u> |
| <u>ACETATE TERM</u> | | | | |
| Bisphenol A | 1500 | 2000 | 0.12 | 136 |
| Bisphenol A | 5000 | 5000 | 0.20 | 156 |
| Hq/Bp 50/50 | 4000 | 4000 | 0.18 | 174 |
| Hq/Bp 50/50 | 6000 | 6800 | 0.22 | 179 |
| <u>CARBOXYL TERM</u> | | | | |
| Hq/Bp 50/50 | 2000 | 2400 | 0.15 | 147 |
| Hq/Bp 50/50 | 5000 | 5800 | 0.23 | 176 |
| Hq/Bp 50/50 | 9000 | 9900 | 0.31 | 189 |
| Hq/Bp 50/50 | 14000 | 14100 | 0.36 | 195 |
| Hq/Bp 50/50 | 15000 | 15800 | 0.41 | 203 |
| Hq/Bp 50/50 | 16000 | 17500 | 0.47 | 210 |

(1) 1-METHYL-2-PYRROLIDINONE, 25°C

(2) 10°C/MIN, N₂, 2nd heating scan

Hq/Bp = Hydroquinone/Biphenol

Table 2. Characterization of Carboxyl Functionally Terminated Poly(arylene ether ketone) Oligomers

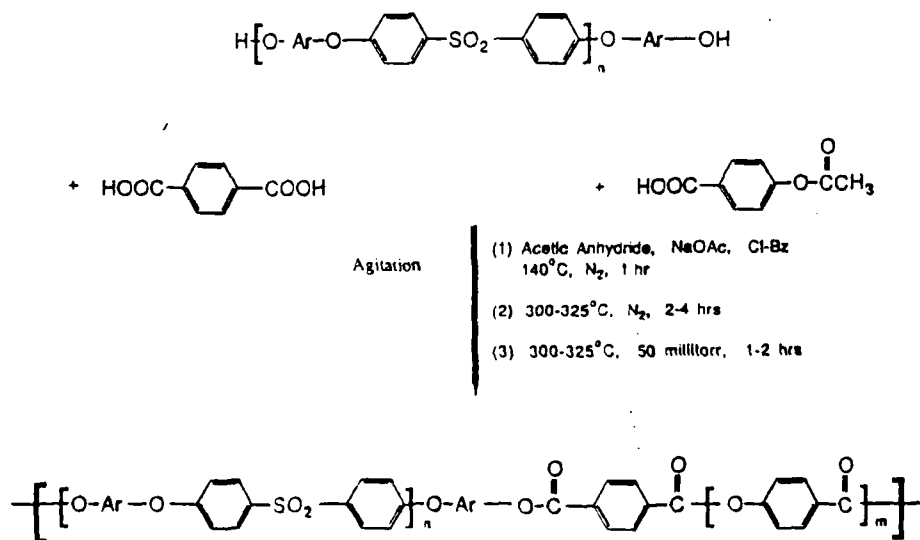
| <u>POLYSULFONE</u> | <u>\bar{M}_n gm/mol</u> | | <u>DSC(2)</u> | |
|----------------------|--------------------------------------|-----------------|----------------------------------|--------------------------|
| | <u>THEORETICAL</u> | <u>TITRATED</u> | <u>$[\eta]^{(1)}$</u> | <u>T_g(°C)</u> |
| <u>CARBOXYL TERM</u> | | | | |
| Bisphenol A | 3000 | 3600 | 0.18 | 136 |
| Bisphenol A | 5000 | 5700 | 0.23 | 140 |
| Bisphenol A | 8000 | 7300 | 0.26 | 147 |
| Bisphenol A | 10000 | 9700 | 0.35 | 147 |

(1) CHCl₃, 25°C

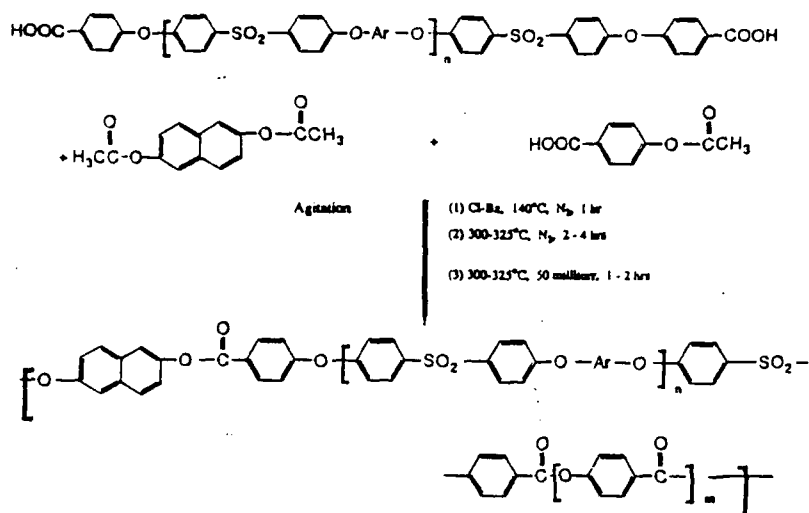
(2) 10°C/MIN, N₂, 2nd heating scan

Preliminary studies of poly(arylene ether sulfone)-poly(oxybenzoate) copolymers have been reported earlier (15,17,19). Those copolymers were synthesized without the use of a solvent which limits the segment size of the poly(arylene ether) to impractically low values due to well-known polymer-polymer incompatibility phenomena. The work reported here deals with segmented copolymers based on poly(oxybenzoate) and poly(arylene ether) sulfone using a solvent such as chlorobenzene which critically enhances the mixing of the polysulfone oligomer and ester forming monomers. The one pot synthetic route to the polysulfone-poly(arylate) segmented copolymers is shown in Schemes 4, 5, 6, and 7. It was found through FT-IR and extraction studies, that if a high degree of agitation and mixing was not employed during the initial stages of the melt acidolysis reaction, p-acetoxibenzoic acid would react with itself forming a homopolymer of poly(oxybenzoate) and the polysulfone oligomer would be chain extended by a few repeat units of oxybenzoate to produce a chloroform soluble fraction. However, when a solvent such as chlorobenzene, which dissolves both the polysulfone oligomer and ester forming monomers, was utilized, true segmented copolymers of polysulfone or polyether ketone poly(oxybenzoate) were formed. This was proven by extracting representative samples in a soxhlet with chloroform for 24 hours and drying to a constant weight. Complete solubility in chlorinated solvents and hot NMP was only observed at 10 weight % POB or lower (Tables 3 and 4). In most cases, very little of the original polysulfone oligomer was observed to be extracted by refluxing chloroform (Tables 5 and 6). This contrasts with our earlier results (19) and also those reported recently by Auman and Percec et al. on similar materials (12). It thus demonstrates the importance of good mixing (eg. mutual solvent and/or good agitation in the early stages of the reaction).

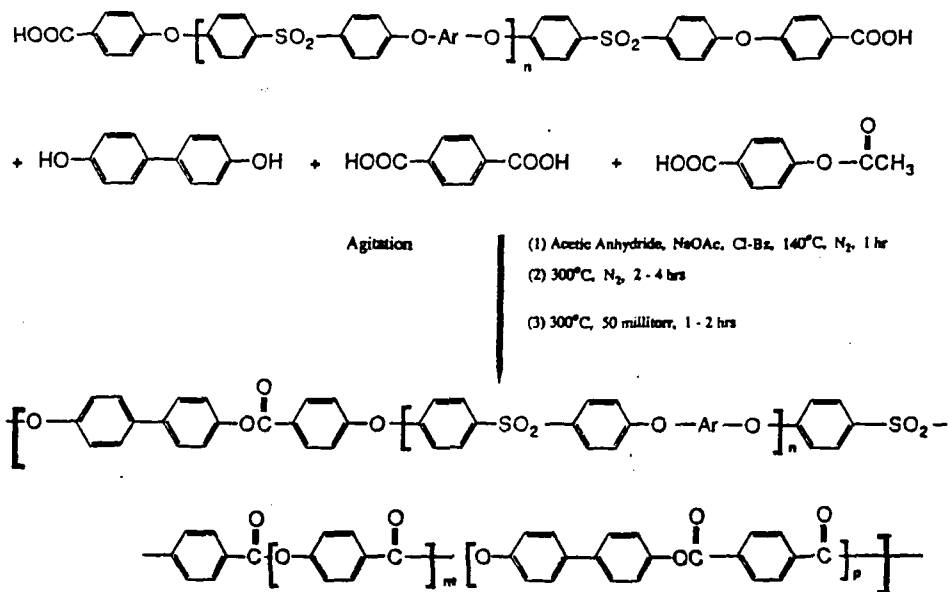
Scheme 4. Synthesis of Poly(arylene ether) Sulfone-Poly(oxybenzoate) Segmented Copolymers via Melt Acidolysis



Scheme 5. Synthesis of Poly(arylene ether sulfone)-Poly(oxygenzoate) Segmented Copolymers Via Melt Acidolysis



Scheme 6. Synthesis of Poly(arylene ether sulfone)-XydarTM Segmented Copolymers Via Melt Acidolysis



Scheme 7. Synthesis of Poly(arylene ether ketone)-Poly(Oxybenzoate) Segmented Copolymers Via Melt Acidolysis

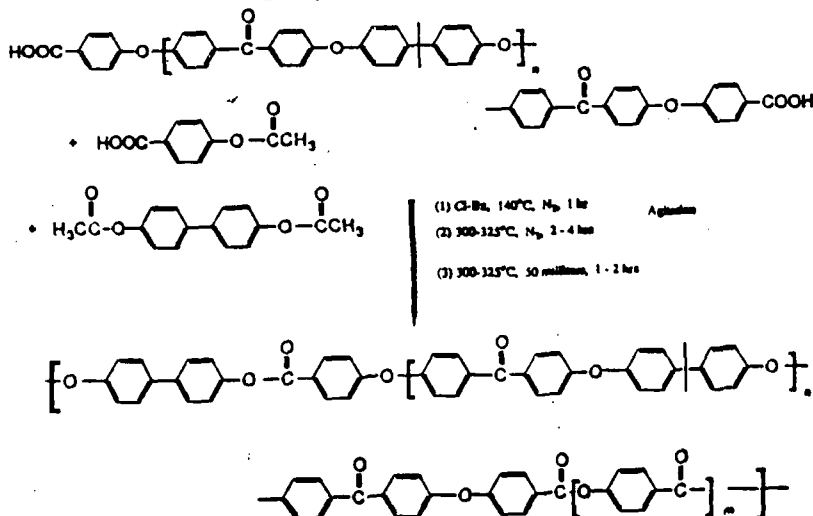


Table 3. Solubilities of a Series of Poly(arylene ether sulfone)-Poly(oxybenzoate) Segmented Copolymers

| | | | <u>SOLVENTS⁽¹⁾</u> | |
|----------------------|-----------|--------------------|-------------------------------------|------------|
| <u>POLYSULFONE</u> | <u>MW</u> | <u>WT% PSF/POB</u> | <u>CH₂Cl₂</u> | <u>NMP</u> |
| <u>ACETATE TERM</u> | | | | |
| BISPHENOL A | 5000 | 95/5 | IS | S |
| Hq/Bp 50/50 | 4000 | 95/5 | IS | S |
| Hq/Bp 50/50 | 4000 | 90/10 | IS | S |
| Hq/Bp 50/50 | 4000 | 80/20 | IS | IS |
| <u>CARBOXYL TERM</u> | | | | |
| Hq/Bp 50/50 | 5800 | 90/10 | IS | IS |
| Hq/Bp 50/50 | 5800 | 80/20 | IS | IS |
| Hq/Bp 50/50 | 9900 | 90/10 | IS | IS |
| Hq/Bp 50/50 | 9900 | 80/20 | IS | IS |
| Hq/Bp 50/50 | 15800 | 95/5 | IS | S |
| Hq/Bp 50/50 | 15800 | 90/10 | IS | IS |
| Hq/Bp 50/50 | 15800 | 80/20 | IS | IS |

(1) 1 WT % IS = INSOLUBLE S = SOLUBLE

(2) 100°C FOR 24 HRS

Table 4. Solubilities of a Series of Poly(arylene ether ketone)-Poly(oxybenzoate) Segmented Copolymers

| | | | <u>SOLVENTS⁽¹⁾</u> | |
|-------------------------|-----------|--------------------|-------------------------------------|------------------------|
| <u>POLYETHER KETONE</u> | <u>MW</u> | <u>WT% PSF/POB</u> | <u>CH₂Cl₂</u> | <u>NMP²</u> |
| <u>CARBOXYL TERM</u> | | | | |
| Bisphenol A | 5700 | 95/5 | S | S |
| Bisphenol A | 5700 | 91/9 | IS | IS |
| Bisphenol A | 5700 | 85/15 | IS | IS |
| Bisphenol A | 5700 | 75/25 | IS | IS |
| Bisphenol A | 5700 | 60/40 | IS | IS |

(1) 1 WT % IS = INSOLUBLE S = SOLUBLE

(2) 100°C FOR 24 HRS

Table 5. Extractions of a Series of Poly(arylene ether sulfone)-Polyoxybenzoate) Segmented Copolymers

| <u>POLYSULFONE</u> | <u><Mn></u> | <u>WT% PSF</u> | <u>% EXTRACTED⁽¹⁾</u> |
|----------------------|-------------------|----------------|----------------------------------|
| <u>ACETATE TERM</u> | | | |
| BISPHENOL A | 5000 | 95 | 33 |
| Hq/Bp 50/50 | 4000 | 95 | 35 |
| Hq/Bp 50/50 | 4000 | 90 | 20 |
| Hq/Bp 50/50 | 4000 | 80 | 10 |
| <u>CARBOXYL TERM</u> | | | |
| Hq/Bp 50/50 | 5800 | 80 | 15 |
| Hq/Bp 50/50 | 9900 | 90 | 22 |
| Hq/Bp 50/50 | 9900 | 80 | 14 |
| Hq/Bp 50/50 | 15800 | 95 | 29 |
| Hq/Bp 50/50 | 15800 | 90 | 18 |
| Hq/Bp 50/50 | 15800 | 80 | 10 |
| Hq/Bp 50/50 | 17500 | 80 | 12 |
| Hq/Bp 50/50 | 17500 | 60 | 6 |
| Hq/Bp 50/50 | 17500 | 40 | 2 |

(1) Soxhlet Extraction with CHCl_3 for 24 hrs; Constant weight after 1 day

Table 6. Extractions of a Series of Poly(arylene ether ketone)-Poly(oxybenzoate) Segmented Copolymers

| <u>POLYETHER KETONE</u> | <u><Mn></u> | <u>WT% PEK</u> | <u>% EXTRACTED⁽¹⁾</u> |
|-------------------------|-------------------|----------------|----------------------------------|
| <u>CARBOXYL TERM</u> | | | |
| Bisphenol A | 5700 | 95 | 100 |
| Bisphenol A | 5700 | 91 | 39 |
| Bisphenol A | 5700 | 85 | 37 |
| Bisphenol A | 5700 | 75 | 28 |
| Bisphenol A | 5700 | 60 | 6 |

(1) Soxhlet Extraction with CHCl_3 for 24 hrs; Constant weight after 1 day

DSC scans of the copolymers indicated a single glass transition, similar to that of the polysulfone or polyether ketone segment, and a single melting endotherm (Tables 7 and 8) was observed at moderate POB concentrations (10-40 wt%). Higher concentrations of POB showed additional higher temperature transitions (Figures 1 and 2) more characteristic of liquid crystalline order.

Table 7. Transition Temperatures of a Series of Poly(arylene ether sulfone)-Poly(arylate Segmented Copolymers)

| <u>POLYSULFONE</u> | <u><Mn></u> | <u>WT% PSF/PAR</u> | <u>DSC(°C)⁽¹⁾</u> | | |
|----------------------|-------------------|--------------------|------------------------------|----------------------|-----------------------|
| | | | <u>T_g</u> | <u>T_m</u> | <u>T_{lc}</u> |
| <u>ACETATE TERM</u> | | | | | |
| Bisphenol A | 5000 | 95/5 | 185 | - | - |
| Hq/Bp 50/50 | 4000 | 95/5 | 203 | - | - |
| Hq/Bp 50/50 | 4000 | 90/10 | 202 | - | - |
| Hq/Bp 50/50 | 4000 | 80/20 | 197 | 302 | - |
| <u>CARBOXYL TERM</u> | | | | | |
| Hq/Bp 50/50 | 5800 | 80/20 | 197 | 302 | - |
| Hq/Bp 50/50* | 5800 | 80/20 | 205 | - | - |
| Hq/Bp 50/50* | 9900 | 80/20 | 212 | - | - |
| Hq/Bp 50/50 | 9900 | 80/20 | 206 | 303 | - |
| Hq/Bp 50/50* | 15800 | 80/20 | 214 | - | - |
| Hq/Bp 50/50 | 15800 | 80/20 | 214 | 322 | - |
| Hq/Bp 50/50 | 17500 | 60/40 | 218 | 326 | 375 |
| Hq/Bp 50/50 | 17500 | 40/60 | 217 | 320 | 370 |

*PSF-XYDAR™ copolymers (semi-crystalline from WAXS patterns)
All other polyester segments based upon p-acetoxybenzoic acid (PSF/POB)
(1) 2nd or 3rd heating scan, 10°C/min, N₂

Table 8. Transition Temperatures of a Series of Poly(arylene ether ketone)-Poly(oxybenzoate) Segmented Copolymers

| <u>POLYETHER KETONE</u> | <u><Mn></u> | <u>WT% PEK/POB</u> | <u>DSC(°C)⁽¹⁾</u> | |
|-------------------------|-------------------|--------------------|------------------------------|----------------------|
| | | | <u>T_g</u> | <u>T_m</u> |
| <u>CARBOXYL TERM</u> | | | | |
| Bisphenol A | 5700 | 95/5 | 157 | - |
| Bisphenol A | 5700 | 91/9 | 159 | 301 |
| Bisphenol A | 5700 | 85/15 | 159 | 304 |
| Bisphenol A | 5700 | 75/25 | 161 | 315 |
| Bisphenol A | 5700 | 60/40 | 161 | 307 |

(1) 2nd or 3rd heating scan, 10°C/min, N₂

Sample: 17.5K PSP-POB (40-60 WT %)
 S11W: 32.9700 mg

DSC

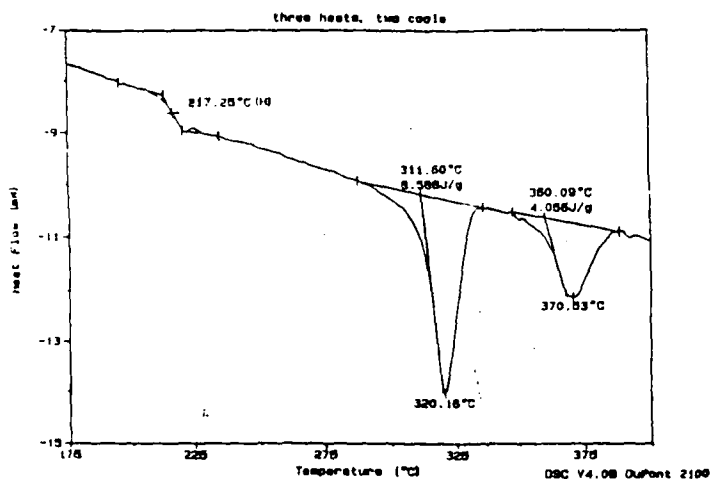


Figure 1

DSC OF PEK<9300>-POB 60%

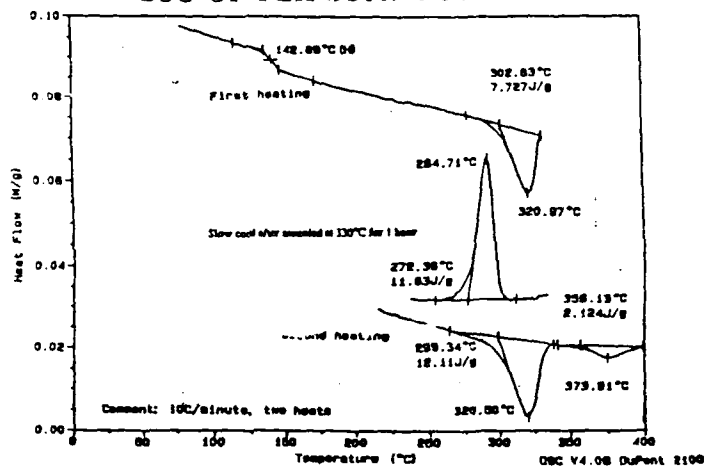


Figure 2

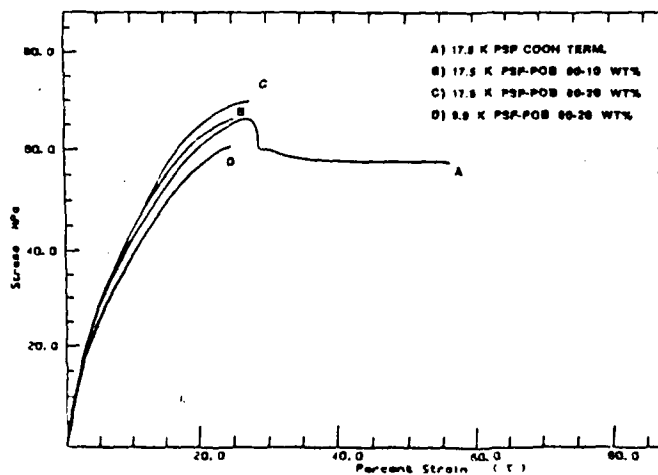
STRESS-STRAIN MEASUREMENTS OF SELECTED POLY(ARYLENE
ETHER SULFONE) - POLY(OXYBENZODIATE) COPOLYMERS

Figure 3

Wide angle diffraction analysis clearly distinguishes between the amorphous poly(arylene ether) oligomers and homopolymers and the ordered segmented copolymers. Wide-angle x-ray scattering (WAXS) patterns also show that the copolymers can be semi-crystalline. A sample viewed between cross polarizers at a temperature below that of the melting endotherm shows a texture similar to that of semi-crystalline polymers (7). However, when viewed between cross polarizers above the temperature of the melting endotherm it shows a texture similar to that expected for liquid crystal polymers (7). Thus, it appears that some form of order, probably liquid crystallinity, exists above the melting endotherm. Although exact molecular weight determinations for the copolymers containing more than ~ 10 weight percent POB are not readily accessible (due to their insolubility in any solvent but strong acids) reasonably high molecular weights are indicated by the ability to compression mold the copolymers into structural adhesives and coherent solvent resistant films at 350°C. Mechanical property values as demonstrated by Instron testing (Figure 3) show that ductile behavior was obtained.

CONCLUSIONS

A one pot melting acidolysis synthetic procedure utilizing chlorobenzene as a solvent in the initial stages successfully yields true segmented copolymers of ductile poly(sulfone) or poly(ether ketone) and polyoxybenzoate. Well defined polysulfone oligomers may be prepared with controlled molecular weights and functionally terminated with hydroxyl, acetate or carboxyl endgroups. These endgroups, coupled with the unproved melt acidolysis procedure, allow for near quantitative incorporation of the isotropic polysulfone into an aromatic, potentially liquid crystalline segmented copolyester. The resulting anisotropic-isotropic copolymers are solvent resistance, semi-crystalline copolymers as poly(oxybenzoate) concentrations greater than approximately 10 weight %.

REFERENCES

1. P. W. Morgan, Macromolecules, 10(6), p. 1381, (1977).
2. J. H. Wendorff, H. Finkelmann and H. Ringsdorf, J. Polym. Sci.: Polym. Symp. 63, 245, (1978).
3. R. W. Lenz and J. K. Jin, "Liquid Crystals and Ordered Fluids" #4, p. 347, 1984.
4. W. J. Jackson, Jr., British Polymer Journal, Vol. 12, p. 154 (1980).
5. W. Volksen, J. R. Lyster, Jr., J. Economy and D. Dawson, J. Polym. Sci.: Polym. Chem. Ed., Vol. 21, p. 2249, (1983).
6. J. Economy, R. S. Storm, V. I. Matkovich and S. G. Lottis, J. Polym. Sci. Chem. Ed. 14, 2807, 1977.
7. A. Ciferri, W. R. Krigbaum and R. B. Meyer, Editors, Polymer Liquid Crystals, Academic Press (1982).
8. G. W. Calundann and M. Jaffe, p. 247-285, Proceedings of the Robert A. Welch Foundation Conferences on Chemical Research XXVI Synthetic Polymers, Houston 1983.

9. J. S. Moore and S. I. Stupp, Macromolecules, 21(6), p. 1217, (1988).
10. P. G. Martin and S. I. Stupp, Macromolecules, 21(6), p. 1222, (1988).
11. S. I. Stupp, J. S. Moore and P. G. Martin, Macromolecules, 21(6), p. 1228, (1988).
12. B. C. Auman and V. Percec, Polymer (London), 29(5), 938 (1988).
13. A. B. Erdemir, D. J. Johnson and J. G. Tomka, Polymer, 27, 441, (1986).
14. R. Rosenau-Eichin, M. Ballauff, J. Grebowicz and E. W. Fischer, Polymer, 29, 518, (1988).
15. J. M. Lambert, E. Yilgor, I. Yilgor, G. L. Wilkes and J. E. McGrath, Polymer Preprints, Vol. 26(2), p. 275, (1985).
16. D. K. Mohanty, J. L. Hedrick, K. Gobetz, B. C. Johnson, I. Yilgor, E. Yilgor, R. Yang and J. E. McGrath, Polymer Preprints, Vol. 23, (1), p. 284, (1982).
17. J. M. Lambert, D. C. Webster, and J. E. McGrath, Polymer Preprints, Vol. 25, (2), p. 14, (1984).
18. A. J. Wnuk, T. F. Davidson and J. E. McGrath, J. Appl. Poly. Sci.: Appl. Polym. Symp. 34, p. 89, (1978).
19. J. M. Lambert, B. E. McGrath, G. L. Wilkes and J. E. McGrath, Vol. 54, p. 1, (1986). Polymeric Materials Science and Engineering; J. M. Lambert, Ph.D. Thesis VPI & SU (1986).
20. R. H. Bott, et al, SAMPE Journal, July 1988.