Polymeric Organic−Inorganic Hybrid Nanocomposites: Preparation of Polyimide-Modified Poly(silsesquioxane) Using Functionalized Poly(amic acid alkyl ester) Precursors

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Received January 31, 1997
Revised Manuscript Received September 3, 1997

Introduction

The sol−gel or spin-on-glass process for the preparation of an inorganic network has been an active research field for nearly three decades. This process is a method for preparing inorganic metal oxides under mild conditions from organic metal halides, alkoxides, esters, etc. The network forming reaction of the sol−gel process involves the simultaneous hydrolysis and condensation of poly(valent) metal alkoxides to produce the gel.[1−14] As the condensation reactions proceed, the continuing network formation causes a contraction in the gel.[15−19] The high interfacial area of the solid−liquid interface coupled with the reduction in chemical potential through condensation provide the incentive for the shrinkage. The shrinkage of the gel and the concurrent expulsion of the condensation byproducts from the pores is known as syneresis. The syneresis or drying process is complex, and Scherer has reported three distinct stages including evaporation, viscous deformation of the solid phase, and the flow of fluid through the pores to generate capillary stress.[15] The development of the stress in the gel phase depends on the relative rates of each of these processes. The redistribution pressure that drives the liquid (i.e., the condensation byproducts) from the wet region of the gel to the dry region is the most pervasive of the capillary stresses identified. Rapid drying causes cracking, due to the large capillary forces generated in the nanoporous structure. As a consequence, films of thicknesses of 1 μM or greater are difficult to dry and usually crack extensively.

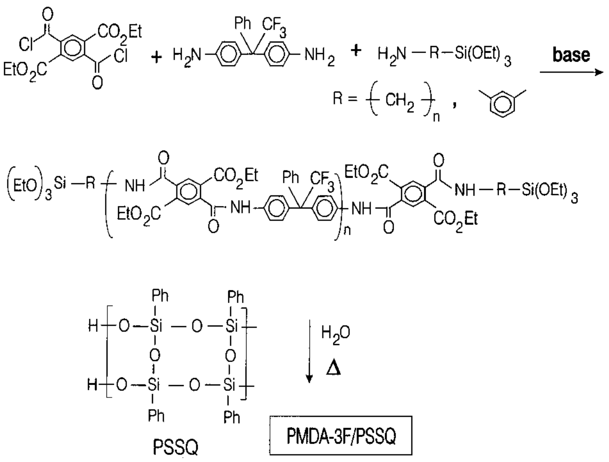
Several approaches have been designed to ameliorate the stresses and strains that arise during gel drying.[20,21] The use of supercritical carbon dioxide is a successful means of elimination of the interfacial tension and the gel capillary stresses associated. Alternatively, Schmidt and co-workers[22] controlled the polymerization rate and stresses in metal alkoxides through the concept of "chemically controlled condensation," where competitive esterification reactions were used to slow the elimination of water. In addition to the manipulation of the processing parameters, another approach toward dealing with the stresses associated with drying involves the modification of the inorganic metal oxide with an appropriately functionalized polymer. Such inorganic−organic hybrids or composites can be designed to offer a range of properties depending on the relative composition of each component, size scale of phase separation, and reactivity between the components.[23−33] Chujo and co-workers[34−36] and others[37−39] have reported that nanometer phase separation is obtained for organic−inorganic composites only when there is inorganic functionality on the organic component and there is a strong interaction (i.e., hydrogen bonding) between the components. Examples of such polymers include triethoxysilyl functional polyoxazolines,[34−36] poly(methyl methacrylate), poly(vinyl acetate),[31] poly(*N*,*N*-dimethylacrylamide),[37] poly(vinylpyrrolidone),[37,40] and others.[37]

For many organic−inorganic composites, high temperatures are required to effect full network formation and completely dehydrate the system. For such systems, high-temperature polymers, in particular, polyimides, have been used as modifiers for spin-on-glass resins. The initial attempts at hybridization involved simply mixing of a poly(amic acid) solution with tetraethylorthosilicate (TEOS) in an aprotic dipolar solvent.[41] In these systems, gross macroscopic phase separation was observed. Partial control of the phase separation and resulting morphology was accomplished by introducing inorganic functionality to the polyimide so as to chemically incorporate the organic component into the TEOS-based network.[42−44] This was accomplished for low inorganic compositions by binding the metal alkoxide precursor to the carboxylic sites of the poly(amic acid).[45,46] Upon imidization, the metal alkoxide is released and further condenses, producing dispersed inorganic particles within the polyimide matrix. Alternatively, Mascia and Kioul reported the use of (glycidylpropyl)trimethoxysilane as a coupling agent to compatibilize TEOS with poly(amic acids).[47−49] The use of the coupling agent served to significantly reduce the size scale of phase separation, which occurred via a spinodal decomposition process. Other key factors in structure control included the molecular weight of the poly(amic acid), the reaction time for the coupling agent, and the nature and concentration of catalyst.[48]

The synthetic procedure for the preparation of polyimide−silica hybrids involves mixing varying quantities of TEOS and water with the poly(amic acid) solution. The resulting mixtures are cast and cured to effect imidization and concurrent network formation. For this condensation, water is essential, and therefore the stability of the poly(amic acid) to hydrolysis is of concern. To this end, we have surveyed an alternative route to polyimide−silica hybrids based on poly(amic acid ethyl ester) precursors to the polyimide. These precursor poly(amic acid esters) (PAE) are hydrolytically stable, allowing isolation, characterization, and copolymerization in a wide variety of solvents and solvent mixtures. In particular, we are interested in introducing inorganic functionality (i.e., triethoxysilyl end groups) to the precursor in a controlled way. We have primarily used the poly(amic acid ethyl ester) precursor route since imidization occurs at a substantially higher temperature than the poly(amic acid) analog.[50] In polyimide−silica hybrids derived from poly(amic acid) solutions, the morphology is strongly influenced by the hydrogen bonding between the organic and inorganic components. If this interaction is lost prior to vitrification (i.e., imidization), significant coarsening during phase separation is observed. The onset of imidization of the poly(amic acid ethyl ester) is 250 °C without a catalyst, and a cure temperature of 350 °C is required for quantitative imidization. The high cure temperature should allow significant vitrification of the gel prior to imidization, providing a kinetic means of controlling the morphology.

S0024-9297(97)00135-6 CCC: $14.00

Scheme 1



Experimental Section

Materials. *N*-Methyl-2-pyrrolidone (NMP) and *N,N′*-dimethylpropyleneurea (DMPU) were purchased from Aldrich and distilled under vacuum from P_2O_5. Methylene chloride was purchased from Aldrich and used as supplied. Pyridine was stored over potassium hydroxide and distilled prior to use. Diethyl dichloropyromellitate was prepared according to a literature procedure[50] and was used as an isomeric mixture comprising 99% meta and 1% para isomers. 1,1-Bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (3FDA) was prepared according to the literature procedure.[51] (*p*-Aminophenyl)-trimethoxysilane was purchased from Gelest Inc. and was used as supplied. This monomer was an isomeric mixture comprising 95% para and 5% meta isomers, as estimated by ^{1}H NMR and GPC. The poly(silsesquioxane) (GR-950F) was obtained from Techneglass Inc. and used as received.

Oligomer Synthesis. Trimethoxysilyl-Functionalized Poly(amic acid ethyl ester) (Scheme 1). To a three-neck flask equipped with an overhead stirrer, nitrogen inlet, and additional funnel was charged 3.2456 g (9.48 mmol) of 3FDA, 0.2218 g (1.04 mmol) of (aminophenyl)trimethoxysilane, 2.0 g (25.00 mmol) of pyridine, and 50 mL of distilled NMP. The reaction mixture was maintained under a positive nitrogen pressure and cooled to 0 °C. The pyromellitic dianhydride (PMDA) diethyl ester diacyl chloride (3.4716 g, 10 mmol) was dissolved in ~100 mL of methylene chloride, quantitatively transferred to the addition funnel, and added dropwise to the cold, stirred reaction mixture. After the addition was complete, the polymerization was allowed to proceed overnight at room temperature. The poly(amic acid ethyl ester) oligomer was isolated by precipitation under high shear conditions (Waring blender) in methanol, filtered off, and dried in a vacuum oven at 60 °C.

Characterization

The inherent viscosities were obtained with 0.5 g/dL solutions in NMP at 30 °C by employing a Cannon Ubbelohde viscometer and were calculated from an average of five different runs. ^{1}H NMR spectra were obtained on a Bruker AC 250 MHz NMR spectrometer in either $CDCl_3$ or deuterated DMSO and are reported in ppm (δ) downfield from TMS. In the case of the trimethoxysilyl-functionalized oligomers, the number average molecular weights were estimated from the ratio of the methyl protons of the ester functionality to the methoxhy protons of the trimethoxysilyl end group. FTIR analyses were carried out on a Nicolet FTIR on films prepared from a solution of poly(amic acid ethyl ester) in THF on NaCl plates. Dynamic TGA was performed on a Perkin-Elmer TGA-7 in air at a heating rate of 10 °C/min. Dynamic DSC was carried out on a DuPont 1090 instrument at 10 °C/min.

Table 1. Characteristics of Trimethoxysilane Functional Poly(amic acid ethyl ester) Oligomer

sample entry	target $\langle M_n \rangle$	η_{inh} NMP, 30 °C (dL/g)	$\langle M_n \rangle$ H NMR
1	10 000	0.17	8,900

Measurement of Fracture Properties. Fracture properties were characterized using a controlled-flaw stressing technique in which the films were exposed to a reactive environment under applied stress. Strips 10 mm wide and 30 mm long were cleaved from the coated silicon wafers and a 5 N indentation made in the center of the strips. The Vickers diamond-pyramid square indenter used produced a contact impression with cracks approximately 30 μm long emanating from the corners that extended through the film “into the substrate” or the silicon substrate. The indented strips were then immersed in water either as indented or in a small four-point bend fixture that applied 70 MPa tension to the outer fiber of the silicon substrate resulting in approximately 6−9 MPa additional stress on the film. Control strips that contained no indentations were also monitored or were exposed to air of approximately 50% relative humidity. The behavior of the cracks was monitored using optical microscopy.

Results and Discussion

The successful implementation of the hybridization approach to toughen spin-on-glass requires the judicious combination of polyimide with the inorganic precursor. The material requirements for the polyimide component are stringent and include high thermal stability, high T_g, and functionalization (vide infra). The polyimide used in this study was the structure formally derived from pyromellitic dianhydride (PMDA) and 1,1-bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (3FDA), a material with a high T_g (440 °C), solubility in common dipolar solvent, and excellent thermal stability.[51] The $Si(OMe)_3$ functional poly(amic acid ethyl ester) oligomers were prepared by the reaction of 3FDA with the diethyl ester diacyl chloride of PMDA in the presence of (4-aminophenyl)trimethoxysilane to control the molecular weight and end-group functionality (Scheme 1). The details of the synthesis and characterization of these oligomers have been published elsewhere.[52] The meta-isomer of the acid chloride was isolated by fractional recrystallization and used in the oligomer synthesis, since polymers prepared in this manner show enhanced solubility and a distinct softening or T_g at approximately 120 °C. The molecular weight (M_n) of the oligomer prepared was 8900 (Table 1).

The inorganic component used is based on a precondensed poly(silsesquioxane) (PSSQ), where the substituent on the silicon atom is phenyl. The structure of PSSQ is variously described as a linear double chain ladder polymer, randomly linked polycyclic cages, or structurally random. Such precondensed polymers show significantly less volume contraction upon condensation than TEOS-based analogs, providing inherently tougher films. In the study, the commercially available PSSQ (GR-950F) was used. This resin has a melting point between 52 and 54 °C, and only 8% weight loss is observed upon curing to 420 °C. The theoretical weight loss of water for the polymer is only 1.5%. The additional weight loss observed is from residual solvent or low molecular byproducts from the synthesis. Films were prepared by casting from NMP or DMPU and cured at 415 °C for 2 h. Crack- and defect-free films

Table 2. Mechanical and Thermal Characteristics of Hybrids

		treatment conditions				
material	thickness	air	water	indent/water	indent/water/stress	isothermal wt loss at 400 °C,[a] wt %/h
PSSQ	0.85 μm	unstable (day)	unstable (days)	unstable extension	unstable extension	
hybrid-1, 20 wt % PAE	3 μm	unstable (day)	unstable (hours)	unstable extension	unstable extension	
(oligomer 1)	2 μm	stable	stable	no estension	large stable extension	0.3
	1 μm	stable	stable	no extension	no extension	
hybrid-2, 23 wt % PAE	3 μm	unstable (days)	unstable (day)	unstable extension	unstable extension	
(oligomer 1)	2 μm	stable	stable	no extension	no extension	0.3
	1 μm	stable	stable	no extension	no extension	

[a] Isothermal weright loss of PSSQ at 400 °C is 0.2 wt %/h.

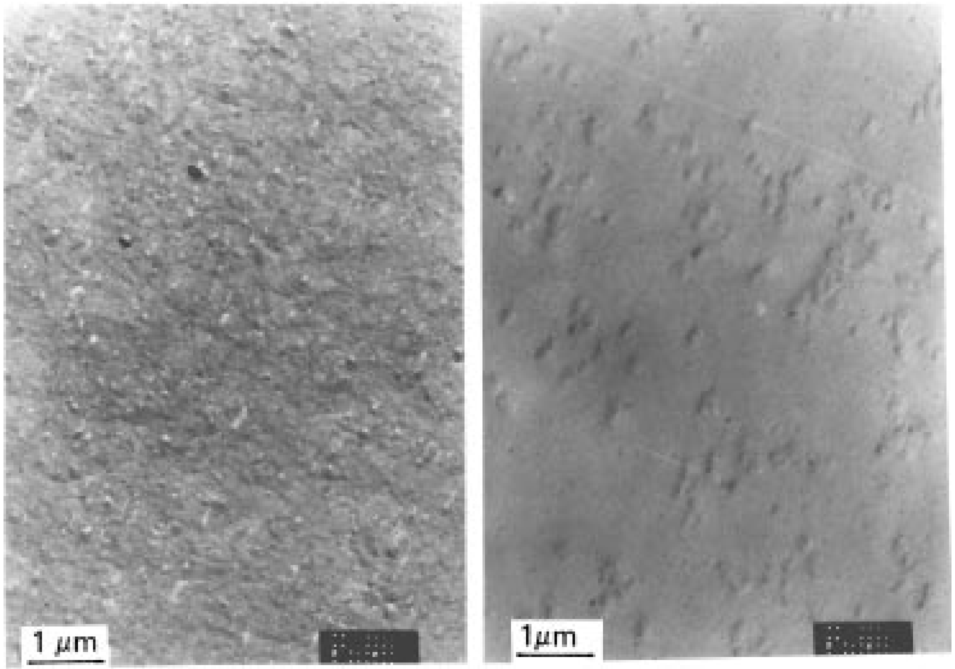


Figure 1. TEM micrograph of hybrid-2 cast from either (right) NMP or (left) DMPU.

with thicknesses between 0.5 and 2.0 μm were prepared. The resulting networks were thermally stable as judged by thermogravimetric measurements (i.e., the isothermal weight loss at 400 °C was less than 0.2 wt %), and no detectable softening point or T_g was observed by thermomechanical measurements.

Homogeneous solutions of the PSSQ and poly(amic acid ethyl ester) were prepared in either NMP or *N*,*N*-dimethylpropyleneurea (DMPU), cast and cured to 410 °C, which effects both imidization and condensation (Scheme 1). The resulting films were defect free and could be prepared with film thicknesses as high as 10 μm, depending on the polyimide composition. Interestingly, the temperature range for imidization is between 250 and 350 °C, which is nearly identical to that for the condensation chemistry and the loss of solvent. The characteristics of the hybrid systems prepared are shown in Table 2. The composition of polyimide in the composite as intentionally maintained low and ranged from 5 to 30 wt %. The thermal stability of the composites was not compromised by the incorporation of the polyimide and was comparable to that of the neat PSSQ.

Over the polyimide compositional ranges studied for the organic–inorganic hybrids, the films cast from DMPU were clear and transparent, whereas films cast from NMP were somewhat translucent, suggesting structures on the order of the wavelength of light for the latter. Shown in Figure 1 are the TEM micrographs of composites containing 20 wt % polyimide and cast from either NMP or DMPU. The sample cast from NMP clearly shows spherical polyimide "rich" regions on the order of 0.2 μm. However, the frequency of these domains does not appear to constitute 20 wt %, which suggests that a significant amount of the polyimide remains in the PSSQ "rich" continuous phase. The TEM micrograph of the sample cast from DMPU shows no large scale phase separation and, in fact, shows regions of electron density contrast well below 100 nm, similar to a microphase-separated block copolymer system. The nature and extent of phase separation in these systems appears to be kinetically controlled and appears to proceed via a nucleation and growth mechanism. These data are significantly different from other polyimide–silica hybrids reported. In these earlier reports, nanostructures were obtained only for high polyimide compositions, where a high viscosity is realized at the cure temperature. Conversely, the hybrids with low polyimide content were macroscopically phase separated (1.0 to 10 μm), irrespective of the nature of the composite (i.e., blend vs functional system). Since the onset of the condensation reaction of the PSSQ is above 200 °C, the samples cast from NMP (bp = 206 °C) have essentially lost most of the solvent prior to vitrification, allowing coarsening of the two dissimilar components that phase separate upon loss of solvent. In contrast, the higher boiling DMPU (bp = 294 °C) keep the mixture homogeneous until vitrification limits the mobility and hence the extent of phase separation. Alternatively, a variety of basic catalysts could be employed to facilitate both the condensation network forming reaction as well as imidization of the poly(amic acid ethyl ester). For instance, *N*-methyldiethanolamine (1−3 wt % of the total solids composition) facilitates each process and produces microphase-separated morphologies, with a number of different solvents.

The preliminary mechanical characteristics of the hybrids cast from DMPU and cured to 410 °C together with those of fused silica, used as a PECVD silica model, are shown in Table 2. A summary of the fracture behavior of the hybrids in comparison with that of bulk silica after 24 h of exposure is given in Table 2. In this table, the term "unstable" refers to spontaneous global fragmentation of the film, "stable extension" refers to the growth of the indentation cracks to a new finite length, and "unstable extension" refers to the growth of cracks completely across the specimen. Although qualitative, these observations clearly suggest the addition of polyimide enhances the resistance of the hybrids to cracking whether spontaneously initiated in the film or induced by deliberate indentation. The critical thickness for suppression of film fragmentation under the conditions appears to be at least 2 μm for each sample studied. However, the sample containing 23 wt % polyimide appears to offer greater resistance to continued crack propagation of introduced cracks over that of the silica model.

The dielectric constant of the matrix PSSQ is 2.8 (1 MHz at 100 °C), which is significantly lower than the value for PECVD silica (ca. 4.0) and presumably results from the significant organic character and perhaps porosity of the PSSQ. The dielectric constant of the polyimide is 2.9, and as expected, the dielectric constants of the hybrids are in the 2.9 range. Refractive index measurements (n_{TE} and n_{TM}, 633 nm) indicate that the electronic properties are optically isotropic.

Acknowledgment. J.L.H. and R.D.M. gratefully acknowledge partial funding from the NSF Center for Polymeric Interfaces and Molecular Assemblies under Cooperative Agreement No. DMR-9400354.

References and Notes

(1) Schmidt, J. *J. Non-Cryst. Solids* **1988**, *100*, 51
(2) Roy, R. *J. Am. Ceram. Soc.* **1969**, *52*, 344.
(3) Dislich, H. *Angew Chem.* **1971**, *83*, 428.
(4) Gottardi, V. *J. Non-Cryst. Solids* **1982**, *48*.
(5) Scholze, H. *J. Non-Cryst. Solids* **1984**, *63*.
(6) Zarzycki, J. *J. Non-Cryst. Solids* **1986**, *82*.
(7) Better Ceramics through Chemistry, *Materials Research Society Symposium Proceedings*; Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds; North-Holland: New York, 1984; Vol. 32.
(8) Better Ceramics through Chemistry II, *Materials Research Society Symposium Proceedings*; Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds.; MRS: Pittsburgh, 1986; Vol. 73.
(9) *Sol-Gel Technology for Thin Films, Preforms, Electronics, and Especially Shapes*; Klein, L. C., Ed.; Noyes: Park Ridge, NJ, 1988.
(10) Brinker, D. J.; Scherrer, G. W. *Sol-Gel Science, The Physics and Chemistry of Sol-Gel Processing*; Academic: San Diego, CA, 1990.
(11) Livage, J.; Henry, M.; Sanchez, C. *Prog. Solid State Chem.* **1988**, *18*, 259.
(12) Sanchez, C.; Ribot, F.; Doeuff, S. In *Inorganic and Organometallic Polymers with Special Properties*; Lane, R. M., Ed.; Nato ASI Series; Kluwer: New York, 1992; Vol. 206, p 267.
(13) Brinker, C. J. *J. Non-Cryst. Solids* **1988**, *100*, 31.
(14) Schmidt, H.; Scholze, H.; Kaiser, A. *J. Non-Cryst. Solids* **1984**, *63*, 1.
(15) Scherrer, G. W. *J. Non-Cryst. Solids* **1986**, *87*, 199.
(16) Brinker, C. J.; Scherrer, G. W.; Roth, E. P. *J. Non-Cryst. Solids* **1985**, *72*, 345.
(17) Scherrer, G. W.; Brinker, C. J.; Roth, E. P. *J. Non-Cryst. Solids* **1985**, *72*, 369.
(18) Scherrer, G. W. *J. Non-Cryst. Solids* **1986**, *87*, 199.
(19) Livage, J. *J. Solid State Chem.* **1986**, *64*, 322.
(20) Yoldas, B. E. *Bull. Am. Ceram. Soc*, **1975**, *54*, 286.
(21) Strawbridge, I. In *Chemistry of Glasses*, 2nd ed.; Paul, A., Ed.; Chapman & Hall: London, 1990; pp 57, 85.
(22) Schmidt, H.; Seiferling, B. *Mater. Res. Soc. Symp. Proc.* **1986**, *73*, 731.
(23) Philipp, G.; Schmidt, H. *J. Non-Cryst. Solids* **1984**, *63*, 283.
(24) Schmidt, H. *J. Non-Cryst. Solids* **1985**, *73*, 681.
(25) Sanchez, C.; Ribot, F. *New J. Chem.* **1994**, *18*, 1007.
(26) Jiang, C-Y.; Mark, J. E. *Makromol. Chem.* **1984**, *185*, 2609.
(27) Ning, Y-P.; Mark, J. E. *J. Appl. Polym. Sci.* **1985**, *30*, 3519.
(28) Mark, J. E.; Ning, Y-P.; Jiang, C-Y.; Tang, M-Y.; Roth, W. C. *Polymer* **1985**, *26*, 2069.
(29) Wang, B.; Wilkes, G. L.; Hedrick, J. C.; Liptak, S. C.; McGrath, J. E. *Macromolecules* **1991**, *24*, 3449.
(30) Fumita, M.; Honda, K. *Polym. Commun.* **1989**, *30*, 200.
(31) Spinu, M.; Brennan, A.; Rancourt, J.; Wilkes, G. L.; McGrath, J. E. *Mater. Res. Soc. Symp. Proc.* **1990**, *175*, 179.
(32) Ellsworth, M. W.; Novak, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 2756.
(33) Novak, B. M.; Dacies, C. *Macromolecules* **1991**, *24*, 5481.
(34) Saegusa, T.; Chujo, Y. *Makromol. Chem., Macromol. Symp.* **1992**, *64*, 1.
(35) Chujo, Y.; Ihara, E.; et al. *Macromolecules* **1993**, *26*, 5681.
(36) Toki, M.; Chow, T.; et al. *Polym. Bull.* **1992**, *29*, 653.
(37) Landry, D. J. T.; Coltrain, B. K.; Wesson, J. A.; Lippert, J. L.; Zumbulyadis, N. *Polymer* **1992**, *33* (7), 1496.
(38) Landry, C. J. T.; Coltrain, B. K.; Brady, B. K. *Polymer* **1992**, *33* (7), 1486.
(39) Fitzgerald, J. J.; Landry, C. J. T.; Pochan, J. M. *Macromolecules* **1992**, *25*, 3715.
(40) Toki, M.; Chow, T. Y.; Ohnaka, T.; Samura, H.; Saegusa, T. *Polym. Bull.* **1992**, *29*, 653.
(41) Morikawa, A.; Iyoku, Y.; Kakimoto, M.; Imai, Y. *Polym. J.* **1992**, *28*, 107.
(42) Morikawa, A.; Iyoku, Y.; Kakimoto, M. Imai, Y. *J. Mater. Chem.* **1992**, *1*, 679.
(43) Johnen, N.; Beecroft, L. L.; Ober, C. K. In *Step Growth Polymers for High Performance Materials: New Synthetic Methods*; Hedrick, J. L., Labadie, J. W., Eds.; ACS Symposium Series 624; American Chemical Society: Washington, DC, p 392.
(44) Iyoku, Y.; Kakimoto, M.; Imai, Y. *High Performance Polym.* **1994**, *6*, 95.
(45) Nandi, M.; Conklin, J. A.; Salvati, L., Jr.; Sen, A. *Chem. Mater.* **1991**, *3*, 201.
(46) Nandi, M.; Conklin, J. A.; Salvati, L., Jr.; Sen, A. *Chem. Mater.* **1990**, *2*, 772.
(47) Mascia, L.; Kioul, A. *J. Mater. Sci.* **1994**, *13*, 641.
(48) Kioul, A.; Mascia, L. *J. Non-Cryst. Solids* **1994**, *175*, 169.
(49) Mascia, L. *Trends Polym. Sci.* **1995**, *3*, 61.
(50) Volksen, W.; Yoon, D. Y.; Hedrick, J. L.; Hofer, D. C. *Mater. Res. Soc. Symp. Proc.* **1992**, *277*, 3.
(51) Rogers, M. E.; Moy, T. M.; Kim, Y. S.; McGrath, J. E. *Mater. Plast. Soc. Symp.* **1992**, *277*, 23.
(52) Srinivasan, S. A.; Hedrick, J. L.; Miller, R. D.; Di Pietro, R. *Polymer* **1996**.

MA970135Y