Imide–Dimethylsiloxane Block Copolymers: Design and Synthesis of a Permanent Buried Oxygen Ion Etch Barrier

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ABSTRACT: Imide–siloxane multiblock copolymers were investigated. A key feature of these copolymers is the preparation of bis(aminopropyl) oligomers via anionic ring-opening polymerization. The molecular weights of the oligomers ranged from 1000 to 5000 g/mol. The oligomers were coreacted with 4,4′-oxydianaline (ODA) and pyromellitic dianhydride (PMDA) diethyl ester chloride in a N-methyl-2-pyrrolidone/THF–solvent mixture in the presence of N-methylmorpholine. The resulting amic ethyl ester siloxane copolymers were isolated and washed to remove homopolymer contamination. Copolymer compositions, determined by ^{1}H-NMR, ranged from 20 to 65 wt % siloxane content and the measured compositions were close to those charged. Solutions of the copolymers were cast and cured (350°C) to effect imidization, producing clear films. The films showed tough ductile mechanical properties with moduli varying with siloxane content. The copolymers displayed good thermal stability with decomposition temperatures in the proximity of 450°C. Multiphase morphologies were observed irrespective of siloxane block lengths or compositions. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 199–208, 1997

INTRODUCTION

Inorganic oxide insulators have typically dominated microelectronic applications which involve the fabrication of multichip modules (MCM) or on-chip wiring, where the latter constitutes device-to-device interconnection and is typically designated as the "back end of the line" (BEOL) wiring. The employment of organic materials in these devices allows for a lower dielectric constant medium, thereby reducing propagation delay and crosstalk and lower manufacturing cost since materials can be spin-coated rather than vacuum-deposited.[1] Such insulating materials must be able to withstand the high temperature associated with the processes used to deposit metal lines and join chips without any degradation, outgassing, or dimensional change. Other major factors

in the use of organic insulators is the control of residual thermal stress, adhesion, and planarization from common organic solvents.

A wide variety of polymers have been evaluated for use in microelectronics applications; however, polyimides have emerged as the favored class of materials.[2–6] The rigid and semirigid polyimides, in particular, PMDA/ODA and BPDA/PDA, show an excellent combination of thermal and mechanical properties as judged by high elongations to break. In addition, these properties are largely retained to 400°C, where above this temperature a partial softening is observed in some cases. These desirable properties reflect the high degree of molecular packing.[7–10] For instance, with PMDA/ODA polyimide, a local smecticlike ordering is found. These rigid polyimides are generally applied by spin coating onto silicon wafers as dilute solutions. Since most of these structures are insoluble, they are applied as a soluble poly(amic acid) precursors typically in aprotic dipolar solvents such as N-methyl-2-pyrrolidone (NMP) or di-

methylacetamide (DMAC).[11] Imidization is then effected by a subsequent heating step denoted as curing.

The fabrication of multilayer polyimide–metal structures used in chip BEOL wiring or module thin-film packaging generally involves reactive ion-etching (RIE) processes to pattern the polyimide film.[12,13] When the channels of a given wiring plane inside the structure are defined by RIE of the polyimide dielectric, an etch stop layer is preferred to protect the underlying polyimide. This etch stop layer allows for overetching, thus providing a manufacturable processing window. Furthermore, the basic process for fabricating these structures without an etch stop or permanent, buried oxygen RIE barrier requires considerably more steps than without, and structures with required planarity cannot be built. Since such a barrier layer will remain in the wiring structure, the material requirements are comparable to the polyimide dielectric and include low dielectric constant, high thermal stability, and adhesion to the adjoining polyimide layers.[13] Furthermore, planarization and gap-filling properties are also important if the metalization of wiring channels is done by lift-off.

The organic materials which possess oxygen RIE resistance are those which contain silicon[14,15] or phosphorus.[15–19] Resistance is achieved provided a sufficiently high composition of silicon or phosphorus exists in the bulk, which, upon exposure to the oxygen plasma, forms a protective oxide layer at the surface. Most of the reported etch stops are designed for microlithography applications and do not have the requisite thermal or mechanical properties to survive microelectronic fabrication.[20] However, one approach to an organic etch stop which has been successful is the use of a block copolymer composed of a thermally stable matrix (polyimide) and a dispersed phase which constitutes the etch stop. Block copolymers in most instances are capable of supermolecular assembly, where the domain sizes are on the order of nanometers and the domain shapes or morphology depends on the relative composition of the components. In the design of an etch stop, the properties should be largely dictated by the high-temperature polymer matrix, since the second component which serves as the etch stop would be the dispersed phase. As a class of materials, polyimides have received little attention as a component in the synthesis of block copolymers, due primarily to their limited solubility. Among the few examples, the imide–siloxane copolymers are

the most widely studied as atomic oxygen and oxygen plasma resistant materials.[21] The general synthetic methodology used for the imide–siloxane block copolymers employs a "monomers–oligomers" approach via the poly(amic acid) precursor to the polyimide. Bis(amino)siloxane oligomers of various molecular weights were coated with a dianhydride and diamine to produce poly(amic acid) solutions which were subsequently cast and cured to imidize the polymer, producing a multiblock architecture. In this approach, the copolymers were not isolated or characterized prior to imidization. Furthermore, this approach is not applicable to the semirigid and rigid rod polyimides.

An alternative synthetic procedure for the preparation of imide–siloxane copolymers has been developed using a poly(amic alkyl ester) intermediate to the polyimide.[22] The poly(amic alkyl ester) precursor offers considerable synthetic flexibility due to improved solubility and allows greater structural variety in both the polyimide backbone and the coblock type and composition. The hydrolytically stable precursors may be isolated, characterized, and purified prior to imidization. Furthermore, since imidization occurs at higher temperatures than that of the poly(amic acid) analog, the copolymers are mobile before imidization, thus allowing microphase separation to proceed more fully. In this article, the modification of rigid and semirigid polyimides through copolymerization is described and the basic thermal and mechanical properties are presented.

EXPERIMENTAL

Materials

The 4,4-oxydianiline (ODA, Davos Chemical Co.) and pyromellitic dianhydride (PMDA, Chriskev Co.) were used without further purification. N-Methyl-2-pyrrolidone (NMP) was vacuum-distilled from P_2O_5 prior to use. Octamethylcyclotetrasiloxane (D_4), oxtaphenylcyclotetrasiloxane (D_4'), and 1,3-bis(aminopropyl)tetramethyldisiloxane were purchased from Petrarch. The tetramethylammonium hydroxide pentahydrate, purchased from Aldrich, was used without further purification. The diethyl pyromellitate diacyl chloride was prepared according to a literature procedure.[11,12]

Oligomer and Polymer Syntheses

Synthesis of Aminopropyl-terminated Dimethyl and Dimethyldiphenylsiloxane Oligomers

The bis(aminopropyl)dimethylsiloxane oligomers and bis(aminopropyl)dimethyldiphenylsiloxane oligomers were synthesized by a base (tetramethylammonium hydroxide pentahydrate) catalyzed-bulk anionic equilibration reaction of D_4 or a mixture of D_4 and D_4', respectively, with bis(aminopropyl)tetramethyldisiloxane, also denoted as the end blocker.[23–25] In the polymerization of the dimethylsiloxane oligomers, the equilibrations were done at 80°C for 24 h. The temperature was then increased to 150°C (5 h) to decompose the base catalyst. The polymerization of the D_4 and D_4' cyclic mixtures required slightly different conditions, owing to the insolubility of D_4' in D_4. The D_4' is, however, soluble in oligomers of dimethylsiloxane. Therefore, the equilibration was performed sequentially. The D_4 end blocker and catalyst were charged and allowed to equilibrate, yielding oligomers after 2–3 h. The cyclic tetramer of diphenylsiloxane was then charged and allowed to coequilibrate. The reaction temperature was maintained at 80°C for 48 h and then increased to 150°C for 5 h to decompose the catalyst. The oligomers were heated (150°C) under a (0.05–0.10 mmHg) vacuum to remove the equilibrium cyclics.

Block Copolymer Synthesis of PMDA/ODA and Polydimethylsiloxane Monomers–Oligomers Approach

The amic ester–aryl ether siloxane copolymers were prepared by the coreaction of the siloxane oligomers with ODA and PMDA diethyl ester diacyl chloride in NMP in the presence of N-methylmorpholine. A detailed procedure designed to prepare an amic–ester siloxane copolymer with a siloxane oligomer 5000 g/mol molecular weight and 20 wt % siloxane compositions is provided. A three-neck flask equipped with an overhead stirrer and addition funnel was charged with PMDA (1.2000 g, 000975 mol) and ODA (0.9005 g, 0.004497 mol) and carefully rinsed in with 20 mL of NMP. Throughout the polymerization, N_2 was passed through the system. The solution was then cooled to −5°C, and N-methylmorpholine (1.076 g, 0.01094 mol) was added to the solution. The PMDA diethyl ester diacyl chloride was dissolved in ca. 25 mL of methylene chloride and added in ∼ 0.5 mL increments over a 2 h period so as to

slowly approach the stoichiometric end point. The polymerizations were allowed to proceed overnight and isolated by precipitation in methanol/water, rinsed with water (to remove excess salts) and subjected to a methanol rinse (to remove possible homopolymer contamination), and dried in a vacuum oven.

Measurements

Films for thermal and mechanical analysis were cast from an NMP/CHP (50/50) solvent mixture, heated to 350°C (5°C/min heating rate), and held for 30 min. Glass transition temperatures, taken as the midpoint of the change in slope of the base line, were measured on a DuPont DSC 1090 instrument with a heating rate of 10°C/min in the tension mode. Isothermal and variable temperature (5°C/min heating rate) thermal gravimetric analysis (TGA) measurements were performed on a Perkin-Elmer Model TGA-7 in a nitrogen atmosphere.

The number-average molecular weights of the aminopropyl-terminated siloxane oligomers were determined by titration with a Fisher computer-aided titrimeter. The siloxane oligomers were dissolved in isopropanol and titrated with 0.1N HCl. The epoxy-terminated hydroxy ether oligomers were dissolved in a 2 : 1 mixture of chlorobenzene and acetic acid and titrated with 0.01N HBr.

RESULTS AND DISCUSSION

The approach used for the preparation of the high-temperature organic etch stop is based on phase-separated block copolymers in which the major component composing the matrix is thermally and mechanically robust, while the minor component contains the etch stop. The thermally stable matrix used for this study is PMDA/ODA polyimide, since it has the requisite thermal and mechanical properties and it is one of the most widely used polymer dielectrics. Polydimethylsiloxane was used as the dispersed component, since it is thermally stable, readily functionalized for copolymerization, and has the required oxygen plasma resistance. In this example, the minor component block must be present in a high enough concentration to serve as an etch stop and be of a high enough molecular weight to produce the desired phase-separated morphology. It is also of interest to control the level of phase separation of the siloxane coblock so as to control the distribution of the sili-

Scheme 1
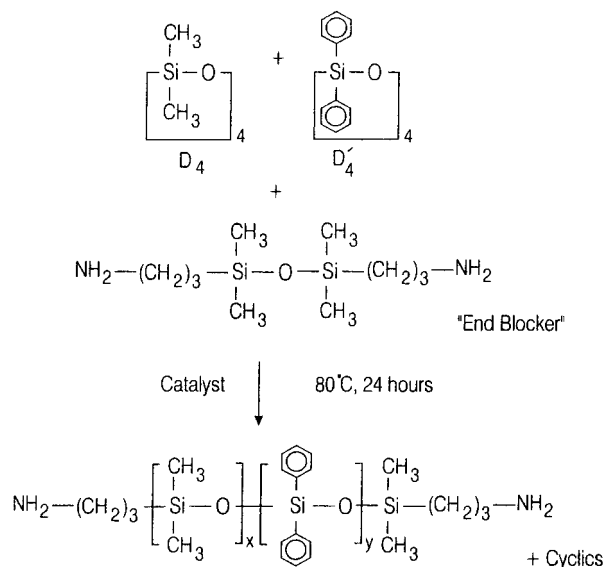
cone etch stop and to study how this effects the etch rate. To this end, siloxane oligomers of low molecular weight were prepared. In addition, a second series of copolymers were prepared in which a portion of the dimethylsiloxane was replaced with diphenylsiloxane. Since diphenylsiloxane is considerably more polar than is the dimethylsiloxane, phase mixing in the copolymer should be promoted.

Bis(aminopropyl)-terminated dimethyl diphenylsiloxane oligomers were synthesized by a base-catalyzed anionic equilibration reaction.[23-25] Bis(aminopropyl)tetramethyldisiloxane (end-blocking agent) was reacted at 80°C with either the cyclic tetramer of dimethylsiloxane, D_4, or diphenylsiloxane, D_4', using tetramethylammonium hydroxide pentahydrate as the catalyst[23,25] (Scheme 1). The dimethylsiloxane oligomers generally require less than 24 h to complete the equilibration. However, the oligomers based on the more reactive cyclic tetramer of diphenylsiloxane required longer reaction times (48 h) so as to avoid blocky structures.[25] The equilibrations were performed in bulk to minimize the cyclic compounds generated upon completion of the reaction. The crystalline cyclic tetramer of diphenylsiloxane, however, was soluble in oligomers of dimethylsiloxane at elevated temperatures. Therefore, the dimethyl diphenylsiloxane equilibrations were performed sequentially, where the end-blocking agent, catalyst, and D_4 were initially charged and allowed to react, generating oligomers followed by the addition of D_4'. Upon completion of the equilibration,

the oligomers were heated to 150°C for 4–5 h to decompose the tetramethylammonium siloxanolate catalyst. Finally, the cyclics remaining from the equilibration, usually 10–15 wt %, were removed by vacuum distillation.

The molecular weights of the bis(aminopropyl)-siloxane oligomers were controlled by the ratio of the end blocker to the cyclic tetramer. Table I contains the characteristics of the oligomers prepared. The molecular weights ranged from 1000 to 5000 g/mol. Dimethylphenylsiloxane oligomers were prepared where the molecular weight was held essentially constant (at 5000 g/mol) and the diphenylsiloxane composition was varied. The glass transition temperatures ranged from −123 to −26°C, where the latter sample contains 75 wt % of diphenylsiloxane.

Polyimides are generally prepared from the condensation of stoichiometric quantities of aromatic bisanhydrides with aromatic diamines to produce soluble poly(amic acid) solutions.[11] Such solutions can be deposited directly and cured thermally to effect imidization. Alternatively, poly(amic acid) solutions can be chemically imidized by dehydration to yield the polyimide directly.[11] However, this limits the polyimide structures to soluble polymers which have limited utility in microelectronic applications. A more versatile precursor to the polyimide is shown in Scheme 2. Pyromellitic dianhydride (PMDA) can be opened by ethanol to give a *meta/para* mixture of half esters which can be separated by fractional recrystallization and converted to the respective acid chlorides.[22] Reaction with ODA produces the corresponding poly(amic ester) which may be isolated and characterized. The poly(amic esters) derived from the *meta* acid chloride showed significantly enhanced solubility in NMP and NMP solvent mixtures. This is an important feature in preparing block copolymers from components of dissimilar solubility.

The copolymer synthesis involved the incremental addition of PMDA diethyl ester diacyl chloride, dissolved in methylene chloride, to a solution of ODA and the functional siloxane oligomer in an NMP/THF solvent mixture in the presence of *N*-methylmorpholine (Scheme 2). Although both the poly(amic ethyl ester) and siloxane oligomer are soluble in NMP, a mixture of the two in NMP produced cloudy solutions. THF added to the NMP solution of the homopolymers produced a clear solution and minimized homopolymer contamination during copolymerization. The solids content for the copolymerizations was

Table I Characteristics of Dimethylsiloxane and Dimethyldiphenylsiloxane Oligomers

Sample Entry	Diphenylsiloxane Compositions (Wt %)	Molecular Weight (g/mol)	T_g (°C)
1a	0	1000	−114
1b	0	5400	−121
2a	25	4800	−109
2b	50	5400	−71
2c	75	5700	−26

maintained between 12–14%. N-Methylmorpholine was used as the acid acceptor since the subsequent salt, N-methylmorpholium hydrochloride, precipitated from the reaction mixture. This is believed to be important since other acid acceptors such as triethylamine form salts which remain in solution and may adversely affect the solubility of the oligomer(s) or subsequent copolymer, lead-

ing to homopolymer contamination. High molecular weight was readily achieved as judged by the dramatic increase in viscosity, characteristic of most condensation polymerizations. The resulting amic ester–siloxane copolymers were precipitated in water and rinsed with methanol to remove salts formed during the polymerization.

Two series of block copolymers were prepared and the characteristics of the copolymers are shown in Tables II and III. In the first series of copolymers, imide–dimethylsiloxane block copolymers were prepared with two dimethylsiloxane block lengths and two compositions. In the second series of copolymers, the siloxane block molecular weight was maintained at approximately 5000 g/mol and diphenylsiloxane was introduced into the siloxane block. The diphenylsiloxane compositions ranged from 0 to 75 wt % as shown in Table I. The monomers–oligomers synthetic route employed produced an $(A—B)_n$ microstructure with segments statistically placed. The average molecular weight of the siloxane block is identical to that of the preformed oligomer. However, the average molecular weight of the imide block is controlled by the stoichiometric imbalance between the ODA and diethyl ester diacyl chloride of PMDA, dictated by the siloxane block length and composition. For example, copolymers containing low molecular weight siloxane blocks at moderately high compositions have polyimide block lengths which are low. This is due to the large stoichiometric imbalance generated between the polyimide monomers by having high compositions of siloxane. This is of considerable importance since the polyimide block length may control the phase purity in the subsequent block copolymers to a large extent.

The dynamic mechanical behavior for the two series of block copolymers are shown in Figures 1–3. Two transitions were observed for each of
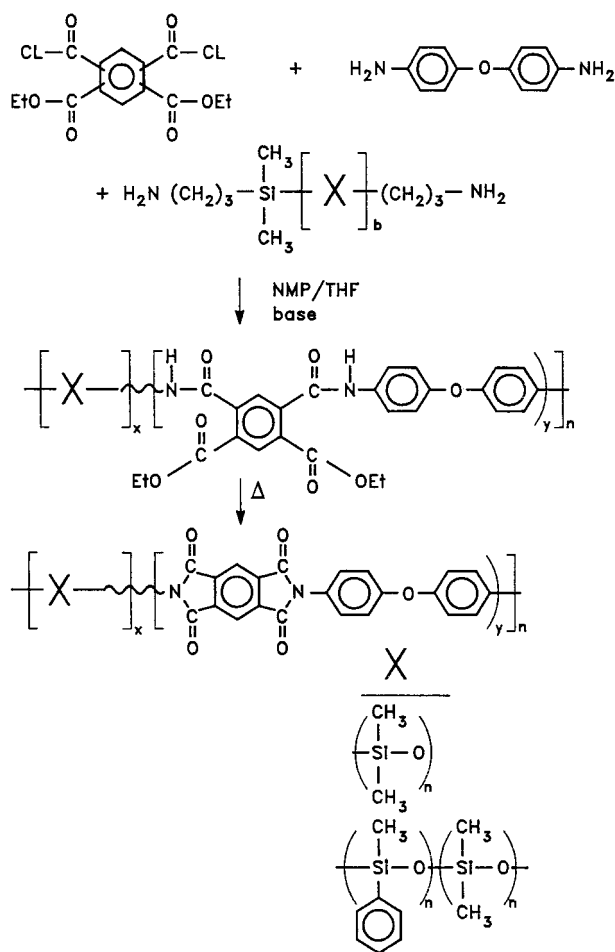
Scheme 2

Table II Characteristics of Imide–Dimethylsiloxane Block Copolymers

| Copolymer Entry | Dimethylsiloxane Block Length (g/mol) | Dimethylsiloxane Composition (Wt %) | $(\eta)^{THF}_{25°C}$ (dL/g) | Polymer Decomposition Temp (°C) | Isothermal Aging, Weight Loss (Wt %/h) | | Dielectric Constant | Oxygen Etch Rate (Å/min)[a] |
					350°C	400°C		
3	1000, 1a	20	0.34	450	0.07	0.06	2.94	65
4	1000, 1a	65	0.41	440	0.1	0.9	3.01	25
5	5400, 1b	20	0.38	450	0.07	0.5	2.71	120
6	5400, 1b	50	0.47	—	0.1	0.75	2.88	40

[a] Polyimide etches at 1200 Å/min under the same conditions.

the copolymers, indicating microphase-separated morphologies. The imide–dimethylsiloxane copolymers containing the high molecular weight siloxane blocks (copolymers 5 and 6) showed siloxane glass transition temperatures identical to the oligomers used in the synthesis and suggest there was little, if any, phase mixing. Furthermore, crystallization and melting of the siloxane block was observed in copolymer 6. The imide transitions in these block copolymers were nearly equal to that observed for PMDA/ODA polyimide cured to similar temperatures. On the other hand, the imide–dimethylsiloxane copolymers prepared from the low molecular weight siloxane oligomers (copolymers 3 and 4) showed siloxane glass transitions higher than those of the initial oligomers. The imide transitions, on the other hand, were substantially depressed from the imide homopolymer cured under the same conditions. This indicates a substantial amount of phase mixing. Furthermore, the transitions were not sharp, but broad, indicative of diffuse phase boundaries. As expected, the copolymers prepared from the diphenylsiloxane oligomers showed significant phase mixing, as evidenced by the T_g shifts, even though the molecular weights of the blocks were high. More graphic evidence of the phase separation is given in Figure 4. An electron micrograph of an imide–dimethylsiloxane copolymer (copoly-

mers 5), having a siloxane block length of 5000 g/mol, is shown, in which the dark areas are the imide phase while the siloxane component appears as the white or light phase. Clearly, discrete domains of dimethylsiloxane can be observed with sharp phase boundaries.

Shown in Figure 5 is a typical small-angle X-ray scattering profile for an imide–dimethylsiloxane copolymer. In this case, the weight fraction of the dimethylsiloxane block is 50%, yielding a 16% Si content. The SAXS data are shown as the scattered intensity as a function of the scattering vector, Q, which is given by $(2\pi)/\lambda$ by $\sin \theta$, where λ is the wavelength of the radiation (1.542 Å) and 2θ is the scattering angle. In agreement with the mechanical data, there is clear evidence of a microphase-separated structure by the appearance of a strong reflection at $Q = 0.0228$ Å^{-1}, which corresponds to a Bragg spacing of 275 Å. In fact, a careful examination of the scattering data shows the appearance of a higher-order peak at 0.0457 Å^{-1}. This higher-order reflection yields a spacing of 138 Å, which is one-half that of the intense reflection at smaller Q. These reflections correspond to the first- and second-order reflection of a lamellar microphase-separated structure composed of polyimide and polydimethylsiloxane layers. However, the suppression of the higher-order reflections, third and higher, indicate that the mi-

Table III Characteristics of Imide–Dimethyldiphenylsiloxane Block Copolymers

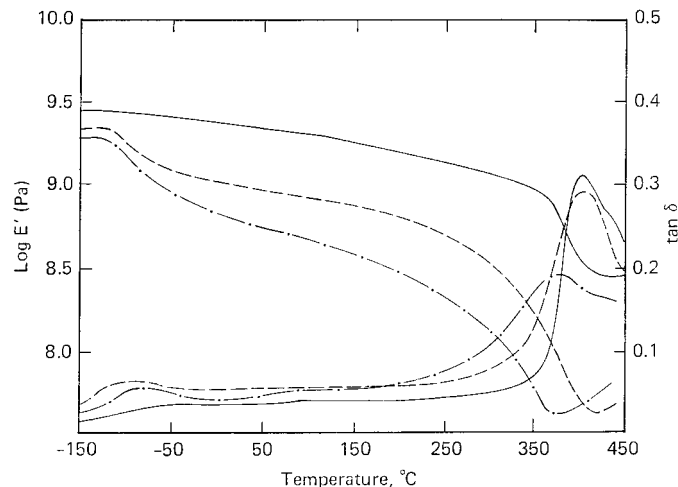| Copolymer Entry	Dimethyldiphenylsiloxane Block Length (g/mol)	Dimethyldiphenylsiloxane Composition in Copolymer (Wt %)	Diphenylsiloxane Incorporation (Wt %)	$(\eta)^{25°C}_{THF}$ (dL/g)	Polymer Decomposition Temperature (°C)	Oxygen Etch Rate (Å/min)
7	4800	20	25	0.39	440	37
8	5400	20	50	0.5	450	—
9	5700	20	75	0.41	450	—

Figure 1 Dynamic mechanical analysis of copolymers (---) 3, (-·-) 4, and (——) PMDA/ODA polyimide.

crophase-separated structure is either highly distorted, i.e., the thickness of the layers is not uniform over large distances, or that the stacking of the lamellae does not persist over large distances. Nonetheless, the extent to which this multiblock copolymer has microphase-separated is striking.

Examination of the SAXS at higher scattering vectors permits the determination of the phase boundary between the siloxane and polyimide microphases. For the copolymer studies here, the phase boundary is ~ 10 Å, which is quite sharp. This reflects the high degree of immiscibility between the two components of the copolymer and the ability for the copolymer to microphase-separate and approach an equilibrium structure owing to the mobility at the elevated temperatures. These results are in keeping with the mechanical properties of these copolymers.

Although not shown, the SAXS from the diphenylsiloxane copolymers monotonically decreased with the scattering vector. While the data indicated that the copolymers were microphase-separated, the extent of microphase separation was far less than that observed from the dimethylsiloxane copolymers. This is, also, in keeping with the mechanical data where a significant amount of phase mixing and broad phase boundaries were evident.

The base mechanical properties (i.e., stress/strain data) for the copolymers are shown in Table IV. A more detailed study of the mechanical properties has been published elsewhere.[26] As expected, the incorporation of the low T_g siloxane block significantly reduced the modulus and stress at break. This reduction was more pronounced for those copolymers where the siloxane block is the continuous phase. These values ap-
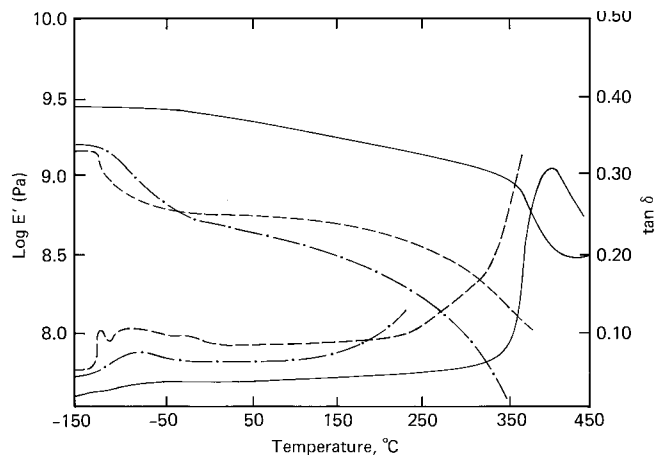

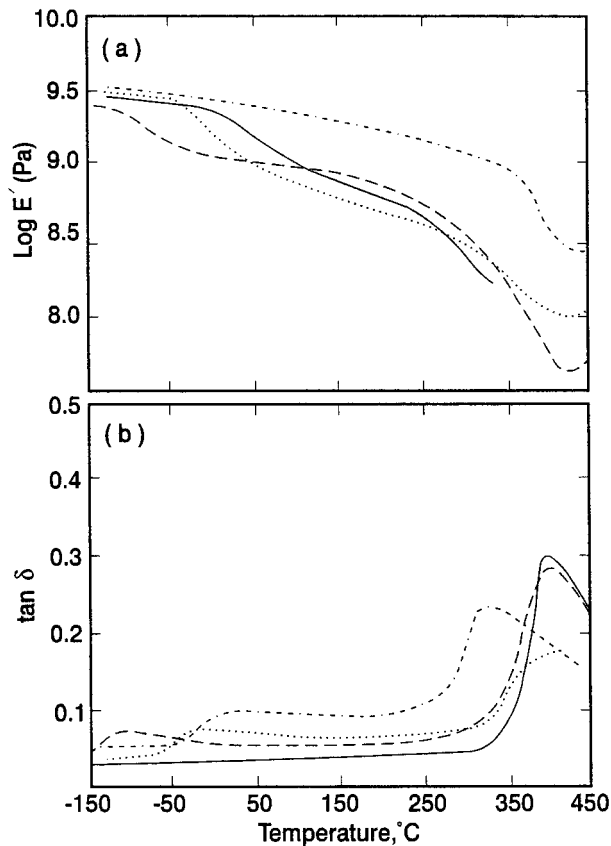**Figure 2** Dynamic mechanical analysis of copolymers (---) 5 and (-·-) 6.

Figure 4 TEM micrograph of copolymer 5.

Figure 3 Dynamic mechanical analysis of copolymers (---) 7, (· · ·) 8, (——) 9, and (-·-·) PMDA/ODA polyimide.

peared, for a given composition, to be independent of the block size or type. The PMDA/ODA polyimide shows no distinct yield point, yet fails at high elongations (at 70%). Likewise, the copolymers showed no distinct yield and failed at extremely high elongations. In copolymer 5, where the siloxane was the continuous phase, the sample behaved more as a filled rubber than as a polyimide.

The thermal stability of the copolymers was assessed by thermal gravimetric analysis and thermal mechanical properties. Table II contains the weight loss as a function of time for samples aged at 350 and 400°C. It is of interest to ascertain the maximum temperature where the bulk of the mechanical properties are retained with minimal weight loss. Markedly different thermal stabilities were observed for the copolymers. Generally, the higher the siloxane content was, the lower was the thermal stability, as judged by weight loss. A notable decrease in thermal stability is observed for each type of siloxane block as the temperature is i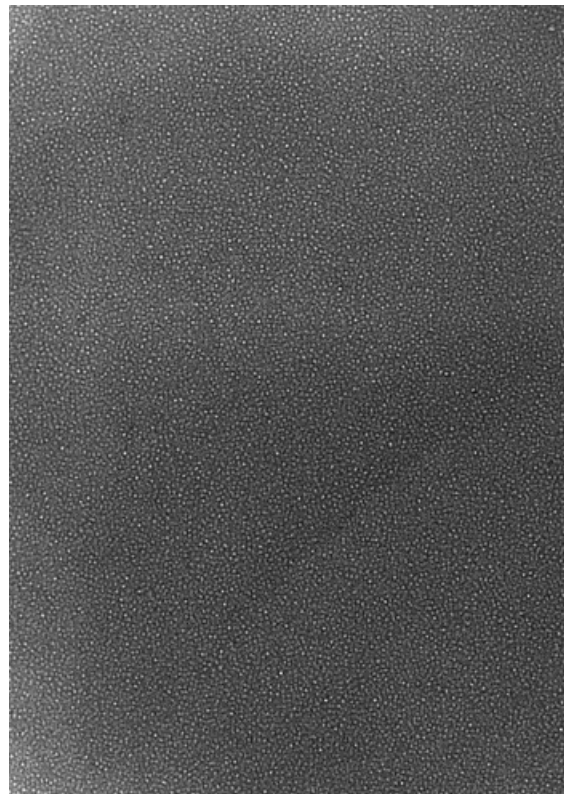ncreased from 350 to 400°C. The isothermal weight loss for the copolymers at 350°C is comparable to the observed for PMDA/ODA polyimide at 400°C. However, at 400°C, the thermal stability is somewhat lower than that of polyimide, regardless of the siloxane block length
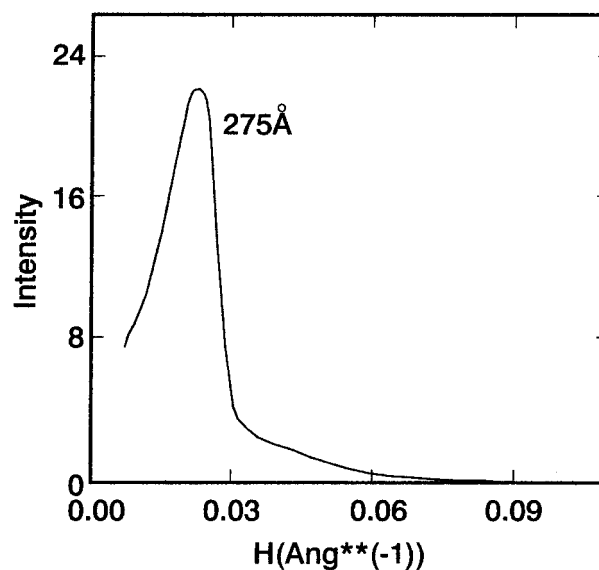

Figure 5 SAXS analysis of copolymer 6.

Table IV Mechanical Properties of Selected Imide–Siloxane Block Copolymers

Copolymer Entry	Modulus (MPa)	Stress at Break (MPa)	Elongation (%)
3	875	60	90
4	120	28	160
5	850	81	90
6	400	51	110

or type. Isothermal dynamic mechanical analysis was also employed where the modulus or stiffness was followed as a function of time at both 350 and 400°C. Shown in Figures 6 and 7 are the isothermal aging studies for copolymers 3 and 5. Copolymer 3 showed a minimal change in the modulus with time; however, at 350°C, an increase in the modulus was observed. Isothermal aging at 400°C produced markedly different results. A significant increase in the modulus was observed. In the case of copolymer 5, isothermal aging at 350°C produced a minimal change in the modulus, due, most likely, to the dilution of the thermally unstable aminopropyl end groups. However, at 400°C, an increase in the modulus was observed.

Each of the copolymers shows a significantly reduced oxygen plasma etch rate from that observed for the polyimide homopolymer. Polyimide etches at a rate of ~ 1200 Å/min, whereas the copolymers etch at a significantly reduced rate and in the proximity of 100 Å/min (Tables II and III). Thus, the desired etch differential (i.e., 10 : 1) was achieved for an ample processing window. Also shown in Table II is the dielectric constant

for selected copolymers and the polyimide control. The introduction of the lower dielectric constant polydimethylsiloxane coblock into polyimide reduced the dielectric constant to the proximity of 2.7–3.0 from 3.2–3.3.

SUMMARY

Imide–siloxane copolymers were successfully prepared and their thermal and mechanical properties and morphology were investigated. Bis(aminopropyl) dimethyl- and dimethyldiphenylsiloxane oligomers were prepared via an anionic ring-opening polymerization. The oligomers were coreacted with ODA and PMDA diethyl ester diacyl chloride in an NMP/THF solvent mixture in the presence of N-methylmorpholine. The poly(amic ethyl ester) intermediate to the polyimide was found to be more versatile than was the poly(amic acid) analog for the preparation of the copolymers since it can be isolated, characterized, and washed to remove homopolymer contamination prior to imidization. In addition, the poly(amic ethyl ester)
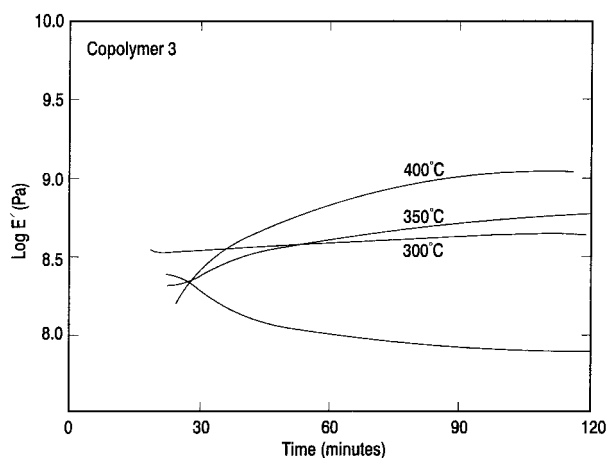

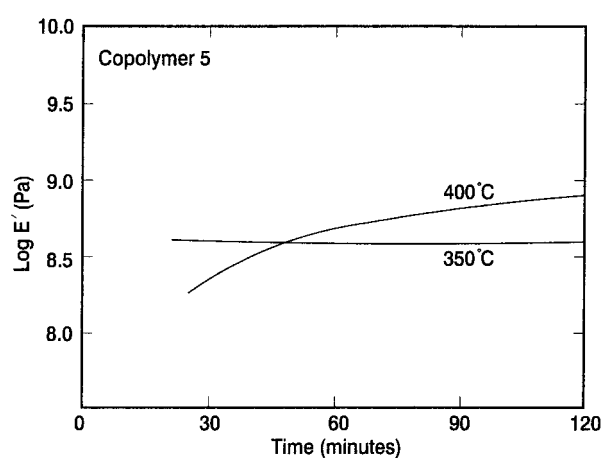**Figure 6** Isothermal dynamic mechanical analysis of copolymer 3.

Figure 7 Isothermal dynamic mechanical analysis of copolymer 5.

is soluble in a wide variety of solvents and solvent mixtures, and since imidization occurs at a higher temperature than for the poly(amic acid)s, vitrification occurs after solvent loss. Furthermore, due to the enhanced solubility of this intermediate, rigid and semirigid polyimides may be employed. Solutions of the copolymers were cast and cured (350°C) to effect the imidization, affording clear films with tough mechanical properties and moduli comparable to the parent polyimide. The thermal stability of the copolymers was somewhat less than that of the polyimide homopolymer with decomposition temperatures in the proximity of 450°C. Multiphase morphologies were observed for both copolymer series irrespective of the siloxane block lengths or compositions. However, higher siloxane block lengths showed that siloxane improved phase purity.

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