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Low-stress polyimide block copolymers

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In order to produce polyimide films *in situ* on silicon substrates, while minimizing the thermally induced residual stresses on cooling from the cure temperature, we have prepared various polyimide–polydimethylsiloxane based block copolymers derived from pyromellitic dianhydride (PMDA) and *p,p′*-oxydianiline (ODA) via the poly(amic-alkyl ester) precursor route. This approach allows more synthetic flexibility than the poly(amic acid) route because it permits the use of a wider range of solvents and solvent mixtures, allowing copolymers with considerable variety in the polyimide backbone, as well as in the coblock, block length and composition. PMDA/ODA containing 20 wt% polydimethylsiloxane blocks of molecular weight 5400 $g\,mol^{-1}$ was found to show no residual thermal stress after curing at 350°C, although its Young's modulus and yield stress remained high (about half those of the PMDA/ODA homopolymer, which showed residual stresses of about 40 MPa for comparable film thicknesses). The rapid stress relaxation is attributed to the relatively good phase separation and minimal perturbation of the molecular ordering and orientation of the PMDA/ODA matrix in this copolymer. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: imide-siloxane block copolymers; thermal stress; relaxation)

INTRODUCTION

Future multichip packaging technologies are expected to benefit from the use of polymers as interlayer dielectrics. These materials must withstand severe thermal, chemical and mechanical stresses associated with microelectronics fabrication. In this respect, polymeric materials have many shortcomings when compared with the inorganic alternatives such as alumina or silicon oxides. Conversely, the lower dielectric constants provided by polymers, relative to those of inorganic dielectric materials, manifest themselves in lower signal propagation delays and the possibility of higher wiring densities for interchip connections[1]. These properties are of vital importance if future packages are to take full advantage of the high switching speeds afforded by advanced chips, and in handling the greater number and density of chip I/Os[2]. The microelectronics industry, therefore, increasingly makes use of polymers as dielectric materials for the thin film wiring to interconnect chips, EC pads and other components on multichip modules, and devices on the chips themselves[1].

Of the few organic polymers which satisfy the criteria for microelectronics fabrication, polyimides have emerged as the favoured class of materials[3–7]. In particular, semirigid aromatic polyimides, such as poly(pyromellitic dianhydride-oxydianiline) (PMDA/ODA), and rigid aromatic polyimides, such as poly(pyromellitic dianhydride-phenylene diamine) (PMDA/PDA) and poly(biphenyl dianhydride-phenylene diamine) (BPDA/PDA), have proven suitable for such applications, owing to their solubility in the poly(amic-acid) precursor form and their excellent combination of thermal and mechanical properties after thermal cure[3–7]. These properties include low thermal expansion coefficients, high moduli and high strengths, which are substantially retained up to 400°C (although, above this temperature softening or flow may occur). Such properties reflect the high degree of molecular packing. For example, the polymer chains of PMDA/ODA polyimide assume locally extended conformations in a smectic-like layered order, and imidization of PMDA/ODA polyimide films in contact with a substrate produces substantial orientation of the molecules parallel to the surface, owing to the confinement of the film on the substrate and volume losses during curing[8,9]. This orientation results in anisotropic physical properties, and a notably high thermal expansion coefficient and low modulus normal to the film plane. Therefore, in considering the properties of semirigid and rigid polyimides, one should recognize that such polymers display extended local conformations, and orientational order, both locally and with respect to the film surface[10]. Indeed, these effects are even more pronounced for the BPDA/PDA and PMDA/PDA polyimides[11–13].

The first step in the fabrication of rigid and semirigid aromatic polyimide films is generally the spin coating of dilute solutions of the poly(amic acid) precursor onto silicon wafers. Spin coating is typically done using aprotic dipolar solvents such as *N*-methyl-2-pyrrolidone (NMP) or dimethyl acetamide (DMAC)[14]. Imidization

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involves a subsequent heat treatment step, referred to as curing. Cure can cause significant stresses to build up owing to solvent evaporation, imidization and the mismatch in the thermal expansion coefficients of the film and the substrate[15–17]. As the number of polymer layers and the overall thickness of the film increases, controlling these stresses becomes increasingly difficult, and they can lead to warpage of the substrate, loss of adhesion or cohesive failure of the polymer or substrate. Currently, stress is controlled at low levels by using polyimides whose thermal expansion coefficients match those of the substrate, that is, rigid and highly ordered polyimides, such as BPDA/PDA and PMDA/PDA. This approach is very limiting with respect to the number of possible rigid rod-like structures obtainable and synthetic flexibility. For example, poly(amic-alkyl ester) precursors generally show higher thermal expansion coefficients and residual thermal stress than their poly(amic-acid) analogies[18–19]. Moreover, as more and more functionality is demanded of polymer dielectric layers, it becomes increasingly difficult to design materials with the desired enhancements (such as photosensitivity) without compromising the existing properties.

The semirigid PMDA/ODA polyimide has a relatively large thermal expansion coefficient of approximately 40×10^{-6}°C and a measured residual thermal stress in the 30–40 MPa range when spin coated and imidized on a silicon substrate[2,20]. Although much higher than for the rigid polyimides, this residual stress is significantly less than would be predicted on the basis of the thermal expansion coefficient and Young's modulus. This difference is clearly a result of stress relaxation during fabrication[21]. Thus, given that the rate and degree of stress relaxation is unmodified PMDA/ODA are not sufficient to overcome difficulties with thermal mismatch stresses in multilayer structures containing dissimilar materials such as ceramic and copper, it is of interest to modify PMDA/ODA polyimide in such a way as to enhance stress relaxation. Indeed, it would be highly useful to have a generic means of modifying semi-rigid and even amorphous polyimides in such a way as to control the stresses which result from thermal expansion coefficient mismatches between substrates and adhered films.

In this article, the synthesis of imide-siloxane block copolymers will be discussed as a route to low stress polyimides, as well as several structural modifications and their effects on the morphology and mechanical properties. Earlier studies on semirigid and rigid polyimide block copolymers have shown that both the ordering and orientation of the molecules are substantially retained, independent of the coblock type or compositions[22–24]. Consequently, attempts to generate rigid polyimide nanofoams by pyrolysis of block copolymers have been largely unsuccessful[25,26]. In this approach, films are prepared by casting microphase separated block copolymers of a thermally stable polyimide block with thermally labile materials, and on a thermal treatment the thermally unstable block undergoes thermolysis, leaving pores with a size and shape dictated by the initial morphology[25]. In PMDA/ODA-based systems, molecular ordering and orientation were found to be critical in determining the stability of the foam structure. Where the characteristic in-plane molecular orientation and molecular ordering of homogeneous PMDA/ODA films were retained, relaxation rates were clearly enhanced in the presence of the pores, leading to collapse of the foam structure well below the matrix T_g. Moreover, there is some suggestion that the presence of pores may enhance stress relaxation rates in step strained imide foams[26]. Thus, the recreation of these effects in a suitably designed block copolymer (where the presence of a second phase should maintain the structural integrity) may be a means of promoting rapid stress relaxation in PMDA/ODA imide films, yielding the sought-after low stress materials. Polydimethylsiloxane was chosen as the coblock because it has a low T_g, low modulus, and should, in principle, provide a large modulus mismatch with the polyimide. Since dimethylsiloxane is nonpolar, microphase-separated copolymers derived from this coblock tend to show high phase purity, whereas the polyimide block is expected to retain the local ordering and orientation, characteristic of the polyimide homopolymer. Moreover, siloxane polymers may be appropriately functionalized for copolymerization and they have the requisite thermal stability to survive the thermal cure.

Polyimides, and in particular semi-rigid and rigid polyimides, have received little attention as components in the synthesis of block and segmented copolymers, owing to their limited solubility and poor hydrolytic stability of the poly(amic acid), which often precludes isolation and subsequent characterization. Despite this, the imide-siloxane copolymers are relatively widely studied[27,28]. The general synthetic route in the preparation of these copolymers is based on a monomer(s)-oligomer approach via the poly(amic-acid) precursor to the polyimide. Bis(amino) siloxane oligomers are co-reacted with either a dianhydride or a combination of a dianhydride and diamine to form a high molecular weight poly(amic-acid) solution, which can be cast into films and cured to effect imidization. This results in a multiblock microstructure with the blocks statistically placed. However, almost all of the imide-siloxane copolymers reported up to now have employed flexible, low T_g imide coblocks.

An alternative synthetic approach to the preparation of imide containing copolymers was taken here. A monomer(s)-preformed oligomer synthetic route was used to prepare amic alkyl ester-siloxane block copolymers. The poly(amic-alkyl ester) precursor to polyimide copolymers allows greater synthetic flexibility than the poly(amic acid) analogue because the former is soluble in a variety of solvents and solvent mixtures, allowing copolymers with greater structural variety in the polyimide backbone, as well as in the coblock, block length and composition[29,30]. The hydrolytically stable poly(amic-ester) precursors may be isolated, characterized and washed to remove homopolymer co-contamination prior to imide formation. Furthermore, the poly(amic-alkyl ester) route may favourably influence the morphology of the subsequent imide copolymer since imidization occurs at higher temperatures, allowing sufficient mobility for equilibrium to develop. The extent of phase separation or phase purity in block copolymers derived from the poly(amic acid) precursors may be limited because vitrification or imidization occurs prior to solvent evolution.

EXPERIMENTAL

Materials

The 4,4′-oxydianiline, ODA (Davos Chemical

Company) and pyromellitic dianhydride, PMDA (Chriskev Company) were used without further purification. *N*-methyl-2-pyrrolidone (NMP) was vacuum distilled from P_2O_5 prior to use. 1,4-Bis[6-(3-aminophenoxy)-3-phenyl-2-quinoxalinyl] benzene was prepared according to literature previously published[31]. Octamethylcyclotetrasiloxane (D_4), octaphenylcyclotetrasiloxane ($D_{4''}$), and 1,3-bis(aminopropyl)tetramethyldisiloxane (end blocker) were purchased from Petrarch. The tetramethylammonium hydroxide pentahydrate purchased from Aldrich was used without further purification.

Diethyl pyromellitate diacyl chloride. Pyromellitic dianhydride, PMDA (50.0 g, 0.230 mol) was suspended in 250 ml of dry ethanol and refluxed for 3 h, yielding a clear solution[29,30]. Evaporation of the ethanol followed by vacuum drying at 50°C for 24 h gave diethyl dihydrogen pyromellitate (mixed isomers) in quantitative yield. The material was then suspended in about 200 ml of dry ethyl acetate in a 500 ml three-necked flask equipped with magnetic stirrers, reflux condenser, and N_2 bubbler. Oxalyl chloride (75 g, 0.591 mol) was then added in three portions over a period of 8–10 h, each addition being followed by 1–2 drops of DMF. The DMF allowed the reaction to proceed at ambient temperature, as shown by vigorous evolution of gas. Stirring was continued overnight and the reaction mixture was then heated to about 60°C in a water bath for an additional 6 h (the total run time was about 28 h). The ethyl acetate was stripped and the residue dried under vacuum at room temperature overnight. The product was twice recrystallized from approximately 150 ml of hexane and vacuum dried giving a yield of approximately 75% with a slight enrichment of the *para*-isomer (a *meta*/*para* ratio of 45/55: ^{1}H-n.m.r. ($CDCl_3$), δ 8.30 and 7.92 (*d*, $1H_1$, *meta*-Ar-H), δ 8.10 (*s*, 1H, *para*-Ar-H) δ 4.50–4.38 (1, 4H, methylene), δ 1.39–1.36 (*t*, 6H, methyl)).

Oligomer and polymer synthesis

Synthesis of aminopropyl terminated dimethyl- and dimethyldiphenylsiloxane oligomers. α,ω-Bis(aminopropyldimethyldiphenyl)siloxane oligomers of various molecular weights were synthesized by the base tetramethylammonium hydroxide pentahydrate catalysed-bulk anionic equilibrium reaction of D_4 and $D_{4''}$ with 1,3-bis(aminopropyl)-tetramethyl disiloxane end blocker[32–34]. The $D_{4''}$ is a crystalline solid and insoluble in the mixture of D_4 and the end-blocking agent. However, the $D_{4''}$ is soluble in oligomers of dimethylsiloxane. Therefore, these coequilibrations had to be performed sequentially. First, the D_4, end-blocking agent, and catalyst were charged and heated to 80°C, yielding oligomers of dimethylsiloxane after about 2 h. The cyclic tetramer of diphenylsiloxane was then charged and allowed to coequilibrate. The oligomers containing the higher siloxane content had to be heated to 150°C to form a homogeneous reaction mixture and then cooled to 80°C. The reaction temperature was held 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 (0.05–0.10 mmHg) vacuum to remove equilibrium cyclics.

The molecular weights of the bis(aminopropyl)-terminated dimethylsiloxane and dimethyldiphenylsiloxane oligomers were controlled by the ratio of the end-blocker to the cyclic tetramer(s). *Table 1* contains characteristics

Table 1 Characteristics of dimethylsiloxane and dimethyldiphenylsiloxane oligomers

Sample entry	Diphenylsiloxane compositions (wt%)	Molecular weight, (g mol^{-1})	T_g (°C)
1a	0	1000	−114
1b	0	5400	−121
2a	25	4800	−109
2b	50	5400	−71
2c	75	5700	−26

of the oligomers synthesized with diphenylsiloxane compositions ranging from 0 to 75 wt%. The molecular weights, determined by potentiometric titrations of the aminopropyl end group with 0.1 N HCl, were maintained in the 5000 g mol^{-1} range to facilitate comparison. The glass transition temperature ranged from −123°C for the poly(dimethylsiloxane) to −26°C for the poly(dimethyldiphenylsiloxane) containing 75 wt% diphenylsiloxane.

Block copolymer synthesis of PMDA/ODA and poly(dimethylsiloxane). The amic ester siloxane copolymers were prepared by the co-reaction of the siloxane oligomers with ODA and PMDA diethyl ester diacyl chloride in NMP in the presence of *N*-methylmorpholine. Details are given here of a procedure designed to prepare an amic-ester siloxane copolymer with a siloxane oligomer of 5000 g mol^{-1} and 20 wt% siloxane. A three-necked flask equipped with an overhead stirrer and addition funnel was charged with oligomer **lb** (*Table 1*) (1.200 g, 0.00024 mol), ODA (1.7400 g, 0.000868 mol), and carefully rinsed in with 25 ml of an NMP-tetrahydrofuran (50/50) solvent mixture. Throughout the polymerization N_2 was passed through the system. The solution was then cooled to −5°C, and *N*-methylmorpholine (1.8047 g, 0.01780 mol) added to the solution. The PMDA diethyl ester diacyl chloride (3.100 g, 0.00892 mol) was dissolved in about 50 ml of methylene chloride, and added in increments over a 2-h period so as to slowly approach the stoichiometric end point. The polymerizations were allowed to proceed overnight, and the product was isolated by precipitation in methanol–water, rinsed with water (to remove excess salts) and then methanol, and finally dried in a vacuum oven.

Modified PMDA/ODA-siloxane block copolymers. Two types of modification were considered. In the first, PMDA/ODA imide-dimethyldiphenylsiloxane copolymers with premixed with diphenylsiloxane compositions ranging from 25 to 75 wt%. Polar diphenylsiloxane is expected to minimize the solubility parameter difference between the imide and siloxane blocks, facilitating phase mixing. In the second modification the imide block was altered by the introduction of a co-monomer. Various compositions of an aryl ether phenylquinoxaline containing diamine, 1,4-bis[6-(3-aminophenoxyl)-3-phenyl-2-quinoxalinyl] benzene, were copolymerized with ODA and the diethyl ester diacyl chloride of PMDA. This monomer was prepared by the reaction of 1,4-(6-fluoro-3-phenyl-2-quinoxalinyl) benzene with 3-aminophenol in the presence of base. Owing to the nonselectivity of the quinoxaline ring formation, three constitutional isomers were generated and retained in the polymer[31]. Imide-aryl ether phenylquinoxaline copolymers have been reported

previously, and it was shown that the copolymers with high phenylquinoxaline compositions sufficiently disrupted the order of the PMDA/ODA sequences to produce an amorphous and isotropic material[31]. The effect of phenylquinoxaline incorporation and subsequent morphology changes on the thermal stress will also be considered.

Measurements

Films for thermal and mechanical analysis of about 50 μm thick were cast from NMP heated to 350°C (5°C min^{-1} heating rate) and held for 30 min at this temperature. Glass transition temperatures, taken as the midpoint of the change in slope of the heat flow rate, were measured on a DuPont DSC 1090 instrument at a heating rate of 10°C min^{-1}. The dynamic mechanical measurements were performed in tension, using a Polymer Laboratories Dynamic Mechanical Analyser (DMTA) at 10 Hz and a heating rate of 10°C min^{-1}. Relaxation measurements and stress–strain curves were obtained using the Polymer Laboratories Minimal™ miniature tensile test apparatus. Isothermal and variable temperature (5°C min^{-1} heating rate) thermal gravimetric analysis (t.g.a.) measurements were performed on a Perkin-Elmer TGA-7 in N_2. Stress measurements, as a function of temperature, were ran *in situ* on a Flexus F2300 thin-film stress analyser with a heating rate of 2°C min^{-1} held for 1 h at 350 or 400°C, then cooled to room temperature at 1°C min^{-1}.

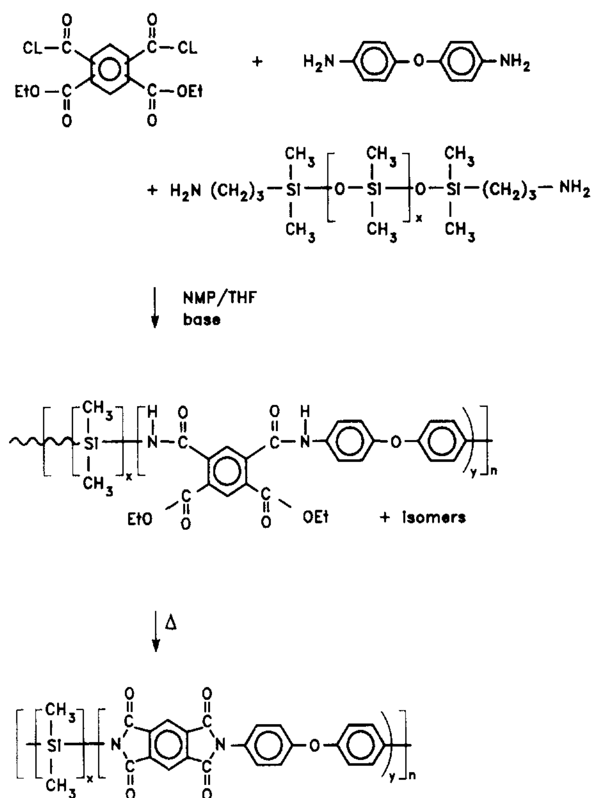
The number average molecular weights, $\bar{M}_n$ of the oligomers were determined by ^{1}H n.m.r. after derivatization of the end groups with trimethylproponyl chloride. Integration of the resonance assigned to the trimethylsilyl groups in the oligomers was compared with the integration of the aromatic protons, and the ratio of the integrated areas per proton gave the degree of polymerization, from which $\bar{M}_n$ was deduced.

RESULTS AND DISCUSSION

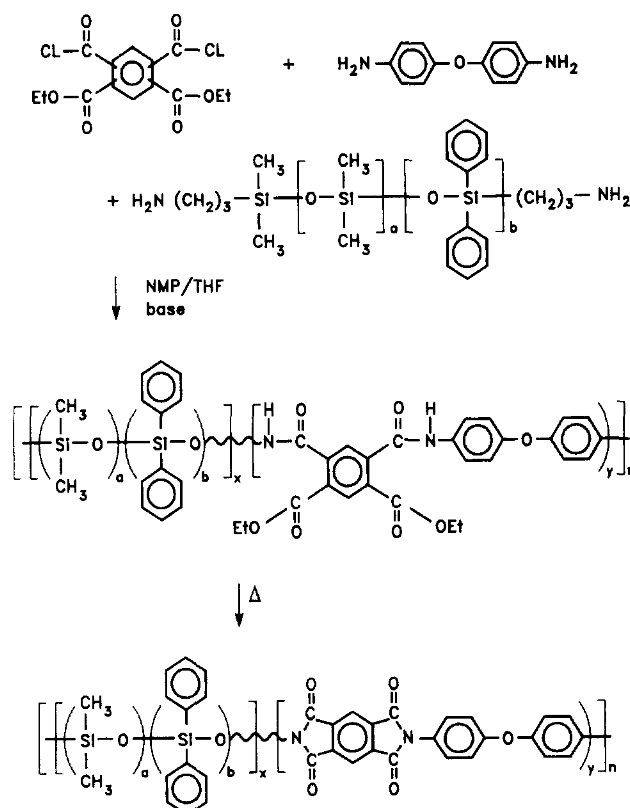
The three series of block copolymers prepared are shown in *Schemes 1–3*. In the first series (*Scheme 1*), the PMDA/ODA-poly(dimethylsiloxane) block copolymers with two block lengths and two dimethylsiloxane compositions were considered and the characteristics of these block copolymers are shown in *Table 2*. In the second series of block copolymers (*Scheme 2*), the siloxane block length was maintained at approximately 5400 g mol^{-1} and the diphenylsiloxane was introduced into the soft block. The diphenylsiloxane compositions ranged from 0 to 75 wt% as shown in *Table 3*. In the third and final series of block copolymers, the structural modifications to the imide block were introduced (*Scheme 3*) in order to disrupt the ordering of the PMDA/ODA sequences. The phenylquinoxaline compositions ranged from 25 to 70 wt% and the characteristics

Table 2 Characteristics of imide-dimethylsiloxane block copolymers

Copolymer entry	Dimethylsiloxane block length (g mol^{-1})	Dimethylsiloxane composition (wt%)
3	1000	20
4	1000	65
5	5400	20
6	5400	50

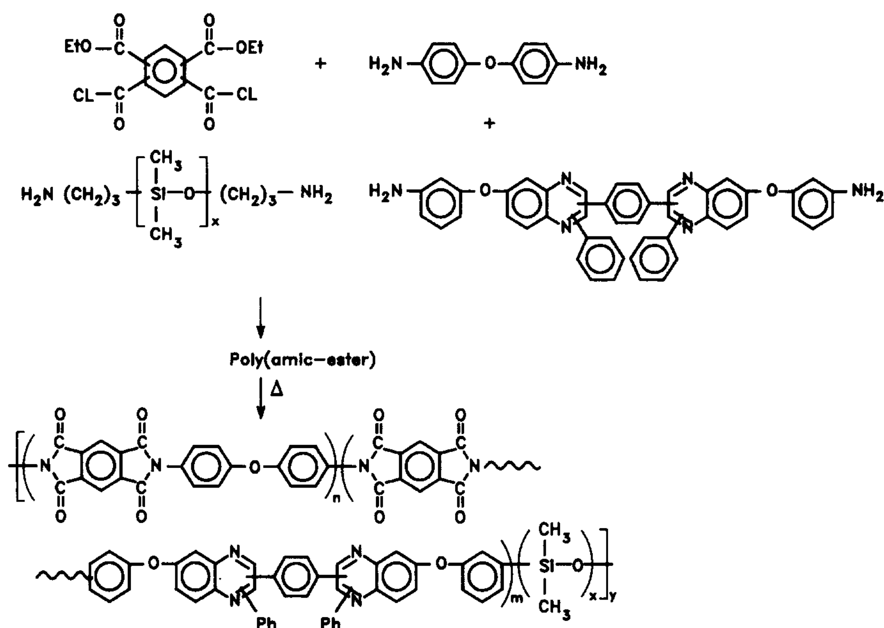


Scheme 1



Scheme 2

of these copolymers are shown in *Table 4*. This synthetic route produced an $(A–B)_n$ type 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



Scheme 3

Table 3 Characteristics of imide-dimethyldiphenylsiloxane block copolymers

Copolymer entry	Dimethyldiphenylsiloxane block length ($g\,mol^{-1}$)	Dimethyldiphenylsiloxane composition in copolymer (wt%)	Diphenylsiloxane incorporation (wt%)
7	4800	20	25
8	5400	20	50
9	5700	20	75

Table 4 Characteristics of imide-phenylquinoxaline-dimethylsiloxane block copolymers

Sample entry	Dimethylsiloxane block length ($g\,mol^{-1}$)	Dimethylsiloxane composition (wt%)	Phenylquinoxaline composition (wt%)
10	5400	20	25
11	5400	20	50
12	5400	20	75

weight of the imide block is controlled by the stoichiometric imbalance between the ODA and PMDA diethyl ester diacyl chloride, dictated by the siloxane block length and composition. Therefore, low siloxane block lengths and high siloxane compositions generate a larger imbalance between the ODA and PMDA diethyl ester diacyl chloride, and consequently a lower imide block length. This is of considerable importance because the polyimide block length may, to a large extent, control the phase purity in the subsequent block copolymers.

The dynamic mechanical behaviour for the three series of block copolymers are shown in *Figures 1–4*. Two transitions were observed for each of the copolymers, indicating microphase separated morphologies. The imide-dimethylsiloxane block containing the high molecular weight siloxane block (copolymers **5** and **6**) showed a siloxane T_g (tan δ peak) identical to that of the oligomer used in the synthesis, and suggests that there was little, if any, phase mixing (*Figure 1* and *Figure 2*). Furthermore, crystallization and melting of the siloxane was observed in copolymer **6** (*Figure 2*). The imide transition in the block copolymer was also nearly identical to the transition observed for PMDA/ODA polyimide cured to the same temperature (*Figure 1*). Conversely, the imide-dimethylsiloxane copolymer prepared from the low molecular weight siloxane oligomer (copolymers **3** and **4**) showed a siloxane T_g somewhat higher than that observed

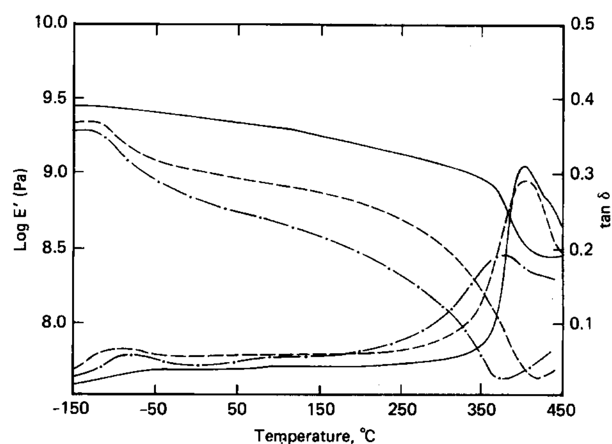


Figure 1 Dynamic mechanical spectra of copolymers **3** (-·-) and **5** (- - -) and PMDA/ODA polyimide

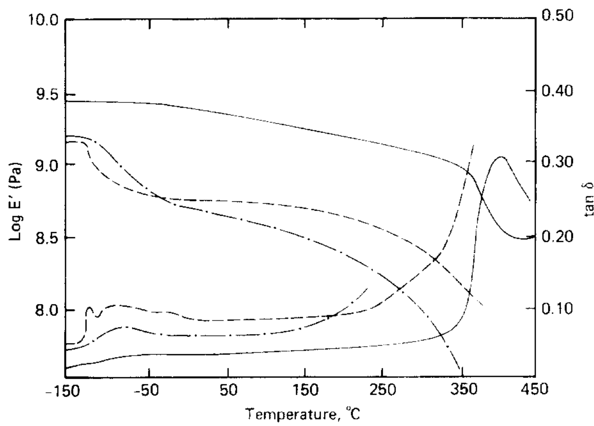


Figure 2 Dynamic mechanical spectra of copolymers **4** (- · -) and **6** (- - -) and PMDA/ODA polyimide

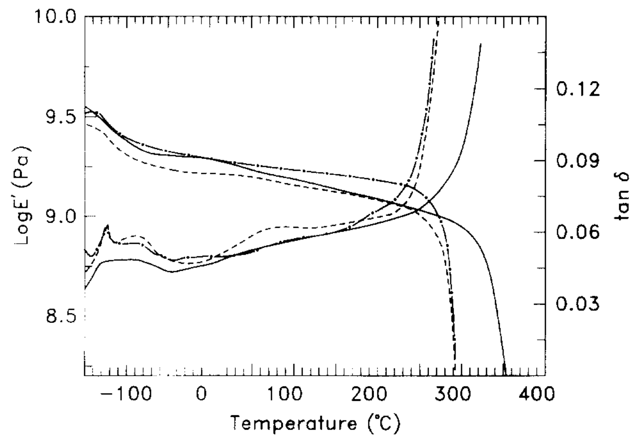


Figure 4 Dynamic mechanical spectra of copolymers **10** (—), **11** (- · · ·) and **12** (- - -)

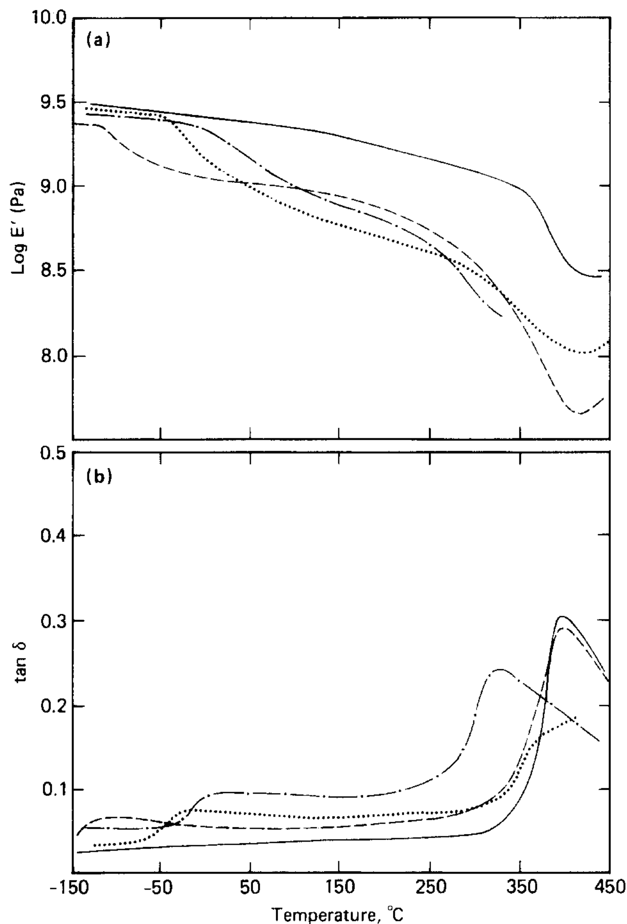


Figure 3 Dynamic mechanical spectra of copolymers **5** (- - -), **8** (····), **9** (- · · ·) and PMDA/ODA polyimide (—)

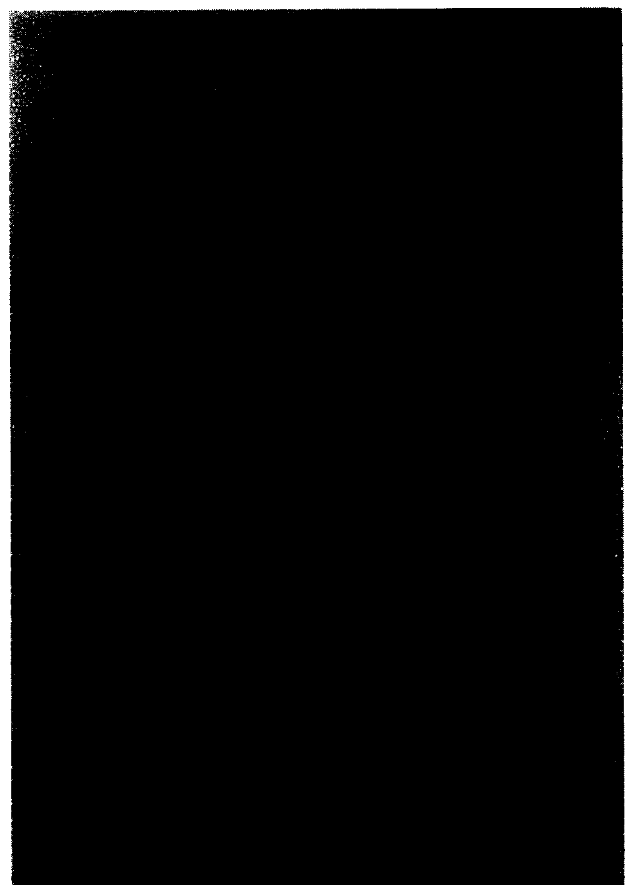


Figure 5 Transmission electron micrograph of copolymer **5**

for the oligomer, and an imide T_g, significantly lower than for the homopolymer cured under the same conditions, which is indicative of a significant amount of phase mixing (*Figure 1* and *Figure 2*). As expected, the block copolymers with the dimethyldiphenylsiloxane coblock also showed significant phase mixing, even when the siloxane block lengths were of high molecular weight (*Figure 3*). Finally, two transitions were seen for all the imide phenylquinoxaline-siloxane copolymers (*Figure 4*). The transitions at $-120°C$ are almost identical to those of the siloxane oligomers and, in each case, crystallization and melting of the siloxane block could be observed, which is consistent with high phase purity. The imide phenylquinoxaline transitions, however, occurred at somewhat lower temperatures than those observed for the imide phenylquinoxaline homopolymers, and this does suggest partial phase mixing. More graphic evidence of a phase-separated morphology is given in *Figure 5*. Here, an electron micrograph of the PMDA/ODA-dimethylsiloxane block copolymer **5** with a siloxane block length of $5400\,g\,mol^{-1}$ is shown, in which the dark regions correspond to the polyimide matrix. The siloxane component appears as discrete domains with little apparent interconnectivity.

The residual thermal stress in the films was investigated

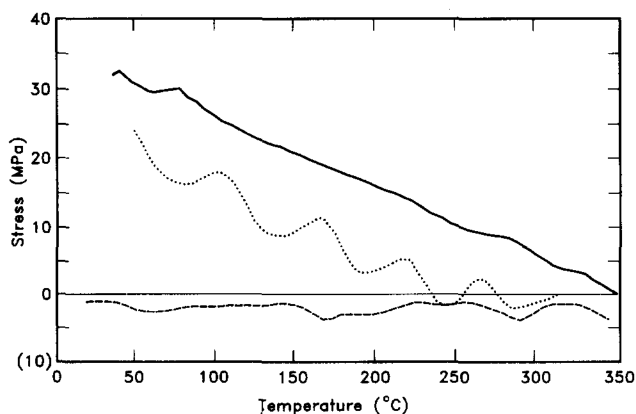


Figure 6 Stress *versus* temperature plots for copolymers **3** (····) and **5** (- - -) and PMDA/ODA polyimide (—)

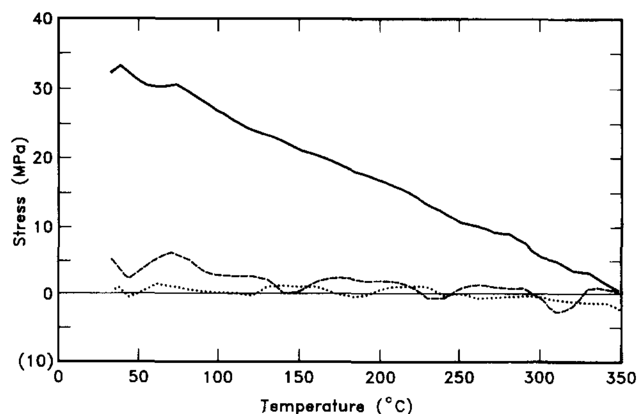


Figure 7 Stress *versus* temperature plot for copolymers **4** (- - -) and **6** (····) and PMDA/ODA polyimide (—)

with a Flexus F2300 stress analyser. The residual stress, σ_f, was calculated from the radii of wafer curvatures before and after polyimide film deposition using the following equation valid under $t_f \ll t_s$:

$$\sigma_f = \frac{E_s t_s^2}{6t_f(1 - v_s)}\left(\frac{1}{R_f} - \frac{1}{R_\infty}\right) \quad (1)$$

where the subscripts f and s represent the polymer film and substrate respectively, E is the Young's modulus, v is the Poisson's ratio and t is the thickness. R_f and R_∞ are the radii of the substrate with and without the polymer film, respectively[35]. During thermal curing and cooling, the stress was monitored in the temperature range 25–350°C.

The stress *versus* temperature profiles for the imide dimethylsiloxane copolymers **3** and **5** with siloxane block lengths of 1000 and 5400 $g mol^{-1}$, respectively, are shown in *Figure 6*, along with that of the PMDA/ODA polyimide, to facilitate comparison (each of the block copolymer samples contained about 20 wt% of polydimethylsiloxane). On cooling from 350°C, copolymer **5** showed no build-up in stress. In the absence of relaxation, the residual thermal stress arising from the mismatch in the thermal expansion coefficients of the substrate and the polymer is proportional to the product of the modulus and the difference in thermal expansion between the substrate and polymer. That is,

$$\sigma = \frac{E \Delta T \Delta \alpha}{1 - v} \quad (2)$$

where T is the temperature, E is the tensile modulus and α is the thermal expansion coefficient. The imide was the continuous phase in copolymer **5**, and both the modulus and the thermal expansion coefficients were high (the modulus was about half that in the PMDA/ODA imide homopolymer, which is consistent with a weight fraction of 20% rubber), so that the lack of stress build-up on cooling must be attributed to relaxation effects. Some stress build-up was seen on cooling copolymer **3**, containing the lower molecular weight dimethylsiloxane coblock. However, this stress was also significantly less than that observed for the PMDA/ODA imide homopolymer. That the imide-dimethylsiloxane copolymers **4** and **5** containing the high volume fractions of dimethylsiloxane showed minimal residual thermal stress on cooling from 350°C (*Figure 7*) was not surprising. In both of these

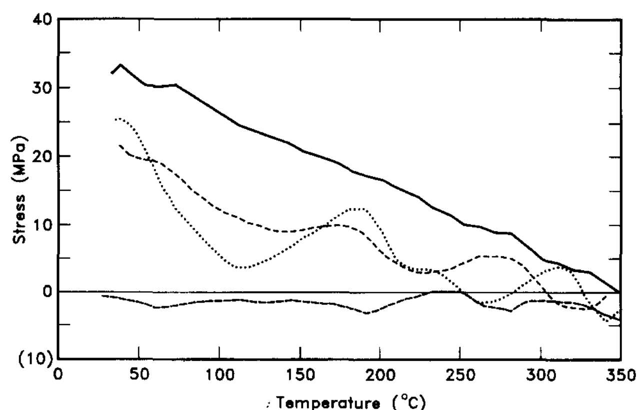


Figure 8 Stress *versus* temperature plots for copolymers **5** (- - -), **8** (····) and **9** (- - -) and PMDA/ODA polyimide (—)

copolymers, the dimethylsiloxane was the continuous phase, giving a correspondingly low E.

The introduction of diphenylsiloxane into the siloxane blocks (copolymers **7–9**), while maintaining a high block length, resulted in stress–temperature profiles which were substantially different from those of the corresponding unmodified imide-dimethylsiloxane copolymers. *Figure 8* shows the stress *versus* temperature profile for copolymers **8** and **9**, along with the profiles for the PMDA/ODA polyimide and copolymer **5**. The residual stresses in the diphenylsiloxane containing copolymers were between 20 and 25 MPa, which is approximately 25 to 40% lower than that of the parent homopolymer, but significantly higher than for copolymer **5** (although comparable with copolymer **3**). It is important to note that for each of the copolymers **3**, **8** and **9**, significant phase mixing was observed, as judged by the dynamic mechanical spectra. Similarly, the dimethylsiloxane-based block copolymers with various phenylquinoxaline contents showed significantly higher residual stresses than copolymer **5** (*Figure 9*).

Of the imide rich copolymers, the absence of residual stress was therefore unique to copolymer **5**, containing the high dimethylsiloxane block lengths, and in which the phase purity was high. *Figure 10* shows the room-temperature relaxation curves at different applied deformations in copolymers **3** and **5**, and also in the PMDA/ODA imide for comparison, providing a further indication of the relatively rapid stress relaxation in the

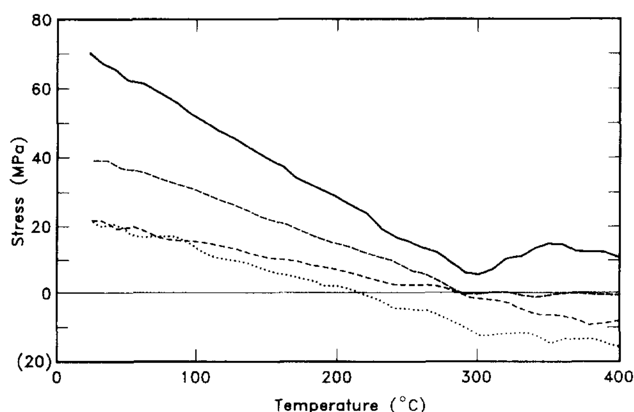


Figure 9 Stress *versus* temperature plots for copolymers **10** (- - -), **11** (····), **12** (- - -) and imide-phenylquinoxaline homopolymer (—)

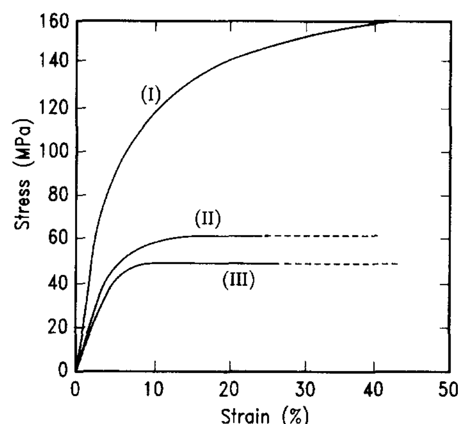


Figure 11 Stress–strain curves for samples deformed in tension at a constant strain rate of $10^{-3}s^{-1}$: (I) PMDA/ODA polyimide; (II) copolymer **3**; (III) copolymer **5**

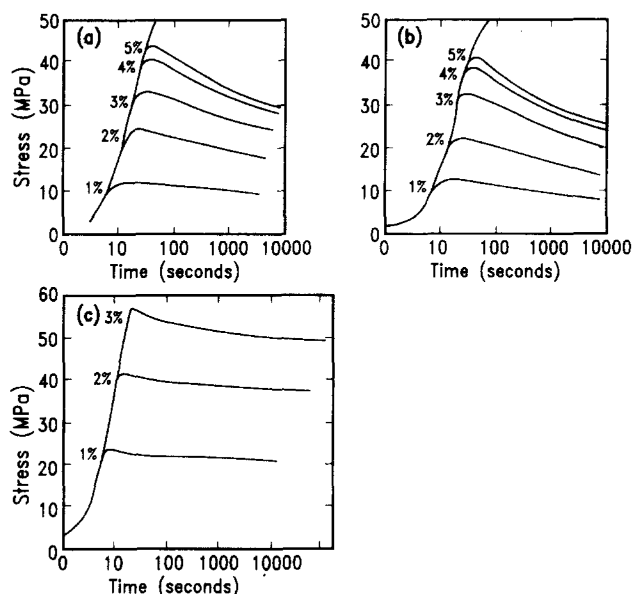


Figure 10 Stress relaxation, after deforming to different strains at a strain rate of about $2 \times 10^{-3}s^{-1}$ (the initial shape of the relaxation curve is an artefact arising from the finite response time of the control system): (a) copolymer **3**; (b) copolymer **5**; (c) PMDA/ODA polyimide

copolymers, and particularly in copolymer **5**. This also manifested itself in ductile behaviour in constant cross-head speed tensile tests, for which stress–strain curves are shown in *Figure 11*. Both copolymers **3** and **5** showed extensive shear banding, followed by stable plastic necking. The PMDA/ODA imide films show no distinct yield point, and fail by rapid crack propagation, albeit at relatively high strains (about 50%).

Previous studies have shown that the liquid crystalline type ordering, characteristic of PMDA/ODA polyimide films, is retained in copolymer **5**. Also, the modulus *versus* temperature profiles are similar in the imide and in the copolymer, and there is strong phase separation. Therefore, we can probably rule out major structural modification to the imide phase at a molecular level in this particular copolymer, so that it is reasonable to assume the response of the matrix to large strains to be similar to that of the homopolymer films. A detailed description of the temporal relaxation behaviour and the global response in the nonisothermal residual stress measurement is beyond the scope of the present article.

However, a plausible qualitative explanation for the enhanced relaxation behaviour of the copolymers is the stress-concentrating effect of the rubbery inclusions, which results in an enhanced relaxation rate for a given global stress or deformation because the local relaxation rates in the matrix are strongly stress dependent.

For the quantitative effect of these stress concentrations, it is simpler to consider the evolution of the global yield stress. Although the PMDA/ODA imide homopolymer does not show a clear yield point, following Argon and Bessonov[36], we assume its behaviour to be that of a linear work hardening elastic–plastic solid. Here, the yield stress can be assigned either to the stress corresponding to the intercept at zero deformation of the tangent to the approximately linear portion of the stress–strain curve at large strains, or to the stress corresponding to achievement of a linear hardening rate. This procedure gives a value of about 130 MPa at room temperature. For an elastic plastic material obeying a Von Mises yield criterion, the effects of both an isolated spherical rubber particle and of an isolated spherical hole on the onset of local yielding for a given global stress in uniaxial tension may be determined from the elastic fields calculated by Eshelby[37,38]. In both cases, for a nonpressure-dependent criterion, the equivalent Von Mises stress is about twice the applied uniaxial stress, so that, given the accompanying dilational stress and the inherent pressure sensitivity of yielding in glass polymers, the onset of local yielding would be expected to occur at global applied stresses of less than half the intrinsic yield stress. Although it is not possible to take into account particle–particle interactions in a simple manner (and it is clear that these cannot be ignored in a composite containing 20 wt% dispersed rubbery inclusions), this analysis gives some indication of the influence of the second phase on yielding, whether or not the particles cavitate. Indeed, careful characterization of poly(methyl methacrylate) (PMMA) and rubber toughened PMMA has led to results consistent with this approach[39]. Thus, the observed drop in the room temperature yield stress in uniaxial tension from 130 MPa in the PMDA/ODA imide homopolymer to about 50 MPa in copolymer **5** (*Figure 11*) may be mainly explicable in terms of the presence of the rubber inclusions. The present room-temperature yield stress results do not therefore merit any attempt to incorporate

specific features at the molecular level (such as orientational anisotropy or local orientational correlations between the particle–matrix interfaces and the matrix).

The higher thermal stresses of the remaining copolymers with low dimethylsiloxane contents, but with significant phase mixing and in certain cases modified matrices, indicate that maintaining either the ordered imide structure or sharp phase boundaries (or both), is important to obtain low stress films. Blurring of the phase boundary may reduce the stress-concentrating effect of the particles and disruption of order in the matrix may affect its intrinsic relaxational behaviour. In the particular case of the semiflexible PMDA/ODA polyimide, it is likely that cooperative motion of bundles showing a high degree of smectic ordering locally contributes to the mechanical response of thin films at elevated temperatures. This mechanism may be suppressed when the ordering is disrupted by, for example, copolymerization with phenylquinoxaline.

CONCLUSION

We have synthesized and characterized semirigid PMDA/ODA-dimethylsiloxane block copolymers and modified PMDA/ODA-polydimethylsiloxane block copolymers obtained via the poly(amic-alkyl ester)-polydimethylsiloxane precursor route. This has considerable advantages over the poly(amic acid) route, both in terms of synthetic flexibility and in the characterization of the oligomers. Our interest in preparing such materials, as laid out in the introduction, was to obtain mechanically and thermally resistant films, while avoiding thermal stresses and associated problems and lack of adhesion, for example after thermal curing at high temperature on a silicon substrate. It was hoped that the addition of the rubbery polydimethylsiloxane would result in the relatively rapid relaxation of these stresses, if good phase separation with the PMDA/ODA imide could be obtained. Indeed, for a PMDA/ODA-polydimethylsiloxane block copolymer with a dimethylsiloxane block length of 5400 $g\,mol^{-1}$, no residual stress was observed at room temperature in films cured at 350°C. In modified films, however, where the phase boundary was less sharp and where, in some cases, the molecular structure of the matrix was altered, some residual stress was measured, although generally much less than in homogeneous PMDA/ODA imide films cured under the same conditions.

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