Structure–property behaviour of soluble polyimide–polydimethylsiloxane segmented copolymers

C. A. Arnold, J. D. Summers, Y. P. Chen, R. H. Bott, D. Chen and J. E. McGrath*

Department of Chemistry and Science and Technology Center, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA

(Received 15 September 1988; accepted 18 November 1988)

New, high-molecular-weight, randomly coupled poly(siloxane imide) *soluble* segmented copolymers have been synthesized from bis(aminopropyl) polydimethylsiloxane oligomers of controlled molecular weights and a series of dianhydride and diamine monomers. A solution imidization procedure was used to convert quantitatively the poly(siloxane amic acid) intermediates to the corresponding polyimides. The solution imidization procedure is based upon the co-amide solvents *N*-methylpyrrolidinone and cyclohexylpyrrolidinone and is conducted at milder temperatures than the classical bulk imidization. The bulk imidization technique requires temperatures of approximately 300°C, in slight excess of the ultimate glass transition. The solution imidization technique, on the other hand, is conducted at approximately 160°C. The poly(siloxane imide) segmented copolymers are flexible, tough, transparent and soluble, and are possible candidates for environmentally stable composite matrix resins, coatings and structural adhesives. Upper glass transition temperatures of many copolymers approach those of the unmodified controls, indicating good microphase separation. Lap shear strengths achieved against surface-treated titanium showed that relatively good adhesion could be achieved under practical bonding conditions. Moreover, the values were basically unchanged as a function of siloxane content at low siloxane levels. Photoelectron spectroscopy demonstrated that the top surface (~ 10 Å) is dominated by the siloxane. Significant reductions in the dielectric constant were obtained by incorporating fluorinated dianhydrides and *hydrophobic* aromatic diamines into the polyimide structure. Lower moisture sorption may also be obtained via siloxane modification and by the use of more non-polar reactants.

(Keywords: segmented copolymers; poly(siloxane imide); polyimide; polydimethylsiloxane)

INTRODUCTION

Polyimides synthesized from aromatic monomers exhibit excellent high-temperature thermal and mechanical properties and, indeed, many applications already exist for this class of materials[1–3]. Unless carefully designed, however, polyimides are often insoluble and intractable in their fully imidized form, presenting serious processing difficulties. Therefore, much effort has been spent on synthesizing tractable, processable polyimides that maintain reasonably high strength and environmental stability. Successful attempts to accomplish this goal have involved the incorporation of flexible bridging units[4–6] or bulky side-groups[7] or the more asymmetric *meta* catenation[8,9] into the otherwise rigid polyimide backbone. In this respect, the incorporation of the flexible siloxane segments into the polyimide backbone structure can yield soluble, processable copolyimides with good thermomechanical properties[10].

The polysiloxane component imparts a number of beneficial properties to the polymeric system into which it is co-reacted, including enhanced solubility, reduced water sorption and gas permeability, good thermal and ultraviolet stability, resistance to degradation in aggressive oxygen environments, impact resistance and modified surface properties[11–18,29]. These particular advantages render polysiloxane-modified polyimides attractive for aerospace, electronic and other high-performance applications.

Another significant method for obtaining improved processability involves the incorporation of monofunctional reagents to obtain non-reactive end-groups and controlled molecular weights. The method of conversion of the poly(amic acid) intermediate to the fully imidized polyimide will also affect processability and solubility, and, to some extent, certain physical properties as well[19].

In addition to enhanced solubility and processability, another current goal of polyimide research is to obtain reduced dielectric-constant behaviour. More hydrophobic, non-polar monomers are capable of yielding polyimide systems with lower dielectric constants than the classical Kapton polyimide. The most significant reductions have been obtained for fluorinated systems and with biphenyl tetracarboxylic dianhydride. Lower moisture sorption may also be obtained by utilizing relatively non-polar reactants[20].

In this work, a series of dianhydride and diamine monomers were systematically chosen as intermediates for the synthesis of polyimide homopolymers and poly(siloxane imide) segmented copolymers. The incorporated polydimethylsiloxane oligomer was varied from 5 to 70 wt%, with molecular weights in the range of 800 to 10 000 g mol^{-1}. The poly(amic acid) intermediates were prepared by a solution synthesis of the reactants in

---

* To whom correspondence should be addressed

0032–3861/89/060986–10$03.00

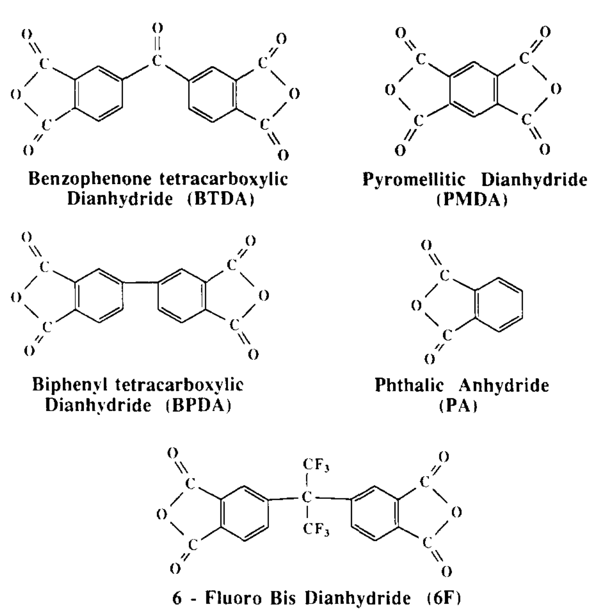

Figure 1 Anhydrides used for polyimide synthesis

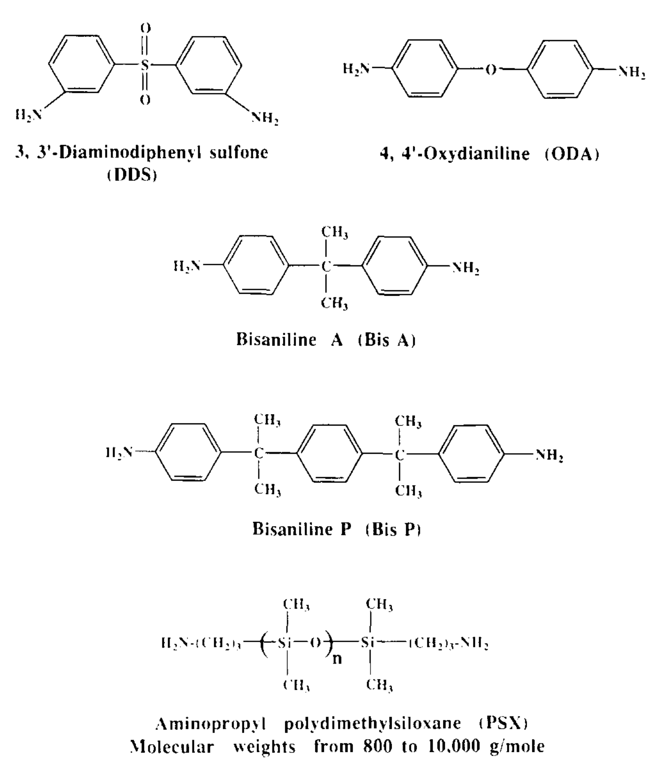

Figure 2 Diamines used for polyimide synthesis

either dimethylacetamide (DMAc) or *N*-methylpyrrolidinone (NMP). A co-solvent, tetrahydrofuran (THF), was utilized in the siloxane-modified systems. The high-molecular-weight amic acids were imidized by two procedures. The classical bulk imidization involved scheduled heating of the amic acid to temperatures slightly greater than the upper glass transition of the resultant fully imidized polyimide. The second approach is a recently developed solution imidization technique utilizing a solvent–azeotroping agent combination to imidize quantitatively the amic acid at milder temperatures of approximately 160°C. Both approaches were successful in producing high-molecular-weight, tough and transparent films. Structure–property relationships, solubility characteristics, surface composition analysis and dielectric behaviour of the homopolymer and copolymers will be reported.

EXPERIMENTAL

Materials

Figures 1 and *2* illustrate the monomers that were utilized in the synthesis of the homopolyimides and copolyimides. The dianhydrides BTDA, PMDA and BPDA were obtained from the Chriskev Corp.; the 6F dianhydride was kindly supplied by Hoechst–Celanese; phthalic anhydride (PA) was obtained from Aldrich Chemical Co. The PA and PMDA were purified by sublimation, and the other dianhydrides were used as received. All of the dianhydrides, however, were subjected to a thermal treatment prior to use.

Of the diamines, DDS was obtained from FIC Corp. and the bisaniline diamines were graciously supplied by Air Products Corp. These diamines were recrystallized prior to use.

All solvents were vacuum distilled after stirring over the drying agent phosphorous pentoxide. Water contents of the solvents, as determined by Karl Fisher automatic titrations, were 100 ppm or less.

The α,ω-aminopropyl polydimethylsiloxane oligomers were synthesized by the equilibration of the cyclic siloxane tetramer, octamethylcyclotetrasiloxane (D_4), and the aminopropyl functional disiloxane (DSX) in the presence of a basic catalyst[21], as illustrated in *Figure 3*. Molecular weights are controlled by the initial ratio of the tetramer to the dimer and can be determined by potentiometric titration of the amine end-groups.

Polymer synthesis

The non-siloxane-containing poly(amic acid) intermediates were synthesized by slowly adding the solid dianhydride to a stirring solution of the chosen diamine. The overall reaction was conducted at room temperature under a nitrogen atmosphere at 15% solids concentration in either NMP or DMAc.

In order to ensure the incorporation of the siloxane oligomer, the siloxane-containing poly(amic acid)s were

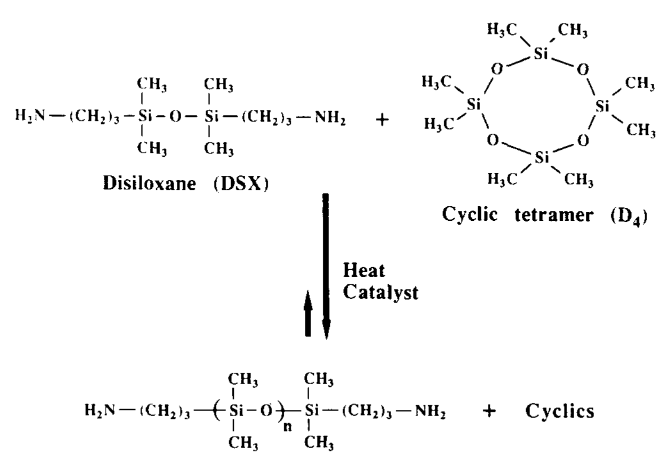

Figure 3 Synthetic scheme for difunctional amine-terminated polydimethylsiloxane oligomers via an equilibration polymerization process. Cyclics are removed via vacuum stripping. Catalyst must be neutralized for maximum stability. M_n is controlled at equilibrium by the initial ratio of D_4 to DSX. Other end-groups are possible with appropriate DSX and catalyst. Actual M_n is determined by titration of amine end-groups or by ^{1}H n.m.r.

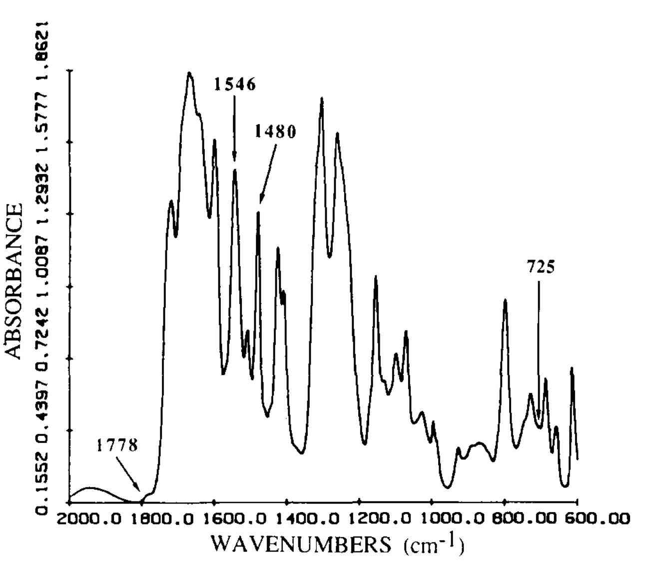

Figure 4 *FT*i.r. of poly(amic acid) based upon BTDA–DDS with 10 wt% siloxane (siloxane $M_n = 950$ g mol^{-1})

synthesized by a slightly different method. First of all, because the siloxane oligomers and aromatic monomers possess vastly different solubility characteristics, a co-solvent system consisting of NMP or DMAc and THF was necessary to accomplish *homogeneous* solution copolymerization. As a general rule, a co-solvent ratio higher in THF was needed to solvate reaction mixtures containing higher molecular weights and/or higher percentages of the siloxane oligomers. Maintaining solubility of the reactants throughout the polymerization process proved critical in obtaining tough, transparent poly(siloxane imide) films of predictable composition.

In addition to the co-solvent system, another technique to ensure the incorporation of the siloxane oligomer was to alter the traditional mode of monomer addition. Thus, the siloxane oligomer was first slowly added to a stirring solution of the dianhydride, effectively capping the siloxane oligomer through reaction of its amine end-groups. The aromatic diamine is then gradually added as a solution to the free dianhydride and anhydride-capped siloxane. Advantageously, the capped siloxanes possess greater solubility in the co-solvent system. By employing these synthetic variations for the poly(siloxane amic acid)s, namely the use of a co-solvent system and the altered mode of monomer addition, siloxane oligomers ranging in molecular weights from 800 to 10 000 g mol^{-1} were successfully incorporated into the BTDA–DDS system in amounts ranging from 5 to 70 wt%. Calculated amounts of phthalic anhydride were also incorporated to limit the molecular weight and control the end-groups. This feature has proved substantially influential in optimizing the adhesive performance and overall thermoplastic behaviour of these materials[13].

Conversion of the poly(amic acid) intermediates to the fully imidized polyimide was accomplished by two different techniques. The first and most common method is bulk thermal imidization, which involves casting the amic acid solution onto a glass plate and removing the solvent in a vacuum oven at 100°C for several hours. To complete the cyclization/dehydration and remove the residual solvent, the films were then subjected to scheduled heating in a forced air oven at 100, 200 and 300°C for an hour at each temperature.

The second technique is a solution imidization conducted at a 15% solids concentration with a co-solvent system of NMP (80%) and cyclohexylpyrrolidinone (CHP, 20%). A much milder temperature of 160°C is required, with cyclization complete after 24 h. The conversion of the amic acid to the fully imidized polymer may be monitored semi-quantitatively by *FT*i.r.[15,22–24], as indicated in *Figures 4* and *5*, corresponding to the amic acid and the polyimide obtained after 24 h at 160°C, respectively. The bands at 1778 and 725 cm^{-1} correspond to the imide structure, while the band at 1546 cm^{-1} is characteristic of the amic acid. Tough, transparent and flexible films were obtained by both imidization techniques, although the choice of the imidization technique affected certain material properties. The general synthetic and imidization schemes for the poly(siloxane imide) segmented copolymers are depicted in *Figure 6*.

Characterization

Intrinsic viscosity measurements yielded relative molecular weights and were performed in NMP at 25°C using a Cannon-Ubbelohde viscometer. Gel permeation chromatography was used to investigate the molecular-weight distribution of the polyimides and was performed on a Waters instrument in tetrahydrofuran with an ultra-violet detector at 254 nm.

Proton nuclear magnetic resonance (n.m.r.) spectroscopy was run on a 270 MHz Bruker instrument for samples dissolved in deuterated dimethylsulphoxide.

Differential scanning calorimetry (d.s.c.) was used to determine the glass transition temperatures (T_g) with a Perkin–Elmer model DSC-4. Scans were run at 10°C min^{-1} with a sensitivity of 10 mcal s^{-1}. Reported values were obtained from a second scan after heating and rapid cooling. Some copolymer transitions were obtained by dynamic mechanical thermal analysis (d.m.t.a.) at a frequency of 1 Hz using a Polymer Laboratories instrument. Thermal gravimetric analysis (t.g.a) was performed on a Perkin–Elmer TMS-2

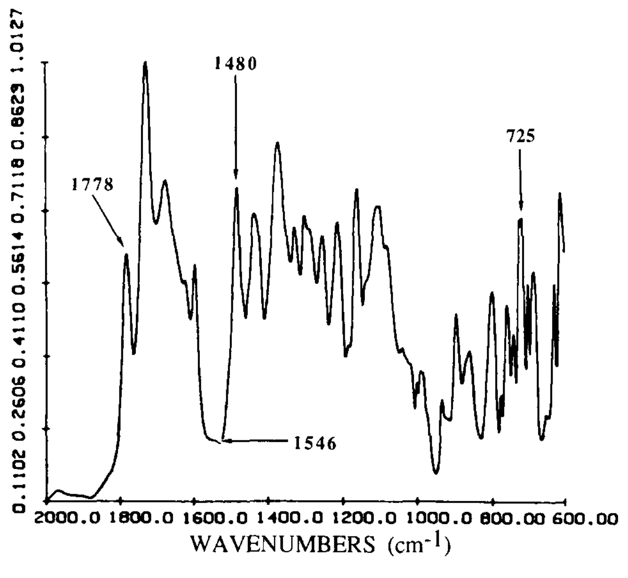

Figure 5 *FT*i.r. of polyimide based upon BTDA–DDS with 10 wt% siloxane obtained after 24 h solution imidization at 160°C (siloxane $M_n = 950$ g mol^{-1})

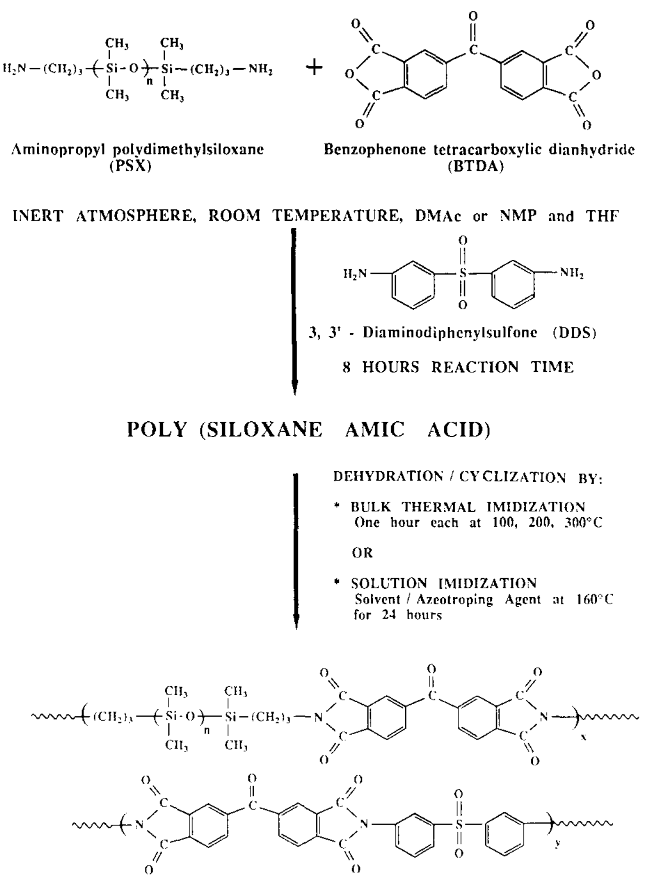

Figure 6 Synthetic scheme for poly(siloxane imide) segmented copolymers

instrument on samples in film form. Scans were run at 10°C min^{-1} in an air atmosphere.

An Instron model 1122 was used to determine the mechanical behaviour of dogbone-shaped specimens of the copolymers. Specimen gauge lengths were 10 mm and specimen widths were 2.76 mm. The extension rate was 5 mm min^{-1}.

Water sorption was monitored by immersing thin films in distilled water at 23°C. The samples were periodically removed and blotted dry, and weighed to determine water uptake.

X-ray photoelectron spectroscopy (x.p.s.) was utilized to determine the surface composition of the copolymer films. Samples were prepared by spin-coating the amic acid intermediate in its reaction solution onto ferrotype plates which had been washed in hexane. The samples were covered with a watchglass to prevent contamination during bulk thermal imidization in a forced air convection oven. After imidization, the samples were washed three times in hexane and placed in clean glass containers with lids. Analysis was performed on a Kratos instrument at exit angles of 15° and 90°. The 15° grazing angle yields compositional data from depths of approximately 10 to 20 Å whereas the 90° normal angle samples depths of approximately 70 to 100 Å.

Single lap shear specimens were prepared by sandwiching a scrim cloth (112E glass) coated with the poly(siloxane imide) resin between two primed titanium adherends. The poly(siloxane amic acid) solution in NMP/THF, which was molecular weight controlled by the addition of phthalic anhydride, was coated onto the scrim cloth and cured in a forced air convection oven using the following schedule:

60°C for 0.5 h
100°C for 0.5 h
160°C for 0.5 h
160°C in vacuum for 0.5 h

This procedure was repeated until an overall thickness for the cloth and resin of 0.023 to 0.033 cm was achieved.

The titanium adherends were sandblasted, treated with Pasa Jell 107, ultrasonically cleaned, and immediately primed with a coating of amic acid solution to preserve the surface treatment. This primer coat was imidized using the same thermal schedule as the scrim cloth.

Single lap shear specimens (1.27 cm overlap) were prepared by pressing the coated scrim cloth between two primed adherends using the following bonding cycle:

Room temperature to 325°C,
  apply 1.4 MPa (200 psi) at 280°C
Hold for 15 to 60 min at 325°C
Cool under pressure to room temperature

Dielectric properties were determined on a Hewlett–Packard Network Analyzer 8510 over the frequency range of 12.5 to 18.0 GHz with a P-band waveguide. The sample specimens were assessed both 'as is', i.e. after remaining at ambient conditions for extended times, and after being dried in a vacuum oven for 12 h (minimum) near the glass transition temperature of the polymer. With the exception of Kapton, only the dielectric values obtained on dry samples are reported. The specimen size was approximately 1 cm x 0.5 cm. The scans were run at room temperature in an air atmosphere, although operation up to 165°C and in different environments over the frequency range of 45 MHz to 26 GHz is also possible.

RESULTS AND DISCUSSION

The removal of moisture from the reaction system was necessary to obtain high-molecular-weight amic acids. Therefore, monomers, solvents and the reaction apparatus were dried prior to use and the low-water-content, distilled solvents were stored in sealed flasks under a nitrogen atmosphere. The solvents were transferred using syringe techniques.

Maintaining solubility of the reactants throughout the polymerization was also a major factor in obtaining high-molecular-weight, tough, transparent samples of predictable composition. Solvents such as methylene chloride, THF and chloroform easily solvate the polydimethylsiloxane oligomers. However, they do not readily dissolve aromatic monomers or the resultant poly(amic acid). On the other hand, dipolar aprotic solvents are good solvents for the aromatic monomers, the growing polymer chain and even the aminopropyl-terminated siloxane dimer. However, they are non-solvents for siloxane oligomers of molecular weight greater than 5000 g mol^{-1}. Based upon these observations, a co-solvent system consisting of a dipolar aprotic solvent such as NMP or DMAc and THF was chosen to synthesize homogeneously the poly(siloxane amic acid) intermediates. Adjustments to the co-solvent ratio were necessary to optimize each reaction for the particular concentration and molecular weight of the siloxane oligomer. In general, to solubilize siloxanes of

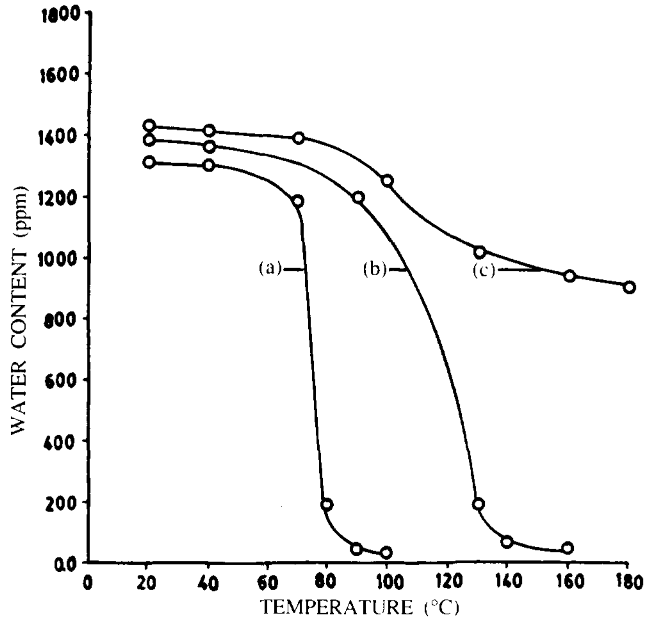

Figure 7 Water contents of reaction solvents as determined by Karl Fisher titrations: (a) CHP only; (b) NMP(80%)/CHP(20%); (c) NMP only

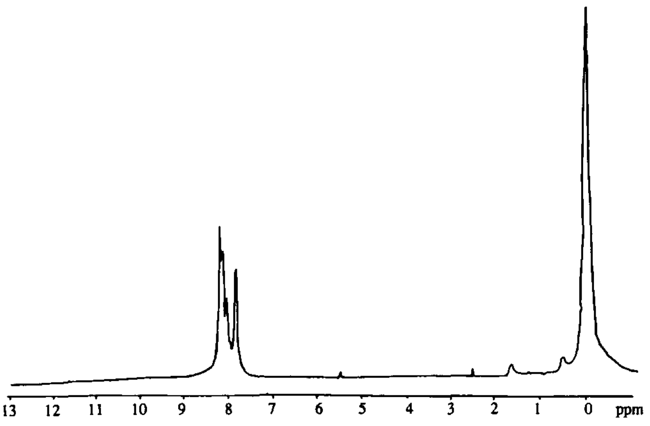

Figure 8 N.m.r. of solution-imidized BTDA–DDS based poly(siloxane imide) copolymer with 40 wt% siloxane charged and 38 wt% siloxane incorporated (siloxane $M_n = 950\ \mathrm{g\ mol^{-1}}$)

higher molecular weights and for greater siloxane concentrations, higher THF contents were necessary.

Solubility of the reaction species was further enhanced by essentially end-capping the siloxane oligomer with the dianhydride in the first step of the reaction sequence. The end-capped siloxane oligomers possessed greater solubility in the reaction mixture of the aromatic monomers and the growing polymer chains, ensuring their incorporation into the amic acid backbone.

The poly(siloxane amic acid) intermediates were converted to the corresponding poly(siloxane imide) segmented copolymers by two techniques. In the case of the bulk thermal imidization, films were exposed to an upper imidization temperature of 300°C for 1 h. This upper temperature, somewhat greater than the glass transition of the resultant fully imidized polymer, was necessary to prevent vitrification before cyclization was complete.

Solution imidization of the amic acid was conducted in a co-solvent system of NMP and CHP (cyclohexylpyrrolidinone) at 160°C for 24 h. At elevated temperatures, CHP effectively acts as an azeotroping agent for water which is formed upon the conversion of the amic acid to the imide. The incompatibility of CHP with water, as determined by automatic Karl Fisher titrations, is demonstrated in *Figure 7*.

A proton n.m.r. spectrum of a BTDA-DDS based copolyimide containing 40 wt% siloxane is shown in *Figure 8*. The siloxane oligomer molecular weight is 950 g mol^{-1}. The spectrum shows a strong resonance at ~0 ppm indicative of the silicon methyls and a series of complicated aromatic proton resonances. The absence of peaks above 10 ppm due to carboxylic acid structures also indicates quantitative imidization. The amount of siloxane in the copolymer, determined by ratioing the integrated peak areas of the aromatic proton region and the silicon methyls, indicated that 95% of the siloxane oligomer was incorporated into the polyimide backbone.

One of the major goals of this endeavour was to solubilize the normally intractable polyimides by the incorporation of siloxane segments, and, optionally, by solution imidization and judicious choice of monomers. For certain monomer combinations, the solution-imidized materials were markedly more soluble than the bulk-imidized systems but their thermal and mechanical properties did not vary significantly. Solubilities of a series of siloxane-modified polyimide copolymers based on BTDA and DDS were evaluated in a variety of solvents as indicated in *Table 1*. Copolymer solubility was found to be a function of the siloxane oligomer (PSX) concentration as well as of the method of imidization. The solution-imidized copolymers and *also the solution-imidized control* (*no siloxane*) were all soluble in dipolar, aprotic solvents such as *N*-methylpyrrolidinone (NMP) and dimethylacetamide (DMAc). The solubility of the solution-imidized copolymers and control in NMP or DMAc ranged from ~10 wt% for the control to ~20 wt% for the copolymers. At 40 wt% siloxane, the solution-imidized copolymers were soluble in a variety of alternative solvents, including tetrahydrofuran (THF), methylene chloride (CH_2Cl_2) and 2-methoxyethyl ether (diglyme). The bulk-imidized materials were less soluble than those which were solution-imidized, requiring at least 10 wt% siloxane at solids concentrations of less than 5% to achieve solubility in NMP and DMAc. The

Table 1 Solubility study of BTDA–DDS based poly(siloxane imide) segmented copolymers: effect of incorporated siloxane[a] and bulk *versus* solution imidization techniques

PSX (wt%)	Imidization method	NMP	DMAc	THF	CH_2Cl_2
Control	Bulk	IS[b]	IS	IS	IS
Control	Soln	Sol	Sol	IS	IS
10	Bulk	MS	MS	IS	IS
10	Soln	Sol	Sol	IS	IS
20	Bulk	MS	MS	IS	IS
20	Soln	Sol	Sol	IS	IS
40	Bulk	MS	MS	IS	IS
40	Soln	Sol	Sol	Sol	Sol
60	Bulk	Sol	Sol	Sol	Sol
60	Soln	Sol	Sol	Sol	Sol

[a] Siloxane molecular weight is 950 g mol^{-1}

[b] IS, insoluble; MS, marginally soluble; Sol, soluble

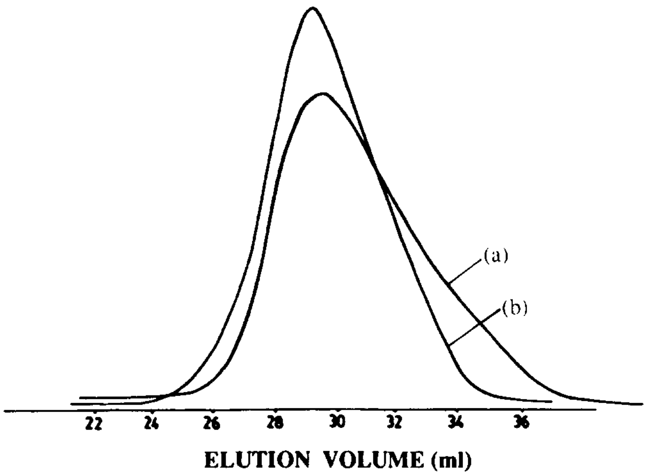

Figure 9 Gel permeation chromatographs of poly(siloxane imide) copolymers based upon BTDA, DDS and siloxane oligomer with $M_n = 950$ g mol^{-1} which were: (a) bulk imidized, 60 wt% siloxane; and (b) solution imidized, 40 wt% siloxane

Table 2 Solubility study of solution-imidized polyimide homopolymers and poly(siloxane imide) segmented copolymers: effect of chemical composition and incorporated siloxane

Polyimide system	NMP	THF	CH_2Cl_2	C_6H_5Cl	Toluene
BTDA–DDS	Sol	IS	IS	IS	IS
BTDA–DDS–10% PSX 800	Sol	Sol	IS	IS	IS
BTDA–Bis A	Sol	IS	Sol	IS	IS
BTDA–Bis P	Sol	MS	Sol	MS	IS
BTDA–Bis P–10% PSX 800	Sol	Sol	Sol	MS	IS
6F–DDS	Sol	MS	MS	IS	IS
6F–Bis P	Sol	Sol	Sol	Sol	Sol
6F–Bis P–10% PSX 800	Sol	Sol	Sol	Sol	Sol

Table 3 Upper glass transitions of BTDA–DDS based poly(siloxane imide) segmented copolymers: effect of incorporated siloxane and bulk *versus* solution imidization techniques

PSX (wt%)	PSX M_n	Imidization method	[η]	T_g (°C) (by d.s.c.)
Control	–	Bulk	–	272
Control	–	Soln	1.36	265
10	900	Bulk	0.62	256
10	900	Soln	0.63	251
10	2100	Bulk	0.78	261
10	2100	Soln	0.73	260
10	5000	Bulk	0.71	264
10	10000	Bulk	0.73	266
20	900	Bulk	0.78	246
20	900	Soln	0.67	240
20	5000	Bulk	0.51	262
40	900	Bulk	0.55	225
40	900	Soln	0.58	218

bulk-imidized control was *not* soluble in dipolar, aprotic solvents.

The differences in solubility between bulk- and solution-imidized polyimides may be partially understood by considering their molecular-weight distributions. Typical gel permeation chromatographs for the bulk- and solution-imidized copolymers are presented in *Figure 9*. Contrasted with the unimodal Gaussian distribution of the solution-imidized sample, the bulk-imidized trace is skewed to low molecular weights. This suggests that abnormal side-reactions may be occurring at the high temperatures (300°C) required to accomplish bulk thermal imidization.

Table 2 indicates the solubilities of some solution-imidized polyimide homopolymers based upon less polar monomers such as Bis P and Bis A diamines or the 6F dianhydride. Utilization of these monomers, rather than the more rigid, polar BTDA or DDS, yields more soluble polyimide systems. Intrinsic viscosities of the copolymers (*Tables 3* and *4*) ranged from 0.50 to 1.88 dl g^{-1}, indicating that high-molecular-weight copolymers were obtained by both imidization techniques over the entire composition and siloxane molecular-weight range.

Solubility and processability may be further enhanced by controlling the overall molecular weight. *Table 5* illustrates that incorporation of a monofunctional reagent, in this case phthalic anhydride, can indeed limit molecular weight, as determined by intrinsic viscosity values. Presumably, most of the end-groups are phthalimide in nature, as depicted in *Figure 10*, although this has not been quantitatively demonstrated. The use of controlled molecular weights offers two pertinent advantages for thermoplastic processing and adhesive applications[30]. First of all, lower-molecular-weight samples exhibit better and more stable melt flow properties and, consequently, superior bond consolidation. Secondly,

Table 4 Upper glass transitions of polyimide homopolymers and poly(siloxane imide) segmented copolymers: effect of chemical composition and incorporated siloxane

Polyimide system	Imidization method	[η]	T_g (°C) (by d.s.c.)
BTDA–DDS	Soln	1.36	265
BTDA–DDS–10% PSX 800	Soln	1.88	251
BTDA–Bis P	Soln	0.72	264
BTDA–Bis P–10% PSX 800	Bulk	0.60	241
6F–DDS	Soln	0.60	270
6F–Bis P	Soln	0.50	267
6F–Bis P–10% PSX 800	Soln	0.79	232

Table 5 Molecular weight and end-group control of 6F–DDS based polyimides by incorporation of phthalic anhydride

Desired M_n	Phthalic anhydride (mol%)	[η]
5000	7.0	0.11
10000	3.5	0.23
20000	1.8	0.37
30000	1.2	0.40
∞	–	1.08

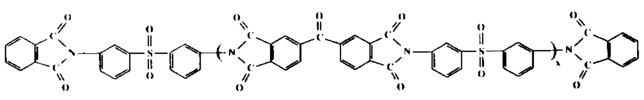

Figure 10 BTDA–DDS polyimide homopolymer with phthalimide end-groups

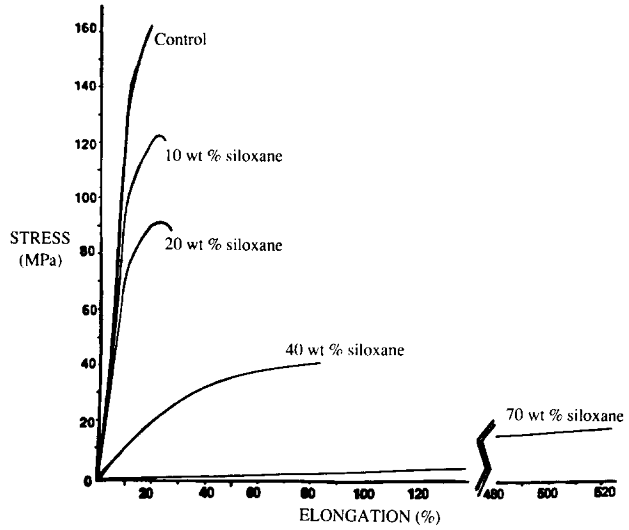

Figure 11 Stress–strain behaviour as a function of siloxane incorporation for a series of BTDA–DDS based poly(siloxane imide) copolymers (siloxane $M_n = 950 \text{ g mol}^{-1}$)

non-functional phthalimide end-groups are unreactive towards potential post-reactions which could occur during bond formation. Such post-reactions could inhibit good wetting of the adherend which might prevent adequate bond consolidation.

Attempts to synthesize PMDA- and BPDA-based polyimides by solution imidization were unsuccessful. Both PMDA–Bis P, PMDA/6F(50 mol% of each dianhydride)–Bis P and BPDA–Bis P amic acid systems precipitated out of solution prematurely, although some imidization had occurred. Accordingly, those systems were only imidized in bulk.

Values of the upper glass transition temperatures of the BDTA–DDS siloxane-modified polyimides were found to be a function of both the level of incorporated siloxane as well as the siloxane molecular weight (*Table 3*). The upper transition temperatures of the solution-imidized materials were found to be only slightly depressed from their bulk-imidized analogues. Generally, the upper transition temperature increased with greater siloxane oligomer molecular weight and with decreasing siloxane incorporation. In many cases, the copolymer's upper transition temperature was depressed only slightly relative to that of the control, indirectly indicating that good microphase separation was achieved. The lower-temperature siloxane transition is difficult to detect by d.s.c. for low levels of siloxane incorporation, i.e. less than 20 wt%. At greater levels of incorporation, however, the transition is detected by both d.s.c. and d.m.t.a. within the range −117 to −123°C. Initial transmission electron micrographs of the solution-imidized BTDA–DDS based copolymers indicate siloxane microphase formation for a 10 wt% siloxane copolymer with a 2000 molecular weight siloxane segment. The domain size is relatively small (~50 Å) and phase contrast is somewhat poor. This may be due to the low siloxane molecular weight and its broad, Gaussian molecular-weight distribution. Microphase separation is enhanced by increasing the siloxane molecular weight to $10\,000 \text{ g mol}^{-1}$. Consequently, the phase contrast sharpens and the domain size increases to ~160 Å.

The upper glass transition temperatures for various polyimide homopolymers are depicted in *Table 4*. Although incorporation of the less polar monomers enhanced solubility, the upper glass transitions of these homopolymers are relatively unchanged from the BTDA–DDS system. Incorporation of siloxane into Bis P–6F based systems, however, more substantially depresses the upper glass transition than for the BTDA–DDS system. Enhanced miscibility of the siloxane component with the Bis P and 6F monomers results in this depression. More phase mixing would occur in this case and substantially decrease the glass transition than if better microphase separation had been obtained.

The thermal–mechanical properties of siloxane-modified polyimides are a function of the weight fraction of incorporated siloxane, the molecular weight of the siloxane blocks and the chemical architecture of both the siloxane and imide segments. Thus, copolymers with high concentrations of incorporated siloxane (greater than 50%), where the siloxane is the continuous phase, behave as thermoplastic elastomers. Copolymers containing low siloxane concentrations result in more rigid materials which behave essentially as modified polyimides. The stress–elongation response for BTDA–DDS based poly(siloxane imide) copolymers illustrates this point (*Figure 11*). At high polyimide compositions, the upper glass transition value and most mechanical properties approach those of the unmodified controls. Overall thermal stability as judged by thermogravimetric analysis is shown in *Figure 12* as a function of siloxane content. Although at siloxane levels as high as 60 wt% the copolymers maintain good thermal stability, degradation occurs at lower temperatures as the siloxane content is increased. The char yield is proportional to the siloxane content, suggesting that the silicate-type structure is the principal degradation product in an air atmosphere and that flammability resistance will be improved for siloxane-modified polymers[25].

Copolymer thermal stability also varies with the siloxane oligomer molecular weight (*Figure 13*). Thermal degradation begins at the aliphatic n-propyl segments linking the siloxane oligomers to the polyimide matrix. Thus, as the siloxane oligomer molecular weight is increased and the concentration of n-propyl linkages in the copolymer backbone decreases, the overall thermal stability is increased. All of the homopolymers exhibit

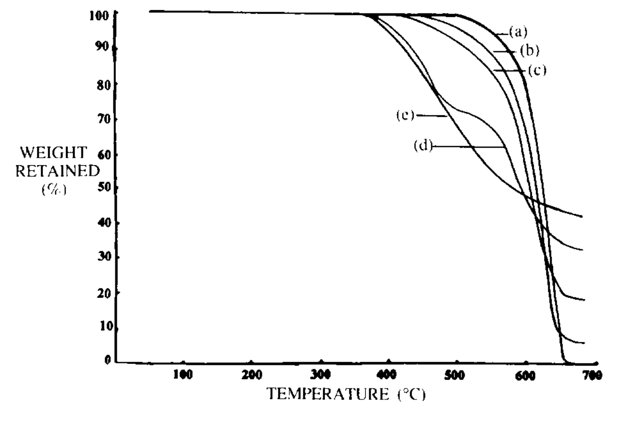

Figure 12 Thermogravimetric analysis as a function of siloxane incorporation for a series of BTDA–DDS based poly(siloxane imide) copolymers (siloxane $M_n = 950 \text{ g mol}^{-1}$): (a) control; (b) 10 wt%; (c) 20 wt%; (d) 40 wt%; (e) 60 wt% siloxane

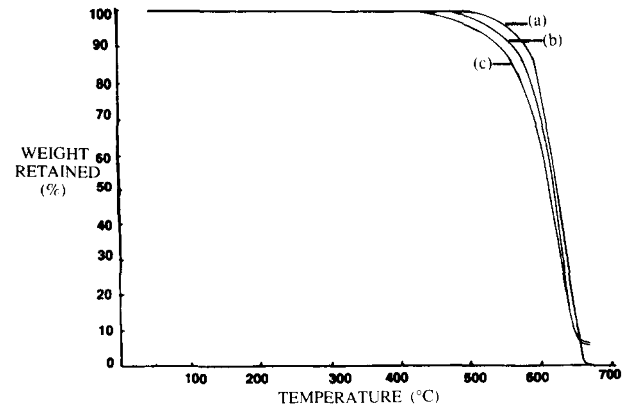

Figure 13 Thermogravimetric analysis as a function of siloxane oligomer molecular weight for a series of BTDA–DDS based poly(siloxane imide) copolymers (10 wt% siloxane incorporation): (a) control; (b) 10000 g mol^{-1}; (c) 950 g mol^{-1}

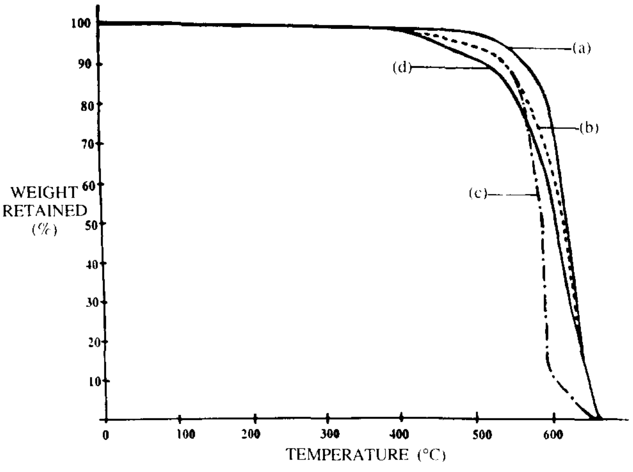

Figure 14 Thermogravimetric analysis for a series of polyimide homopolymers: (a) BTDA–DDS; (b) BTDA–Bis P; (c) 6F–DDS; (d) 6F–Bis P

excellent high-temperature stability, as depicted in the thermograms of *Figure 14*.

The great difference in solubility parameters of the siloxane and imide segments provides a driving force for microphase separation, particularly when higher-molecular-weight siloxane oligomers are incorporated. Because the siloxane component possesses a relatively low surface energy, it will migrate to the air or vacuum interface, yielding a surface dominated by the covalently anchored siloxane component. X-ray photoelectron spectroscopy studies (x.p.s. or e.s.c.a.) demonstrated that the surface composition was predominantly siloxane, even when the bulk siloxane compositions were relatively low (*Table 6*). Thus, one is able to achieve a surface characteristic of the siloxane component while tailoring the physical properties which are characteristic of the bulk.

The conversion of polysiloxane to silicon dioxide in oxygen plasma has been documented within the literature as well as in our laboratories[26–28]. In aggressive oxygen environments, the surface siloxane segments convert to a ceramic-like silicate (SiO_2) which provides a protective overlayer for the bulk material. This transformation is of extreme interest to both the electronics and aerospace industries for the enhancement of oxygen plasma etch resistance and for the *in situ* formation of protective coatings on organic polymeric materials.

Another major benefit of the hydrophobic siloxane surface is the dramatic reduction in the amount of water absorbed by the copolymer compared with the unmodified homopolymer analogue. The results for siloxane-modified copolyimides based on BTDA and DDS are shown in *Figure 15*. As the siloxane content is increased, water sorption decreases sharply. Incorporation of the lower-molecular-weight siloxane oligomer further reduces water sorption. Monomers of relatively low polarity, such as the Bis P diamine or 6F dianhydride, also exhibit low water sorption compared to their more polar analogues. An applied benefit of this result is realized in adhesive bonding studies in hot/wet environments. Durability of single lap shear joints was determined for a BTDA–DDS based copolyimide at 80°C in a 100% relative humidity environment. While the durability is enhanced three-fold by the incorporation of

Table 6 X-ray photoelectron spectroscopy of BTDA–DDS based poly(siloxane imide) segmented copolymers

PSX (wt%)	PSX M_n	Take-off angle (deg)	PSX (wt%) at surface
5	950	15	85
5	950	90	34
10	950	15	77
10	950	90	35
10	10000	15	87
10	10000	90	39
20	950	15	87
20	950	90	53
40	950	15	86
40	950	90	63

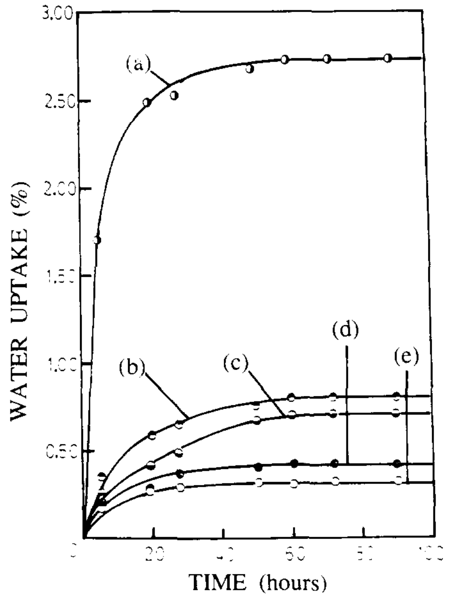

Figure 15 Water sorption for a series of poly(siloxane imide) copolymers based upon BTDA–DDS: (a) control, no siloxane; (b) 30 wt% siloxane (M_n=2500); (c) 30 wt% siloxane (M_n=910); (d) 50 wt% siloxane (M_n=2500); (e) 50 wt% siloxane (M_n=910 g mol^{-1})

Table 7 Adhesive strengths of BTDA–DDS based poly(siloxane imide) segmented copolymers[a]

PSX (wt%)	Single lap shear strength (MPa) (psi)	[η]
0	20.6 (3000)[b]	–
5	16.5 (2400)	–
10	19.9 (2900)[b]	0.40
20	14.4 (2100)	0.36
40	12.4 (1800)	0.34

[a] Siloxane oligomer molecular weight is 950 g mol^{-1}

[b] Data obtained from most recent series of experiments

10% siloxane, the room-temperature ultimate strength (2900 psi) is almost identical to that obtained for the unmodified control (3000 psi).

Preliminary adhesive data on controlled molecular-weight copolymers are shown as single lap shear strengths in *Table 7*. The incorporation of low to moderate amounts of siloxane, where the siloxane molecular weight is 950 g mol^{-1}, *does not* significantly detract from the adhesive characteristics of these materials. Additionally, the high-temperature adhesive properties of these materials are excellent, with copolymers containing up to 20% siloxane retaining approximately 50% of their adhesive strength at 200°C. As previously mentioned, the use of controlled molecular weights and controlled end-groups (*Figure 10*) yields superior bond consolidation. Only at high levels of siloxane incorporation do the room-temperature lap shear strengths fall below 2000 psi, indicating the potential utility of these copolymers as atomic-oxygen-resistant structural adhesives.

A critical issue in this study was the possibility of controlling the dielectric behaviour by molecular structure design of the homopolyimides and their siloxane-modified counterparts. The dielectric behaviour at 15 GHz for different homopolymer and copolymer systems is summarized in *Table 8*. The classical, commercially available Kapton (PMDA–ODA) system shows a dielectric constant of approximately 3.3 at 15 GHz. Introducing less polar diamines than ODA, such as Bis P, significantly drops the dielectric constant to ~2.7. Bis P was found to decrease the dielectric constant for both BTDA- and 6F-based systems as well, relative to the more commonly studied DDS diamine. Attempts to synthesize PMDA-based soluble systems using the Bis P diamine were not successful, even when the 6F dianhydride comprised 50 mol% of the total anhydride component. However, both Bis P and 6F lowered the dielectric constant of PMDA-based, bulk-imidized polyimides. The most dramatic reductions in the dielectric constant were obtained by utilizing the 6F dianhydride, where values approaching 2.5 were achieved. In some cases, incorporation of siloxane further reduces the dielectric constant. The dielectric behaviour was relatively unchanged over the wide frequency range of 12.5 to 17.5 GHz, suggesting that the values may be extrapolated down to lower frequencies which are of current interest, e.g. 10 MHz.

CONCLUSIONS

In summary, it has been possible to prepare a variety of poly(imide siloxane) segmented copolymers which demonstrate useful thermal, mechanical, adhesive and dielectric properties. Other interesting properties include hydrophobic character, u.v. stability and oxygen plasma resistance. The synthesis and characterization of these materials is continuing with an emphasis placed on the production of thermoplastic, soluble, low-dielectric-constant, hydrophobic matrix resins and structural adhesives.

Table 8 Influence of molecular structure on the dielectric behaviour of polyimide homopolymers and poly(siloxane imide) segmented copolymers

Polyimide system	Dielectric constant[b]
PMDA–ODA[a] (Kapton, ambient)	3.32
PMDA–ODA[a] (dry)	3.24
PMDA–Bis P[a]	2.70
PMDA(50 mol%)/6F(50 mol%)–Bis P[a]	2.62
BTDA–DDS[a]	3.17
BTDA–DDS–10% PSX 800	3.09
BTDA–Bis P[a]	2.77
BTDA–Bis A	3.10
6F–DDS[a]	2.87
6F–Bis P	2.62
6F–Bis P–10% PSX 800	2.61
6F–Bis P–10% PSX 800[a]	2.54

[a] Bulk imidized

[b] Dielectric constant at 15 GHz

ACKNOWLEDGEMENTS

Various portions of this research were supported by the Air Force Office of Scientific Research, Defense Advanced Research Projects Agency and National Aeronautics and Space Administration, and these are gratefully acknowledged.

REFERENCES

1 St Clair, A. K. and St Clair, T. L. *ACS Symp. Ser.* 1987, **346**, 437
2 Mittal, K. (Ed.), 'Polyimides: Synthesis, Characterization, and Applications', Plenum Press, New York, 1984, Vols. 1 and 2
3 Davis, C. T. *ACS Symp. Ser.* 1984, **242**, 259
4 Burks, H. D. and St Clair, T. L. in 'Polyimides: Synthesis, Characterization, and Applications' (Ed. K. L. Mittal), Plenum, New York, 1984, Vol. 1, pp. 117–35
5 Young, P. R. and Wakelyn, N. T., Proceedings from the Second International Conference on Polyimides, Ellenville, NY, 1985, pp. 414–25
6 Critchley, J. P. and White, M. A. *J. Polym. Sci., Polym. Chem. Edn.* 1972, **10**, 1809
7 Harris, F. W., *et al.* 'Polyimides: Synthesis, Characterization, and Applications' (Ed. K. L. Mittal), Plenum, New York, 1984, Vol. 1, pp. 3–14
8 St Clair, A. K., St Clair, T. L. and Smith, E. N. *Polym. Prepr.* 1976, **17**, 359
9 St Clair, T. L. and Yamaki, D. A., 'Polyimides: Synthesis, Characterization, and Applications (Ed. K. L. Mittal), Plenum, New York, 1984, Vol. 1, pp. 99–116
10 Arnold, C. A., Summers, J. D., Bott, R. H., Taylor, L. T., Ward, T. C. and McGrath, J. E. *SAMPE Symp.* 1987, **32**, 586
11 Lee, C. L. *SAMPE Symp.* 1985, **30**, 52
12 Berger, A. *SAMPE Symp.* 1985, **30**, 64
13 Bott, R. H., Summers, J. D., Arnold, C. A., Taylor, L. T., Ward, T. C. and McGrath, J. E. *J. Adhes.* 1987, **23**, 67
14 McGrath, J. E., Sormani, P. M., Elsbernd, C. S. and Kilic, S. *Makromol. Chem., Macromol. Symp.* 1986, **6**, 67
15 Summers, J. D., PhD Thesis, VPI&SU, 1988
16 Johnson, B. C., PhD Thesis, VPI&SU, 1984
17 Andolino Brandt, P. J., PhD Thesis, VPI&SU, 1986

18 Johnson, B. C., Yilgör, I. and McGrath, J. E. *Polym. Prepr.* 1984, **25** (2), 54

19 Arnold, C. A., Summers, J. D., York, G., Bott, R. H., Taylor, L. T., Ward, T. C. and McGrath, J. E. *Polym. Prepr.* 1987, **28** (2), 217

20 Arnold, C. A., Summers, J. D., Chen, Y.-P., Chen, D., Graybeal, J. D. and McGrath, J. E. *SAMPE Symp.* 1988, **33**, 960

21 McGrath, J. E., Sormani, P. M., Elsbernd, C. S. and Kilic, S. *Makromol. Chem., Macromol. Symp.* 1986, **6**, 67–80

22 Summers, J. D., Arnold, C. A., Bott, R. H., Taylor, L. T., Ward, T. C. and McGrath, J. E. *Polym. Prepr.* 1986, **27** (2), 403

23 Summers, J. D., Arnold, C. A., Bott, R. H., Taylor, L. T., Ward, T. C. and McGrath, J. E. *SAMPE Symp.* 1987, **32**, 613

24 Summers, J. D. and McGrath, J. E. *Polym. Prepr.* 1987, **28** (2), 230

25 Kambour, R. P. *J. Appl. Polym. Sci.* 1981, **26**, 861

26 Arnold, C. A., Chen, D., Chen, Y.-P., Graybeal, J. D., Bott, R. H., Yoon, T., McGrath, B. E. and McGrath, J. E. *Polym. Mater., Sci. Eng.* 1988, **60**

27 Slemp, W. S., Santos-Mason, B., Sykes, G. F. and Witte, W. G., Jr, AAIA-85-0421, AIAA 23rd Aerospace Meeting, January 1985

28 Visentine, J. T., Lejer, L. J., Kuminecz, J. F. and Spiker, I. K., AIAA-85-0415, AIAA 23rd Aerospace Meeting, January 1985

29 Summers, J. D., Elsbernd, C. S., Sormani, P. H., Brandt, P. J. A., Arnold, C. A., Yilgor, I., Riffle, J. S., Kilic, S. and McGrath, J. E. *ACS Symp. Ser.* No. 360, American Chemical Society, Washington, 1988, p. 180

30 Bott, R. H., Summers, J. D., Arnold, C. A., Taylor, L. T., Blankenship, C. P., Ward, T. C. and McGrath, J. E. *SAMPE J.* 1988, **24**, 7