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Synthesis and Characterization of Triphenylphosphine Oxide-Containing Poly(Aryl Imide)-Poly(Dimethyl Siloxane) Randomly Segmented Copolymers

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SYNTHESIS AND CHARACTERIZATION OF TRIPHENYLPHOSPHINE OXIDE-CONTAINING POLY(ARYL IMIDE)-POLY(DIMETHYL SILOXANE) RANDOMLY SEGMENTED COPOLYMERS

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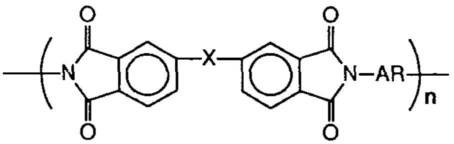
ABSTRACT

Poly(aryl imide)-poly(dimethyl siloxane) randomly segmented copolymers were synthesized by essentially a one-step solution imidization process in a solvent system consisting of predominately *o*-dichlorobenzene with a small amount of *n*-methylpyrolidone. This solvent combination was selected because of its ability to afford homogeneous solutions throughout the polymerization process. This enabled copolymers of any desired poly(dimethyl siloxane) composition to be prepared. A hydrolytically stable triphenylphosphine oxide containing diamine, bis(3-aminophenoxy-4′-phenyl)phenylphosphine oxide, was utilized as a chain extender and together with oxydiphthalic anhydride formed the hard segment in these copolymers. The soft segment was formed from α,ω-aminopropyl poly(dimethyl siloxane) oligomers of controlled molecular weight. The presence of phosphorus and silicon contributes several unique properties to the system, including enhanced solubility, thermal stability, and flame resistance. High molecular weight copolymers containing up to 60% (w/w) of the poly(dimethyl siloxane) segments were successfully prepared using this method. Gel permeation chromatography analysis, based on a universal calibration curve in $CHCl_3$, was performed to determine the molecular weights and distribution. These copolymers with 40–60% (w/w) poly(dimethyl siloxane) exhibited upper T_g values ranging from 130 to 180°C and showed substantial char yields at 750°C in air, which increased with siloxane content. Dynamic mechanical analysis confirmed the anticipated microphase behavior by the presence of two separate glass-transition regions. Both small angle x-ray scattering and transmission electron microscopy measurements determined on well-characterized transparent cast films were used to better demonstrate the multiphase nature of these copolymers.

INTRODUCTION

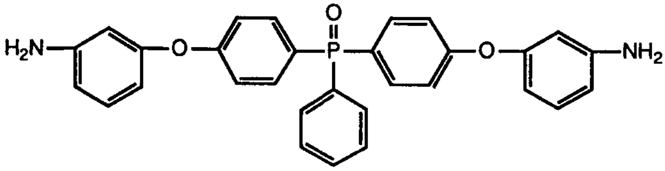
Wholly aromatic polyimides are well known to be high performance materials that exhibit several excellent properties which are utilized in the aerospace and microelectronics industries and elsewhere [1, 2]. A generic polyimide structure is shown below, where X is often a flexible connecting link such as —O—, —$C(CF_3)_2$, etc.



The number of practical applications of aromatic polyimides are limited because of solubility and processibility considerations.

The very nonpolar poly(dimethyl siloxane) is a liquid at room temperature and has a glass-transition temperature of −120°C. Segmented copolymers based on poly(aryl-imide)-poly(dimethyl siloxane) structures have been extensively investigated in recent years [3–9]. These segmented copolymers usually display a microphase separation, and the properties of the copolymers will be partially derived from both components. The poly(dimethyl siloxane) block imparts a number of beneficial properties including improved solubility, reduced water absorption, high gas permeability, good resistance to aggressive oxygen environments, modified surface properties, and improved flame resistance [3]. The poly(aryl imide) component contributes stiffness, strength, and thermal stability to the copolymer. From these property profiles one may suggest that segmented poly(aryl imide)–poly(dimethyl siloxane) copolymers may be of use in a variety of high-performance areas such as aerospace, matrix resins, structural adhesives [10], and electronic and biomaterials applications.

In general, the preparation of these copolymers in our laboratory required the use of a cosolvent to accommodate the different polarities of the polyimide and poly(dimethyl siloxane) components. Mixtures of *n*-methylpyrrolidone/tetrahydrofuran (NMP/THF) in various percentages have previously been reported [11]. Importantly, unless a proper cosolvent mixture is utilized, the very nonpolar poly(dimethyl siloxane) component can macrophase separately during copolymerization from the more polar aromatic polyimide component which limits the amount of poly(dimethyl siloxane) that can effectively be chemically incorporated. However, we recently demonstrated that if the very soluble noncoplanar triphenylphosphine oxide containing diamine, bis(3-aminophenoxy-4′-phenyl)phenyl phosphine oxide, *m*-BAPPO, **1**, was used in conjunction with a moderately polar dianhydride, such as oxydiphthalic anhydride (ODPA), a solvent system consisting of predominantly *o*-dichlorobenzene (*o*-DCB) with a small amount of NMP can be utilized to prepare solution-imidized copolymers. This method allows for the preparation of copolymers of essentially any desired poly(dimethyl siloxane) composition. The *o*-DCB serves as both a solvent and dehydrating or azeotroping agent in this process.



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This flexible aryl aromatic diamine has been previously reported [12–14]. In addition, the use of this phosphine oxide moiety is of great interest since it provides fire resistance to both thermosetting and thermoplastic systems as well as thermooxidative stability. Moreover, it may undergo selective complexation to metals [15]. Furthermore, in contrast to the phosphorus—oxygen—carbon bond found in phosphites and related materials, the phosphorus—carbon bond is much more stable hydrolytically [10].

From the anticipated property profiles discussed above, it was believed that polymeric materials containing both polysiloxane and triphenylphosphine oxide polyimide components would be of interest. This paper describes the synthesis and characterization of flexible poly(dimethyl siloxane)-triphenylphosphine oxide containing poly(aryl imide) randomly segmented copolymers that were conducted in (predominantly) *o*-DCB which yielded a homogeneous solution at 175°C. The microphase separation behavior of the system was investigated by the use of dynamic mechanical analysis (DMA), small angle x-ray scattering (SAXS), and transmission electron microscopy (TEM).

EXPERIMENTAL

Solvents and General Reagents

Aminopropyl-terminated poly(dimethyl siloxane) oligomers with number-average molecular weights of either 800 or 2600 g/mol were prepared via the ring-opening equilibration polymerization of the cyclic tetramer, D_4, and bisaminopropyltetramethyldisiloxane as described earlier from our laboratory [16]. *m*-BAPPO was also prepared in our laboratory as reported earlier [17]. Oxydiphthalic anhydride was obtained from Chriskev Corporation and dried in a vacuum oven at 180°C for 24 hours prior to use. The solvents *o*-DCB and NMP were dried over phosphorus pentoxide for 24 hours, vacuum distilled, and stored in sealed flasks under nitrogen.

Polymerizations

The synthesis of a 50 wt% poly(dimethyl siloxane)/ODPA/*m*-BAPPO copolymer with a polysiloxane oligomer number-average molecular weight of 2600 is described below.

A 4-neck 250 mL round-bottom flask was equipped with a mechanical stirrer, nitrogen inlet, reverse Dean-Stark trap with a condenser and a thermometer. *o*-DCB (20 mL) and NMP (3 mL) were then charged to the flask. The reactor was heated to 175°C with a silicone oil heat-transfer bath. Next, 2.500 g (0.956 mmol) of the aminopropyl-terminated poly(dimethyl siloxane) oligomer ($\langle M_n \rangle = 2600$) was charged to the reactor followed by 1.148 g (3.701 mmol) ODPA. The reaction was stirred and allowed to react under nitrogen for 30 minutes and then 1.352 g (2.745 mmol) of the chain extender *m*-BAPPO was added. All of the reagents were washed into the reactor with a small amount of *o*-DCB. The total amount of solvent used was thus 30 mL *o*-DCB and 3 mL NMP. The concentration of the reaction was calculated to be around 15% solids. The reaction was conducted at 175°C for 24 hours to afford a homogeneous, somewhat viscous solution. The reactor was then cooled, and the very viscous solution was precipitated into rapidly stirred methanol. The fibrous copolymer was dried in a vacuum oven at 140°C for 48 hours. TGA analysis indicated the removal of all solvent was achieved.

Copolymer Film Preparation

Tough transparent films of the segmented copolymers could be prepared by casting from viscous 10% (w/v) chloroform solutions onto clean glass plates. These films were first dried at room temperature for 12 hours and subsequently at 140°C in a vacuum oven for 24 hours. TGA results show that all of the solvent was removed using this drying procedure.

Polymer Characterization

Intrinsic viscosity measurements were conducted in chloroform using a Cannon-Ubbelohde viscometer at 25°C. The molecular weights of the prepared copolymers were determined via gel permeation chromatography (GPC). The instrument was a Waters GPC/ALC150-C chromatograph equipped with a differential refractometer detector (RI) and an on-line differential viscometric detector (DV) Viscotek model 100 coupled in parallel. The samples were run in chloroform at 30°C at a concentration of 2.90 mg/mL with a flow rate of 1 mL/min using a universal calibration curve based on narrow polystyrene standards. The values for these segmented copolymers, though informative, should be considered approximate in view of the difficulties in characterizing block copolymers of these types. The different polymer–solvent interactions of the poly(dimethyl siloxane) and poly(aryl imide) segments with the chloroform may affect the hydrodynamic volume calculated, which could possibly lead to erroneous GPC interpretations.

Thermooxidative stability was assessed using a Dupont Model 2100 TGA with a heating rate of 10°C per minute from room temperature to 750°C in an air atmosphere.

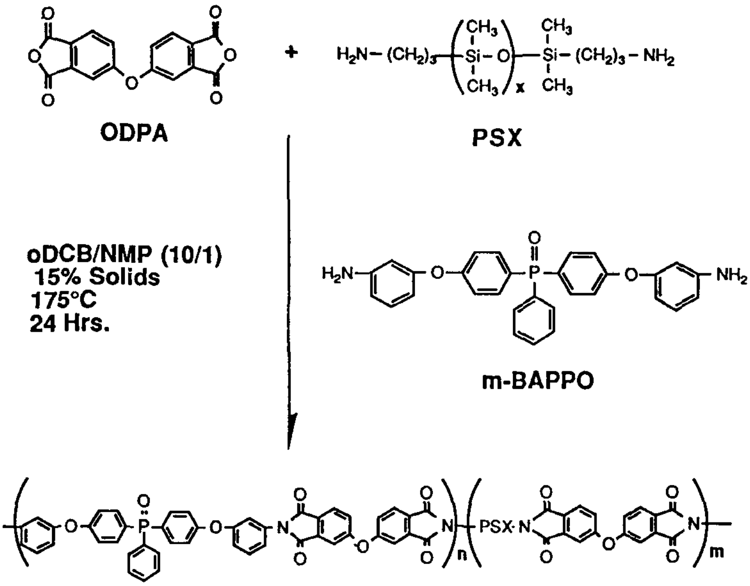
Microphase Analysis

A Perkin-Elmer DMA-7 Dynamic Mechanical Analyzer operated at a frequency of 1 Hz was utilized to determine the upper- and lower-phase transitions of the copolymers. SAXS was conducted using a Siemens-Kratky camera system in conjugation with an M. Braun position sensitive detector. CuK_α radiation having a wavelength of 1.56 Å was used. The slit smeared data was obtained with a slit having a width of 100 μm. TEM was performed on a Phillips 420T Electron Microscope.

RESULTS AND DISCUSSION

Preparation of Poly(Aryl Imide)-Poly(Dimethyl Siloxane) Randomly Segmented Copolymers

The synthesis of the poly(aryl imide)-poly(dimethyl siloxane) randomly segmented copolymers is described in Scheme 1. The more reactive nature of the aliphatic diamine in the poly(dimethyl siloxane) oligomer suggests that the order of addition of the reagents could be very important. Thus, the aminopropyl-terminated poly(dimethyl siloxane) oligomers were first reacted (at 175 °C) with the entire stoichiometric amount of the dianhydride ODPA. This procedure had the goal of producing an anhydride-terminated endcapped poly(dimethyl siloxane) oligomer along with the free excess dianhydride remaining in solution. The less reactive aromatic diamine, *m*-BAPPO, was then added as a "chain extender" to form the hard glassy segment and thus complete the polymerization process.



SCHEME 1. Synthesis of poly(aryl imide)-poly(dimethyl siloxane) randomly segmented copolymers.

A reaction temperature of 175°C was sufficient to remove the water evolved in the amide-acid to imide ring-closing step in the presence of *o*-DCB. This removal of water is, of course, crucial to obtaining fully cyclized high molecular weight material [18]. This procedure appears to result in the formation of more uniformly segmented copolymers and thus may alleviate the possibility of undesired macrophase separation during the reaction.

Molecular Weights

The relatively high values for the intrinsic viscosity for these polymers generally indicate that in all cases high molecular weight copolymers have been prepared (Table 1). GPC results derived by means of a universal calibration curve in chloroform also indicate the existence of high molecular weight polymers.

Discrepancies from a polydispersity approaching that of a most probable distribution, $M_w/M_n = 2.0$, are likely related to the segmented structure of the polymers, although the method of preparation or the size of the poly(dimethyl siloxane) oligomer may also be important.

The representative GPC chromatograms shown in Fig. 1 are unimodal and appear to be free of residual cyclics.

Thermal Analysis

Table 2 shows some characteristics of a systematic series of copolymers where the poly(dimethyl siloxane) number-average molecular weights include both 800 ($X_n = 10$) and 2600 ($X_n = 35$) g/mol. Thermogravimetric analysis studies showed that the polyimide is more thermally stable than the poly(dimethyl siloxane), as expected. However, the char yields taken at 600 and 750°C increase with poly(dimethyl siloxane) content. From these high char yields, along with our prior experiences with the triphenylphosphine oxide materials, it is suggested that these prepared films of controllable stiffness should be relatively flame resistant [19].

TABLE 1. Intrinsic Viscosity and Molecular Weight Determinations via GPC on Poly(Aryl Imide)-Poly(Dimethyl Siloxane) Segmented Copolymers[a]

Sample	M_n	M_w	M_w/M_n	[η], dL/g	[η], dL/g[b]
ODPA/*m*-BAPPO/40% PSX(2614)	107,000	446,000	4.16	0.90	1.64
ODPA/*m*-BAPPO/50% PSX(2614)	100,000	290,000	2.88	0.95	0.96
ODPA/*m*-BAPPO/60% PSX(2614)	110,000	316,000	2.88	0.91	0.86
ODPA/*m*-BAPPO/50% PSX(2614) (30 K)	31,000	69,000	2.20	0.40	

[a] Based on universal calibration with narrow polystyrene standards in $CHCl_3$ at 30°C.
[b] Via Cannon-Ubbelohde viscometer at 25°C in $CHCl_3$.

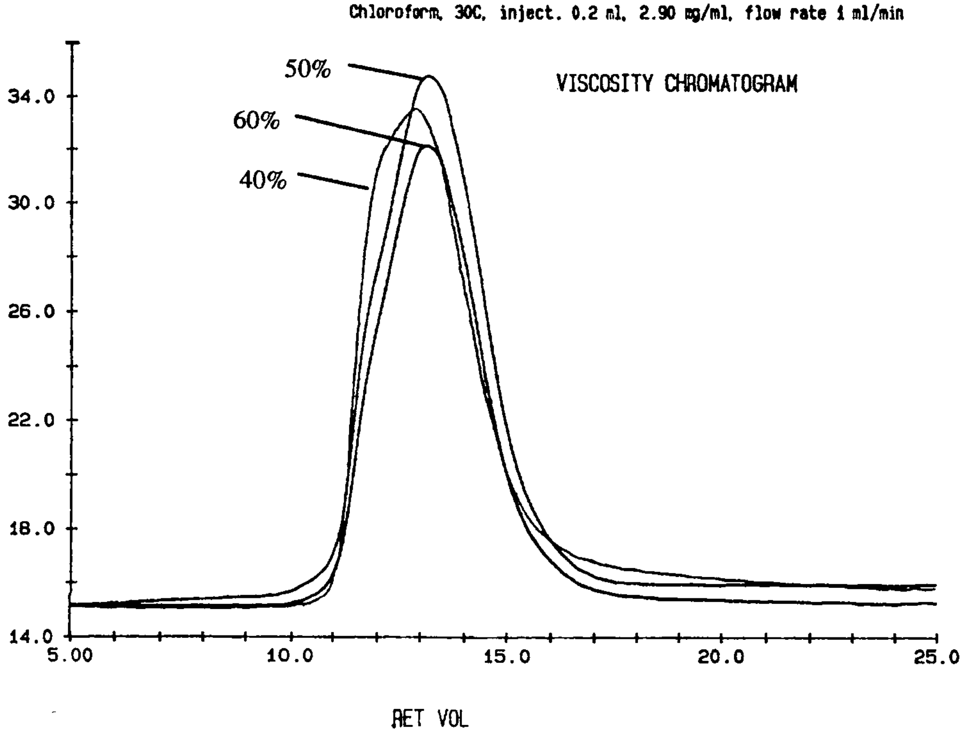


FIG. 1. GPC chromatograms of poly(aryl imide)-poly(dimethyl siloxane) randomly segmented copolymers of 40-60% (w/w) PSX(2600).

Dynamic Mechanical Behavior

Clear, tough films could be easily cast from chloroform solutions. This generally supports the suggestion that complete incorporation of the polysiloxane oligomers has been achieved, although some fractionation could have occurred during copolymer isolation. The refractive index of poly(dimethyl siloxane) is much lower

TABLE 2. Thermal Analysis Characteristics of Poly(Aryl Imide)-Poly(Dimethyl Siloxane) Segmented Copolymers

Sample	T_g, °C, by DMA	TGA, °C, 5% WL air	CHAR, % at 750°C
ODPA/*m*-BAPPO, control	216[a]	531	12
ODPA/*m*-BAPPO/50% PSX(800)	130	457	20
ODPA/*m*-BAPPO/40% PSX(2614)	180	434	25
ODPA/*m*-BAPPO/50% PSX(2614)	150	431	29
ODPA/*m*-BAPPO/60% PSX(2614)	140	413	42

[a] Determined on Dupont 910 DSC.

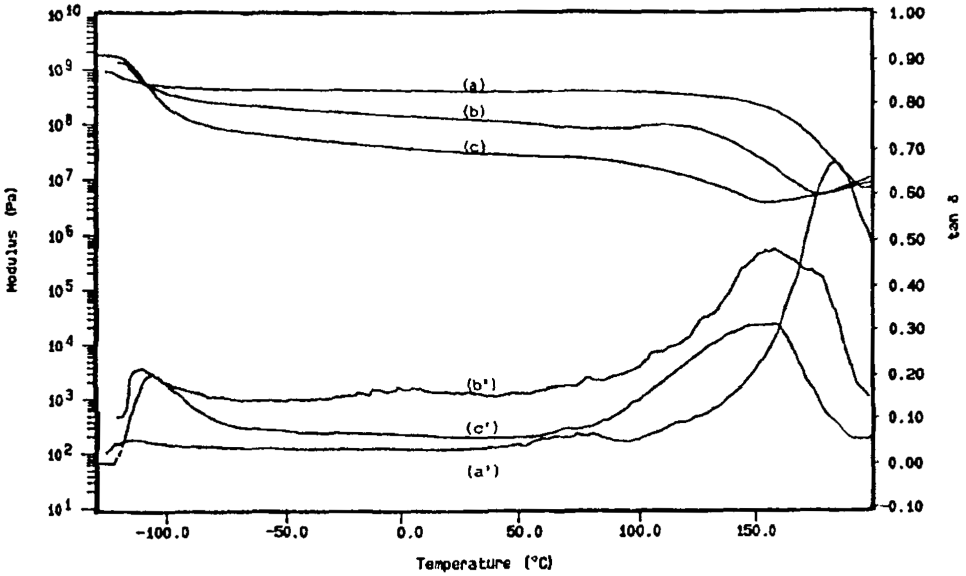


FIG. 2. Dynamic mechanical behavior of poly(aryl imide)-poly(dimethyl siloxane) segmented copolymers as a function of PSX % (w/w) content (all samples have 2600 g/mol segments). Modulus: (a) 40%, (b) 50%, (c) 60%. Tan δ: (a') 40%, (b') 50%, (c') 60%.

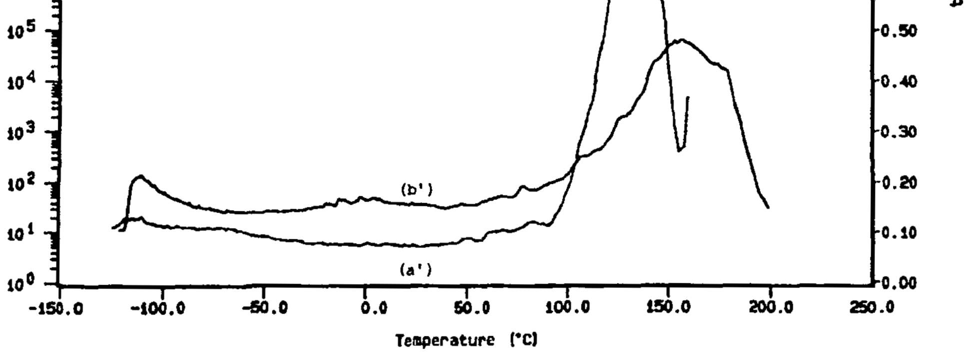


FIG. 3. Dynamic mechanical behavior of poly(aryl imide)-poly(dimethyl siloxane) segmented copolymers as a function of polysiloxane $\langle M_n \rangle$ [both samples contain 50% (w/w) PSX]. Modulus: (a) 2600 g/mol, (b) 800 g/mol. Tan δ: (a') 2600 g/mol, (b') 800 g/mol.

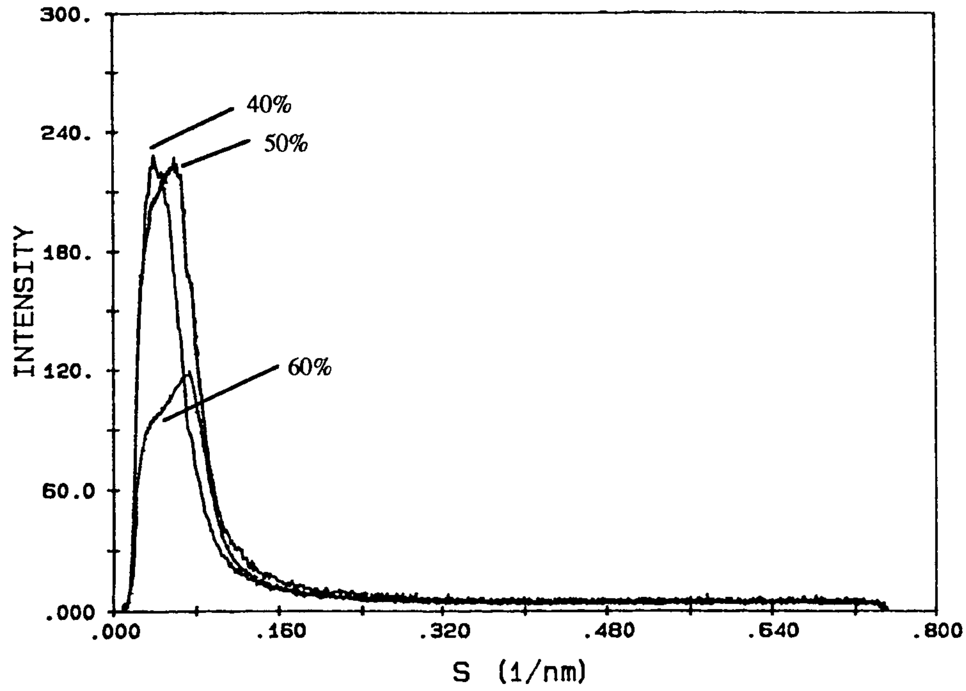
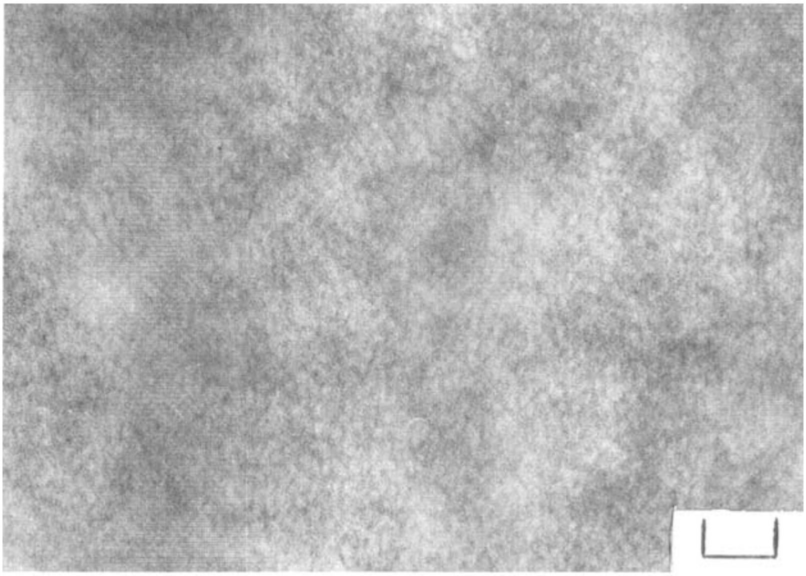


FIG. 4. SAXS profiles of poly(aryl imide)-poly(dimethyl siloxane) randomly segmented copolymers of 40–60% (w/w) PSX(2600).

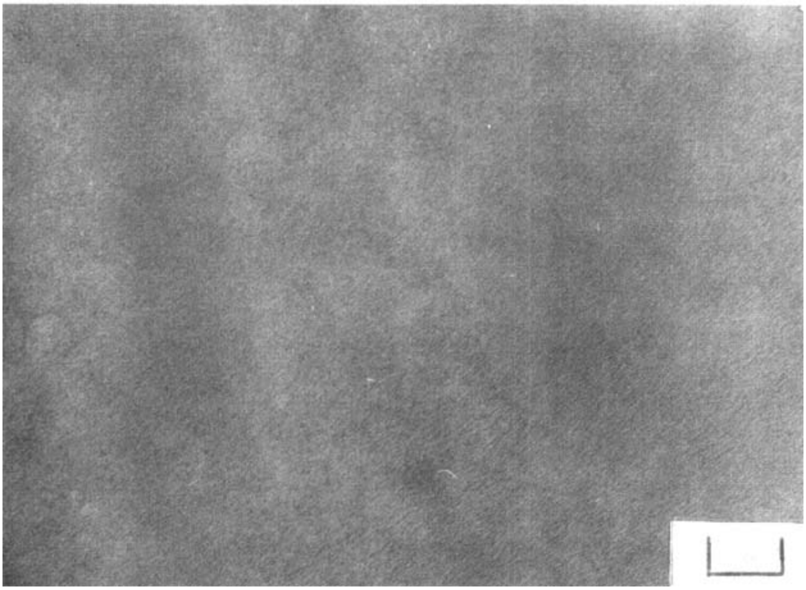
TABLE 3. Average Interdomain Distances, Average Polysiloxane, and Polyimide Domain Sizes as Determined by SAXS

Composition	PSX, $\langle M_n \rangle$	d, nm[a]	PSX, $\langle r_0^2 \rangle^{1/2}$, nm	Imide domain, nm
ODPA/*m*-BAPPO/50% PSX(800)	800	10.0	1.74	8.3
ODPA/*m*-BAPPO/40% PSX(2614)	2614	23.0	3.36	19.6
ODPA/*m*-BAPPO/50% PSX(2614)	2614	16.6	3.36	13.2
ODPA/*m*-BAPPO/60% PSX(2614)	2614	14.3	3.36	10.9

[a] As estimated from smeared data.

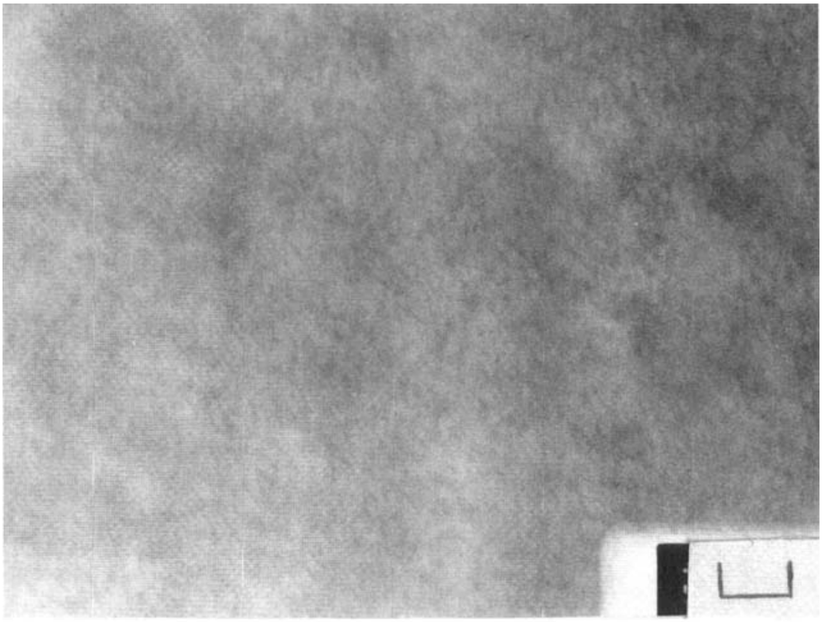


(A) 50% (w/w) PSX(2600 g/mol)

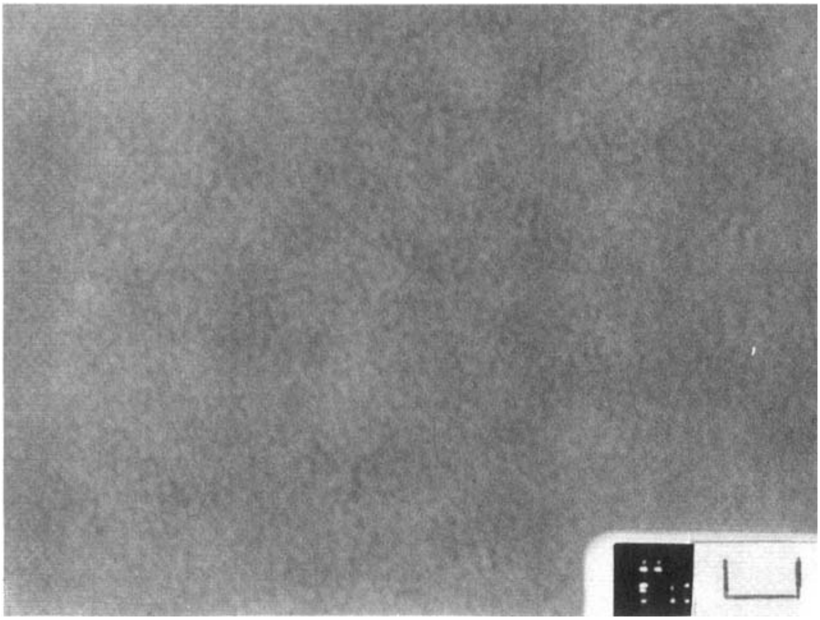


(B) 50% (w/w) PSX(800 g/mol)

FIG. 5. Micrographs of poly(aryl imide)-poly(dimethyl siloxane) copolymers (bar = 5.4 Å).



(C) 40% (w/w) PSX(2600 g/mol)



(D) 60% (w/w) PSX(2600 g/mol)

FIG. 5 (continued).

than that of poly(aryl imides). Thus, if even a few percent of homopoly(dimethyl siloxane) or homopolyimide were present, the cast films would be expected to be hazy as a result of the larger-scale macrophase separation. This was not observed with the copolymers described herein and, together with the solution and compositional characterization, suggests that contamination is minimal. The amount of polysiloxane incorporated was determined by solid-state ^{13}C NMR and was found to be consistent with that of the feed. Solution ^1H NMR can sometimes give erroneously low results if micelle formation occurs and if inappropriate relaxation times are utilized. Thus it should not automatically be considered as an appropriate tool for determining the poly(dimethyl siloxane) content. The use of undried deuterated solvents has also recently been observed to lead to low siloxane values [8].

DSC measurements, taken from a Dupont 910 DSC, were unfortunately unable to clearly discern any thermal transitions in these copolymers, perhaps a result of the large content of polysiloxane in the copolymers. Therefore, DMA studies were performed on clear cast films, and these demonstrated the existence of both an upper and a lower glass-transition temperature. This is consistent with the expected two-phase behavior of these copolymers with the lower and upper glass-transition temperature values derived from the poly(dimethyl siloxane) and poly(aryl imide) microphases, respectively. Figures 2 and 3 show the dynamical behavior of these copolymers. The values for the glass transitions were taken at the maximum value of the tan δ relaxation.

The control polyimide should, in principle, yield a glass-transition temperature similar to the polyimide microphase in a highly microphase-separated poly(aryl imide)–poly(dimethyl siloxane) segmented copolymer. From Table 2, the upper glass-transition temperature of the copolymers prepared from 2600 $\langle M_n \rangle$ poly(dimethyl siloxane) decreases from 180 to 140°C as the weight fraction of poly(dimethyl siloxane) is increased from 40 to 60 wt%. The fact that both of these T_g values are below the homopolymer T_g of 216°C generally indicates that all samples may have a certain degree of phase mixing, although an alternate interpretation could be that the sequence length of the polyimide is reduced and that this depresses T_g. The first possibility would suggest that as more polysiloxane is incorporated, the size of the polyimide domain will decrease, yielding more surface area and thus a build-up of free energy, which may promote more phase mixing.

Table 2 also indicates that as the poly(dimethyl siloxane) oligomer number-average molecular weight is decreased from 2600 to 800 g/mol, the value of the upper T_g decreases from 150 to 130°C at 50% (w/w) poly(dimethyl siloxane). In view of our earlier experience, this suggested that a longer siloxane molecular weight might be desirable in order to decrease the amount of phase miscibility, although its was recognized that melt processibility might become more difficult.

Small-Angle X-Ray Scattering and Transmission Electron Microscopy

To better understand the two-phase behavior of these copolymers, SAXS and TEM studies were performed. Representative scattering profiles are shown in Fig. 4, and the calculated interdomain distances are provided in Table 3. The estimated interdomain distances were determined from the maximum in the scattering profile using Bragg's law [20]. All of the samples demonstrated a distinct maximum in intensity, with the possible exception being the 40% (w/w) PSX(2600) sample. The maximum in this case was very difficult to positively identify because it appeared to occur at the onset of scattering.

Flory and coworkers have demonstrated that the mean squared unperturbed end-to-end distance for poly(dimethyl diloxane) chains can be expressed as [21]

$$\langle r_0^2 \rangle = 6.3nl^2$$

where $l = 0.164$ nm for an Si—O bond and $n = 35$ and 10 for the 2600 and 800 number-average molecular weight polysiloxane oligomers, respectively. Assuming that Gaussian chain statistics can be utilized and that the size of the average poly(dimethyl siloxane) domain is only dependent on the molecular weight of the polysiloxane oligomer and independent of the amount incorporated, the average size of the poly(aryl imide) domain should be equal to the determined interdomain distance less the mean-average end-to-end distance for the poly(dimethyl siloxane) oligomers. These values must be viewed as approximate and are meant to demonstrate trends in the system, for they are intended to represent a system with a lamellar morphology. Randomly segmented copolymers are not generally considered to be of the lamellar type.

Assuming a constant morphology, the data on Table 3 indicate that as the amount of poly(dimethyl siloxane) incorporated is increased, or the amount of poly(aryl imide) is decreased, the interdomain distance decreases as a result of smaller poly(aryl imide) domains. In contrast, if the $\langle M_n \rangle$ of the poly(dimethyl siloxane) is increased, the interdomain distance increases due to a larger poly(dimethyl siloxane) domain. For the most part, the values of the interdomain distances correspond well with the proposed multiphase morphology of the system described above.

Figure 5 illustrated TEM micrographs of the prepared copolymers. These micrographs were taken at 25°C. Staining of the samples was not necessary because of the vast differences in the electron density associated with the poly(dimethyl siloxane) and poly(aryl imide) segments. It is generally considered safe to assume that the darker regions on the micrographs are representative of the poly(dimethyl siloxane) phases. Changes in the morphology are likely to occur at different temperatures. Thus, when viewing these micrographs, it is essential to realize that these pictures cannot be totally related to the DMA plots shown previously. From these micrographs, one can easily observe the more homogeneous nature of the copolymer with the lower molecular weight poly(dimethyl siloxane), $\langle M_n \rangle$ 800 g/mol. The samples which contain the poly(dimethyl siloxane) segment with an $\langle M_n \rangle$ of 2600 g/mol clearly show microphase separation and support our earlier analysis of this system.

CONCLUSIONS

The synthesis of triphenylphosphine oxide containing poly(aryl imide)–poly(dimethyl siloxane) randomly segmented copolymers was successfully achieved in essentially a one-step solution imidization process. The use of the phosphine oxide containing diamine, *m*-BAPPO, as a chain extender enabled fully cyclized copolyimides to be prepared. These copolymers afforded flexible, transparent, and tough solvent-cast films. The two-phase behavior of these systems was demonstrated by the presence of two glass-transition temperatures as observed by DMA analysis, as well as by the existence of a maximum in the SAXS profiles and by the observed microphase-separated domains from TEM. The resulting thermal gravimetric analysis degradation behavior, along with prior experience with the phosphine oxide material, suggest that these systems would be interesting flame-resistant high-performance materials which could be designed to be either rubberlike, flexible coatings or rigid thermoplastics.

ACKNOWLEDGMENTS

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