

Synthesis and properties of xylenyl ether-dimethylsiloxane triblock polymers

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SUMMARY

Poly(xylenyl ether-dimethylsiloxane) (PXE-PDMS) triblock polymers were successfully prepared by a hydroxyl-silylamine condensation route as potential modifiers for poly(styrene) (PS) and related materials. This synthesis route affords A-B-A triblock polymers where A represents PXE and B poly(dimethylsiloxane). These new copolymers are more versatile than poly(styrene-dimethylsiloxane) block polymers (as poly(styrene) modifiers) since the PXE is miscible with PS at all molecular weights and compositions. These triblock polymers formed unimodal molecular weight distributions, transparent and tough films, and microphase-separated morphologies as determined by a number of techniques.

INTRODUCTION

Multiphase organosiloxane copolymers have many desirable properties, including low temperature flexibility, high thermal oxidative stability, low surface energy, and high gas permeability. Consequently, both surface and bulk mechanical properties of existing polymers may be controllably modified in a desirable way by the synthesis of appropriate dimethylsiloxane-containing block and graft copolymers (1-3). The propensity of dimethylsiloxane segments toward phase separation (4,5) allows both rubber toughening and surface segregation to take place in virtually all systems studied. We have utilized these concepts in the study of the surface and bulk modification of poly(styrene) and related structures.

Poly(styrene-dimethylsiloxane) block copolymers are readily synthesized by anionic organolithium polymerization (6,7), however the utility of these materials as poly(styrene) modifiers is limited by molecular weight mismatch effects, i.e., compatible systems result only when the poly(styrene) homopolymer molecular weight is below that of the poly(styrene) block (8,9). Our interest in xylenyl ether polymers is based on the ability of these materials to form infinitely miscible mixtures with poly(styrene) at all compositions and molecular weights (10,11). Block polymers of dimethylsiloxane with xylenyl ether would thus be highly desirable as modifiers of the surface and bulk properties of poly(styrene).

Several recent reports have appeared concerning the utilization of the monofunctional phenolic hydroxyl at the poly(xylenyl ether) (PXE) chain-end for subsequent end group chemistry (12,13). Our research has focused on the utilization of this reactive hydroxyl for block polymer synthesis (14,15). Noshay and coworkers (16) developed the phenolic hydroxyl-silylamine condensation reaction as a route to poly(dimethylsiloxane) copolymers from hydroxyl-functional oligomers. This functional end group chemistry has been applied to a variety of copolymer systems (17,18). Poly(2,6-diphenyl-1,4-phenylene oxide-dimethylsiloxane)

block copolymers have been synthesized by the condensation of the phenol end group of this crystallizable phenylene oxide with alkylamino-terminal (-NHR) poly(dimethylsiloxane) (19). We have successfully prepared PXE-PDMS triblock polymers by the phenolic hydroxyl-silylamine condensation route, as shown in Scheme I. The synthesis and properties of these versatile materials will be discussed in this paper.

EXPERIMENTAL

Materials

The octamethylcyclotetrasiloxane (D_4) and a silylamine-terminal dimethylsiloxane end-blocker were products of Petrarch and were used without further purification. Tetramethylammonium hydroxide was a product of Aldrich Chemical Company. The poly(xylenyl ether) oligomers (PXE) were kindly supplied by the General Electric Company.

Synthesis

The siloxanolate (pseudo-catalytic) initiator used in the poly(dimethylsiloxane) equilibration reactions was prepared by the reaction of one equivalent of tetramethylammonium hydroxide pentahydrate with 4.5 equivalents of D_4 . The reaction was carried out in refluxing benzene for 24 hours. Water was removed with the aid of a Dean-Stark trap.

Silylamine-terminal dimethylsiloxane oligomers of controlled molecular weight were prepared in anhydrous conditions under argon via the bulk anionic equilibration of the silylamine terminal dimethylsiloxane oligomer ($M_n = 500\text{g/mol}$) with D_4 at 80°C for 24 hours. The polymerization was initiated with the siloxanolate pseudo-catalyst.

Block copolymers were synthesized in a three neck, 250 cc flask equipped with an overhead stirrer, reverse Dean-Stark trap fitted with a condenser, and an inlet/outlet to allow for argon flow-through. This apparatus was assembled hot and purged with argon. The PXE oligomer was dried in a vacuum oven overnight at 80°C , then dissolved in dry chlorobenzene (distilled from calcium hydride) and heated to reflux. Several aliquots of chlorobenzene were removed (via the Dean-Stark trap) to ensure dehydration of the system. At this time an addition funnel containing the PDMS oligomer dissolved in dry chlorobenzene was attached to the reaction flask. The PDMS solution was slowly added to the refluxing PXE solution. Dimethylamine evolution began immediately, indicating the condensation was proceeding. As the addition of PDMS oligomer continued, the reaction solution became progressively more viscous, particularly as the stoichiometric point was approached. At this point, the time between incremental additions was increased. A slight excess of PDMS oligomer was added to insure full conversion of PXE to copolymer. The product was precipitated in a 15-fold excess of isopropanol, filtered, and washed for 24 hours in a large excess of hot isopropanol. The product was dried for 24 hours in a vacuum oven at $60\text{--}80^\circ\text{C}$.

Characterization

Number average molecular weights of the silylamine-terminal dimethylsiloxane oligomers were determined by potentiometric titration with 0.1N HCl (20). Molecular weights of the PXE oligomers were determined by light scattering measurements in chloroform. Block copolymers were characterized by size exclusion chromatography with a Waters GPC-1 in chloroform at 30°C using an ASI

four-column set with a wide porosity range, calibrated with poly(styrene) standards. Intrinsic viscosity measurements of PXE oligomers and subsequent copolymers were determined using a Cannon-Ubbelohde dilution viscometer, in chloroform at 25°C.

Films of the block copolymers were prepared by casting chlorobenzene solutions on glass plates, slowly heating (5°C/min.) under nitrogen to 220°C, annealing at that temperature for 30 minutes, followed by slow cooling. Dynamic mechanical properties of the copolymers were determined with a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA) at 10Hz with a 10°C/min. heating rate. Mechanical properties were determined with an Instron tensile tester at ambient temperature with a strain rate of 5mm/min. Glass transition temperatures were measured with a DuPont DSC 910 at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Synthesis

Dimethylaminosilyl-terminal dimethylsiloxane oligomers of various molecular weights were successfully synthesized by a bulk anionic equilibration reaction using a basic catalyst. A silylamine-terminal dimethylsiloxane oligomer ($M_n = 500\text{g/mole}$) was employed as an end-blocker (chain-transfer agent) and equilibrated with the cyclic tetramer of dimethylsiloxane (D_4). Ring opening polymerization was initiated with a tetramethylammonium siloxanolate pseudo-catalyst. The ratio of D_4 to end-blocker determined the final equilibrium molecular weight. In the early stages of these bulk polymerizations, a large increase in viscosity was observed. Apparently, the cyclic tetramer of dimethylsiloxane is more labile toward anionic attack than the end-blocker, and this selectivity affords high molecular weight early in the reaction. Subsequent cleavage by small siloxanates acts to lower the molecular weight soon after this early stage of the polymerization. Similar viscosity-time relationships have been observed in other siloxane equilibrations (21). Upon completion of the equilibration (24 hours is generally sufficient), the reaction was heated to 150°C (3-5 hours) to decompose the siloxanolate to volatile products. We chose not to remove the equilibrium cyclics (about 15 wt.%) after the equilibration to keep handling of this moisture sensitive material to a minimum. The cyclics were ultimately removed after the block polymer synthesis in an extraction step. Table 1 contains the number average molecular weights of the silylamino-terminal oligomers as determined by potentiometric titration of the end groups.

TABLE 1

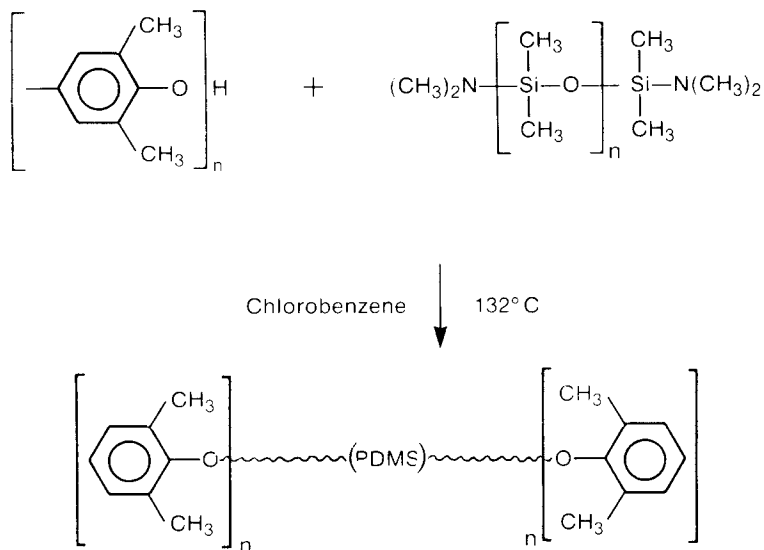
Characteristics of dimethylamino-terminal polydimethylsiloxane oligomers

<u>Sample</u>	<u>Theory</u>	<u>< Mn >, g/mol</u>	<u>Experimental</u>
1	4,000		4,000
2	10,000		9,000

Sample #	$[\eta]_{25^\circ\text{C}}^{\text{chl.}}$ dl/gm	P.I. ^A	$\langle M_w \rangle^{\text{B}}$ (g/mol)	$\langle M_N \rangle^{\text{C}}$ (g/mol)	T_g °C
1	0.30	2.3	32,000	14,000	210
2	0.48	2.3	46,000	20,000	215

^APolydispersity Index
^BDetermined by light scattering in chloroform
^CDetermined by NMR

The PXE-PDMS triblock polymers were synthesized in refluxing chlorobenzene via the silylamine-phenolic hydroxyl condensation, as shown in Scheme I. The synthesis involved the addition of small increments of the functional PDMS oligomer dissolved in chlorobenzene to an anhydrous solution of PXE in refluxing chlorobenzene. Table 2 lists the intrinsic viscosities, number and weight average molecular weights, and the glass temperatures of the monofunctional PXE oligomers employed in this work. Dropwise addition of a solution of the siloxane oligomer to the PXE/chlorobenzene solution facilitated clean conversion to triblock. As the stoichiometric endpoint was approached, the time between additions was increased in an effort to achieve full triblock formation, minimizing homopolymer and diblock contamination. The utility of this approach depends on the fast reaction of the phenol with the dimethylsilylamine. In fact, in refluxing chlorobenzene, the reaction



Scheme I

occurs immediately, as witnessed by the prompt evolution of dimethylamine. Further siloxane oligomer was charged (past the stoichiometric amount) to insure full triblock conversion while minimizing diblock and poly(xylenyl ether) contamination. The excess PDMS is easily extracted (isopropanol or hexane) after the reaction, while PXE homopolymer would be much more difficult to remove. Provided mutual solubility of the oligomers exists in chlorobenzene, clean block polymer formation readily occurs, by virtue of the high reactivity of the dimethylsilylamine end group with phenolic hydroxyl. Ortho substitution on the phenolic does not appear to retard this condensation (at 132°C). The structure of the formed triblock polymer is quite well defined, as only unlike oligomers react, the PXE oligomer is monofunctional, and the PDMS oligomer is perfectly difunctional. Molecular weight analysis by GPC shows that this approach is successful in forming high purity PXE-PDMS-PXE triblock polymers. Figure 1 shows the GPC traces of a PXE oligomer before and after reaction with a functional PDMS oligomer. Lack of broadening of the polydispersities indicates minimal homopolymer and diblock polymer contamination. Table 3 contains the characterization data of the triblock polymers. In agreement with the GPC data, intrinsic viscosities show a marked increase in molecular weight for the copolymers. Block polymers of PDMS ($M_n = 4000$ g/mole) with a variety of PXE molecular weights have been prepared. Solvent cast films of these materials afford clear, tough films. Proton NMR analysis of siloxane content agrees fairly closely with charge ratios (Table 4).

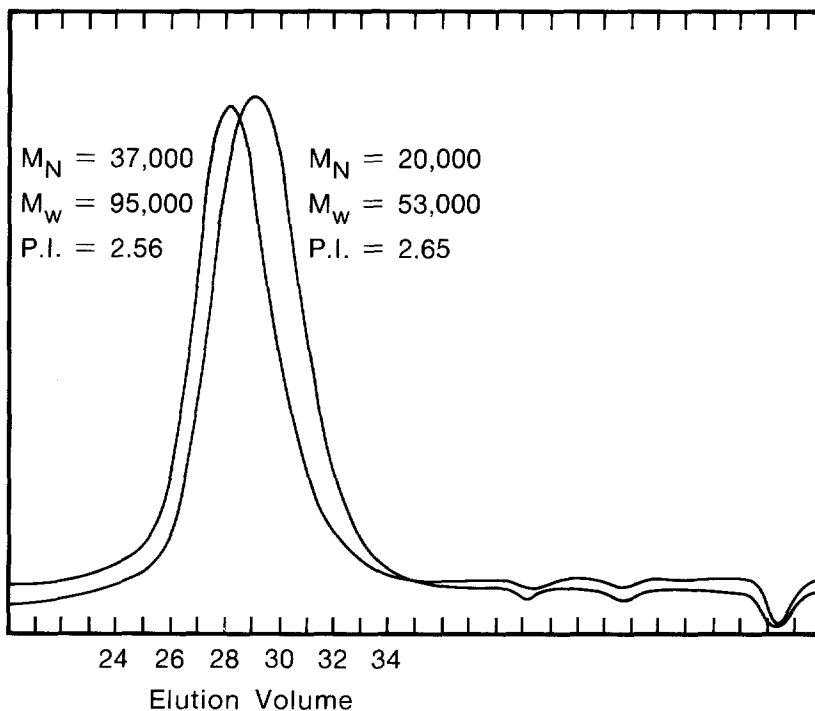


Figure 1. Size exclusion chromatograms of PXE Homopolymer (20K) and PXE-PDMS-PXE (20K-4K-20K).

It is of interest to prepare PXE-PDMS triblock polymers of much higher siloxane content. A limitation of the above synthesis in its current form is the inability to prepare clean triblock materials with high PDMS content (molecular weight). Attempts to prepare triblocks with a siloxane center block of $M_n = 9,000$ g/mole were unsuccessful (see Table 3). After addition of a portion of the siloxane oligomer, the reaction became cloudy. Phase separation in solution was not surprising in light of the solubility parameter difference and appreciable molecular weights of these "oligomers". Once phase separation occurred, the solution never reacted to a high enough extent to become homogeneous, presumably due to the inaccessibility of the end groups. We attempted to overcome this synthetic limitation by a number of strategies, including greater dilution, slower addition, and even addition of small amounts of previously prepared triblock of lower siloxane molecular weight to compatibilize the oligomers. All of these attempts produced materials which formed cloudy solutions and hazy, brittle films, suggesting low conversion to triblock.

Properties

Solvent-cast films of the triblock polymers containing the 4000 g/mole PDMS were transparent and tough. Dynamic mechanical spectra of the copolymers and the PXE homopolymer control are shown in Figure 2. These data, consistent with DSC results, clearly illustrate the two phase morphology of the copolymers. The tensile modulus, E' , drops slightly in the -120°C range, a slightly lower temperature than the β transition of pure PXE (-90°C). This modulus drop is associated with the glass temperature of the PDMS phase. The low temperature $\tan\delta$ peak of the lower PXE molecular weight material (copolymer 1) is at a slightly higher temperature than the peak of copolymer 2, the higher PXE molecular weight copolymer. This indicates a degree of phase mixing as the PXE molecular weight decreases. Other evidence for phase mixing can be observed in the depression of the PXE α transition in copolymer 1. However, the modulus between the PDMS and PXE transitions remains constant over a wide temperature range, indicating a sharp boundary between phases.

TABLE 3

Characteristics of xylenyl ether-dimethylsiloxane triblock polymers

Copolymer #	Oligomer $\langle M_n \rangle$, g/mol		$[\eta]_{25}^{chl.}$ dl/g
	PDMS	PXE	
1	4,000	14,000	0.50 (0.30) ^A
2	4,000	20,000	0.70 (0.48) ^A
3	9,000	14,000	^B
4	9,000	20,000	^B

^AIntrinsic viscosity of PXE oligomer

^BCloudy solutions

TABLE 4

Mechanical properties of xylenyl ether-dimethylsiloxane triblock copolymers

Sample	Wt. % PDMS ^A	E MPa	σ_y MPa	σ_T MPa	Elong. %
PXE(14)/PDMS(4)/ PXE(14)(Copolymer 1)	13.5	900	-	47	6.0
PXE(20)/PDMS(4)/ PXE(20)(Copolymer 2)	8.5	1000	55	52	40.0
PXE(20) (Control)	0	1250	-	65	6.0

^ADetermined by NMR

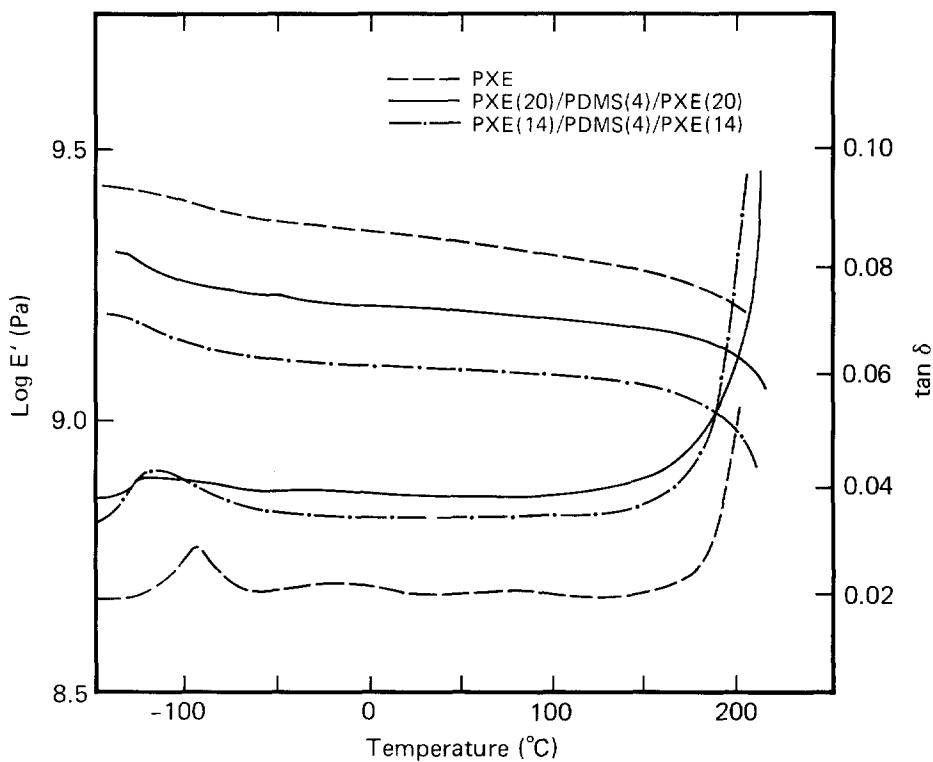


Figure 2. Dynamic mechanical behavior of PXE homopolymer and PXE-PDMS triblock polymers.

Table 4 lists the mechanical properties of the copolymers and the PXE homopolymer control, as determined by tensile testing. The incorporation of the soft or elastomeric phase has a somewhat detrimental effect on the modulus, in agreement with the dynamic mechanical data. High elongations were observed in copolymer 2, which contains the higher PXE block lengths. In contrast, copolymer 1, which contains the lower PXE block length shows poor elongation, presumably due to the low molecular weight of the triblock polymer. The PXE homopolymer on which this triblock is based is a non-film forming material and is quite brittle.

These materials form compatible blends with poly(styrene), dramatically altering both surface and bulk properties even at very low triblock compositions (15). These blends were found to consist of a miscible PXE/PS continuous phase, plus a microphase-separated PDMS phase possessing high surface activity. The ramifications of the surface activity and compatibilization properties of these triblock polymers on their behavior in oxygen plasma environments will be discussed in forthcoming publications.

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