Synthesis of Xylenyl Ether–Arylene Ether Sulfone Triblock Copolymers as Potential Modifiers for Polystyrene and Related Structures

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ABSTRACT: We have successfully synthesized xylenyl ether–arylene ether sulfone triblock polymers. The use of a preformed silyl ether terminated xylenyl ether oligomer to react with a preformed aryl fluoride terminated sulfone oligomer in the presence of cesium fluoride is a successful route to prepare well-defined triblock poly(arylene ethers). An *N*-methylpyrrolidone/toluene solvent mixture at reflux temperatures was used as the reaction medium, which serves to dissolve the oligomers and at least partially dissolve the catalyst. Model polymerizations were performed to demonstrate both the feasibility of the synthetic route and the use of the solvent system. The high molecular weight triblock copolymers were characterized by GPC and intrinsic viscosity measurements. The use of this synthetic route precludes ether interchange reactions typical of conventional poly(arylene ether) syntheses, and both homo- and heterogeneous morphologies were observed depending on the block lengths used.

Introduction

Copolymers of poly(xylenyl ether) (PXE) and poly(arylene ether sulfone) (PSF) have been prepared as potential impact modifiers for polystyrene. The PXE is miscible with polystyrene at all molecular weights and compositions and should provide good interfacial adhesion between the immiscible polysulfone and polystyrene. These materials are believed to be more versatile than other glassy–glassy copolymer structures such as polystyrene–polysulfone copolymers.[1] Polystyrene homopolymers of different molecular weights are not necessarily miscible with styrene containing block copolymers as many workers have found in siloxane-styrene copolymers blended with homopolystyrene.[2,3]

Generally, poly(arylene ethers) are synthesized by a nucleophilic aromatic substitution of a bisphenol and an activated halide by using potassium carbonate[4] or sodium hydroxide[5] to form the more reactive bisphenate. Unfortunately, well-defined block copoly(arylene ethers) have not been prepared by this route. Ether linkages between aromatic rings are typically stable to phenoxides, but when these linkages are activated by sulfone or ketone groups they are labile under step growth or polycondensation conditions, thus preventing the formation of block structures.[6,7] It has been reported by many workers[6-9] that a significant amount of ether interchange occurs at temperatures above 120 °C.

Matzner and co-workers[10] have recently reported in the patent literature the synthesis of xylenyl ether arylene ether sulfone ABA and $(AB)_n$ copolymers prepared from the condensation of a dialkali metal salt of a diphenol and the alkali metal salt of poly(xylenyl ether) with dihalo benzenoid compounds bearing electron-withdrawing groups. However, the activated ether linkages formed during the polymerization may be susceptible to ether interchange reactions leading to a homogeneous system.

Tigerthal et al.[11] have also reported the synthesis of xylenyl ether–arylene ether sulfone ABA copolymers prepared by an oxidative coupling reaction of a difunctional phenolic hydroxyl-terminated tetramethylbisphenol A polysulfone oligomers with 2,6-dimethylphenol or a redistribution reaction of monofunctional phenolic hydroxyl-terminated xylenyl ether oligomer. This synthetic approach does not allow the preparation of multiphase materials most probably due to the similar solubility parameters of the two components and the relatively short block lengths used. In addition, the choice of the poly(arylene ether sulfone) in this synthetic approach is somewhat limited.

Our synthetic procedure for the preparation of the xylenyl ether–arylene ether sulfone triblock copolymers is similar to that used by Kricheldorf et al.[12] in the synthesis of homo- and copoly(arylene ethers). These workers demonstrated that block copoly(arylene ethers) could be synthesized from silylated bisphenols and activated dihalides in a bulk polymerization at elevated temperatures in the presence of a catalyst. Cesium fluoride was found to be the most effective catalyst. The usefulness of the catalyst depends on the formation of the dissolved fluoride ions, which are believed to cleave the Si–O bond of the silylated bisphenols. The fluoride ion is most useful because it is a strong nucleophile and the subsequent Si–F bond in the leaving group is more stable than any other silicon bond.

This novel synthetic route allows the synthesis of both random and block copolymers. The statistical or random copolymers were synthesized by a one-step process in which all the monomers were added simultaneously. The block copoly(arylene ether sulfone ketone) materials were synthesized in a two-step process in which the ketone block was prepared first, followed by the sulfone block. Two glass transition temperatures were obtained at segment molecular weights of 5000 g/mol, which is indicative of a microphase-separated morphology.

Experimental Section

N-Methyl-2-pyrrolidone (NMP) was dried by stirring it over calcium hydride under a nitrogen flow for 24 h. The solvent was then vacuum distilled at approximately 70 °C to avoid degradation. Toluene was used without further purification. Cesium fluoride was purchased from Aldrich and used without further purification.

Bisphenol A (2,2-bis(4-hydroxyphenyl)propane) (Bis-A) was purchased from Aldrich and recrystallized from toluene. Difluorodiphenyl sulfone (DFDPS) was also obtained from Aldrich and recrystallized from an ethyl acetate/hexane (50/50) mixture. Dimethyl(trimethylsilyl)amine was purchased from Petrarch and used without further purification. Tetramethylbisphenol A (2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propane) (TMBA) was purchased from Applied Organic Silicones and was recrystallized from an ethyl acetate/hexane (50/50) mixture.

Monofunctional phenolic hydroxyl terminated PXE oligomers were kindly supplied by the General Electric Corporation. Two different molecular weights were obtained with intrinsic viscosities

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of 0.29 and 0.46 dL/g in chloroform (25 °C).

A typical synthesis of an aryl fluoride terminated polysulfone oligomer was conducted in a four-necked, 500-mL, round-bottom flask equipped with a mechanical stirrer, gas inlet, thermometer, Dean Stark trap, and condenser. For a synthesis designed to prepare a 10 000 g/mol ($\langle M_w \rangle$) bisphenol A based polysulfone (Bis-A PSF), the flask was charged with 20.774 g (0.091 mol) of Bis-A and 25.425 g (0.100 mol) of DFDPS. These monomers were carefully washed into the flask with NMP. The final volume of NMP was approximately 225 mL. To this solution, approximately 150 mL of toluene was added as an azeotroping agent. Finally, approximately 22 g of K_2CO_3 base was added. Note that K_2CO_3 was used in a 40–50% excess. This reaction mixture was then heated until the toluene began to reflux. An optimum reflux temperature range appeared to be about 140–150 °C. Water is generated during the phenoxide formation and was azeotroped from the system. Refluxing must proceed until no more water is observed, which may take 3–5 h. The temperature was then increased to 170 °C for 3–5 h; completion or near completion was estimated qualitatively by the time at which the viscosity increased dramatically. The polymer was then filtered and coagulated in a 10× volume of a 50/50 methanol and water mixture. The polymer was then dried for 24 h in a vacuum oven at 80 °C.

Both TMBA and the PXE oligomers were silylated with a 5× molar excess of dimethyl(trimethylsilyl)amine in refluxing chloroform for 30 h. A typical silylation of a 23 000 g/mol PXE oligomer was conducted in a 1-L, round-bottom flask equipped with a condenser. The PXE (50 g) was charged and dissolved in 350–425 mL of refluxing chloroform (~60 °C). Approximately 2.5 g of dimethyl(trimethylsilyl)amine was dissolved in chloroform and added slowly (5 min) to the refluxing PXE solution. A constant nitrogen flow was maintained to prevent hydrolysis of the silyl ether bond. After 24 h excess silylating agent was added and maintained at reflux temperature for an additional 6 h. The chloroform and excess silylating agent was then vacuum distilled off and the silylated PXE was stored in a vacuum oven until used.

Tetramethylbisphenol A polysulfone (TMBA PSF) was synthesized in a four-necked flask equipped with a mechanical stirrer, gas inlet, thermometer, Dean Stark trap, and condenser. Approximately 0.3 g of CsF was charged to the flask along with 190 mL of NMP and 150 mL of toluene. The mixture was allowed to reflux between 130 and 140 °C for 6 h to dehydrate the catalyst. For a synthesis designed to prepare high molecular weight polymer, 17.68 g of silylated TMBA and 10.492 g of DFDPS were charged and carefully washed down with NMP. The total volume of NMP was 200 mL. The reaction mixture was heated until the toluene began to reflux (approximately 140–150 °C). The reaction mixture was refluxed for 24 h to ensure dehydration and to aid in the removal of the trimethylsilyl fluoride byproduct. The reaction mixture was then heated to 180 °C by the removal of the toluene, and allowed to react for an additional 36 h. Completion or near completion of the polymerization was estimated by the point the viscosity increased dramatically. The polymer was then filtered, coagulated in a 10× volume of a 50/50 methanol and water mixture and dried in a vacuum oven at 80 °C for 24 h.

The synthetic procedure used for the preparation of the xylenyl ether–arylene ether triblock copolymers (PXE/PSF/PXE) is similar to that used for the TMBA PSF. To a four-necked, round-bottom flask equipped with a gas inlet, thermometer, mechanical stirrer, and Dean Stark trap with a condenser, 0.3 g of CsF was charged along with 225 mL of NMP and 175 mL of toluene. The mixture was allowed to reflux (140–150 °C) for 6–8 h to dehydrate the catalyst. For a synthesis designed to prepare a PXE/PSF/PXE triblock copolymer, 23 g of a monofunctional silyl ether terminated PXE oligomer with a block length of 46 000 g/mol and 5 g of a difunctional aryl fluoride terminated bisphenol A based polysulfone with a block length of 20 000 g/mol were charged and allowed to reflux (~140 °C) for 24 h. The temperature was slowly raised to 180 °C by the removal of toluene and allowed to react for an additional 36–48 h. The copolymer was coagulated in a 10× volume excess of a 50/50 mixture of methanol and water and dried in a vacuum oven (80 °C) for 24 h.

Glass transition temperatures, taken as the midpoint of the change in slope of the base line, were measured on a Du Pont DSC 1090 instrument with a heating rate of 10 °C/min. Films for thermal analysis measurements were cast from chlorobenzene and heated to 250 °C (5 °C/min heating rate) and held for 1 h. This thermal history produced materials which displayed the desired two-phase morphologies. Intrinsic viscosity measurements of the oligomers and subsequent copolymers were determined by using a Cannon-Ubbelhodhe dilation viscometer in chloroform (25 °C). GPC measurements were performed on a Waters 150-C instrument in tetrahydrofuran (35 °C).

Table I
Characteristics of Tetramethylbisphenol A Polysulfone

sample	$[\eta]_{25°C}^{chl}$, dL/g	T_g, °C
TMBA PSF	0.40	235
Udel (control)	0.45	190

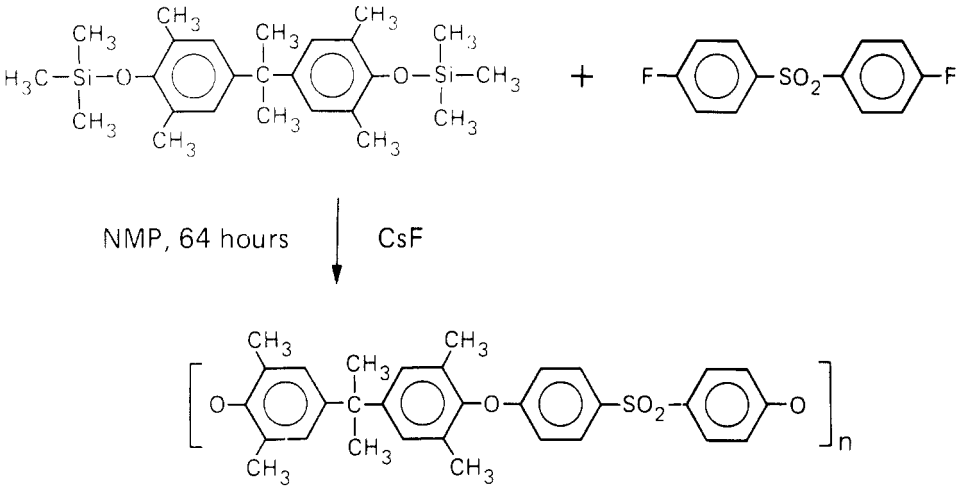
^{13}C NMR spectra were obtained on a Bruker AM500 NMR spectrometer, operating at a ^{13}C NMR frequency of 125.8 MHz. ^{13}C NMR chemical shifts are referenced relative to TMS. The inverse-gated decoupling experiment was used to eliminate NOE from ^{13}C intensities; ^{13}C relaxation times were reduced by the addition of $Cr(ac)_2$. ^{13}C resonance assignments of the fluorinated end group carbons were confirmed by ^{13}C NMR with ^{19}F decoupling. Comparison of end group carbon intensities to those of interior aromatic carbons yielded M_n.

Results and Discussion

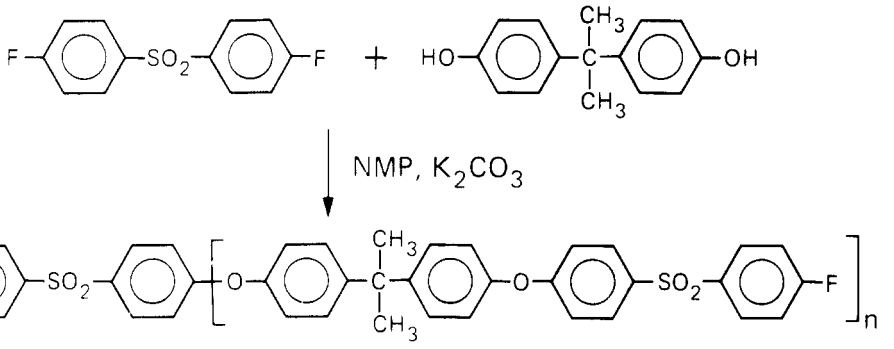
In contrast to the bulk polymerizations used by Kricheldorf et al.,[12] a solvent system was believed to be more useful for the preparation of the triblock copolymers. The high melt viscosity associated with microphase-separated glassy–glassy copolymers[14,15] together with the thermal instability of the PXE block precluded the use of bulk polymerizations at elevated temperatures. A NMP/toluene solvent mixture at reflux temperatures was used as the reaction medium which provides both reduced viscosities and milder polymerization conditions. NMP is an aprotic dipolar solvent which solvates the polysulfone and, at elevated temperatures, the PXE. In addition, the NMP dissolves or at least partially dissolves the cesium fluoride (CsF) catalyst which may be very important in cleaving or complexing with the silyl ether end functionality of the xylenyl ether oligomer. Toluene was required to aid in dissolving the less polar PXE block and, at reflux temperatures with NMP, serves to dehydrate the catalyst, solvents, and oligomers so as to prevent hydrolysis of the silyl ether end group and facilitate the removal of the trimethylsilyl fluoride byproduct.

Prior to the synthesis of the oligomeric precursors and subsequent copolymers, model reactions were performed to demonstrate the utility of the copolymerization and the use of the solvent system. Silylated tetramethyl bisphenol A (TMGA) was reacted with 4,4′-difluorodiphenyl sulfone as shown in Scheme I. This model polymerization closely resembles both the steric and electronic effects of the copolymerization of the aryl fluoride terminated polysulfone with the silyl ether terminated PXE. A NMP/toluene solvent mixture was used together with a catalytic amount of CsF, and high molecular weight was achieved in 48–55 h (180 °C). Table I contains some of the characteristics of the tetramethylbisphenol A polysulfone (TMBA PSF) synthesized together with a high molecular weight commercially available polysulfone (Udel) for comparative purposes. High molecular weight polymer was obtained as indicated by the intrinsic viscosity measurement, and the T_g was 235 °C, which is consistent with other reports of high molecular weight TMBA PSF.[16] Carbon-13 NMR spectroscopy was used to confirm the structure of the TMBA PSF synthesized by this novel route. Figure 1 contains the carbon-13 spectrum of the TMBA PSF which is consistent with other reports[16,17] of TMBA PSF synthesized by more conventional routes. These experi-

Scheme I



Scheme II



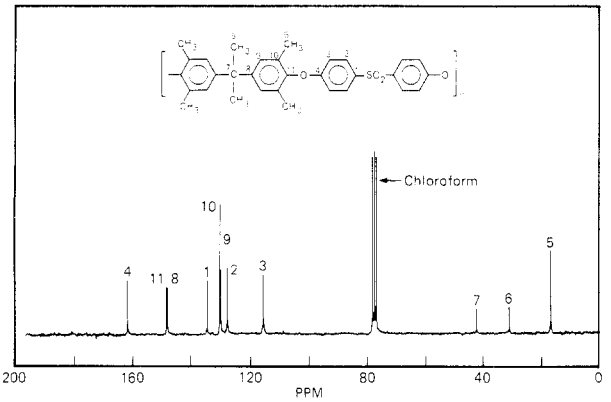


Figure 1. Carbon-13 NMR spectrum of tetramethylbisphenol A polysulfone synthesized by the silyl ether/CsF route.

ments clearly illustrate the feasibility of the copolymerization of the preformed aryl halide terminated PSF and silyl ether terminated PXE oligomers using the NMP/toluene solvent mixture in the temperature range 175–180 °C.

The *N*-methyl-2-pyrrolidone/potassium carbonate (NMP/K_2CO_3) synthesis technique was used to prepare the aryl fluoride terminated polysulfone oligomers (Scheme II).[4,16,17] Poly(arylene ether sulfones) have previously been synthesized by either potassium carbonate/dimethyl acetamide[18] or by aqueous caustic/dimethyl sulfoxide techniques.[5,6] Although these methods are very useful, they are not entirely suitable for the synthesis of high molecular weight polymers. One of the problems associated with the later technique is the insolubility of the bisphenate intermediates. Moreover, partial hydrolysis of the activated aromatic dihalide could occur, which would create a stoichiometric imbalance and limit both the molecular weight and functionality.

Table II
Characteristics of Arylene Ether Sulfone Oligomers

sample	$[\eta]_{25°C}^{chl}$, dL/g	$\langle M_n \rangle$, g/mol theory	$\langle M_n \rangle$, g/mol ^{13}C NMR	$\langle M_w \rangle$, g/mol, light scattering	PI	T_g, °C
1	0.18	5000	4700	10000	2.0	165
2	0.31	10000	11700	20000	2.0	178
3	0.36	15000	15000	29200	2.0	186
4	0.42	20000	21500	38600	2.0	189
Udel	0.40					190

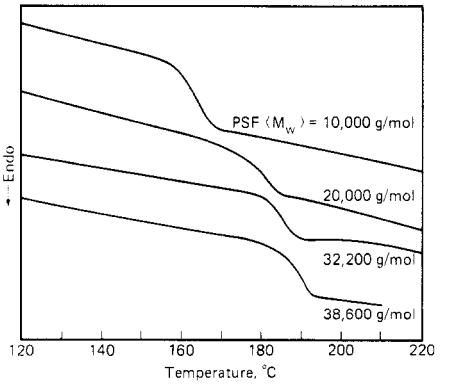


Figure 2. DSC thermograms for the aryl fluoride terminated poly(arylene ether sulfone) oligomers.

The Carothers equation was used to calculate the excess of difluorodiphenyl sulfone required to give the appropriate molecular weight and aryl fluoride termination. Table II contains the intrinsic viscosities, polydispersity index (PI), weight- and number-average molecular weights, and glass transition temperatures of the Bis-A PSF oligomers synthesized. The T_g's for the Bis-A PSF oligomer series ranged from 165 to 190 °C, depending on the molecular

Table III
Characteristics of Xylenyl Ether Oligomers

sample	$[\eta]_{25°C}^{chl}$, dL/g	$\langle M_w \rangle$,[a] g/mol	$\langle M_n \rangle$,[b] g/mol	PI[c]	T_g, °C
1	0.30	32000	14000	2.3	210
2	0.48	46000	20000	2.3	215

[a] Determined by light scattering in chloroform. [b] Determined by ^{1}H NMR spectroscopy. [c] Determined by GPC in tetrahydrofuran.

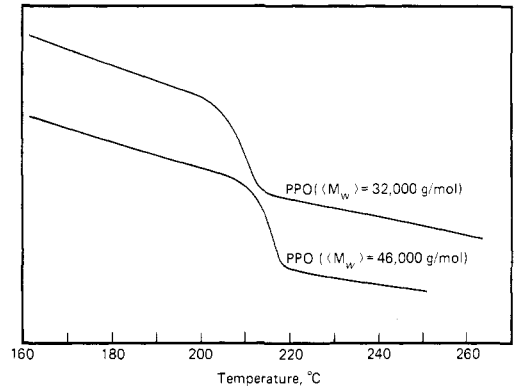


Figure 3. DSC thermograms for the poly(xylenyl ether) oligomers.

weight (Figure 2). The determination of absolute molecular weight of the aryl fluoride terminated oligomers is considerably more difficult than phenolic hydroxyl terminated sulfone oligomers previously reported[19] where end group analysis either by titration[20] or ^{1}H NMR[21,22] techniques may be used to obtain the number-average molecular weights. In the case of the aryl fluoride terminated oligomers, light scattering and quantitative ^{13}C NMR were used to determine the absolute weight and number-average molecular weights of the oligomers.

The light scattering measurements provided weight-average molecular weights which ranged from 10000 to 40000 g/mol, consistent with the predicted values. The ^{13}C NMR end group analysis established the number-average molecular weight and confirmed the aryl fluoride termination. The molecular weights ranged from 5000 to 21500 g/mol and once corrected for the polydispersity showed excellent correlation with the molecular weights obtained by light scattering. As expected, the intrinsic viscosities increased according with the molecular weight.

Table III contains the intrinsic viscosities, polydispersity index (PI), weight-average molecular weights, number-average molecular weights, and glass transition temperatures of the PXE oligomers. The weight-average molecular weights determined by light scattering in chloroform and ranged from 32000 to 46000 g/mol, and the latter sample is of sufficient molecular weight to be film forming and show ductile mechanical properties. The number-average molecular weights were determined by ^{1}H NMR. The PXE oligomers were silylated at the phenolic hydroxyl chain end and comparison of the integrated alkylsilyl peak to the aromatic peak allowed the number-average molecular weight to be calculated. PXE is synthesized by an oxidative coupling or redistribution reaction of 2,6-dimethylphenol, affording the most probable molecular weight distribution in the 2.3 range, and comparison of the weight- and number-average molecular weights obtained by light scattering and ^{1}H NMR, respectively, show good agreement. The T_g's are high and range from 210 to 215 °C (Figure 3).

The xylenyl ether–arylene ether sulfone copolymers were synthesized from the aryl halide terminated PSF oligomers and the monofunctional silyl ether terminated PXE oligomers in a NMP/toluene mixture (Scheme III). In a typical copolymerization, the solvent mixture and catalyst were charged and allowed to reflux for approximately 12 h to dehydrate the catalyst. Stoichiometric amounts of the aryl fluoride terminated PSF and silyl ether terminated PXE were charged and refluxed at 145–150 °C for 24 h. The reaction was slightly turbid at this time. The reaction temperature was increased (175–180 °C) by the removal of the toluene through the Dean Stark trap and was allowed to proceed for an additional 48–64 h. At this time the polymerization became clear and viscous. Aliquots were periodically removed and films cast on a hot plate at 220 °C. Free homopolymer generally produces a cloudy or hazy film because of the difference in refractive indexes of the two components. Cloudy films were obtained early in the copolymerization; however, longer reaction times usually produced clear films.

Table IV
Characteristics of Xylenyl Ether–Arylene Ether Sulfone Copolymers

$\langle M_w \rangle$ of oligomers		characteristics of copolymers		
PSF	PXE	$[\eta]_{25°C}^{CHCl_3}$, dL/g	$\langle M_w \rangle / \langle M_n \rangle$	T_g, °C
10000	32000	0.52	2.2	212
10000	46000	0.86	2.4	215
20400	32000	0.52	2.3	191, 213
20400	46000	0.80	2.7	192, 217
29200	32000	0.60	2.0	187, 215
29200	46000	0.80	2.0	190, 215
38600	32000	0.60	2.9	190, 213
38600	46000	0.92	2.0	187, 215

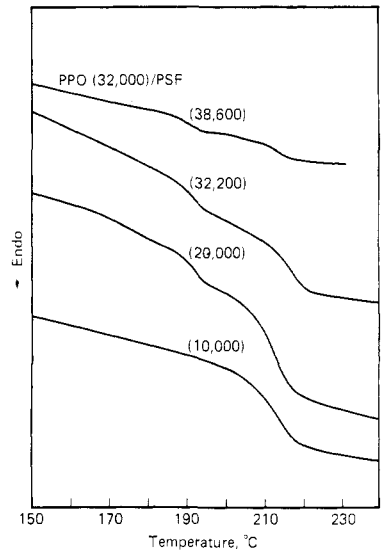
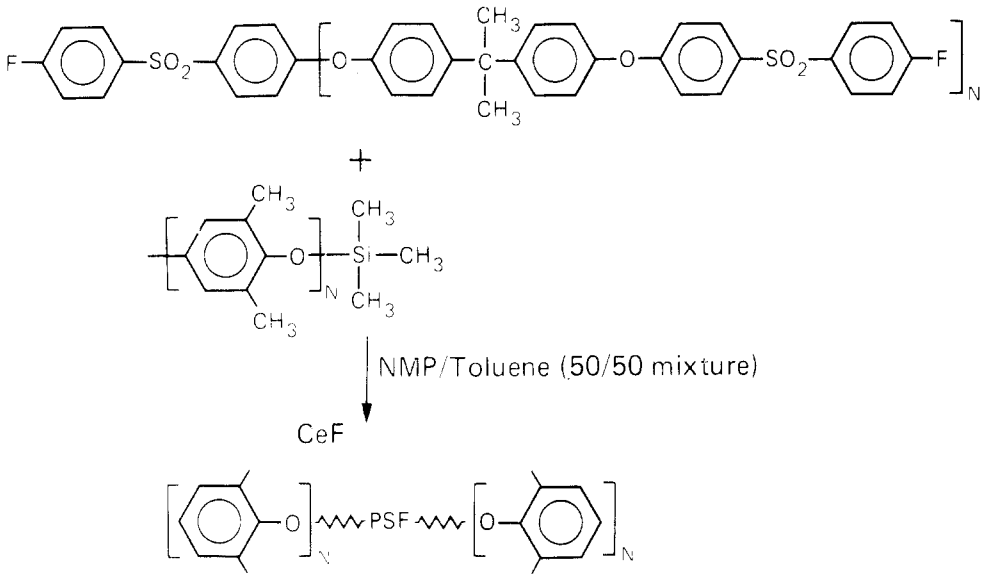


Figure 4. DSC thermograms of PXE/PSF/PXE triblock copolymers containing the 32000 g/mol PXE block and the various PSF block lengths.

Table IV contains the weight-average molecular weights of the initial oligomers and the intrinsic viscosities, molecular weight distributions, and glass transition temperatures of the triblock structures synthesized. In each case high molecular weight was obtained as shown by the intrinsic viscosity measurements and the values fall according to the relative block lengths used. The copolymers prepared formed clear, tough films, suggesting minimal homopolymer contamination. The molecular weight distributions for the copolymers were all monomodal (single peaked), with polydispersity between 2.0 and 2.9 further indicating minimal homo- and diblock contamination.

The DSC results (Table IV) indicate both homo- and heterogeneous morphologies are possible by this synthetic route, and the morphology appears to be strongly de-

Scheme III



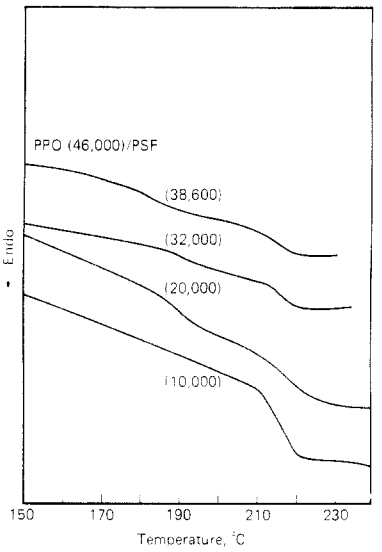
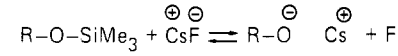


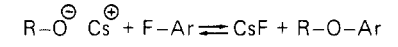
Figure 5. DSC thermograms of PXE/PSF/PXE triblock copolymers containing the 46 000 g/mol block and the various PSF block lengths.

pendent on the block lengths used. Figures 4 and 5 contain the DSC scans for the various copolymers containing the 32 000 and 46 000 g/mol PXE blocks, respectfully. Clearly, a two-phase morphology develops at polysulfone block lengths above 10 000 g/mol as evidenced by the two glass transition temperatures. These data are consistent with earlier reports by Ward et al.[14] on polysulfone–polycarbonate glassy–glassy copolymers where block lengths having a number-average molecular weight of 16 000 g/mol were required to produce a two-phase morphology. More recently, block and random phenylquinoxoline–arylene ester copolymers have been reported by Labadie and coworkers,[23,24] which also show similar effects. Two-phase morphologies were observed in these copolymers when block lengths of approximately 12 000 g/mol or larger were used. In contrast, glassy–glassy di- and triblock polystyrene–poly(α-methylstyrene) copolymers have shown single-phase morphologies with block lengths as high as 200 000 g/mol.[25,26]

The T_g's of the polysulfone component, for those copolymers which were prepared with the lower molecular weight polysulfone oligomers, are up to 15 °C higher than that of the initial oligomers. Apparently, the extent of phase separation or more precisely the phase purity is limited at these lower polysulfone block lengths irrespective of the PXE block length. In contrast, the copolymers containing the 38 000 g/mol polysulfone block show improved phase purity, particularly when the higher molecular weight PXE oligomer is used.

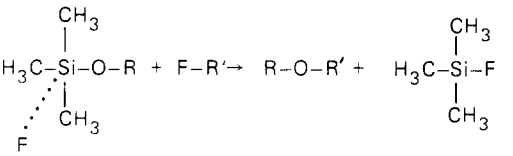
In contrast to the conventional synthetic route for the preparation of poly(arylene ethers), the use of the silyl ether terminated PXE and CsF to displace the aryl fluoride terminated polysulfone precludes interchange reactions affording multiphase materials. Kricheldorf and co-workers[12] proposed the following mechanism for the polymerization using silylated bisphenols and CsF:





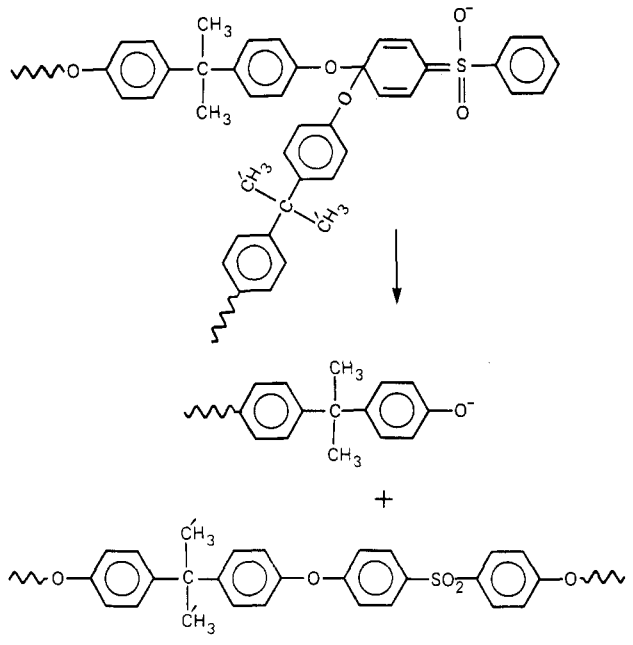
However, this mechanism is not consistent with the development of multiphase materials. That is, according to their scheme the polymerization proceeds through a phenoxide intermediate and at these reaction temperatures activated ether linkages are nearly as reactive as the corresponding halides to phenoxides which will lead to ether interchange and homogeneous morphologies. This exchange can occur on either of the two aromatic rings; however, the ring attached directly to the sulfone linkage is the preferentially attacked due to the formation of the highly energetic Meisenheimer complex (Scheme IV).[16]

A more plausible mechanism for the synthesis may involve a complexation of the fluoride ion with the silicone activating the silyl ether toward nucleophilic aromatic substitution as shown below



Ether interchange is precluded in this case because this "activated" nucleophile is considerably weaker than the corresponding phenoxide. Thus the nucleophilic aromatic substitution reaction will only occur at the aryl fluoride end groups which are stronger electrophiles than the activated ether linkages.

Scheme IV



It is also important to point out that fluoride ion under relatively harsh conditions (i.e., saturated KF solution at 200 °C) has been reported to promote ether exchange reactions by nucleophilic attack on the activated ether linkage.[27] We have employed milder polymerization conditions and significantly lower fluoride ion concentrations to minimize the exchange reaction. Furthermore, the xylenyl ether block is not activated toward these exchange reactions, thus the block structure should always be retained.

Summary

We have successfully synthesized ABA triblock copolymers of poly(xylenyl ether) and poly(arylene ether sulfone). Generally, poly(arylene ethers) are synthesized by a nucleophilic aromatic substitution reaction of a bisphenate and an activated halide in an aprotic dipolar solvent forming ether linkages which are activated. These activated ether linkages are labile to phenoxides preventing the formation of well-defined block copolymers. The use of a silyl ether terminated PXE oligomer to react with an aryl fluoride terminated polysulfone oligomer in the presence of CsF is a successful route to produce well-defined triblock copolymers. Ether interchange reactions were precluded and both homo- and heterogeneous morphologies were produced. Future publications will discuss the morphology, properties, and aging characteristics of the copolymers as well as their blends with polystyrene.

Registry No. (TMBA)(DFDPS) (copolymer), 118400-67-2; (TMBA)(DFDPS) (SRU), 32034-67-6; (DFDPS)(Bis-A) (copolymer), 41209-98-7; (DFDPS)(Bis-A) (SRU), 25135-51-7; (DFDPS)(Bis-A)(2,6-dimethylphenol) (block copolymer), 118400-68-3; CsF, 13400-13-0.

References and Notes

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