Polymer Bulletin 27, 665–671 (1992)

Polymer Bulletin

Solid state properties of xylenyl ether-aryl ether sulfone triblock copolymers

James L. Hedrick

IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, CA 95120-6099, USA

Summary

The morphology and mechanical properties of a series of xylenyl ether-aryl ether sulfone ABA triblock copolymers were studied, where the A represents the xylenyl ether block (PXE) and the B represents aryl ether sulfone block (PSF). The copolymers investigated were composed of PXE block lengths of 16,000 or 23,000 g/mol together with aryl ether sulfone oligomers with molecular weights ranging from 5,000 to 20,000 g/mol. Both homo- and heterogeneous morphologies were observed depending on the composition of the copolymers. The copolymers with the high polysulfone block lengths showed higher phase demixing. The triblock copolymers showed the expected tough ductile mechanical properties, as judged by the high elongations (50-165%).

Introduction

Multiphase polymeric materials in the form of block, graft and segmented and ion containing copolymers with thermoplastic elastomer properties have achieved significant commercial status and a number of reports concerning their preparation and properties have appeared in the literature. In contrast, there has been considerable less attention in the area of block copolymers composed of two or more hard or glassy components. The factors effecting microphase separation, mechanical properties, physical aging and other properties in such block polymers are still unclear. However, several workers have reported that block lengths and segmental interaction parameters are important features.

Numerous examples of glassy-glassy copolymers have appeared in the literature including poly(styrene)-poly(methylacrylate (1), poly(alpha methyl styrene)-poly(methyl methacrylate) (2), poly(styrene-arylonitrile) (3), and others (4). However, poly(styrene)-poly(alpha methyl styrene) copolymers are perhaps the most noteworthy since many of the fundamental aspects of their morphology (i.e., phase separation) have been investigated (5). Poly(styrene)-poly(alpha methyl styrene) di- and triblock polymers with various block lengths have been prepared by anionic polymerization. Single phase morphologies were observed at all block lengths as high as 200,000 g/mol and block architectures. These results are in good agreement with the theoretical predictions of Krause (6,7) who pointed out that such structures should be homogeneous with block lengths as high as 800,000 g/mol.

Conversely, McGrath and co-workers (8) have reported the synthesis of block polymers based on polysulfone and polycarbonate. It was demonstrated that the structure of solubility parameter of the sulfone block used together with the relative molecular weights governs the microphase separation. Two phase morphologies resulted when block lengths exceeding 20,000 g/mol were coupled or when copolymers composed of intermediate block lengths (16,000 g/mol) were given the appropriate thermal history. Similarly, Labadie et al. (9,10) have reported the synthesis, properties and morphology of aryl ester-phenylquinoxaline copolymers in which microphase separated morphologies were observed when block lengths of 12,000 g/mol or greater were used. The effects of having a two phase glassy-glassy structure influenced such properties as ductility, modulus and melt viscosity.

We have recently reported the synthesis of glassy-glassy ABA triblock copolymers of poly(xylenyl ether) and poly(aryl ether sulfone) (11). Generally, poly(aryl ethers) are prepared by a nucleophic aromatic substitution reaction of a bisphenate and an activated dihalide in an aprotic-dipolar solvent forming aryl ether linkages. These ether linkages, activated by sulfone, ketone or similar moieties, are also labile towards displacement by phenoxides preventing the formation of well defined block copolymers. This is known as ether interchange.

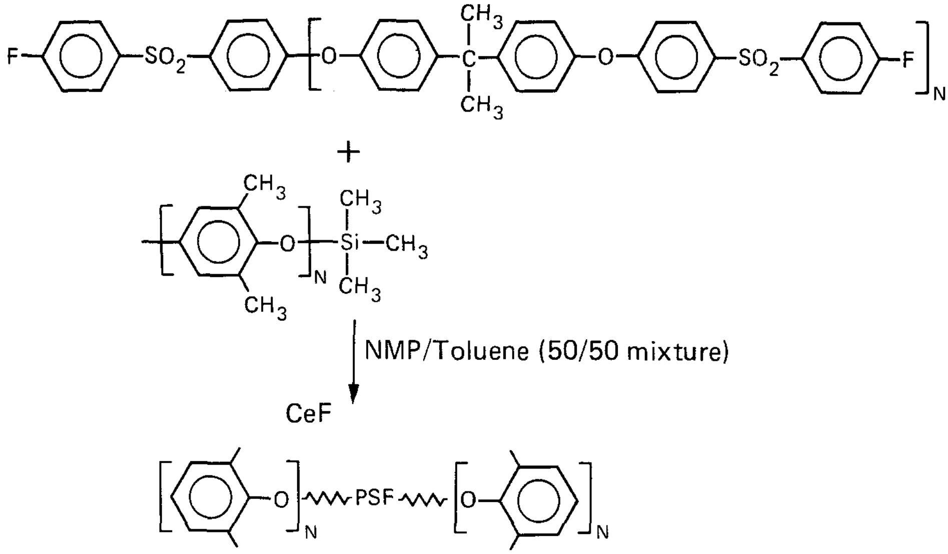
Kircheldorf and co-workers (12) have reported the preparation of block copoly(aryl ethers) from silylated bisphenols and activated halides in a bulk reaction using cesium fluoride (CSF) as the catalyst. We employed this synthetic novel approach for the synthesis of xylenyl ether-aryl ether sulfone triblock copolymers (11). This synthetic route precludes ether interchange associated with conventional poly(aryl ether) synthesis as well as redistribution reactions which may occur during oxidative coupling of xylenyl ether, thereby affording well defined triblock copolymers. Two glass transition temperatures were observed provided sufficient block lengths were used indicative of the development of a heterogeneous morphology. In this communication, the morphology and mechanical properties of the copolymers will be discussed in more detail.

Experimental

The synthetic route to the preparation of the xylenyl ether – aryl ether sulfone triblock copolymers is given elsewhere. Films of the copolymers were cast from chlorobenzene at approximately 15% solids and heated to 225°C (5°C/min.) and held for 1h to remove the solvent. Glass transition temperatures, taken as the mid-point of the change in slope of the baseline, were measured on a DuPont DSC 1090 instrument with a heating rate of 10°C/min. Intrinsic viscosity measurements of the oligomers and subsequent copolymers were determined using a Cannon-Vbbelhodhe dilation viscometer in chloroform (25°C). GPC measurements were performed on a Waters 150-C instrument in tetrahydrofuran (35°C). Stress-strain measurements were made on an Instron Tensile Testor at a strain rate of 10 mm/min. (23°C). The dynamic mechanical measurements were made on a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA) at 10 Hz and a heating rate of 10°C/min. in the tension mode.

Results and Discussion

Xylenyl ether – aryl ether sulfone triblock copolymers were prepared by the step growth polymerization of preformed xylenyl ether (PXE) and aryl ether sulfone PSF oligomers (Scheme I) (11). Table 1 contains the number and weight average molecular weights, and calorimetry results for the oligomers. The weight average molecular weights, determined by light scattering, ranged from 32,000 to 46,000 g/mol for the PXE oligomers and from 10,000 to 38,200 g/mol for the PSF oligomers. The number average molecular weights, determined by NMR, ranged from 16,000 to 23,000 g/mol for the PXE oligomer and from 5,000 to 19,200 for the PSF oligomers. The T_g's, ranging from 210 to 215°C for the PXE oligomers and from 165 to 190°C for the PSF oligomers, were strongly molecular weight dependent.



Scheme 1

Table 1

Characteristics of the Xylenyl Ether (PXE) and Aryl Ether Sulfone (PSF) Oligomers

Oligomer	$<M_n>^a$ (g/mol)	$<M_w>^B$ (g/mol)	$[n]^{25°C}$ (dl/g)	T_g^C (°C)
PXE	14,000	32,000	0.30	210
PXE	20,000	46,000	0.48	215
PSF	4,700	10,000	0.18	165
PSF	11,700	20,000	0.31	178
PSF	15,000	29,200	0.36	186
PSF	21,500	38,600	0.42	189

[A] Determined by ^{13}CNMR or H NMR.
[B] Determined by light scattering chloroform.
[C] Determined by DSC, heat rate 10°C/min.

Table 2 contains the characteristics of the triblock copolymers synthesized, including the intrinsic viscosities, molecular weight distributions and calorimetric results, as well as the molecular weights of the preformed oligomers. In each case, high molecular weight was achieved as judged by the intrinsic viscosity measurements, and the values fall according to the relative block lengths used. The copolymers formed clear, tough films as cast from chlorobenzene, suggesting minimal homopolymer contamination. The molecular weight distributions for the copolymers were all monomodal with polydispersities between 7.0 and 7.9, further indicating minimal homopolymer or diblock contamination.

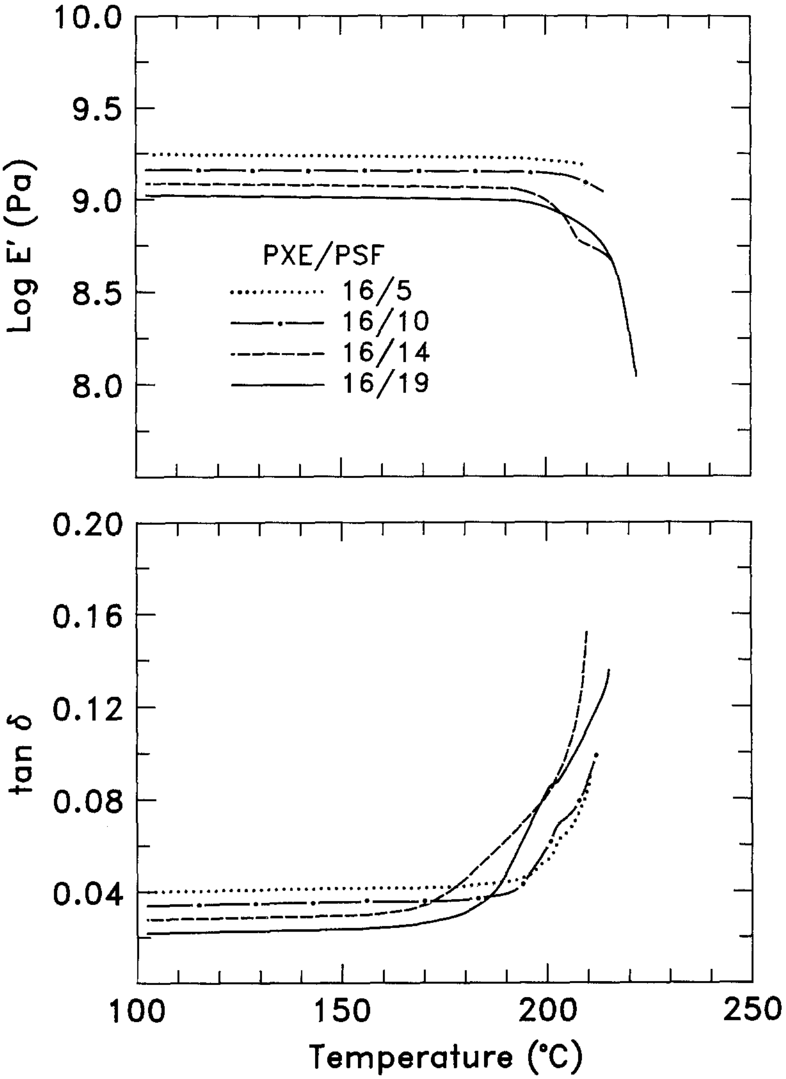


Figure 1. Dynamic mechanical behavior of xylenyl ether aryl ether sulfone block polymers.

Table 2
Characteristics of Xylenyl Ether-aryl Ether Sulfone Copolymers

$\langle M_n \rangle$, (g/mol) of oligomers used in synthesis		Characteristics of Copolymers		
PXF	PXE	$[\eta]^{CHCl_3}_{25^\circ C}$ (dl/g)	$\langle M_w \rangle$ / $\langle M_n \rangle$	T_g (°C)
4,700	14,000	0.52	2.2	212
4,700	20,000	0.86	2.4	215
14,700	14,000	0.52	2.3	191,213
11,700	20,000	0.80	2.7	192,217
15,000	14,000	0.60	2.0	187,215
15,000	20,000	0.80	2.0	190,215
21,500	14,000	0.60	2.9	190,213
21,500	20,000	0.92	2.0	187,215

The calorimetry results indicate both homogeneous and heterogeneous morphologies were obtained by this synthetic route, and that the morphology appears to be strongly dependent on the block lengths used (Table 2). The copolymers containing low PSF block lengths (5,000 g/mol) show only one T_g irrespective of the PXE block length, indicative as a single phase morphology. Interestingly, the T_g is nearly the same or even somewhat higher than that of the PXE oligomer (Table 1). We believe that this is a molecular weight effect resulting from the chain extension of the PXE with the low molecular weight sulfone oligomer.

Conversely, the copolymers containing higher molecular weight PSF block lengths (10,000 – 19,200 g/mol) show two T_g's irrespective of the PXE block lengths, indicative of a microphase separated morphology. The T_g of the polysulfone segment or block for those copolymers which were prepared with the lower molecular weight PSF oligomers have T_g's up to 15°C higher than the unreacted oligomers for each of the PXE block lengths (Tables 1 and 2). Apparently, the extent of phase separation or, more precisely, the phase purity is limited at these lower PSF block lengths. In contrast, the triblock copolymers containing PSF block lengths of 19,200 g/mol show minimal phase demixing, particularly at the higher PXE block length.

The dynamic mechanical thermal analysis (DMTA) results for the triblock copolymers containing PXE block lengths of 16,000 and 23,000 are shown in Figures 1 and 2 for each of the PSF block lengths, respectively. These results, consistent with the calorimetry measurements, clearly illustrate that both single and two phase morphologies were obtained as well as the dependence of the PSF block length on the morphology. A single transition is observed for those copolymers containing the lowest PSF block length (5,000 g/mol). The T_g is somewhat higher than expected and probably results from the chain extension of the PXE oligomer with the PSF oligomer as discussed earlier. The copolymers containing the higher molecular weight PSF block lengths clearly show a two phase morphology as evidenced by the two damping transitions observed in the $\tan\delta$ associated with respective T_g's of the PSF (~ 190°C) and PXE (~ 215°C).

As expected, the magnitude of the $\tan\delta$ transition for the PSF block increases with increasing block length reflecting the higher volume fraction of the polysulfone component. Furthermore, this transition shifts to lower temperatures with increasing PSF molecular weight indicative of higher phase demixing for each of the PXE block lengths.

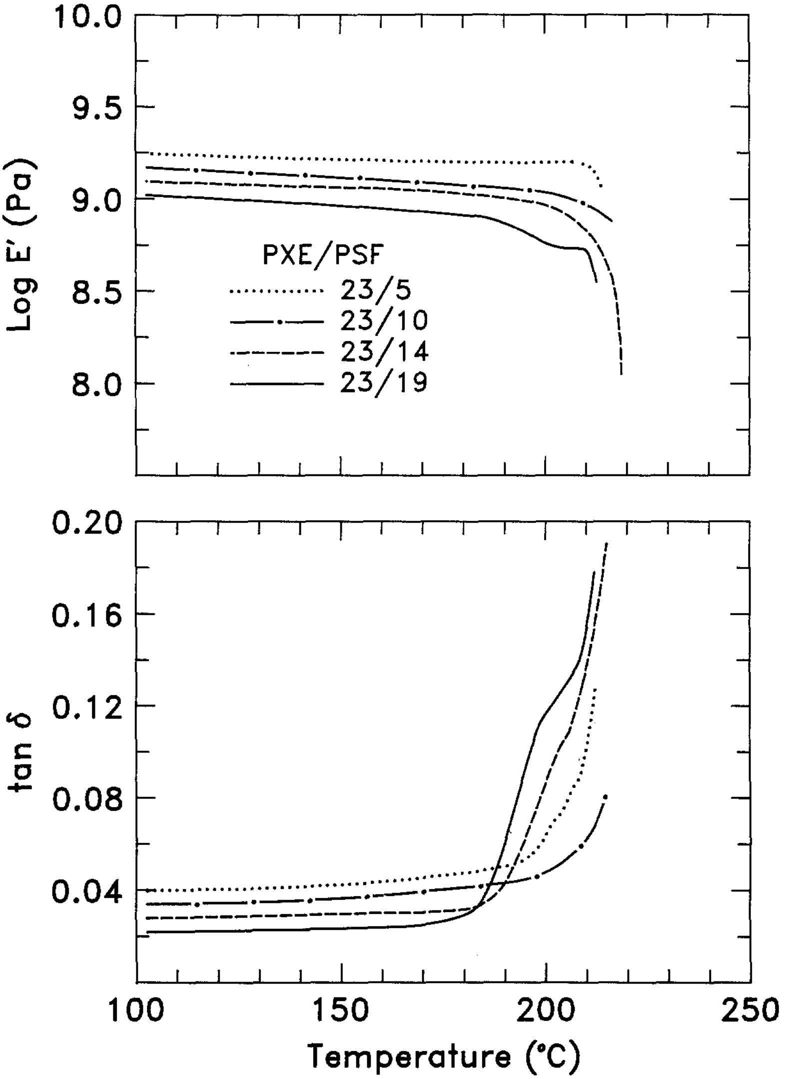


Figure 2. Dynamic mechanical behavior of xylenyl ether aryl ether sulfone block polymers.

These data are consistent with earlier reports by McGrath and coworkers (8) on polysulfone – polycarbonate copolymers and Labadie and co-workers (7,10) on poly(aryl esterphenylquinoxaline) copolymers. In these copolymer series, molecular weights between 12,000 and 16,000 g/mol were required to produce a two phase morphology. In our copolymer systems, slightly lower polysulfone oligomer molecular weight was necessary to produce a two phase morphology. This may result from the difference in block architectures of each of the copolymer systems. The PXE/PSF/PXE copolymers have a triblock architecture, whereas the other copolymer systems are multiblock or of the $(A\text{-}B)_n$ type, and equilibrium may be more readily approached with the former type of block architecture.

The mechanical properties for the triblock copolymers are given in Table 3. The copolymers showed the expected tough ductile mechanical properties as characterized by the high elongations (50-165%). The copolymers yielded and necked similar to other engineering thermoplastics. The moduli were high and comparable to those of the homopolymers.

Table 3

Mechanical Properties of Xylenyl Ether – Aryl Ether Sulfone Triblock Copolymers

$\langle M_n \rangle$ (g/mol) of Oligomers PSF	PXE	Modulus (MPa)	Yield Stress (MPa)	Tensile Stress (MPa)	Elongation (%)
4,700	14,000	1600	72	59	17
4,700	20,000	1460	76	69	60
11,700	14,000	1560	72	68	11
11,700	20,000	1400	78	84	158
15,000	14,000	1480	74	75	103
15,000	20,000	1480	76	83	165
21,500	14,000	1420	72	67	72
21,500	20,000	1550	76	73	65

References

1. Baer M-J (1964) J Polym Sci A-2,2: 417.
2. Hsine G, Yasukawa T, Marakami K (1970) Die Makromol Chemie 139: 285
3. Perry E, J Polym Sci (1964) J Polym Sci 8: 2605
4. Webster D-C, McGrath J-E (1983) Contemporary Topics in Polymer Science. In: Bailey W-J (ed.), 4
5. Robeson L-M, Matzner M, Fetters L-J, McGrath J-E (1974) Recent Advances in Polymer Blends, Grafts and Blocks. In: Sperling L-H (ed.). Plenum, New York.
6. Krause, S, Dunn D-J (1974) Polym Lett 12: 591.
7. Krause S, Dunn D-J, Seyed-Mozzaffari A, Biswas A-M (1977) 10: 786.
8. Ward T-C, Wnuk A-J, Shchori E, Viswanathan R, McGrath J-E (1979) ACS Adv in Chem Series 176. In: Cooper S-L, Estes G (eds.).
9. Labadie J-W, Hedrick J-L, Hofer D-C (1987) J Polym Sci, Polym Chem Ed, submitted.
10. Labadie J-W, Hedrick J-L, Hofer D-C (1987) Polym Bull, submitted.
11. Hedrick J-L, Brown H-R, Hofer D-C, Johnson R (1988) Macromolecules, accepted.
12. Kircheldorf H-R, Bier G (1984) Polymer 25: 1151.

Accepted December 30, 1991