Miscibility in blends of phenylsulfonylated poly(2,6-dimethyl-1,4-phenylene oxide) and poly(*p*-fluorostyrene-*co*-*o*-fluorostyrene)

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Miscibility and phase separation in blends of random copolymers of *p*-fluorostyrene and *o*-fluorostyrene [P(*p*FSt-*co*-*o*FSt)] with phenylsulfonylated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) copolymers in which the degree of sulfonylation ranges from 4 to 92 mol% have been studied by differential scanning calorimetry (d.s.c.) at temperatures up to 320°C. It was found that miscibility depends on isomeric composition, the degree of sulfonylation, and temperature. Certain blends exhibit lower critical solution temperature (*LCST*) behaviour.

(Keywords: miscibility; copolymers; isomeric effects)

INTRODUCTION

There has been much interest in miscible polymer blends in which one or both of the constituents are random copolymers. The miscibility behaviour of mixtures of two random copolymers containing a common segment has been studied[1–4], and the general case of miscibility of two copolymers containing a total of four distinct repeat units has also been reported[5]. In earlier publications we have presented the results of miscibility and phase behaviour studies of blends of styrenic copolymers and partially sulfonylated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO)[6–8] and of blends of SPPO copolymers and halogen-substituted styrene homopolymers[9]. The blends characteristically are miscible for certain ranges of compositions, a behaviour which can be formally explained on the basis of the usual mean-field analysis without invoking specific interactions. This of course does not preclude the possible contribution of favourable interactions between specific moieties in the respective copolymers[10–13].

In this contribution we report on the miscibility and phase behaviour of blends of SPPO copolymers and poly(*p*-fluorostyrene-*co*-*o*-fluorostyrene) [poly(*p*FSt-*co*-*o*FSt)], i.e. amorphous blends of two random copolymers containing a total of four repeat units: a system of the type $(A_{1-x}B_x)_{n1}/C_{1-y}D_y)_{n2}$. The criterion for miscibility in this study is based on differential scanning calorimetry (d.s.c.) measurements of the glass transition temperature(s). The six interaction parameters required for a mean-field analysis of this system[10] are available from previous studies, and it was found that this parameter set accounted for the present data with good agreement.

EXPERIMENTAL

Materials

*P(*p*FSt-*co*-*o*FSt) copolymers.* High-molecular-weight, random copolymers of *p*FSt and *o*FSt were prepared by free-radical polymerization of *p*- and *o*-fluorostyrene in toluene at 60°C, using AIBN as initiator and following the procedure previously described[14]. *Figure 1a* shows the structures of the two repeating units (*o*FSt and *p*FSt), and *Table 1* presents relevant data for these copolymers. The copolymers used are essentially identical to those employed in studies reported in ref. 14.

SPPO copolymers. SPPO copolymers of different degrees of phenylsulfonylation (from 4 to 92 mol%) were prepared by Friedel–Crafts sulfonylation of PPO, also as previously described[15,16]. *Figure 1b* shows the structures of the two repeating units (PO and SPO) of these copolymers.

Blend preparation. The copolymer blends were prepared by dissolving equal quantities of the pure components in toluene and coprecipitating them from solution into a large excess of methanol. The resulting precipitates were filtered and dried at 80°C in vacuum for 60 h. The dried mixtures were then used in d.s.c. experiments.

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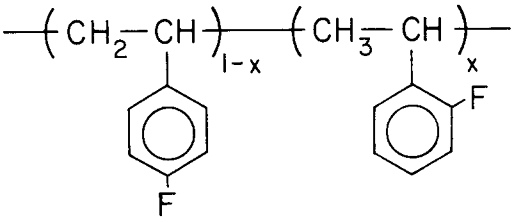
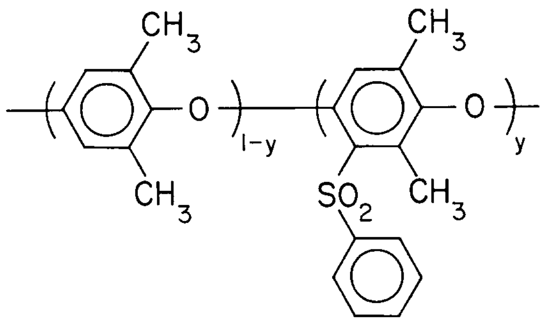


a. Poly (pFSt-co-oFSt)



b. SPPO copolymer

Figure 1 Structures of repeat units in (a) P(*p*FSt-*co*-*o*FSt) and (b) SPPO copolymers

Table 1 Characteristics of copolymers

Copolymer composition (mole fraction of *o*FSt), *x*	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	T_g(°C)
P(*p*FSt)			
0	8.27	4.86	104
P(*p*FSt$_{1-x}$-*co*-*o*FSt$_x$)			
0.14	8.4	4.9	103
0.23	9.0	5.2	103
0.34	10.6	6.2	102
0.44	10.6	5.9	102
0.57	9.5	5.1	100
0.62	9.7	5.3	100
0.72	8.6	4.4	99
0.84	8.6	4.7	98
0.90	11.1	6.4	98
0.93	12.9	7.5	97
P(*o*FSt)			
1.00	8.8	4.6	95

Measurements

Differential scanning calorimetry (Perkin–Elmer DSC-2) was used to determine blend miscibility. Sample sizes were approximately 20 mg, and a heating rate of 20°C min^{-1} in nitrogen was employed. Glass transition temperature(s) were the only distinctive features of the d.s.c. thermograms. The T_g was taken as the temperature at which the heat capacity reached one-half of the total heat capacity change as observed on the thermogram.

Ancillary thermogravimetric measurements (Perkin–Elmer TGS-2) were made (at a heating rate of 10°C min^{-1} with a nitrogen purge) to determine the maximum temperature that could be used in this study. It was found for a range of blends that the observed weight loss between 200° and 320°C was only slightly dependent on the blend composition. For example, the analysis of a blend of the styrenic copolymer with 34 mol% *o*FSt and the SPPO copolymer with 45 mol% substitution exhibited weight losses of 0.3, 0.4 and 1.3% for samples annealed at 250, 280 and 320°C, respectively. It was concluded that thermal degradation was not an important factor in this study for measurements up to 320°C.

RESULTS AND DISCUSSION

Calorimetric studies

A previous publication reported the phase behaviour of the homopolymers P(*o*FSt) and P(*p*FSt) with both PPO and SPPO. Neither homopolymer is miscible with PPO[17], but in the mixtures with SPPO, miscibility was found for a range of sulfonylations, although the compositions at which miscibility occurred were very different for the two systems[9].

Miscibility in the present system, P(*p*FSt-*co*-*o*FSt)/SPPO, was studied for blends of random styrenic copolymers containing 14 to 93 mol% *o*FSt (*Table 1*) and SPPO copolymers with various degrees of sulfonylation, namely, 3.5, 8.6, 12, 17, 25.4, 27, 31, 36.7, 39, 47, 56, 61, 63, 68, 75, 84, 88 and 92 mol% substitution. First, the influence of the styrenic copolymer composition on miscibility was studied. Selected SPPO copolymers were mixed with P(*p*FSt-*co*-*o*FSt) samples as described above in a weight ratio of 50:50. A d.s.c. experiment consisted of heating a sample at the fastest available rate to a temperature above the T_g for the respective sulfonylated copolymer. After annealing, the samples were quenched to ambient temperature as rapidly as possible in the instrument. The quenched samples were reheated at 20°C min^{-1} to determine whether one or two phases were present. An initial scan was made to produce a uniform thermal history for all polymers. The reported glass transition temperatures are derived from the second scan. The usual single T_g criterion was used for assessing miscibility. The T_g data for the 50/50 wt% blends are given in *Table 2*.

On the basis of these analyses, a copolymer–copolymer composition diagram displaying the miscibility domain and the miscibility–immiscibility boundary for 50/50 wt% as-precipitated blends was constructed and is shown in *Figure 2*. The bottom left-hand corner of the miscibility map corresponds to a blend of pure P(*p*FSt) and PPO; the bottom right-hand corner corresponds to a blend of pure P(*o*FSt) and PPO. In both cases, the blends are immiscible, as previously determined[17]. PPO is, however, miscible with a range of P(*p*FSt-*co*-*o*FSt) copolymers (containing 62 to 90 mol% *o*FSt); the location of this miscibility window also agrees with earlier data[14] in which the samples were equilibrated between 180 and 215°C.

As can also be seen in *Figure 2*, miscibility for the SPPO/P(*p*FSt-*co*-*o*FSt) blends lies in a band between the two ordinates, with a distinct narrowing as the *o*FSt content in the styrenic copolymers increases.

The as-precipitated miscible blends were further analysed by annealing at 200, 280 and 320°C. The annealing experiments were carried out in the d.s.c., and the typical protocol consisted of heating a sample known to be homogeneous to the selected annealing temperature and holding it at that temperature for 15 min. Samples were then quenched to ambient temperature, and T_g

Table 2 Influence of the degree of sulfonylation of SPO copolymers on the miscibility in the blends with poly(*p*FSt-*co*-*o*FSt)

SPO content, mol% (T_g, °C)	Temperature (°C)	*o*FSt content, mol% (T_g, °C)									
		14 (103)	23 (103)	34 (102)	44 (102)	57 (100)	62 (100)	72 (99)	84 (98)	90 (98)	93 (97)
3.5 (222)	200	112, 217	117, 217	137^a	147	147	147	147	147	146	146
	280	–	–	118, 218	120, 217	–	–	–	–	–	–
	320	–	–	–	–	137^a	–	–	–	–	–
8.6 (229)	200	114, 218	154	154	153	154	154	152	152	149	150
	280	–	122, 222	–	–	–	–	–	–	–	–
	320	–	–	–	–	–	–	–	–	–	–
12 (236)	200	135^a	154	154	152	150	150	148	148	147	147
	280	122, 217	–	–	–	–	–	–	–	–	–
	320	–	–	–	–	–	–	–	–	–	–
17 (242)	200	151	151	151	151	150	150	149	149	149	149
	280	–	–	–	–	–	–	–	–	–	–
	320	–	–	–	–	–	–	–	–	140^a	122, 227
25.4 (253)	200	157			157				155	112, 235	112, 235
	280	–			–				–	–	–
	320	–			–				112, 235	–	–
27 (254)	200	160	160	160	159	152	152	147	117, 237		
	280	–	–	–	–	–	–	137, 247	–		
	320	–	–	–	–	–	137^a	132, 240	–		
31 (258)	200							117, 240			
	280							–			
	320							–			
36.7 (264)	200				155		112, 240				
	280				–		–				
	320				122, 240		–				
39 (265)	200	163	162	162	153	117, 247	112, 245	112, 242	112, 242	112, 238	
	280	–	–	–	122, 242	–	–	–	–	–	
	320	–	–	123, 262	–	–	–	–	–	–	
47 (268)	200	167	167	142, 245	112, 237	105, 237	105, 237	103, 255	102, 255	100, 257	
	280	–	122, 247	–	–	–	–	–	–	–	
	320	122, 247	–	–	–	–	–	–	–	–	
56 (271)	200	167	112, 253	113, 256		102, 260	120, 260			101, 260	
	280	112, 247	–	–		–	–			–	
	320	–	–	–		–	–			–	
61 (279)	200	168									
	280	120, 253									
	320	–									
63 (281)	200	117, 267	112, 260	112, 259	102, 260	102, 277	102,276	103, 276	102, 277	102, 277	102, 275
	280	–	–	–	–	–	–	–	–	–	–
	320	–	–	–	–	–	–	–	–	–	–
68 (285)	200	112, 272	109, 277	107, 280	107, 280	102, 282	102, 282	102, 282	102, 282	102, 282	102, 282
	280	–	–	–	–	–	–	–	–	–	–
	320	–	–	–	–	–	–	–	–	–	–
75 (292)	200	112, 272	108, 278			101, 280			102, 285	102, 285	
	280	–	–			–			–	–	
	320	–	–			–			–	–	
84 (298)	200	112, 275	106, 280				100, 287			100, 290	
	280	–	–				–			–	
	320	–	–				–			–	
88 (301)	200	112, 287			101, 290				100, 295		
	280	–			–				–		
	320	–			–				–		
92 (306)	200	110, 297		105,297					99, 297	99, 297	
	280	–		–					–	–	
	320	–		–					–	–	

Values given are T_g (°C) for samples heated to the temperatures indicated

^{a} Ambiguous result

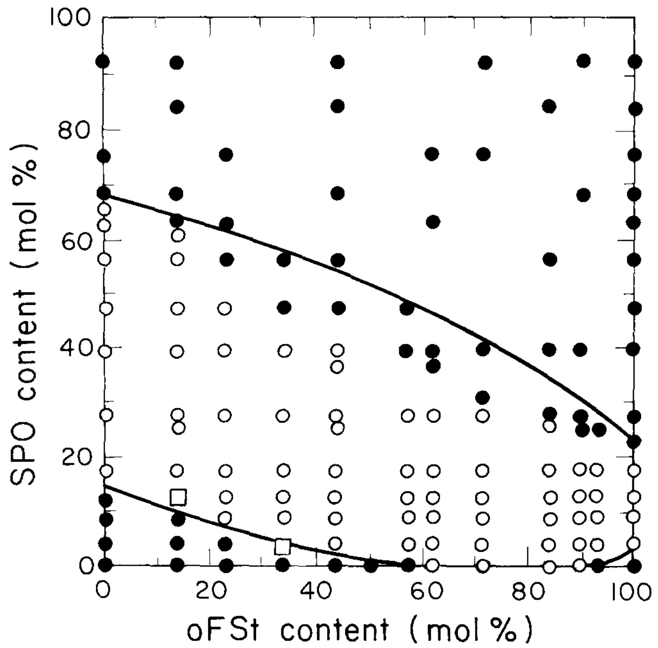


Figure 2 Miscibility of 50/50 wt% blends of P(*p*FSt-*co*-*o*FSt) and SPPO copolymer, as precipitated. (○) one phase; (●) two phases; (□) intermediate situation. The solid lines represent the calculated miscibility–immiscibility boundaries (see text)

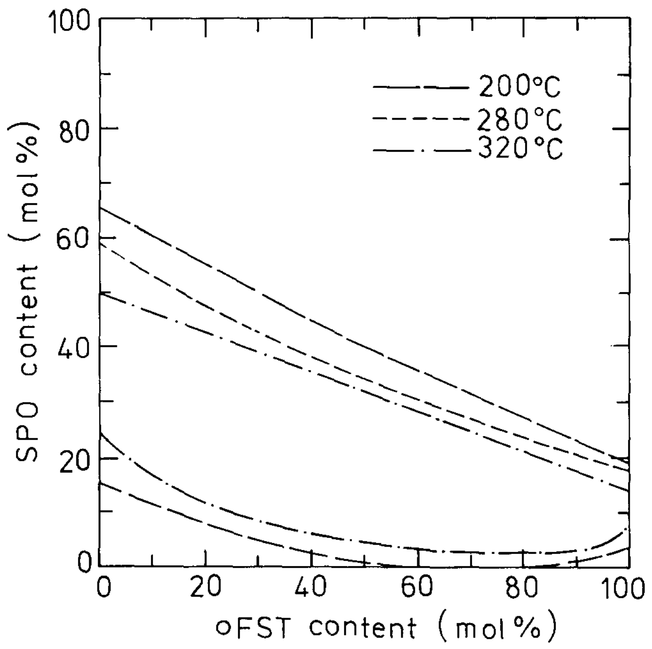


Figure 3 Miscibility–immiscibility boundaries of 50/50 wt% blends of P(*p*FSt-*co*-*o*FSt) and SPPO copolymer, annealed at 200, 280, and 320°C, respectively. Data points have been omitted for clarity. The 280 and 320°C boundaries in the lower section of the diagram essentially overlap

behaviour determined by reheating[14]. Phase separation was typically observed in blends lying close to but within the miscibility–immiscibility boundary shown in *Figure 2*.

Figure 3 shows the experimental miscibility–immiscibility boundaries at 200, 280 and 320°C. (Data points are omitted for clarity.) First we note that the boundaries exhibited no change after annealing of the blends at 200°C, relative to those of the as-precipitated blends shown in *Figure 2*. At the higher annealing temperatures of 280 and 320°C, however, the miscibility domain became progressively smaller. The respective isothermal boundaries are closely spaced within the experimentally accessible temperature range and subject to the usual experimental error.

It may be generally concluded that miscibility in this system diminishes as the equilibrium temperature increases, a result implying lower critical solution temperature (*LCST*) behaviour. To demonstrate this behaviour directly, copolymer blends of different compositions were prepared. The results for two copolymer pairs with compositions located near the miscibility–immiscibility boundaries are shown in *Figures 4* and *5*. The former shows a conventional phase diagram for blends containing styrenic copolymer containing 14 mol% *o*FSt and SPPO copolymer containing 12 mol% sulfonylated units. The phase diagram clearly demonstrates the existence of an *LCST*. Polymer blends containing styrenic copolymer with 34 mol% *o*FSt and SPPO copolymer with 47 mol%

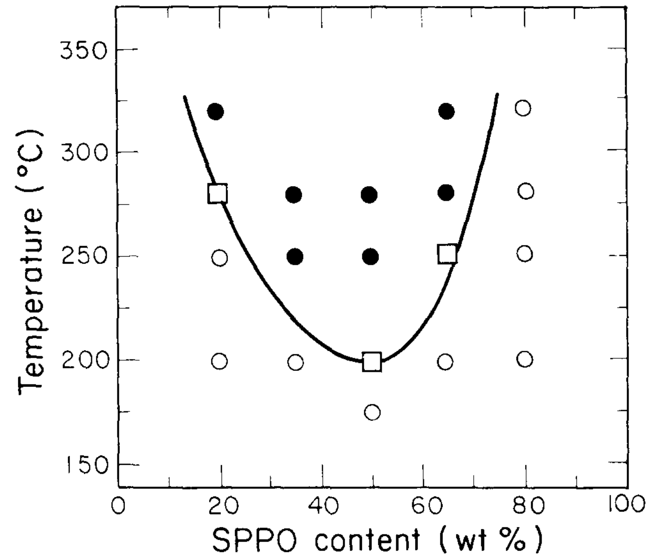


Figure 4 Phase diagram of a blend containing P(*p*FSt-*co*-*o*FSt) with 14 mol% *o*FSt and SPPO with a degree of sulfonylation of 12 mol%. (○) One phase; (●) two phases; (□) intermediate situation

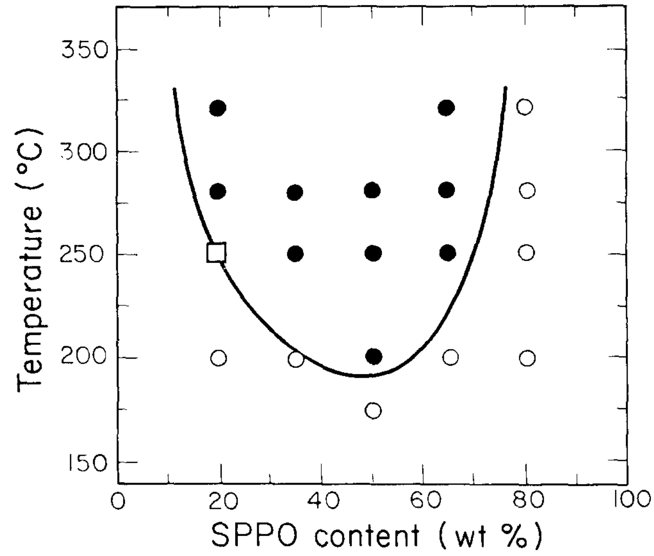


Figure 5 Phase diagram for a blend containing P(*p*FSt-*co*-*o*FSt) with 34 mol% *o*FSt and SPPO with a degree of sulfonylation of 47 mol%. (○) One phase; (●) two phases; (□) intermediate situation

substitution showed similar behaviour (*Figure 5*). These results show also that the boundaries separating the one- and two-phase regimes for 50/50 mixtures correspond approximately to the loci of the *LCST*s for the given systems.

Segmental interaction parameters

The results show, as expected, that the degree of sulfonylation of SPPO is a predominant factor in determining miscibility; this behaviour again demonstrates the influence of relatively small structural changes on miscibility in copolymer blends. A quantitative account of these results can be obtained by using the segmental interaction parameters according to the now well-established mean-field theory of copolymer phase behaviour[10]. The present system constitutes a blend of the type $(A_{1-x}B_x)_{n1}/(C_{1-y}D_y)_{n2}$, where A, B, C and D in this case represent *p*-fluorostyrene (*p*FSt), *o*-fluorostyrene (*o*FSt), 2,6-dimethyl-1,4-phenylene oxide (PO), and the phenylsulfonylated phenylene oxide (SPO) units, respectively[9]. For this system, there are six interaction parameters corresponding to each non-identical pairwise interaction. The expression for χ_{blend} can be written

$$\chi_{\mathrm{blend}}=(1-x)(1-y)\chi_{\mathrm{AC}}+y(1-x)\chi_{\mathrm{AD}}+x(1-y)\chi_{\mathrm{BC}}+xy\chi_{\mathrm{BD}}-x(1-x)\chi_{\mathrm{AB}}-y(1-y)\chi_{\mathrm{CD}} \qquad (1)$$

where segmental interaction parameters between the different monomer units are indicated by their subscripts. In this system, all the parameters can be calculated from previously published contributions. The values of $\chi_{\mathrm{AB}}=0.058$, $\chi_{\mathrm{AC}}=0.037$ and $\chi_{\mathrm{BC}}=0.0052$ were calculated from the experimental data for the miscibility behaviour of the PPO/P(*p*FSt-*co*-*o*FSt)[14] and PPO/P(*o*FSt-*co*-*o*ClSt)[18] systems and from the value $\chi=0.02$ for the PO,*o*ClSt segment pair[19]. The first three values differ slightly from the original published estimates; the present refined values were obtained by a recalculation of the data, using a revised estimate for the key PPO–PS interaction parameter[19]. From the results obtained for the system P*p*FSt/SPPO, the interaction parameters χ_{AD} and χ_{CD} were calculated to be 0.093 and 0.318, respectively[9]. The remaining interaction parameter, $\chi_{\mathrm{BD}}=0.252$, was calculated from the miscibility observations for P*o*FSt/SPPO blends[9]. From these interaction parameters (valid at 200°C) and from the configurational entropy term, $\chi_{\mathrm{blend}}^{\mathrm{crit}}$ ($\equiv 0.005$), the location of the miscibility–immiscibility boundary was calculated (equation (1)) without any adjustable parameters and is shown as a solid line in *Figure 2*. Considering the fact that these parameters were obtained from a rather wide range of experiments involving many different permutations of homo- and copolymers, the agreement implies a reasonably satisfactory degree of predictability in determining miscibility–immiscibility boundaries in these systems.

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