Miscibility in blends of sulfonylated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) with homopolymers of halogen-substituted styrene derivatives

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(Received 27 April 1992)

Miscibility and phase behaviour in blends of poly(*p*-fluorostyrene) (PpFSt), poly(*o*-fluorostyrene) (PoFSt), poly(*p*-chlorostyrene) (PpClSt), poly(*o*-chlorostyrene) (PoClSt), poly(*p*-bromostyrene) (PpBrSt) and poly(*o*-bromostyrene) (PoBrSt) with partially sulfonylated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) copolymers [i.e. systems of the type $(A)_{n_1}/(C_{1-y}D_y)_{n_2}$] have been studied by d.s.c. as a function of temperature and degree of sulfonylation. For all the *para*-substituted styrene polymers/SPPO blends studied, limited miscibility regimes are found. A miscibility regime is also found for PoFSt/SPPO blends. However, PoClSt and PoBrSt are not miscible with any SPPO. Using the mean-field approach, we have calculated all the pertinent segmental interaction parameters for these blends. In several systems, certain blends have been found to exhibit lower critical solution temperature behaviour.

(Keywords: miscibility; blends; halogen-substituted styrene derivatives; sulfonylated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO))

INTRODUCTION

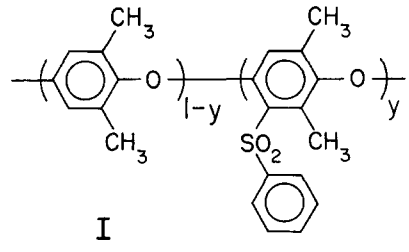
A series of novel random copolymers containing up to 92 mol% phenylsulfonyl-substituted 2,6-dimethyl-1,4-phenylene oxide repeat units together with the unsubstituted units has been prepared. These copolymers appear to be a new class of materials that could be useful either as blend constituents or as engineering thermoplastics[1–3]. In several earlier publications we have reported the results of miscibility and phase behaviour studies of blends of two random copolymers with four distinct repeat units, i.e. styrenic copolymers with partially sulfonylated PPO (SPPO)[2,4]. Studies of the miscibility in blends of copolymers of alternating α-methylstyrene and maleimide units and SPPO[3], in blends of SPPO and poly(styrene-*co*-maleic anhydride)[5] and in blends of SPPO with poly(α-methylstyrene-*co*-maleic anhydride)[5] have also been made. In all these systems, the mole fraction of sulfonyl groups in the SPPO copolymer profoundly affected miscibility.

In a continuation of our studies of the miscibility of SPPO random copolymers, we have systematically investigated miscibility in blends of the six homopolymers of *p*-(*o*-)fluorostyrene, *p*-(*o*-)chlorostyrene and *p*-(*o*-)bromostyrene with the SPPO copolymers. It should also be noted that blends of these six homopolymers with PPO itself have all been found to be immiscible[6–8]. It is reasonable to assume that the bulky and very polar phenylsulfonyl group attached to the phenylene oxide (i.e. the SPO unit) will also influence miscibility in these systems, and that the miscibility phenomena can be accounted for on the basis of a mean-field treatment, as previously described[9].

EXPERIMENTAL

Materials

Homopolymers of *ortho*-(*para*-)fluorostyrene, of *ortho*-(*para*-)chlorostyrene and of *ortho*-(*para*-)bromostyrene of high molecular weight were prepared by free radical polymerization of the respective monomers at 60°C in toluene solution with 2,2′-azobis(isobutyronitrile) (AIBN) as initiator. The polymers were purified by dissolution in toluene and precipitation in methanol. Monomers and solvents were purified and dried in the usual way. AIBN was purified by crystallization from methanol.



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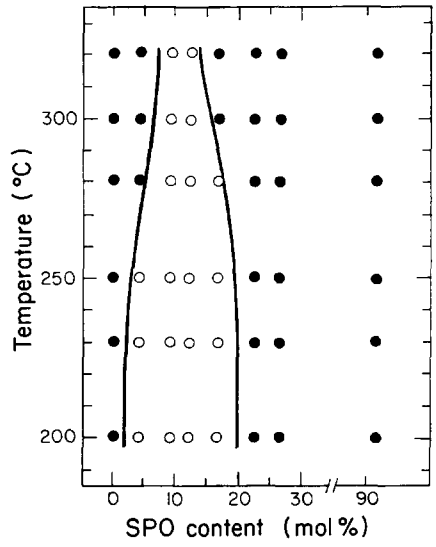

Figure 1 Miscibility of 50/50 wt% blends of PoFSt and SPPO copolymers: (○) one phase; (●) two phases

Sulfonylated PPO copolymers (SPPO, I) containing systematically varied levels of phenylsulfonylation ranging from 4 to 92 mol% were prepared by Friedel–Crafts sulfonylation of PPO[1,3]. The amount of phenylsulfonylation in each copolymer was determined by elemental analysis and from analysis of ^{1}H n.m.r. spectra. The substitution was assumed to be such that the products could be regarded as random copolymers of the derivatized and underivatized moieties.

Polymer blends were prepared by dissolving appropriate quantities of the pure components in chloroform and precipitating the solution into a large excess of methanol. The prepared blends were dried at 100°C in vacuum for 60 h. In one series of experiments, the dried precipitate was used for d.s.c. studies. In other experiments, the dried, precipitated blends were compression moulded under a pressure of 1.4×10^5 kPa at 220°C.

Physicochemical measurements

Glass transition temperature (T_g) measurements of polymers and of the 50/50 wt% polymer blends were carried out by using a Perkin-Elmer DSC-2 at a heating rate of 20°C min^{-1} under nitrogen. The T_g was taken as the inflection point in the heat capacity discontinuity in the second scan. Thermogravimetric measurements of the powdered samples were made by using a Perkin-Elmer TGA-2 thermobalance with a heating rate of 10°C min^{-1} under nitrogen. Molecular weights, based on calibration with monodisperse polystyrene standards (Polymer Laboratories), were determined by g.p.c. (Varian HPGPC, model 8500) in tetrahydrofuran at 25°C. The poly(*o*-fluorostyrene) (PoFSt), poly(*p*-fluorostyrene) (PpFSt), poly(*o*-chlorostyrene) (PoClSt), poly(*p*-chlorostyrene) (PpClSt), poly(*o*-bromostyrene) (PoBrSt) and poly(*p*-bromostyrene) (PpBrSt) samples were characterized by average molecular weights of $\bar{M}_w$ 88 500, $\bar{M}_n$ 46 500; $\bar{M}_w$ 82 700, $\bar{M}_n$ 48 600; $\bar{M}_w$ 160 200, $\bar{M}_n$ 76 900; $\bar{M}_w$ 157 300, $\bar{M}_n$ 87 300; $\bar{M}_w$ 112 300, $\bar{M}_n$ 65 900; and $\bar{M}_w$ 154 000, $\bar{M}_n$ 86 000, respectively.

RESULTS AND DISCUSSION

Miscibility in the blends was characterized by d.s.c. as described above, usually over the entire temperature range at which equilibrium could be attained, i.e. between 200°C and 320°C. The usual single T_g criterion was used for assessing miscibility. Blends that were found to exhibit miscibility over a range of copolymer composition at 200°C were investigated further at the higher temperatures. The thermal stability of the blends was evaluated as necessary by t.g.a., in which representative samples were predried at 200°C in the t.g.a. furnace to remove traces of absorbed water, then heated from 50 to 320°C and the weight loss determined. It was found that the weight loss for each SPPO/homopolymer system studied was <0.5 wt% at the highest temperature (320°C). Therefore, it was concluded that thermal degradation was not an important factor in this investigation.

It should be noted that we found no difference in miscibility, as determined by d.s.c. measurements, of a precipitated powder of the blends or a compression-moulded film.

PoFSt/SPPO and PpFSt/SPPO blends

In both systems a window of miscibility in a temperature–copolymer composition plot was found as a function of the degree of sulfonylation, although the composition ranges were very different for the two systems. For the PoFSt/SPPO systems, miscibility was found (at 200°C) in samples containing from 4 to 17 mol% SPO. Phase separation was found at higher temperatures in a number of samples, as shown in *Figure 1*. The annealing experiments were carried out in the d.s.c. by applying a previously described procedure[10]. From *Figure 1*, it is evident that the maximum miscibility in the PoFSt/SPPO system is in blends containing ~9 mol% SPO.

The miscibility window in PpFSt/SPPO blends extended from 17 to 66 mol% SPO at 200°C. It was found that the boundary between one- and two-phase behaviour is also temperature dependent, as is shown in *Figure 2*. Thus polymer blends with copolymer containing 17 mol% SPO phase separated at 280°C. For the blend with the 63 mol% SPO copolymer, partial phase separation at 280°C was found. The maximum in the miscibility window in this system occurs at an SPO content of ~40–50 mol%. The two boundaries separating the one- and two-phase regimes correspond approxi-

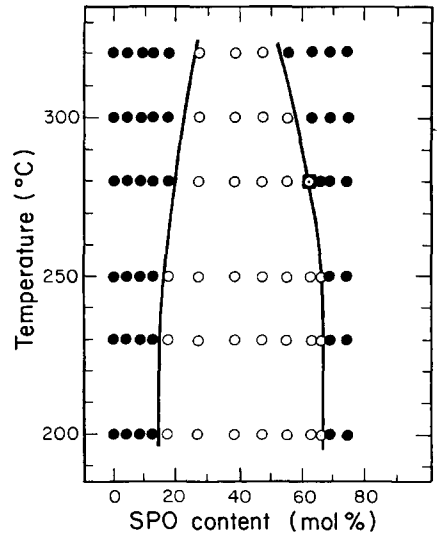

Figure 2 Miscibility of 50/50 wt% blends of PpFSt and SPPO copolymers: (○) one phase; (●) two phases; (□) intermediate situation

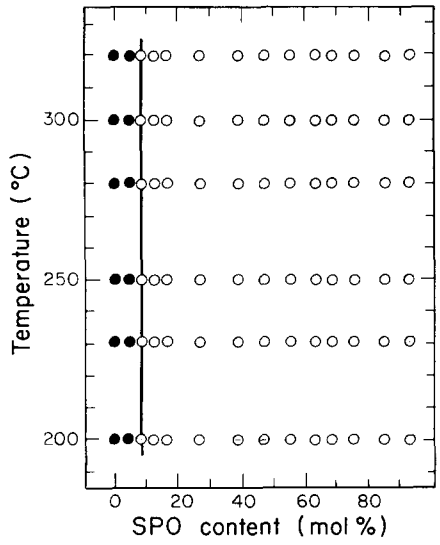

Figure 3 Miscibility of 50/50 wt% blends of PpClSt and SPPO copolymers: (○) one phase; (●) two phases

mately to the loci of the lower critical solution temperatures for the given systems.

PoClSt/SPPO and PpClSt/SPPO blends

Blends of PoClSt/SPPO exhibited two T_gs for all SPPO samples studied, i.e. with copolymer samples containing from 4 to 92 mol% SPO. (PoClSt is also known to be immiscible with PPO itself.) In PpClSt/SPPO blends, however, miscibility was observed in blends with copolymers containing >9 mol% SPO (*Figure 3*). No changes in miscibility were observed for any of the samples at higher temperatures (*Figure 3*). Moreover, the glass transition width in d.s.c. thermograms did not change, a result indicating an intimate level of mixing in these blends. Clearly the slope of the miscibility–immiscibility boundaries is too high to be measured in the accessible region of the temperature–copolymer composition diagram.

PoBrSt/SPPO and PpBrSt/SPPO blends

PoBrSt/SPPO blends exhibited the same immiscibility that was observed for the corresponding chlorinated styrene derivatives. Blends of PoBrSt with SPPO copolymers containing from 4 to 92 mol% SPO were investigated.

In PpBrSt/SPPO blends, miscibility was found in samples containing copolymers with >12 mol% SPO (*Figure 4*). It is evident from *Figure 4* that in these systems no changes in miscibility could be observed upon heating the samples to higher temperatures.

Segmental interaction parameters

The behaviour of the blends in this study demonstrates again the effect of relatively small structural changes on miscibility in polymers. A quantitative accounting of these results can be obtained by calculating the segmental interaction parameters according to the mean-field theory of copolymer phase behaviour[9]. The present systems represent blends of a homopolymer $(A)_{n_1}$ and a copolymer $(C_{1-y}D_y)_{n_2}$, where C and D in this case represent 2,6-dimethyl-1,4-phenylene oxide (PO) and the sulfonylated phenylene oxide (SPO) units, respectively, n_1 and n_2 are the degrees of polymerization and y is the mole fraction of the D unit in the copolymer. In this investigation, the molecular weights of the constituents were sufficiently high that the configurational entropy correction to the free energy, $O(n_{1,2}^{-1})$, is negligible. In a given system there are three interaction parameters corresponding to the three non-identical segment interactions. For such systems, the resulting expression for χ_{blend} takes the form:

$$\chi_{blend} = (1-y)\chi_{AC} + y\chi_{AD} - y(1-y)\chi_{CD} \quad (1)$$

where the interaction parameters describing the interactions between different monomer units are indicated by their subscripts. For blends of SPPO and any of the four homopolymers (PoFSt, PpFSt, PpClSt and PpBrSt), copolymer compositions, expressed in mole fraction of SPO, of the 50/50 wt% blend at the miscibility–immiscibility boundary at 200°C (i.e. at $\chi_{blend}=0$) were 0.02 and 0.19; 0.17 and 0.67; 0.09; and 0.10, respectively, with an average error of ± 0.03 in mole fraction units.

The data provided by the present experiments together with results from earlier studies have been used to calculate the interaction parameters for all binary combinations of halogen-substituted styrene derivatives with the unsubstituted (PO) and with the sulfonyl-substituted (SPO) moieties (see *Table 1*).

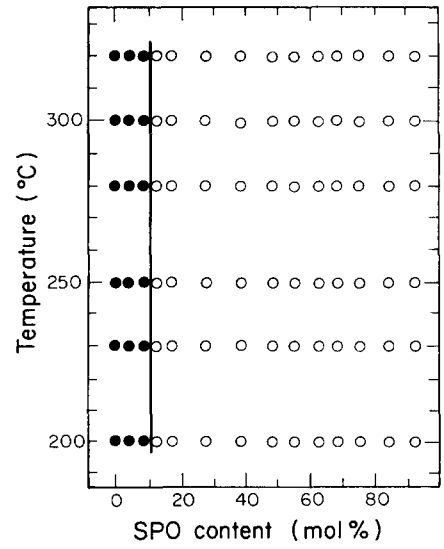

Figure 4 Miscibility of 50/50 wt% blends of PpBrSt and SPPO copolymers: (○) one phase; (●) two phases

Table 1 Segmental interaction parameters at 200°C

Segment pair	χ_{ij}
PO,pFSt	0.037[a]
PO,oFSt	0.005[a]
SPO,pFSt	0.093
SPO,oFSt	0.252
PO,pClSt	0.03[b]
PO,oClSt	0.02[b]
SPO,pClSt	0.017
SPO,oClSt	0.28[c]
PO,pBrSt	0.035[a]
PO,oBrSt	0.029
SPO,pBrSt	0.013
SPO,oBrSt	0.27[c]
PO,SPO	0.318

[a] Calculated on the basis of data in refs 11–14
[b] From ref. 13
[c] Calculated from data in ref. 15

PoFSt/SPPO and PpFSt/SPPO blends

From the previously published data for miscibility behaviour of PPO/poly(oFSt-*co*-oClSt)[11] and PPO/poly(oFSt-*co*-pFSt)[12], and from a previously estimated value of 0.02 for $\chi_{PO,oClSt}$[13], the values of $\chi_{PO,oFSt}$ and $\chi_{PO,pFSt}$ were calculated to be 0.0052 and 0.037, respectively, at 200°C.

Because a value of $\chi_{PO,pFSt}$ has already been calculated, there remain two unknowns, which can be obtained for the PpFSt/SPPO system from the equation using the two critical points in *Figure 2*. The values obtained (200°C) are $\chi_{SPO,pFSt}=0.093$ and $\chi_{PO,SPO}=0.318$. The copolymer composition y_T that represents the maximum in the window of miscibility[9] for this system is given by:

$$y_T=\frac{1}{2}-\frac{\chi_{SPO,pFSt}-\chi_{PO,pFSt}}{2\chi_{PO,SPO}}=0.40 \qquad (2)$$

The present data thus predict that a maximum in the miscibility window occurs at 40 mol% sulfonylated PO, a result consistent with the experimental data.

The PoFSt/SPPO system was analysed in a similar way. Using the value for $\chi_{PO,oFSt}$ (0.0052 at 200°C), the two unknowns were calculated by using the two critical compositions shown in *Figure 1*. The values obtained are $\chi_{SPO,oFSt}=0.252$ and $\chi_{PO,SPO}=0.317$ (the value of 0.318 was taken for $\chi_{PO,SPO}$ in all further calculations). From these results and equation (1), it follows that the calculated maximum in the window of miscibility is at a mole fraction sulfonylation of 0.10, in good agreement with experimental results.

PpClSt/SPPO blend

Figure 3 shows the phase behaviour of the PpClSt/SPPO system. The unknown $\chi_{SPO,pClSt}$ parameter at 200°C was calculated by using previously estimated data: $\chi_{PO,pClSt}=0.03$[13], $\chi_{PO,SPO}=0.318$, and the value of y at the boundary, 0.09; from this, $\chi_{SPO,pClSt}$ was calculated to be 0.017.

PpBrSt/SPPO blend

Figure 4 shows the phase behaviour of the PpBrSt/SPPO system. We needed additional data to calculate interaction parameters for this system. The value of $\chi_{PO,pBrSt}$ at 200°C was obtained from the phase behaviour in the temperature–copolymer composition plane of the PPO/poly(St-*co*-pBrSt) system[14]. It was found that $\chi_{PO,pBrSt}=0.035$. Applying equation (1) to the boundary conditions with $\chi_{PO,pBrSt}=0.035$ and $\chi_{PO,SPO}=0.318$, we found that $\chi_{SPO,pBrSt}=0.013$.

PoClSt/SPPO and PoBrSt/SPPO blends

For these systems, immiscibility over the entire SPPO copolymer composition range was found. The expressions for χ_{blend} for the respective systems are given by equations (3) and (4):

$$\chi_{blend}=(1-y)\chi_{PO,oClSt}+y\chi_{SPO,oClSt}-y(1-y)\chi_{PO,SPO} \qquad (3)$$

$$\chi_{blend}=(1-y)\chi_{PO,oBrSt}+y\chi_{SPO,oBrSt}-y(1-y)\chi_{PO,SPO} \qquad (4)$$

From the calculated values of the segmental interaction parameters $\chi_{PO,oClSt}$, $\chi_{PO,SPO}$ and $\chi_{PO,oBrSt}$ at 200°C (*Table 1*) in equations (3) and (4), it is readily determined that miscibility for these systems is only possible if $\chi_{SPO,oClSt}<0.139$ and $\chi_{SPO,oBrSt}<0.13$. The values for the interaction parameters of the SPO,oClSt and SPO,oBrSt pairs calculated from the experimental data for the poly(oClSt-*co*-pClSt)/SPPO and poly(oBrSt-*co*-pBrSt)/SPPO systems were found to be 0.28 and 0.27[15], values consistent with the experimental results presented here.

From the segmental interaction parameters for the PoClSt/SPPO system (*Table 1*), it can be seen that $\chi_{PO,SPO}>\chi_{SPO,oClSt}>\chi_{PO,oClSt}$. The fact that $\chi_{PO,SPO}\cong\chi_{SPO,oClSt}$ implies that repulsion between PO and SPO units is too small to compensate for the positive values of $\chi_{PO,oClSt}$ and $\chi_{SPO,oClSt}$, and immiscibility thus occurs over the whole range of compositions. As found experimentally, immiscibility in the PoBrSt/SPPO system also occurs over the whole composition range. From the calculated values for $\chi_{PO,oBrSt}$ (from data in ref. 14), $\chi_{SPO,oBrSt}$ (from data in ref. 15), and $\chi_{PO,SPO}$ (*Table 1*), it follows that the explanation for immiscibility in this system is the same as that for the PoClSt/SPPO system. It is interesting to observe that two of the three χs for this system differ only slightly from the corresponding interaction parameters in the fluorine-containing system; nevertheless, the differences are sufficient to account for the large differences in miscibility behaviour.

The results clearly show that the location of the halogen atom in the benzene ring, rather than the electronegativity or the bulkiness of the halogen atom, is a predominant factor in determining miscibility.

Miscibility in blends of SPPO and an *ortho*-substituted styrene derivative in the three halogens studied is influenced by this steric factor. In blends of SPPO and a *para*-substituted styrene derivative, in contrast, the interaction between the benzene ring in polystyrene and the benzene ring in sulfonylated PPO is affected by the electronegativity of the *para* substituent.

Finally it is interesting to observe from the values in *Table 1* that, although all the χ_{ij}s are positive, in some cases the absolute values are small, of the order of 10^{-2}. This finding implies that blends in which the constituents have degrees of polymerization of the order of magnitude of the reciprocal would be miscible. For example, it is predicted that PpBrSt will become miscible with completely sulfonylated PPO if the respective molecular weights were of the order of 10 000.

ACKNOWLEDGEMENT

This work was supported by the National Science Foundation of the United States of America through funds made available to the US–Yugoslav Joint Board of Scientific and Technical Cooperation.

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