

1998

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Phase behaviour in blends of poly[styrene-co-*ortho*(*para*)-bromostyrene] and phenylsulfonylated poly(2,6-dimethyl-1,4-phenylene oxide) copolymers

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(Received 21 February 1997; accepted 4 August 1997)

Random copolymers of styrene with *ortho*- or *para*-bromostyrene differ substantially in their blend behaviour with partly sulfonylated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO). Copolymers of styrene with *ortho*-bromostyrene exhibit a very narrow window of miscibility in comparison with styrene-*para*-bromostyrene copolymer blends with SPPOs. The experimental results can be accounted for on the basis of individual segmental interaction parameters by applying mean-field theory. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: copolymer-copolymer miscibility; segmental interaction parameters; styrene copolymers)

INTRODUCTION

In contrast to the analogous fluorinated and chlorinated systems, blends of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and poly(*ortho*-bromostyrene-co-*para*-bromostyrene) [poly(*o*BrSt-co-*p*BrSt)] are immiscible over the entire copolymer composition range¹. The poly(*ortho*-bromostyrene) [poly(*o*BrSt)] and poly(*para*-bromostyrene) [poly(*p*BrSt)] homopolymers are also immiscible with PPO¹. However, poly[styrene-co-*ortho*(*para*)bromostyrene] [poly(St-co-*o*(*p*)BrSt)] in blends with PPO show miscibility-immiscibility behaviour which is a function of the copolymer composition^{1,2}. The modification of the PPO molecule by the introduction of the phenylsulfonyl group to form phenylsulfonylated PPO (SPPO) has a further influence on the miscibility of the above-mentioned bromine-containing polymers³. Thus poly(*o*BrSt) was found to be immiscible with any SPPO, independent of the degree of sulfonylation. It was also found that miscibility in blends of poly(*p*BrSt) with SPPO depends on the degree of sulfonylation of PPO³. Mixtures containing SPPO with > 12 mol% sulfonylation are miscible with poly(*p*BrSt). Miscibility of copolymers of *o*BrSt and *p*BrSt was found to depend on the copolymer composition as well as on the degree of sulfonylation of the SPPO⁴. On the basis of these results it can be expected that for SPPO copolymers in blends with poly[St-co-*o*(*p*)BrSt] both the degree of sulfonylation and the composition of the latter will determine miscibility.

This paper presents results for miscibility of blends of random copolymers of styrene with *o*(*p*)BrSt with SPPO of different degrees of sulfonylation, and analyses these results on the basis of the respective segmental interaction parameters by applying mean-field theory⁵.

EXPERIMENTAL

Materials

The poly(*o*BrSt) and poly(*p*BrSt) homopolymers and the poly[St-co-*o*(*p*)BrSt] copolymers were prepared by free-radical polymerization in toluene at 60°C with azo-*bis*-isobutyronitrile (AIBN) as initiator. The polymerization was carried out in thermostatted glass vials under purified nitrogen. After the required reaction time the vial was cooled and the copolymer was precipitated by addition to cold methanol. The precipitated copolymer was filtered and dried in vacuum at 60°C overnight. The conversion was limited to ~20 wt%. The copolymer compositions, T_g values and molecular weights of the copolymers prepared are presented in Table 1.

PPO powder (General Electric Co.; $M_w = 35\,000$, $M_n = 17\,000$, g.p.c.) was purified by dissolution in toluene and was used in the preparation of SPPO copolymers.

Random SPPO copolymers were obtained by Friedel-Crafts phenylsulfonylation of PPO⁶. SPPO copolymers with a range of sulfonylation from 3.8 to 91 mol% were prepared.

Polymer blends were prepared by dissolving appropriate quantities of the pure components in chloroform and precipitating by pouring into a large excess of methanol. Blends were dried at 100°C in vacuum for 60 h. The dried 'as precipitated' blends were used in d.s.c. experiments.

Physicochemical measurements

The styrene-bromostyrene copolymer compositions were determined by bromine analysis, while the degree of phenylsulfonylation of the SPPO copolymers was determined by elemental analysis and from ¹H n.m.r. spectrometry. Molecular weights, based on calibration with monodisperse polystyrene standards (Polymer

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Table 1 Characteristics of poly(St-co-*o*BrSt) and poly(St-co-*p*BrSt) copolymers and of phenylsulfonfylated copolymers (SPPO)

| Sample | T_g (°C) | Molecular weight | | |
|---|------------|------------------|------------------|-----------|
| | | M_w (10^4) | M_n (10^4) | M_w/M_n |
| Poly(St-co- <i>o</i> BrSt) ^a | | | | |
| 10.9 | 114 | 10.7 | 6.4 | 1.7 |
| 20.4 | 118 | 9.4 | 5.8 | 1.6 |
| 27.8 | 120 | 10.3 | 6.3 | 1.6 |
| 40.9 | 124 | 10.6 | 6.4 | 1.6 |
| 48.6 | 130 | 11.0 | 6.5 | 1.7 |
| 55.5 | 137 | 11.9 | 7.4 | 1.6 |
| 63.2 | 139 | 11.2 | 6.5 | 1.7 |
| 75.4 | 140 | 9.6 | 5.7 | 1.7 |
| 88.0 | 153 | 12.2 | 7.0 | 1.7 |
| Poly(St-co- <i>p</i> BrSt) ^b | | | | |
| 10.6 | 116 | 11.4 | 6.2 | 1.8 |
| 18.6 | 120 | 10.7 | 6.6 | 1.6 |
| 26.0 | 125 | 12.1 | 7.3 | 1.6 |
| 33.6 | 127 | 13.6 | 8.3 | 1.6 |
| 44.2 | 130 | 12.5 | 7.7 | 1.6 |
| 55.8 | 135 | 14.1 | 8.6 | 1.6 |
| 67.5 | 139 | 13.9 | 8.3 | 1.7 |
| 80.1 | 145 | 16.0 | 9.2 | 1.7 |
| 90.4 | 147 | 16.4 | 9.8 | 1.7 |
| SPPO copolymers ^c | | | | |
| 3.5 | 222 | 0.393 | 0.147 | 2.67 |
| 9.3 | 230 | 0.430 | 0.172 | 2.50 |
| 11.5 | 236 | 0.438 | 0.160 | 2.74 |
| 15.5 | 241 | 0.445 | 0.167 | 2.67 |
| 19.4 | 247 | 0.481 | 0.178 | 2.70 |
| 25.4 | 253 | 0.500 | 0.180 | 2.78 |
| 29.0 | 255 | 0.520 | 0.173 | 3.01 |
| 36.7 | 263 | 0.610 | 0.210 | 2.90 |
| 45.0 | 268 | 0.580 | 0.200 | 2.90 |
| 49.3 | 261 | 0.590 | 0.200 | 2.95 |
| 55.0 | 271 | 0.593 | 0.190 | 3.12 |
| 60.8 | 277 | 0.615 | 0.220 | 2.80 |
| 66.0 | 284 | 0.710 | 0.248 | 2.86 |
| 75.0 | 292 | 0.730 | 0.245 | 2.98 |
| 84.0 | 298 | 0.730 | 0.230 | 3.17 |
| 87.0 | 301 | 0.720 | 0.210 | 3.43 |
| 91.0 | 306 | 0.780 | 0.230 | 3.39 |

^a*o*BrSt content (mol%)^b*p*BrSt content (mol%)^cDegree of sulfonation of SPPO (mol%)

Laboratories) were determined by g.p.c. (Varian HPGPC model 8500, μ -Styragel columns, in THF at room temperature).

Glass transition temperatures (T_g) of the polymers and polymer blends were measured with a Perkin-Elmer DSC-2 at a heating rate of 20°C min⁻¹ under nitrogen. T_g was taken as the inflection point of the heat capacity discontinuity in the second scan.

Thermogravimetric measurements were made with a Perkin-Elmer TGS-2 thermobalance at a heating rate of 10°C min⁻¹ under nitrogen.

RESULTS AND DISCUSSION

The composition of all blends of SPPO and poly[St-co-*o*(*p*)BrSt] studied was 50/50 wt%. Miscibility in the blends was characterized by d.s.c. The usual single- T_g criterion was used for assessing miscibility. Initially miscible polymer blends, i.e. 'as precipitated' blends, were further analysed by annealing at temperatures of 200, 250 and 300°C. The annealing experiments were performed in the d.s.c. by applying the usual protocol⁷, which consisted in heating the samples to the chosen temperature, annealing for 15 min and quenching to ambient temperature as rapidly as possible. The quenched samples were then reheated at

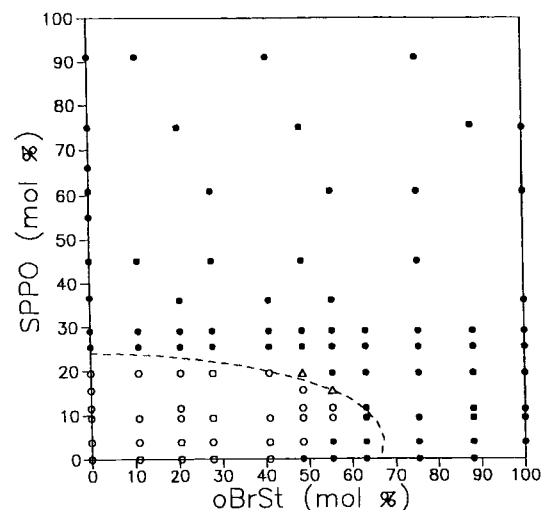


Figure 1 Miscibility of 50/50 wt% blends of poly(St-co-*o*BrSt) and SPPO copolymers, annealed at 200°C. (O) One phase; (●) two phases; (Δ) intermediate situation; (---) calculated miscibility-immiscibility boundary (see text)

20°C min⁻¹ to determine whether one or two phases were present.

Thermal stability of the blends was evaluated by thermogravimetric analysis by measuring weight loss. It was found that weight loss for each blend system studied was < 1.4 wt% at the highest temperature used, 300°C. Hence it was concluded that thermal degradation was not of importance in these experiments.

Poly(St-co-*o*BrSt)–SPPO blends

In this system, for the blends 'as-precipitated' and for those annealed at 200°C, a single T_g was observed for the poly(St-co-*o*BrSt) copolymers with *o*BrSt content from 10.9 to 48.9 mol% and for SPPO copolymers of sulfonation degree from 3.8 to 19.4 mol%. In these compositions the only uncertainty encountered was for the sample containing 48.9 mol% *o*BrSt, which showed partial miscibility with SPPO of sulfonation degree 19.4 mol%. Copolymers containing 55.5 mol% of *o*BrSt are miscible when blended with SPPO of degrees of sulfonation 9.3 and 11.5 mol% respectively and are partly miscible with blends of SPPO with degree of sulfonation 15.5 mol%. All other blends exhibited two T_g values. These results are shown in Figure 1, in which data for blends containing the respective homopolymers are also shown.

All blends miscible at 200°C were further examined at 250 and 300°C. The miscibility boundaries for some composition ranges significantly overlapped (Figure 2). For the blends annealed at 300°C, the only further difference observed was that the samples with 55.5 mol% *o*BrSt became immiscible with SPPOs of degrees of sulfonation 9.3 and 11.5 mol%.

Poly(St-co-*p*BrSt)–SPPO blends

The miscibility domain for this system is quite wide for all poly(St-co-*p*BrSt) copolymers containing from 10.6 to 90.4 mol% *p*BrSt and for SPPO copolymers of widely differing degrees of sulfonation. The miscibility domain is narrowed for the blends with lower contents of *p*BrSt in the copolymer. Thus, for example at a *p*BrSt content of 10.6 mol%, miscibility was found with the SPPO copolymers of degrees of sulfonation from 3.8 to 19.4 mol%.

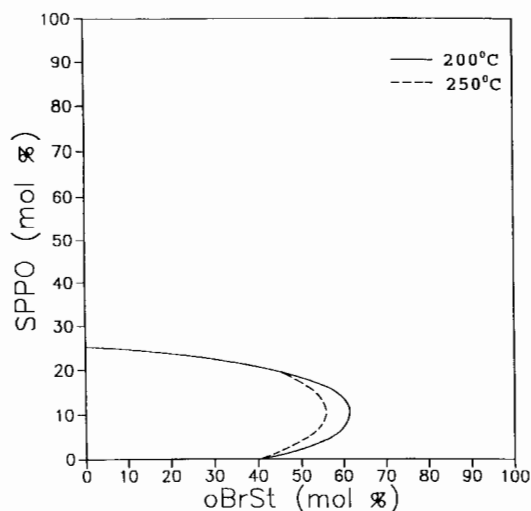


Figure 2 Miscibility of 50/50 wt% blends of poly(St-co-*o*BrSt) and SPPO copolymers, annealed at 200 and 250°C. Individual data points omitted for clarity

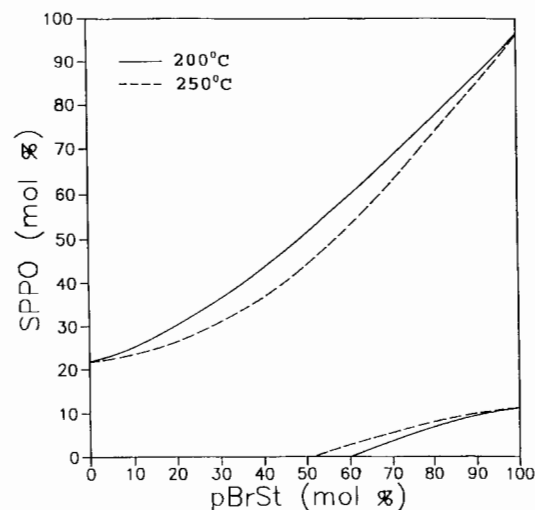


Figure 4 Miscibility of 50/50 wt% blends of poly(St-co-*p*BrSt) and SPPO copolymers, annealed at 200 and 250°C. Individual data points omitted for clarity

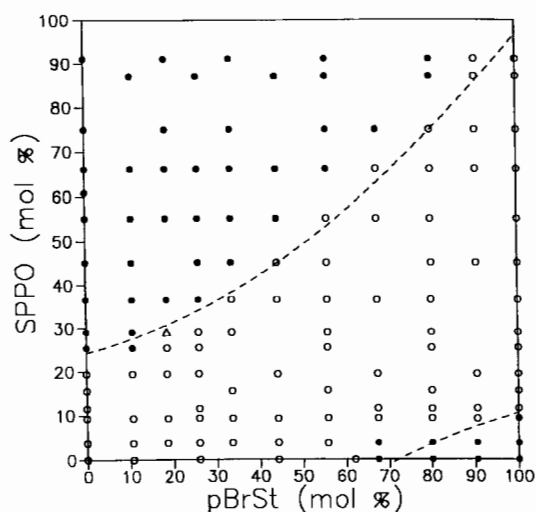


Figure 3 Miscibility of 50/50 wt% blends of poly(St-co-*p*BrSt) and SPPO copolymers, annealed at 200°C. (○) one phase; (●) two phases; (Δ) intermediate situation; (---) calculated miscibility–immiscibility boundary

With a *p*BrSt content of 55.8 mol% in the copolymer the miscibility window for blends containing SPPO copolymers is for sulfonation degrees from 3.8 to 55 mol%. For copolymers of the highest *p*BrSt content, 90.4 mol%, miscibility is observed with SPPOs with degrees of sulfonation from 8.3 to 91 mol%. These results (Figure 3) are the same for ‘as-precipitated’ blends and for blends annealed at 200°C.

On annealing the miscible blends at 250°C, some changes were observed, Figure 4. At 300°C there were no further changes in comparison with the results at 250°C. The decrease in miscibility for both systems with increasing temperature indicates that these blends show LCST behaviour.

Segmental interaction parameters

By using the mean-field approach⁵, the phase behaviour of these blends of SPPO with poly(St-co-*o*BrSt) and poly(St-co-*p*BrSt) can be analysed. The overall interaction

Table 2 Segmental interaction parameters, χ_{ij} , at 200°C

| Segment pair | χ_{ij} |
|--------------------|---------------------|
| PO, <i>o</i> BrSt | 0.029 ^a |
| SPO, <i>o</i> BrSt | 0.270 ^a |
| PO, <i>p</i> BrSt | 0.035 ^a |
| SPO, <i>p</i> BrSt | 0.013 ^a |
| PO,SPO | 0.318 ^a |
| St,PO | -0.043 ^b |
| St,SPO | 0.385 ^c |
| St, <i>o</i> BrSt | 0.007 |
| St, <i>p</i> BrSt | 0.051 |

^aFrom ref.3

^bFrom ref.9

^cFrom ref.10

parameter, χ_{blend} , for the copolymer–copolymer blend systems of the type $(A_{1-x}B_x)_{n_1}/(C_{1-y}D_y)_{n_2}$ can be expressed as a linear combination of the segmental interaction parameters:

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

in terms of the respective copolymer compositions and DPs. For the blend systems in this study, A, B, C and D represent St, *o*BrSt or *p*BrSt, PPO and SPPO units respectively. The first four terms on the right-hand side of equation (1) define additive interactions between the non-bonded component monomer units in the mixtures of the two copolymers, weighted according to the copolymer compositions; the remaining two terms reflect intramolecular interactions between the two different monomers constituting each of the copolymers.

A quantitative determination of χ_{ij} requires the best fit of the observed miscibility–immiscibility boundaries as a function of copolymer composition and the mean-field equation to be obtained by a minimization procedure⁸. For the present systems, five of the six χ_{ij} parameters required in equation (1) are already available from our earlier investigations^{3,9,10}. The sixth χ_{ij} , namely χ_{AB} , was treated as an adjustable parameter and was obtained by fitting the miscibility–immiscibility boundary to the mean-field equation.

Table 3 Coefficients in equation (5) and miscibility conditions for systems

| System | <i>a</i> | <i>b</i> | <i>c</i> | <i>d</i> | <i>e</i> | <i>f</i> | <i>b</i> ² | <i>b</i> ² – 4 <i>ac</i> | Centre of hyperbola, <i>f</i> (<i>x_c</i> , <i>y_c</i>) (<i>x_c</i> , <i>y_c</i>) | <i>f</i> (<i>x_c</i> , <i>y_c</i>) |
|---------------------------------|----------|----------|----------|----------|----------|----------|-----------------------|-------------------------------------|--|--|
| Poly(St-co- <i>o</i> BrSt)–SPPO | 0.0070 | – 0.187 | 0.318 | 0.065 | 0.110 | – 0.047 | 0.035 | 0.026 | 237.5; 52.5 | > 0 |
| Poly(St-co- <i>p</i> BrSt)–SPPO | 0.0510 | – 0.450 | 0.318 | 0.027 | 0.110 | – 0.047 | 0.203 | 0.138 | 48.4; 17.0 | < 0 |

The conformational entropic term $\chi_{\text{blend}}^{\text{crit}}$ was calculated from the degree of polymerization of the respective blend components by the usual expression:

$$\chi_{\text{blend}}^{\text{crit}} = \frac{1}{2} \left[\frac{1}{\sqrt{n_1}} + \frac{1}{\sqrt{n_2}} \right]^2 \quad (2)$$

For the systems considered in this study, the value of 0.004 was used for $\chi_{\text{blend}}^{\text{crit}}$, corresponding to $n_1 = 1000$ and $n_2 = 300$ (Table 1) and the data given in ref. 6.

The values of the unknown segmental interaction parameters for the two systems, i.e. $\chi_{AB} \equiv \chi_{\text{St},o\text{BrSt}}$ and $\chi_{AB} \equiv \chi_{\text{St},p\text{BrSt}}$, were obtained on the basis of experimental data for SPPO–poly[St-co-*o*(*p*)BrSt] blends obtained in this study, previous miscibility results for PPO–poly[St-co-*o*(*p*)BrSt] and PS–poly[St-co-*o*(*p*)BrSt] blends² and χ parameters given in refs 3, 9 and 10. The dashed lines in Figures 1 and 3 represent calculated miscibility–immiscibility boundaries at 200°C for the SPPO–poly(St-co-*o*BrSt) and SPPO–poly(St-co-*p*BrSt) systems respectively. It can be seen that a good correlation was obtained between theoretical evaluation and experiment. The values of the segmental interaction parameters for all binary combinations of SPPO with poly(St-co-*o*BrSt) and poly(St-co-*p*BrSt) derived in this way, together with the results from earlier studies, are listed in Table 2.

The miscibility–immiscibility boundary, at which $\chi_{\text{blend}} = \chi_{\text{blend}}^{\text{crit}}$, can be described by a function expressed in terms of *x* and *y* such that

$$f(x, y) = \chi_{\text{blend}} - \chi_{\text{blend}}^{\text{crit}} = 0 \quad (3)$$

Equation (1) can be written in quadratic form:

$$\begin{aligned} x^2\chi_{AB} + y^2\chi_{CD} + (\chi_{AC} - \chi_{AD} - \chi_{BC} + \chi_{BD})xy \\ + (\chi_{BC} - \chi_{AB} - \chi_{AC})x + (\chi_{AD} - \chi_{AC} - \chi_{CD})y \\ + (\chi_{AC} - \chi_{\text{blend}}^{\text{crit}}) = 0 \end{aligned} \quad (4)$$

or generally,

$$ax^2 + by^2 + cxy + dx + ey + f = 0 \quad (5)$$

from which solutions can be readily obtained in the *xy* plane. Hence all constants of the generalized quadratic equation are directly related to the χ_{ij} parameters. The geometric form of *f*(*x*, *y*) depends on the sign and magnitude of the χ_{ij} parameters. Because the degree of polymerization of all the blend constituents is relatively high, miscibility in these copolymer systems is overwhelmingly a consequence of specific binary interactions. The shape of the miscibility boundary curves is determined by the difference in interaction strengths between different copolymer segments.

The generalized quadratic equation predicts the isothermal miscibility–immiscibility boundary to be hyperbolic for both blend systems investigated in this study, i.e. the

condition¹¹:

$$b^2 - 4ac > 0 \quad (6)$$

is fulfilled for both cases (Table 3). For the SPPO–poly(St-co-*o*BrSt) system (Figure 1) the miscibility domain lies within one branch of the hyperbola. Its location is determined by the sign of *f*(*x*, *y*) in the centre of the hyperbola (Table 3)¹⁰. For the SPPO–poly(St-co-*p*BrSt) system (Figure 3) the miscibility domain is defined by the area between the two branches of the hyperbola. Consideration of the *b*² term (Table 3), which represents the contribution of segmental dissimilarity, shows that the SPPO–poly(St-co-*p*BrSt) system should exhibit a wider miscibility regime than the SPPO–poly(St-co-*o*BrSt) blend system, in agreement with the experimental results, Figures 1 and 3.

To summarize these results, it is evident that good agreement exists between the miscibility–immiscibility boundaries obtained experimentally and those calculated by a mean-field approach. It is also evident that the interaction parameters derived previously^{3,9,10} are sufficiently quantitative to be of predictive value for the copolymer systems studied here. Moreover, the results show that the degree of phenylsulfonylation of SPPO is the principal factor determining miscibility in these systems.

ACKNOWLEDGEMENTS

This work was supported by the National Science Foundation (USA) and the Ministry of Science, Republic of Croatia, as a joint project between INA–Research and Development, Zagreb and the Polymer Science and Engineering Department, University of Massachusetts, Amherst, MA. F.E.K. also acknowledges support from AFOSR.

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