

# Miscibility in Blends of Sulfonated Poly(2,6-dimethyl-1,4-phenylene oxide) and Poly(*p*-bromostyrene-*co*-*o*-bromostyrene)

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## SYNOPSIS

Miscibility in blends of random copolymers of *p*-bromostyrene (*p*BrSt) and *o*-bromostyrene (*o*BrSt) [P(*p*BrSt-*co*-*o*BrSt)] with partially sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) have been studied by differential scanning calorimetry (DSC). For an SPPO of given degree of sulfonation, a miscibility window in terms of the isomeric composition of the brominated copolymer was seen; the location and width of the window was a function of sulfonation. In general, copolymers with a higher content of *p*BrSt exhibit miscibility with SPPOs with higher degrees of sulfonation. Upon annealing to temperatures of 280° and 320°C, only small changes in the miscibility regime were observed. The miscibility behavior was analyzed on the basis of the mean-field theory in terms of the individual segmental interaction parameters. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

The miscibility of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with polymers of brominated styrene derivatives has been extensively studied.<sup>1-3</sup> *Ortho*- and *para*-bromostyrene homopolymers were found to be immiscible with PPO.<sup>1</sup> The miscibility of poly(*o*-(*p*-)bromostyrene-*co*-styrene)/PPO blends depends on the copolymer composition,<sup>1,2</sup> with maxima in the brominated styrene contents which is isomer dependent. Miscibility and phase separation behavior in PPO and poly(*o*-(*p*-)fluorostyrene-*co*-*o*-(*p*-)bromostyrene) blends has also been studied. Of the four possible copolymer permutations, miscibility was observed only for PPO/(poly(*o*-fluorostyrene-*co*-*p*-bromostyrene) blends containing between 11 and 73 mol % *p*-bromostyrene.<sup>3</sup> It has also been established that none of the copolymers of *o*-BrSt and *p*-BrSt are, themselves, miscible with PPO.<sup>1</sup> This differs, therefore, from the behavior of the corresponding fluorinated and chlorinated

systems. All these results can be accounted for on the basis of first-order mean-field theory.<sup>4</sup>

In a continuation of our studies of the miscibility of random copolymers and homopolymers of halogenated styrene derivatives, we have investigated miscibility in blends of these materials with partially sulfonated PPO (SPPO).<sup>5-7</sup> For all the *p*-substituted styrene homopolymers with SPPO blends studied (i.e., with F, Cl, and Br), limited miscibility regimes have been found.<sup>5</sup> Miscibility was also observed in P(*o*FSt)/SPPO blends. However, P(*o*ClSt) and P(*o*BrSt) are not miscible with SPPO of any degree of sulfonation.<sup>5</sup> For blends of SPPO with P(*p*FSt-*co*-*o*FSt)<sup>6</sup> and with P(*p*Cl-*co*-*o*Cl)<sup>7</sup> it was found that the window of miscibility depends on both the copolymer composition and the degree of sulfonation of the SPPO. This is in accord with the copolymer miscibility theory, from which it is anticipated that intrachain repulsion of the sulfonated and nonsulfonated segments in the SPPO chain would, in general, enhance miscibility.

We now report on the miscibility and phase behavior of SPPO/P(*p*BrSt-*co*-*o*BrSt) blends, particularly relevant in light of the immiscibility of PPO itself with these copolymers. Again, the experimental

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results will be discussed in the context of a mean-field treatment.<sup>4</sup>

## EXPERIMENTAL

### Materials

Poly(*p*BrSt-*co*-*o*BrSt) of high molecular weights and varying isomer composition were prepared by free radical polymerization in toluene as previously described.<sup>2</sup> Molecular weights and glass transition temperatures of the samples used are listed in Table I.

PPO, supplied by General Electric Co., was purified by dissolution in toluene and precipitated in an excess of methanol ( $M_w = 35000$ ;  $M_n = 17000$ ). SPPO copolymers containing systematically varying levels of phenylsulfonation (3.5, 8.6, 12, 16, 25, 31, 39, 46, 55, 63, 68, 75, 84, 87, and 92 mol %) were prepared by a Friedel-Crafts sulfonation of PPO.<sup>8,9</sup> Polymer blends (50/50 wt %) were prepared by coprecipitation from toluene solutions. The resulting precipitates were filtered and dried under vacuum at 80°C for about 60 h. The dried precipitate was used in the DSC experiments.

### 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°/min under nitrogen was employed. Glass transition temperature(s) were taken as the

inflection point in the heat capacity discontinuity in the second scan. The annealing experiments also were carried out in the DSC. In a typical experiment, a given sample was heated at the highest available rate to a selected temperature and held at this temperature for 15 min. The sample was then rapidly quenched to room temperature and subsequently scanned at 20°C/min, to observe whether one or two discontinuities in the heat capacity were present.

The thermal stability of the blends was evaluated by thermogravimetric analysis (Perkin-Elmer TGS-2) in which samples were heated at a rate of 10°C/min with a nitrogen purge. These samples were predried at 200°C in the TGA furnace to remove traces of absorbed water and then heated from 50° to 320°C to determine weight loss.

Molecular weights, based on a calibration with monodisperse polystyrene standards (Polymer Laboratories), were determined by GPC (Varian HPGPC, Model 8500) using  $\mu$ -Styragel columns in tetrahydrofuran at 25°C.

## RESULTS AND DISCUSSION

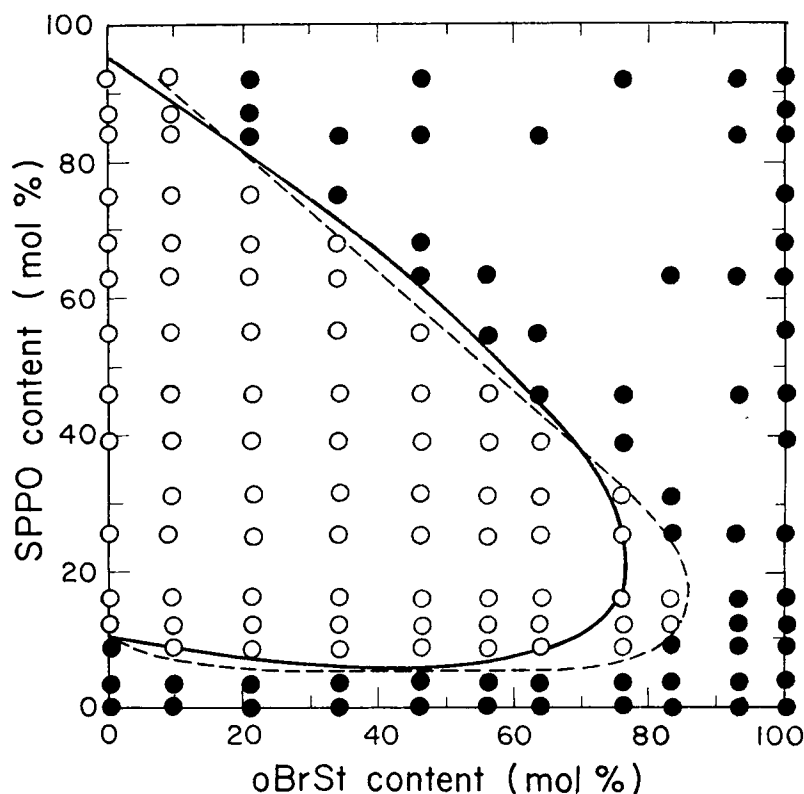
The thermal stability of the blends at temperatures up to 320°C was determined by measuring the weight loss in TGA experiments. The maximum weight loss in all cases was below 1 wt %. From these data it was concluded that thermal degradation was not an important factor in this study.

The miscibility of the blends was determined by the usual criterion of a single glass transition in the DSC measurements. Blends that were found to exhibit miscibility using samples precipitated as described above, were investigated further at annealing temperatures of 200°, 280°, and 320°C.

Figure 1 summarizes the results for 50/50 wt % blends annealed at 200°C, plotted in terms of copolymer contents. As previously shown,<sup>5</sup> miscibility occurs in P(*p*BrSt)/SPPO blends with SPPOs sulfonated from 12 to 92 mol % (left ordinate). None of the blends containing pure PPO were miscible, and immiscibility was also found for all blends with SPPO of sulfonation degree of 3.5 mol %, regardless of bromostyrene copolymer composition. As can be seen, miscibility in other SPPO/P(*p*BrSt-*co*-*o*BrSt) blends is significantly influenced by the degree of sulfonation of the SPPO. P(*o*BrSt) is, however, immiscible with any SPPO.<sup>5</sup> It should be noted that the as-precipitated blends show essentially the same behavior as those annealed at 200°C except for the blend with the SPPO (sulfonation degree of 92 mol %) in which miscibility was observed. At annealing temperatures of 280° and

**Table I** Molecular Weights and Glass Transition Temperatures of P(*p*BrSt-*co*-*o*BrSt) Copolymers

Copolymer Composition (Mol Fraction of <i>o</i> BrSt) $\chi$	$M_w \times 10^{-5}$	$M_n \times 10^{-5}$	$T_g$ (°C)
P( <i>p</i> BrSt)			
0.0	1.5	0.86	144
P( <i>p</i> BrSt <sub>1-x</sub> - <i>co</i> - <i>o</i> BrSt <sub>x</sub> )			
0.10	2.2	1.2	144
0.21	2.2	1.2	144
0.34	2.2	1.1	144
0.46	2.3	1.2	144
0.56	2.3	1.2	145
0.64	2.3	1.1	145
0.76	2.4	1.2	147
0.83	2.4	1.2	147
0.93	2.4	1.2	147
P( <i>o</i> BrSt)			
1.0	1.12	0.66	147



**Figure 1** Miscibility of 50/50 wt % blends of P(*p*BrSt-*co*-*o*BrSt)/SPPO: (○) one phase; (●) two phases; 200°C. Dashed line: experimental miscible-immiscible boundary, 200°C. The solid curve is the boundary calculated with a two adjustable parameter fit (see text) at 200°C.

320°C, relatively minor changes in miscibility were observed; the area of the miscibility domain decreases somewhat at the higher temperatures, implying that this system also demonstrated LCST behavior.

The influence of blend composition on glass transitions was studied for samples containing SPPO copolymers containing 16, 46, and 75 mol % sulfonation, respectively, with brominated styrene

copolymers containing 9.7 mol % *o*BrSt (Fig. 2) and for the blend of SPPO with the sulfonation degree of 16 mol % with copolymer containing 75 mol % *o*BrSt (Fig. 3). In all these miscible blends the dependence of the glass transition temperatures on composition show only small deviations from linearity. The  $T_g$ -composition curves can be fitted with the usual Gordon-Taylor equation:<sup>10</sup>

$$T_g = (W_1 T_{g1} + kW_2 T_{g2}) / (W_1 + kW_2) \quad (1)$$

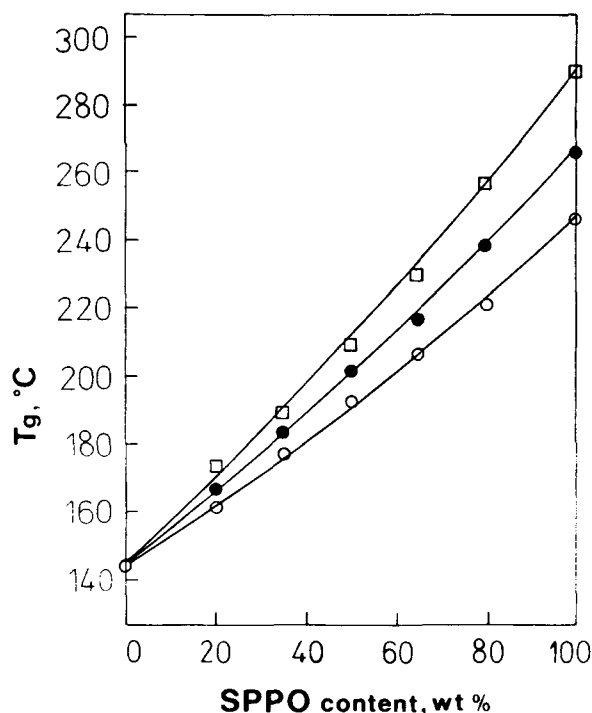
where  $T_g$ ,  $T_{g1}$ , and  $T_{g2}$  are the measured glass transition temperatures of the blend, and of pure components 1 and 2, respectively,  $W_1$  and  $W_2$  are the respective weight/fractions, while  $k$  is an adjustable semiempirical constant obtained here by a least squares fit. It was found that a value  $k = 0.85 \pm 0.01$  fit all the data in Figure 2;  $k = 0.76$  gave the best fit for the blend containing the SPPO with the lower degree of sulfonation, Figure 3. Prud'homme<sup>11</sup> has suggested that  $k$  values represent a semiquantitative measure of interaction; we could not draw this conclusion on the basis of our limited data or of that in earlier, related, studies.<sup>6,7,9</sup>

**Table II** Segmental Interaction Parameters at 200°C

Segment Pair	$\chi_{ij}$
PO,SPO	0.318 <sup>a</sup>
SPO, <i>o</i> BrSt	0.27
<i>p</i> BrSt, <i>o</i> BrSt	0.065
PO, <i>p</i> BrSt	0.035 <sup>a</sup>
PO, <i>o</i> BrSt	0.029 <sup>b</sup>
SPO, <i>p</i> BrSt	0.013 <sup>a</sup>
$\chi_{blend}^{crit}$	0.004

<sup>a</sup> Reference 5.

<sup>b</sup> Reference 2.



**Figure 2** Glass transition temperatures (points and squares), and fitted curves (—) versus composition for blends: (O) P(*p*BrSt-*co*-*o*BrSt) containing 9.7 mol % *o*BrSt, with SPPO of the sulfonylation degree of 16 mol %; (●) P(*p*BrSt-*co*-*o*BrSt) containing 9.7 mol % *o*BrSt, with SPPO of the sulfonylation degree of 46 mol %; (□) P(*p*BrSt-*co*-*o*BrSt) containing 9.7 mol % *o*BrSt with SPPO of the sulfonylation degree of 75 mol %.

### Segmental Interaction Parameters

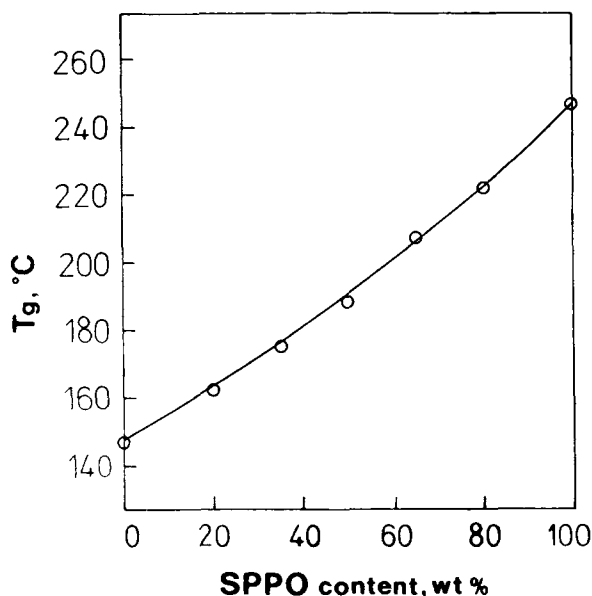
The data provided by these experiments, together with results from previously published studies, have been combined to calculate the individual segmental interaction parameters. These calculations are based on a first-order mean-field theory of phase behavior in copolymer blends.<sup>4</sup> The expression for the overall interaction parameters,  $\chi_{\text{blend}}$ , of two copolymers, i.e., blends of the type  $(A_{1-x}B_x)_{n1}/(C_{1-y}D_y)_{n2}$ , is given by the equation:

$$\begin{aligned} \chi_{\text{blend}} = & (1-x)(1-y)\chi_{AC} \\ & + (1-x)y\chi_{AD} + x(1-y)\chi_{BC} + xy\chi_{BD} \\ & - x(1-x)\chi_{AB} - y(1-y)\chi_{CD} \quad (2) \end{aligned}$$

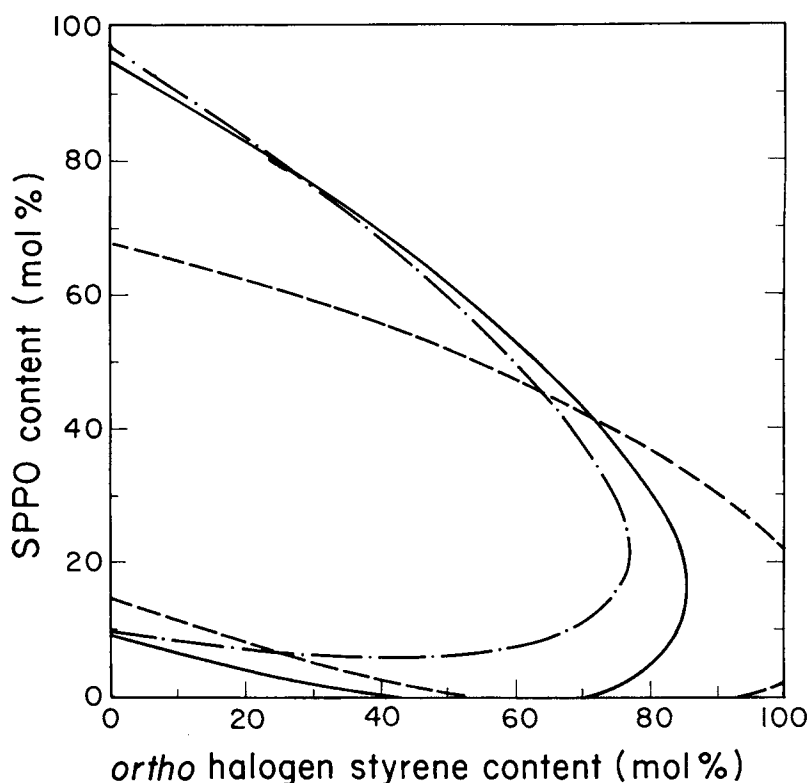
In the present case A, B, C, and D represent *p*BrSt, *o*BrSt, PO, and SPO units, respectively. Six binary segmental interaction parameters are, thus, required to describe the system. The segmental interaction parameter for the PO,*o*BrSt segment pair at 200°C (0.029) has been obtained from the miscibility stud-

ies of the PS/(St-*co*-*o*BrSt) and PPO (St-*co*-*o*BrSt) blends.<sup>2</sup> Three further binary segmental interaction parameters,  $\chi_{\text{PO},p\text{BrSt}}$ ,  $\chi_{\text{SPO},p\text{BrSt}}$ , and  $\chi_{\text{PO},\text{SPO}}$ , were obtained from the experimental data discussed in reference 5. The remaining parameters,  $\chi_{p\text{BrSt},o\text{BrSt}}$  and  $\chi_{o\text{BrSt},\text{SPO}}$ , were obtained from a best least-squares fit of the present data taking into account that the entropic, molecular weight related, term  $\chi_{\text{blend}}^{\text{crit}} = 0.004$ . The results are collected in Table II. Experimental results and the calculated boundary are in good, but not perfect, agreement as expected for a two parameter fit (Fig. 1), and to this extent support the validity of the simple mean-field theory.<sup>4</sup> The shape of the elliptical boundary curves, especially near the extrema, is highly sensitive to the value of the  $\chi_{ij}$ ; we estimate the latter are accurate to  $\pm 10\%$ .

The results show that the polar phenylsulfonyl group attached to the phenylene oxide segment has a predominant effect on miscibility in these systems. A comparison of the miscibilities of the three halogenated styrene copolymers with SPPO is instructive (Fig. 4). It can be seen that the results for the brominated and chlorinated systems are qualitatively similar and highly asymmetric with respect to the isomer contents of the respective copolymers. The wide miscibility window along the *para*-substituent ordinate implies that this is a result of the



**Figure 3** Glass transition temperature experimental data (points) and fitted curve (—) versus composition for the blend P(*p*BrSt-*co*-*o*BrSt) containing 9.7 mol % *o*BrSt with SPPO of the sulfonylation degree of 16 mol %.



**Figure 4** Miscibility domains for the *para,ortho* halogen substituted styrene copolymers with SPPO copolymers, 200°C. Fluoro- (---), chloro- (—), and bromo- (- · -) substituted systems, references 5 and 6, and this work, respectively.

severe repulsion between the SPO and PO moieties; *ortho*-substitution is a strong inhibitor of miscibility, demonstrated by the total absence of miscibility along the *ortho*-substituent ordinate. In the case of fluoro-substitution, the isomeric effect is considerably smaller and the miscibility domain is more nearly described by a band parallel to the abscissae whose width is primarily a result of the aforementioned repulsion between the substituted and unsubstituted phenylene oxide moieties. Thus, the *ortho-para*-substituent effect in the fluoro-system accounts for the observed asymmetry, but cannot as yet be explained in any reasonable *a priori* manner.

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