

## Miscibility–immiscibility behaviour in blends of phenylsulfonated Poly(2,6-dimethyl-1,4-phenylene oxide) and Poly[styrene-co-*ortho*(*para*)-chlorostyrene]

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### Abstract

Miscibility in blends of random copolymers of poly[styrene-co-*ortho*(*para*)chlorostyrene] with partially sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) has been studied. Evidence from DSC measurements shows the window of miscibility is influenced by both, the chlorine atom position on the benzene ring and the degree of sulfonation of SPPO. Copolymers containing *para*-chlorostyrene exhibit miscibility window with SPPO of much higher degree of sulfonation than the corresponding copolymers of styrene with *ortho*-chlorostyrene. Good agreement was obtained between the miscibility–immiscibility boundaries obtained experimentally and by those calculated in terms of the individual segmental interaction parameters using a mean-field approach. © 1997 Elsevier Science B.V.

**Keywords:** Miscibility; Poly[styrene-co-*ortho*(*para*)chlorostyrene]; Poly(2,6-dimethyl-1,4-phenylene oxide); DSC

### 1. Introduction

Previously, it was shown that blends of high molecular weight poly(*ortho*-chlorostyrene) [poly(oClSt)] or poly(*para*-chlorostyrene) [poly(pClSt)] with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) are immiscible at all blend compositions [1,2]. Miscibility of PPO blends with random copolymers of styrene (St) and oClSt or pClSt, depends on the copolymer composition and, to some extent, on the location of the substituent on the aromatic ring [1–3]. Recently, we also investigated miscibility in blends of poly(oClSt)

and poly(pClSt) homopolymers with partially sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) copolymers (SPPO) [4]. Blend of SPPO/poly(oClSt) exhibited two  $T_g$ 's for all SPPO samples studied, i.e. with copolymer samples containing from 4 to 92 mol% SPPO. In poly(pClSt)/SPPO blends, however, miscibility was observed in blends with copolymers containing more than 9 mol% SPPO. No changes in miscibility were observed for any of these samples at the temperatures up to 593 K. Since these blends are thermally very stable, there appears to be a new class of materials. In the continuation of our studies of the miscibility of SPPO copolymers, we have investigated miscibility of poly(St-co-oClSt) and poly(St-co-pClSt) copolymers with SPPO of different degrees of sulfonation. On the basis of previous

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results, we would expect that miscibility would be a function of the composition of both copolymer species. The miscibility behaviour was analyzed on the basis of the mean-field theory in terms of the individual segmental interaction parameters [5].

## 2. Experimental

### 2.1. Materials

Random poly(St-co-oClSt) copolymers containing from 9.2 to 90 mol% oClSt and the poly(St-co-pClSt) copolymers with pClSt content from 10.4 to 89.7 mol% and the respective poly(oClSt) and poly(pClSt) homopolymers were prepared by solution polymerization in toluene at 60°C with azo-bis-isobutyronitrile (AIBN) as initiator. To minimize composition drift, the degree of conversion was held to below 20%. The relevant characterization data are presented in Table 1.

PPO powder (General Electric) was purified by dissolution in toluene ( $M_w = 35\,000$ ,  $M_n = 17\,000$ ; GPC) and was used in the preparation of SPPO copolymers. A series of random SPPO copolymers with the degrees of sulfonylation from 3.8 to 91 mol% (see Table 1) were prepared by Friedel–Crafts sulfonylation of PPO [6,7]. Polymer blends were prepared by co-precipitation of desired quantities of the polymer components from toluene solution with methanol. The dried precipitate (“as-precipitated”) was used for DSC studies.

### 2.2. Physico-chemical measurements

The copolymer composition was determined from the halogen content by elemental analysis. The average molecular weights were determined by GPC at room temperature in THF (Varian HPGPC model 8500, a  $\mu$ -Styrogel column).

Thermogravimetric measurements were made by Perkin–Elmer TGS-2 at a heating rate of 10°C/min with a nitrogen purge.

The glass-transition temperatures ( $T_g$ 's) were measured using Perkin–Elmer DSC-2 at heating rate of 20°C/min under nitrogen.  $T_g$  was taken as the half-height of the corresponding heat capacity change on the thermogram.

Table 1

Molecular weights and  $T_g$ 's of poly(St-co-oClSt) and poly(St-co-pClSt) of different copolymer compositions and sulfonylated PPO copolymers of different degrees of sulfonylation

Sample	$T_g$ (K)	Mol. wt. $\times 10^{-5}$		
		$M_w$	$M_n$	$M_w/M_n$
<i>Poly(St-co-oClSt)</i> <sup>a</sup>				
9.2	386	1.083	0.670	1.6
19.6	388	1.235	0.759	1.6
25.3	389	1.387	0.860	1.6
36.1	392	1.283	0.782	1.6
47.5	392.5	1.332	0.825	1.6
57.7	396	1.433	0.904	1.6
65.9	399	1.425	0.817	1.7
76.1	403	1.555	0.960	1.6
90.0	407	1.420	0.835	1.7
<i>Poly(St-co-pClSt)</i> <sup>b</sup>				
10.4	384	1.236	0.764	1.6
19.3	388	1.229	0.752	1.6
24.1	391.5	1.252	0.744	1.7
40.0	393	1.105	0.673	1.6
50.0	395	1.093	0.648	1.7
59.0	398	1.126	0.700	1.6
65.8	400	0.990	0.531	1.9
78.8	402	0.928	0.572	1.6
89.7	404	0.869	0.520	1.6
<i>SPPO copolymers</i> <sup>c</sup>				
3.8	495	0.393	0.147	2.67
9.3	503	0.430	0.172	2.50
11.5	509	0.438	0.160	2.74
15.5	514	0.445	0.167	2.67
19.4	520	0.481	0.178	2.70
25.4	526	0.500	0.180	2.78
29.0	528	0.520	0.173	3.01
36.7	536	0.610	0.210	2.90
45.0	541	0.580	0.200	2.90
49.3	534	0.590	0.200	2.95
55.0	544	0.593	0.190	3.12
60.8	550	0.615	0.220	2.80
66.0	557	0.710	0.248	2.86
75.0	565	0.730	0.245	2.98
84.0	571	0.730	0.230	3.17
87.0	574	0.720	0.210	3.43
91.0	579	0.780	0.230	3.39

<sup>a</sup> oClSt content in mol%.

<sup>b</sup> pClSt content in mol%.

<sup>c</sup> Degree of sulfonylation of SPPO in mol%.

### 2.3. Calorimetric studies

Since thermal history of the samples has influenced the glass-transition temperature, an initial scan was

made to produce a uniform thermal history in all polymers and polymer blends. Therefore, the reported glass-transition temperatures are from the second scan. All the blends studied were amorphous, and the only distinctive features of the thermograms were glass transitions. The thermal stability of the blends at temperatures up to 573 K was determined by measuring the weight loss in TGA experiments. The maximum weight loss in all cases was < 1.5 wt%, thus indicating 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 “as-precipitated” samples were investigated further at annealing temperatures of 473, 523 and 573 K, respectively. Annealing experiments were carried out in the DSC by applying the usual procedure [8], which consisted in 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  $T_g$  behaviour determined on reheating.

#### 2.4. Poly(St-co-oClSt)/SPPO blends

Miscibility was studied for blends of random styrenic copolymers containing from 9.2 to 90 mol% oClSt and SPPO copolymers with the degrees of sulfonylation from 3.8 to 91 mol% substitution. Fig. 1 summarizes the results for 50/50 wt% blends annealed at 473 K, plotted in terms of copolymer content. It should be noted that the “as-precipitated” blends show the same behaviour as those annealed at 473 K. As it can be seen from Fig. 1, the miscibility exists for the blends containing copolymers with oClSt content from 9.2 to 65.9 mol% and SPPO copolymers with a degree of sulfonylation from 3.8 to 19.4 mol%. For copolymers with 76.1 and 90 mol% of oClSt content, immiscibility was found to be independent of the SPPO sulfonylation degree. The dashed lines represent the calculated miscibility–immiscibility boundaries obtained on the basis of the segmental interaction parameters (see below). The bottom left-hand corner of the miscibility map corresponds to a blend of pure PS and PPO; the bottom right corner corresponds to a blend of pure poly(oClSt) and PPO

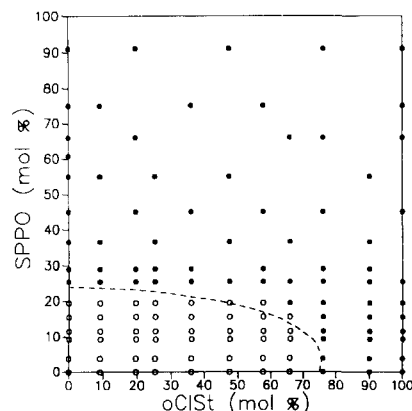


Fig. 1. Miscibility of 50/50 wt% blends of poly(St-co-oClSt) and SPPO copolymers, annealed at 473 K: (○) – one phase; and (●) – two phases.

which is immiscible as previously determined [2,3]. For the PPO/poly(St-co-oClSt) blends miscibility depends on the oClSt content in the copolymer; thus, copolymer blends with oClSt content from 9.2 to 65.9 mol% are miscible with PPO at 473 K, as evident from the abscissa in Fig. 1 [3].

Blends annealed at 473 K, which were miscible, were further analyzed by annealing at the 523 and 573 K. At these temperatures, small changes in the location of the miscibility–immiscibility boundaries were observed for the blends containing copolymers with 47.5, 57.7 and 65.9 mol% oClSt. For the copolymer with 65.9 mol% of oClSt, immiscibility was observed for the blends with SPPO content of 3.8 and 15.5 mol%. Copolymer blends with oClSt content of 47.5 and 57.7 mol% and SPPO copolymers 19.4 mol% sulfonylation also exhibited immiscibility at these temperatures. The phase of none of the other blends separated during annealing at temperatures of 523 or 573 K.

#### 2.5. Poly(St-co-pClSt)/SPPO blends

The miscibility behaviour of this system, for the “as-precipitated” blends and blends annealed at 473 K, is shown in Fig. 2. Miscibility was studied in blends containing poly(St-co-pClSt) with pClSt content from 10.4 to 89.7 mol% and SPPO of the sulfonylation degrees from 3.8 to 91 mol%. A miscibility window exists for nearly all poly(St-co-pClSt) compositions and for different degrees of sulfonyla-

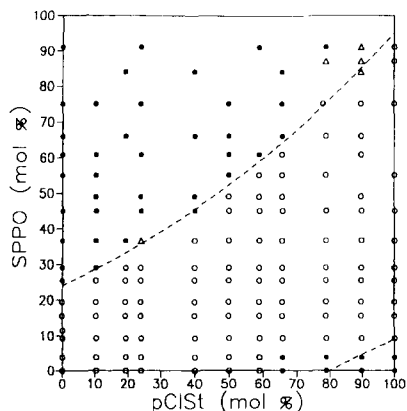


Fig. 2. Miscibility of 50/50 wt% blends of poly(St-co-pClSt) and SPPO copolymers, annealed at 473 K: (○) – one phase; (●) – two phases; and (△) – intermediate situation.

tion of the SPPO with a distinct narrowing as the pClSt content in the copolymers decreases. Thus, for example, miscibility was found in blends containing styrene copolymers with a pClSt content of 89.7 mol% and SPPOs with degrees of sulfonylation from 9.3 to 91 mol%. At pClSt content of 50 mol% miscibility occurs for blends with SPPO having degrees of sulfonylation from 3.8 to 49 mol%. For blends of poly(St-co-pClSt) containing 10.4 mol% of pClSt, miscibility was observed with SPPO copolymers having degree of sulfonylation from 3.8 to 19.4 mol%. In Fig. 2, the left- and right-hand ordinates represent data obtained for blends of the homopolymers PS and poly(pClSt) with SPPO respectively.

We also examined the higher temperature behaviour of these blends by annealing at 523 and 573 K. The results at these temperatures are practically indistinguishable from those for blends annealed at 473 K. Blends of poly(St-co-pClSt) containing 19.3 mol% pClSt with SPPO of the sulfonylation degree of 25.4 mol% become immiscible at 523 K, while blends with pClSt content of 50, 59 and 65.8 mol% with SPPO of the sulfonylation degrees of 49, 55 and 60.8 mol%, respectively, become partially miscible at 523 and 573 K.

## 2.6. Segmental interaction parameters

These miscibility behaviours have been accounted for on the basis of the mean-field theory. The overall interaction parameter,  $\chi_{\text{blend}}$ , between two random

copolymers  $(A_1 - xB_x)_{n_1}$  and  $(C_1 - yD_y)_{n_2}$ , derived by the 1st-order mean-field theory, according to the treatment of ten Brinke et al. [5] is

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

where  $x$  and  $y$  denote the copolymer compositions. At the critical point of miscibility, the interaction parameter,  $\chi_{\text{blend}}$ , is equal to the entropic term,  $\chi_{\text{blend}}^{\text{crit}}$ . Thus, the miscibility-immiscibility boundary is determined by the following relation:

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

where

$$\chi_{\text{blend}}^{\text{crit}} = 0.5(n_1^{-0.5} + n_2^{-0.5})^2 \quad (3)$$

Eq. (2) may be written in general quadratic form:

$$ax^2 + bxy + cy^2 + dx + ey + f = 0 \quad (4)$$

from which solution represents the miscibility-immiscibility boundary in the  $1 \geq x, y \geq 0$  domain in a Cartesian coordinate system in which the abscissa and ordinate represents the composition of the respective copolymers.

The shape and the size of the boundary of the miscibility domain is a function of the signs and relative magnitudes of the six segmental interaction parameters,  $\chi_{ij}$ , representing all possible binary interactions, and the degrees of polymerization of the copolymers,  $n_1$  and  $n_2$ , as defined by Eq. (2). Depending upon the values of the segmental interaction parameters, the generalized quadratic equation (Eq. (4)) predicts that the isothermal miscibility-immiscibility boundary can be, according to the sign of  $b^2 - 4ac$  when plotted in a Cartesian coordinate system [9]: an ellipse, if  $b^2 - 4ac < 0$ , a parabola, if  $b^2 - 4ac = 0$ ; or a hyperbola, if  $b^2 - 4ac > 0$ .

The experimental isothermal phase diagrams of random copolymer blends of SPPO with poly(St-co-oClSt) and poly(St-co-pClSt) at 473 K, i.e. miscibility as a function of mole percent of sulfonylated PPO, are shown in Figs. 1 and 2. It can be clearly seen that

copolymers of styrene with pClSt exhibited miscibility with SPPO with a higher degree of sulfonylation than the copolymers containing oClSt. Miscibility in these systems depends on the extent of chlorination and the position of the chlorine on the benzene ring and also upon the degree of sulfonylation of PPO. The results observed in this investigation are consistent with our earlier studies of the miscibility of halogen substituted styrene polymers/copolymers with SPPO [4].

Employing the theory outlined here, the interaction parameters in Eq. (1) or, equivalently, in Eq. (2) can be determined from the experimentally observed miscibility boundaries as a function of copolymer composition, as it was discussed in our previous papers [10–12]. In order to provide unambiguously meaningful values of the required  $\chi_{ij}$  parameters, additional data from the earlier investigations of phase behaviour for different polymer blend systems consisting of the same polymer segments were employed.

For both the systems investigated, the parameter  $\chi_{\text{blend}}^{\text{crit}} = 0.004$  was calculated from the average degrees of polymerization (Eq. (3), Table 1).

For both SPPO/poly(St-co-oClSt) and SPPO/poly(St-co-pClSt) systems, five of the  $\chi_{ij}$  parameters required in the Eq. (1) are already available from earlier investigations [4,13,14]. The sixth  $\chi_{ij}$  parameter, representing interactions between St and SPO segments (i.e.  $\chi_{AD}$ ) was treated as an adjustable parameter. Based on the experimental miscibility–immiscibility boundary, for the systems described in the present paper, on our earlier experimental data for the miscibility behaviour of the SPPO/PS system [15] and previously determined and published  $\chi_{ij}$  parameters, the  $\chi_{\text{St,SPO}}$  parameter at 473 K was estimated applying the mean-field equation so that the best fit of the data have been found. It may be mentioned that the results obtained by Cimmino et al. [14] for  $\chi_{\text{St,oClSt}}$  and  $\chi_{\text{St,pClSt}}$  were already tested and used in our earlier

Table 2  
Segmental interaction parameters,  $\chi_{ij}$ , at 473 K

Segment pair	$\chi_{ij}$
PO, oClSt	0.02 <sup>a</sup>
SPO, oClSt	0.28 <sup>a</sup>
PO, pClSt	0.03 <sup>a</sup>
SPO, pClSt	0.017 <sup>a</sup>
PO, SPO	0.318 <sup>a</sup>
St, PO	−0.043 <sup>b</sup>
St, oClSt	0.0027 <sup>c</sup>
St, pClSt	0.0792 <sup>c</sup>
St, SPO	0.385

<sup>a</sup> From Ref. [4].

<sup>b</sup> From Ref. [13].

<sup>c</sup> From Ref. [14].

work [16]. The dashed lines in Figs. 1 and 2 represent calculated miscibility–immiscibility boundary at 473 K for SPPO/poly(St-co-oClSt) and for SPPO/poly(St-co-pClSt) systems. It can be seen from these figures that a very good correlation was obtained between theoretical evaluations and experiments. The calculated value for the estimated interaction parameter  $\chi_{\text{St,SPO}}$  is included in Table 2, together with the results from earlier studies.

The generalized quadratic equation predicts that the isothermal miscibility–immiscibility boundary is hyperbolic for both blend systems investigated in this study, i.e. the condition for the miscibility boundary  $b^2 - 4ac > 0$  is fulfilled, as can be seen from Table 3. Since  $\chi_{AB}$  and  $\chi_{CD}$  have the same sign, a hyperbolic boundary can be observed if the product  $\chi_{AB}\chi_{CD}$  is small.

The A, C and D units representing St, PO and SPO, respectively, are common to both copolymer–copolymer blend systems investigated in this study. In the two system, the B unit represents oClSt or pClSt, respectively, and greatly influences the phase behaviours of the copolymer blends. For this reason, the

Table 3

The coefficients *a*, *b*, *c*, *d*, *e* and *f* from Eq. (4) and the miscibility conditions for blend systems studied

System	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	$b^2$	$b^2 - 4ac$	Center of hyperbola, ( $x_c$ ; $y_c$ )	$f(x_c, y_c)$
Poly(St-co-oClSt)/SPPO	0.0027	−0.168	0.318	0.060	0.110	−0.047	0.028	0.025	229.3; 43.3	> 0
Poly(St-co-pClSt)/SPPO	0.0792	−0.441	0.318	−0.006	0.110	−0.047	0.194	0.094	47.5; 15.7	< 0

role of the interactions  $\chi_{AB}$ ,  $\chi_{BC}$  and  $\chi_{BD}$  in inducing miscibility were analyzed.

The relationship between various  $\chi_{ij}$ 's for SPPO/poly(St-co-oClSt) is:

$$\chi_{AD} > \chi_{CD} > \chi_{BD} \gg \chi_{BC} > \chi_{AB} > \chi_{blend}^{crit} > \chi_{AC}$$

and for SPPO/poly(St-co-pClSt) system:

$$\chi_{AD} > \chi_{CD} \gg \chi_{AB} > \chi_{BC} > \chi_{BD} > \chi_{blend}^{crit} > \chi_{AC}$$

As mentioned above, all permutations of homopolymers in these two systems, with the exception of PPO and PS, are immiscible, as reflected in the positive values of the respective  $\chi_{ij}$  parameters. Thus, for both the aforementioned blends, the miscibility domain includes the point ( $x = 0$ ,  $y = 0$ ), corresponding to the miscibility of PS and PPO, as a consequence of the attractive interaction between St and PPO monomer units. The miscibility domains for both copolymer-copolymer blend systems are bounded by the intercept on the axes  $x = 0$  and  $y = 0$ , corresponding to the miscibility of PS with a range of SPPOs and to the miscibility PPO with a range of composition of poly(St-co-oClSt) and poly(St-co-pClSt). The miscibility domain includes also the intercept on the line  $x = 1$  as a consequence of the partial miscibility of SPPO/poly(pClSt) blends. It is thus obvious that the miscibility can be significantly increased by decreasing  $\chi_{BD}$ .

The miscibility domain may be located either within or outside the hyperbolic boundaries, as can be seen from Figs. 1 and 2. Table 3 summarizes the numerical coefficients of the terms in Eq. (4), and the miscibility conditions, to determine the nature of the miscibility domains. Analysis of the geometrical properties of the curves represented by Eq. (4) indicates that the coefficients  $d$  and  $e$  are directly related to the centre and the loci of the focal points of the curves. Examination of the condition for the miscibility boundary as was described by Chai and Karasz [17] leads to the conclusion that the  $b^2$  term represents the contribution of segmental dissimilarity in the two copolymers. The greater the chemical difference of the two units in the copolymer, the larger is this term and, thus, favours a hyperbolic miscibility boundary. From Table 3, it can be seen that the absolute values of the  $d$  and  $e$  coefficients are significantly smaller than the absolute value of the coefficient  $b$  (i.e. the coeffi-

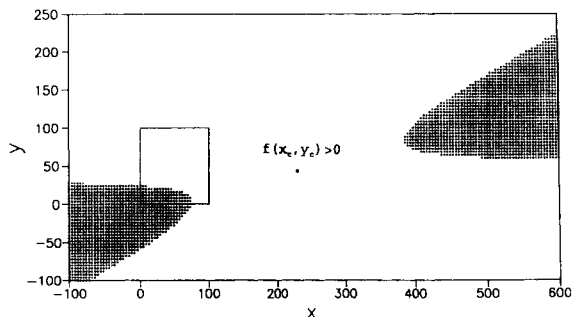


Fig. 3. Calculated miscibility map for poly(St-co-oClSt)/SPPO blend, with extended  $x$  and  $y$  axes. Physical meaning is limited to the square region  $[0,0; 0,100; 100,0; \text{and } 100,100]$ .

cient which is related to axial rotation) for the SPPO/poly(St-co-pClSt) system. For the SPPO/poly(St-co-oClSt) system, these differences are not so emphatic. It can be seen from Fig. 2, that the miscibility domain at 473 K in this system is defined by the area between two branches of a hyperbola. The location of the miscibility domain is determined by the sign of  $f(x,y)$  (Eq. (2)) at the center of hyperbola;  $f(x_c, y_c)$  for this system is negative and the miscibility domain is, therefore, outside the hyperbola. For the SPPO/poly(St-co-oClSt) system (Fig. 1), the situation is the opposite:  $f(x_c, y_c)$  is positive and the miscibility domain lies within one branch of the hyperbola.

Fig. 3 shows, in an enlarged coordinate system, the calculated miscibility map for SPPO/poly(St-co-oClSt) with the portion of the domain which has physical meaning outlined. The calculated miscibility map, where the shaded and open areas represent the miscibility and immiscibility regimes, respectively, shows clearly that the former lies within the hyperbola.

In the first case (in which the miscibility domains lies outside the hyperbola), the reason is the very large intermolecular segmental interaction  $\chi_{AD}$  compared to intramolecular parameter  $\chi_{AB}$ . The second case (miscibility within the hyperbola) can be related to repulsion in the copolymers. The repulsion of the *ortho*-substituted styrene with SPO unit ( $\chi_{BD}$ ) is much greater than that of *para*-substituted styrene. This isomeric effect is far more pronounced than in the corresponding interaction of the substituted styrene units with PO ( $\chi_{BC}$ ). These steric effect, therefore, account for the miscibility behaviour of SPPO/poly[St-co-o(p)ClSt] systems.

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