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Phase Behavior in Copolymer Blends of Poly(*p*-chlorostyrene-co-*o*-chlorostyrene) and Phenylsulfonylated Poly(2,6-dimethyl-1,4-phenylene oxide)

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SYNOPSIS

The miscibility of random copolymers of *o*-chlorostyrene and *p*-chlorostyrene [P(*o*ClSt-co-*p*ClSt)] with partially phenylsulfonylated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) copolymers has been studied, using differential scanning calorimetry (DSC) to establish T_g behavior. It already has been established that the isomeric effect of the chlorine substitution on miscibility is large. Thus the *para*-chloro-substituted styrenic homopolymer is miscible with all SPPOs containing more than ~ 5 mol % phenylsulfonylation, whereas the *ortho*-chloro-substituted homopolymer is immiscible with the entire range of SPPO copolymer compositions (and also with the respective homopolymers). As a result of this asymmetric behavior of the homopolymers, the width of the window of miscibility in blends now investigated containing copolymers with high *p*ClSt content and SPPO is much greater than in the corresponding blends containing copolymers with large mole fraction of *o*ClSt. These differences are reflected in the corresponding χ parameters calculated from analysis of the data. It was also found that the miscibility is temperature dependent and that the regime in the copolymer-copolymer composition plane shrank as the equilibrium temperature increased, results indicative of LCST behavior. © 1994 John Wiley & Sons, Inc.

Keywords: Miscibility • copolymers • isomeric effects • halostyrenes • phenylene oxide polymers

INTRODUCTION

In several earlier publications^{1–4} we reported the miscibility and phase separation behavior in blends of chloro-substituted styrenic polymers with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). In these studies, the miscibilities of homopolymer-homopolymer pairs as well as homopolymer-copolymer systems were investigated. It was shown that blends of high molar mass poly(*ortho*-chlorostyrene) [P(*o*ClSt)] or poly(*para*-chlorostyrene) [P(*p*ClSt)] and PPO are immiscible at all blend compositions.¹ Miscibility of PPO blends with random copolymers of halogen-substituted styrene (St), *o*ClSt or *p*ClSt, depends on the copolymer compo-

sition as well as on the location of the substituent on the aromatic ring.^{2,3} Thus P(*p*ClSt-co-*o*ClSt)/PPO blends display two miscibility-immiscibility transitions:⁴ copolymers of low and high *p*ClSt content are immiscible with PPO, whereas those with a *p*ClSt content between 23 and 64 mol % form homogeneous blends. Miscible blends close to these boundaries undergo phase separation upon annealing at elevated temperatures, a result indicating the existence of a lower critical solution temperature (LCST).

Recently we also investigated miscibility in blends of P(*o*ClSt) and P(*p*ClSt) homopolymers with partially phenylsulfonylated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO), which can be regarded as a copolymer of substituted and unsubstituted moieties.⁵ These copolymers are regarded as the most thermally stable modified PPOs. They appear

to be a new class of materials that could be useful either as blend constituents or as engineering thermoplastics. Using a mean-field approach,^{6,7} we analyzed the phase behavior in these systems in terms of binary segmental interaction parameters.

In this contribution we present results obtained for the study of miscibility in blends of random copolymers of P(*p*ClSt) and P(*o*ClSt) with SPPO copolymers of different degrees of sulfonylation. On the basis of previous results, we would expect that miscibility would be a function of the composition of both copolymer species.

EXPERIMENTAL

Materials

Random P(*p*ClSt-co-*o*ClSt) copolymers containing from 4 to 95 mol % *o*ClSt and the respective P(*p*ClSt) and P(*o*ClSt) homopolymers were prepared by solution polymerization in toluene at 60°C, with azo-*bis*-isobutyronitrile as initiator.⁴ The relevant characterization data are presented in Table I.

PPO powder was supplied by General Electric and was purified by dissolution in toluene and precipitation in an excess of methanol ($M_w = 35,000$; $M_n = 17,000$).

A series of random SPPO copolymers (Structure I) with degrees of sulfonylation of 3.5, 8.6, 12, 17, 19.4, 27, 31, 39, 46, 55, 63, 68, 74, 84, 87, and 92 mol

%, were prepared by Friedel-Crafts sulfonylation of PPO. The electrophilic substitution reactions were carried out in nitrobenzene solution in the presence of AlCl_3 , under nitrogen at temperatures ranging from 45 to 80°C. After the required reaction time, the AlCl_3 complex was destroyed by adding the reaction mixture to methanol acidified with HCl. The precipitated polymer was filtered off, washed with additional acidified methanol and water, and then vacuum dried to constant weight.^{8,9}

Polymer blends were prepared by dissolving appropriate quantities in 50/50 wt % composition of the pure components in toluene and precipitating from the solution with an excess of methanol. The blends were then dried in vacuo for 60 h at 80°C. The dried mixtures were used in the DSC experiments.

Physicochemical Measurements

Glass transition temperature (T_g) determinations were carried out with a Perkin-Elmer DSC-2 at a heating rate of 20°C min⁻¹ in nitrogen. The T_g was taken as the midpoint of the heat capacity rise.

Thermogravimetric measurements (to investigate stability of the blends) were made using a Perkin-Elmer TGS-2 thermobalance at a heating rate of 10°C min⁻¹ with nitrogen purge.

Copolymer molecular weights, based on calibration with monodisperse polystyrene standards (Polymer Laboratories), were determined by GPC (Varian HPGPC, Model 8500), using μ -Styrogel columns with tetrahydrofuran (THF) as solvent, at 25°C.

RESULTS AND DISCUSSION

Miscibility Behavior

Miscibility was ascribed to those blends that displayed a single glass transition in the DSC thermogram. All the blends studied were amorphous, and the only distinctive features of the thermograms

Table I. Characteristics of Copolymers

Copolymer Composition (Mole Fraction of <i>o</i> ClSt) x	M_w $\times 10^{-5}$	M_n $\times 10^{-5}$	T_g (°C)
P <i>p</i> ClSt			
0	1.6	0.87	132
P(<i>o</i> ClSt _{<i>x</i>} -co- <i>p</i> ClSt _{1-<i>x</i>})			
0.04	1.9	1.1	131
0.10	2.3	1.3	131
0.21	2.2	1.1	130
0.32	2.2	1.1	129
0.45	2.3	1.2	126
0.55	2.3	1.2	127
0.64	2.3	1.2	126
0.72	2.2	1.0	127
0.82	2.0	1.0	127
0.91	1.8	0.9	126
0.95	1.9	1.0	126
P <i>o</i> ClSt			
1.00	1.6	0.77	126

were glass transitions. To produce a uniform thermal history in all the blends, an initial scan was made. The reported glass transition temperatures are from the second scan.

Miscibility-immiscibility behavior was first studied for the blends as precipitated (i.e., the blends that were obtained by coprecipitation of an equal amount of each component from toluene solution by methanol). Figure 1 shows the results in terms of a miscibility-immiscibility boundary in a copolymer-copolymer composition plot. For example, miscibility was found in blends containing copolymers with an SPPO content equivalent to degrees of sulfonylation from 3.5 to 92 mol % and styrene copolymers with an *o*ClSt content of 10 mol %. At higher *o*ClSt contents of the P(*p*Cl-co-*o*ClSt) copolymer, the window of miscibility became progressively narrower. As another example, for blends of the chlorinated copolymer containing 95 mol % *o*ClSt, miscibility was observed with SPPO copolymers ranging from 8.6 to 17 mol % substitution. In Figure 1 the left- and right-hand ordinates represent data obtained for the blends of homopolymers P(*p*ClSt) and P(*o*ClSt) with SPPO copolymers, respectively, the blends having the thermal/solvent

Figure 1. Miscibility of 50/50 wt % blends of P(*p*ClSt-co-*o*ClSt)/SPPO copolymers: (○) one phase; (●) two phases; (□) intermediate situation. The dashed line represents the experimentally obtained boundary between miscible and immiscible blends for as-precipitated copolymer blends and those annealed at 200°C. The solid curve is the theoretical boundary between miscible and immiscible blends calculated on the basis of a single adjustable parameter fit of segmental interaction parameters at 200°C.

Figure 2. Miscibility of 50/50 wt % blends of P(*p*ClSt-co-*o*ClSt)/SPPO copolymers annealed at 280°C; (○) one phase; (●) two phases; (□) intermediate situation. The dashed line represents the experimentally obtained boundary between miscible and immiscible blends.

histories as described above. By extrapolation, Figure 1 also implies miscibility for a blend of P(*p*ClSt) and a fully sulfonylated (but experimentally unavailable) SPPO polymer. These limiting miscibility behaviors in the P(*p*ClSt)/SPPO system and immiscibility in the P(*o*ClSt)/SPPO system has been accounted for on the basis of mean-field theory.⁶

We also examined the temperature behavior of certain blends by annealing at fixed temperatures of 200, 280, and 320°C, respectively. As usual, the annealing experiments were carried out in a DSC cell by applying a previously described procedure.⁴ The results at 200°C are indistinguishable from those for the as-precipitated blends (dashed line, Fig. 1). At higher annealing temperatures (280°C, Fig. 2 and 320°C, Fig. 3), small but measurable changes in the miscibility-immiscibility boundaries were observed. The area of the miscibility regime became progressively smaller as the annealing temperature increased. The miscibility window along the axis representing pure PPO with the respective copolymers disappeared at the higher temperatures implying that the LCST for these systems lies between 200 and 280°C.

Thermostability

Blends of SPPO/P(*p*ClSt-co-*o*ClSt) are stable in N₂ up to 320°C in terms of the experiment described above, as was shown by measuring weight loss thermogravimetrically. Each blend was heated to the appropriate annealing temperature (200, 280, or

320°C) and maintained at that temperature for 15 min. It was found that observed weight loss depended very little on blend composition; at the highest test temperature under the specified conditions, maximum weight losses were less than 1.5%. From these data, it was concluded that thermal degradation was not significant in this study.

Segmental Interaction Parameters

In a mean-field analysis,⁶ the P(*o*ClSt-co-*p*ClSt)/SPPO system can be represented as blends of two random copolymers; it is of the type $(A_{1-x}B_x)_{n1}/(C_{1-y}D_y)_{n2}$. For such blends, the overall segmental interaction parameter χ_{blend} is related to the six segmental interaction parameters representing the nonidentical binary interactions of the monomeric units and the copolymer compositions by

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

where *A* and *B* represent the *para*- and *ortho*-chlorostyrene mers, respectively; *C* and *D* represent the PO and the phenylsulfonylated PO units (SPO), respectively.

Five of the χ parameters (at 200°C) required in this analysis already are available. Thus χ_{AD} and χ_{CD} were obtained from recent studies of phase boundaries in SPPO/P(*p*ClSt) blends;⁵ χ_{AB} , χ_{AC} ,

Table II. Segmental Interaction Parameters at 200°C

Segment Pair	χ_{ij}
PO,SPO	0.318 ^a
SPO, <i>o</i> ClSt	0.282
<i>o</i> ClSt, <i>p</i> ClSt	0.094 ^b
PO, <i>p</i> ClSt	0.030 ^c
PO, <i>o</i> ClSt	0.020 ^c
SPO, <i>p</i> ClSt	0.017 ^a
χ_{crit}	0.0035

^a From ref. 5.

^b From Ref. 10.

^c From Ref. 11.

and χ_{BC} were taken from earlier data in the literature.^{10,11} The sixth χ parameter, representing interactions between *o*ClSt and SPO (i.e., χ_{BD}) was treated as an adjustable parameter for the experimental results obtained in this study. The value of the conformational entropy term χ_{crit} , 0.0035, was calculated from the degree of polymerization of the respective blend components and from the usual result that the boundary is represented by $\chi_{\text{blend}} = \chi_{\text{crit}}$. Taking the above into account and using eq. (1), χ_{BD} was found to be 0.282 (Table II).

The experimental miscibility domain for blends of SPPO and P(*p*ClSt-co-*o*ClSt) at 200°C is shown in Figure 1 by a dashed line. The solid curve represents the miscibility-immiscibility boundary calculated on the basis of the segmental interaction parameters discussed above and listed in Table II.

CONCLUSIONS

The results observed in this investigation are consistent with earlier studies of miscibility of halogenated styrene polymers with PPO and substituted PPO. With the exception of PPO and styrene itself all the several permutations of homopolymers in these series are immiscible, as reflected in the positive values of the respective χ parameters. One of the more unusual features to emerge concerns the strong isomeric effect of the placement of the halogen substituent on the styrene ring in the interaction of this unit with the phenylsulfonylated PO mer.

The repulsion of the *ortho*-substituted styrene with SPPO is always much greater than that of the *para*-substituted mer. The ratio of the respective binary interaction parameters [i.e., $\chi_{\text{SPO}/o\text{-XSt}}/\chi_{\text{SPO}/p\text{-XSt}}$ (where X = F, Cl or Br)] is 2.7, 16, and 21 for the fluorinated,⁵ chlorinated (present work), and brominated⁵ series. This isomeric effect

Figure 3. Miscibility of 50/50 wt % blends of P(*p*ClSt-co-*o*ClSt)/SPPO copolymers annealed at 320°C: (O) one phase; (●) two phases; (□) intermediate situation. The dashed line represents the experimentally obtained boundary between miscible and immiscible blends.

is far more pronounced than in the interaction of the halogen-substituted styrene units with PO itself, where the ortho-substituted ring typically is mildly favored over the para-substituted ring. Clearly a steric effect accentuated by the presence of the phenylsulfonated moiety must account for this behavior. We anticipate that interactions derived from molecular modeling calculations now under way will illuminate underlying factors responsible for this very marked effect. In view of the results described we consider that steric effects could account to some extent to the miscibility behavior of SPPO/poly(*p*ClSt-co-*o*ClSt) blends.

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