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MISCIBILITY AND PHASE BEHAVIOUR IN POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE) AND POLY(FLUOROSTYRENE-CO-BROMOSTYRENE) BLENDS

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Abstract—Copolymers of *ortho*(*para*)fluorostyrene and *ortho*(*para*)bromostyrene with a range of copolymer compositions were prepared by free radical polymerization in toluene solution using azobis(isobutyronitrile). The miscibility and phase behaviour of these copolymers in blends with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) have been studied by differential scanning calorimetry. Of the four possible copolymer systems, miscibility was observed only for PPO/poly(*o*-fluorostyrene-co-*p*-bromostyrene) blends in which the copolymer contains between 11 and 73 mol% *p*-bromostyrene. High temperature phase separation in the miscible blends is a function of copolymer composition and of the thermal history. The results can be explained on the basis of the mean field theory of phase behaviour for homopolymer-copolymer systems.

INTRODUCTION

Miscibility in blends of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) or polystyrene (PS) and random copolymers of styrene with fluorinated [1-3], chlorinated [4-6] and brominated [7, 8] styrene derivatives has been reported in a previous series of publications; in contrast, PPO and PS are generally immiscible with the respective halogenated homopolymers. The copolymers of *o*-fluorostyrene with *p*-fluorostyrene, [9] and the corresponding chlorinated [6, 10, 11] and brominated styrene derivatives [7] have also been prepared and their behaviour in blends with PPO and with PS studied. The behaviour of mixed halogen-containing styrene copolymers, poly(fluorostyrene-co-chlorostyrene) with PPO (PS) has also been reported [12, 13]. In several of these systems, miscibility can be found for a certain range of copolymer compositions, but in these cases miscibility extends only up to a certain temperature at which point phase separation occurs; phase behaviour in these binary mixtures is thus of the lower critical solution temperature (LCST) type. The general explanation for this behaviour is based on a first-order mean field theory recently introduced [14-16].

In this paper we present results of the study of the miscibility of PPO with copolymers of fluoro- and bromo-substituted styrene derivatives. Table 1 lists the unit structures of the copolymers and the codes used. The observed phase behaviour and polymer-copolymer miscibility is accounted for in terms of the first order mean field theory for homopolymer-copolymer systems.

EXPERIMENTAL

Polymerization and polymer characterization

Homopolymers of *o*-fluorostyrene [poly(*o*-FS)], *p*-fluorostyrene [poly(*p*-FS)], *p*-bromostyrene [poly(*p*-BrS)], and *o*-bromostyrene [poly(*o*-BrS)], and copolymers consisting of permutations of these monomers were prepared by solution polymerization in toluene at 60°C using azobis(isobutyronitrile) (AIBN) as the initiating species. The procedure was identical to that reported in previous publications [2, 4, 5]. The polymerization was stopped when the reaction was between 10 and 30% complete to minimize copolymer composition drift, by dilution with additional toluene and precipitation into methanol. The precipitated dried powders were characterized and used in the blend studies. Copolymer compositions were determined by fluorine [17] and bromine [18] elemental analysis.

The reactivity ratios of the monomers were evaluated according to the methods of Fineman and Ross (F-R) [19] and Kelen and Tüdös (K-T) [20-22]. The reactivity ratios calculated by least squares analysis are given in Table 2. These data together with the results shown in Figs 1 and 2 show that copolymerization is favoured over homopolymerization and that monomer units in the polymer show some tendency to alternate.

Characterization of the polymer samples included determinations of molecular weight and glass transition temperature. The former were determined by GPC at 25°C in tetrahydrofuran. The GPC (Varian Model 8500) was calibrated using monodisperse polystyrene samples of known molecular weights. The molecular weights, $\bar{M}_n$ and $\bar{M}_w$, and the ratio $\bar{M}_w/\bar{M}_n$ are therefore given in the form of "polystyrene equivalent" molecular weights in Table 2.

The glass transition temperatures, T_g , for the pure components and the blends were measured for compression moulded films, using a Perkin-Elmer DSC-2. The T_g was taken as the temperature at which the heat capacity reached one half of the total heat capacity change as observed on the thermogram. These data are also listed in Table 3.

† The stabilities of the pure components and of the blends were investigated by thermogravimetric analysis with a Perkin-Elmer TGS-2 under a N₂ atmosphere.

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Table 1. Unit structures and codes of the copolymers used

Unit structure	Code
$\left[\text{CH} \begin{array}{c} \\ \text{C}_6\text{H}_4\text{F} \end{array} - \text{CH}_2 - \text{CH}_2 - \text{CH} \begin{array}{c} \\ \text{C}_6\text{H}_4\text{Br} \end{array} \right]_n$	Poly(<i>o</i> -FS-co- <i>p</i> -BrS)
$\left[\text{CH} \begin{array}{c} \\ \text{C}_6\text{H}_4\text{F} \end{array} - \text{CH}_2 - \text{CH}_2 - \text{CH} \begin{array}{c} \\ \text{C}_6\text{H}_3\text{Br} \end{array} \right]_n$	Poly(<i>o</i> -FS-co- <i>o</i> -BrS)
$\left[\text{CH} \begin{array}{c} \\ \text{C}_6\text{H}_4\text{F} \end{array} - \text{CH}_2 - \text{CH}_2 - \text{CH} \begin{array}{c} \\ \text{C}_6\text{H}_4\text{Br} \end{array} \right]_n$	Poly(<i>p</i> -FS-co- <i>p</i> -BrS)
$\left[\text{CH} \begin{array}{c} \\ \text{C}_6\text{H}_4\text{F} \end{array} - \text{CH}_2 - \text{CH}_2 - \text{CH} \begin{array}{c} \\ \text{C}_6\text{H}_3\text{Br} \end{array} \right]_n$	Poly(<i>p</i> -FS-co- <i>o</i> -BrS)

Table 2. Copolymer reactivity ratios Fineman-Ross (F-R) and Kelen-Tüdös (K-T) equation

Copolymer	m_1	m_2	r_1 (F-R)	r_2 (F-R)	r_1 (K-T)	r_2 (K-T)
Poly(<i>o</i> -FS-co- <i>p</i> -BrS)	<i>o</i> -FS	<i>p</i> -BrS	0.56	0.85	0.57	0.83
Poly(<i>o</i> -FS-co- <i>o</i> -BrS)	<i>o</i> -FS	<i>o</i> -BrS	0.52	0.77	0.46	0.81
Poly(<i>p</i> -FS-co- <i>p</i> -BrS)	<i>p</i> -FS	<i>p</i> -BrS	0.44	0.91	0.42	1.10
Poly(<i>p</i> -FS-co- <i>o</i> -BrS)	<i>p</i> -FS	<i>o</i> -BrS	0.58	0.67	0.60	0.73

Fig. 1. Copolymer composition vs feed composition for poly(*o*-FS-co-*p*-BrS) (●) and poly(*o*-FS-co-*o*-BrS) (○). Fig. 2. Copolymer composition vs feed composition for poly(*p*-FS-co-*p*-BrS) (■) and poly(*p*-FS-co-*o*-BrS) (□).

Table 3. Copolymer characterization

Sample*	T_g (°C)	Mol. wt $\times 10^{-5}$		
		$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
Poly(<i>o</i> -FS-co- <i>p</i> -BrS)				
0.05 <i>p</i> -BrS	100	1.34	0.77	1.74
0.11 <i>p</i> -BrS	102	1.65	0.98	1.68
0.22 <i>p</i> -BrS	108	1.74	0.94	1.85
0.27 <i>p</i> -BrS	112	1.79	1.05	1.70
0.36 <i>p</i> -BrS	117	1.88	0.99	1.90
0.45 <i>p</i> -BrS	122	1.65	0.70	2.36
0.60 <i>p</i> -BrS	128	1.75	0.93	1.88
0.68 <i>p</i> -BrS	132	1.94	1.11	1.75
0.73 <i>p</i> -BrS	135	1.48	0.86	1.72
0.77 <i>p</i> -BrS	138	2.04	1.18	1.73
0.86 <i>p</i> -BrS	143	2.19	1.27	1.72
Poly(<i>o</i> -FS-co- <i>o</i> -BrS)				
0.03 <i>o</i> -BrS	102	1.23	0.69	1.78
0.17 <i>o</i> -BrS	105	1.23	0.52	2.33
0.24 <i>o</i> -BrS	108	1.37	0.61	2.24
0.30 <i>o</i> -BrS	112	1.43	0.61	2.34
0.23 <i>o</i> -BrS	117	1.51	0.74	2.03
0.47 <i>o</i> -BrS	125	1.63	0.69	2.36
0.57 <i>o</i> -BrS	131	1.92	0.74	2.59
0.69 <i>o</i> -BrS	137	1.86	0.94	1.98
0.78 <i>o</i> -BrS	144	2.07	1.10	1.88
0.90 <i>o</i> -BrS	147	2.60	1.29	2.02
0.91 <i>o</i> -BrS	148	1.89	1.09	1.73
Poly(<i>p</i> -FS-co- <i>p</i> -BrS)				
0.13 <i>p</i> -BrS	116	1.69	0.99	1.71
0.21 <i>p</i> -BrS	118	1.80	1.02	1.76
0.28 <i>p</i> -BrS	121	2.12	1.23	1.72
0.43 <i>p</i> -BrS	125	1.80	1.11	1.62
0.55 <i>p</i> -BrS	131	1.81	0.99	1.83
0.65 <i>p</i> -BrS	136	2.16	1.26	1.71
0.74 <i>p</i> -BrS	141	2.18	1.17	1.86
0.84 <i>p</i> -BrS	144	2.20	1.04	2.12
0.92 <i>p</i> -BrS	147	2.28	1.08	2.11
Poly(<i>p</i> -FS-co- <i>o</i> -BrS)				
0.12 <i>o</i> -BrS	119	1.03	0.58	1.78
0.20 <i>o</i> -BrS	121	1.10	0.60	1.83
0.26 <i>o</i> -BrS	125	1.18	0.69	1.71
0.36 <i>o</i> -BrS	128	1.30	0.76	1.71
0.46 <i>o</i> -BrS	133	1.38	0.81	1.70
0.60 <i>o</i> -BrS	137	1.62	0.94	1.72
0.76 <i>o</i> -BrS	141	1.69	0.93	1.82
0.87 <i>o</i> -BrS	144	1.86	1.11	1.68
0.97 <i>o</i> -BrS	147	1.95	1.19	1.64

*Numbers indicate mole fraction *para*-bromo or *ortho*-bromostyrene in the respective copolymer.

PPO (General Electric Co.) was purified by dissolving in toluene and precipitating from methanol. Molecular weight determination by GPC at 25°C in THF gave values: $\bar{M}_w$: 35,000 and $\bar{M}_n$: 17,000.

Blends and film preparation

The respective copolymers and homopolymers were blended with PPO by coprecipitation from dilute toluene solution into a large quantity of methanol. The dried, precipitated blends were compression moulded under a pressure of 1.4×10^5 kPa at 180°C for the homopolymer blends and 190°C for the copolymer blends.

RESULTS AND DISCUSSION

PPO-copolymer miscibility

PPO/poly(*o*-FS-co-*p*-BrS) blends. The miscibility of the blends was determined by observation of the nature of the glass transition behaviour in the DSC measurements. Figure 3 shows the DSC thermograms of 50/50 wt% PPO/poly(*o*-FS-co-*p*-BrS) blends. It can be seen that those blends involving copolymers which contain 11 to 73 mol% *p*-BrS display only one T_g . In contrast, blends containing copolymers of 5 and of 77 or more mol% *p*-BrS are immiscible; they exhibit two T_g 's which are close in value to the T_g 's of the pure components.

PPO/poly(*o*-FS-co-*o*-BrS), PPO/poly(*p*-FS-co-*p*-BrS) and PPO/poly(*p*-FS-co-*o*-BrS) blends. Copolymers of *o*-FS and *o*-BrS, of *p*-FS and *p*-BrS, and of *p*-FS and *p*-BrS display different behaviour in blends with PPO. All samples studied (containing from 3 to 91 mol% *o*-BrS for *o*-FS-co-*o*-BrS copolymers, 13–92 mol% *p*-BrS for *p*-FS-co-*p*-BrS copolymers and 12–97 mol% *p*-BrS for *p*-FS-co-*p*-BrS copolymers) show two T_g 's in the DSC thermograms

at essentially the T_g 's of the constituents and are therefore considered immiscible.

Thermally induced phase separation

It is known that polymer blends with an observed "miscibility window" at low temperatures often exhibit phase separation at higher temperatures. This behaviour has been experimentally demonstrated for many combinations of PPO with halogen-substituted styrene derivatives [1, 8–13]. In view of this behaviour, it was also interesting to analyze the miscible PPO/poly(*o*-FS-co-*p*-BrS) systems by annealing at temperatures up to 300°C. As for other blends, the experiments were carried out in the DSC. In these studies, an annealing time of 15 min was selected as sufficient to obtain phase equilibrium in the sample but not long enough to induce degradation of either component. After annealing, the samples were quenched to ambient temperatures and subsequently scanned at 20°C/min revealing either one or two discontinuities in the heat capacity curve according to whether or not phase separation had taken place.

By annealing blends which were miscible at the moulding temperature of 190°C, phase separation at different temperatures was observed for different copolymer compositions. Thus for the copolymer containing 73 mol% *p*-BrS, phase separation occurred at 250°C. The mixture containing 68 mol% *p*-BrS separated at 280°C while the blends containing 60 mol% *p*-BrS did not phase separate even after annealing at 300°C. Figure 4 shows a diagram of temperature vs copolymer composition which summarizes the results of the annealing experiments and shows the effect of temperature on the miscibility window. It is evident that blends containing copolymers of between 11 and 60 mol% *p*-BrS cannot be phase separated by annealing at temperatures up to 300°C.

From Fig. 4 it can also be seen that the boundary between one and two phases is characteristically

Fig. 3. DSC thermograms of 50/50 wt% mixtures of PPO/poly(*o*-FS-co-*p*-BrS) blends. Numbers indicate mole fraction of *p*-BrS in the copolymer.

Fig. 4. Miscibility of 50/50 wt% blends of PPO and poly(*o*-FS-co-*p*-BrS) as a function of copolymer composition: (○) one phase, (●) two phases.

temperature dependent; it corresponds approximately to the loci of the lower critical solution temperatures for this respective system. In contrast to other systems of this type [1, 9], the maximum in the window of miscibility cannot be experimentally attained.

Further insight into the thermal behaviour of PPO/poly(*o*-FS-co-*p*-BrS) blends can be obtained from Fig. 5 which shows the phase diagram for the particular blend containing the copolymer with 68 mol% *p*-BrS as a function of blend composition. All blends are miscible at 250°C but at 280°C, for a blend composition of 50/50 wt%, it can be seen that the sample is phase separated; for the blend compositions of 20/80 and 80/20 wt% PPO, the sample is homogeneous and at 40/60 and 60/40 wt% PPO, an intermediate situation exists. It should be noted that, for the blends of 20/80 and 80/20 wt%, it is difficult to determine the phase behaviour using DSC because of the relatively small amounts of the second components.

For the PPO/poly(*o*-FS-co-*p*-BrS) blends containing copolymers of 60 mol% *p*-BrS annealed at 300°C, no changes in miscibility were observed as shown by the presence of a single T_g . In addition, the widths of the glass transitions remain relatively constant indicating an intimate level of mixing in these blends.

Since these studies were conducted at high temperatures, it was desirable to determine the thermal stabilities of the materials under the experimental conditions. The thermal stabilities of the systems investigated were determined at temperatures between 200°C and 300°C using TGA. No weight loss was observed at 200°C and even at 300°C PPO/poly(*o*-FS-co-*p*-BrS) blends experienced a loss of less than 0.4%. It was thus concluded that thermal degradation was not an important factor in this study.

Segmental interaction parameters

The behaviour of the blends in this study demonstrates again the effect of relatively small structural changes on miscibility in polymers. The data provided by these experiments together with results from studies of blends of other halogenated styrene systems have been combined to provide individual segmental interaction parameters. These calculations are based on a first-order mean field theory of phase behaviour developed by ten Brinke *et al.* [15], and

Fig. 5. Phase diagram for the PPO/poly(*o*-FS-co-*p*-BrS) system in which the copolymer contains 73 mol% *p*-BrS: (○) one phase; (◐) intermediate situation; (●) two phases.

others [14, 16]. According to the theory, miscibility in systems of the type studied here does not require any specific interaction but rather is due to a "repulsion" between the different covalently bonded monomers comprising the copolymers. It predicts that miscible polymer systems can occur in which none of the respective segmental interaction parameters is in fact negative. This is most likely to be the case when the copolymer segments differ substantially in polar character.

The expression for the overall interaction parameter, χ_{blend} , of a homopolymer A_{n_1} and a copolymer $(C_y D_{1-y})_{n_2}$ takes the simple form

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

where y is the copolymer composition expressed as the volume fraction of C segments; the definition of the respective χ parameters is obvious from their subscripts. For high molecular weight blend components, the miscibility/immiscibility boundary is given by $\chi_{\text{blend}} = 0$. Equation (1) will be used to estimate or obtain lower limits for the χ parameters involved in blends of PPO and the following copolymers: poly(*o*-FS-co-*p*-BrS), poly(*o*-FS-co-*o*-BrS), poly(*p*-FS-co-*p*-BrS) and poly(*p*-FS-co-*o*-BrS).

PPO/poly(*o*-FS-co-*p*-BrS)

The equation for χ_{blend} for this system is given by

$$\chi_{\text{blend}} = y\chi_{\text{PO}, o\text{-FS}} + (1-y)\chi_{\text{PO}, p\text{-BrS}} - y(1-y)\chi_{o\text{-FS}, p\text{-BrS}} \quad (2)$$

Since a value for $\chi_{\text{PO}, o\text{-FS}}$ (0.013 at 200°C) was previously published [15], there remain two unknown χ 's which can be calculated from the equations corresponding to the two critical points in Fig. 4. The values obtained, at 200°C, are

$$\chi_{\text{PO}, p\text{-BrS}} = 0.044 \quad \text{and} \quad \chi_{o\text{-FS}, p\text{-BrS}} = 0.171 \quad (3)$$

The copolymer composition y_i which represents the maximum in the window of miscibility for this system is given by [15]

$$y_i = \frac{1}{2} + \frac{\chi_{\text{PO}, p\text{-BrS}} - \chi_{\text{PO}, o\text{-FS}}}{2\chi_{o\text{-FS}, p\text{-BrS}}} \quad (4)$$

The present data thus predict that a maximum occurs for a copolymer containing 0.59 mol fraction *o*-FS, which is consistent with the experimental results (Fig. 4).

PPO/poly(*o*-FS-co-*o*-BrS), PPO/poly(*p*-FS-co-*p*-BrS) and PPO/poly(*p*-FS-co-*o*-BrS) blends

For these systems, immiscibility over the entire copolymer composition range was found. The expressions for χ_{blend} for the respective systems are given by Eqns (5)–(7):

PPO/poly(*o*-FS-co-*o*-BrS):

$$\chi_{\text{blend}} = y\chi_{\text{PO}, o\text{-FS}} + (1-y)\chi_{\text{PO}, o\text{-BrS}} - y(1-y)\chi_{o\text{-FS}, o\text{-BrS}} \quad (5)$$

PPO/poly(*p*-FS-co-*o*-BrS):

$$\chi_{\text{blend}} = y\chi_{\text{PO}, p\text{-FS}} + (1-y)\chi_{\text{PO}, p\text{-BrS}} - y(1-y)\chi_{p\text{-FS}, p\text{-BrS}} \quad (6)$$

PPO/poly(*p*-FS-co-*o*-BrS):

$$\chi_{\text{blend}} = y\chi_{\text{PO}, p\text{-FS}} + (1-y)\chi_{\text{PO}, o\text{-BrS}} - y(1-y)\chi_{p\text{-FS}, o\text{-BrS}} \quad (7)$$

By using available data [15] for the lower bounds at 200°C for $\chi_{\text{PO}, o\text{-FS}}$, $\chi_{\text{PO}, p\text{-FS}}$, $\chi_{\text{PO}, o\text{-BrS}}$, and $\chi_{\text{PO}, p\text{-BrS}}$ in Eqns (5)–(7), it is readily determined that miscibility for these systems is only possible if $\chi_{o\text{-FS}, o\text{-BrS}} > 0.28$; $\chi_{p\text{-FS}, p\text{-BrS}} > 0.30$; and $\chi_{p\text{-FS}, o\text{-BrS}} > 0.44$. The results indicate that “repulsion” between *o*-FS and *o*-BrS in, for example, the system PPO/poly(*o*-FS-co-*o*-BrS) is too weak in comparison to the repulsion between the PPO and *o*-FS and the PPO and *o*-BrS segments. The lack of miscibility in the other two systems can be explained in the same way.

The results presented here further support the validity of the simple mean field treatment [15] and may be used to explain the behaviour in other PPO(PS)/halogen-substituted styrene copolymer blends [11, 13].

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