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Phase behavior of blends of poly(2,6-dimethyl-1,4-phenylene oxide)/polystyrene/poly(*o*-chlorostyrene-*co*-*p*-chlorostyrene) copolymer

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Abstract

The phase behavior of ternary blends of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), polystyrene (PS) and a 50/50 mole % statistical copolymer of *o*-chlorostyrene and *p*-chlorostyrene [p(*o*ClS–*p*ClS)] has been investigated by differential scanning calorimetry (DSC) and analyzed in terms of a Flory–Huggins mean-field segmental interaction parameter treatment. Both PS/PPO and PPO/p(*o*ClS–*p*ClS) binary blends exhibit single glass transition temperatures over the full composition range whereas the PS/p(*o*ClS–*p*ClS) system displays a substantial immiscibilty window which extends into the ternary phase diagram. In principle, ternary systems provide enhanced opportunities relative to binary systems for evaluating segmental interaction parameters χ_{ij}s from experimental data because of the high sensitivity of phase boundary locations to these parameters and to component molecular weights. In this system the effect of these parameters on the phase boundary was studied experimentally and compared to calculated values.

Keywords: Ternary blends; Phase diagram; Interaction parameter

1. Introduction

The phase behavior of ternary polymer blends has been investigated on numerous occasions both theoretically and experimentally in terms of a mean field approach [1–3] or by more comprehensive treatments such as the lattice fluid theory of Sanchez and Lacombe [4]. Such systems may be usefully but not inclusively divided into those that contain three homopolymers [1–4], two homopolymers and a random copolymer [5–8] or three random copolymers [9–11]. In this contribution the phase behavior of the amorphous ternary system, polystyrene (PS), poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and a (50/50) mole % random copolymer of *o*- and *p*-chlorostyrene [p(*o*ClS–*p*ClS)] was studied experimentally and the data fitted in terms of the six relevant binary interaction parameters χ_{ij}, which in principle are temperature and composition dependent. The effect of changes in the molecular weight of one of the components, PS, on the phase behavior was also investigated. All six χ_{ij}s are available in the literature but in each case a range of values has been reported [12–15]. The fit of the experimental and calculated phase boundaries which is sensitive to the choice of the respective χ_{ij}s offers the possibility of extracting a more accurate and consistent set of interaction parameters compared to those presently available from studies of binary blends.

The high sensitivity of the details of the phase diagram to the choice of χ_{ij}s was shown by Su and Fried in their calculation of spinodals for ternary homopolymer blends [1]. These authors also showed that even when all the binary pairs of the blend constituents are miscible, for certain choices of χ_{ij}s an immiscibility regime could be found within the ternary phase diagram. In the usual ternary phase diagram representation where the apexes, labelled 1, 2 and 3 correspond to the pure components 1, 2 and 3, respectively, Su and Fried also showed that if two binary interaction parameters, e.g. χ_{13} and χ_{23}, were equal then the phase boundary defining the immiscibility regime (if it exists) of the third, 1–2 pair as component 3 is added is not a function of $\chi_{13}(\equiv \chi_{23})$ and the spinodal region itself is a symmetrical projection from the 1,2 axis. Cowie also discussed this important result for a system containing three copolymers, which, however, can be treated as a ternary quasi-homopolymer system if the molar compositions of the

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respective copolymers are held constant [16]. The corollary is that if χ_{13} is not equal to χ_{23} then the location of the boundary or boundaries will be a function of all the χ_{ij}. If we consider the case (relevant here, see below) in which χ_{13} and χ_{23} are sufficiently negative to provide total miscibility of the respective 1,3 and 2,3 component pairs, whereas χ_{12} is such that a regime of immiscibility is found, then for any given χ_{12} the asymmetry of the boundary will be a function of $|\chi_{13} - \chi_{23}|$ (the so called $\Delta\chi$ effect). Li and Ping extended this analysis to take into account molecular weight asymmetries of the three components which could in certain cases compensate for $|\chi_{13} - \chi_{23}|$ effects [17]. It is noted that molecular weight effects have also been used in binary blend phase studies to enhance the accuracy of χ_{ij} determinations [18–21]. Although fitting the phase boundaries in binary and ternary systems is the most common technique for determining χ_{ij}s [22,23], other techniques including melting point depression in the case that one or more blend components is crystalline [24] or SANS measurements [13] are well established.

Of the six segmental parameters in the PPO/PS/[p(*o*ClS–*p*ClS)] system which is the focus of our attention, the largest literature disagreement is found in $\chi_{S/PO}$, the styrene and 2,6-dimethyl-1,4-phenylene oxide segmental interaction parameter [12–15,25–28]. The two homopolymers are known to be miscible for all molecular weights and experimentally accessible temperatures and therefore (with one exception, [25]) all published values for $\chi_{S/PO}$ are negative, ranging from -0.986 to -0.021; some of this variation may be due to temperature effects. There is also some variability in the published values [14,15,29] for the other five χ_{ij} relevant to this system but the uncertainty is far lower than is the case for $\chi_{S/PO}$.

In the present study, the binary interactions of the copolymer $\chi_{i/\mathrm{cop}}$, where i = PS, PPO, with the two respective homopolymers can be treated according to the established methods [14,15]. Thus,

$$\chi_{i/\mathrm{cop}} = x\chi_{i/o\text{-ClS}} + (1-x)\chi_{i/p\text{-ClS}} - x(1-x)\chi_{o\text{-ClS}/p\text{-ClS}} \quad (1)$$

where x = mole fraction of *o*-ClS in the copolymer. The present system can thus be regarded as a quasi-homopolymer ternary blend which can be treated in terms of the three binary parameters $\chi_{S/PO}$, $\chi_{S/\mathrm{cop}}$ and $\chi_{PO/\mathrm{cop}}$.

2. Experimental

2.1. Blend preparation

The properties and sources of the polymers used in this study are shown in Table 1. The samples for DSC measurements were prepared by dissolving selected compositions of the three components in toluene at a total polymer concentration of 2 wt %, and recovering the blends by precipitation from a 12:1 excess of methanol. The resulting precipitate was dried under vacuum at 70 °C for five days. In addition, some blends were prepared by casting from the appropriate solution on to a mercury surface at room temperature. The solution-cast films were dried and then held under vacuum at 70 °C for five days. After eliminating thermal and solvent histories of the two types of sample by further annealing (see below) no measurable differences between the two types of samples could be observed.

Table 1
The properties of the polymers used in this work

Samples	M_w	M_w/M_n	T_g (°C)	Source
PS	99,000	1.06	97	Polyscience
PS	115,000	1.06	98	Polyscience
PS	250,000	1.04	101	Polyscience
PS	600,000	1.10	103	Polyscience
PPO	52,000	1.20	214	Aldrich
p(*o*ClS–*p*ClS)	160,000	1.33	121	Springborn Laboratory

2.2. DSC measurements

The thermal properties of the amorphous samples were measured by differential scanning calorimetry (DSC Perkin Elmer Model 7). Temperature calibration was performed using indium (T_m = 156.6 °C). Blend samples, 15–20 mg, were heated under nitrogen using the following annealing protocol. The samples were heated from 25 to 230 °C at a heating rate of 50 K min^{-1}., held at this temperature for 15 min, quenched to 25 °C at the same rate, and scanned at 20 °C min^{-1}. Glass transition temperatures were taken as the inflection point in the heat capacity discontinuity observed in the second scan. The appearance of a single composition dependent T_g was taken as evidence for equilibrium miscibility in this system at 230 °C. Multiple T_gs reflected immiscibility. No difference in phase behavior could be detected when the annealing temperature was varied between 200 and 250 °C.

3. Results and discussion

The binary pairs PPO and PS, and PPO and the [p(*o*ClS–*p*ClS)] copolymer are completely miscible while the third binary pair, PS/ p(*o*ClS–*p*ClS) is only partially miscible. Thus in the ternary phase diagram a single phase boundary defines the system with a region of immiscibility of PS and the copolymer that extends into the interior of the diagram, Fig. 1. Any ternary composition containing over 10 or more weight % PPO is miscible. The data shown is for a blend which contains a PS fraction of molecular weight 99,000 (degree of polymerization (dp) = 960).

To simplify the discussion we will denote the weight fractions Φ_1, Φ_2 and Φ_3 corresponding to pure PS, copolymer and PPO as the phase diagram apexes 1, 2 and 3, respectively. It can be seen that the intersections of the

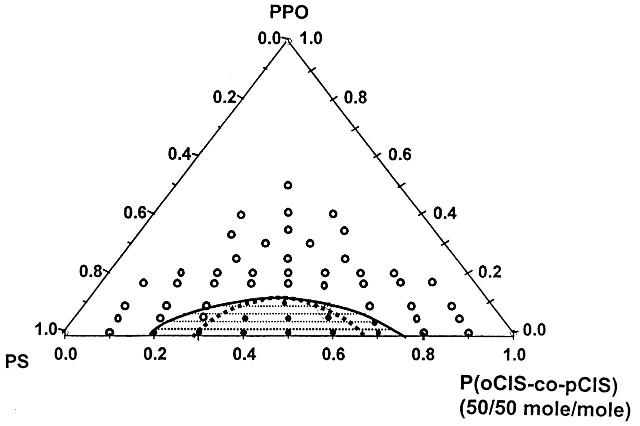

Fig. 1. Phase diagrams for blends of PS/PPO/[p(*o*ClS–*p*ClS)] (—) binodal boundary, (· · ·) spinodal boundary, ○ miscible blend, ● immiscible blend. The degrees of polymerization are $m_1 = 960$, $m_2 = 1200$, $m_3 = 430$, where 1, 2 and 3 refer to PS, the copolymer and PPO, respectively. The interaction parameters used are $\chi_{\mathrm{S/cop}} = 0.0021$, $\chi_{\mathrm{S/PO}} = -0.015$, $\chi_{\mathrm{PO/cop}} = -0.015$, see text.

phase boundary with the binary composition line 1–2 are almost symmetrical about the mid point $\Phi_1 = \Phi_2 = 0.5$. The observed asymmetry is a result of the nonequality of the degrees of polymerization of the respective components PS (dp = 960) and the copolymer (dp = 1200). However the immiscibility region projecting into the interior of the phase diagram, i.e. for $\Phi_3 > 0$, from the 1,2 axis is symmetrical within the resolution of the experimental data. This observation implies that the special condition, $\chi_{13} = \chi_{23}$, obtains.

In the mean field approximation, the general equation for the spinodal phase boundary in a ternary system is given by [30]

$$\begin{aligned} & m_1\Phi_1 + m_2\Phi_2 + m_3\Phi_3 - 2[m_1m_2(\chi_1 + \chi_2)\Phi_1\Phi_2 \\ & \quad + m_1m_3(\chi_1 + \chi_3)\Phi_1\Phi_3 + m_2m_3(\chi_2 + \chi_3)\Phi_2\Phi_3] \\ & \quad + 4m_1m_2m_3(\chi_1\chi_2 + \chi_1\chi_3 + \chi_2\chi_3)\Phi_1\Phi_2\Phi_3 = 0 \end{aligned} \tag{2}$$

where m_i = degree of polymerization of component i,

$$\chi_i = (\chi_{ij} + \chi_{ik} - \chi_{jk})/2 \tag{3}$$

and

$$\Sigma\Phi_i = 1$$

In the special case $\chi_{13} = \chi_{23}$ Eq. (3) yields the following:

$$\chi_1 = \chi_2 = \chi_{12}/2 \tag{4}$$

$$\chi_3 = \chi_{13} - \chi_{12}/2 \tag{5}$$

and Eq. (2) reduces to

$$\begin{aligned} & m_1\Phi_1 + m_2\Phi_2 + m_3\Phi_3 - 2[m_1m_2\chi_{12}\Phi_1\Phi_2 \\ & \quad + m_1m_3\chi_{13}\Phi_1\Phi_3 + m_2m_3\chi_{13}\Phi_2\Phi_3] \\ & \quad + m_1m_2m_3(4\chi_{13}\chi_{12} - \chi_{12}^2)\Phi_1\Phi_2\Phi_3 = 0 \end{aligned} \tag{6}$$

which defines the phase boundary or boundaries for the symmetrical case.

Further, if the condition $\chi_{i3} < \chi_{i3}^{\mathrm{cr}}$ holds, where χ_{i3}^{cr} is the critical value of the interaction parameter for the i,3 segment pair and is given by $[0.5(m_i^{-0.5} + m_3^{-0.5})^2]$ and if $\chi_{12} > \chi_{12}^{\mathrm{cr}}$ then the single phase boundary for the system will extend from the 1–2 axis and it will be given by

$$2m_1m_2\chi_{12}\Phi_1\Phi_2 - m_1\Phi_1 - m_2\Phi_2 = 0 \tag{7}$$

within the limits of the mean field treatment and for the condition specified above.

This equation for the boundary is independent of the value of $\chi_{13}(\equiv \chi_{23})$ [16] and also of m_3 in this approximation. If χ_{13} and/or χ_{23} are greater than the respective critical values then second (and third) region(s) of immiscibility will extend from the respective binary composition axes. In the present case the binary 1–2 interaction parameter can be calculated from Eq. (1) and the available data: $\chi_{\mathrm{S}/o\text{-}\mathrm{ClS}} = 0.005$ [15], $\chi_{\mathrm{S}/p\mathrm{ClS}} = 0.0792$ [18], and $\chi_{o\text{-}\mathrm{ClS}/p\text{-}\mathrm{ClS}} = 0.16$ [14] to yield $\chi_{\mathrm{S/cop}} \equiv \chi_{12} = 0.0021$. Fig. 1 shows that this value yields a very good fit to the experimental data. It also indicates that the values used for the three χ_{ij}s are at a minimum consistent with the present results; additional phase boundary data using copolymers with a range of monomer ratios are required to confirm (or otherwise) their individual correctness. The corresponding binodal boundary and the tie lines [6] are also shown in Fig. 1.

In Fig. 2, phase boundaries calculated for a small range of values of χ_{12} are shown, demonstrating the high sensitivity of the location of the boundary to χ_{12}.

The symmetry of the phase boundary implies that $\chi_{\mathrm{S/PO}} \equiv \chi_{\mathrm{PO/cop}}$ (given the dp asymmetries constitute a

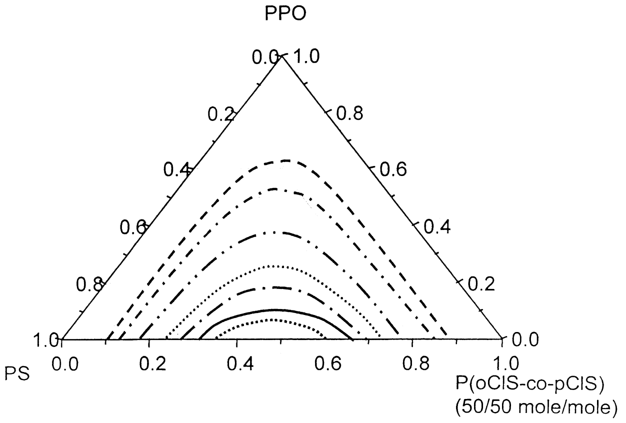

Fig. 2. Calculated spinodal boundaries for several values of $\chi_{\mathrm{S/cop}}$ (· · ·) 0.0020, (—) 0.0021, (– · –) 0.0023, (· · ·) 0.0025, (-···-) 0.0030, (-·-·-·) 0.0040, (---) 0.0050. The other χ_{ij} and the m_i used are the same as in Fig. 1.

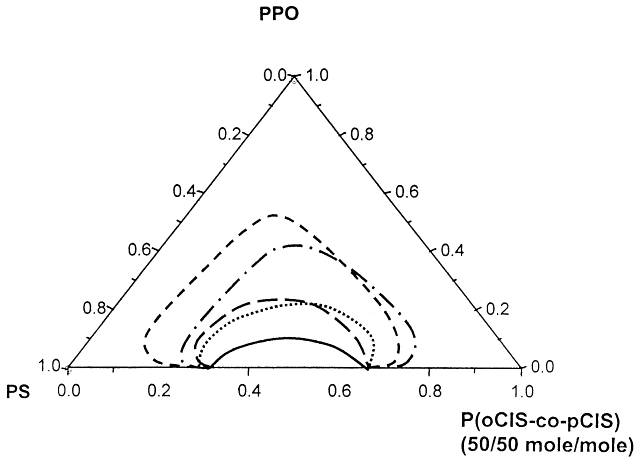

Fig. 3. Calculated spinodal boundaries for several values of $\chi_{S/PO}$. (---) -0.005, (– –) -0.010, (—) -0.015, (···) -0.020, (– · –) -0.025. The other χ_{ij} and the m_i used are the same as in Fig. 1.

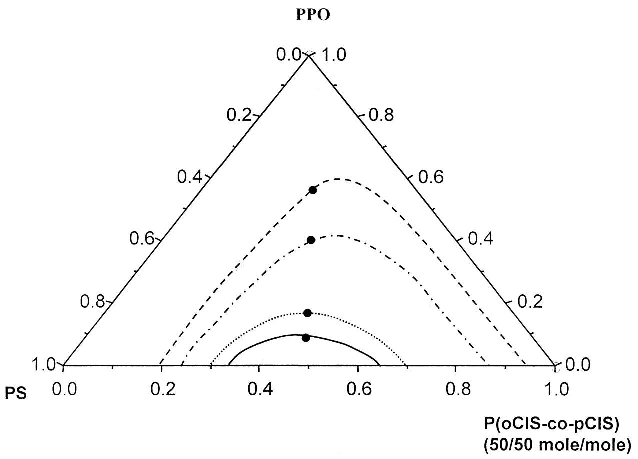

Fig. 4. Calculated spinodal boundaries for several values of m_{PS} the polystyrene degree of polymerization. The filled circles correspond to the experimentally determined miscibility-immiscibility transition points for the respective blends. The parameters used other than mPS are as in Fig. 1. (—) $m_{PS} = 960$, (···)1105, (– · –)2405, (---) 5770.

minor correction) as noted above. The parameter $\chi_{PO/cop}$ can be calculated from Eq. (1) and the available data $\chi_{PO/o\text{-}CIS} = 0.02$ [15], $\chi_{PO/pCIS} = 0.03$ [15], and $\chi_{o\text{-}CIS/p\text{-}CIS} = 0.16$ [15] and is equal to -0.015. This value for $\chi_{S/PO}$ therefore lies slightly below the range of previously published value for this parameter. To show the effect of non-equivalence of $\chi_{S/PO}$ and $\chi_{PO/cop}$ we have calculated the phase boundaries for a range of $\chi_{S/PO}$ while holding the two other binary χ_{ij}s constant using Eq. (2), see Fig. 3. These calculations taken into account the different dps of the components. The effect of asymmetry in the $\chi_{S/PO}$ and $\chi_{PO/cop}$ parameters is apparent. It may be observed that the size of the immiscibility regime passes through a minimum for $\chi_{13} = \chi_{23}$. This minimum is due to a balance in the competitive interactions as represented by the magnitude of $|\chi_{13} - \chi_{23}|$. It should be noted that the asymmetries exhibited in Fig. 3 are contributed to by the inequalities of the PS and copolymer degrees of polymerization.

The large effects of changes in the degree of polymerization on the phase boundary is shown in Fig. 4. The experimental data for the miscibility-immiscibility transition for blends containing PS fractions of differing dp along the line joining the 50/50 wt% PS copolymer mixture with the point $\Phi_3 = 1$ (i.e. pure PPO) are shown by filled circles. The full lines show the complete calculated boundaries for these blends using $\chi_{13} = \chi_{23}$ and Eq. (7). The agreement between the calculated and the experimental data is excellent. The increasing asymmetry of the immiscibility region as the difference in the degree of polymerization of the components increases is also apparent. As expected the most symmetrical boundary is for a PS fraction with a d.p. of 1105, this being closest to the dp of the copolymer, 1200. The experimental phase boundaries represent equilibrium conditions at 230 °C. As already stated, no differences could be detected in any of the measured boundaries on varying the annealing temperature of the blends between 200 and 250° We can therefore assert that the χ_{ij}s are valid at 230 °C.

4. Conclusion

It has been shown that the study of the phase behavior of ternary systems can provide a useful sensitive adjunct for the precise determination of binary interaction parameters. However, in the present case the coincidental equivalence of two of the binary interaction parameters prevented a full assessment of the six segmental parameters needed to completely define this A/B/CD system. By systematically changing the composition of the copolymer this restriction can be removed and a complete evaluation of the parameter set may be feasible.

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