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Phase Behavior in Copolymer Blends: Poly(2,6-dimethyl-1,4-phenylene oxide) and Halogen-Substituted Styrene Copolymers

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ABSTRACT: A recently introduced mean field theory of phase behavior in polymer/copolymer systems is extended to random copolymer/copolymer systems. Miscibility in these systems does not require any specific interaction but rather a "repulsion" between the different covalently bonded monomers of the copolymers. Conversely, immiscibility may occur in systems with specific interaction due to an "attraction" between the different covalently bonded monomers of the copolymers. Using the mean field approach, we discuss in detail the phase behavior in polymer/copolymer systems. The requirements for the occurrence of a symmetric or an asymmetric (im)miscibility window in a temperature–copolymer composition diagram are derived. Using this treatment, we calculate all the segmental interaction parameters for blends of poly(2,6-dimethyl-1,4-phenylene oxide) with poly(*o*-chlorostyrene-*co*-*p*-chlorostyrene), poly(*o*-fluorostyrene-*co*-*p*-fluorostyrene), poly(styrene-*co*-*o*-chlorostyrene), poly(styrene-*co*-*p*-chlorostyrene), poly(styrene-*co*-*o*-fluorostyrene), and poly(styrene-*co*-*p*-fluorostyrene). The absence of miscibility in blends of poly(2,6-dimethyl-1,4-phenylene oxide) with any poly(*o*-bromostyrene-*co*-*p*-bromostyrene) copolymer is explained.

Introduction

It is well-known that high molar mass polymers are, in general, only miscible if there is a favorable specific interaction between them. According to the more recent theories of polymer mixing such as the equation of state[1,2] and the lattice–fluid theory,[3] the Gibbs free energy of mixing contains three different contributions: the combinatorial entropy of mixing, the exchange interaction, and a so-called free volume term. Although, as elaborated in particular by Koningsveld and co-workers,[4,5] this is in many respects too simple a picture, it clearly explains why specific interactions are a prerequisite for the miscibility of polymers. In this case the combinatorial entropy of mixing in negligible whereas the free volume contribution is positive and hence unfavorable for mixing.

There are, nevertheless, an increasing number of exceptions to this rule, but they all have one thing in common: at least one of the components is a random copolymer. An example in which both components are copolymers is given by poly(butadiene-*co*-styrene) and poly(vinyl chloride-*co*-vinyl acetate).[6] These are known to be miscible for a particular range of the copolymer compositions. However, none of the binary combinations of the homopolymers polybutadiene, polystyrene, poly(vinyl chloride), and poly(vinyl acetate) are miscible, an indication in effect of the absence of any specific interactions between them. Other examples that will be considered in some detail in this paper include poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with poly(*o*-chlorostyrene-*co*-*p*-chlorostyrene) (poly(*o*ClS-*co*-*p*ClS))[7,8] or with poly(*o*-fluorostyrene-*co*-*p*-fluorostyrene) (poly(*o*FS-*co*-*p*FS).[9,29]

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In these systems miscibility if found for a certain range of copolymer compositions, but for a given system only up to a certain temperature at which phase separation occurs. The phase behavior in these binary mixtures is therefore of the LCST (lower critical solution temperature) type. In the temperature–copolymer composition plane a miscibility window is obtained, delineating the locus of the LCST's. A comparison between the windows for the PPO/poly-(*o*ClS-*co*-*p*ClS) and for the PPO/poly(*o*FS-*co*-*p*FS) systems shows that their location is different. Whereas the maximum in the miscibility window for the first system occurs approximately at the center of the copolymer composition axis, for the second system it is shifted to the *o*-fluorostyrene-rich side of the diagram. We also note that a miscibility window is not observed in the PPO/poly(*o*-bromostyrene-*co*-*p*-bromostyrene) (poly(*o*-BrS-*co*-*p*-BrS)) system.[10]

Kambour et al.[11] recently formulated a Flory–Huggins type of theory for mixtures of homopolymers and random copolymers. They argued that such a system can be miscible, for a suitable choice of the copolymer composition, without the presence of any specific interaction because of a so-called "repulsion" between the two different monomers comprising the copolymer. In the first section we will introduce this theory in a slightly extended form applicable for blends of two different copolymers. Paul and Barlow[35] also developed a similar model for miscibility of copolymers in blends.

Using this theory, we will address a number of questions. First, some general arguments are given for the occurrence of exclusively LCST-type phase behavior in these kind of systems. Although the arguments are similar to the ones usually presented in discussions of blends of homopolymers, some differences appear because of the possible absence of any specific interaction in the systems under consideration. Next, it will be shown that the presence

of a miscibility window in certain blends of homopolymers and copolymers follows in a very simple way from the theory. It results simply from the fact that the net interaction parameter is a quadratic function of the copolymer composition. The shape and location of the miscibility window are shown to be determined by the difference in interaction strength between a homopolymer segment and the two different copolymer segments. Some arguments will be presented for the possible occurrence of an immiscibility window in blends of a homopolymer and a copolymer in which all three different monomers interact favorably (all χ's negative).

Additional experimental results[7,8,10,12] have been obtained for blends of PPO and copolymers of styrene with one of the ortho- or para-halogenated styrenes. Together with known values for the segmental interaction parameters in the PPO/PS[11,21] and PS/poly(oClS)[27] systems, the interaction parameters for PPO and for PS with poly(o- and p-chlorostyrenes) and for poly(oClS) with poly(pClS) can be calculated by using the theory and the experimental results mentioned above. Knowledge of the phase behavior in the PPO/poly(oFS-co-pClS) systems[9,30] is available and has been used for the calculation of the interaction parameters of the analogous fluorinated systems. Finally, arguments are given to account for the known immiscibility of PPO and poly(oBrS-co-pBrS) of every copolymer composition.

As mentioned above, the calculations are based on a simple Flory–Huggins-type mean field model, containing a number of oversimplifications, known to be at best approximately valid. The most obvious shortcomings of this model will be discussed in the next section. They do not invalidate, however, the main results of this paper.

Theoretical Model

Statistical mechanical treatments of polymer systems are usually based on the quasi-lattice model introduced by Meyer.[13] A polymer molecule is assumed to consist of a number of segments, each occupying one lattice site. The excluded volume effect is taken into account by the requirement that a site can be occupied only once. The central problem is the the calculation of the number of ways of placing the polymer chains on the lattice. Well-known approximate solutions to this problem were first obtained by Flory[14] and by Huggins.[15] They obtained expressions for the free energy of mixing by combining the derived combinatorial entropy of mixing with a Hildebrand–van Laar–Scatchard enthalpy of mixing characterized by an interaction parameter χ. It soon became clear that a reinterpretation of χ as a free energy parameter was necessary to obtain reasonable agreement with experimental results.[16] The discovery of the LCST phenomenon[17] gave rise to the development of the equation-of-state theory by Flory and co-workers[1,2] and of the lattice–fluid theory by Sanchez and Lacombe.[3] These treatments give explicit expressions for χ as a function of temperature and composition.

For a binary mixture of two random copolymers, one consisting of monomers A and B and the other of monomers C and D, an expression for the free energy of mixing ΔG can be derived in a manner similar to the original Flory–Huggins treatment (cf. ref 36). For this case, however, six χ-parameters are involved. The resulting expression is

$$\Delta G/RT = (\phi_1/N_1) \ln \phi_1 + (\phi_2/N_2) \ln \phi_2 +$$
$$\phi_1\phi_2\{xy\chi_{AC} + (1 - x)y\chi_{BC} + x(1 - y)\chi_{AD} + (1 - x)(1 - y)\chi_{BD} - x(1 - x)\chi_{AB} - y(1 - y)\chi_{CD}\} \quad (1)$$

where x and y denote the copolymer compositions, ex-

pressed in volume fractions, of the two copolymers $(A_xB_{1-x})_n$ and $(C_yD_{1-y})_n$ of volume fractions ϕ_1 and ϕ_2 and degree of polymerization N_1 and N_2, respectively, and the definition of the respective χ-parameters is obvious from their subscripts. The derivation of eq 1 is based on the assumption that a real homogeneous mixture is obtained. In the case of block or graft copolymers this is valid only if the sample does not contain the usual microdomain structures. This implies an upper bound for the various segment block lengths, which have to be relatively short compared to the magnitudes of the interaction parameters. The above expression is identical with the Flory–Huggins one for a binary mixture of homopolymers if the following definition is made:

$$\chi_{blend} \equiv xy\chi_{AC} + (1 - x)y\chi_{BC} + x(1 - y)\chi_{AD} + (1 - x)(1 - y)\chi_{BD} - x(1 - x)\chi_{AB} - y(1 - y)\chi_{CD} \quad (2)$$

For a mixture of a homopolymer of A($x = 1$) and a copolymer $(C_yD_{1-y})_n$ this simplifies to

$$\chi_{blend} = y\chi_{AC} + (1 - y)\chi_{AD} - y(1 - y)\chi_{CD} \quad (3)$$

Finally, for a mixture of two copolymers that differ only in copolymer composition, eq 1 reduces to (A = C, B = D)

$$\chi_{blend} = (x - y)^2\chi_{CD} \quad (4)$$

In a somewhat different form this equation was used by Scott[33] to show that copolymers of high molar mass must be reasonably uniform in chemical composition, or the system will be thermodynamically unstable with respect to separation into two or more phases. Furthermore, Roe and Zin[34] applied it to evaluate the χ-parameter for polystyrene and polybutadiene from the observed cloud point curve for polystyrene and a random or a block copolymer of styrene and butadiene. Equations 3 and 4 were also given by Kambour et al.[11] As in the usual Flory–Huggins theory, a critical point occurs at a temperature for which χ_{blend}^{crit} equals χ_{blend}, given by

$$\chi_{blend}^{crit} = \frac{1}{2}(N_1^{-1/2} + N_2^{-1/2})^2 \quad (5)$$

The composition at the critical point is given by

$$\phi_1^{crit} = N_2^{1/2}/(N_1^{1/2} + N_2^{1/2}) \quad (6)$$

For blends of very high molar mass polymers, N_1 and N_2 are so large that χ_{blend}^{crit} is zero. Miscibility therefore corresponds to $\chi_{Blend} < 0$ and immiscibility to $\chi_{blend} > 0$. Equations 2 and 3 clearly show that the first case can occur even if all the segmental interaction parameters are positive; χ_{blend} will be negative if the parameters characterizing the interaction between the different monomers of the same copolymer (χ_{AB} and χ_{CD} in eq 2) are sufficiently large. Kambour et al.[11] introduced the term "repulsion effect" for these cases. A number of specific examples were given in the Introduction.

There are several assumptions involved in the theoretical model discussed above. The most important ones are the following: (a) the segmental interaction parameters are taken to be composition independent; (b) both components of the mixture are considered to be monodisperse; (c) free volume effects are neglected. These are considered below in some detail.

The first assumption is clearly an oversimplification since the χ-parameters are, in general, composition dependent as has been observed for several blends.[18-21] One of the main reasons for this relates to a difference in segmental surface areas. As a consequence, critical compositions may differ considerably from those predicted by equation 5.[22,23] This is, however, exceptional, and experimental results[12] suggest that it does not happen for the

systems considered in this paper. The calculations of the various segmental interaction parameters, presented below, combine results for blends at different copolymer compositions. The resulting values must therefore be regarded as composition averaged. This neglect of composition dependence may well introduce some error.

Another source of possible errors in our treatment arises from the polydispersity of the polymers. Thus, the critical point, in general, will no longer coincide with the minimum of the cloud point curve.[24] The border lines of the miscibility regions presented in the literature are therefore the loci of minima of cloud point curves rather than true LCST's. The assumption, however, that χ_{blend} is approximately zero on these border lines is unlikely to introduce more than a very small error.

Finally, the derivation of the free energy expression, eq 1, takes into account only the combinatorial entropy of mixing and the exchange interaction. The reinterpretation of the segmental interaction parameters as essentially free energy parameters does not change the exchange character of the latter contribution. In addition, there are clearly free volume contributions that will be reflected in the values of the segmental χ-parameters calculated from eq 2 or 3. As mentioned above, such calculations combine experimental results for a number of copolymer blends. Because the free volume effects may differ for different blends, this again introduces some errors. The identification of a segmental χ-parameter of a copolymer blend, such as χ_{AC} in eq 3, with the χ-parameter appropriate to a blend of homopolymers consisting of monomers A and C, respectively, is therefore not entirely correct.

Temperature Dependence of χ_{blend}

All the systems considered in this paper have one property in common: the observed phase behavior is of the LCST type. Conseqently, the χ-parameters of these blends must increase as a function of temperature, at least for the copolymer compositions for which phase separation occurs. To explain this we will restrict ourselves to mixtures of a homopolymer and a copolymer for simplicity. According to the Prigogine–Flory theory, as reviewed by Patterson and Robard,[25] the χ-parameter of a binary mixture of polymers contains two contributions: an exchange interaction and a free volume term. Making suitable assumptions, one can write the former, in analogy to eq 3, as

$$\chi_{blend}^{int}(T) = \frac{c}{\tilde{v}(T)T}(yX_{AC} + (1 - y)X_{AD} - y(1 - y)X_{CD})$$

$$(7)$$

where T is the temperature, c is a constant, $\tilde{v}$ is the reduced volume of the mixture, and X_{AC}, X_{AD}, and X_{CD} are "real" interaction parameters. Flory and co-workers[26] also introduced empirical entropy parameters, which will be neglected here. Introducing an effective interaction parameter by

$$X_{eff} \equiv yX_{AC} + (1 - y)X_{AD} - y(1 - y)X_{CD} \qquad (8)$$

creates a situation completely analogous to that for a mixture of homopolymers. For $X_{eff} > 0$, χ_{blend}^{int} decreases as a function of temperature whereas it increases as a function of temperature for $X_{eff} < 0$. For some given values of X_{AC}, X_{AD}, and X_{CD}, possibly all positive, either of these cases may be obtained for a suitable choice of copolymer composition y. On the other hand, the free volume contribution always increases as a function of temperature, as is the case for blends of homopolymers. The different possibilities are schematically illustrated in Figure 1. If X_{eff} is positive, χ_{blend} is also positive and miscibility does
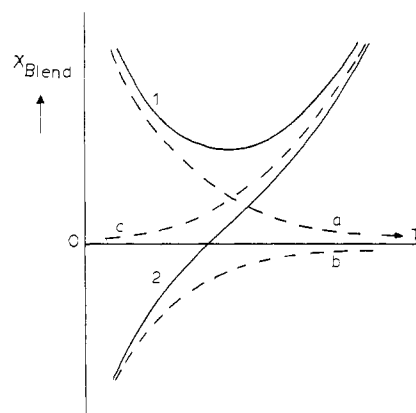

Figure 1. Schematic illustration of the blend interaction parameter χ_{blend} as a function of temperature. The free volume contribution is given by curve c, whereas curves a and b represent the interaction contribution for $X_{eff} > 0$ and $X_{eff} < 0$, respectively. The corresponding temperature dependence of χ_{blend} is given by curves 1 and 2.

not occur. If, on the other hand, X_{eff} is negative, χ_{blend} increases as a funtion of temperature, resulting in LCST behavior. The interesting feature is that either of the two situations may be obtained by a suitable choice of y. The statement that the common type of phase diagram in miscible blends of high molar mass polymers is of the LCST type remains valid for blends containing copolymers.

Miscibility Window

As argued before, the miscibility of systems consisting of a homopolymer and a copolymer is determined by the sign of the quadratic function $f(y)$ defined by

$$f(y) = y^2\chi_{CD} + y(\chi_{AC} - \chi_{AD} - \chi_{CD}) + \chi_{AD} - \chi_{blend}^{crit} \qquad (9)$$

where χ_{blend}^{crit}, given by equ 5, will be neglected in the following discussion. A number of different cases will be considered.

a. χ_{AC}, χ_{AD}, **and** χ_{CD} **Positive.** In this case, $f(y)$ is a convex function of y, which may have two, one, or no zeros for a given temperature. As is clear from the discussion in the last section, any such zeros of $f(y)$ can only occur in the copolymer composition range for which X_{eff}, given by eq 8 is negative. For values of y in between the possible zeros y_{min} and y_{max} of X_{eff}, $f(y)$ is an increasing function of temperature, whereas for y values outside this region, $f(y)$ is a decreasing function of T at least for low temperatures. The behavior of $f(y)$ as a function of temperature is schematically illustrated in Figure 2, together with the resulting window of miscibility.

b. χ_{AC}, χ_{AD}, **and** χ_{CD} **Negative.** Because χ_{CD} is negative, $f(y)$ is a concave function of y. Again $f(y)$ may have two zeros, say y_1 and y_2, for certain temperatures. This time, however, values of y in between y_1 and y_2 represent immiscible systems, and taking into account the temperature behavior of $f(y)$, we obtain a window of immiscibility. This possible behavior is schematically illustrated in Figure 3. In this case the window of immiscibility results from an "attraction" effect in contrast to the "repulsion" effect introduced before. So far, no systems with this type of behavior have been reported.

c. χ_{AC} **Negative,** χ_{AD} **and** χ_{CD} **Positive.** This situation occurs among others for mixtures of PPO and a copolymer of styrene and one of the 2- or 4-halogenated styrenes. Because χ_{AC} is negative, $f(y)$ is negative, and the system miscible, for y sufficiently close to 1. The zeros of f therefore occur for $0 < y < 1$ and $y > 1$. The latter does
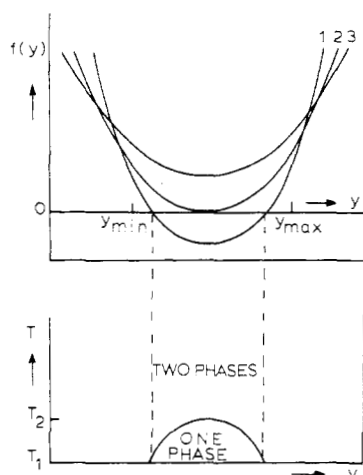
Figure 2. Schematic illustration of the connection between the behavior of $f(y)$ as a function of copolymer composition y and temperature T and the miscibility window in the temperature–copolymer composition plane. Curves 1, 2, and 3 are for the temperatures $T_1 < T_2 < T_3$. y_{min} and y_{max} are the zeros of the effective blend interaction X_{eff} given by eq 8.
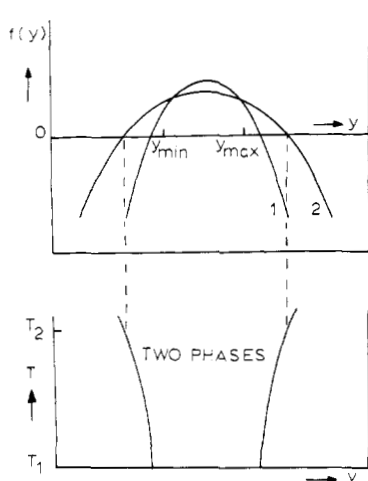

Figure 3. Schematic illustration of the connection between the behavior of $f(y)$ as a function of copolymer composition y and temperature T and the immiscibility window in the temperature–copolymer composition plane. Curves 1 and 2 are for temperatures $T_1 < T_2$. y_{min} and y_{max} are the zeros of the effective blend interaction X_{eff} given by eq 8.

not correspond to a realistic physical situation. Figure 5 depicts this result.

The maximum in the miscibility window corresponds to the situation for which the minimum of $f(y)$ is zero. This requirement results in a relation between the copolymer composition y_t at the maximum and three χ-parameters:

$$y_t = \frac{1}{2} + \frac{\chi_{AD}(T_t) - \chi_{AC}(T_t)}{2\chi_{CD}(T_t)} \tag{10}$$

where T_t denotes the temperature of the maximum. There are clearly three distinct cases possible:

1. $y_t \sim \frac{1}{2} \rightarrow \chi_{AD}(T_t) - \chi_{AC}(T_t) \ll \chi_{CD}(T_t)$

2. $y_t > \frac{1}{2} \rightarrow 0 < \chi_{AD}(T_t) - \chi_{AC}(T_t) \leq \chi_{CD}(T_t)$ $\quad$ (11)

3. $y_t < \frac{1}{2} \rightarrow 0 < \chi_{AC}(T_t) - \chi_{AD}(T_t) \leq \chi_{CD}(T_t)$

Examples of (1) and (2) will be given in the next section. Similar conclusions can be drawn from the location of the minimum of the immiscibility region for systems mentioned under (b). Most likely, however, an immiscibility window will have no minimum, as illustrated in Figure 3.
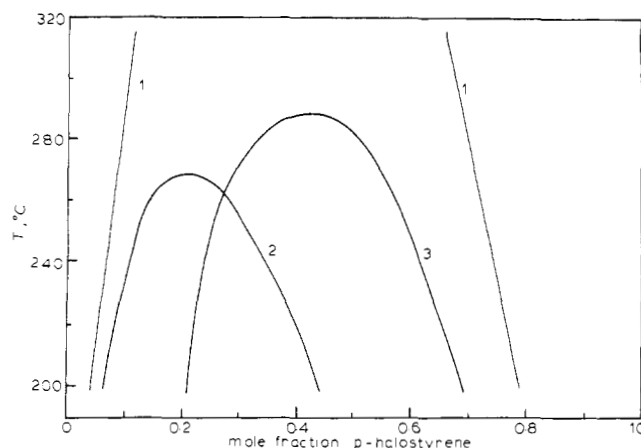

Figure 4. Miscibility of PPO with random copolymers of o-fluorostyrene and p-chlorostyrene (curve 1), o-fluorostyrene and p-fluorostyrene (curve 2), and o-chlorostyrene and p-chlorostyrene (curve 3). The insides of the curves represent the miscibility regions. The experimental data are taken from ref 7, 9, 29, and 30, respectively.

The phase behavior in the polymer/copolymer systems discussed above differs substantially from that in the ternary systems of homopolymers corresponding to the monomers involved. The conditions for miscibility in ternary systems are[31,32]

$$G_{22} > 0 \tag{12}$$

$$G_{22}G_{33} - G_{23}{}^2 > 0 \tag{13}$$

where G_{ij} signifies $(\partial^2 \Delta G/(\partial \phi_i\, \partial \phi_j))_{P,T}$. ϕ_i and ϕ_j are the mole fractions of components i and j, respectively. The free energy of mixing ΔG is, in the usual mean field approximation, given by

$$\Delta G/RT = (1 - \phi_2 - \phi_3)/N_1 \ln (1 - \phi_2 - \phi_3) +$$
$$\phi_2/N_2 \ln \phi_2 + \phi_3/N_3 \ln \phi_3 +$$
$$(1 - \phi_2 - \phi_3)\phi_2\chi_{12} + (1 - \phi_2 - \phi_3)\phi_3\chi_{13} + \phi_2\phi_3\chi_{23} \tag{14}$$

Condition 12 implies that miscibility in a ternary system of high molar mass polymers is only possible if all three χ-parameters are negative. If all three χ-parameters are positive, a situation corresponding to case a considered above, the immiscibility is obvious. For a range of ϕ_2,ϕ_3 values, the free energy of mixing given by eq 14 will be positive. If all three χ-parameters are negative the system may be miscible but phase separation may also occur, depending on the precise values.

Segmental Interaction Parameters

Equation 3 will now be used to calculate the χ-parameters involved in blends of PPO and one of the following copolymers: poly(S-co-oClS), poly(S-co-pClS), poly-(oClS-co-pClS), poly(S-co-oFS), poly(S-co-pFS), and poly(oFS-co-pFS). A value of 0.004 will be used for χ_{blend}^{crit}, corresponding to $N_1 = 300$ and $N_2 = 1000$. The phase behavior for most of these systems has already been published[7-9,12,29] and is summarized in Figures 4 and 5.

a. Chlorinated Systems. Figures 4 and 5 show a total of four critical points for these systems for moderate temperatures: two in the PPO/poly(oClS-co-pClS) systems and one in each of the PPO/poly(S-co-oClS) and PPO/poly(S-co-pClS) systems. Thus we have four equations containing six different χ-parameters. Hence additional information is needed. It is known that blends of high molar mass poly(oClS) and polystyrene are only miscible for a sufficiently low molar mass of the latter component.[10,27] Consequently, it can be shown that $\chi_{S,oClS}$ is very small, of the order of 0.005. There is also considerable
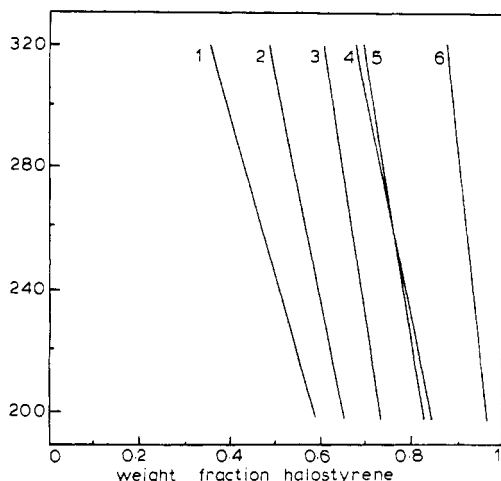
Figure 5. Miscibility of PPO with random copolymers of styrene and o-bromostyrene (curve 1), p-fluorostyrene (curve 2), p-bromostyrene (curve 3), o-chlorostyrene (curve 4), p-chlorostyrene (curve 5), and o-fluorostyrene (curve 6). Miscibility occurs to the left of these curves. The experimental results are taken from ref 7, 10, and 12.

Table I
Segmental Interaction Parameters at 200 °C

segment pair	χ_{ij}	segment pair	χ_{ij}
PO/S	−0.1	PO/S	−0.1
PO/oClS	0.03	PO/oFS	0.013
PO/pClS	0.045	PO/pFS	0.09
S/oClS	0.005	S/oFS	0.09
S/pClS	0.09	S/pFS	0.08
oClS/pClS	0.16	oFS/pFS	0.17

information available regarding the PPO/PS system. Melting point depression data,[21] heat of mixing data,[28] and the observed phase behavior of PS, PPO, and their brominated derivatives[11] all suggest a value of approximately −0.1 for $\chi_{PO,S}$. It should, however, be noted that the melting point depression data also indicate a significant composition dependence for $\chi_{PO,S}$. Since no definite information is available concerning the temperature dependence of $\chi_{S,oClS}$ and $\chi_{PO,S}$, it will be assumed that the available values are a reasonable approximation at a temperature of about 200 °C. The values of the other interaction parameters, also at 200 °C, follow then from the observed phase behavior at this temperature. The choice of 200 °C is motivated by the observation that the free volume effects, which are not well-known, become increasingly important as temperature is raised. The final results are listed in Table I, from which it follows that

$$\frac{\chi_{PO,pClS} - \chi_{PO,oClS}}{2\chi_{oClS,pClS}} \simeq 0.05 \qquad (15)$$

Assuming that this result is also approximately valid at the temperature of the maximum in the miscibility window of the PPO/poly(oClS-co-pClS) system, eq 10 predicts that this maximum will occur for a copolymer composition of 0.55 mole fraction oClS, in good agreement with the experimental result. This is not surprising since this assumption implies that the copolymer composition at the maximum will be the average of the copolymer compositions of the two critical points at 200 °C (i.e., the miscibility window is symmetrical with respect to composition).

b. Fluorinated Systems. To calculate the χ-parameters for these systems, we again need additional information. Besides $\chi_{PO,S}$, for which a reasonable value was given above, one more parameter must be known. This can be obtained from the phase behavior in the PPO/

Table II
Lower Bounds for Segmental Interaction Parameters at 280 °C

segment pair	lower bound	segment pair	lower bound
PO/oClS	0.04	PO/pFS	0.09
PO/pClS	0.04	PO/oBrS	0.13
PO/oFS	0.012	PO/pBrS	0.06

poly(oFS-co-pClS) system,[9,30] which is also presented in Figure 4. The interaction parameters of this blend are $\chi_{PO,oFS}$, $\chi_{PO,pClS}$, and $\chi_{oFS,pClS}$. Since a value for $\chi_{PO,pClS}$ was derived before, there are only two unknowns, which can be calculated from the equations corresponding to the two critical points. Alternatively, the phase behavior in the PPO/poly(oFS-co-oClS) system[9,30] could be used. In both cases, the exact location of the critical point at the oFS side of the phase diagram is poorly known. This may introduce a considerable error in the calculated values for the χ-parameters. Table I summarizes the values for the χ-parameters as they follow from this analysis. In this case

$$\frac{\chi_{PO,pFS} - \chi_{PO,oFS}}{2\chi_{oFS,pFS}} \simeq 0.23 \qquad (16)$$

in agreement with condition 2 of expression 11.

c. Brominated Systems. In contrast to the chlorinated and fluorinated systems, blends of PPO and poly(oBrS-co-pBrS) are immiscible over the entire copolymer composition range.[10] The data for the phase behavior in PPO/poly(S-co-oBrS) and PPO/poly(S-co-pBrS) alone are clearly insufficient to calculate the various interaction parameters. However, useful lower bounds for $\chi_{PO,oBrS}$ and $\chi_{PO,pBrS}$ can be derived from these observations. As an example the PPO/poly(S-co-oBrS) system will be considered. This blend has an LCST at 280 °C for a weight fraction, which is a lower bound for the volume fraction, of styrene of about 0.57. The χ-parameter of this blend is given by

$$\chi_{blend} = y\chi_{PO,S} + (1 - y)\chi_{PO,oBrS} - y(1 - y)\chi_{S,oBrS} \qquad (17)$$

Assuming that $\chi_{PO,S}$ is still about −0.1 at 280 °C, the positive value of $\chi_{S,oBrS}$ (polystyrene and poly(oBrS) are immiscible) implies

$$\chi_{PO,oBrS} > 0.13 \qquad (18)$$

This procedure can be repeated for the other five blends of PPO with copolymers of styrene and pBrS, o-ClS, pClS, oFS, and pFS, respectively. The results are listed in Table II. A comparison between these lower bounds at 280 °C and the actual values, as derived before, at 200 °C suggests that even at the latter temperature, $\chi_{PO,oBrS}$, and $\chi_{PO,pBrS}$ may exceed these lower bounds of 0.13 and 0.06, respectively. Additional support for this can be found in the paper by Kambour et al.,[11] where $\chi_{PO,pBrS}$ was calculated to be 0.22 at about 120 °C, more than 3 times the above given lower bound. Returning to the PPO/poly(oBrS-co-pBrS) system, for which the χ-parameter is given by

$$\chi_{blend} = y\chi_{PO,oBrS} + (1 - y)\chi_{PO,pBrS} - y(1 - y)\chi_{oBrS,pBrS} \qquad (19)$$

it follows from the lower bounds for $\chi_{PO,oBrS}$ and $\chi_{PO,pBrS}$ that miscibility is only possible if

$$\chi_{oBrS,pBrS} > 0.38 \qquad (20)$$

This requirement clearly explains the lack of miscibility in PPO/poly(oBrS-co-pBrS): the "repulsion" between oBrS and pBrS is, although probably large, too small to compensate the rather large values of $\chi_{PO,oBrS}$ and $\chi_{PO,pBrS}$.

Concluding Remarks

The experimental results in Figure 5 show that the ability of the halogen substituent to induce incompatibility in PPO/PS blends is given by

$$o\text{-Br} > p\text{-F} > p\text{-Br} > o\text{-Cl} \simeq p\text{-Cl} > o\text{-F} \qquad (21)$$

The calculated values for $\chi_{PO,oClS}$, $\chi_{PO,pClS}$, $\chi_{PO,oFS}$ and $\chi_{PO,pFS}$ together with the calculated lower bounds for $\chi_{PO,oBrS}$ and $\chi_{PO,pBrS}$ satisfy the same ordering and thus rationalize the observed phase behavior. The physical origin of this ordering is not well understood. Two effects seem to oppose each other: the electronegativity of the halogen atoms, which decreases from F to Br, and their size, which increases from F to Br. Also the differences between F and Br or Cl are much larger than between Br and Cl. The present work is nevertheless an important step forward because it establishes for the first time an ordering in the "interaction" between PPO and the various halogenated styrenes. This could not simply be concluded from the observed phase behavior in blends of PPO and copolymers of styrene and one of the ortho- or para-halogenated styrenes, since the phase behavior in each blend is determined by three different interaction parameters, two of which are unique. Furthermore, it presents a method of calculating interaction parameters from miscibility data, which is perhaps experimentally simpler and yet of comparable accuracy with other techniques.

The calculation of the various χ-parameters is partly based on the observed phase behavior, summarized in Figures 4 and 5. In addition to this, reasonable values for $\chi_{PO,S}$ and $\chi_{S,oClS}$ had to be introduced. A lack of information with respect to the temperature dependence of the latter makes a calculation of the other interaction parameters as a function of temperature, and a detailed analysis of the miscibility windows, impossible at present. The necessary additional information can be obtained by measuring the phase behavior in the PS/poly(oClS-co-pClS) system as a function of copolymer composition. According to the predictions based on the data presented in Table I, this system will be miscible for a copolymer composition between 0.55 and 0.95 mole fraction oClS at a temperature of 200 °C. A determination of the miscibility window will result in two extra equations and will allow the calculation of the χ-parameters at different temperatures. This will be the subject of a future publication.

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