Macromolecules **1983**, *16*, 753–757

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Registry No. Sodium polyacrylate, 9003-04-7; poly(sodium ethenesulfonate), 9002-97-5; sodium polymethacrylate, 54193-36-1; lithium polyacrylate, 25656-42-2; potassium polyacrylate, 25608-12-2; rubidium polyacrylate, 39936-29-3; poly(acrylic acid), 9003-01-4; acetic acid, 64-19-7; sodium ethanesulfonate, 5324-47-0; EDTA, 60-00-4; PSS, 62744-35-8; $TbCl_3$, 10042-88-3; NaCl, 7647-14-5.

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Phase Behavior of Polystyrene, Poly(2,6-dimethyl-1,4-phenylene oxide), and Their Brominated Derivatives

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ABSTRACT: Polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PXE) have been brominated selectively to produce in each case a series of copolymers and ultimately two new homopolymers. Limits of miscibility of the copolymers with the homopolymers have been defined in terms of the copolymer compositions in 11 unique binary, ternary, and quaternary blend series. Segment–segment χ values have been derived from an interpretation of the binary blend miscibility limits in the Flory–Huggins framework and used to predict ternary blend results successfully. Relative segment–segment repulsion inside copolymers is seen to be an important driving force for mixing frequently.

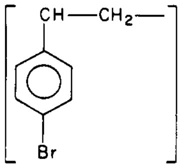
Introduction

Miscibility in polymer–polymer blends is a subject of widespread theoretical as well as practical interest currently. In the past decade or so the number of blend systems that are known to be miscible has increased considerably.[1] Moreover, a number of systems have been found that exhibit upper or lower critical solution temperatures, i.e., complete miscibility only in limited temperature ranges.[1-6] Modern thermodynamic theories have had limited success to date in predicting miscibility behavior in detail.[7] These limitations have spawned a degree of pessimism regarding the likelihood that any practical theory can be developed that can accommodate the real complexities that nature has bestowed on polymer–polymer interactions.

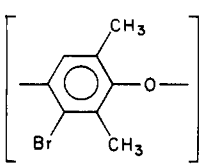
The purpose of this paper is fourfold: first, to describe several related polymer blend systems that are convenient for experimental and theoretical studies of miscibility limits; second, to show how classical Flory–Huggins segmental interaction parameters can be derived from these miscibility limits; third, to show to what extent these parameters are true constants, i.e., to what extent they are useful in predicting the miscibility characteristics of other blend systems containing the same segment pairs; and fourth, to highlight, for blends containing copolymers, the importance to blend miscibility of the segment–segment interactions internal to the copolymer itself.

Experimental Procedures

The subject blends were made from polystyrene (PS), poly(2,6-dimethyl-1,4-phenylene oxide), trivially named poly(xylenyl ether) (PXE), and their brominated derivatives. Both parent resins can be easily and controllably brominated in solution up to one bromine per repeat unit without the need for adding a catalyst. (Experimental conditions used: (a) For PXE, $CHCl_3$ as solvent; stoichiometric liquid bromine added; absence of light: 3–6-h reaction time.[8] For PS, nitrobenzene as solvent; ca. 5/4 stoichiometric liquid bromine added; absence of light; 1-day reaction time. The latter reaction is sluggish; unreacted bromine at the end of the reaction period was titrated with pentene before the polymer was precipitated.) The bromine substitution occurs in each case in one position on the aromatic ring only and, due to deactivation, once only on each ring. Thus, in the case of complete bromination two new homopolymers are formed, poly(*p*-bromostyrene) and poly(3-bromo-2,6-dimethyl-1,4-phenylene oxide):



PBr$_1$S



PBr$_1$XE

Lesser degrees of bromination result in random copolymers of (a) styrene with *p*-bromostyrene, coded PBr$_x$S and, (b) xylenyl

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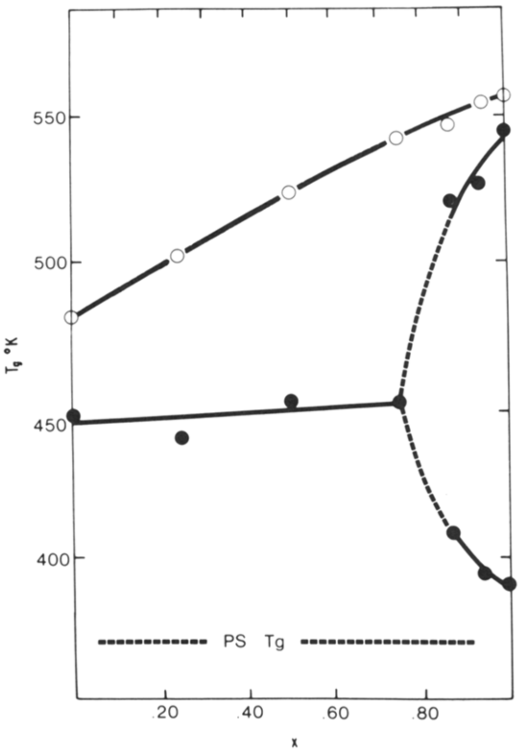

Figure 1. $\bar{x}$ dependence of DSC T_g's in 30/70 wt % blends of polystyrene and PXE brominated to various levels. Dashed lines: T_g's of pure PBr$_{\bar{x}}$XE's and of polystyrene.

ether with 3-bromoxylenyl ether, coded PBr$_{\bar{x}}$XE, $0 < \bar{x} < 1$, where $\bar{x}$ indicates the average fraction of repeat units that is brominated.

Degrees of bromination and chemical structures produced (i.e., bromine adduct purity) were determined by ^{1}H and ^{13}C NMR. Gel permeation chromatographs verified that no change in chain length (i.e., no chain scission) occurred in either resin during reaction.

The blends described below were based on a monodisperse PS of $\bar{M}_w = 97\,000$, a PXE of $\bar{M}_w = 75\,000$, $\bar{M}_w/\bar{M}_n = 2.1$, and their brominated derivatives.

Blend Preparation. Blends were prepared by codissolution in chloroform or chlorobenzene followed by film casting from these solutions. Chloroform solutions were cast at ambient temperature. Films containing PXE were cast from chlorobenzene at 120 °C, which prevented PXE crystallization. (Crystallization does not occur with any of the PBr$_{\bar{x}}$XE's.) [Neither solvent identity nor casting temperature was found to affect miscibility behavior significantly.]

Tests of Miscibility. Three tests for miscibility were used. Bromination changes refractive indices so markedly that optical transparency was generally reliable evidence of single-phase behavior. The existence of two T_g's in systems containing PXE and/or PBr$_{\bar{x}}$XE's [whose T_g's (210–280 °C) are much higher than those of PBr$_{\bar{x}}$S's (100–130 °C)] was a reliable indicator of two phases. Finally, both scanning and transmission electron microscopy were useful in detecting bromine-rich phases, especially in blends in which the brominated resin(s) was low in bromine content. In general, consistent results were obtained by these three methods.

T_g's were determined for copolymers and blends with a Perkin-Elmer DSC-II scanning calorimeter. The T_g's of two series of blends, each series at fixed blend compositions (e.g., 50 wt % PXE), are displayed vs. copolymer compositions $\bar{x}$ in Figures 1 and 2. Above a critical value $\bar{x}_c$ two well-separated T_g's existed. By comparison with the T_g's of the pure components it appears that each of the two phases contains a large amount of one component and a small amount of the other.

Microscopy was carried out on an International Scientific Instrument ISI-40 scanning electron microscope. The micrographs in Figure 3 are images of the same area of a two-phase film formed by secondary electron modulation and bromine X-ray emission modulation. The specimen is a cast film. The viewing surface

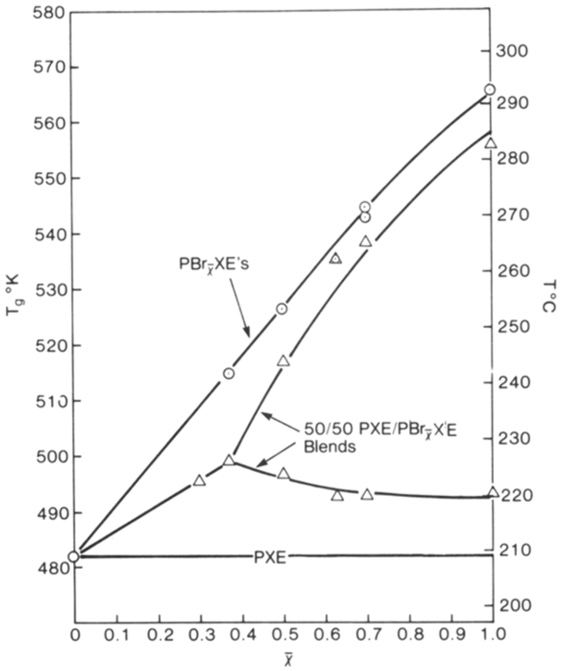

Figure 2. $\bar{x}$ dependence of DSC T_g's in 50/50 wt % blends of PXE and PXE brominated to various levels.

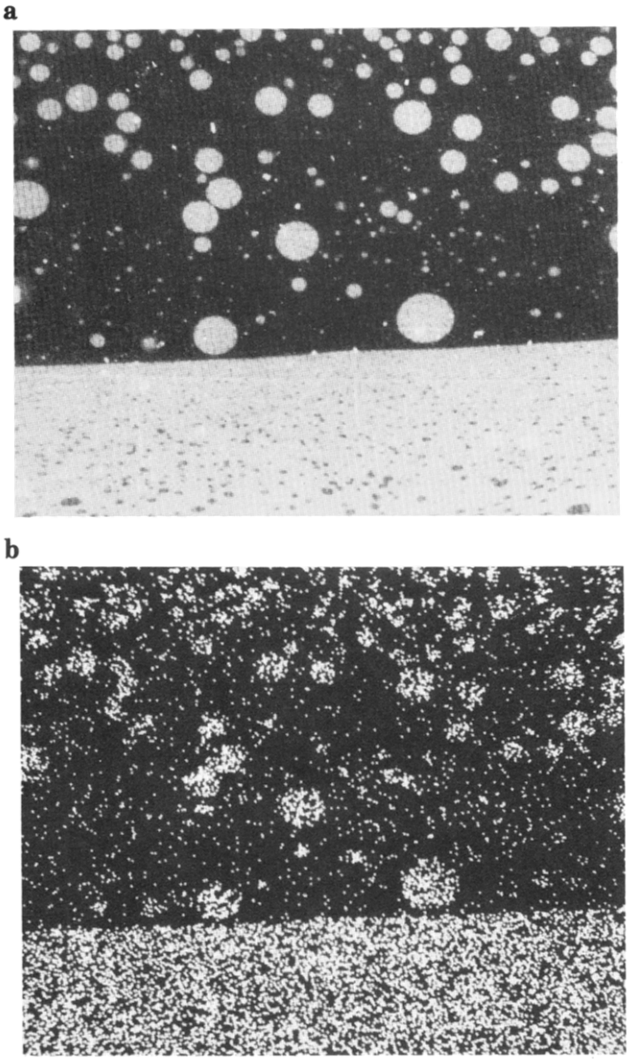

Figure 3. Scanning electron micrographs of cross section of cast film containing 30 wt % polystyrene and 70 wt % PBr$_1$XE. Images formed by (a) secondary electron modulation and (b) bromine X-ray emission. Magnification 450×.

Table I
Blend Compositions and Critical Levels of Bromination for Phase Separation

	volume fraction						
blend	PXE	PBr$_1$XE	PS	PBr$_1$S	PBr$_{\bar{x}_c}$XE	PBr$_{\bar{x}_c}$S	x_c(obsd)
30/70 PXE/PBr$_{\bar{x}}$XE	0.33				0.67		0.38
50/50 PS/PBr$_{\bar{x}}$XE			0.57		0.43		0.75
50/50 PXE/PBr$_{\bar{x}}$S	0.56					0.44	0.47
50/50 PS/PBr$_{\bar{x}}$S			0.51			0.49	0.10
50/50 PBr$_1$XE/PBr$_{\bar{x}}$XE		0.47			0.53		0.48
50/50 PBr$_1$S/PBr$_{\bar{x}}$XE				0.48	0.52		0.78
50/50 PBr$_1$XE/PBr$_{\bar{x}}$S		0.42				0.58	0.15
50/25/25 PXE/PBr$_{\bar{x}}$XE/PBr$_{\bar{x}}$S	0.54				0.23	0.23	0.37 0.40[a]
50/25/25 PS/PBr$_{\bar{x}}$XE/PBr$_{\bar{x}}$S			0.52		0.24	0.24	0.16
25/25/50 PXE/PS/PBr$_{\bar{x}}$XE	0.27		0.28		0.45		0.45 0.54[a]
25/25/25 PS/PXE/PBr$_{\bar{x}}$S	0.26		0.27			0.47	0.29 0.30[a]
25/25/25/25 PS/PXE/PBr$_{\bar{x}}$S/PBr$_{\bar{x}}$XE	0.26		0.27		0.23	0.24	0.26

[a] Calculated.

is the film cross section. The areas that give rise to high X-ray emission in Figure 3b are the same as those giving high secondary electron emission in Figure 3a, thus confirming the use of the latter modulation technique in identifying bromine-rich areas. [The later technique is in fact much more sensitive and less time-consuming.] The morphology seen is thought to be a kinetic artifact arising from the occurrence of phase separation during the film drying process.

Experimental Results

PXE and PS have long been known to be completely miscible as evidenced by a large number of techniques.[9] In the current study PBr$_1$XE and PBr$_1$S were also found to be completely miscible. Neither of the latter derivative homopolymers is miscible with either parent homopolymer however. Each of the four homopolymers was mixed (usually at 50 wt %) with members of the two series of copolymers. There are eight possible binary blend series, of which six are unique in terms of the kinds of segments they contain; the critical level of bromination for phase separation $\bar{x}_c$ was determined for each of these six. In addition, blends at the 25/25/50 wt % levels were made in the four possible ternary blend series that contain one or both of the parent resins; in any blend containing 25 parts each of a PBr$_{\bar{x}}$S and a PBr$_{\bar{x}}$XE, copolymers of matched bromine levels only were used (i.e., $\bar{x}$ was same for both). Finally, blends in the quaternary series containing both parent resins were made, again using in any given blend a PBr$_{\bar{x}}$S and a PBr$_{\bar{x}}$XE of matched bromine level.

Table I lists all polymer blend series made and the values found in each blend series for $\bar{x}_c$. Figure 4 displays $\bar{x}_c$ vs. blend composition for all series containing one or both of the parent resins; a large variation in $\bar{x}_c$ is seen, depending on which parent resin(s) and which brominated resin(s) are in the particular series.

Qualitatively, it is clear from the results for the four binary blend series in Figure 1 that (1) bromination changes the physicochemical nature of PS much more than that of PXE and (2) bromination tolerance is greater if the copolymer is mixed with the opposite parent resin (e.g., PBr$_{\bar{x}}$XE with PS), which fact is consistent with the favorable heat of mixing of PS and PXE.[10]

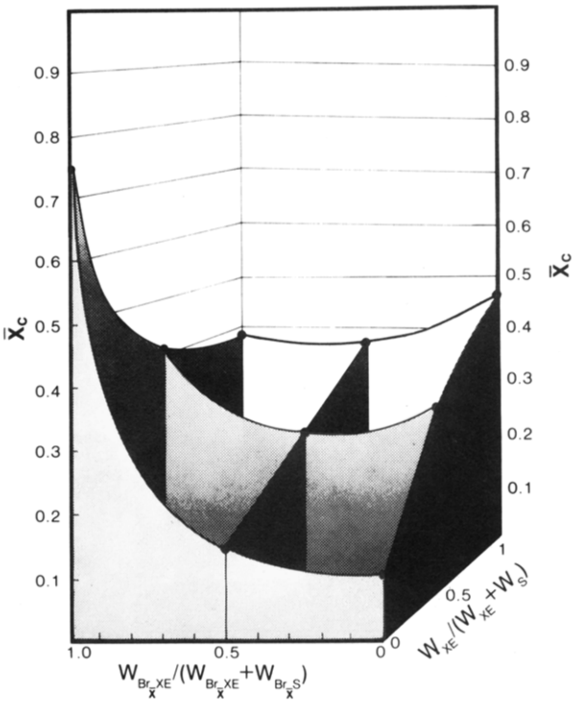

Figure 4. Dependence of bromination tolerance $\bar{x}$ vs. blend composition. In any blend containing both a PBr$_{\bar{x}}$S and a PBr$_{\bar{x}}$XE the $\bar{x}$'s of two copolymers are equal. See Table I for blend compositions.

Theory

The following analysis has been developed based on the assumptions that (a) for mixtures in which $\bar{x} = \bar{x}_c$ a critical solution temperature lies at or close to the film-casting temperature, (b) the presence of residual solvent at the point of "glassification" during film casting has modified $\bar{x}_c$ only slightly, and (c) the Flory–Huggins theory can be used in conjunction with the Gibbs conditions for critical temperatures to develop equations that rationalize the observed values of $\bar{x}_c$ in the various blend series.

Binary Blends. For a blend at the point of phase separation that contains equal volume fractions of two resins A and B of the same chain length N (approximately our case), the last assumption leads to

$$\chi_{AB}{}^{c} = 2/N \tag{1}$$

where $\chi_{AB}{}^{c}$ is the Flory–Huggins polymer–polymer interaction parameter, the superscript denoting critical be-

Table II
Segmental Interaction Parameters and Corresponding Local Contributions to the Free Energy of Mixing

segment pair	χ_{ij}	ΔF_m, cal/mol
S/XE	−0.986	−59
BrS/BrXE	−0.0563	−34
XE/BrXE	0.0156	9
S/BrXE	0.0395	24
S/BrS	0.200	120
XE/BrS	0.2215	133

havior.[11] χ_{AB} can be expressed in terms of the segment-segment χ's (χ_{ij}'s) applicable to the various interactions in the blends as shown below.

For the simplest kind of binary blend (homopolymer A with its own copolymer B) there is one χ_{ij} only. It is found by expressing the local free energy of mixing ΔF_m (i.e., that part of ΔF related to χ) in terms of (1) the "self" free energy (local) of the copolymer

$$\Delta F_B^1 = \bar{x}^2\omega_{jj} + 2(1 - \bar{x})\bar{x}\omega_{ij} + (1 - \bar{x})^2\omega_{ii}$$

where ω is the local ΔF for the interaction of two segments, the subscript j indicates the bromine-containing segment, and $\bar{x}$ is the degree of bromination, and (2) the interaction free energy of an A chain with a B chain:

$$\Delta F_{AB}^1 = (1 - \bar{x})\omega_{ii} + \bar{x}\omega_{ij}$$

When A and B are mixed the local free energy of mixing is found to be

$$\Delta F_m^1 = \bar{x}^2[\omega_{ij} - {}^1\!/_2(\omega_{ii} + \omega_{jj})] = \bar{x}^2\Delta\omega_{ij} = \bar{x}^2\chi_{ij}kT \quad (2)$$

which differs from the standard expression for the mixing of one half mole each of A and B by the factor $\bar{x}^2$.

Combination of (1) and (2) yields for $\bar{x} = \bar{x}_c$

$$\chi_{12} = \chi_{AB}^c/\bar{x}_c^2 = 2/N\bar{x}_c^2 \quad (3)$$

For binary blends in which the homopolymer contains i segments and the copolymer j and k segments, the generalization of (3) is

$$\chi_{AB}^c = 2/N = (1 - \bar{x}_c)\chi_{ij} + \bar{x}_c\chi_{ij} - \bar{x}_c(1 - \bar{x}_c)\chi_{kj} \quad (4)$$

There are six χ_{ij}'s in our ensemble of blends and six binary blends unique in the kinds of segments each contains. Incorporation of the corresponding six values of $\bar{x}_c$ from Table I in the six equations of the type (4) allows for simultaneous determination of all six χ_{ij}'s.

Tertiary Blends. The Gibbs conditions for critical behavior in ternary blends are more complex than those for binaries.[12] Combination with the Flory–Huggins equation leads to a set of cumbersome equations from which analytical solutions for the χ_{ij}'s are not easily extracted. Rather the χ_{ij}'s from the binary blends were used to generate plots of the appropriate Gibbs determinant Δ vs. $\bar{x}$ at constant polymer volume fraction. At the critical point, according to Gibbs

$$\Delta = \begin{bmatrix} \dfrac{\partial^2\Delta F}{\partial\phi_1{}^2} & \dfrac{\partial^2\Delta F}{\partial\phi_1\partial\phi_2} & \dfrac{\partial^2\Delta F}{\partial\phi_1\partial\phi_3} \\ \dfrac{\partial^2\Delta F}{\partial\phi_1\partial\phi_2} & \dfrac{\partial^2\Delta F}{\partial\phi_2{}^2} & \dfrac{\partial^2\Delta F}{\partial\phi_2\partial\phi_3} \\ \dfrac{\partial^2\Delta F}{\partial\phi_1\partial\phi_3} & \dfrac{\partial^2\Delta F}{\partial\phi_2\partial\phi_3} & \dfrac{\partial^2\Delta F}{\partial\phi_3{}^2} \end{bmatrix} = 0$$

Thus, the value of $\bar{x}$ at $\Delta = 0$ should equal the experimental value of $\bar{x}_c$. A comparison of the two values of $\bar{x}_c$ provides a test of the theory and its utility in predicting blend behavior.

Theoretical Results

All values of χ_{ij} are listed in Table II along with their counterpart ΔF_m^1's for mixing together one half mole each of the two segmental units. Consistent with the miscibility observations the S/XE and the BrS/BrXE χ_{ij}'s are negative (i.e., favor mixing) while all those between unbrominated and brominated segments are positive (i.e., unfavorable to mixing). Predicted values of $\bar{x}_c$ for the ternary blends are compared with experimental values in Table I. Agreement is considered to be reasonably good.

Discussion

Limitations in the Current Approach. Compatibility behavior in our system is broadly rationalized by the theory presented here. Therefore this approach, based on the simple Flory–Huggins theory, must be judged an attractive one for initial mapping of polymer–polymer miscibility behavior. However, this approach is not capable of predicting miscibility behavior in fine detail.

Critical solution temperatures for blends like ours are already known to be very sensitive to copolymer composition (i.e., to $\bar{x}$), changing perhaps by hundreds of degrees for a 20% change in $\bar{x}$.[3] The current approach does not assess the enthalpic and entropic components of χ (not to mention their own temperature dependences). Thus, without casting (or annealing) films over a wide temperature range, we cannot assess the temperature dependence of miscibility, i.e., the temperature dependence of x_c.

It is also worth reiterating that we have applied theory strictly applicable to spinodals to phenomena related to the cloud curves in each system. Moreover, we have ignored the ca. 5–15% residual solvent still present in the drying film at the point that its T_g rises through the casting temperature. Presumably the strong sensitivity of miscibilities to bromine levels allows these liberties to be taken.

Finally, it is suspected that χ_{ij} is not entirely independent of local environment. [However, to the extent that it is independent of local environment the values generated here may be useful in deriving new χ_{ij}'s from other, already available, blend miscibility data (e.g., PXE/P*o*Cl$_{\bar{x}}$S[13,14]).]

Sources of Bromine Tolerance. Regardless of its limitation the treatment presented shows that there are two qualitatively different local free energy sources that

Table III
Sources of Bromine Tolerance in Poly-i Plus j/k-Copolymer Binary Blends As Revealed by Terms Calculated for Eq 4 at $x = x_c$

i	j/k	ij term	ik term	−jk term	−jk term (% of total negative)
S	BrXE/XE	+0.02963	−0.02465	−0.00293	11
XE	BrS/S	+0.1041	−0.05226	−0.04982	49
BrS	BrXE/XE	−0.04391	+0.04873	−0.00268	6
BrXE	BrS/S	−0.00845	+0.03358	−0.02550	75

contribute to the miscibility of a homopolymer containing i segments with a copolymer containing j and k segments. Miscibility is aided by negative χ_{ij} and χ_{jk} of course, but also by a *positive* χ_{jk}. The importance of the latter is best comprehended by comparing the signs and magnitudes of the three terms in eq 4 at the critical point of certain of the binary blends. The three terms are calculated and entered in Table III for each of the four blends in which i $\neq$ j or k. The first and second terms in (4) arise from the interaction *between* the polymers, and the third term arises from the interaction of the j and k units *within* the copolymer. Because the third term is subtracted in (4), it contributes favorably to χ_{AB} (i.e., negatively) only when χ_{jk} is *positive*. In Table III the jk term for (3) is tabulated as a percentage of the total of the terms in (4) that favor mixing; the calculation of these terms is done at $\bar{x} = \bar{x}_c$. The point of this tabulation is to show that internal copolymer segmental "repulsion" can often be the dominant term favoring the mixing of a homopolymer and a copolymer. ("Repulsion" is used in a relative sense here; i.e., $\Delta\omega_{jk}$ is positive.) It suggests, in the extreme, that polymer systems exist in which none of the segment–segment χ's are negative yet in which miscibility occurs. This is most likely to be the case when the j and k segments differ greatly in polar character (as is the case with butadiene and acrylonitrile) and the i segment has an intermediate character (as is probably the case, for example, with vinyl chloride or methyl methacrylate); thus copolymer internal repulsion could account for the miscibility of poly(vinyl chloride) with, e.g., butadiene–acrylonitrile copolymers of intermediate compositions.[1]

Acknowledgment. We thank S. Y. Hobbs and V. H. Watkins for providing the scanning electron micrographs, P. E. Donahue and E. A. Williams for the nuclear magnetic resonance analysis, and D. M. White and J. Verbicki for guidance regarding the brominations.

Registry No. PS, 9003-53-6; PXE (SRU), 24938-67-8; 2,6-dimethylphenol homopolymer, 25134-01-4.

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Dynamical Aspects of Phase Separation in Polymer Blends

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ABSTRACT: We have investigated the time development of structure in polystyrene/poly(vinyl methyl ether) blends using conventional light scattering techniques. We show that by utilizing the light scattering invariant and the angular dependence of scattering, one may quantitatively describe the early stages of phase separation within the framework of the linearized Cahn–Hilliard expression. By extrapolating the measured diffusion constant to where it undergoes a sign change, one may also determine the spinodal curve from this procedure.

Introduction

Although phase separation is a dynamical process, previous studies concerned with phase separation in polymer blends have concentrated on determining equilibrium properties, i.e., the phase diagram. van Aartsen[1,2] combined the Flory–Huggins free energy expression and Cahn–Hilliard equations to estimate the effect of spinodal decomposition in polymer/small-molecule systems and proposed an empirical method to define the spinodal temperature by monitoring the total isothermal light scattering intensity as a function of time. Others[3,4] have applied the Ornstein–Zernike–Debye theory to determine the spinodal curve. This procedure involves extrapolating light scattering as a result of density fluctuations to zero angle at a series of temperatures and extrapolating the temperature dependence of the zero-angle intensity to the temperature at which the scattering becomes discontinuous. All measurements are taken in the one-phase region to avoid complications caused by critical opalescence.[5] The utility of this procedure was illustrated in work performed on the polystyrene/cyclohexane system.[3,4] Goldsbrough et al. have experimentally extended Scholte's procedure by applying pulse induced scattering (PICS) techniques to determine the spinodal curve.[6] The PICS method is based on the assumption that it is possible by means of a rapid "thermal pulse" to jump into the metastable region, measure scattering as a result of fluctuations, and return to the one-phase region before appreciable phase separation has occurred. Analysis of PICS data is identical with Scholte's original procedure; however, the spinodal curve is determined via a shortened extrapolation length. The thermodynamic understanding of polymer blend phase diagrams has been advanced by the theoretical treatments

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[†] Contribution No. 3072.