counterion loadings remained constant within experimental error.

The phosphoric acid cation-exchange resins are reasonably stable under experimental conditions encountered in the course of additional characterization measurements to be reported in the accompanying[43] and subsequent[3] publications. In these papers, the water contents, ion-exchange selectivities, electrical conductances, and infrared spectra will be reported and interpreted.

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Miscibilities in Monodisperse Mixtures of Polystyrene, Poly(*p*-bromostyrene), and Their Copolymers

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ABSTRACT: The phase behavior of cast films of mixtures of narrowly disperse polystyrene (I), poly(*p*-bromostyrene) (II), and their copolymers (III) was studied. Miscibility limits were characterized as functions of the degree of polymerization N and copolymer composition. The N dependence of x_c, the critical comonomer concentration of bromostyrene for phase separation in I–III mixtures, is accounted for with a simple mean field model (i.e., a composition-independent, positive segmental interaction parameter χ_{12} for the styrene–bromostyrene pair) for $0 < x_c < 0.4$ and $100 < N < 8000$. At $N < 100$ and $x_c > 0.4$, a downward drift in χ_{12} seems to emerge. Studies of I–III, II–III, and III–III mixtures, all at one N, also reveal a small reduction of χ_{12} with increase in average bromostyrene concentration in the blend. The size and magnitude of this dependence are rationalized in terms of enhanced coupling of the bromostyrene dipoles in the low dielectric medium afforded by blends of high styrene content. The composition dependence of χ_{12} is similar to that found in a study of the upper critical solution temperature behavior in a single I–III blend system of medium molecular weight described in the following paper. The combined results of these studies indicate that for high molecular weights as well as low molecular weights, the phase separations produced are related to upper critical solution temperatures.

The study of polymer–polymer blend miscibility from a fundamental viewpoint is made difficult by several problems, some of which are material in nature. One of the foremost is finding or producing a set of closely related blends, all of the members of which exhibit phase boundaries between their T_g's and their decomposition temperature.

A second problem arises from polymer chain length and chain length dispersity, both of which affect miscibility characteristics through the well-known combinatorial entropy factor. Miscibility studies, each employing a copolymer series of a range of chemical compositions (e.g., styrene/halostyrene copolymers)[1-3] mixed with another resin, perhaps a homopolymer, have been hampered by two aspects of copolymer synthesis: (1) Each copolymer in the series has been made by polymerizing monomers, so that obtaining resins all of the same chain length and chain length dispersity is difficult. (2) Since the copolymers have been free radical or condensation polymers, ratios of $\bar{M}_w$ to $\bar{M}_n$ have been 2 or greater.

These problems can be avoided by following a synthetic route to copolymers (and ultimately another homopolymer) that involves appropriate chemical modification of a parent polymer of narrow molecular weight distribution. Probably the most natural choice for such a study is anionic polystyrene because of the wide range of molecular weights and the narrow dispersities of commercially available resins. Mixtures of each copolymer produced with its parent resin and/or other copolymers then allow for the most easily interpretable miscibility studies to be made.

The objective of the current study was to test the validity of applying phase separation theory based on the Flory–Huggins theory combined with the Gibbs conditions for critical points to binary polymer mixtures cast from solution.[4] Two aspects of the theory were examined: chain length dependence and blend composition dependence of χ_{12}, the segmental interaction parameter. The first examination employed a set of polystyrenes covering a wide molecular weight range. Each member of the set was brominated to varying degrees, and the copolymer products were then mixed with their parent polystyrene to determine comonomer concentrations just necessary for phase separation. The second examination employed the full range of bromostyrene/styrene copolymers as well as poly(p-bromostyrene), all derived from a single polystyrene. In the manner pioneered by Molau[6] and later used by Kollinsky and Markert,[7] these derivatives were blended with each other in order to characterize the comonomer concentration discrepancies between the two blended polymers just necessary for phase separation as a function of the average comonomer content in the blend.

Experimental Section

The polystyrenes used in this work were anionic polymers of $\bar{M}_w/\bar{M}_n = 1.06$ typically. They were purchased from Pressure Chemical Co. Brominations of phenyl rings were carried out in nitrobenzene, a solvent of sufficiently high dielectric constant that no catalyst of the usual type (e.g., ferric bromide) was needed. For each reaction 5 g of polystyrene was dissolved in 50 mL of solvent in an Erlenmeyer flask containing a Teflon-coated magnetic stirrer. The flask was covered with aluminum foil to prevent the light-catalyzed free radical reactions that would otherwise produce backbone bromination. The appropriate amount of liquid bromine was pipetted into the stirred flask. HBr evolution began almost immediately and continued for many hours. At the end of about 22 h the unreacted bromine was destroyed by adding liquid pentene to the flask. To effect 100% of the desired extent of reaction in this time, e.g., addition of one bromine atom to each styrene ring, a 20% excess of bromine liquid over the stoichiometric amount was required. The quenched reaction mixture was then poured in a thin stream into ca. 5 volumes of methanol in a high-speed blender. The precipitated polymer was filtered, washed with more methanol, and dried in a vacuum oven at 80–100 °C until no odor of nitrobenzene remained.

A fairly good estimate of the degree of bromination achieved could be obtained by pentene titration of the unreacted bromine. Ultimately, however, degrees of bromination (precise to ±1%) were determined from ^{13}C nuclear magnetic resonance spectra. These were also used to verify that bromination occurred exclusively on the aromatic ring, and there only in the para position. It is believed that bromination occurs randomly along the chain because adjacent rings are separated from each other by three aliphatic carbons and because steric hindrance between para positions of adjacent rings is negligible, as indicated for example by conformational energy calculations.[8]

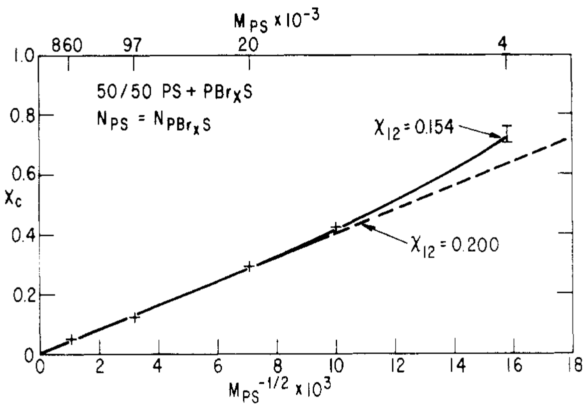

Figure 1. Conditions for phase separation in set A films: dependence of critical mole fraction x_c of p-bromostyrene in copolymer vs. molecular weight of the admixed parent polystyrene.

Polymer blends (50/50 (w/w)) were made by codissolution in chloroform. Films were cast from these solutions at ambient temperatures. These films were inspected for clarity, which was taken as evidence of the existence of one phase. Mixtures that were very cloudy were deemed markedly incompatible. Between these two extremes of behavior in a given series of mixtures there would usually be found one or two compositions, the films of which were opalescent; i.e., they evidenced haze to the eye at low light scattering angles. These films were considered to lie on the verge of compatibility, a judgment buttressed by scanning calorimetry and by phase contrast microscopy on these and the clear films. Differences in ^{13}C NMR measured bromostyrene concentration between two copolymers of 3–4 mol % were generally enough so that when the copolymers were mixed respectively with another, suitably chosen material, the first cast film would be clear to slightly hazy and the second would be quite hazy or cloudy. Thus, the optical "transition" had a width of 3–4 mol % bromostyrene.

In this way miscibility determinations were made on two sets of blends: Set A involved polystyrene from $M = 4000$ to $M = 860\,000$. From each polystyrene a subset of brominated derivatives was made; each derivative PBr$_x$S ($0 < x < 1$), where x is the molar-average degree of bromination in the polymer chain, was mixed with the parent polystyrene in order to determine the critical bromination level x_c necessary for the onset of two-phase behavior in the cast films. By this procedure the dependence of x_c on M of the parent PS was determined.

Set B involved polystyrene of $M = 97\,000$ and its brominated derivatives. The derivatives were mixed with the parent resin and each other (i.e., PBr$_x$S plus PBr$_y$S, where $y > x$ by some fraction). In this way the critical *difference* in bromination level $y_c - x_c$ for the onset of phase separation was determined as a function of average bromine level $(y_c + x_c)/2$ in the mixture.

Results

Figure 1 displays x_c vs. $M^{-1/2}$ of the parent PS for set A. A straight line passing through the origin correlates the results down to $M_{PS} < 10\,000$. Only x_c from $M_{PS} = 4000$ departs from the correlation.

Figure 2 displays $y_c - x_c$ vs. $(y_c + x_c)/2$ for set B. The error bars are derived from the ^{13}C NMR precision and the clear-to-cloudy film transition width principally. In spite of the uncertainties, the best fit straight line to the data suggests a doubling in $y_c - x_c$ over the whole range of bromine contents. Although there are only two points evident at the right-hand end of Figure 2, one of these represents two separate determinations in that two different bromostyrene homopolymers, each mixed with the same copolymer, gave similar, somewhat hazy films, the haze levels of which indicated that $x_c - y_c$ was close to the critical value.

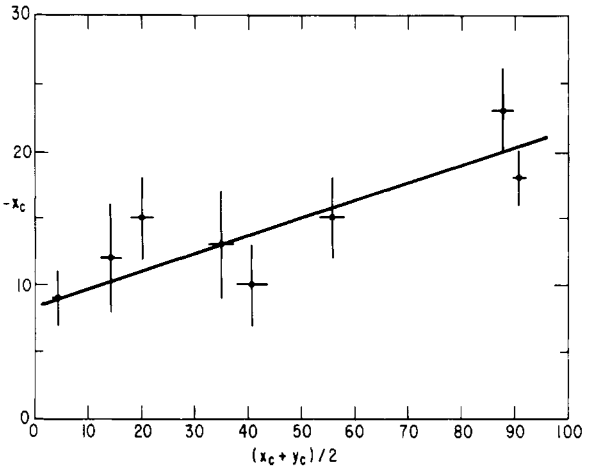

Figure 2. Conditions for phase separation in set B films: critical molar difference $y_c - x_c$ vs. molar average $(y_c + x_c)/2$ of *p*-bromostyrene in the two admixed polymers. All resins are of the same chain length.

Comparison with Theory. An analysis based on the Flory–Huggins theory for the phase behavior of binary and ternary blends of related materials has been developed recently.[4] The underlying assumptions of this development are as follows: (a) A critical solution temperature lies fairly close to the film casting temperature whenever $x \simeq x_c$; (b) the presence of residual solvent at the point of glassification during film casting has a negligible effect on the phase behavior observed; (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 x_c. The use of 50/50 (w/w) blends, rather than those compositions corresponding to the critical solution temperatures introduces negligible error in x_c determination. This is so because of the breadth of the coexistence curve and the extreme sensitivity of the curve's location on the temperature scale to copolymer bromine content. Thus in one case[9] the coexistence temperature at 50/50 composition differs from the critical temperature (70/30 composition) by about 10 °C; by contrast, a change of 1 or 2% in copolymer composition was found sufficient to shift the whole coexistence curve upward by 100 °C.

For similar reasons the amount of residual solvent in the cast film at the point of glassification (ca. 5–10%) is believed to have negligible effects on x_c determination.

The densities of poly(*p*-bromostyrene) and polystyrene are 1.57 and 1.04 g/cm^3. This leads to a difference of only 17% in the sizes of the lattice sites occupied by the two respective chain units. Moreover, in each of the mixtures but one described below, the two polymers mixed together (homopolymer plus copolymer or copolymer plus copolymer) differ by 40% or less in composition. Therefore the *average* size of the lattice site of the units in one component differs from the average site size in the other by 7% or less. These differences are considered to be negligible.

Set A Blends. For set A the appropriate expression for $x = x_c$ is[4,5]

$$\chi_{12} = 2/Nx_c^2 \tag{1}$$

where χ_{12} is the styrene–bromostyrene segmental interaction parameter and N is the degree of polymerization ($N_A = N_B$ for each subset). If χ_{12} is a constant independent of concentration and molecular weight, then

$$x_c \propto N^{-1/2} \tag{2}$$

with intercept at the origin. This behavior is seen in Figure 1 for polystyrene molecular weights of 10 000–860 000 or above and values of x_c up to 40%. The value of χ_{12} in this M_{PS} range averages 0.20, which is close to the value estimated previously[4] based solely on the results for M_{PS} = 97 000 and its derivatives. The datum at M_{PS} = 4000 and x_c = 0.76 suggests a positive deviation from linearity in the correlation, i.e., a greater tolerance for bromine at lower molecular weights and higher average bromine content.

Set B Blends. Set B blends provide a much more stringent test of the constancy of χ_{12} with change in the medium since the concentration range covered is much greater (5–90% vs. 0–38% average bromostyrene content in sets A and B, respectively).

For set B the expression analogous to (1) is easily shown to be

$$\chi_{12} = 2/N(y_c - x_c)^2 \tag{3}$$

Thus, for constant $N_A = N_B$, which is the case for set B, the bromination difference tolerance should be constant across the whole copolymer composition range if χ_{12} is independent of composition. This result does not fit the experimental trend seen in Figure 2, however. (The use of 50/50 (w/w) blends rather than the 50/50 (v/v) blends required by eq 3 cannot explain the discrepancies: In the case of the largest density difference between copolymer pairs in Figure 2 (0.48/0.62), the χ's calculated with weight fractions and volume fractions differ by less than 1%.)

The mean field approach attributes all nonideality to the van Laar segment/segment exchange free energy.

$$\Delta\omega_{12} = \omega_{12} - \tfrac{1}{2}[\omega_{11} + \omega_{22}] \tag{4}$$

where ω_{12}, ω_{11}, and ω_{22} are the near-neighbor energies of styrene/bromostyrene, styrene/styrene, and bromostyrene/bromostyrene segments, respectively. The free energy absorbed when 1 mol of styrene and 1 mol of bromostyrene segments are mixed to form 1 mol of styrene/bromostyrene contacts is $\Delta\omega_{12} = \chi_{12}RT \simeq 120$ cal at room temperature. While all blend results indicated an endothermal $\Delta\omega_{12}$, Figure 2 suggests that the magnitude of $\Delta\omega_{12}$ decreases (i.e., the styrene/bromostyrene "tolerance" increases) with increasing bromostyrene content in the medium. This trend is consistent with the value of χ_{12} necessary to rationalize the datum at x_c = 0.76 in Figure 1. This result is also confirmed by the detailed study of the coexistence curve of a single copolymer pair.[9] In short, the three sets of experiments are consistent in suggesting that χ_{12} decreases with bromine increase.

A dependence of χ on composition is a phenomenon of polymer mixtures frequently observed. It is also a phenomenon that may occur for any of a number of reasons. For most systems studied the precise source(s) of such dependence is apparently not known. While recognizing that there are many possible sources, we wish to suggest in what follows one specific, physically realistic source that seems capable of rationalizing most or all of the dependence seen here.

In the systems under study chemical effects (e.g., ionic or hydrogen bonding) are not expected, so that pairwise additivity of segment energies should be a good approximation. The major contributions to molecular attraction in the absence of hydrogen bonding and charge transfer are dispersion, induction, and dipole–dipole coupling.[10] Induction energies are generally small,[10,11] and thus an explanation of the downward drift in χ_{12} with bromine content in terms of dipole–dipole attractions between the bromostyrene units is considered. While it must be admitted that this specific mechanism is only one of many that come to mind, it seems to have two advantages over other choices: (1) the most prominent *chemical* distinction between halogenated and unhalogenated hydrocarbons is electronic polarity, and so seems to us to be a "natural" candidate; (2) there are no free parameters available for the calculation, so that either it gives the correct magnitude of the effect or it does not.

Specifically, we assess the influence of the bulk dielectric constant of the medium in which the dipole pairs sit upon their mutual interaction free energy as measured by the term ω_{22} (the only term on the right side of eq 4 that is affected). The interaction energy U_{dipole} between two (bromostyrene) dipoles μ and μ' in a vacuum is

$$U_{\text{dipole}} = -\left[\frac{\mu\mu'}{4\pi\epsilon_0 r^3}\right](2 \cos \Theta \cos \Theta - \sin \Theta \sin \Theta \cos \Phi) \tag{5}$$

where r is their scalar separation, Θ and Φ are the spherical vector orientation angles, and ϵ_0 is the permittivity of free space. The thermal average of eq 5 over all orientations gives

$$\langle U_{\text{dipole}} \rangle = -\frac{2\mu^2\mu'^2}{3r^6RT(4\pi\epsilon_0)^2} \tag{6}$$

a near-neighbor effect that falls off as r^{-6}. In bulk each segment has about 12 neighbors, and dipole field intensity lines are reduced by the dielectric constant. Approximating the local dielectric constant by its average bulk value $\bar{\epsilon}$, we write the dipole–dipole stabilization of a bromostyrene pair as

$$\langle U_{\text{dipole}} \rangle = -(\bar{\epsilon})^{-2}\frac{2\mu^2\mu'^2}{3r^6RT(4\pi\epsilon_0)^2} \tag{7}$$

An estimate of this energy is found by using the gas-phase moment of bromobenzene (μ = 2.7 D) and the average separation between segments $\bar{r} = 3.35 \times 10^{-8}$ cm in bulk bromostyrene. The dielectric constants of polystyrene and poly(bromostyrene) are 2.55 and 5.5.[8] From eq 7 dipolar contributions at 300 K to ω_{22}/RT are

$$\frac{\langle U_{\text{dipole}} \rangle}{RT} \sim +0.20 \text{ in a styrene environment}$$
$$\sim +0.04 \text{ in a bromostyrene environment}$$

The larger dielectric constant of bromostyrene shields the interacting dipole fields and *destabilizes* bromostyrene pairs relative to such pairs in the low dielectric of styrene itself. The magnitude of the effect is (probably) fortuitously close to the χ_{12} differences deduced from Figure 2 using eq 1, namely, 0.2 and 0.05 in styrene and bromostyrene, respectively. It is certainly true that the sign and magnitude of the dipole–dipole stabilization energy are consistent with the observed composition dependence of the segment–segment interaction $\Delta\omega_{12}$. The present "dielectric shielding" model ought to be applicable in any blend system composed of polar and nonpolar segments. In fact, one may predict that polar-rich compositions will in general be more tolerant of composition differences. Barnum et al.[13] have recently emphasized the possible importance of dipole interactions in polymer blend systems.

Finally, it is worth noting that this study and its companion,[9] taken together, imply that the phase separation behavior seen in these systems must be associated with upper critical solution temperatures over the whole range of chain lengths.

Conclusions

The molecular weight dependence of the critical bromination level for phase separation, x_c, may be understood in terms of the mean field model previously presented. The composition dependence of the model parameter χ_{12} corresponds to an increased tolerance of styrene for bromostyrene at high bromostyrene levels, and its sign and magnitude seem to be susceptible to rationalization in terms of dielectric shielding of bromostyrene dipoles from each other. Finally, the unity of results over the entire range of molecular weights, together with the UCST behavior reported for one of the lower chain length blends in the succeeding paper, indicates that UCST's are associated with phase separation over the whole range of those blends.

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