Critical Behavior of Binary Liquid Mixtures of Deuterated and Protonated Polymers

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Binary mixtures of protonated and perdeuterated 1,4-polybutadiene have been examined by small-angle neutron scattering and are shown to exhibit an upper critical solution temperature. The scattering results above the critical temperature are described by the mean-field theory of de Gennes for homogeneous binary polymer mixtures. These results contradict the universally held assumption that mixtures of deuterated and protonated polymers of otherwise identical chemical structure form ideal solutions.

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The method of "staining" individual macromolecules by isotope labeling has been extensively applied to the investigation of polymer chain conformation,[1-3] polymer-polymer miscibility,[4,5] and high-polymer diffusion[6-8] in the melt state. Neutron scattering,[1-6] forward recoil spectroscopy,[7] and infrared microdensitometry[8] techniques have each been utilized in pursuing these issues by exploiting the large differences in mass and neutron-scattering cross section between hydrogen and deuterium nuclei. All such investigations are premised on the assumption that amorphous high–molecular-weight protonated and deuterated polymers, characterized by otherwise identical chemical structures, form ideal solutions. However, several recent studies investigating critical phenomena in binary polymer blends[9] and solutions[10] have yielded isotope-dependent critical temperatures, and Bates *et al.*[3] have observed polymer block clustering with increasing molecular weight in mixtures of deuterated and protonated block copolymers, suggesting that this result might also derive from an isotope effect. These experimental observations indirectly question the ideal-solution assumption. Furthermore, Buckingham and Hentschel[11] have calculated that a binary mixture of high–molecular-weight deuterated and protonated polymer should exhibit an upper critical solution temperature. This prediction is notable for two reasons: (1) Nonideal mixing has never been reported in mixtures of protonated and deuterated amorphous polymers, and (2) there exists no documented example of upper critical solution temperature behavior in mixtures of high–molecular-weight polymers; because of free-volume effects[12] lower critical solution temperatures have been universally observed. In this Letter we conclusively demonstrate with small-angle neutron scattering (SANS) measurements that binary mixtures of fully protonated and perdeuterated 1,4-polybutadiene are in fact characterized by an upper critical solution temperature. These results establish that segregation effects must be accounted for in the application of isotope labeling to the investigation of polymer chain structure and dynamics in high–molecular-weight polymer melts.

Monodisperse perdeuterated and protonated (normal) 1,4-polybutadienes were synthesized and characterized with use of previously reported techniques.[13] The microstructure of the protonated samples was determined by ^{13}C-NMR analysis to be exactly equivalent to that characterizing perdeutero-1,4-polybutadiene prepared under the same conditions.[9,14] The weight average degree of polymerization N_W and polydispersity index N_W/N_N for the three polymers presently considered are listed in Table I. All reported results are based on the weight-average degree of polymerization.[15] Binary blends were prepared by dissolving each component in excess cyclohexane followed by solvent stripping and drying under vacuum (10^{-5} Torr). Scattering cells were assembled by squeezing a blend between quartz plates. This procedure was conducted under vacuum in order to eliminate the development of bubbles.

Neutron-scattering spectra were obtained on the 30-m SANS instrument at the National Center for Small-Angle Scattering Research located at Oak Ridge Na-

TABLE I. Polymer molecular characteristics.

Sample	Isotope	Weight-average degree of polymerization N_W ($\pm 10\%$)	Polydispersity index N_W/N_N (± 0.02)
B2	^{2}H	4600	1.10
B3	^{1}H	4200	1.12
B5	^{1}H	960	1.05

tional Laboratory. 4.75-Å-wavelength neutrons ($\Delta\lambda/\lambda \cong 5\times10^{-2}$) were collimated with pinholes and counted with a position-sensitive area detector. Two-dimensional scattering data were corrected for background intensity, sample-cell scattering, and sample thickness and transmission. The isotropic two-dimensional scattering data were radially averaged to one-dimensional form and reduced to units of absolute differential scattering cross section per unit solid angle (cm^{-1}, $\pm10\%$) by calibration of the instrument with an irradiated aluminum secondary standard. This standard was in turn calibrated by use of the incoherent scattering from water and vanadium and the coherent scattering from a well-characterized, partially labeled polystyrene sample. A series of SANS spectra were collected at each temperature (± 0.1 °K) during several heating and cooling cycles in order to verify that the reported results reflect an equilibrium state.

We have examined two sets of mixtures prepared by blending sample B2 with samples B3 and B5 (see Table I), denoted by B2B3(Φ) and B2B5(Φ) where Φ refers to the volume fraction of perdeuterated polymer. Two of these specimens, B2B3(0.50) and B2B5(0.31), lying at or near the critical composition[15]

$$\Phi_c = N_2^{1/2}[N_1^{1/2}+N_2^{1/2}]^{-1}, \tag{1}$$

are presently discussed, where N_1 and N_2 refer to the degree of polymerization of the perdeutero and normal species, respectively. Figure 1 depicts three representative SANS spectra obtained from sample B2B5(0.31) between 247 and 363 °K. It should be noted that 1,4-polybutadiene is characterized by a glass transition temperature of approximately 183 °K,[13] so that the samples remained in the liquid state during all measurements. The scattering spectrum from sample B2B3(0.5), obtained at 296 °K, is shown in Fig. 2.

de Gennes[15] has calculated the correlation function for homogeneous binary mixtures of amorphous polymers on the basis of the mean-field random-phase approximation,

$$S^{-1}(q) = [N_1\Phi g_D(R_{g_1},q)]^{-1} + [N_2(1-\Phi)g_D(R_{g_2},q)]^{-1} - 2\chi, \tag{2}$$

$$g_D(R_g,q) = 2[R_g^2q^2 + e^{-R_g^2q^2} - 1]/R_g^4q^4,$$

in which $q = 4\pi\lambda^{-1}\sin(\theta/2)$ is the scattering wave vector, N is the number of segments per polymer molecule, and $R_g = a(N/6)^{1/2}$ is the radius of gyration for a Gaussian coil where $a = 6.9$ Å for 1,4-polybutadiene.[14,16] χ, known as the Flory parameter,[15] describes segment-segment interactions. In the case $\chi = 0$, the system is ideal, while for $0<\chi<\chi_s$ the system remains homogeneous but is characterized by composition fluctuations. For $\chi>\chi_s$ the homogeneous state becomes unstable and the mixture undergoes phase separation, where

$$\chi_s = \{(N_1\Phi)^{-1} + [N_2(1-\Phi)]^{-1}\}/2 \tag{3}$$

defines the spinodal point. The predicted scattering intensity is given by

$$I(q) = V^{-1}(b_\mathrm{H} - b_\mathrm{D})^2 S(q), \tag{4}$$

where V is the segmental volume, and b_H and b_D are the coherent scattering lengths of the protonated and deuterated segments.

We have analyzed the neutron scattering data from

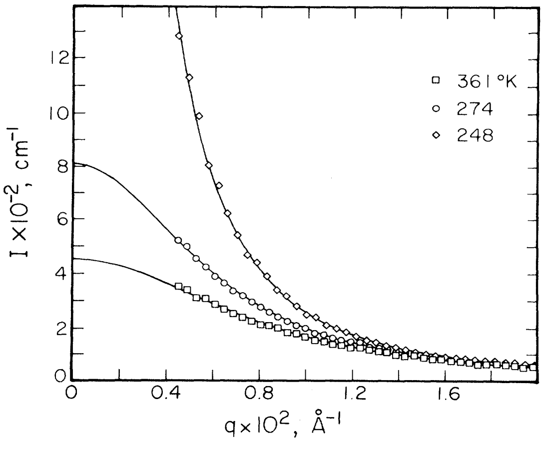

FIG. 1. Coherent small-angle neutron scattering from sample B2B5(0.31), a binary mixture of protonated and perdeuterated 1,4-polybutadiene at the critical composition. The curves were obtained from the predicted homogeneous-mixture scattering function by adjusting the segment-segment interaction parameter χ.

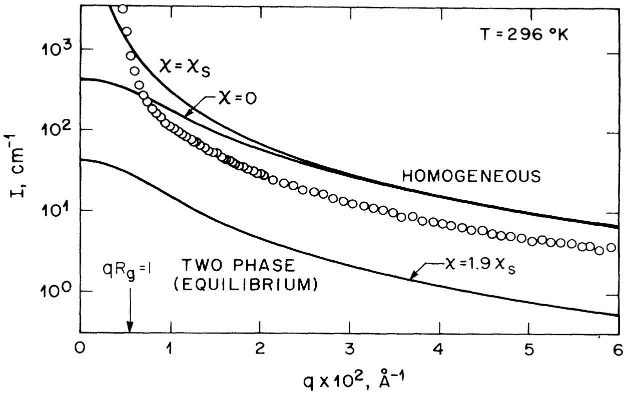

FIG. 2. Coherent small-angle neutron scattering from sample B2B3(0.50), a phase-separated (metastable) binary blend of protonated and perdeuterated 1,4-polybutadiene. The curves are the calculated scattering intensities for a homogeneous mixture in the limits of ideal mixing ($\chi = 0$) and single-phase stability ($\chi=\chi_s$), and for the equilibrium two-phase state based on the experimentally determined interaction parameter ($\chi = 1.9\chi_s$).

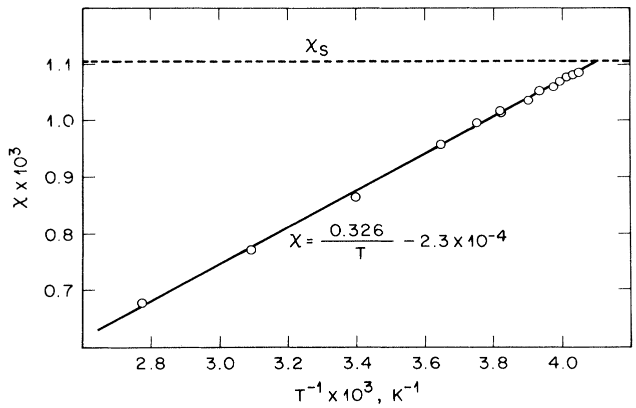

FIG. 3. Temperature dependence of the segment-segment interaction parameter χ, obtained by fitting the theoretical homogeneous binary-blend correlation function to the small-angle neutron-scattering data from sample B2B5(0.31).

sample B2B5(0.31) on the basis of the homogeneous mixture structure factor $S(q)$ given by Eq. (2). The predicted scattering intensities represented by the solid curves in Fig. 1 have been best fitted to the data by adjustment of the interaction parameter χ, which has been found to be inversely related to temperature,

$$\chi = (0.326 \pm 0.004) T^{-1} - (2.3 \pm 1.7) \times 10^{-4},$$

as illustrated in Fig. 3; all other parameters including SANS intensity have been independently determined. The uncertainty in the constant term of $\chi(T)$ is a reflection of the errors associated with measuring N (Table I) and calibrating the SANS instrument for absolute intensity. These results quantitatively account for the experimental data and conclusively demonstrate that this mixture is characterized by an upper critical solution temperature. It should be noted that the SANS data do not extend to low enough wave vector ($qR_g \geqslant 0.8$) to justify direct use of the Ornstein-Zernike analysis.[15] We have also measured $\chi = 8.7 \times 10^{-4}$ at 296 °K for a blend away from the critical point, B2B5(0.65), indicating that the segment-segment interaction parameter does not depend strongly on composition over the range $0.31 \leqslant \Phi \leqslant 0.65$.

In contrast with sample B2B5(0.31), the SANS data from sample B2B3(0.50) *cannot* be described by the homogeneous-mixture correlation function based on the experimental parameters in either of the limits $\chi = 0$ or $\chi = \chi_s$, as illustrated by the upper curves in Fig. 2. This behavior is expected in light of the results presented in Fig. 3, which connote that the homogeneous mixed state for sample B2B3(0.50) should be unstable ($\chi/\chi_s = 1.9$) at 296 °K because of an increased degree of polymerization (Table I). As a result of the exceedingly long diffusion times associated with high-polymer melts,[15] the demixing process in polymer blends is generally arrested in a nonequilibrium metastable state distinguished by finite-size domains. The forward scattering observed in Fig. 2 ($qR_g \sim 1$) is attributed to the existence of such a domain structure. This conclusion has been verified by the observation of a peak in the small-angle scattering of visible light ($qR_g << 1$), which is characteristic of binary blends which have undergone phase separation into roughly micron-size domains. As illustrated in Fig. 2, the observed scattering intensity at $qR_g > 1$ lies significantly below that corresponding to the homogeneous mixed state, but in excess of that calculated for two-phase equilibrium on the basis of $\chi = 1.9\chi_s$. This intermediate level of scattering reflects a significant degree of interfacial mixing, which is a consequence of the combined effects of the close proximity of this sample to the critical point[17] and the large interfacial surface area associated with the aforementioned domain structure. Overall, the SANS data depicted in Fig. 2 conclusively confirm that sample B2B3(0.50) has undergone phase separation as predicted.

What then is the nature of the interaction between protonated and deuterated polymers which results in this unexpected phase behavior? Buckingham and Hentschel[11] have observed that there exists a small difference in molar specific volume, $\Delta V/V \cong 10^{-2}$–10^{-3}, between nearly all pairs of deuterated and protonated organic molecules. They argue that upon mixing of such pairs of polymer molecules, specific-volume variations are redistributed such that the resulting solution is characterized by a single segmental volume. Hence the change in free energy associated with the mixing of protonated and deuterated polymer is modeled in two steps: (1) compression or expansion of each component to the final segmental volume of the mixture, and (2) mixing of the components at constant volume. This leads to the prediction of an upper critical solution temperature, which for the purpose of comparison with the present results can be cast in terms of the critical degree of polymerization,

$$N_c = 4k_B T\kappa / V(\Delta V/V)^2, \tag{5}$$

where $\kappa = 5.3 \times 10^{-10}$ Pa^{-1} is the isothermal compressibility of polybutadiene,[16] k_B is the Boltzmann constant, and the degree of polymerization of each component has been taken to be the same. $\Delta V/V$ and V for perdeuterated and protonated 1,4-polybutadiene were experimentally determined to be $(4.0 \pm 1.0) \times 10^{-3}$ and 1.0×10^{-22} cm^3/segment, respectively. Thus, the predicted critical degree of polymerization at 296 °K is $3.5 \times 10^3 \leqslant N_c \leqslant 9.7 \times 10^3$. This value can be compared with the SANS-determined χ

by use of the symetrical versions ($N_1 = N_2 = N$) of Eqs. (1) and (3), $N_c = 2/\chi$. On the basis of the interaction parameter determined at 296 °K (Fig. 3), the corresponding experimentally determined critical degree of polymerization is $N_c = (2.3 \pm 0.5) \times 10^3$. Hence the calculation of Buckingham and Hentschel predicts both the temperature dependence and relative magnitude of the observed isotope effect. It is the size of macromolecules and the corresponding reduction in combinatorial entropy which makes this effect significant in binary blends of amorphous polymers.

These findings clearly indicate the necessity of accounting for isotope effects when applying the isotope labeling technique to the investigation of chain conformation, multicomponent mixing, and dynamics in high–molecular-weight polymer melts. They also demonstrate a new class of materials with which to study critical phenomena and phase behavior in polymer mixtures, including interfacial mixing near critical points[17] as discussed above, and phase-separation dynamics. Of particular significance is the ability to manipulate precisely the critical temperature and composition of a mixture by varying the degree of polymerization of the monodisperse components.

In conclusion, we have demonstrated that binary blends of high–molecular-weight protonated and perdeuterated 1,4-polybutadiene are characterized by an upper critical solution temperature, in contradiction to the typical assumption of ideal solution behavior.

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