

Isotope-Induced Quantum-Phase Transitions in the Liquid State

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Isotopic binary liquid mixtures are universally characterized by an upper critical solution temperature as a consequence of zero-point motion in conjunction with the anharmonicity of the interatomic potential. This quantum effect is predicted, and demonstrated by small-angle neutron-scattering measurements, to be manifest at ambient temperatures for mixtures of deuterated and protonated polymers. Prior evidence of such phase behavior has been restricted to liquid mixtures of ^3He and ^4He .

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We have recently discovered^{1,2} that binary liquid mixtures of deuterated and protonated polymers are characterized by an upper critical solution temperature. In this Letter we show quantitatively that such phase behavior is a direct manifestation of zero-point motion in combination with interatomic-potential anharmonicity. This quantum effect is universal to all isotopic liquid mixtures, resulting in phase separation as $T\Delta S_M \rightarrow 0$, where ΔS_M represents the difference in entropy between the mixed and the unmixed states. Until recently^{1,2} this condition had only been realized for mixtures of ^3He and ^4He , which can exist in the liquid state as $T \rightarrow 0$.³ For polymers in the liquid state $\Delta S_M \sim N^{-1}$ (see below), where N represents the number of segments in a molecule. Hence, all isotopic liquid polymer mixtures will undergo phase separation at a finite temperature as $N \rightarrow \infty$. This phenomenon is experimentally verified for binary liquid mixtures of fully deuterated and protonated (normal) polystyrenes and polybutadienes.

The change in free energy per segment associated with the mixing of deuterated and protonated polymers of degree of polymerization N_D and N_H can be approximated by^{4,5}

$$\frac{\Delta F_M}{k_B T} = \frac{\Phi_H}{N_H} \ln \Phi_H + \frac{\Phi_D}{N_D} \ln \Phi_D + \Phi_H \Phi_D \chi, \quad (1)$$

where $\Phi_D (= 1 - \Phi_H)$ represents the volume fraction of deuterated segments, k_B is the Boltzmann constant, and χ is the Flory-Huggins parameter.^{4,5} The first two terms in Eq. (1) describe the combinatorial entropy while the third term accounts for both segment-segment interaction energy and noncombinatorial entropy.

It is well known that substitution of a deuterium atom for a hydrogen atom in a molecule reduces the

average bond length as a consequence of zero-point vibrations and the anharmonicity of the interatomic potential. This reduction in bond length with deuterium substitution is primarily in evidence in the liquid state as a decrease in both the molecular volume and the polarizability. Therefore, we estimate the overall segment-segment interaction parameter to be the sum of two terms,

$$\chi = \chi_v + \chi_d, \quad (2)$$

where χ_v and χ_d account for the difference in segment volume and van der Waals forces between deuterated and protonated liquid polymers, respectively. This is equivalent to splitting of the mixing process into two steps⁶: (1) compression or expansion of each component to the segmental volume of the mixture, and (2) mixing of the components at constant volume.

The correction to the mixing free energy which accounts for the difference in segment volume between deuterated (V_D) and protonated (V_H) polymers is

$$\chi_v = (1/k_B T) \sum_{i=H,D} \int_{V_i}^V P dV, \quad (3)$$

where the equation of state is given by

$$P = P_i + (1/\kappa_i) \ln(V_i/V), \quad (4)$$

in which V is the segment volume of the mixture, and the compressibility κ_i has been taken to be independent of pressure. In the limit of vanishing external pressure ($P_i=0$) and $V^{-1}(V_H - V_D) \ll 1$, and with neglect of the excess volume of mixing, $V \cong \Phi_H V_H + \Phi_D V_D$,

$$\chi_v \cong (1/k_B T) (V_H - V_D)^2 / 2\kappa V, \quad (5)$$

where the polymer compressibility is assumed to be independent of isotopic state ($\kappa = \kappa_H \cong \kappa_D$).

The second term of Eq. (2) corresponds closely to the original Flory-Huggins⁵ description of the segment-segment interaction parameter,

$$\chi_d = \chi_{d,\epsilon} - \chi_{d,S}, \quad (6)$$

$$\chi_{d,\epsilon} = (1/k_B T) [\epsilon_{HD} - \frac{1}{2}(\epsilon_{HH} + \epsilon_{DD})], \quad (7)$$

where ϵ indicates a segment-pair interaction energy. Since deuterocarbon and hydrocarbon polymers are expected to be characterized by purely dispersion forces we have identified these terms by the subscript d . $\chi_{d,S}$ accounts for the noncombinatorial entropy change associated with the dispersion interactions. This parameter is not readily calculated, although it must be emphasized that $\chi_{d,\epsilon} \geq 0$ and to a good approximation it does not depend on temperature.⁷

We estimate ϵ from the familiar London formula⁸ based on a uniform segment density⁹ V^{-1} for distances greater than a cutoff length $(3V/4\pi)^{1/3}$. Thus Eq. (7) reduces to

$$\chi_{d,\epsilon} \cong \frac{1}{k_B T} \frac{2}{3} \frac{\pi^2}{V^2} I(\alpha_H - \alpha_D)^2, \quad (8)$$

where α and I represent the segment polarizability and ionization potential, respectively (note that $I_H/I_D = 1 \pm 0.01$ for organic molecules). The difference in segment polarizabilities is approximated from the n carbon-hydrogen (C—H) or carbon-deuterium (C—D) bonds per segment and the corresponding bond polarizabilities,¹⁰

$$\alpha_H - \alpha_D = n(\alpha_{C-H} - \alpha_{C-D}). \quad (9)$$

Bell¹¹ has measured the polarizability of a carbon-hydrogen bond to be 1.0145 times greater than that of a carbon-deuterium bond; this derives from the slightly more extended electron distribution that results from the longer bond length in the protonated molecule.

We are now in a position to calculate the interaction energy, $\chi_v + \chi_{d,\epsilon}$, for deuterated and protonated

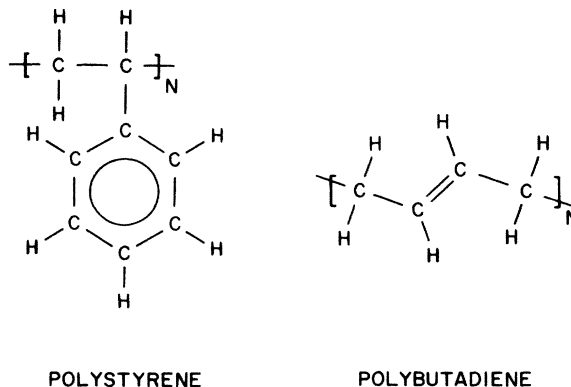


FIG. 1. Two-dimensional projections of the segment molecular structure for the protonated polymers discussed in the text.

liquids, based solely on measurable quantities. As shown below, it is this portion of the segment-segment interaction parameter that can be accurately determined experimentally. Two cases are presently considered, polybutadiene and polystyrene; two-dimensional projections of the segment molecular structure are illustrated in Fig. 1. The calculated values of χ are given in Table I, along with parameters used in the calculations.

As demonstrated in a previous Letter,¹ the isotope effect can be accurately determined for liquid polymers by means of coherent small-angle neutron scattering (SANS) measurements. The SANS intensity is given by

$$I(q) = V^{-1}(b_H - b_D)^2 S(q), \quad (10)$$

where $q = 4\pi\lambda^{-1} \sin(\theta/2)$ is the scattering wave vector, and b_H and b_D are the coherent scattering lengths of the protonated and deuterated segments, respectively. For homogeneous binary polymer mixtures, the structure factor is given in the random-phase approximation by⁴

$$S^{-1}(q) = [N_H \Phi_H g_D(R_{g,H}, q)]^{-1} + [N_D \Phi_D g_D(R_{g,D}, q)]^{-1} - 2\chi, \quad (11)$$

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

TABLE I. Polymer segment parameters.

	$10^{22} V$ (cm ³)	$10^{25} (V_H - V_D)$ (cm ³)	$10^{10} \kappa$ (Pa ⁻¹)	I (eV)	$10^{25} (\alpha_H - \alpha_D)$ (cm ³)	$T\chi_v$ (± 0.02)	$T\chi_{d,\epsilon}$ (± 0.01)	$T(\chi_{\text{calc}} + \chi_{d,S})$	χ_{meas}
Polybutadiene	1.00 (298 K) ^a	4.1 ± 0.4^a	5.3 (298 K) ^b	9 ± 0.3^c	0.557 ^d	0.12	0.21	0.33 ± 0.02	$(0.326 \pm 0.04) T^{-1}$ $-(2.3 \pm 1.7) \times 10^{-4}$
Polystyrene	1.75 (400 K) ^e	5.1 ± 0.7^f	8.2 (460 K) ^e	8.8 ± 0.3^c	0.743 ^d	0.07	0.12	0.19 ± 0.02	$(0.20 \pm 0.01) T^{-1}$ $-(2.9 \pm 0.4) \times 10^{-4}$

^aReference 12.

^bReference 15.

^cReference 16.

^dReferences 8 and 11.

^eReference 13.

^fReference 14.

where $R_g = a(N/6)^{1/2}$ is the radius of gyration for a Gaussian coil; the statistical length $a \cong 6.9 \text{ \AA}$ for 1,4-polybutadiene¹² and 6.7 \AA for atactic polystyrene.² By appropriate choice of N_D , N_H , and Φ_D , a binary isotopic polymer mixture can be brought near the critical point for demixing^{4,12}; near this point small variations in χ induce large changes in $I(q)$ for $qR_g \leq 1$. Since χ represents the only experimentally undetermined parameter in Eqs. (10) and (11), a fitting of SANS data obtained as a function of temperature from a near-critical binary polymer mixture with $S(q)$ provides a determination of $\chi(T)$. As a consequence of making all measurements on a single mixture, with a single instrumental setup, the systematic experimental uncertainties in N and in calibrating the SANS instrument (each $\pm 5\%$ – 10%) appear almost exclusively in the constant term, $\chi_{d,s}$. Thus, this technique gives a precise determination of the temperature-dependent part, $\chi_v + \chi_{d,e}$, of the interaction parameter.

Using this method, we have measured $\chi(T)$ for fully deuterated and protonated polymers, for the two cases illustrated in Fig. 1. The results for 1,4-polybutadiene have been described in a previous

Letter¹ and are reported in Table I. Figure 2 shows the SANS results obtained at several temperatures from a binary mixture of fully deuterated and protonated atactic polystyrenes near the critical point ($N_D = 1.15 \times 10^4$, $N_H = 8.7 \times 10^3$, $\Phi_D = 0.50$). The methods of sample preparation and SANS data acquisition and reduction are as previously described.² The solid curves shown in Fig. 2 were obtained by use of Eqs. (10) and (11) with adjustment of χ ; all other parameters have been independently determined. The dependence of χ on inverse temperature is illustrated in Fig. 3, and reported in Table I.

Both measured segment-segment interaction energy parameters are predicted, within experimental uncertainty, by the method described above (Table I). Furthermore, the measured sign of $\chi_{d,s}$ is consistent with that dictated by the calculated dispersion forces. This clearly confirms the nature of these isotope-induced liquid-state phase transitions.

It should be noted that these effects are intrinsic to all isotopic liquid mixtures. However, in all known

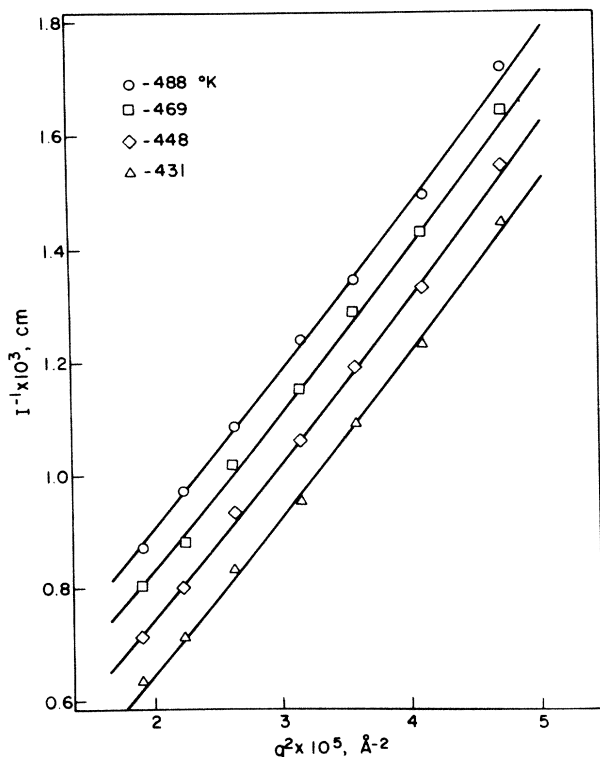


FIG. 2. Coherent small-angle neutron scattering from a homogeneous binary liquid mixture of fully deuterated and protonated polystyrenes near the critical point for demixing. The curves were obtained by use of the predicted homogeneous-mixture scattering function with adjustment of the segment-segment interaction parameter χ .

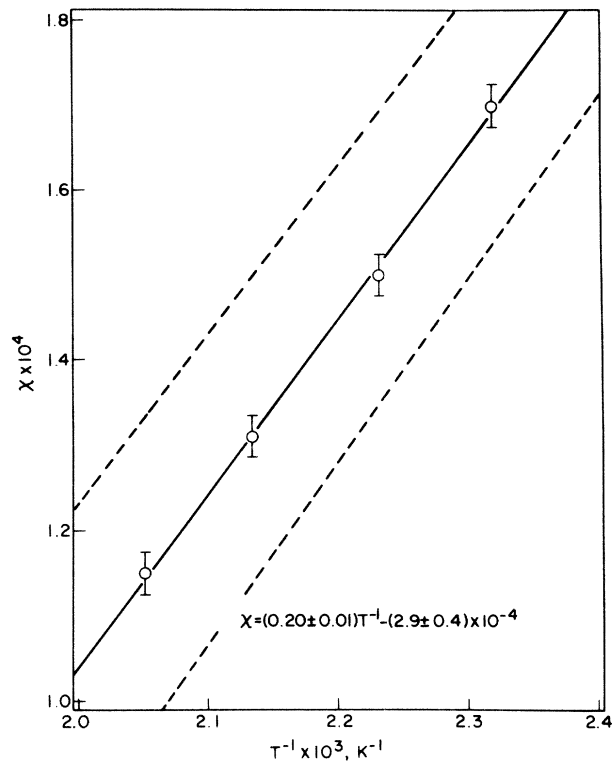


FIG. 3. Temperature dependence of the segment-segment interaction parameter obtained from the SANS results for a binary mixture of fully deuterated and protonated polystyrenes near the critical point. The dashed curves indicate the uncertainty in $\chi(T)$ corresponding to the estimated uncertainty in degree of polymerization N and SANS intensity calibration.

cases except helium and polymers, crystallization or vitrification obscures observation of the effect. For liquid mixtures of ^3He and ^4He , $\chi_{d,e}, \chi_{d,S} \approx 0$, within the context of the present analysis, and we calculate an upper critical solution temperature $T_c \approx 0.6$ K which is relatively close to the actual (tricritical) temperature $T = 0.87$ K. Quantitative treatment of the phase behavior of isotopic liquid-helium mixtures obviously requires the incorporation of additional statistical and quantum corrections,¹⁷ which are insignificant in the case of polymers at ambient temperatures.

In summary, we have demonstrated that liquid mixtures of deuterated and protonated polymers of sufficiently high degree of polymerization are characterized by an upper critical solution temperature that is quantitatively shown to result from the combined effects of zero-point motion and the anharmonicity of the interatomic potential.

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⁴P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell Univ. Press, Ithaca, NY, 1979).

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⁶A. D. Buckingham and H. G. E. Hentschel, *J. Polym. Sci. Polym. Phys. Ed.* **18**, 853 (1980), have used a similar approach in calculating the free energy of mixing for isotopic polymer mixtures, but incorrectly concluded that $V_D > V_H$ and $\chi_d \approx 0$.

⁷ $\chi_{d,S}$ represents the excess entropy which results from nonrandom mixing in a strictly regular solution as discussed by R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge Univ. Press, London, 1960), Chap. 8.

⁸J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).

⁹Since $\chi_{d,e}$ is determined solely by the density of carbon-hydrogen and carbon-deuterium bonds [see Eq. (9)] this actually corresponds to the more realistic assumption of a uniform density of these bonds.

¹⁰This approximation is supported by the fact that the difference in refractive indices between deuterated and protonated organic molecules is accurately predicted by the Lorentz-Lorenz relationship using Eq. (9).

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¹⁴We have estimated $V_H - V_D$ for polystyrene to be equivalent to that reported for toluene and methycyclohexane by L. S. Bartell and R. R. Roskos, *J. Chem. Phys.* **44**, 457 (1966).

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¹⁶Polymer-segment ionization potentials have been estimated based on those reported for structurally related molecules in *Handbook of Chemistry and Physics* (CRC Press, Boca Raton, FL, 1975), 56th ed.

¹⁷This is evidenced by the termination of the λ line at the top of the miscibility gap leading to tricritical behavior, and by the intersection of the coexistence curve at a finite (6.5%) ^3He concentration at $T=0$. Nevertheless, it has been clearly demonstrated (see G. Baym, Ref. 3, p. 439) that phase separation in liquid ^3He - ^4He mixtures derives primarily from the difference in mass (volume) between these two isotopes.