Thermodynamics of Isotopic Polymer Mixtures: Poly(vinylethylene) and Poly(ethylethylene)

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ABSTRACT: Binary mixtures of normal (protonated) and perdeuteriated poly(vinylethylene), and of poly(ethylethylene), containing 50% by volume deuteriated polymer, have been examined by small-angle neutron scattering (SANS). Evaluation of SANS data obtained between 26 and 100 °C, using the RPA theory for binary polymer mixtures, reveals that both isotopic systems are characterized by a small positive Flory-Huggins segment-segment interaction parameter, $5 \times 10^{-4} < \chi < 10^{-3}$, and an upper critical solution temperature (UCST). This isotope effect primarily derives from the reduction in carbon-hydrogen bond length that results from substituting deuterium for hydrogen in nonpolar organic liquids; the shorter carbon deuterium bonds are directly manifested as a smaller segment volume, $(V_H - V_D)/V = 0.0019 \pm 0.0004$ and 0.0039 ± 0.0004 for poly(vinylethylene) and poly(ethylethylene), respectively. A prediction for the excess free energy of mixing for isotopic polymer mixtures, based on the measured differences in segment volumes and the associated differences in segment polarizabilities, accounts for the experimental findings. Two other published theories, based solely on the segment volume isotope effect, are also discussed. We conclude that nonideal mixing is a universal characteristic of deuteriated and protonated polymers.

I. Introduction

Until recently, deuteriated and "normal" (protonated) polymers, which are otherwise chemically indistinguishable, have generally been assumed to form ideal mixtures. This has been implicit in most small-angle neutron scattering (SANS) studies of bulk polymers, which usually rely on the large difference in neutron coherent scattering lengths between hydrogen and deuterium to achieve scattering contrast without imparting a chemical dissimilarity. In several recent papers we have challenged this assumption[1-4] based on SANS studies of mixtures of perdeuteriated and normal 1,4-polybutadiene and atactic polystyrene, which indicate that isotopic polymer mixtures are characterized by a small positive Flory-Huggins segment-segment interaction parameter, $10^{-4} < \chi < 10^{-3}$, and an upper critical solution temperature (UCST). Green and Doyle[5] have confirmed our measurements of $\chi(T)$ for perdeuteriated and normal atactic polystyrene[4] based on FRS measurements of the thermodynamic slowing down of cooperative diffusion in mixtures of these isotopes. And Lapp et al.[6] report a small, positive interaction parameter for homogeneous mixtures of normal and perdeuteriated polydimethylsiloxane. Thus, there exists growing evidence that polymer isotopes do not form ideal solutions, although this conclusion is not universally accepted.[7]

Buckingham and Hentschel[8] were first to point out that deuteriated and protonated polymers should exhibit an upper critical solution temperature as a consequence of the small difference in segment volumes between isotopes; their prediction is an extension of that presented earlier by Prigogine[9] for liquid mixtures of ^{3}He and ^{4}He. More recently we have suggested that the polymer isotope effect derives from the change in C-H bond length with deuterium substitution,[4] which leads to a reduction in *both* segment volume and polarizability (Buckingham and Hentschel incorrectly concluded that $V_D > V_H$ where V represents the segment volume). Singh and Van Hook[10] have presented an alternative interpretation for the polymer isotope effect based solely on the segment volume isotope effect. However, their prediction derives from the same bond length variation addressed by us and therefore is fundamentally similar in origin.

In order to quantitatively evaluate the polymer isotope effect and to expand the number of chemically distinct species documented as exhibiting this behavior, we have prepared two new sets of isotopic mixtures: perdeuteriated and normal poly(vinylethylene) and poly(ethylethylene). These two polymers are particularly attractive for studying this phenomenon since the latter is obtained by hydrogenating or deuteriating the former, leading to an increase in the ratio of hydrogen-to-carbon, and a significant modification of physical properties, without changing the degree of polymerization. This eliminates a potentially significant source of error in the evaluation of the isotope effect for chemically different polymers. The presently reported SANS results, obtained from mixtures containing 50% by volume perdeuteriated polymer, demonstrate that both systems have a UCST, consistent with our previous findings. A comparison of the experimentally determined and predicted Flory-Huggins parameters indicates that nonideal mixing for polymer isotopes derives primarily from the effects of deuterium (hydrogen) substitution on the characteristics of the carbon-hydrogen (deuterium) bond.

II. Experimental Methods

A. Synthesis and Characterization. "Normal" (protonated) and perdeuteriated poly(vinylethylene)—often refered to as 1,2-polybutadiene—were prepared by using the anionic polymerization technique. Polymerizations were conducted in rigorously purified cyclohexane at 20 °C employing *tert*-butyllithium as the initiator. Bis(piperidinyl)ethane was added to the cyclohexane-*tert*-butyllithium solutions at approximately five times the active anion concentration ($\sim 5 \times 10^{-4}$ M) in order to obtain essentially complete 1,2 addition of butadiene.[11,12] Protonated and deuteriated butadiene monomers were obtained from Matheson Co. and MSD Isotopes, respectively, and were purified by successive vacuum distillation from butyllithium and dibutylmagnesium; the supplier reported that the perdeuteriated monomer contained 99.1 atom % deuterium based on mass spectroscopic analysis. The polymerizations were terminated after 18 h by the addition of a small amount of degassed methanol,

Table I
Molecular Characterization Results

sample	n_D[a]	$10^{-3}N_N$[b]	N_w/N_N[c]	$10^{-3}N_w$[d]	ρ,[e] g cm^{-3}	$10^{22}V$,[f] cm^3	$\Delta V/V$
PVE1	5.946	1.27	1.03	1.33	0.9883 ± 0.0003	1.0095 ± 0.0003	0.0019 ± 0.0004
PVE2	0	1.69	1.03	1.71	0.8881 ± 0.0003	1.0114 ± 0.0003	
PEE1	7.736	1.31	1.03	1.33	0.9941 ± 0.0003	1.0675 ± 0.0003	0.0039 ± 0.0004
PEE2	0	1.64	1.03	1.71	0.8694 ± 0.0003	1.0717 ± 0.0003	

[a] Deuterons per repeat unit. [b] Determined by membrane osmometry. [c] Determined by SEC. [d] $^1/_2(N_{N,PVE} + N_{N,PEE})(N_W/N_N)$. [e] Determined by density gradient column at 23.0 °C. [f] Repeat unit volume at 23.0 °C.

followed by precipitation of the product in excess methanol, and drying under vacuum. Poly(vinylethylene) was stored in a dark, high-purity helium environment.

A portion of each poly(vinylethylene) was hydrogenated or deuteriated in order to obtain the corresponding normal and perdeuteriated poly(ethylethylene). These reactions were conducted in nitrogen sparged cyclohexane at approximately 1% (w/v) polymer concentration, making use of a calcium carbonate supported palladium catalyst (Strem Chemical Co.) and ca. 500 psi of hydrogen or deuterium. The product was subsequently filtered and recovered by precipitation in methanol followed by vacuum drying. Infrared analysis of these hydrogenated (deuteriated) polymers confirmed complete reaction within the precision of the experimental method (<0.5%).

The number average degrees of polymerization, N_N, and polydispersity indices, N_W/N_N, were determined by membrane osmometry and size exclusion chromatography (SEC), respectively. The former measurements were conducted with a Wescan Model 230 membrane osmometer using concentrations between 1 and 8 g/L of polymer in toluene at 30 °C. These results are listed in Table I. Within experimental uncertainty the poly(ethylethylene), henceforth denoted PEE, is characterized by the same number average degree of polymerization as the corresponding poly(vinylethylene), to be referred to as PVE. This result is consistent with the previous study of these materials[12] and confirms the absence of spurious chemistry during the hydrogenation reactions. SEC measurements were obtained from a Waters 150C instrument fitted with six microstyrogel columns (10^2–10^6 Å pores) with THF employed as the mobile phase at 30 °C. All four polymers were found to have polydispersity indices (N_W/N_N and N_Z/N_W) of 1.03. On basis of this result and the average of the n_N values obtained for each PEE–PVE pair, we have determined the weight average polymerization indices reported in Table I. Owing to the care exercized in obtaining these results, the listed N_W values are estimated to be precise to within 3%.

We have determined the deuterium content of sample PEE1 by counting the total number of protons in 0.1 g of this polymer using a solid-state NMR spectrometer. The NMR proton counting technique was independently calibrated with a weighed amount of normal adamantane and checked for precision by comparing the NMR determined proton concentration from a perdeuteriated polybutadiene with that estimated from the level reported in the monomer; these independent measurements agreed within experimental error (0.1%). As indicated in Table I sample PEE1 contains 7.736 deuterons per repeat unit, which is somewhat less than is expected on the basis of the stoichiometric addition of deuterium to the PVE precursor, which contains 5.95 deuterons per repeat unit. This higher than anticipated concentration of protons derives from the exchange of hydrogen from the normal cyclohexane solvent onto the palladium catalyst, and subsequently onto the polymer; there are apparently no other adverse effects associated with this well known exchange reaction.

The densities of normal and perdeuteriated PEE and PVE were determined at 23.00 ± 0.05 °C by the density gradient column technique. Two separate columns were prepared from degassed solutions of methanol and ethylene glycol, covering densities from 0.86 to 0.92 g cm^{-3} (hydrogenous samples) and 0.97 to 1.00 g cm^{-3} (perdeuteriated samples). Both columns were immersed in a thermostated temperature bath and calibrated with a set of glass float standards (±0.0001 g cm^{-3}) supplied by Fisher Scientific. Measurements were made by using polymer samples which had been heated (~75 °C) under vacuum for 24 h and subsequently stored under a purified helium atmosphere. Small (~10^{-2} g) specimens introduced into the density gradient column settled to a constant level within several hours. Density measurements were taken from at least four specimens, which were consistently found to equilibrate at a single level, within the precision of the method. The results of these measurements are listed in Table I. Also listed in Table I are the repeat unit volumes V which have been calculated from the listed densities and atomic compositions.

B. Sample Preparation. We have prepared two mixtures containing 50% by volume perdeuteriated polymer by using the perdeuteriated and normal polymers listed in Table I; these are refered to as PVE12(0.5) and PEE12(0.5). Mixing was accomplished by dissolution of both components in rigorously purified hexane under inert-gas conditions followed by filtration (1 μm), solvent evaporation, and drying under vacuum to a constant weight. For the PVE mixture, this entire procedure was conducted in the absence of oxygen in order to ensure against side reactions such as chain branching and gelation.

Neutron scattering specimens were prepared by allowing an aliquot of a sample mixture to flow onto a $^1/_{16}$ in. thick by 1-in. diameter optical quality quartz disk, within the area defined by a 1.5 cm (inside diameter) by 0.125 cm thick aluminum spacer; this process was conducted under vacuum at 50 °C. The specimen was then placed in a high-purity helium environment and covered with a second quartz disk, thus forming a uniform thickness cell. Scattering cells were sealed by using epoxy while under helium. We have found that this procedure yields a very stable neutron scattering specimen which is well-protected from the ambient environment.

C. SANS Measurements. Small-angle neutron scattering (SANS) measurements were obtained by using the 30-m instrument at the National Center for Small Angle Scattering Research located at Oak Ridge National Laboratory. A detailed description of this instrument can be found elsewhere.[13] Measurements were made at sample-to-detector distances (SDD) of 19, 6.9, and 2.6 m by using a radiation wavelength of $\lambda = 4.75$ Å with a distribution (fwhm) of $\Delta\lambda/\lambda = 0.06$. This combination provided access to a range of scattering wavevectors $3 \times 10^{-3} \leq q \leq 2 \times 10^{-1}$ Å^{-1} where $q = 4\pi\lambda^{-1} \sin(\theta/2)$. In all cases the neutron beam area at the sample was defined by a 0.8-cm diameter cadmium pinhole while the source aperture size and distance from the sample were adjusted for each SDD in order to optimize the neutron flux on the sample. Scattered neutrons were collected on a 64 × 64 cm area detector, corrected for background and empty cell scattering and for sample thickness and transmission. The samples examined in this work produced isotropic two-dimensional scattering patterns that were azimuthally averaged to the one-dimensional form of intensity versus momentum transfer q. These results were reduced to units of absolute scattering intensity (cm^{-1}) based on the calibration methods that we have recently published elsewhere.[14]

The background scattering contributions to the total measured scattering intensities of the mixtures have been estimated on the basis of the q-independent SANS intensities obtained from each of the unmixed homopolymers; an illustration of such scattering from liquid polybutadienes has recently been given elsewhere.[3] Both the incoherent and coherent background intensities have been calculated by using the method reported by Hayashi et al.[15] and independently verified by O'Reilly et al.,[16] and these have been subtracted from the total measured intensities of the mixtures.

III. Results

A. SANS Data Evaluation. The absolute coherent scattering intensity from a homogeneous (single phase) binary isotopic polymer mixture is given by

$$I(q) = V^{-1}[b_H - b_D]^2 S(q) \qquad (1)$$

where b_H and b_D refer to the coherent scattering lengths of the normal and deuteriated repeat units, respectively. We define the reference volume to be $V = \Phi_H V_H + \Phi_D V_D$, where Φ_D refers to the volume fraction of deuteriated polymer ($\Phi_D + \Phi_H = 1$). Since V_H very nearly equals V_D (see Table I), it is not necessary to correct b or terms appearing in the structure factor $S(q)$ for minor difference in repeat unit volumes; the corresponding errors in interpreting $I(q)$ are less than 0.1%. The reference volume has been calculated at each measurement temperature on the basis of the segment volumes listed in Table I and an estimated thermal expansion coefficient $V^{-1}\partial V/\partial T = 6 \times 10^{-4}$ K^{-1}.[17]

de Gennes[18] has derived the structure factor for homogeneous binary polymer mixtures using the random phase approximation (RPA)

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

where

$$g_D(R_g,q) = 2\left[R_g^2 q^2 + e^{-R_g^2 q^2} - 1\right] \Big/ R_g^4 q^4 \quad (3)$$

and $R_g = a(N/6)^{1/2}$ represents the polymer coil radius-of-gyration based on Gaussian statistics. The parameter χ in eq 2 accounts for the thermodynamic interactions between the H and D polymer segments (repeat units) in a mixture. Our primary focus is this paper is the evaluation of χ, known as the Flory–Huggins interaction parameter, as a function of temperature for homogeneous mixtures of perdeuteriated and normal poly(vinylethylene) and poly(ethylethylene).

The interaction parameter χ can be directly related to the zero-angle scattering intensity. Combining eq 2 and 3, in the limit $q \rightarrow 0$, yields

$$S(q) = \frac{\frac{1}{2}(\chi_s - \chi)^{-1}}{1 + q^2\xi^2} \quad (4)$$

where ξ corresponds to the composition fluctuation length

$$\xi = \frac{a}{6}[\Phi_H \Phi_D(\chi_s - \chi)]^{-1/2} \quad (5)$$

and χ_s represents the limit of thermodynamic stability

$$\chi_s = \tfrac{1}{2}[(\Phi_H N_H)^{-1} + (\Phi_D N_D)^{-1}] \quad (6)$$

The intercept of an Ornstein–Zernlike plot ($I^{-1}(q)$ versus q^2) therefore provides for a direct determination of χ, based solely on independently measured parameters. Unfortunately this was not a viable method for extracting χ from the PVE and PEE SANS data for the following reasons. We found that some of the mixtures exhibited a small amount of excess scattering intensity at the lowest q values attainable on the 30-m SANS instrument. This spurious scattering is not related to the H–D composition fluctuations in the mixtures since the unmixed samples also exhibit this effect as illustrated in Figure 1. Because this forward scattering is considerably more prevalent in the hydrogenated (deuteriated) polymers, we believe it to be primarily due to residual hydrogenation catalyst which was not removed by filtration. In order to guarantee that such scattering did not interfere with the quantitative determination of χ, we have discarded all the data below $q = 7 \times 10^{-3}$ Å^{-1}; above this scattering wavevector the contribution of this spurious background intensity to that of the mixtures becomes insignificant. For the polymers examined, the range $q \geq 7 \times 10^{-3}$ Å^{-1} does not satisfy the condition $qR_g \ll 1$ which is presumed in the derivation of eq 4. Therefore, we have extracted the value of χ from our SANS data by making use of the full theoretical structure factor given by eq 2. This necessitated the additional determination of the statistical length a.

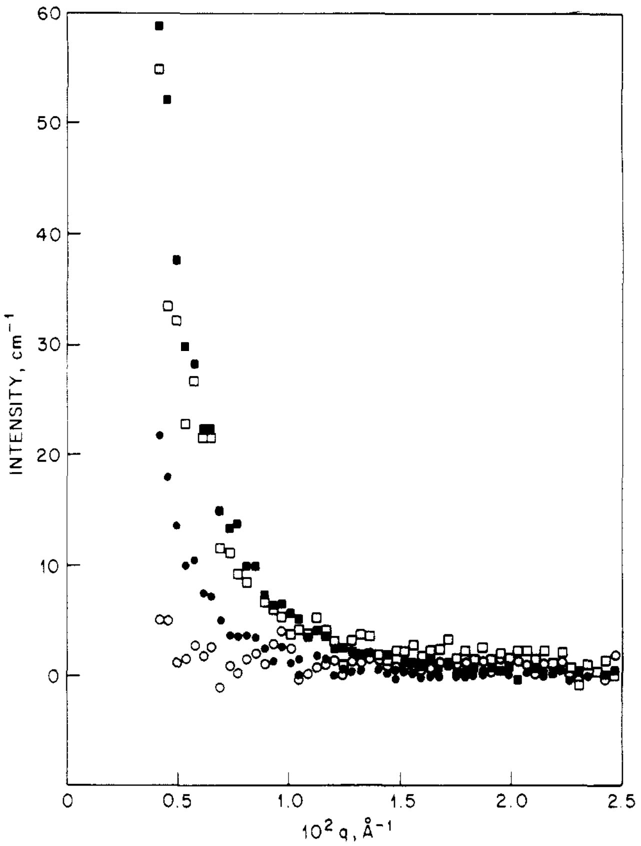

Figure 1. Total small angle neutron scattering (SANS) obtained from perdeuteriated (solid circles) and protonated (empty circles) poly(vinylethylene) and from perdeuteriated (solid squares) and protonated (empty squares) poly(ethylethylene). Scattering intensity at $q < 10^{-2}$ Å^{-1} derives mainly from impurities, which are predominantly residual (unfiltered) hydrogenation catalyst in the case of poly(ethylethylene) (square symbols). Analysis of SANS data obtained from 50/50 mixtures of these polymers has been restricted to $q > 7 \times 10^{-3}$ Å^{-1}.

In prinicple, the statistical repeat length can be obtained directly from the SANS data at $qR_g \gg 1$ where eq 2 reduces to

$$S(q) = 12\Phi_H\Phi_D/q^2a^2 \quad (qR_g \gg 1) \quad (7)$$

This method of determining a has been previously exploited by us in studying the isotope effect in 1,4-polybutadiene[1,3] and actactic polystyrene.[2] In Figure 2 are presented the SANS data obtained at 2.6 m from mixtures PEE12(0.5) and PVE12(0.5). It is apparent from this log–log plot that neither of these polymers conform to the predicted Gaussian coil configuration ($I \sim q^{-2}$) at length scales much smaller than R_g, where R_g ranges from 73 to 101 Å. A similar behavior has been documented by O'Reilly et al.[16] for stereoregular poly(methylmethacrylates). In our opinion the observed power law behavior reflects, in part, local segment correlations not accounted for in the Gaussian coil model, which are expected to contribute significantly to the scattering intensity at $qa \gtrsim 1$. Consequently, we have restricted the determination of a to the SANS data obtained at 19 m, which corresponds to length scales nearer the radius of gyration.

Presented in Figures 3 and 4 are Ornstein–Zernike plots of the 19-m SANS results for mixtures PVE12(0.5) and PEE12(0.5). The regions indicated by the rectangles have been expanded in Figures 5 and 6. We have determined the statistical segment length a and segment–segment in-

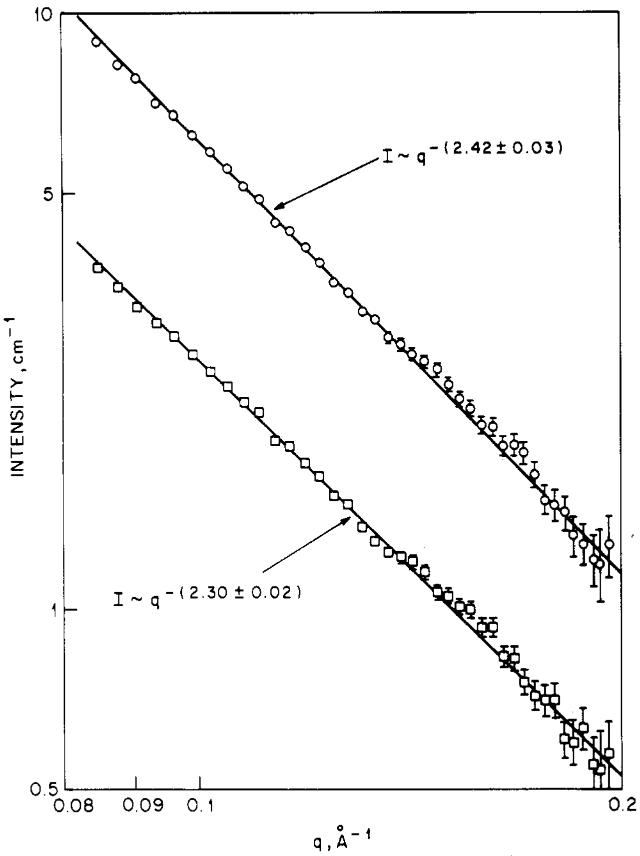

Figure 2. Coherent small angle neutron scattering from 50/50 mixtures of perdeuteriated and protonated poly(vinylethylene) (squares) and poly(ethylethylene) (circles) for $qR_g \gg 1$. Solid lines are least-squares fits, indicating that these polymers do not conform to Gaussian statistics ($I \sim q^{-2}$) for $qR_g \gtrsim 6$.

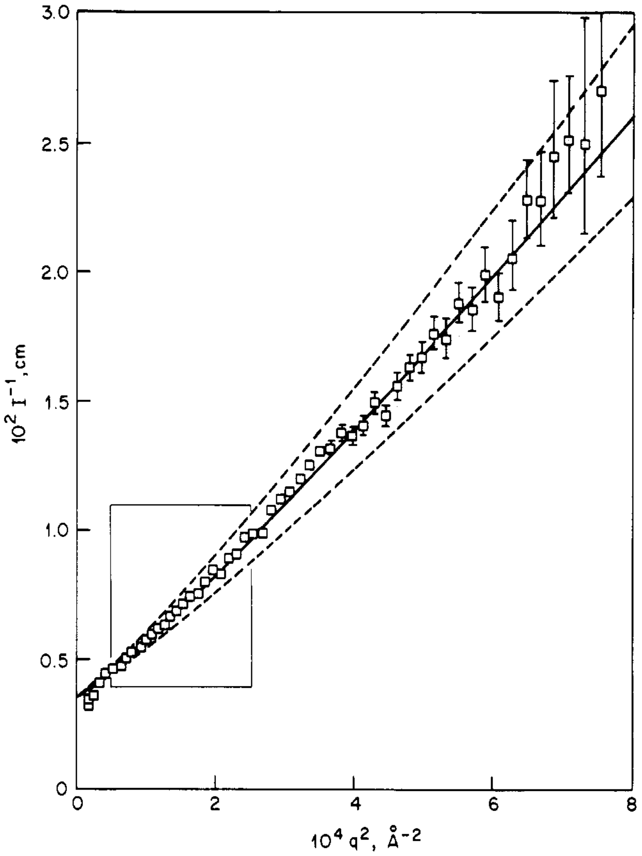

Figure 3. Coherent small angle neutron scattering from a 50/50 mixture of perdeuteriated and protonated poly(vinylethylene) at 37 °C. Curves correspond to the RPA prediction based on $\chi = 6.75 \times 10^{-4}$, which has been determined by least-squares fitting of the data within the rectangular box; this region has been expanded in Figure 5. Solid curve corresponds to a statistical segment length a = 6.0 Å. Sensitivity to variations in a is illustrated by the upper (a = 6.4 Å) and lower (a = 5.6 Å) dashed curves.

teraction parameter χ (see following sections) for each mixture by fitting eq 2 to the SANS data as illustrated in Figures 3–6. In Figures 3 and 4 are depicted the sensitivities of the predicted scattering intensities to variations in a at fixed χ. The results of this analysis are a_{PVE} = 6.0 Å and a_{PEE} = 4.9 Å. A similar evaluation of the SANS data from mixtures ranging in composition from 10 to 90% perdeuteriated polymer reveals that to within 0.1 Å this value does not depend on composition; a full discussion of these SANS results will be presented in a separate paper.[19] These SANS determined statistical segment lengths are equivalent, within experimental error, to those obtained by Xu et al.,[12] $a_{\mathrm{PVE},\Theta}$ = 5.8 Å and $a_{\mathrm{PEE},\Theta}$ = 5.0, from Θ temperature intrinsic viscosity measurements on identically prepared polymers.

To summarize this section, we find that the SANS results from poly(vinylethylene) and poly(ethylethylene) isotopic mixtures for $qR_g \lesssim 3$ are qualitatively described by the RPA theory based on Gaussian statistics and a small positive χ parameter (see following section). The SANS determined statistical segment lengths, a_{PVE} = 6.0 ± 0.2 and a_{PEE} = 4.9 ± 0.1 Å, are in close agreement with those determined by intrinsic viscosity measurements at the Θ temperature.[12]

B. Segment–Segment Interaction Parameter χ. The thermodynamic segment–segment interaction parameter has been measured as a function of temperature for the mixtures PVE12(0.5) and PEE12(0.5). SANS data for the highest and lowest temperatures at which measurements were taken are shown in Figures 5 and 6; intermediate temperature data, which fall systematically between these limiting results, have been omitted for clarity. All measurements have been made well above the respective glass transition temperatures, $T_{g,\mathrm{PVE}} \cong -4$ °C and $T_{g,\mathrm{PEE}} \cong -30$ °C.[12] As with the previous two isotopic systems we have studied,[1-4] increasing temperature leads to a reduction in the scattering intensity, indicative of an upper critical solution temperature. These SANS data have been fit with eq 2 by adjustment of χ, keeping a constant as previously discussed. The results of this fitting procedure are shown by the solid curves in Figures 5 and 6. Also indicated for comparison, by the dashed curves, are the calculated scattering intensities in the limits of ideal mixing ($\chi = 0$) and single-phase stability ($\chi = \chi_s$). Listed in Table II are the χ parameters determined for each mixture as a function of temperature. These results have been plotted versus inverse temperature in Figures 7 and 8, from which we obtain (solid lines)

$$\chi_{\mathrm{PVE}} = (0.175 \pm 0.013)T^{-1} + (1.15 \pm 0.40) \times 10^{-4} \quad (8)$$

and

$$\chi_{\mathrm{PEE}} = (0.279 \pm 0.006)T^{-1} - (0.40 \pm 0.18) \times 10^{-4} \quad (9)$$

The errors indicated in eq 8 and 9 correspond to the standard deviations in the parameters obtained from the least-squares fits of the points found in Table II and Figures 7 and 8. In addition to these statistical errors, $\chi(T)$ is subject to systematic errors due to the uncertainty in the intensity calibration and molecular weight determinations. These systematic uncertainties are indicated by the dashed lines in Figures 7 and 8 and constitute errors of 10 and 6% in $\chi_{\mathrm{PVE}}(T)$ and $\chi_{\mathrm{PEE}}(T)$, respectively. Thus, within the combined statistical and systematic errors, the

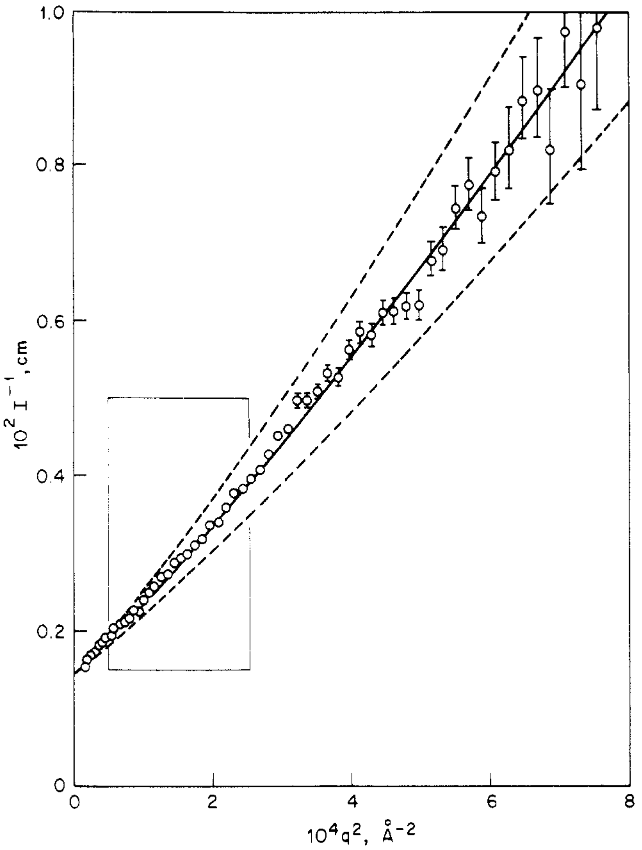

Figure 4. Coherent small angle neutron scattering from a 50/50 mixture of perdeuteriated and protonated poly(ethylethylene) at 26 °C. Curves correspond to the RPA prediction based on $\chi = 8.93 \times 10^{-4}$, which has been determined by least-squares fitting of the data within the rectangular box; this region has been expanded in Figure 6. Solid curve corresponds to a statistical segment length of a = 4.9 Å. Sensitivity to variations in a is illustrated by the upper (a = 5.3 Å) and lower (a = 4.5 Å) dashed curves.

Table II
SANS Determined χ Parameters for 50/50 Isotopic Mixtures

	$10^4\chi$	
temp, K	poly(vinylethylene)[a]	poly(ethylethylene)[b]
299		8.9_3
310	6.7_5	8.6_5
320	6.6_7	8.3_0
330	6.4_1	8.0_7
340	6.3_0	7.8_2
350	6.2_0	7.5_8
360	6.0_7	7.4_2
373	5.76_6	7.0_5

[a] Mixture PVE12 (0.5); subject to a 10% systematic error. [b] Mixture PEE12 (0.5); subject to a 6% systematic error.

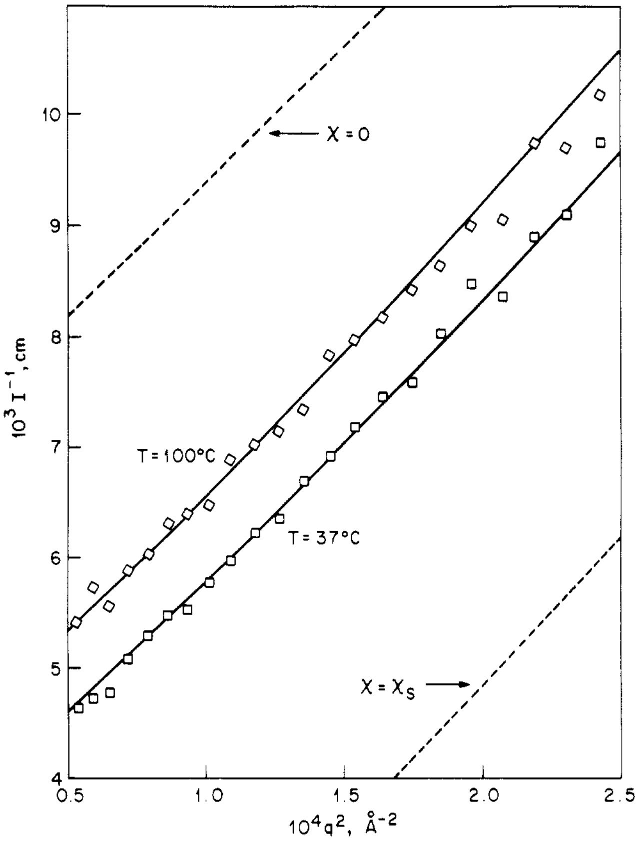

Figure 5. Temperature-dependent coherent small angle neutron scattering obtained from a 50/50 mixture of perdeuteriated and protonated poly(vinylethylene). Solid curves have been fit to the data by using the RPA theory with adjustment of χ. The results of this fitting procedure for all measurement temperatures are listed in Table II. The dashed curves have been calculated for the limits of ideal mixing (χ = 0) and thermodynamic stability ($\chi = \chi_s$).

constant term in eq 8 and 9 are negligible in comparison with the temperature-dependent term, over the range of measurement temperatures (299–373 K).

IV. Discussion

A. Effect of Isotopic Substitution. Our analysis of the SANS results from binary mixtures of perdeuteriated and normal poly(vinylethylene) and poly(ethylethylene) clearly demonstrates that these isotopic mixtures do not form ideal solutions. This corroborates our previous findings for isotopic mixtures of 1,4-polybutadiene[1,3] and atactic polystyrene.[2,4] Collectively, these experimental results strongly support our previous contention[2,4] that this thermodynamic property constitutes a universal behavior, intrinsic to all isotopic (polymer) pairs. As discussed below, we believe the polymer isotope effect can be traced to the fundamental differences between carbon–hydrogen and carbon–deuterium bonds.

At ambient temperatures (~300 K) the interatomic spacing (bond length) for carbon and hydrogen, in a hydrocarbon molecule, is primarily dictated by ground state (zero-point) vibrations ($h\nu/kT \simeq 14$). Substituting deuterium for hydrogen lowers the zero-point energy, and, as a consequence of the anharmonicity of the interatomic potential, also slightly reduces the bond length. A direct manifestation of this bond length reduction is a measurable decrease in molar volume.[20] In Table III are listed the reported molar volumes of four isotopic pairs of simple organic liquids. In each case perdeuteriation leads to a slight reduction in molar volume, $0.0022 \leq \Delta V/V \leq 0.0034$ where $\Delta V = V_H - V_D$. Bartell and Roskos[20] have shown that this effect is primarily a consequence of the change in C–H bond length. These results from simple organic liquids are consistent with our findings for the isotopes of PVE and PEE (Table I), $\Delta V/V = 0.0019 \pm 0.0004$ and 0.0039 ± 0.0004, respectively. Therefore, we conclude that the observed polymer segment volume isotope effect also derives from the reduction in C–H bond length with deuterium substitution.

Owing to the slight reduction in electron distribution that results from a shorter bond length, the carbon–deuterium bond polarizability is somewhat less than that characterizing carbon and hydrogen. R. P. Bell[21] first demonstrated this effect over 40 years ago using gas-phase polarizability measurements from normal and perdeuteriated methane, for which $\alpha_{C-H} = 1.01445\alpha_{C-D}$, where

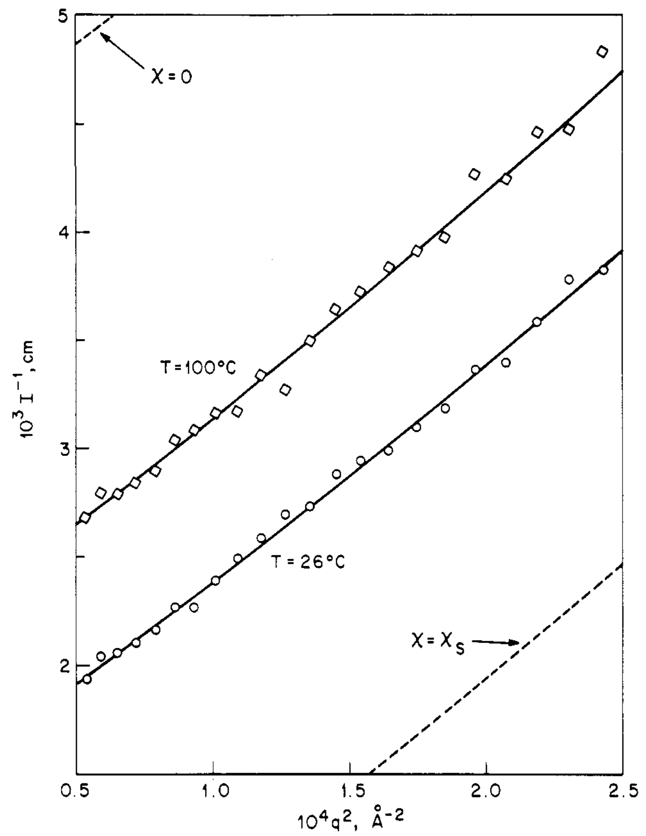

Figure 6. Temperature-dependent small angle neutron scattering obtained from a 50/50 mixture of perdeuteriated and protonated poly(ethylethylene). Solid curves have been fit to the data by using the RPA theory with adjustment of χ. The results of this fitting procedure for all measurement temperatures are listed in Table II. The dashed curves have been calculated for the limits of ideal mixing ($\chi = 0$) and thermodynamic stability ($\chi = \chi_s$).

Table III
Isotope Effects on Simple Organic Liquids

	benzene	toluene	isoprene	cyclohexane
H/C	1	1.14	1.6	2
V_H, cm^3 mol^{-1}	88.867[a]	106.284[a]	100.14[b]	108.102[a]
V_D, cm^3 mol^{-1}	88.626[a]	105.983[a]	99.92[b,f]	107.737[a]
$\Delta V/V$	0.0027	0.0028	0.0022	0.0034
n_H	1.50110[c]	1.4961[d]	1.4219[b]	1.42630[c]
n_D	1.49911[c]	1.4942[e]	1.4189[b]	1.42181[c]
$\alpha_{C-H}/\alpha_{C-D}$	1.0164	1.0146	1.0170[f]	1.0181

[a] Reference 20. [b] Reference 28. [c] Reference 29. [d] Reference 30. [e] Reference 31. [f] Based on a reported[28] 97.5 atom % deuterium.

α_{C-H} refers to the carbon–hydrogen bond polarizability. This polarizability effect is manifested in the liquid state as a *reduction* in the refractive index n upon substituting deuterium for hydrogen as indicated in Table III; solely on the basis of the volume change, one would expect on *increase* in refractive index. We have estimated the ratio $\alpha_{C-H}/\alpha_{C-D}$ for organic liquids by making use of the Lorentz–Lorenz relationship for the molecular polarizability

$$\alpha = \frac{n^2 - 1}{n^2 + 2}\,\frac{3}{4}\,\frac{V}{\pi} \tag{10}$$

in conjunction with the assumption of additive bond polarizabilities. Neglecting off-diagonal terms in the bond polarizability tensor[22]

$$\alpha = \tfrac{1}{3} \sum_{\text{bonds}} (\alpha_{\parallel} + 2\alpha_{\perp}) \tag{11}$$

where $\alpha_{\parallel}$ and $\alpha_{\perp}$ refer to the parallel and perpendicular components of the overall bond polarizability. On the basis of reported[22] values for $\alpha_{\parallel}$ and $\alpha_{\perp}$ and with the assumption that that carbon–carbon bond polarizabilities are unaffected by deuterium substitution, we have calculated $\alpha_{C-H}/\alpha_{C-D}$ for each of the four isotopic liquid pairs listed in Table III. These liquid phase results, $\langle \alpha_{C-H}/\alpha_{C-D} \rangle = 1.0165$, are in good agreement with the gas-phase measurement reported by Bell.

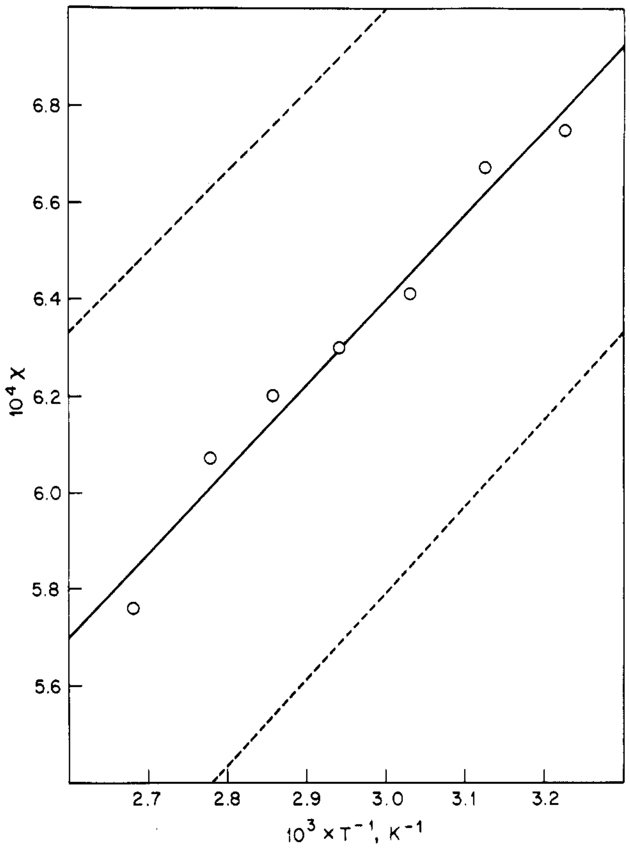

Figure 7. Temperature dependence of the segment–segment interaction parameter determined by using the SANS results from a 50/50 mixture of perdeuteriated and protonated poly(vinylethylene). The solid line corresponds to $\chi(T) = (0.175 \pm 0.013)T^{-1} + (1.15 \pm 0.40) \times 10^{-4}$. The dashed lines represent the estimated systematic error in $\chi(T)$ deriving from the uncertainties in SANS intensity calibration (±5%) and polymer degree of polymerization (±3%).

B. Thermodynamics of Binary Isotopic Polymer Mixtures. The segment–segment interaction energies for nonpolar isotopic mixtures derive from purely dispersive forces. Therefore, the thermodynamic mixing parameter χ can be estimated classically[23]

$$\chi = \frac{1}{k_B T}[\epsilon_{HD} - \tfrac{1}{2}(\epsilon_{HH} + \epsilon_{DD})] \tag{12}$$

where k_B is the Boltzmann constant and H and D refer to the light (hydrogenated) and massive (deuterated) repeat units, respectively. Equation 12 is equivalent to the original Flory–Huggins liquid lattice description of χ with the exception that the lattice coordination number is presently included in the energy terms ϵ. We approximate the dispersion energies from the leading term of the familiar Drude (London) model[22]

$$\epsilon_{HD} = -\tfrac{3}{2}\left[\frac{h\nu_{0,H}\nu_{0,D}}{\nu_{0,H} + \nu_{0,D}}\right]\hat{\alpha}_H\hat{\alpha}_D \int_0^\infty \frac{4\pi}{r^4}\rho(r)\,dr \tag{13}$$

where $\hat{\alpha}$ represents the lattice site polarizability. For a

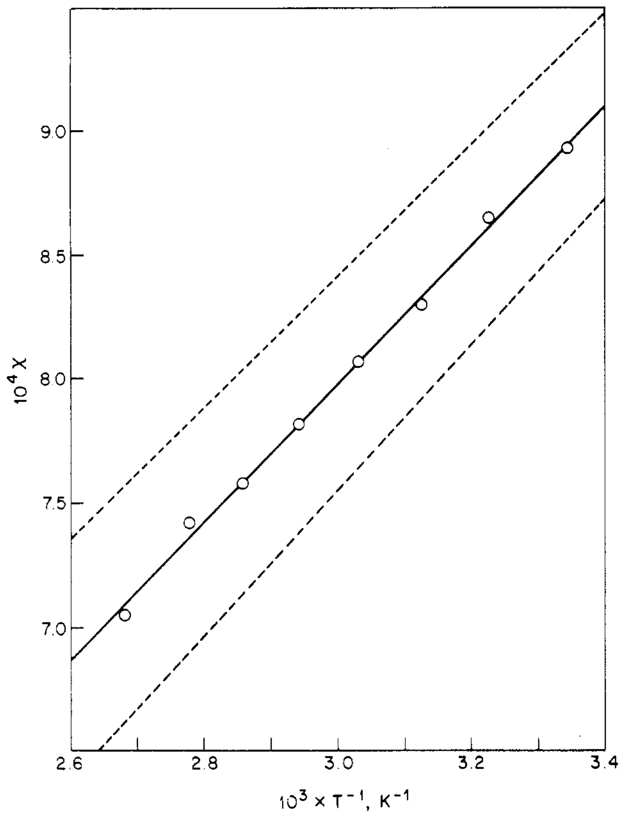

Figure 8. Temperature dependence of the segment–segment interaction parameter determined using the SANS results from a 50/50 mixture of perdeuteriated and protonated poly(ethylethylene). The solid line corresponds to $\chi(T) = (0.279 \pm 0.006)T^{-1} - (0.40 \pm 0.18) \times 10^{-4}$. The dashed lines represent the estimated systematic error in $\chi(T)$ deriving from the uncertainties in SANS intensity calibration (±5%) and polymer degree of polymerization (±3%).

uniform site density $\rho(r) = \hat{V}^{-1}$ at distances greater than an assumed cutoff length $(3\hat{V}/4\pi)^{1/3}$, eq 11 reduces to

$$\epsilon_{\mathrm{HD}} = \frac{8\pi^2}{3}\left[\frac{h\nu_{0,\mathrm{H}}\nu_{0,\mathrm{D}}}{\nu_{0,\mathrm{H}} + \nu_{0,\mathrm{D}}}\right]\left(\frac{\alpha}{V}\right)_{\mathrm{H}}\left(\frac{\alpha}{V}\right)_{\mathrm{D}} \tag{14}$$

Substituting the ionization potential I for $h\nu_0$ and noting that for organic molecules larger than ethane $I_{\mathrm{H}} \cong I_{\mathrm{D}} = I$ (± 0.1%)[24] yield

$$\epsilon_{\mathrm{HD}} = \frac{4\pi^2}{3}I\left(\frac{\alpha}{V}\right)_{\mathrm{H}}\left(\frac{\alpha}{V}\right)_{\mathrm{D}} \tag{15}$$

from which we obtain (eq 10)

$$\chi = \frac{2\pi^2 I}{3k_{\mathrm{B}}T}\left[\left(\frac{\alpha}{V}\right)_{\mathrm{H}} - \left(\frac{\alpha}{V}\right)_{\mathrm{D}}\right]^2 \tag{16}$$

Thus, the interaction parameter χ can be estimated directly from the refractive indices (see eq 10) or from the values of α/V calculated from the bond polarizabilities and experimentally determined segment volumes.

Here we note the derivation presented above differs somewhat from that reported earlier by us.[4] In our previous derivation of χ, we treated the volume and polarizability effects separately. The volume difference was accounted for in a manner analogous to that presented by Buckingham and Hentschel[8] (see below), e.g., compression or dilation of each isotope to the volume characterizing the mixture, while the polarizability difference was evaluated as described above, but at constant segment volume. If the measured volume difference were a consequence of *intermolecular* vibrations, this approach might be justified. However, under the condition that *both* volume and polarizability variations derive from the same *intramolecular* zero-point energy difference, as indicated in the previous section, the separate treatment of these effects is redundant. In other words, hypothetically compressing the C–H bond to the length of the C–D bond simultaneously eliminates the disparity in bond polarizability. In our present derivation we have eliminated this redundancy.

A final comment on eq 16 concerns corrections due to nonrandom mixing. Our derivation of the energy parameter χ corresponds to a strictly regular solution treatment, that assumes completely random mixing. There are two sources of error associated with this assumption. First, there exists a correlation between nearest neighbors on a polymer chain that will slightly diminish the number of intermolecular contacts, thereby modifying the local concentration from that given by the macroscopic mixing stoichiometry. In the Flory treatment[23] this is accounted for by reducing the effective lattice coordination number. Such a correction slightly decreases the predicted value of χ without influencing its temperature dependence. In the light of the uncertainties in determining the parameters of eq 16 (see below), such a modification is unwarranted. Second, the quantitative description of a regular solution must account for the excess entropy of mixing associated with specific segment interactions. A comprehensive evaluation of this nonrandom mixing effect has been presented by Fowler and Guggenheim.[25] For the situation presently considered ($\Phi = {}^1/_2$) the nonrandom mixing corrected energy parameter χ can be expressed as a power series in the Flory–Huggins parameter

$$\bar{\chi} = \chi + \frac{1}{4z}\chi^2 + O(\chi^3) + ... \tag{17}$$

where $z \approx 10$ represents the number of effective (nearest-neighbor) segment contacts. In the case of simple liquids ($N = 1$) the χ^2 and higher order terms make a significant contribution to $\bar{\chi}$. For example, these corrections account for about 10% of the critical value of $\bar{\chi}$ for phase separation.[25] However, in the limit of small χ, such as one encounters in homogeneous polymer mixtures, these nonrandom mixing corrections are negligible and $\bar{\chi} \cong \chi$. This is particularly true for isotopic mixtures where $10^{-4} < \chi < 10^{-3}$. Thus we expect the measured excess free energy measured by SANS to be directly proportional to the inverse temperature as indicated by eq 16.

Two other theories for the excess free energy of isotopic polymer mixtures have been presented in the literature. Buckingham and Hentschel[8] were first to suggest that isotopic polymer mixtures should exhibit an upper critical solution temperature. On the basis of a modified version of a theory previously presented by Prigogine,[9] they calculated

$$\chi_{\mathrm{BH}} = (1/k_{\mathrm{B}}T)(V_{\mathrm{H}} - V_{\mathrm{D}})^2/2\kappa V \tag{18}$$

where $V = V_{\mathrm{H}} \cong V_{\mathrm{D}}$ and κ is the isothermal compressibility which is assumed to be independent of isotopic state. Very recently Singh and Van Hook[10] have criticized this result and presented their own theory for such mixtures. Both of these theories account for the excess free energy of mixing by evaluating the change in free energy associated with compressing and dilating each isotope to the molar volume characterizing the mixture. Singh and Van Hook argue that this process must be conducted "congruently" in order to preserve the equivalence in potential energy surfaces between isotopes. Their result, cast in Flory–Huggins terminology, is

$$\chi_{\mathrm{SVH}} = \frac{r\gamma}{2}\frac{(V_{\mathrm{H}} - V_{\mathrm{D}})}{V}u_{\mathrm{H}}[1 - (\mu_{\mathrm{H}}/\mu_{\mathrm{D}})^{1/2}] \qquad (19)$$

where r is the number of protons (deuterons) per repeat unit, $u_{\mathrm{H}} = h\nu_s/kT$ for which ν_8 is the C–H stretching frequency, and $\gamma = \mathrm{d}\ln u_{\mathrm{H}}/\mathrm{d}\ln V$ is the associated Gruneisen coefficient. $\mu_{\mathrm{H}}/\mu_{\mathrm{D}}$ represents the ratio of reduced masses for the C–H and C–D oscillators. In the following section we compare the predictions of eq 16, 18, and 19 with our experimental results for poly(vinylethylene) and poly(ethylethylene).

C. Comparison with Experiment. All three expressions for the excess free energy of isotopic mixtures (eq 16, 18, and 19) predict an upper critical solution temperature (UCST) for phase separation, i.e. $\chi \sim T^{-1}$. The SANS results summarized in Figures 7 and 8 along with similar results reported previously by us for 1,4-polybutadiene[1,3] and atactic polystyrene[2,4] conclusively confirm this prediction. To our knowledge isotopic blends are the only class of high molecular weight polymer mixtures that appear to universally exhibit UCST behavior. High polymer mixtures are generally characterized by lower critical solution temperatures (LCST) as a consequence of the differences in equation-of-state parameters[26] between chemically different species. Our results indicate that deuterium substitution does not significantly influence the latter thermodynamic properties.

Quantitative comparison of the experimentally determined interaction parameters listed in Table II with our predictions (BWF, eq 16), and those by Buckingham and Hentschel (BH, eq 18), and Singh and Van Hook (SVH, eq 19) requires the estimation of several parameters. For eq 16 we need to estimate the ionization potentials for poly(ethylethylene) and poly(vinylethylene). We adopt $I = 10 \pm 1$ eV for poly(ethylethylene) on the basis of the values characterizing the higher linear and branched saturated alkanes.[24] Terminal unsaturation of the pendant ethyl groups will reduce this ionization potential by approximately 10% to 9 ± 1 eV by analogy with the trend observed with simple alkanes and alkenes.[24] The segmental polarizabilities have been estimated by using eq 11 with $\alpha_{\mathrm{C-H}} = (1.0165 \pm 0.0015)\alpha_{\mathrm{C-D}}$ as described previously and indicated in Table III. For eq 18 and 19 we need to estimate the isothermal compressibility κ and C–H stretching mode Gruneisen coefficient γ, respectively. Since the isothermal compressibilities of poly(ethylethylene) and poly(vinylethylene) have not been reported, we assume a value typical for elastomers,[17] $\kappa = (5.3 \pm 0.5) \times 10^{-10}$ Pa^{-1}. Singh and Van Hook[10] quote $\gamma = 0.035$ as the characteristic Gruneisen coefficient for the C–H stretching modes in solids. We adopt this value for poly(ethylethylene) and poly(vinylethylene) but note that γ can vary by a factor of 2–3 between the various C–H stretching modes in an organic molecule,[27] placing a large degree of uncertainty on this assignment. Deuterium substitution may also influence this parameter.[27]

Before comparing our experimental results with the predictions, we comment briefly on an assumption common to all three. Equations 16, 18, and 19 provide estimates for the classically defined segment–segment interaction parameter that is independent of both composition and molecular weight. As described in a separate publication,[19] the SANS determined interaction parameter for these isotopic mixtures actually depends on both these parameters. However, for $\Phi_{\mathrm{D}} = 0.5$ the corrections to eq 12 are quite small (<5%) and can be safely ignored in the context of the present discussion.

Table IV
Comparison of Predictions and Experiment at 296 K

	$10^4\chi_{\mathrm{PVE}}$	$10^4\chi_{\mathrm{PEE}}$	$\chi_{\mathrm{PEE}}/\chi_{\mathrm{PVE}}$[b]
expt	7.1 ± 0.9	9.1 ± 0.6	1.27 ± 0.10
BWF (eq 16)	5.4 ± 0.9	6.0 ± 1.0	1.1 ± 0.3
BH (eq 18)	0.83 ± 0.38	3.8 ± 0.5	4.6 ± 2.2
SVH (eq 19)	7.6 ± 1.7[a]	20.7 ± 2.1[a]	2.7 ± 0.7

[a] The estimated error does not include the uncertainty in the Gruneisen coefficient which may be a factor of 2–3. [b] The errors in these numbers do not include the systematic errors which contribute to the uncertainties in the individual χ measurements.

A comparison of the segment–segment interaction parameters obtained from the experimental measurements (eq 8 and 9) with those calculated from eq 16, 18, and 19 is given in Table IV. We have chosen to make this comparison at 296 K, the temperature at which the segment molar volumes were determined, in order to avoid errors associated with our estimate of the thermal expansivity (see section IIIA). Also listed in Table IV is the ratio $\chi_{\mathrm{PEE}}/\chi_{\mathrm{PVE}}$ for the experimental and predicted interaction parameters. We believe that a comparison of the predicted and experimental ratio $\chi_{\mathrm{PEE}}/\chi_{\mathrm{PVE}}$ provides the best means for evaluating these theories since systematic errors are in large part eliminated; sources of systematic error include intensity calibration in the SANS experiments, selection of the cutoff length in eq 13, and selection of a Gruneisen coefficient in eq 19. Between the three predictions eq 16 most closely accounts for the experimental results. The predictions of eq 18, both for the absolute magnitude of the interaction parameters and their ratio, are significantly different than the measured values. In the case of eq 19, the prediction for poly(vinylethylene) is in excellent agreement with the experimental result, while that for poly(ethylethylene) is more than twice the measured value. Both results lie within the large uncertainty associated with assignment of a Gruneisen coefficient. However, if this coefficient does not vary significantly between poly(vinylethylene) and poly(ethylethylene), then the predicted ratio of interaction parameters is significantly overestimated by eq 19 (see Table IV).

The relatively close agreement between the experimental results and those predicted by us and Singh and Van Hook for the polymer isotope effect lend strong support to our contention that this phenomenon derives primarily from the fundamental difference between C–H and C–D bonds and that all isotopic polymer mixtures should exhibit such behavior. We believe that isotopic polymer mixtures provide nearly ideal materials with which to investigate the thermodynamics and dynamics of liquids in general, as a consequence of this small well-defined molecular variation.

V. Summary and Conclusion

We have examined binary mixtures of perdeuteriated and normal poly(vinylethylene) and poly(ethylethylene) by small-angle neutron scattering (SANS). These mixtures, containing 50% by volume perdeuteriated polymer, are characterized by Gaussian statistical segment lengths, which are in close agreement with those determined from intrinsic viscosity measurements at the Θ temperature, and by finite positive Flory–Huggins segment–segment interaction parameters. Both interaction parameters depend inversely on temperature, indicating upper critical solution temperature (UCST) behavior; all four isotopic polymer systems studied to this date exhibit UCST behavior.

The polymer isotope effect is attributed to the decrease in C–H bond length which accompanies substitution of deuterium for hydrogen; this derives from the combined effects of zero-point motion and interatomic potential anharmonicity. As a result, both the segment polarizability and molar volume are lower for the deuteriated species. On the basis of the Flory–Huggins lattice model for χ and with the use of the London equation to describe the intersegmental dispersion forces, we have calculated the segment–segment interaction parameters for deuteriated and normal polymers. These predictions, which are based on bond polarizabilities taken from the literature and directly measured polymer segment volumes, compare well with the experimentally determined values. Two other published theories for nonideal isotopic polymer mixtures, based solely on the segment volume isotope effect, have also been examined and found to be in qualitative agreement with experiment.

In conclusion, the results of this work, taken together with our previous findings for isotopic mixtures of 1,4-polybutadiene and atactic polystyrene firmly establishes that in general deuteriation and protonated polymers, otherwise of identical chemical structure, do not form ideal solutions, contradictory claims not withstanding.[7]

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Registry No. PVE, 9003-17-2; PVE (deuteriated), 29989-19-3; PEE, 9003-28-5; PEE (deuteriated), 113111-12-9.

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Preparation of Asymmetric Three-Arm Polybutadiene and Polystyrene Stars

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ABSTRACT: The synthesis of three-armed polybutadiene and polystyrene stars is described for the case where one of the three arms differs in molecular weight from the remaining two. The preparative approach involves the reaction of methyltrichlorosilane with the chain end active centers under conditions unfavorable to chain coupling or linking, i.e., the synthesis of linear doublet chains or three-arm stars. Some observations regarding thermal-induced post-polymerization side reactions that distort the near-monodisperse nature of the molecular weight distributions obtainable for polybutadiene are described. Preparative conditions must be selected to avoid such side reactions if "model" branched polybutadienes are required.

Introduction

The behavioral differences of branched and linear polymers of equal molecular weights have been a topic of academic and commercial interest. Polymers that undergo chain transfer events or are prepared in the presence of polyfunctional monomers are randomly branched and have broad molecular weight and branching distributions. These factors contribute to the overall behavior of a polymer. Thus, in order to isolate and interpret the effects of branching on physical properties, the polymer must be composed of only one type of branched structure and this structure must be defined.

Star-shaped polymers prepared by the use of multifunctional chlorosilane compounds,[2-39] divinylbenzene,[40-47] or other linking agents[48-54] represent the simplest type of branched structures and, therefore, have received detailed

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