Table I
^{13}C Spin-Lattice Relaxation Times T_{1C} of the Carbons of Amylose

	water content,[a] %	T_1/s			
		C1	C4	C2,3,5	C6
A-amylose	0	20.3	17.6	16.3	3.7
	100	8.9	6.6	5.1	1.6
B-amylose	0	21.0	18.3	16.1	3.0
	101	8.7	8.9	7.5	1.9

[a] (g of water)/(g of polymer) × 100.

mixture of gauche–trans and trans–gauche.[5] However, it can be concluded from the chemical shift (62.7 ppm) of the C6 carbon that the CH_2OH group of A-amylose adopts the gauche–trans conformation.[9,10]

Table I lists ^{13}C T_1 values of A- and B-amyloses measured by Torchia's pulse sequence.[6] Although each line has at least two components with different T_1's, longer T_1's are assumed to be the values of the crystalline component. The T_1 values of the pyranose ring carbons are of the order of 5–9 s for the hydrated A- and B-amyloses, whereas the values are significantly longer in the dry state. Almost the same effect of hydration on T_1 values was observed in the case of the samples soaked in D_2O. It is therefore concluded that water enhances the torsional motion about the α-1,4-glycosidic linkage even in the crystalline region. Such high molecular mobility of the amylose chains may stem from the flexibility of the sixfold structure.[4,5] In contrast, cellulose molecules containing β-1,4-glycosidic linkages adopt the twofold helical structure, which is an almost linear conformation without flexibility.[16-19] This rigid structure will be reflected in much longer T_1 values obtained for different cellulose samples in both dry and hydrated forms.[3,9,20]

The T_1's of the C6 carbons of the two polymorphs of amylose are shorter than those of the ring carbons in both the dry and hydrated forms, indicating that the CH_2OH groups undergo enhanced torsional motion about the exocyclic C5–C6 bond. This is also in contrast to the result[3,9,20] of cellulose crystals; the T_1 values of their C6 carbons are of almost the same order as those of their ring carbons, suggesting hindrance of the torsional motion about the C5–C6 bond. Such a difference in the torsional mobility of the CH_2OH groups between amylose and cellulose may be related to the difference in hydrogen bonding. In A- and B-amyloses most of the hydrogen bonds are formed along the helical chain[4,5] and thus the mobility of CH_2OH groups is also closely associated with the high flexibility of the helical chains. On the other hand, all CH_2OH groups are fixed by inter- and intrachain hydrogen bonding in cellulose I and II[16-19] and furthermore the main chains are also very limited in molecular mobility.[20] More detailed analysis of molecular chain conformation and dynamics will be published elsewhere for regenerated samples in the A, B, and V forms.

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Nonideal Mixing in Binary Blends of Perdeuterated and Protonated Polystyrenes

Recently, we demonstrated[1] that amorphous mixtures of normal (protonated) and perdeuterated 1,4-polybutadienes are characterized by an upper critical solution temperature (UCST), contradicting the widely held assumption that such isotopic mixtures form ideal solutions. This effect was shown[1] to derive from a small difference in segment volume between the perdeuterated and normal species, as predicted by Buckingham and Hentschel.[2] In the symmetric case ($N_D = N_H = N$), the predicted critical degree of polymerization for amorphous isotopic polymer mixtures is

$$N_c = 4k_B T\kappa / V(\Delta V/V)^2 \qquad (1)$$

where k_B is the Boltzmann constant, T is the UCST, and β_T is the isothermal compressibility. V represents the average segment volume for the mixture, and ΔV is the difference in volumes between the normal and perdeuterated (undiluted) segments. On the basis of the symmetric version of the Flory–Huggins approximation to the mixing free energy,[3] the critical degree of polymerization is given by

$$N_c = 2/\chi \qquad (2)$$

where χ is commonly referred to as the "segment–segment interaction parameter". We therefore expect all mixtures of normal and perdeuterated polymers to exhibit a small *positive* interaction parameter, $\chi \sim T^{-1}$, since such isotopic substitution produces changes in molecular volume in essentially all organic compounds.[4] In this communication we report our initial findings concerning the phase behavior of amorphous mixtures of perdeuterated and normal atactic polystyrenes. These results are consistent with our expectation of a universal isotope effect in amorphous polymers.

Monodisperse atactic (anionic) polystyrenes were obtained from Pressure Chemical Co.; the degrees of polymerization and polydispersity indices, as reported by the supplier, are listed in Table I. Binary mixtures (≈0.1-

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Table I
Molecular Characteristics for 50/50 Mixtures[a] of Perdeuterated and Normal Polystyrenes

mixture	$N_D \times 10^{-3}$ [b]	$N_H \times 10^{-3}$ [b]	$\chi \times 10^4$ [c]	$\chi_s \times 10^4$ [d]
PSHD1	5.0	5.5	1.5 ± 0.3	3.8
PSHD2	11.5	8.7	1.9 ± 0.2	2.0
PSHD3	11.5	15.4		1.5

[a] Volume percentages. [b] N_D and N_H are the degree of polymerizations (ca. ±5%) of the perdeuterated and normal (protonated) polystyrenes, respectively, as reported by the supplier. The reported polydispersity indices for $N \times 10^{-3}$ = 5.0, 5.5, 8.7, 11.5, and 15.4 are 1.15, 1.06, 1.10, 1.3, and 1.10. [c] Segment–segment interaction parameter determined by fitting the theoretical homogeneous binary mixture structure factor (eq 4) to the SANS data. The reported error derives from the uncertainties in N and in the absolute intensity calibration of the SANS instrument. [d] Calculated (eq 7) limit for single-phase stability.

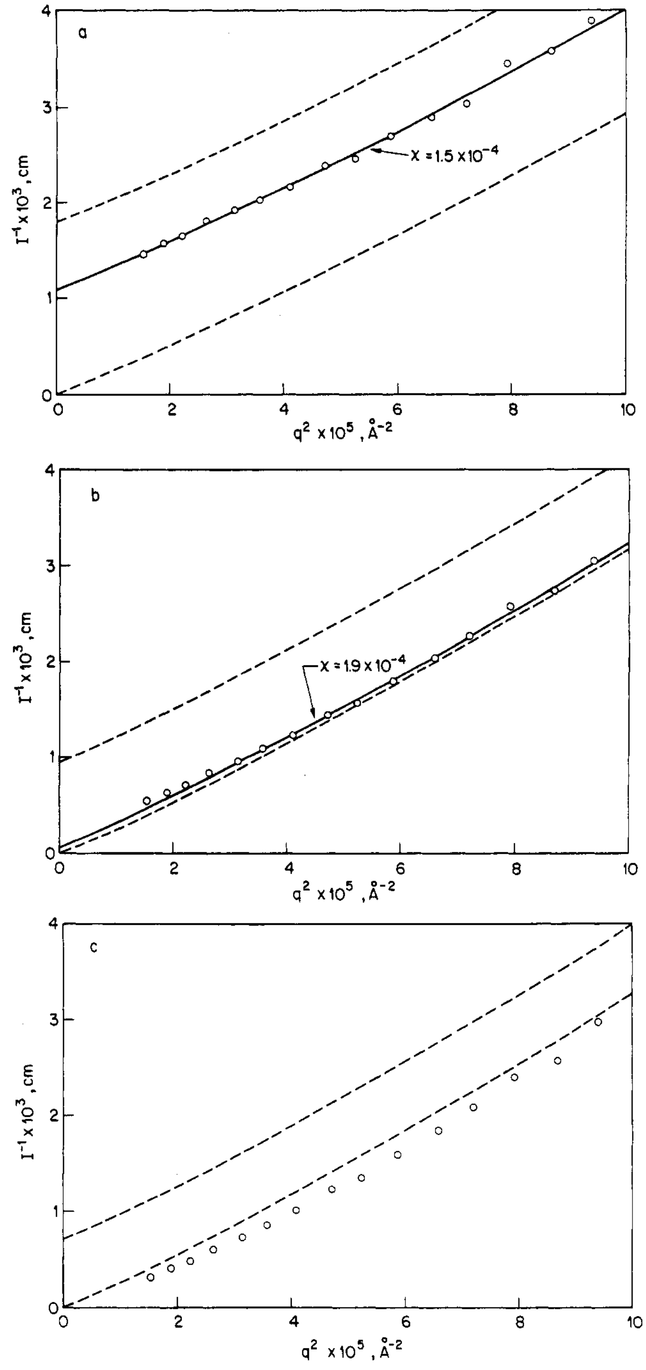

Figure 1. Coherent small-angle neutron scattering from binary mixtures of perdeuterated (50% by volume) and normal atactic polystyrenes (annealed at 160 °C) in order of increasing degree of polymerization: (a) PSHD1; (b) PSHD2; (c) PSHD3. The curves have been calculated from the theoretical correlation function for homogeneous binary polymer mixtures (eq 4), where the upper and lower dashed curves in each panel correspond to the limits of ideal mixing (χ = 0) and single-phase stability (χ = χ_s), respectively.

mm-thick films) containing 50% (by volume) perdeuterated and 50% normal (protonated) polystyrenes were prepared by solvent casting from a toluene solution (<1% w/v), containing both polymer components, followed by vacuum drying at 130 °C. These mixtures are identified in Table I. Stacks of solvent-cast films were subsequently pressure (5 MPa)-molded under vacuum (<10^{-1} torr) into approximately 1-mm-thick specimens. Molding was conducted for 12 h at 200 °C followed by 12 h of annealing at 160 °C and quenching (<3 s) to room temperature. This procedure provides sufficient time for the establishment of equilibrium composition fluctuations in the homogeneous mixtures (see below), at the annealing temperature, and "freezes" the resulting structure into a glassy state.

Small-angle neutron scattering (SANS) data were obtained, in units of absolute intensity (cm^{-1}, ±5%), from the 30-m instrument at the National Center for Small Angle Scattering Research, Oak Ridge National Laboratory. Instrument calibration techniques and data reduction methods have been described elsewhere.[5] We have found that our methods of sample preparation almost completely eliminate the complication known as "void scattering" as reported by others[6] studying polystyrene by SANS. This was verified by examining entirely protonated and deuterated (blank) specimens prepared under the same conditions as the mixtures. These results were also used to correct the SANS data, obtained from the mixtures, for incoherent scattering. The resulting coherent scattering data are presented in Ornstein–Zernicke form[3] (reciprocal intensity vs. q^2) in Figure 1, where $q = 4\pi\lambda^{-1} \sin(\theta/2)$ represents the scattering wave vector.

The coherent neutron scattering intensity from a binary polymer mixture is given by

$$I(q) = V^{-1}(b_H - b_D)^2 S(q) \tag{3}$$

where V is the polymer segment volume and b_H and b_D are the coherent scattering lengths[7] of the normal and deuterated segments. de Gennes[3] has calculated the structure factor for homogeneous (one phase) binary polymer mixtures

$$S(q) = [N_D \Phi g_D(R_{gD},q)]^{-1} + [N_H(1 - \Phi) g_D(R_{gH},q)]^{-1} - 2\chi \tag{4}$$

where Φ and N_D correspond to the volume fraction and degree of polymerization of the deuterated component. g_D is the Debye function

$$g_D(R_g,q) = 2\left[R_g^2 q^2 + e^{-R_g^2 q^2} - 1\right] \Big/ R_g^4 q^4 \tag{5}$$

$$R_g^2 = a^2 N/6 \tag{6}$$

in which a (=6.7 Å for polystyrene[8]) is the segment (Kuhn) length. In the case of ideal mixing χ = 0, while for $0 < \chi < \chi_s$ the mixture is characterized by composition fluctuations, where the limit of single-phase stability is given by

$$\chi_s = [(N_D \Phi)^{-1} + (N_H(1 - \Phi))^{-1}]/2 \tag{7}$$

We have determined the segment–segment interaction parameter for perdeuterated and normal polystyrene by fitting eq 4 to the SANS data for mixtures PSHD1 and PSHD2 (Table I) as indicated by the solid curves in Figures 1a,b. Clearly, the theoretical scattering function

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quantitatively accounts for these SANS results. It should be emphasized that χ represents the *only* fitting parameter in this analysis. Within experimental error, equivalent values of χ have been determined from these two separate mixtures, as indicated in Table I. Also illustrated in Figure 1 (dashed curves) are the calculated scattering curves in the limits of ideal mixing ($\chi = 0$) and single-phase stability ($\chi = \chi_s$).

On the basis of an average measured value of $\langle \chi \rangle = 1.7 \times 10^{-4}$ (Table I), the homogeneous state for sample PSHD3 is calculated (eq 7) to be thermodynamically unstable ($\chi/\chi_s = 1.12$) at $T = 160$ °C. The SANS results depicted in Figure 1c lead us to conclude that this mixture has indeed begun to phase separate; i.e., the low-q scattering intensity deviates in form and magnitude from that predicted for homogeneous mixtures ($0 \leq \chi \leq \chi_s$). This SANS behavior is analogous to that previously described for a phase-separated isotopic mixture of 1,4-polybutadienes.[1]

A preliminary investigation of the temperature dependence of χ for perdeuterated and normal polystyrenes has confirmed that these mixtures are also characterized by an UCST. A specimen of mixture PSHD2 was annealed at 215 °C for 12 h, quenched to room temperature, and examined by SANS, revealing $\chi = 1.3 \times 10^{-4}$; this constitutes a 32% reduction[9] from the value determined at 160 °C (Table I). We are presently examining the detailed temperature and composition dependence of χ for this system. These results will be presented in a future report.

Finally, it is interesting to note that Strazielle and Benoit[10] have observed that perdeuterated and normal polystyrenes are characterized by slightly different solution thermodynamic properties. By analyzing the temperature dependence of the second virial coefficient of polystyrene–cyclohexane solutions near the Θ temperature, they estimated the difference in solubility parameters (cohesive energy densities) between normal and perdeuterated polystyrenes to be $\delta_H - \delta_D = 0.038$ (0.048) (cal/cm^3)$^{1/2}$, where the value in parentheses incorporates corrections for excluded volume effects. Following Hildebrand,[11] the segment–segment interaction parameter can be approximated as

$$\chi = \frac{V_m}{RT}(\delta_H - \delta_D)^2 \tag{8}$$

where V_m is the segment molar volume. Thus, *10 years ago*, the isotope effect in molten polystyrene could be estimated to be $\chi = 1.7 \times 10^{-4}$ (2.7×10^{-4}) at 160 °C!

In conclusion, we have definitively demonstrated with small-angle neutron scattering measurements that mixtures of perdeuterated and normal polystyrenes are characterized by a small, positive interaction parameter, $\chi = (1.7 \pm 0.4) \times 10^{-4}$ at $T = 160$ °C, and an upper critical solution temperature. These findings parallel our previous discovery of an isotope effect in binary mixtures of perdeuterated and normal 1,4-polybutadienes;[1] extrapolation of $\chi(T)$ determined for 1,4-polybutadienes[1] yields $\chi = (5.2 \pm 1.8) \times 10^{-4}$ at 160 °C.[12] It is our conviction that *all* amorphous mixtures of deuterated and protonated polymers will exhibit such phase behavior, as anticipated by Buckingham and Hentschel.[2]

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Registry No. Perdeuterated polystyrene (homopolymer), 27732-42-9; polystyrene (homopolymer), 9003-53-6; neutron, 12586-31-1.

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Observation of a Persistent Methacrylate Radical in the Decomposition of Methyl 2,2′-Azobis(isobutyrate) and the Polymerization of Methyl Methacrylate

Conformational and electronic states of the propagating polymer radicals of vinyl monomers such as acrylates, acrylonitriles, and acrylamides have been studied by means of ESR spectroscopy[1] under different conditions, i.e., in a frozen matrix or in a heterogeneous solution, from an actual polymerization system because of the difficulty in obtaining a high concentration of polymer radical. To avoid such deviation of the experimental conditions ESR studies using low molecular weight radicals such as captodative substituted radicals[2] have been carried out under similar conditions to those of an actual polymerization system. Recently, we employed 2,2′-azobis(isobutyronitrile) (AIBN) and methyl 2,2′-azobis(isobutyrate) (MAIB) as covenient models for the propagating polymer radicals in the polymerization of methacrylonitrile and methyl methacrylate (MMA).[3] Subsequently we found that the primary radical from MAIB, a model for the poly(MMA) radical, showed interesting behavior in the ESR spectrum and product distribution.

We describe herein the observation by ESR of a persistent methacrylate radical generated from the decomposition of MAIB or the chain-transfer reaction in the radical polymerization of MMA.

Sample solutions in an ESR cell were degassed by the freeze–thaw technique and finally filled with helium gas. ESR spectra were recorded on a JEOL JES-FE2XG spectrometer operating at X-band (9.5 GHz) with a TE mode cavity while heating or irradiating (1-kW Xe lamp) the sample in the cavity.

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