polyacrylamide gels investigated here do not depend on the history of the sample but only on its concentration. The scaling-law predictions are obeyed.

The shear elastic moduli of the gels reported in this work contrast with the osmotic behavior in that their value depends strongly on their initial concentration and cross-linking density. Even if the concentration dependence of μ upon swelling were linear, as might naively be expected, E/μ would diverge as the gel was deswollen. The observed variation of μ is, however, even slower than predicted, making the apparent divergence even stronger. Only under conditions of equilibrium swelling do E and μ recover their expected ratio.

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Magic-Angle Carbon-13 Nuclear Magnetic Resonance Analysis of the Interface between Phases in a Blend of Polystyrene with a Polystyrene–Polybutadiene Block Copolymer

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ABSTRACT: Magic-angle cross-polarization ^{13}C NMR spectra have been obtained at 15.1 MHz of polystyrene, of random mixtures of polystyrene with perdeuteriopolystyrene, and of a blend of perdeuteriopolystyrene with a polystyrene–polybutadiene block copolymer. Proton $T_{1\rho}$'s (as observed by high-resolution ^{13}C NMR) and intermolecular cross-polarization transfer rates (from protons on one chain to carbons on another) are both dependent on the mixing of protonated and deuterated chains. Results from such independent measures of effective mixing of chains within the deuterated polystyrene–block copolymer blend lead to the conclusion that the interfacial region surrounding the phase-separated rubber domains is unstructured.

Introduction

Adding rubber to polystyrene produces a two-phase material with an impact strength greater than that of polystyrene by itself.[1] The rubber particles imbedded in the polystyrene matrix presumably inhibit macroscopic crack propagation associated with an incipient brittle failure of the polystyrene phase and so improve toughness.[1] Rubber–polystyrene AB block copolymers can also be used to toughen polystyrene. Phillips markets such copolymers under the designation "K-resins". Blending K-resins with polystyrene produces not only a material with good impact resistance but also one which is almost optically clear. The molecular weight of the polybutadiene block of the copolymer determines the rubber particle size. Blended K-resins typically result in dispersed rubber particles too small to be light scattering centers.

A natural question arises as to the nature of the interface between phases when a rubber–polystyrene block copolymer has been blended with polystyrene. Does the polystyrene covalently attached to a rubber particle form a surrounding shell? Or is there some sort of an interfacial gradient from the rubber phase to the polystyrene matrix, a transition which involves the polystyrene chains of the copolymer and provides improved adhesion between the phases?

To answer this question we have used cross-polarization magic-angle[2] ^{13}C NMR to compare mixtures of perdeuteriopolystyrene and polystyrene with a blend of perdeuteriopolystyrene and K-resin. The mixing of polystyrene chains from two sources can be determined experimentally by ^{13}C NMR if chains from one of them are deuterium labeled. In these experiments, proton $T_{1\rho}$'s are obtained from the final slopes of plots of observed carbon magnetization generated by long, matched spin-lock cross-polarization transfers from protons to carbons.[3] A separate proton $T_{1\rho}$ is obtained from each polystyrene-carbon resonance resolved by magic-angle spinning, thereby providing considerably more insight than can be achieved by direct ^{1}H NMR measurements. These proton $T_{1\rho}$'s are sensitive to spatially dependent proton–proton spin diffusion[4] and so, in a mixture or blend of protonated and deuterated chains, are a measure of the proximity of protonated polystyrene chains with one another. In addition, intermolecular cross-polarization transfers from protons on one chain to deuterated carbons on another chain can be used to characterize the mixing of protonated and deuterated polystyrene chains. The combination of these independent results leads to the conclusion that the interfacial region in the deuterated polystyrene/K-resin blend in fact shows no structural features but rather consists of randomly mixed protonated and deuterated polystyrene chains.

Experiments

Carbon-13 magic-angle experiments were performed at 15.1 MHz, using a Beams-Andrew design rotor (0.7-cm^3 sample volume) and 2-kHz spinning speeds. Matched spin-lock cross-polarization transfers employed H_1's of 44 kHz. Standard radio-frequency pulse sequences and four-phase quadrature routing schemes were used throughout.[5]

Measurements were made on an atactic high-molecular-weight polystyrene (Monsanto), polystyrene-d_8 polymerized from 98 atom % styrene-d_8 (Merck), and mixtures of the two polymers containing 90 and 73 wt % polystyrene-d_8, respectively. Uniform mixtures were made by dissolution of both polymers in chloroform

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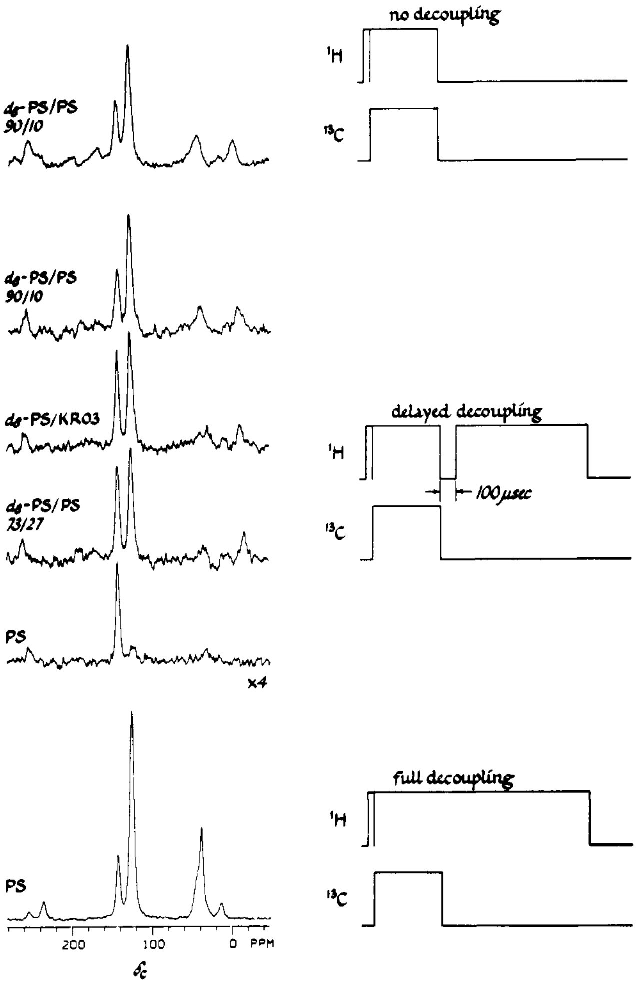

Figure 1. Magic-angle cross-polarization ^{13}C NMR spectra of polystyrene (PS), mixtures of PS with perdeuteriopolystyrene (PS-d_8), and a blend of PS-d_8 with a Phillips K-resin (KR03) under a variety of decoupling conditions. Matched spin-lock, 2-ms, 44-kHz single contacts were employed.

followed by precipitation in methanol. The dried powders were compression molded above T_g as 0.5-mm-thick disks which were quenched in ice water. The disks were stacked to fill the magic-angle rotor.

Measurements were also made on a blend of two parts by weight polystyrene-d_8 with one part Phillips KR03 K-resin. The latter is a block copolymer of polystyrene and polybutadiene containing 23 wt % polybutadiene. A more detailed description of KR03 is available elsewhere.[6] The blend was made above the softening temperature of polystyrene with a two-roll mill, followed by a 10-min compression molding at 200 °C. The resulting material consisted of an apparently uniform, slightly hazy, reasonably void-free, 1-mm-thick sheet from which disks for the NMR rotor were punched. Electron micrographs of the blend showed dispersed rubber particles, most of which were about 0.05 μm in diameter. The ratio of deuterated to protonated polystyrene in this blend of perdeuteriopolystyrene with KR03 is 73/27.

Results

A standard cross-polarization magic-angle ^{13}C NMR spectrum of polystyrene (Figure 1, bottom) consists of three lines, a quaternary-carbon resonance (δ_C 145), a combination aromatic-carbon resonance (δ_C 125), and a main-chain aliphatic-carbon resonance (δ_C 40). Spectra of mixtures or blends of perdeuteriopolystyrene with either polystyrene or K-resin have the same appearance. In particular, no cross-polarization signal arising from the almost liquid-like polybutadiene component of the K-resin is observed.

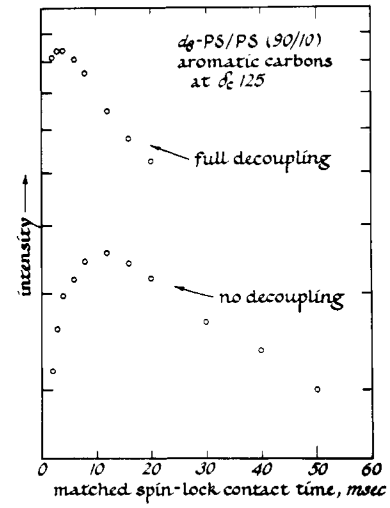

Figure 2. Carbon signal intensity for a homogeneous mixture of perdeuteriopolystyrene and polystyrene (10% by weight polystyrene) as a function of matched spin-lock contact time. The pulse sequences of Figure 1 were used.

For long, matched spin-lock contact times, the carbon magnetization, in general, tracks the $T_{1\rho}$ decay of the abundant protons since proton and carbon spin systems are in thermodynamic equilibrium.[7] A complication arises for samples containing perdeuteriopolystyrene, however. A slow cross-polarization transfer from protons of one chain to deuterated carbons on another chain prevents a steady-state condition from being reached. Thus, semilog plots of carbon intensity as a function of contact time between 2 and 20 ms are not linear (Figure 2, top).

The origin of this complication can be confirmed in a cross-polarization experiment in which no dipolar decoupling is used during data acquisition. Without dipolar decoupling, it is known that high-resolution cross-polarization carbon signals from protonated chains are not observed.[8] Magic-angle spinning by itself is, however, sufficient to produce high-resolution cross-polarization signals from deuterated chains (Figure 1, top). The evolution of this signal with contact time (Figure 2, bottom) contains information about static dipolar interactions[7] between protons of one chain and deuterated near and distant carbons of other chains.

The same shape cross-polarization curve was, in fact, observed for all protonated–deuterated mixed systems examined, including curves for both aliphatic and aromatic carbons. These curves are characterized by an initial rise with an apparent time constant of about 3–4 ms and an asymptotic decay with an apparent time constant of about 30–50 ms (Figure 2, bottom). In general, the relative intensity of the carbon signals observed with no decoupling, compared to that with full decoupling, increases with increasing perdeuteriopolystyrene concentration. In particular, this is true for the quaternary aromatic-carbon line at δ_C 145 (Table I). (The reason for the choice of scaling factor used in Table I will become apparent later in the discussion of results.)

One way to obtain the $T_{1\rho}$(H) of the protonated chains in a mixed protonated–deuterated system is from the difference of curves such as those shown in Figure 2. The top curve is due to both protonated and deuterated carbons while the bottom curve is due to deuterated carbons only. Thus, the difference can be associated exclusively with protonated carbons. A limitation with this procedure is that foregoing dipolar decoupling to obtain a signal only from deuterated carbons results in a line shape with some residual proton–carbon dipolar broadening. While this is

Table I
Polystyrene Quaternary-Carbon Signal Intensities[a] under Various Proton-Decoupling Conditions[b]

system	full decoupling[c]	delayed decoupling[d]	no decoupling[e]
polystyrene (PS)	1.00	0.48	nil
PS-d_8/PS (90/10)	1.54	1.15	0.54
PS-d_8/PS (73/27)	1.19	0.62	0.19
PS-d_8/KR03	1.19	0.66	0.19

[a] Matched spin-locked contact times of 2 ms. [b] Full decoupling *minus* no decoupling scaled to unity (see text). [c] Deuterated chains and all of the protonated chains. [d] Deuterated chains and part of the protonated chains. [e] Only deuterated chains.

Table II
Proton $T_{1\rho}$ from Proton-Carbon Cross-Polarization Direct-Difference Signals: Full Decoupling Minus Delayed Decoupling Experiments[a,b]

carbon/ system	$T_{1\rho}$(H), ms			
	PS-d_8/PS (90/10)	PS-d_8/ KR03	PS-d_8/PS (73/27)	PS
aliphatic	9.4	6.8	7.6	5.3
aromatic (at δ_C 125)	10.0	7.6	8.0	5.6

[a] Estimated error ± 5%. [b] Matched spin-locked contact times of 2 ms.

not a big effect, it is enough to make questionable a straightforward comparison of intensities (peak heights in particular) in the two halves of the difference experiment.

Instead, we have used a difference between a fully decoupled spectrum and a delayed decoupled spectrum.[9,10] For polystyrene, a 100-μs delay is sufficient to remove virtually the entire contribution to the protonated aromatic-carbon line at δ_C 125 (Figure 1, middle). Contributions from deuterated carbons are, of course, unaffected by this delay. For the quaternary-carbon line at δ_C 145, only half (48%) of the intensity survives the 100-μs delay for protonated polystyrene, while in mixed deuterated–protonated systems, *all* of the quaternary-carbon intensity from the deuterated chains, but only about half from the protonated chains, survives the delay (Table I).

Thus, a fully decoupled minus delay decoupled *difference* spectrum arises from just the protonated chains in a mixed system. Furthermore, the line shapes observed in this difference spectrum are the same as in the standard dipolar-decoupled situation since the decoupling is on throughout the data acquisition. We have performed such difference experiments in real time by alternately accumulating a positive signal from the full-decoupling half of the experiment and a negative signal from the delayed-decoupling half. Carbon magnetization in the resulting spectra, as a function of spin-lock contact time, can then be treated in the usual way to obtain $T_{1\rho}$(H) (Figure 3).

A compilation of these $T_{1\rho}$ values is presented in Table II. Entries represent single relaxation times since only straight-line $T_{1\rho}$ difference plots were observed. Values of both aliphatic- and aromatic-proton $T_{1\rho}$'s for the deuterated-polystyrene blend with K-resin are about the same (within experimental error) as those for the random mix of 73% by weight deuterated and 27% protonated polystyrene.

As mentioned above, a delay in decoupling of 100 μs is enough to ensure the absence of a protonated-carbon polystyrene resonance, but this delay does not suppress completely the aromatic quaternary-carbon signal (at δ_C 145) from an ordinary protonated chain. Thus, in a mixed protonated–deuterated system, the ratio of the two aromatic-carbon lines under delayed decoupling becomes a measure of the proton–deuterium mixing. The lower field aromatic-carbon line arises, in part, from protonated chains (and so acts as an internal standard), while the higher field aromatic-carbon line arises only from deuterated carbons, cross-polarized by protons on neighboring chains. As shown in Figure 1, the ratio of the two aromatic-carbon lines for the deuterated-polystyrene blend with K-resin is about the same as that for the 73/27 random mixture of deuterated and protonated polystyrenes.

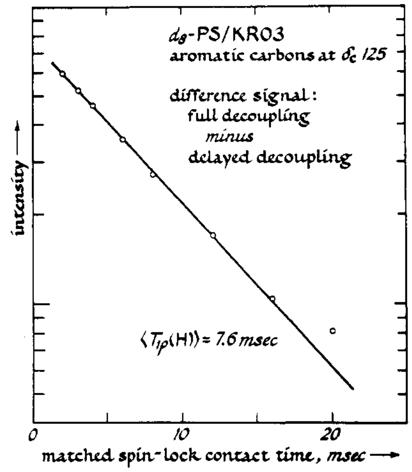

Figure 3. Carbon difference signal intensity for a blend of perdeuteriopolystyrene and Phillips K-resin (KR03) as a function of matched spin-lock contact time. The pulse sequences of Figure 1 were used.

Discussion

$T_{1\rho}$(H). The increase in $T_{1\rho}$(H) for both aliphatic and aromatic protons of polystyrene with increasing dilution by deuterated polystyrene (Table II) shows that *inter*chain relative motions are an important part of the proton rotating-frame spin–lattice relaxation. Substituting deuteriums for protons reduces the strength of internuclear dipolar coupling and hence increases the relaxation time.[4] The fact that only a single $T_{1\rho}$(H) is observed, even for the 90/10 deuterated–protonated mixed-polystyrene system, means that *intra*chain proton–proton spin diffusion is effective enough to generate a single average value. This suggests that the intra- and interchain relative motions contributing to relaxation in polystyrene are widespread and not restricted to a few local centers of relaxation. Otherwise isolation by deuterated chains of these local centers would probably result in multiple $T_{1\rho}$(H)'s since even rapid intrachain spin diffusion could not completely average values over extended stretches of a single protonated chain.[11]

For the blend of a perdeuteriopolystyrene with K-resin, a single $T_{1\rho}$(H) is also observed, increased from the polystyrene value by about 50% (Table I). This result leads to the immediate conclusions that the protonated polystyrene of the K-resin does not form a dense shell around the polybutadiene particles, and, in addition, does not form occlusions, or domains, imbedded within the dispersed rubber phase. In either event, a $T_{1\rho}$(H) relaxation plot, or component of a relaxation plot, characteristic of pure polystyrene would be observed. The experimental $T_{1\rho}$(H) for the blend (which contains 73% of its polystyrene deuterated) is about the same as that for a 73/27 random mix of deuterated and protonated polystyrene, suggestive of, but not necessarily proof for, a conclusion that the polystyrene chains of the K-resin are themselves randomly mixed with those of the matrix.

The similarity in the aliphatic- and aromatic-proton $T_{1\rho}$(H)'s for the various mixes and blends of polystyrene, as compared to pure polystyrene, shows that there was no H-D chemical exchange during the blending, mixing, and molding processes. If exchange did occur, differential relaxation effects would be observed for the chemically more labile and exchangeable aromatic protons and their $T_{1\rho}$(H). Substitution of a deuterium for a proton on an aromatic ring would produce a substantial decrease in the efficiency of intramolecular dipolar coupling and spin-lattice relaxation for the remaining protons of that ring. Naturally, this confirmation of the absence of any exchange effect is straightforward only with the resolution of the magic-angle ^{13}C NMR experiment.

Proton-Carbon Cross-Polarization from Protonated to Deuterated Chains. The evolution with increasing cross-polarization contact time of the deuterated-carbon magnetization has a deceptively simple appearance (Figure 2, bottom). Actually the functional dependence of this curve is given by[12]

$$S = \frac{S_M}{T_{IS}} \frac{e^{-t/T_{1\rho}(H)} - e^{-t(1/T'_{\rho L}+1/T_{IS})}}{1/T'_{\rho L} + 1/T_{IS} - 1/T_{1\rho}(H)} \qquad (1)$$

where S is the deuterated-carbon magnetization, S_M is the maximum magnetization available in a matched spin-lock cross-polarization experiment, T_{IS} is the proton-deuterated carbon matched spin-lock time constant, $T_{1\rho}$(H) is the proton rotating-frame relaxation time, and $T'_{\rho L}$ is the deuterated-carbon spin-lattice rotating-frame relaxation time in the presence of a proton spin-lock radio-frequency field. The initial slope of the curve is dominated by the smallest of the three time constants, and the final slope by the largest of the three. The deuterated-carbon spin-lattice relaxation time, $T'_{\rho L}$, at 44 kHz is about 10 times the usual protonated $\langle T_{1\rho}(C)\rangle$, or 100 ms.[11] From Table I, $T_{1\rho}$(H) in the mixed deuterated-protonated polystyrene systems is between 7.6 and 10 ms. Thus, the initial time constant of 3-4 ms observed for all three mixed or blended deuterated-protonated systems must be dominated by a T_{IS}(SL) for a proton-to-deuterated carbon cross-polarization transfer. The similarity in time constants for all three systems means this transfer probably occurs from similarly positioned, single, nearest-neighbor protons. Much larger values of T_{IS}(SL) can also be expected for slow transfers originating from more distant protons, so that even a nominal final slope (which may require several hundred milliseconds to reach) will reflect both cross-polarization and spin-lattice processes. Because of the presence of this wide distribution of cross-polarization rates, a full quantitative treatment of the transfer from protons to deuterated carbons is far more complicated than the situation represented by eq 1.

On the basis of the preceding discussion, we conclude that the ratios of intensities of aromatic-carbon lines observed in the delayed-decoupling experiment employing a cross-polarization contact time of 2 ms (Figure 1, middle) are free from serious complications due to differing $T_1\rho$(H)'s for different systems. This would not be true if, say, the ratios were examined after intermediate-length 10-ms cross-polarization contacts. Thus, the fact that the ratio of intensities for the 73/27 random mixture is about the same as that for the deuterated-polystyrene blend with K-resin (which has the same total deuterated-protonated polystyrene composition) is strong evidence that the polystyrene chains of the K-resin are indeed randomly mixed within the matrix. This conclusion is supported by the similarity of the ratios of the 2-ms spin-lock quaternary-carbon intensities with and without decoupling for the K-resin blend and the 73/27 random mixture (Table I). Such ratios are also a measure of the effectiveness of the protonated chains in generating carbon polarization from deuterated polystyrene and hence of the mixing of protonated and deuterated chains.

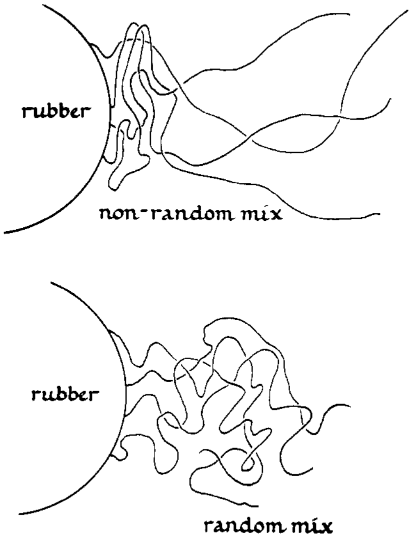

Figure 4. Schematic drawings representing two possibilities for the mixing of protonated polystyrene chains (solid lines) covalently linked to polybutadiene domains with perdeuteriopolystyrene chains (not shown) of an assumed unstructured matrix.

Random Mixing of Protonated and Deuterated Chains. To illustrate the strength of the evidence supporting random mixing, we consider a specific example contrasting nonrandom and random mixing (Figure 4). Only the protonated chains covalently attached to rubber are shown in this figure. These chains are assumed mixed with the unstructured deuterated chains of the matrix nonrandomly (top) and randomly (bottom). Actually, separate $T_{1\rho}$(H)'s would probably be observed for the concentrated and dispersed protonated chains of any distribution as exaggeratedly nonrandom as that of Figure 4.[11] However, single $T_{1\rho}$(H)'s are conceivable if more subtle gradients occurred which nevertheless still resulted in significantly nonrandom mixing.

The question arises as to whether the delayed-decoupling spectrum of polystyrene-d_8/K-resin (Figure 1, middle), which looks so much like the polystyrene-d_8/polystyrene (73/27) spectrum, could also be constructed by adding together spectra from mixtures of two different compositions, say, polystyrene-d_8/polystyrene (90/10) and pure polystyrene. We see that in fact this can be done easily by using as the only criterion the ratio of the intensity of the quaternary-carbon signal (δ_C 145) to that of the rest of the aromatic carbons (δ_C 125). Since polystyrene does not have a significant δ_C-125 line in the delayed-decoupling experiment, we need only add enough of its spectrum to that of the polystyrene-d_8/polystyrene (90/10) mixture to increase the ratio of intensities δ_C 145/δ_C 125 from 0.52 to 0.84. The former is the value observed for the polystyrene-d_8/polystyrene (90/10) mixture and the latter for the polystyrene-d_8/K-resin blend (Figure 1, middle).

Table I has been constructed to aid in this synthesis. The relative signal intensities have been scaled so that one (arbitrary) unit of mass of *protonated* polystyrene contributes an intensity of 1 to the fully decoupled quaternary-carbon line for each of these mixtures. That is, the table was constructed by using experimental relative intensities for each of the three different decoupling conditions, scaled so that the intensity difference between the

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no-decoupling spectrum, which does not detect protonated chains, and the full-decoupled spectrum, which detects them quantitatively, is unity. It is useful to scale intensities this way since the delayed-decoupling spectra we are about to compare reflect contributions from only part of the protonated chains.

We now construct a spectrum which has a fraction f of protonated polystyrene as a deuterated–protonated (90/10) mixture and the remaining fraction $(1 - f)$ as pure polystyrene so as to produce an intensity ratio δ_C 145/δ_C 125 of 0.84. We use the relative contributions of these two components to observed delayed decoupling intensities (Table I) and so find $f = 0.404$ by solving the proportion

$$\frac{1.15f}{1.15f + 0.48(1 - f)} = \frac{0.52}{0.84}$$

For this mixture, the weighted average of the relaxation rates for the two kinds of aromatic protons (40.4% in polystyrene-d_8/polystyrene (90/10) and 59.6% in polystyrene) predicts $T_{1\rho}(\mathrm{H}) = 6.8$ ms, as compared to 7.6 ms observed for the polystyrene-d_8/K-resin blend. In addition, the overall composition combines $0.404 + 0.596 = 1$ part of polystyrene with $9 \times 0.404 = 3.636$ parts of polystyrene-d_8 to give 21.6% polystyrene as compared with 27% in the actual K-resin blend. Not only do these two sets of figures not agree particularly well, they cannot *both* be made to agree better by altering the composition of the heterogeneous mixture. In fact, the only way to achieve better agreement is to make the components of the heterogeneous mixture less different. Thus, we are led to the conclusion that the *combined* evidence of our several different measurements is only consistent with a random or near-random mixing model.

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Small-Angle Neutron Scattering from Sulfonate Ionomers

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ABSTRACT: Small-angle neutron scattering experiments (SANS) have been performed on sulfonated polystyrene ionomers. Sulfonate concentrations were studied over the range 0–8.5 mol %. The radius of gyration of the polystyrene ionomers showed a regular increase with increasing sulfonate content. The radius of gyration was insensitive to thermal annealing and remained unchanged at temperatures well above the glass transition temperature.

Introduction

Ionomers are defined as linear polymers with predominantly nonpolar backbones which contain 10 mol % or less of neutralizable side groups. The backbone may or may not be crystalline. Despite extensive studies carried out on ionomers, the important question of the state of aggregation of the salt groups in the bulk remains unanswered. The literature concerning ionomers has become vast and a suitable introduction to the subject may be found in two recent books and a review.[1-3] From the structural studies involving various techniques, including electron microscopy, X-ray scattering, neutron scattering, vibrational spectroscopy, and Mössbauer spectroscopy, several different models have been suggested. We shall here be concerned with only one of these which we believe to be generally applicable. For a discussion of the others, the reader should consult ref 1–3. The model envisages the presence of at least two kinds of ionic aggregates. These will be referred to as clusters and multiplets to conform to the nomenclature of Eisenberg.[2] The clusters have dimensions in the 10–50-Å range, contain 50–100 ion pairs, and possess an internal structure. The multiplets consist of isolated ion pairs or quartets. The model implies a multiphase structure for ionomers. For amorphous ionomers two phases are present: a dispersed phase consisting of the clusters and a continuous phase consisting of the hydrocarbon matrix and the multiplets. Examples of ionomers in this category are poly(butadienecarboxylates) and poly(styrenecarboxylates). Crystalline ionomers contain a third phase consisting of the crystallized portions of the backbone. The best known examples of ionomers in this category are the poly(ethylenecarboxylates).

The most striking feature present in both the X-ray and neutron scattering patterns of ionomers is a peak corresponding to a Bragg spacing from 20 to 60 Å, depending upon the chemical structure of the ionomer and the presence or absence of polar impurities such as water. This peak appears for all salt forms but is absent in the acid form. It persists in the melt up to decomposition tem-

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