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Chain Motion of Partially Deuterated Polystyrene above the Glass Transition Temperature As Revealed by Deuterium NMR Spectroscopy

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ABSTRACT: Deuterium NMR spectra of polystyrene containing deuterium in 10–20% of the center of the polymer chain were examined in the temperature range 380–470 K. The results coincide with those of Spiess and co-workers for polymers containing deuterium along the entire polymer chain. Below 390 K there is no motional averaging of the deuterium spectrum although it is possible to measure NMR correlation functions sensitive to molecular reorientation with appropriate three-pulse sequences. Above 430 K the spectrum is averaged into a Lorentzian line that narrows as the temperature is raised. Above 430 K the pseudo-solid echo that results in some other deuterated polymer melts from a pair of 90° pulses in quadrature was not formed. It appears that, in the presence of the spectral averaging produced by motion between chain entanglements, reptative motion out of the entanglements is fast enough at temperatures above 430 K to average any residual couplings that might otherwise exist. Nevertheless, this motion would be much too slow to average the complete spectrum by itself. The results suggest that deuterium NMR spectroscopy may not be as useful for the study of very slow reorientation in polymer melts as are forms of NMR spectroscopy that have a longer effective time scale such as ^{13}C and ^{1}H NMR.

Introduction

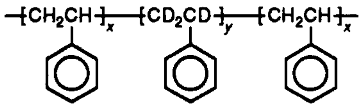
The loss of molecular orientation that occurs in stretched polystyrene films during annealing above the glass transition temperature has been followed with infrared spectroscopy.[1-5] Recovery of isotropic orientation is nonexponential and can be divided into three stages.[6,7] The initial loss of chain orientation accompanies Rouse motion between chain entanglements. The second stage occurs as the chain segments retract within the deformed tubes formed by surrounding chains. The third stage involves movement of the chains out of the original tubes into new, undeformed tubes.

Reorientation of each polymer chain also takes place in samples without a net overall orientation. Nuclear magnetic resonance spectroscopy offers a means to examine polymer reorientation in such materials,[8,9] whose dynamic properties could differ somewhat from those of the oriented samples.[10,11] Even in isotropic samples, however, intermolecular constraints should force molecular reorientation to occur nonexponentially, in stages. Interestingly, at 430 K deuterium NMR spectroscopy appears to be insensitive to any multistage reorientational process that may occur in polystyrene.[12-16]

Nevertheless, ^{13}C NMR line widths of molten polystyrene and polystyrene in concentrated solution do show a molecular weight and concentration dependence that suggests that intermolecular constraints play an important role in controlling the motions of polystyrene that are important to NMR spectroscopy.[17,18] There is also wide evidence that chain entanglements affect the NMR spectra of other polymers.[19-31] Furthermore, the nuclear interactions characteristic of the solid phase are only partially averaged in many polymer melts[19-23] and concentrated solutions.[24,25] Special pulse sequences[26,27] and magic-angle spinning,[28-31] which depend on the presence of solidlike interactions, are still effective for many molten polymers and concentrated solutions. Apparently, fast motion in the melts averages most of the interactions of the solid away but leaves a residual interaction that is lost only slowly. Detailed relaxation studies also must be interpreted in terms of restricted motion induced by chain entanglements.[32-36]

Thus the high-temperature deuterium NMR results for polystyrene are puzzling.[11-15] Above the glass transition temperature we would expect that there would be spectral evidence of hindered movement of the polystyrene chains and that some solidlike character of the melts would persist. The NMR resonances should be non-Lorentzian, and it should be possible to focus "pseudo-solid" quadrupolar echos.

The previous results might be understood if the spectra were dominated by signals from the chain ends, whose motion is much more free than that of the chain centers. We have now examined the deuterium NMR spectrum of polystyrene samples containing deuterium in only the innermost portions of the chain (I). The results for these materials are essentially the same as those for the polymers that are deuterated along the entire polymer chain. For both systems the chain motion of molten polystyrene above 430 K and of polystyrene in concentrated solution is indistinguishable from isotropic diffusion in terms of its effect on the deuterium NMR spectrum. Even at 380 K NMR correlation functions are reasonably well approximated by calculations based on isotropic rotational diffusion of the polymer chains.[36] We show, nevertheless, that the NMR results can be rationalized with the infrared studies and with the viscoelastic properties of polystyrene that indicate that chain motion is much more complicated than simple isotropic rotational diffusion.



I

Experimental Section

Purification of Materials. Styrene (Aldrich) was stirred over finely ground calcium hydride for 1–2 days before vacuum distillation. The distilled monomer was then stored at −25 °C in a brown bottle until further use. Immediately prior to

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polymerization, it was distilled from dibutyl magnesium (DBM), available as a 25% solution in heptane from Lithco. Typically, 60 mL of styrene required 4–5 mL of DBM, added until the pale yellow associated with the complexation of DBM to the olefin site in styrene persisted. Styrene-d_2 (98 atom % deuterated at the CH_2 site; Merck) was simply distilled from DBM immediately before use.

sec-Butyllithium is available from Lithco as a 1.31 M solution in hexane. It was used as received and was stable at −25 °C for several months. Tetrahydrofuran (Kodak; reagent grade) was distilled under nitrogen from sodium and benzophenone immediately before use.

Preparation of Initiator. Naphthalene (Aldrich; scintillation grade) was sublimed at 30 °C immediately prior to use. Approximately 1.5 g of finely sliced sodium (Aldrich) was placed in a Schlenk vessel under nitrogen purge. An equivalent weight of sublimed naphthalene was then added. The vessel was capped with a rubber septum, and positive nitrogen was maintained. Tetrahydrofuran (50 mL) was added with a syringe at room temperature. There was immediately a green color indicative of the presence of radical anions. The solution was allowed to stand for 18 h and was decanted with a cannula into a flame-dried bottle.

Polymerizations. All glassware was rigorously cleaned and dried in an oven at 120 °C for 24 h. For small-scale polymerizations the reactor was a 250 mL, one-neck round-bottomed flask equipped with a magnetic stirrer and rubber septum. The reactor was flame dried and allowed to cool under nitrogen purge. Tetrahydrofuran was added with a syringe, and the vessel was submerged in a −78 °C bath. Polymerizations were done with either a monofunctional initiator (*sec*-butyllithium) or a bifunctional initiator (the sodium/naphthalene radical anion).

For the monofunctional initiator purified styrene monomer was inserted into the reactor with a syringe followed by addition of the calculated amount of the *sec*-butyllithium with a syringe. The orange of the polystyryl lithium anion formed immediately. The polymerization of each block was allowed to proceed for 20 min to ensure complete conversion. Deuterated monomer was added immediately after polymerization of the first block. The triblock polymer was completed by addition of a final charge of styrene.

For the bifunctional initiator the solution of deuterated styrene was placed in the reactor at the start of the reaction. The solution of the radical anion was added with a syringe, leading to immediate formation of a red color. The polymerization was allowed to proceed to 20 min before addition of styrene to generate the triblock copolymer. For the difunctional initiator only two monomer charges were necessary for formation of the triblock copolymer.

For both initiators the polymerization was terminated with degassed, HPLC-grade methanol. The copolymers were precipitated into a 10-fold excess of methanol and were isolated by vacuum filtration before drying under vacuum at 100 °C overnight.

The molecular weights of the polymers were characterized by size-exclusion chromatography (SEC) in THF at 25 °C with ultrastyragel columns of 10^6, 10^5, 10^4, and 10^3 Å. The instrument was a variable-temperature Waters gel-permeation chromatograph equipped with a differential refractive index detector. Polystyrene standards (Polymer Laboratories) were used for the construction of calibration curves.

The polymer with low molecular weight examined with NMR spectroscopy was prepared with the monofunctional initiator and was labeled PS-48. It had $\bar{M}_n = 47\,800$ and $\bar{M}_w/\bar{M}_n = 1.50$. Because this polymer gave NMR spectra equivalent to those from the sample with higher molecular weight, the relatively broad molecular weight distribution was not considered to be a problem. The polymer with higher molecular weight that was used was prepared with the bifunctional initiator and was labeled PS-120. It had $\bar{M}_n = 120\,000$ and $\bar{M}_w/\bar{M}_n = 1.30$.

Deuterium NMR spectra were recorded with a Bruker CXP-100 spectrometer operating a home-built probe at 41.445 MHz in a narrow-bore magnet. The sample was melted into a 7-mm ceramic spinner from Doty Scientific, Inc., that is normally used for magic-angle spinning. It was sealed with a Macor top equipped with O-rings. Because the observation temperatures were below 473 K, no effort was made to exclude oxygen from the samples to slow down oxidative degradation.

The probe temperature was controlled with standard Bruker equipment. The temperature of a reference thermocouple placed in a dummy sample in the probe on the bench top was within 2 K of the temperature set on the Bruker controller for the temperature range used for actual observations.

The 90° pulse width measured on a small bulb of deuterium oxide in the center of the coil was typically 3.2 μs. The average time for a 90° pulse over the entire polymer sample was about 4.0 μs, however.

Spectra recorded below 400 K were determined by Fourier transformation of the quadrupolar echo formed with two 90° pulses separated by 25 μs. The spectral width was normally 1.67 MHz, digitized in 1 K data points.

For experimental consistency spectra recorded above 430 K were usually acquired with the same, two-pulse sequence used for lower temperature spectra. Nevertheless, it was verified that a quadrupolar echo did not actually form at these temperatures. The NMR resonances obtained by Fourier transformation of the signal following two pulses had the same shape as those obtained by Fourier transformation of the signal following a single pulse.

At temperatures for which motion is too slow to average the observed NMR spectrum, spectral interchange can be detected with three-pulse sequences. In one type of experiment a second pulse 90° out of phase from the first creates varying degrees of "quadrupolar order" or "spin alignment", depending on the time development of the spin system between the pulses.[37] For nuclei having a quadrupolar frequency ω_1 between the first and second pulses, the amount of quadrupolar order formed is proportional to $\sin \omega_1 t_1$, where t_1 is the time between the pulses. The maximum amount of quadrupolar order for any given value of t_1 is formed with a flip angle of the second pulse of 45°.

During a mixing period t_m following the second pulse, the components of quadrupolar order are partially interchanged by molecular motion. The third pulse transforms the interchanged components of quadrupolar order back into transverse magnetization. Maximum conversion again occurs for a pulse width of 45°. The frequency associated with each component of magnetization after the third pulse differs from that before the second pulse because of molecular reorientation occurring during the mixing period. The overall signal intensity measured at a time t_1 after the third pulse is $\langle \sin \omega_1 t_1 \sin \omega_2 t_1 \rangle$, where ω_2 is the frequency of the magnetization component after the third pulse and the angular brackets denote an ensemble average. Measurements made for a set of t_m values map out a correlation function whose detailed shape is a function of t_1.

Similar experiments can be performed in which the second pulse has the same, or opposite, phase as the first pulse does. The second pulse now partially transforms transverse magnetization into Zeeman order. The amount of Zeeman order formed is proportional to $\cos \omega_1 t_1$ and is maximized for a 90° pulse. Following a 90° third pulse, a correlation function having the form $\langle \cos \omega_1 t_1 \cos \omega_2 t_1 \rangle$ can be measured after a time t_1 following the third pulse.

The time t_m is limited in the case of Zeeman order by the spin–lattice relaxation time and in the case of quadrupolar order by the relaxation time of quadrupolar order, which is similar in magnitude to that of the spin–lattice relaxation time. Spin–lattice relaxation in PS-120 was nonexponential. The decay curve could be broken into a major component (75%) having a relaxation time of 1.5 s and a minor component (25%) having a relaxation time of 0.2 s. Actual values of t_m used for the measurements extended to 0.6 s. Thus the fast-relaxing component of magnetization is largely lost during the longest values of t_m. Phase cycling was used to cancel artifacts created by such nuclear relaxation.

The maximum quadrupolar frequency for aliphatic deuterium nuclei in the labeled polystyrenes is about 125 kHz. Accordingly, the correlation functions should oscillate with a period of about 8 μs. Measurements optimally are made with t_1 values as short as a few microseconds. For such short times the widths of the pulses themselves must explicitly be taken into account.[38,39] For both types of correlation functions t_1 is lengthened by half the width of the first pulse. For the correlation function of cosines the effective length of t_1 is also lengthened by half the width of the second pulses. For the correlation function of sines the second pulse adds to the effective length of t_1, but to a degree that varies

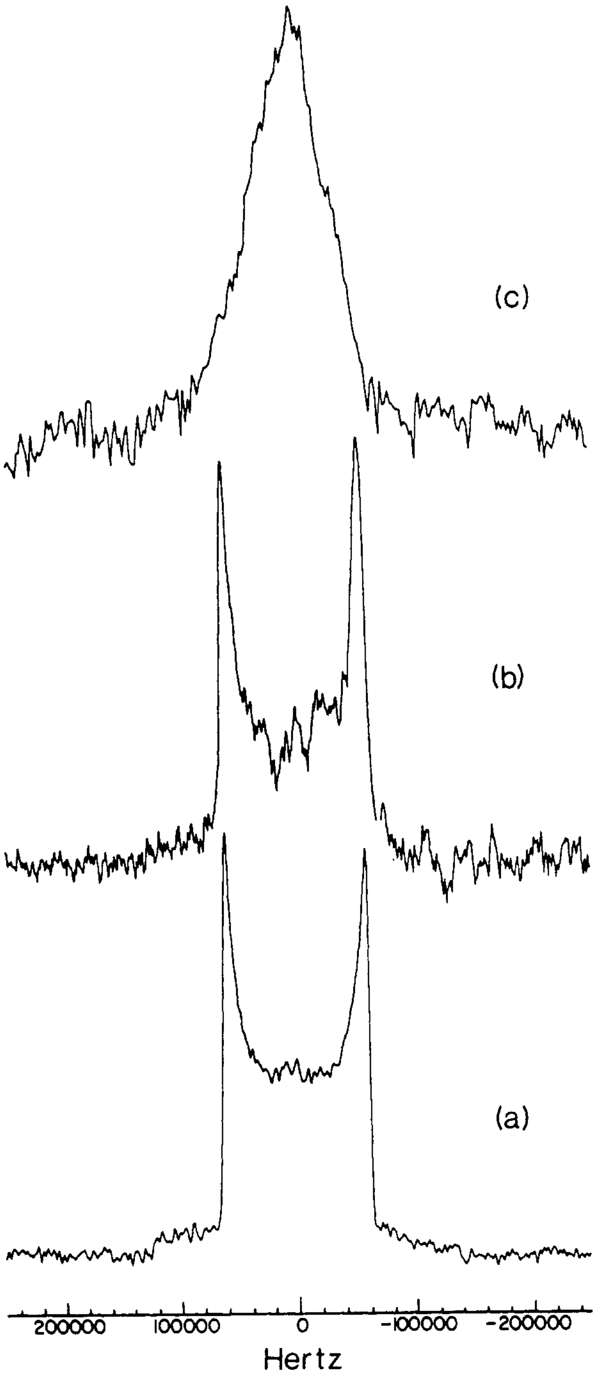

Figure 1. Deuterium NMR spectra of PS-48 taken at temperatures of (a) 390, (b) 400, and (c) 430 K.

with the particular value of ω_1 for each magnetization component.[38,39] For reasonably strong pulses the length of the second pulse can simply be ignored.[39]

The pulse sequence leading to the correlation functions is the same as that used for generation of two-dimensional exchange deuterium NMR spectra.[40-44] Actual generation of two-dimensional spectra with such a pulse sequence requires measurements with a wide range of t_1 values. The intensity of the deuterium NMR signal for the polystyrenes did not permit generation of two-dimensional spectra, which would provide additional details about the mechanism of chain reorientation.

Calculations of the correlation functions were made with programs written in BASIC for a Macintosh II computer. Details of the calculations are described below.

Results

Deuterium NMR spectra for PS-48 as a function of temperature are shown in Figures 1 and 2. The spectrum taken at 390 K is equivalent to that of a rigid solid. Distortion from molecular motion is apparent, however, in the spectrum taken at 400 K. Furthermore, there was an overall reduction in the signal-to-noise ratio of the spectrum as the temperature was raised from 390 to 400 K. At temperatures between 400 and 430 K the intensity of the quarupolar echo dropped almost to zero and no spectra were recorded. Almost complete loss of the quadrupole echo after a two-pulse sequence is an indication that the molecules are undergoing almost isotropic rotational motion.[38]

At 430 K a signal following the second pulse in the two-pulse sequence was again evident. This signal was now not actually a quadrupolar echo, however, but the remains of the free-induction-decay signal generated by the first pulse. Careful comparison of the signal intensity in one-

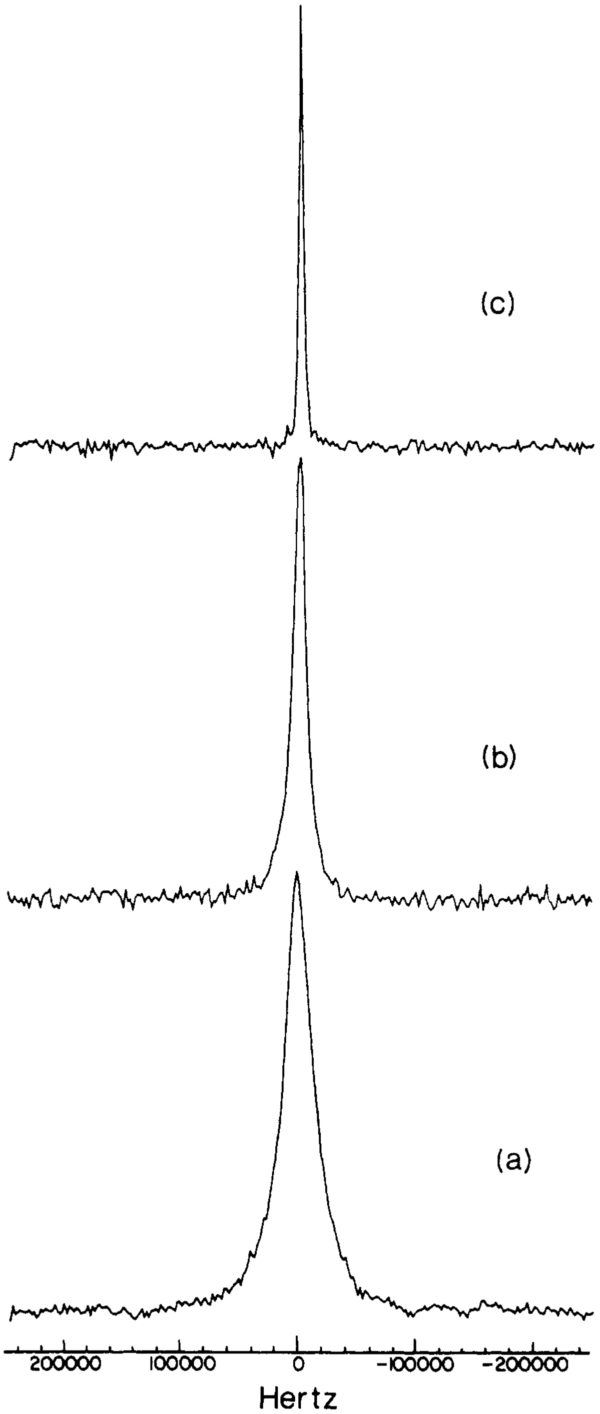

Figure 2. Deuterium NMR spectra of PS-48 taken at temperatures of (a) 440, (b) 450, and (c) 470 K.

Table I
Widths of the Deuterium NMR Signals of PS-48

temp, K	line width, Hz	correlation time, s
430	27000	1.51×10^{-6}
440	11500	6.04×10^{-7}
450	4500	2.54×10^{-7}
470	1300	8.41×10^{-8}

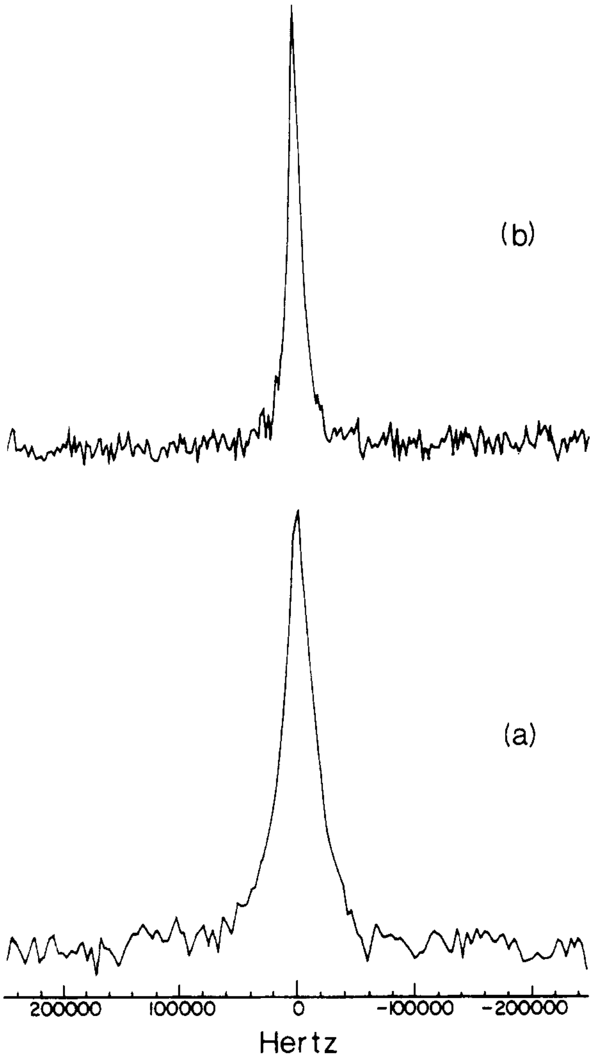

Figure 3. Deuterium NMR spectra of PS-120 taken at (a) 440 and (b) 450 K.

Table II
Widths of the Deuterium NMR Signals of PS-120

temperature, K	line width, Hz	correlation time, s
380		2.0
430	27000	1.38×10^{-6}
440	11500	5.78×10^{-7}
450	4500	2.32×10^{-7}
470	1300	6.76×10^{-8}

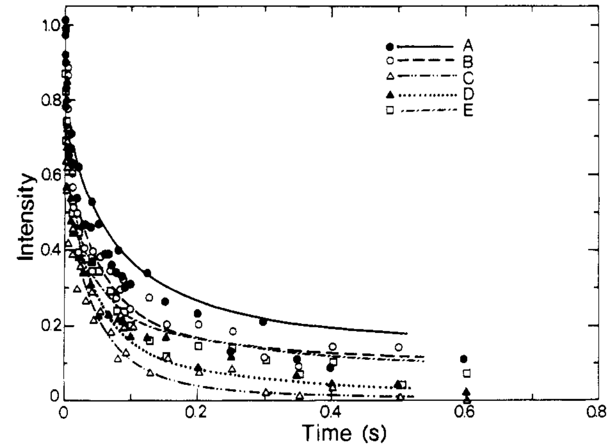

Figure 4. Correlation function $\langle \sin \omega_1 t_1 \sin \omega_2 t_1 \rangle$ for PS-120 measured at 380 K with corrected t_1 values of (a) 13.08, (b) 15.08, (c) 17.08, (d) 19.08, and (e) 21.08 μs. The solid lines were calculated for isotropic diffusion with a correlation time of 2.0 s as described in the text.

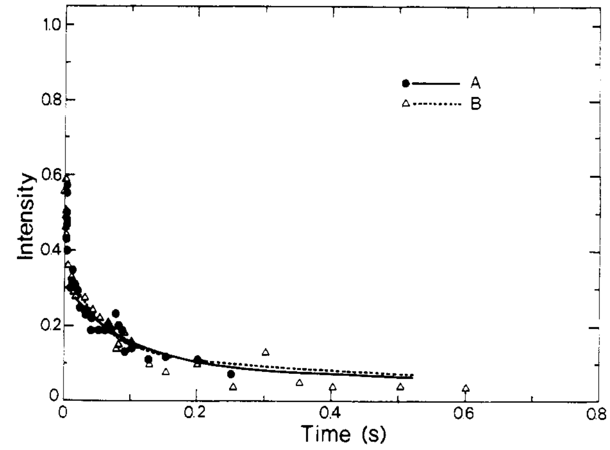

Figure 5. Correlation function $\langle \cos \omega_1 t_1 \cos \omega_2 t_1 \rangle$ measured for PS-120 at 380 K with corrected t_1 values of (a) 11.44 and (b) 17.44 μs. The solid lines were calculated for isotropic diffusion with a correlation time of 2.0 s as described in the text.

and two-pulse expeiments showed that the second pulse had no effect at all on the signal. The spectral resonance obtained from the signal by Fourier transformation had only a fraction of the width of the spectrum taken at 390 K.

As the temperature was increased above 430 K, the signal in the spectrum continued to sharpen. At each temperature its shape was almost perfectly Lorentzian with the widths at half-height shown in Table I.

PS-120 gave the spectra shown in Figure 3 at 440 and 450 K. These spectra almost perfectly reproduce those from PS-48 shown in Figure 2 at comparable temperatures. Thus the deuterium spectra appear to be insensitive to molecular weight within the range investigated. Measured line widths are shown in Table II.

The homogeneous line width was reduced in one sample upon the addition of 31 mg of dibutyl phthalate to 64 mg of PS-120. This facilitated detection of any inhomogeneous line width that might have existed. At 460 K the width at half-height of the deuterium NMR signal was 326 Hz. Once again, however, no quadrupolar echo formation was detected at either this temperature or at other temperatures between 420 and 460 K. The inhomogeneous line width is either very small or nonexistent.

At temperatures that are too low for there to be significant spectral averaging from motion, it is still possible to detect motion with deuterium NMR spectroscopy by measuring how the echo in a three-pulse experiment is attenuated as a function of the time between the second and third pulses.[11,23,37,44] As is explained in the Experimental Section, it is possible to record functions of both the form $\langle \sin \omega_1 t_1 \sin \omega_2 t_1 \rangle$ and the form $\langle \cos \omega_1 t_1 \cos \omega_2 t_1 \rangle$, where ω_1 is the frequency of a particular magnetization component between the first and the second pulse and ω_2 is the frequency of the magnetization component after the third pulse. The angular brackets denote an ensemble average.

A series of sine correlation functions recorded for PS-48 at 380 K with corrected t_1 values between 13.08 and

Table III
Calculated Correlation Times (s)[a]

temp	I[b]	II[c]	III[d]	IV[e]	exptl[f]
380	2.0[g]	2.0[g]	2.0[g]	2.0[g]	2.0
430	4.85×10^{-6}	1.22×10^{-5}	1.96×10^{-6}	1.52×10^{-6}	1.38×10^{-6}
440	1.37×10^{-6}	3.81×10^{-6}	5.79×10^{-7}	6.22×10^{-7}	5.78×10^{-7}
450	4.76×10^{-7}	1.42×10^{-6}	2.11×10^{-7}	2.08×10^{-7}	2.32×10^{-7}
470	8.78×10^{-7}	2.98×10^{-7}	4.38×10^{-8}	3.65×10^{-8}	6.76×10^{-8}

[a] From the equation $\log a_T = -c_1(T - T_{ref})/(c_2 + (T - T_{ref}))$ where $a_T = \tau_c/\tau_{ref}$. [b] For $c_1 = 13.7$, $c_2 = 50.0$, $T_{ref} = 373$ K. [c] For $c_1 = 12.7$, $c_2 = 49.8$, $T_{ref} = 373$ K. [d] For $c_1 = 13.7$, $c_2 = 40.0$, $T_{ref} = 373$ K. [e] For $c_1 = 13.7$, $c_2 = 49.8$, $T_{ref} = 375$ K. [f] From Table I. [g] Assumed.

21.08 μs are shown in parts A–E of Figure 4. Two cosine correlation functions for the same sample are shown in parts A and B of Figure 5.

Discussion

The deuterium NMR spectra of polystyrene that is deuterated in only the central portion of the chain are similar to those of Spiess and co-workers for polystyrene that is deuterated along the whole chain.[11-15] Below 390 K the spectral shape is essentially unaffected by motion; above 430 K it is collapsed into a homogeneous Lorentzian signal.

Long-lived chain entanglements in the polystyrene melts would be expected to lead to collapsed deuterium NMR spectra with non-Lorentzian shapes. In the presence of long-lived constraints a C–D bond is inhibited from sampling all directions in space. There is a residual quadrupolar interaction, the magnitude of which depends on the orientation of the axis connecting the chain entanglements with respect to the direction of the magnetic field. This residual coupling results in a very small splitting of the NMR signals from each deuterium nucleus. The observed signal for an isotropic melt is the superposition of all such signals. In general, there is no overall, observable splitting, but the signal is inhomogeneously broadened and clearly has a non-Lorentzian shape.[45-50] The signal is homogeneously broadened by incomplete averaging caused by motion of the chain segments between the chain entanglements.

The residual inhomogeneous line width in polymer networks is only on the order of 100 Hz.[45-50] This is small compared to the observed line widths given in Tables I and II. To a first approximation, the entire line width for the deuterated polystyrenes above 430 K can be considered to be homogeneous. The NMR line widths can then be used to provide an estimate for the time scale on which orientation is lost. For this purpose we approximate the motion as isotropic rotational diffusion. Rapid isotropic diffusion leads to a Lorentzian NMR signal with a width at half-height of $\omega_p{}^2\tau_c$, where $\omega_p{}^2$ is the second moment of the spectrum of the rigid solid and τ_c is the correlation time for diffusion.[51] The second moment of the deuterium NMR powder line shape for the deuterated polystyrene is about 1.23×10^{11} s^{-1}. We calculate the correlation times for chain reorientation in polystyrene at each of the observation temperatures that are shown in the final columns of Tables I and II.

The NMR correlation functions can be used to get an effective correlation time at 380 K, again based on the approximation of the overall motion as isotropic diffusion. For reorientational diffusion, the joint probability function, $\Gamma(\theta_1,\theta_2,t)$, that a given axially symmetric vector has an orientation θ_2 at time t and that it had the orientation θ_1 at time 0 can be expanded as a series in the Legendre polynomials $P_\nu(\cos\theta_1)$ and $P_\nu(\cos\theta_2)$.[42,52]

$$\Gamma(\theta_1,\theta_2,t) = \frac{\sin\theta_1}{2}\frac{\sin\theta_2}{2}\sum_{\nu=0}^{\infty}(2\nu + 1)P_\nu(\cos\theta_1) \times P_\nu(\cos\theta_2)\exp[-\nu(\nu + 1)t_m/(6\tau_c)] \quad (1)$$

The NMR correlation functions $F_p(t_1,t_m)$ then have the form

$$F_p(t_1,t_m) = \int_0^{\pi/2}d\theta_1\int_0^{\pi/2}d\theta_2\, p(\omega_1t_1)\, p(\omega_2t_1)\, \Gamma(\theta_1,\theta_2,t_m) \quad (2)$$

where $p(\phi) = \cos\phi$ or $\sin\phi$ and $\omega_n = (6\pi e^2qQ/8h) \times P_2(\cos\theta_n)$. Thus the NMR ccorrelation functions can be calculated for various values of τ_c and t_1.

In practice, the series expansion in eq 1 must be used with great caution. The exponent corresponding to the largest value of ν should be large for the shortest time of interest. A reasonable requirement is that $\nu(\nu + 1)t_m/(6\tau_c) > 5$ for the largest value of ν and the smallest value of t_m used. If the smallest time $t_m = 0.02\tau_c$, then the largest ν should be about 39. The Legendre polynomials $P_n(\cos\theta_1)$ oscillate with shorter and shorter periods in θ_1 as n becomes larger. If a large number of terms are retained in the series, very fine steps in the orientational angles must be used in any series approximation to the integrals in eq 2.

These restrictions mean that short-time simulation of the correlation functions cannot practically be made with the series expansion for a reasonable number of terms in the series expansion. For relatively long times we were able, however, to simulate the experimental correlation functions reasonably well for $\nu_{max} = 40$ with $\tau_c = 2.0$ s^{-1} down to mixing times of several milliseconds. The calculated functions are shown as solid lines in Figures 4 and 5. The change in the correlation functions with varying t_1 is especially well reproduced.[14]

The temperature dependencies of the calculated correlation times (Tables I and II) are reasonably consistent with those expected on the basis of the WLF equation.[53] Predicted high-temperature correlation times were calculated for each of the two sets of WLF parameters quoted by Ferry[53] as shown in Table III. The overall trends of the NMR observations are matched by the WLF results, although the parameters of Barlow given by Ferry match the results somewhat better than do those of Plasek. An even better fit results from slightly modified parameters as shown in column 3 of Table III. A simple shift in the reference temperature without readjustment of the other WLF parameters also gives an improved fit (column 4). The apparent shift in the reference temperature would be consistent with a constant error in temperature measurement. Because control of the temperature in an NMR probe to less than 1 or 2 K is difficult, such an error is quite possible. In any case, the agreement of the correlation times predicted by the WLF equation and those determined by NMR spectroscopy indicates that similar motions control both the narrowing of the NMR spectrum and the viscoelastic properties of molten polystyrene.

Clearly, however, the assumption of isotropic rotational diffusion is inappropriate for molten polystyrene. Infrared dichroism[3-8] and ^{13}C NMR spectroscopy[10] show that chain entanglements severely constrain the polymer motion. Reorientation should occur in stages, the final loss of orientational correlation taking place on a time scale several orders of magnitude longer than the initial loss. How is it possible to rationalize this expectation with the deuterium NMR spectra?

At 393 K both motion of the chain segments between entanglements and reptative movement out of the entanglements are too slow to average the NMR spectrum. Chain motion can be detected with deuterium NMR only through the NMR correlation functions. The correlation functions most strongly reflect chain motion between entanglements. Only a small residual orientational correlation that is hard to observe is left by this motion. The residual correlation decays very slowly, on a time scale much longer than that of nuclear spin–lattice relaxation.

At temperatures between 400 and 430 K, the deuterium NMR spectrum is highly averaged by rotational motion. It is no longer possible to measure NMR correlation functions as before. It is not even possible to measure the spectrum accurately.

Above 430 K most of the spectrum is averaged by the fast process. There could be a residual inhomogeneous broadening, but it would be small, on the order of 100–200 Hz. It is quite possible that even this small residual inhomogeneous broadening is completely absent, however. The infrared results suggest that the fast process is about 10^3 or 10^4 more rapid than the slow process. If the correlation time for the fast process at 430 K is about 10^{-6} s, it is quite reasonable that the time constant of the slower process is about 10^{-3} s. Motion on a time scale of 10^{-3} s is appropriate to average a residual coupling of 100–200 Hz. Thus, even though the slow process is incapable of averaging the entire deuterium spectrum, it may be fast enough at 430 K and higher temperatures to average the residual couplings left by the fast process.

Because the deuterium quadrupole interaction is relatively large, motion must occur on a relatively short time scale to average the deuterium NMR spectrum. Sample temperatures must be high for orientational motion to occur on this time scale. At these elevated temperatures it is more difficult to separate components of the overall reorientational motion than it would be at lower temperatures. Unfortunately, for polystyrene it is not possible to obtain an NMR spectrum with pulse techniques over much of the temperature range that would be of interest. NMR correlation functions can be measured at still lower temperatures, but very slow reorientational motion now occurs on a time scale longer than that of spin–lattice relaxation. These facts prevent the application of deuterium NMR spectroscopy to the study of very slow motions in polystyrene and, perhaps, other polymers.

Conclusions

Although chain entanglements can lead to residual inhomogeneous broadening of the deuterium NMR signals of polymer melts, these should not universally be expected. At temperatures well above the glass transition temperature it may be impossible to separate the effects of constrained motion of polymer chains from that of isotropic rotational diffusion.

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