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Rouse and Reptation Dynamics of Linear Polybutadiene Chains Studied by ^{2}H NMR Transverse Relaxation

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ABSTRACT: Deuterium NMR has been used to investigate two different types of dynamics of linear polybutadiene chains in the melt. The transverse relaxations of short Rouse chains of molecular weight 640−3000 were biexponential, which has been attributed to separate decays of the methylene and methine deuterons. Interpretation of the transverse relaxation rates using a model for Rouse dynamics, combined with molecular simulations, gave the shortest Rouse unit as approximately 4.4 monomers and the shortest Rouse time as 8.3×10^{-7} s. The reptation dynamics of higher molecular weight entangled chains were investigated using ABA isotopic triblock copolymers, of total molecular weight 14000−135000, where A is protonated polybutadiene of molecular weight greater than the entanglement molecular weight and B is a deuterated block. These polymers were specifically synthesized so that the fast motion of the Rouse-like chain ends should not complicate the signal. The fundamental parameters found for the Rouse chain were used in the reptation model, assuming fast dynamics, and gave an entanglement molecular weight, M_e, of 5380 or approximately 21 Rouse units. This M_e is more than twice the conventional value, obtained from rheology, and is more suggestive of the critical molecular weight M_c, consistent with previous NMR work. The theoretical analysis used in this work is based on the assumption that the chain dynamics are fast on the time scale set by the NMR deuterium quadrupolar interaction. The highest molecular weight samples were found to not satisfy this criterion and indicate the molecular weight at which a new theoretical approach is needed.

Introduction

The objective of this paper is to use the deuterium NMR transverse relaxation to quantify the molecular dynamics of polybutadiene, above and below the entanglement molecular weight (M_e). In a number of previous papers,[1−6] we have shown how an exact solution for the transverse relaxation can be developed and adapted using appropriate approximations, to study the dynamics of Rouse chains,[1] reptating chains,[2] and cross-linked networks.[3] Experimental examples include proton NMR studies of polyethylene[4,6] and poly(ethylene oxide).[5]

This work uses similar methodologies to study the dynamics of monodisperse polybutadiene chains, of molecular weights above and below M_e, using the deuterium transverse relaxation. One reason for using deuterated samples relates to the chemical structure of polybutadiene. Employment of the models[1−3] used to interpret the proton NMR requires the assumption of noninteracting proton pairs, such that the transverse relaxation is almost solely due to dipolar interactions between two protons comprising a pair. This criterion is clearly not satisfied in polybutadiene. However, the polybutadiene structure is not a problem when considering the deuterium relaxation, which results from quadrupolar interactions, and we will show that the Rouse parameters can be determined satisfactorily using the deuterium NMR relaxation. Another reason for using deuterated materials relates to the two distinct types of dynamics of entangled chains that usually results in biexponential-type transverse relaxations and can make analysis difficult. Kimmich[7] has proposed that the ends of polymer chains undergo Rouse dynamics, similar to free chains of low molecular weight, whereas the middle of the chain undergoes reptation. He showed, through analysis of biexponential fits to experimental data, that the effective molecular weight of the ends performing Rouse motion is independent of the molecular weight of the chain, and approximately equal to two entanglement lengths. We have also shown recently[8] that the free induction decay (FID) from the end entanglement section of a polybutadiene star arm, of arm M_w 30000, is single-exponential, consistent with Rouse dynamics. Without specific isotopic labeling, namely the synthesis of polymers with NMR-active nuclei in known locations, the resulting NMR signal must contain contributions from all parts of the chain, with a whole range of dynamics. Slowly reorientating sections of the chain, such as those constrained by entanglements, will have a rapidly decaying transverse relaxation which will be significantly obscured by the more gradual decay of the signal from fast-moving chain ends. To overcome these problems, in the present work, we have selectively deuterated the middle section of entangled chains, leaving the end sections in excess of two entanglement lengths protonated. With these samples, it has been possible to focus exclusively on the part of the chain which undergoes reptation, without the signal from the chain ends dominating the transverse relaxation. A recently derived result[6] for the free induction decay, calculated from the reptation spectrum, is employed to interpret the data.

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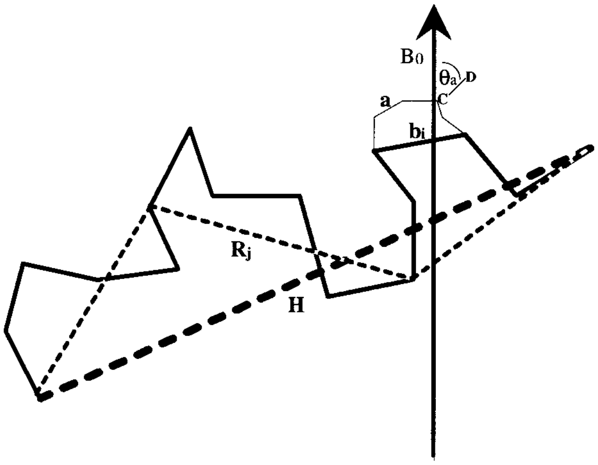

Figure 1. A schematic picture of the scale invariant model used to interpret the NMR transverse relaxation. N_a monomers are connected to form a **b** unit (Rouse unit), N_b Rouse units comprise the vector **R**, equal to an entanglement length, and N_R entanglement lengths form the polymer chain **H**.

Theory

Transverse NMR Relaxation. Interactions of the quadrupole moment of the deuterium atom with the electric field gradient associated with the C−D bond (which is attached to the polymer backbone) cause the dephasing of the transverse nuclear magnetization. This decay is sensitive to both the correlation times of the various chain segments and to the melt structure.

The transverse relaxation function $M(t)$ for a C−D bond is given by[9]

$$M(t) = \left\langle \cos\left[\frac{3\nu_0}{8}\int_0^t \left(\frac{3\cos^2\theta_a(t') - 1}{2}\right) \mathrm{d}t'\right]\right\rangle \tag{1}$$

where ν_0 is the static quadrupolar coupling constant for deuterium and $\theta_a(t')$ is the (fluctuating) angle between the C−D bond and the applied magnetic field, as shown in Figure 1. The local dynamics of $\theta_a(t')$ are many orders of magnitude faster than the collective motions (Rouse modes) of the polymer chain. Cohen-Addad[10] has shown how the fast local NMR details can be averaged to give a rescaled model more applicable to investigating the collective motions. This method has been further developed by Brereton.[9] In this approach several monomers, N_a, described by the bond vectors $\mathbf{a}_j$, are connected together to form a statistical unit **b** (such that $\underline{b} = \sum_{j=1}^{N_a}\underline{a}_j$) and **b** can be considered to be equivalent to a Rouse unit. The model is illustrated schematically in Figure 1. The NMR interaction is averaged over this length scale to give

$$\nu_0(2z^2 - x^2 - y^2) \rightarrow \frac{\kappa}{N_a}\nu_0\left(\frac{2Z^2 - X^2 - Y^2}{N_a}\right) \tag{2}$$

where (x,y,z) are the coordinates of the bond and (X,Y,Z) are the end coordinates of a sequence of the N_a bonds, ν_0 is the quadrupolar coupling constant for deuterium, and κ is a numerical constant associated with the NMR average over the atomic details. The transverse relaxation function $M(t)$ for the chain can now be written in terms of the **b** vectors as[9]

$$M(t) = \left\langle \cos\left[\frac{3\Delta_b}{2b^2}\int_0^t \mathrm{d}t'\{2b_z^{\,2}(t') - b_x^{\,2}(t') - b_y^{\,2}(t')\}\right]\right\rangle \tag{3}$$

where b is the root-mean-square length of the Rouse unit and Δ_b is the rescaled quadrupolar interaction constant corresponding to the segment b given by

$$\Delta_b = \frac{\kappa\nu_0}{4N_a} \tag{4}$$

For freely jointed rods, κ is 0.6. In general, κ is given by

$$\langle P_2(\cos\theta)\rangle_{\sum_{j=1}^{N_a}(a_j=b)} = \frac{\kappa}{N_a}\langle P_2(\cos\phi)\rangle + \text{terms} \sim (N_a^{\;-2}) \tag{5}$$

where, in the present case, θ is the angle between the C−D bond in a methylene or methine group and the end-to-end vector of a chain comprising N_a repeat units and ϕ is the angle that the end-to-end vector makes with the applied field. The evaluation of κ will be discussed later in the Results and Discussion.

The $\langle\cdots\rangle$ in eq 3 indicates an averaging of the NMR-active statistical segment over all available conformations, in the time interval $0-t$, subject to any constraint that the environment imposes on the segment (e.g., cross-links or entanglements). It is through this averaging that the NMR spin is sensitive to the polymer chain environment. The problem posed by the evaluation of eq 1 has been treated in a series of papers.[1−3,9]

The calculation of the transverse relaxation, given by eq 3, is accomplished by using the second-moments approximation. The range of validity of this approximation has been studied[9] and for the present NMR problem requires the relaxation times to be faster than Δ_b^{-1}. The necessary dynamical information needed to complete the calculation only involves the bond vector correlation function $\langle \underline{b}_j(t)\cdot\underline{b}_j(0)\rangle$. This is available for both Rouse and reptation dynamics. The result[1] using the Rouse model is given by

$$M(t) = \exp\left(-\left[\frac{6\ln N_b}{\pi}\Delta_b^{\,2}\tau\right]t\right) \tag{6}$$

where τ is the shortest Rouse time and N_b the number of b (Rouse) units per chain. The longest Rouse relaxation time is given by $N_b^{\,2}\tau$ and the validity of the result is dependent on the fast relaxation time condition, which in practice[9] has been found to be

$$\Delta_b N_b^{\,2}\tau < 10 \tag{7}$$

We will show that for Rouse chains this condition is easily satisfied for all molecular weights up to the entanglement point.

At larger chain lengths when N_b becomes greater than N_e, the number of Rouse units in an entanglement length, entanglements with other chains superimposes a slower reptation motion on the relatively fast Rouse modes. To accommodate the possibility of a different dynamics at larger scales, we consider a further rescaling of N_e Rouse units described by the bond vectors $\{\mathbf{b}_j\}$ onto a larger vector $\mathbf{R}_j$ given by

$$\underline{R}_j = \sum_{j=1}^{N_e} \underline{b}_j \tag{8}$$

This is shown in Figure 1. The NMR interaction strength is also rescaled as

$$\Delta_b \rightarrow \frac{\Delta_b}{N_e} \tag{9}$$

The entire polymer chain with an end-to-end vector **H** is now considered as a chain of N_R vectors $\{\underline{R}_J\}$ such that

$$\sum_{j=1}^{N_R} \underline{R}_j = \underline{H} \tag{10}$$

We will use the experimental NMR results to identify the $\{\underline{R}_j\}$ vectors with entanglement lengths, so that for a chain of molecular weight M_w and entanglement weight M_e

$$N_R = \frac{M_w}{M_e} \tag{11}$$

Again, it is assumed that reptation dynamics are fast. The slowest reptation mode is given by $\tau_R = N_R^3(N_e^2\tau)$ and this must be compared to the rescaled interaction Δ_b/N_e. In practice,[9] it has been shown that the condition for fast dynamics is

$$\frac{\Delta_b}{N_e}\tau_R \leq 10 \quad \text{or} \quad \Delta_b N_R^{\,3} N_e \tau \leq 10 \tag{12}$$

When this criterion is satisfied, the result for the transverse relaxation is given[6] by

$$M(t) = \exp\left(-\left[\frac{18 N_R \ln N_R}{\pi}\Delta_b^{\,2}\tau\right]t\right) \tag{13}$$

Experimental Section

Samples. The samples used for this work were synthesized and characterized at the IRC in Polymer Science and Technology at the University of Durham. Anionic polymerization using high-vacuum methods was used to synthesize all the polymers discussed here. Hydrogenous butadiene was obtained from Aldrich and passed through a drying column before use. Deuteriobutadiene was obtained from the reductive dechlorination of hexachlorobutadiene using the procedure of Craig and Fowler.[11] All polymerizations were carried out using rigorously dried benzene as the solvent and *sec*-butyllithium as the initiator. Low-molecular-weight polybutadienes were allowed to react at 40 °C for 3−4 h before terminating by the addition of nitrogen-purged methanol. The ABA isotopic triblock copolymers (where A is hydrogenous and B deuterated polybutadiene) were synthesized by the sequential addition of monomers. Blocks with molecular weights of less than 10000 g mol^{-1} were allowed to react for 3−4 h before the addition of the next quantity of monomer. Block molecular weights greater than 10000 g mol^{-1} were allowed to react overnight before adding more of the monomer. At each stage of the polymerization (i.e., at each monomer addition process), a sample of the polymer was removed for molecular-weight determination. At the completion of polymerization the reaction was terminated by adding nitrogen-purged methanol and the polymer precipitated out into chilled methanol. Molecular weights were determined by size exclusion chromatography on tetrahydrofuran solutions using both refractive index and viscosity detectors which had been calibrated using polybutadiene standards.

Table 1. Molecular Weights of Each Section of the Butadiene−Deuteriobutadiene−Butadiene A−B−A Triblock Copolymers and Their Total Molecular Weight (All g mol^{-1})

protonated end section (A)	deuterated mid section (B)	protonated end section (A)	total M_w
5900	2700	5400	14000
6800	9900	8200	24900
5500	18200	3300	27000
14750	2050	19600	36400
4800	37200	6400	48400
5900	114300	20700	135000

Monodisperse deuteriobutadiene chains of relatively low molecular weight were synthesized in order to investigate short-chain dynamics through ^{2}H NMR. These were fully deuterated and have molecular weights of 640, 940, 1250, 1450, 2100, and 3000 g mol^{-1}.

To study reptation, the ends of the high-molecular-weight entangled chains had to be rendered invisible to ^{2}H NMR as they undergo fast Rouse diffusion and would dominate the transverse relaxation, as previously mentioned. To probe only the sections of chain-performing reptation, the ends of the chains (blocks A) were hydrogeneous butadiene, whereas the middle (block B) was deuteriobutadiene. The molecular weights of the isotopic triblock copolymers are reported in Table 1. The entanglement molecular weight M_e of polybutadiene, calculated from literature values[12] of the plateau modulus, is 1970 g mol^{-1}. A length of the hydrogeneous chain at each end, with the molecular weight considerably in excess of this, was therefore considered a sufficient target molecular weight to mask any Rouse dynamics.

Nuclear Magnetic Resonance. The NMR measurements were carried out at the IRC in Polymer Science and Technology at the University of Leeds, using a Chemagnetics CMX-200 spectrometer, corresponding to a frequency of 30.7 MHz for deuterium.

The employment of the theory described is dependent upon the experimentally observed transverse relaxation being interpretable in terms of molecular motion. The Levitt Freeman[13] version of the Carr Purcell pulse sequence has therefore been used, which removes the static field inhomogeneities and other inhomogeneous interactions, which would otherwise affect the simple free induction decay. The Levitt Freeman pulse sequence is written

$$\left(\frac{\pi}{2}\right)_x - T - \left[\left(\frac{\pi}{2}\right)_x \pi_y \left(\frac{\pi}{2}\right)_x - 2T\right]_n$$

This self-compensating sequence ensures that every second echo is correct, providing that diffusional processes are not significant. The $(\pi/2)$ pulse was 4 μs and the dephasing time T typically ∼0.1−0.5 ms. A total of $n/2$∼300 points was acquired, at the peak of every second echo, with the resultant free induction decay being the average of about 16 accumulations, with a recycle delay of 3 s. All measurements were carried out at 25 °C.

The standard quadrupolar echo pulse sequence $(\pi/2)_x - T - (\pi/2)_y$ was used to record the rigid-lattice spectrum at −130 °C for calculation of the quadrupolar coupling constant, with a pulse width of 2 μs, 1 MHz spectral width, an interpulse spacing, T, of 70 μs, and a recycle delay of 10 s.

Molecular Simulations. For the calculation of the parameter κ (eq 4), a 100 repeat unit length of polybutadiene was constructed containing a random sequence of cis and trans units, using *Insight* software.[14] Random conformations of this chain were then generated using the RIS Monte Carlo method (RMMC). This method explores the torsion space of the chain with a Monte Carlo algorithm. Some of the same approximations as the RIS (rotational isomeric state) theory are used (such as only including short-range interactions in calculating the chain energy; thus, the chain is modeled as in the melt or

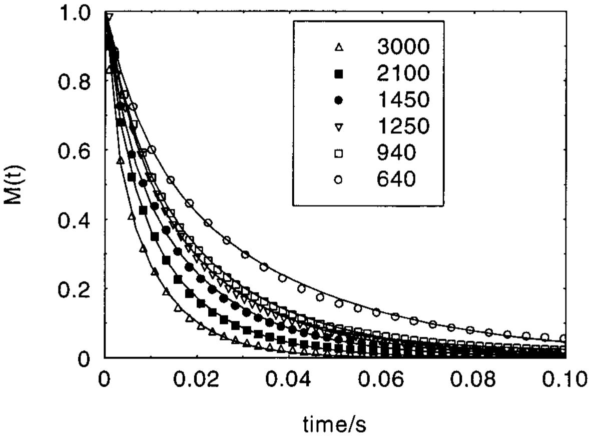

Figure 2. The deuterium transverse relaxations for low-molecular-weight polybutadiene, with fits to a double exponential (eq 16). M_w is indicated. For clarity, not all data points are included.

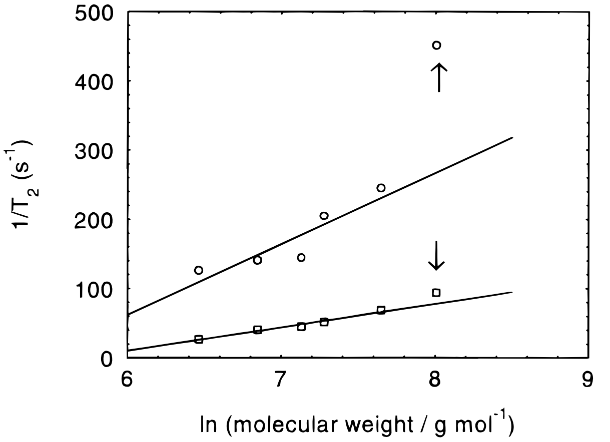

Figure 3. The transverse relaxation rate, $1/T_2$, for the low-molecular-weight samples, versus ln M_w for the methylene (□) and methine (○) deuterons, showing fits to eq 15. The points marked are not included in the fits.

theta solution); however, unlike RIS the torsion angles are allowed to vary continuously. At each step in the simulation a rotatable backbone torsion is chosen at random and rotated to a new random angle. The energy of the chain in its new conformation is evaluated and the move accepted if $\exp[-(E_{new} - E_{old})/kT]$ is greater than a random number chosen between 0 and 1. To equilibrate the system, 10^5 steps were run and then a further 5×10^6 steps to generate conformations for processing. Conformations were saved every 5×10^4 steps to yield 100 conformations. A temperature of 300 K was used and the energies calculated using the polymer consortium force field (PCFF). For a particular length segment, the orientation parameter required is $P_2(\cos\theta)$ where θ is the angle between the end-to-end vector of the segment and the C$-$D vector in the methylene or methine group in the center of this segment. For a particular segment length an average of this value is calculated over all possible origins along a chain and over all stored conformations. The first two and the last two repeat units on the chain were ignored in all calculations, and so, for instance, there were 95×100 possible segments of length 2 units. The results are shown in Figure 5.

Results and Discussion

Rouse Chains. Equation 6 expresses the Rouse model for transverse relaxation and can be rewritten as

$$M(t) = \exp\left[\frac{-6}{\pi} t \Delta_b^{\,2} \tau (\ln M_w - \ln m)\right] \qquad (14)$$

where m is the molecular weight of a Rouse unit. Experimentally, the transverse relaxation from a low-molecular weight Rouse chains is expected to be single-exponential, defined by the relaxation time, T_2, and so we can write

$$\frac{1}{T_2} = \frac{6}{\pi} \Delta_b^{\,2} \tau (\ln M_w - \ln m) \qquad (15)$$

Figure 2 shows the transverse relaxations obtained from the six low-molecular-weight samples. None of these transverse relaxations are single-exponential. However, this is because polybutadiene contains two chemically different deuterons, namely methylene and methine present in a 2:1 ratio, having different T_2 values. The experimental pulse sequence used will remove the chemical shift differences, but the two separate decays will be superimposed, leading to a biexponential transverse relaxation. Each transverse relaxation was therefore fitted to eq 16, where $T_2^{\,a}$ and $T_2^{\,b}$ relate to the methine and methylene deuterons, respectively.

$$M(t) = \left(\frac{1}{3}\right) \exp(-t/T_2^{\,a}) + \left(\frac{2}{3}\right) \exp(-t/T_2^{\,b}) \qquad (16)$$

The fits to eq 16 are shown in Figure 2. From eqs 4 and 15, it can be seen that the fundamental parameters N_a and τ can be found from the plot of $1/T_2$ against ln M_w which will have a slope equal to $(6/\pi)\Delta_b^{\,2}\tau$, and intercept equal to $-(6/\pi)\Delta_b^{\,2}\tau(\ln m)$. This plot is shown in Figure 3 and shows acceptable linear relationships for both deuterons, in accordance with the NMR model for Rouse dynamics, up to and including 2100 g mol^{-1}. The sample of molecular weight 3000 g mol^{-1} shows deviation from linear behavior, suggesting the onset of entanglement constraint, such that the free Rouse model is no longer appropriate.

The logarithm of the molecular weight of a Rouse unit, ln m, is the ratio of the intercept to the slope, and the values of m obtained are given in Table 2. As can be seen from Table 2, m determined from the two separate deuterons is the same, within experimental error, justifying the procedure used in separating the transverse relaxation into two different decays.

The number of monomers in a Rouse unit can be found by dividing m by the monomer molecular weight, which is 60 for deuteriobutadiene. This gives an average value of 4.4 ± 0.5 monomers, corresponding to approximately 18 backbone chain bonds. Cohen-Addad et al.[15] have used a similar model for the short time component of proton transverse relaxations for low-molecular-weight *cis*-polybutadiene at 274 K. They regard the subunit to be equivalent to the entanglement length for both *cis*-polybutadiene[15] and poly(dimethylsiloxane),[16] which is reasonable as they have used a model which assumes the subunit to be effectively frozen on the NMR time scale.

The shortest Rouse time, τ, is determined from the slope of the straight line fits of Figure 3. However, as can be seen, there are two different slopes, one for each of the two types of deuteron. At an atomic level, the reason for this is most probably due to the C$-$D bonds within methylene and methine units having different average correlation times, giving rise to two different T_2 values, which then show different trends with molecular weight. However, within the context of the

Table 2. Rouse Parameters Found from Analysis of the Relaxation Rate of the Methine and Methylene Deuterons, via Equation 15

deuteron	slope[a]	intercept[a]	m (g mol^{-1})	N_a	κ	Δ_b (10^3 s^{-1})	τ (10^{-7} s)
methine	102	−553	226	3.8	0.73	7.924	8.45
methylene	33.6	−191	294	4.9	0.55	4.630	8.15
average			260 ± 34	4.4 ± 0.5			8.30 ± 0.15

[a] From Figure 3.

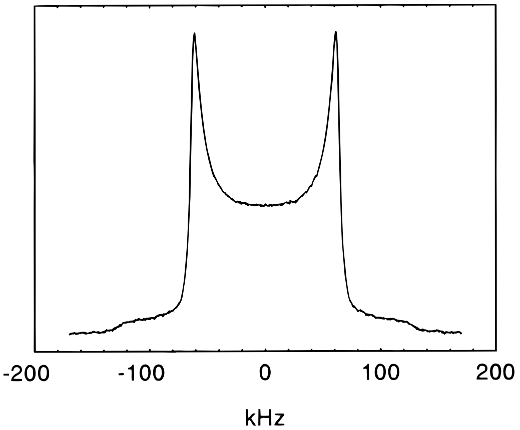

Figure 4. Solid-state deuterium NMR spectrum of polybutadiene, at −130 °C.

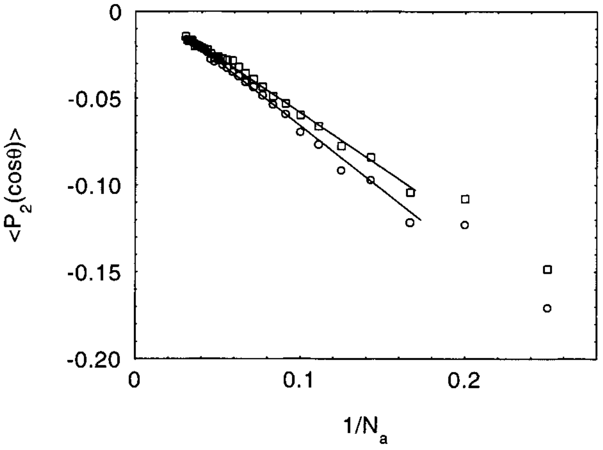

Figure 5. Orientation factor $\langle P_2(\cos\theta)\rangle$ versus N_a^{-1} for the C−D bond within methylene (□) and methine (○) groups.

model we are using, for Rouse dynamics, the possibilities for the origin of these two slopes can be interpreted as (i) different fundamental Rouse times (τ values) exhibited by the methine and methylene groups or (ii) different values of Δ_b for each group. We consider that the former possibility can be dismissed, as the shortest Rouse unit comprises 4.4 monomers, which is clearly too coarse a scale to be affected by atomic details. Any intrinsic correlation time difference between the methylene and methine deuterons will be lost as their motions are rescaled onto the motion of the larger vector describing the Rouse unit. Consequently, τ must be independent of the type of deuteron used to calculate it. We can interpret the two slopes therefore as different values of Δ_b, the interaction strength, obtainable from eq 4. The value for the quadrupolar coupling constant ν_0 can be determined experimentally from the low-temperature, rigid-lattice spectrum of the polymer (the "Pake pattern"). Figure 4 shows the spectrum for deuteriopolybutadiene at −130 °C, at which temperature the polymer chain is expected to be immobile as it is approximately 40 °C below its glass-transition temperature. The quadrupolar coupling constant can be found from the separation between peaks, $\Delta f = 123.75$ Hz, through

$$\nu_0 = \frac{4}{3}\Delta f \qquad (17)$$

Only one Pake pattern is seen at −130 °C, indicating a single ν_0 for each deuteron. From eq 17 a static quadrupolar coupling constant of 165 kHz is found, consistent with literature values.[17] The only possibility left, therefore, is two values for κ. As mentioned in the Theory section, this is a factor arising from the averaging of the local atomic details to give the smallest scale invariant unit described by the bond vector **b**. Numerical simulation methods (see Experimental Section) were used to find $\langle P_2(\cos\theta)\rangle$ for the methine and methylene C−D bonds for chain segments of N_a polybutadiene repeat units, setting the angle ϕ to zero for convenience. κ is then, to a good approximation, the slope of the plot of $\langle P_2(\cos\theta)\rangle$ versus N_a^{-1}, as suggested by eq 5. This plot is shown in Figure 5, for N_a up to 30 repeat units. The data for the short units are less reliable because of the difficulty of choosing a C−D bond near the exact center of the segment. For the longer segments the standard error in $\langle P_2(\cos\theta)\rangle$ is of the order of 0.005. The values of κ obtained by this method are −0.55 and −0.73, for the methylene and methine deuterons, respectively. The methine bond produces a higher κ because it is a stiffer bond, being located adjacent to the double bond on the main chain, which is also consistent with this deuteron having a shorter T_2. A similar procedure has been carried out by Gronski et al.,[18] who used Monte Carlo methods to find $\langle P_2(\cos\theta)\rangle$ for just the methylene group in polybutadiene, as a function of N_a. Analysis of their data gives a value of −0.2 for κ. However, in their case, $\langle P_2(\cos\theta)\rangle$ does not tend toward zero at high N_a, reaching an asymptotic value of about −0.14, an anomaly which the authors mention but do not specifically address. We therefore regard our present simulation as providing better estimates. Accordingly, substituting our values for κ into eq 4 yields values for τ, obtained from the slopes relating to the methylene and methine deuterons, of 8.15×10^{-7} and 8.45×10^{-7} s, respectively, as seen in Table 2. These values are very similar, again justifying the procedure used for that of separating the transverse relaxation into two different decays. The values are also similar to those in the literature,[19] in which des Cloizeaux uses dynamic mechanical measurements to give τ for polybutadiene as 1.2×10^{-6} s.

Finally, as mentioned in the Theory section, the Rouse model is valid only in the region where $\Delta_b N_b^2 \tau < 10$. Using the values found, the condition is $N_b < 140$. In Figure 3, it can be seen that the highest M_w that still obeys the Rouse model is 2100, for which $N_b \approx 8$, comfortably satisfying the above criterion. Even the sample of $M_w = 3000$, which shows a departure from the model, has $N_b \approx 11$.

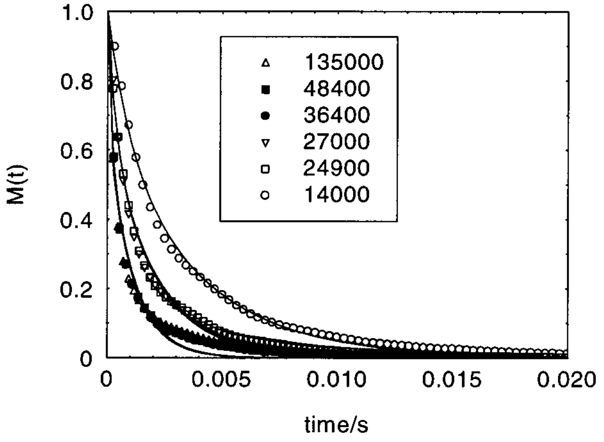

Figure 6. The deuterium transverse relaxations for high-molecular-weight, entangled polybutadiene chains, with fits to a double exponential. M_w is indicated. The poor quality of the fits at high molecular weight is indicative of the breakdown of the second-moments approximation.

Reptating Chains. For the high-molecular-weight chains, the transverse relaxation rate can be related to eq 13, in the same manner as before, to give

$$\frac{1}{T_2} = \frac{18}{\pi}\Delta_b^{\,2}\,\tau N_R \ln N_R \tag{18}$$

The verification of eq 18 has the significance of showing that NMR transverse relaxation can perceive reptation.

In a manner similar to the analysis of the unentangled chains, the T_2 value was used as a measure of the decay of the net magnetization. As expected from the analysis of the transverse relaxations obtained from unentangled chains, the data could not be fitted well by a single exponential, but was fitted adequately, up to a certain molecular weight, by a biexponential, as shown in Figure 6. It is important to emphasize here the distinction between the biexponential behavior seen in this work and that which is normally seen in unlabeled, entangled chains. In the latter case, as mentioned in the Introduction, the biexponential transverse relaxation is the result of contributions from two entirely different types of dynamics. The end sections, of the order of an entanglement length, are undergoing fast Rouse-like dynamics, whereas the central section is undergoing reptation. In our case, by using isotopic labeling, we have eliminated from the transverse relaxation the contribution from the ends, and we regard the biexponential behavior to be due to the two types of deuteron present, both of which are undergoing the same dynamics, but which relate to different values of Δ_b. As long as the dynamics of the central reptating section are fast, such that the second-moments approximation is valid, the transverse relaxation for any particular deuteron in this section of the chain will be a single-exponential.

To interpret the results within the context of the reptation model as expressed by eq 18, $1/T_2$ for each decay was plotted against M_w (Figure 7). The factor $((18/\pi)\Delta_b^2\tau)$ in eq 18 was calculated by using the results from the Rouse analysis, and hence, M_e, the entanglement molecular weight, was the only fitting parameter. The highest one or two molecular weight samples clearly deviate from the model and are not included in the fit. Table 3 shows the results from this analysis for the methylene and methine deuterons. Again, the justification for analyzing the transverse relaxation in terms of two separate decays is provided by the very similar value for the number N_e of Rouse units in an entanglement length, 22 and 19, respectively. The average value for M_e, 5380, is significantly higher than literature values of 1970 for M_e obtained from rheology.[12] However, this is consistent with similar NMR work by Ries et al.[5] where the M_e of poly(ethylene oxide) was found to be twice that of the literature value obtained from mechanical measurements, suggesting that this NMR method is more sensitive to M_c, the critical molecular weight. The M_e found through NMR corresponds to the number of Rouse units N_e which sum to give larger vectors, **R**, as $M_e = N_e m$. It is possible to rescale from Rouse units to a larger vector, **R**, which is a step length of the primitive path. **R** is not necessarily the diameter of the tube perceived by dynamic mechanical measurements.

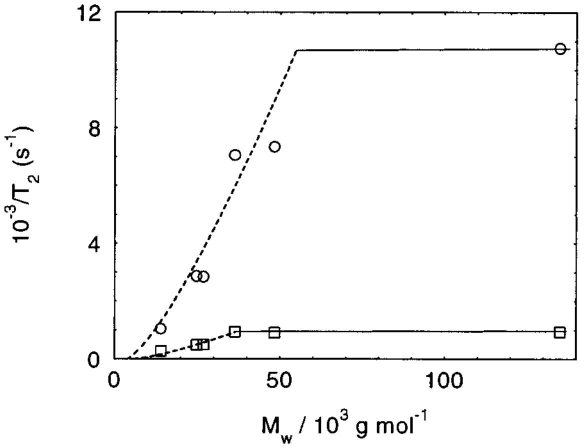

Figure 7. The transverse relaxation rate, $1/T_2$, of the high-molecular-weight samples, versus M_w for the methylene (□) and methine (○) deuterons. The broken lines are the fits to eq 18.

Table 3. Entanglement Molecular Weight, M_e, and the Number of Rouse Units in an Entanglement Length, N_e, Obtained from Fits to Equation 18 for Methylene and Methine Deuterons

deuteron	M_e (g mol^{-1})	N_e ($=M_e/m$)
methine	4250 ± 750	19 ± 3
methylene	6500 ± 1500	22 ± 5
average	5380 ± 1130	21 ± 4

$1/T_2$ is found to be proportional to $N_R \ln N_R$ for molecular weights up to about 36400, or $N_R \sim 7$, thus verifying eq 18 for these shorter entangled polymers. The theoretical model uses the standard reptation model and the second-moments approximation. The sharp deviation from the fit at a high molecular weight suggests that the longest chains, namely those of M_w equal to 48000 and 135000, are too slow for the second-moments approximation to hold. This also results in poor fits to the transverse relaxations in Figure 6. The criterion for the applicability of the second-moments approximation is given from eq 12 as

$$\Delta_b N_R^{\,3} N_e\,\tau \le 10$$

From Table 2 we have $\Delta_b \sim 6 \times 10^3$ s^{-1} and $\tau \sim 10^{-6}$ s^{-1}, and we have just deduced that $N_e \sim 21$, hence $\Delta_b N_R^3 N_e \tau \sim 0.1(N_R^3)$. The second-moments approximation is therefore predicted to hold for $N_R \le 5$ or $M_w \le$ 27000, in reasonable agreement with the value found.

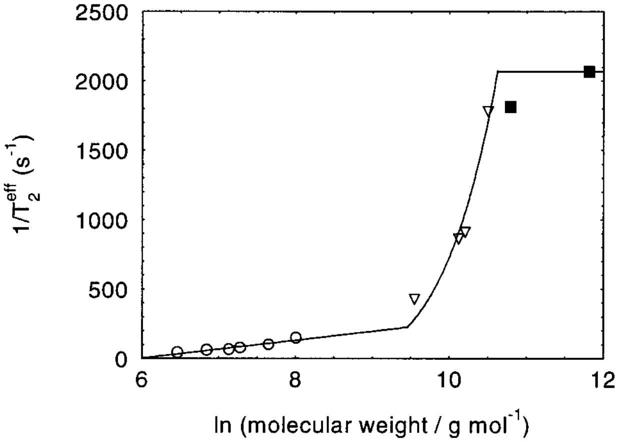

Figure 8. The average relaxation rate, $(T_2^{\rm eff})^{-1}$ versus $\ln(M_w)$ for all samples, showing the transition from Rouse to reptation dynamics, and the breakdown of the second-moments approximation.

The problem of analyzing the transverse relaxation when the second-moments approximation does not hold has been addressed and will be considered for polybutadiene in a forthcoming paper.

Finally, an overall perspective on both the Rouse and reptation dynamical regimes is provided by Figure 8. In this figure, for clarity, the presence of two Δ_b values has been ignored, and also the data has been analyzed in terms of an "effective T_2", $T_2^{\rm eff}$, which is simply the time taken for the transverse relaxation to fall to 1/e of its initial amplitude. In Figure 8, the plot of $(T_2^{\rm eff})^{-1}$ versus $\ln(M_w)$ shows very clearly the crossover between Rouse and reptation dynamics, and then at higher molecular weight, the point at which the second-moments approximation fails.

Conclusions

We have shown that the NMR model for the evaluation of polymer chain Rouse parameters, previously applied to proton NMR data, is applicable to deuterated polybutadiene. This theory, in combination with molecular simulations, gives the shortest Rouse time, τ, as 8.3×10^{-7} s, similar to values found from rheology, and the number of monomers in a Rouse unit, N_a, was found to be 4.4. A new feature has been the deconvolution of the deuterium transverse relaxation into two separate decays from the two different deuterons, a procedure that appears to be justified by the fact that the parameters are independent of the choice of deuteron. Two-dimensional techniques would undoubtedly be a better method of separating the different decays, which is an area we are currently pursuing. The recently derived model[6] for the NMR transverse relaxation based on the reptation spectrum has been used to study a series of high-molecular-weight deuterated polybutadienes, where the end sections have been rendered invisible by protonation. The molecular weight between entanglements, as perceived by NMR, was found to be 5380. The theory based upon reptation, which uses the second-moments approximation, was found to be valid only below a molecular weight of about 27000, in reasonable accord with the experimental results, and suggesting that, above this molecular weight, at least the slowest reptation mode is slow with respect to the NMR experimental time.

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