89-4; *cis*-1-nonyl-2-hexylcyclobutanol, 102396-77-0; octyl bromide, 111-83-1; 9-octylnonadecan-10-one, 112421-75-7; 9,11-dioctylnonadecan-10-one, 112421-76-8.

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Local Dynamics of Poly(*cis*-1,4-butadiene) Studied by Coupled Spin Relaxation

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ABSTRACT: The dynamics of an entangled linear polymer, poly(*cis*-1,4-butadiene), are studied by the coupled spin relaxation of a methylene group ($^{13}CH_2$). Relaxation experiments are performed on the solid, using magic-angle spinning, and in solution with CD_2Cl_2 at concentrations of 10–80 mol % monomer. By extrapolating the data taken between 10 and 40 mol % monomer to infinite dilution, four unique spectral densities are measured for the methylene. These can be expressed in terms of correlation times describing the reorientation of d-orbital-like functions oriented along a Cartesian axis system. The ratio of τ_{zz} to τ_{yy} to τ_{xy} is 2.4:1.0:0.48. These anisotropies of motion are very similar to those recently found for nonane and heneicosane. The anisotropy also agrees well with that calculated for a "crank-like" motion of polyethylene in a recent simulation.

I. Introduction

Understanding chain dynamics is important in a wide variety of problems, ranging from an understanding of the microscopic basis of the macroscopic properties of polymers to an understanding of transport of small molecules through biological membranes. Recent advances in computational methods have made theoretical modeling of such processes possible.[1-4] Experimental verification of

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such models is difficult, however. Techniques such as dielectric relaxation, dynamic light scattering, and infrared or Raman bandshapes are probes of orientational motion. All share some common disadvantages when studying chain molecules in that they probe overall motions of the molecules and/or depend on vibrational modes that are not always easy to resolve or localize. Dipolar spin relaxation and fluorescence anisotropy decay are well-localized in the molecule, but the latter technique usually requires insertion of a foreign probe into the polymer. This paper presents a study of the dynamics of poly(*cis*-1,4-butadiene) (CBD) in the solid and as a function of concentration in solution utilizing the dipolar relaxation of a coupled spin system, $^{13}CH_2$. As noted above, dipolar spin relaxation is well-localized in the molecule and does not require structure perturbing labels. Furthermore, the multiplet relaxation of scalar coupled spins provides a richness of information not available in more conventional studies.

Spin relaxation is well-known as a powerful tool for studying dynamic processes in condensed phases. Generally, relaxation experiments measure spin–lattice (T_1) or spin–spin (T_2) relaxation times for the dipolar interaction of a pair of spins in a molecule. These experimental parameters are related to differing combinations of autocorrelation spectral densities (J_{ijij}, where ij specifies a pair of spins) which are in turn the Fourier transforms of the time autocorrelation functions which describe the orientation of an internuclear dipolar vector at a given time relative to its position at some earlier time.[5] As such these parameters provide information into the dynamic behavior of the relevant vector.

Rigid molecules for which a small step diffusion model is appropriate can have their diffusion tensor completely characterized by observing the relaxation behavior of several pairs of dipolar coupled spins whose orientations in the molecule are linearly independent.[6] The orientational dynamics of a chain molecule are much more complex to describe than those of a rigid molecule represented by a diagonalized diffusion tensor. Even if the chain motion is diffusional, it is likely to require more than three constants to characterize the motion of a given segment.[7] Also, the flexibility of the chain means that separate dipolar interactions are not rigidly oriented relative to each other. Thus the amount of information about the dynamical behavior of any given chain segment available from spin relaxation experiments would appear to be limited. In studies using this methodology subsequent interpretation proves to be highly model dependent.

Fortunately, the dipolar relaxation of several scalar coupled spins provides information which improves this situation. The fundamental theory of spin relaxation for coupled spins has been available in terms of density matrix treatments and Redfield–Bloch theory for many years.[5,8] Relating the formalism to experimental observables is not trivial but has been done for a number of spin systems, primarily by Werbelow and Grant[9] and Vold and Vold.[10] The main feature of this description of coupled spin relaxation is a description of the time evolution of individual transition intensities (lines in the NMR spectrum) by a set of coupled differential equations. The transitions are coupled to each other and to the lattice by coefficients expressed in terms of both autocorrelation and cross-correlation spectral densities. By monitoring the relaxation behavior of a set of transitions, the various spectral densities may be extracted.

As noted above, the autocorrelation spectral densities and conventional relaxation times are closely related. The unique feature of a complete analysis of coupled spin relaxation, then, is the ability to extract cross-correlation spectral densities. These techniques have been used to study several small molecules[11–14] and chain molecules in lipid bilayers.[15,16] Application of these techniques to a chain molecule (n-nonane) in solution has also now been completed.[17,18]

CBD was chosen as the subject of study for several reasons. It is structurally a relatively simple molecule, consisting of only two kinds of main-chain carbons and no side chains, and this level of complexity is susceptible to simulation by theorists. It is also a simple spin system (two kinds of carbon and of hydrogen). To be able to compare dynamics in the solid state to those in solution requires a molecule where high-resolution ^{13}C spectra may be obtained in the solid without decoupling (a requirement of the coupled spin relaxation experiment). High-resolution ^{13}C spectra of solid CBD may be obtained with magic angle spinning (MAS) alone.

II. Experimental Section

The CBD was provided by the Firestone Tire and Rubber Co., Akron, OH. Deuteriated methylene chloride was purchased from MSD Isotopes, Rahway, NJ.

Samples of CBD in CD_2Cl_2 solution were made consisting of 10, 20, 40, 60, and 80 mol % monomer. To speed achievement of homogeneity the samples were warmed at 308 K for several days. Each sample was subjected to three freeze–pump–thaw cycles and sealed in a 10-mm NMR tube under vacuum. The solid sample was cut into small pieces and packed into an Andrews type MAS rotor. On spinning the sample redistributed in the rotor to become a cylinder coating the inside of the rotor body.

Both standard solution and MAS ^{13}C spectra were obtained at 50.3 MHz on a Bruker CXP-200 spectrometer. MAS spectra were obtained by using an Andrews type spinner in a single double-tuned coil; the spinning rate was 2500 Hz. For all spectral data, tables of 1K were acquired over a sweep width of 3000 Hz. The data were later zero filled to 8K. Recycle delays were adjusted to be at least 10 times the nominal T_1 of the sample. All ^{13}C and ^1H pulses were applied on resonance. Typically 16 different delay times were used for each experiment. These were ordered randomly to reduce systematic errors. The number of scans per delay time varied depending on the sample but was typically 300–600. All experiments were performed at 293 ± 1 K.

Line intensities were obtained from manual reading of peak amplitudes. This method proved superior to either software integration or cut-and-weigh methods. Multi-parameter curve fitting was performed as reported previously,[13] except that instead of a direct search algorithm a steepest descent routine (Stepit, copyright 1965 J. P. Chandler, available from Quantum Chemistry Program Exchange) was used. Fitting parameters included pulse efficiencies, initial intensities, a line-width scaling factor, and dipolar and random field spectral densities.

III. Results

The relaxation of the methylene spin system may conveniently be expressed in terms of a number of magnetization modes: (1) $^a\nu_1$, the total ^{13}C magnetization; (2) $^a\nu_2$, the total ^1H magnetization; (3) $^a\nu_3$, the difference between the inner and outer line intensities of the ^{13}C multiplet; and (4) $^a\nu_4$, the difference between the singlet and triplet transitions contributing to the center line of the ^{13}C triplet.[9] These four modes couple together and are perturbed by any rf pulse affecting either ^{13}C or ^1H.

Three different initial perturbations of the $^{13}CH_2$ spin system were used. (1) a ^{13}C 180° pulse inverting the entire methylene triplet; (2) a ^1H 180° pulse inverting the proton doublet (both as described previously[11]); and (3) a low power ^{13}C pulse inverting only the central line of the ^{13}C triplet. For this perturbation the so-called intermediate soft pulse was used as described by Bovee.[19]

The initial perturbation of the spin system was followed

Table I
Methylene Spectral Densities from the Relaxation of Poly(*cis*-1,4-butadiene)

	mol % monomer					
	10	20	40	60	80	100
J_{CHCH}	0.093 ± 0.006	0.100 ± 0.004	0.105 ± 0.003	0.136 ± 0.012	0.218 ± 0.019	0.294 ± 0.004
J_{CHCH}	0.010 ± 0.003	0.004 ± 0.002	0.005 ± 0.004	0.015 ± 0.002	0.019 ± 0.003	0.026 ± 0.006
$J_{\mathrm{HH'HH'}}$	0.088 ± 0.013	−0.017 ± 0.014	−0.35 ± 0.08	−1.7 ± 0.3	−4.7 ± 1.2	−2.0 ± 0.2
$J_{\mathrm{CHHH'}}$	0.045 ± 0.004	0.053 ± 0.003	0.063 ± 0.004	0.084 ± 0.010	0.13 ± 0.03	0.210 ± 0.014
j_{C}	−0.01 ± 0.02	−0.006 ± 0.014	0.044 ± 0.012	0.06 ± 0.04	0.08 ± 0.06	0.508 ± 0.019
j_{H}	0.146 ± 0.018	0.34 ± 0.02	1.20 ± 0.11	4.6 ± 0.7	12 ± 3	5.8 ± 0.6

by a variable delay period and a ^{13}C sampling pulse as in a normal inversion recovery experiment. As only the ^{13}C magnetization was monitored, $^{a}\nu_2$ was not directly observed. $^{a}\nu_4$ was resolved by using an intensity exchange pulse on the ^{1}H magnetization coincident with the sampling pulse as described by Fuson and Prestegard.[20]

In the limit of extreme narrowing, the dipolar relaxation of a methylene group (^{13}CH$_2$) is completely described by four frequency independent spectral densities (J_{CHCH}, $J_{\mathrm{CHCH'}}$, $J_{\mathrm{HH'HH'}}$, and $J_{\mathrm{CHHH'}}$). These can be obtained from fitting the experimental data to the theoretical expressions for the relaxation as described previously.[11] The relaxation expressions for the solid sample spun at the magic angle are exactly the same as that for the solution samples except that contributions at zero frequency are replaced by contributions at the spinning frequency and twice the spinning frequency.[21]

In addition to the dipolar spectral densities and experimental parameters, we include random field spectral densities in the fit to account for any other relaxation mechanisms operating in the sample. For the methylene spin system a complete set of random field spectral densities would include an autocorrelation term at the carbon (j_{C}), an autocorrelation term at each hydrogen (j_{H}), and a cross-correlation term between the two hydrogens ($k_{\mathrm{HH'}}$). Previous work[11,15] has always found that j_{H} and $k_{\mathrm{HH'}}$ are statistically indistinguishable and they have been locked to each other in the fit. This result has been confirmed, and the same practice is followed herein.

The spectral densities obtained from fitting the relaxation data are listed in Table I (also see Figure 1). The dominant trends in the results are straightforward. J_{CHCH}, $J_{\mathrm{CHCH'}}$, and $J_{\mathrm{CHHH'}}$ all increase with increasing monomer concentration. There is some fluctuation in $J_{\mathrm{CHCH'}}$, probably due to the extremely small magnitude of this spectral density relative to experimental precision.

A significant difficulty in the data analysis is revealed upon examining the values of $J_{\mathrm{HH'HH'}}$ for the methylene group. Fitted values for the more concentrated samples are negative, which is contrary to theory for an autocorrelation spectral density of a motion described by small step motion. The source of the difficulty is revealed by noting the very large magnitudes of the proton random field terms (j_{H}) for the same samples. These terms characterize relaxation mechanisms other than the dipolar relaxation of the coupled spin system, including intermolecular dipolar interactions (which are assumed to be responsible for the large magnitudes in the concentrated solutions). The values of $J_{\mathrm{HH'HH'}}$ and j_{H} generated by the fitting routine are correlated (correlation coefficients on the order of 0.4), and when one has a large value, it can have the effect of dominating the value of the other. Thus values of $J_{\mathrm{HH'HH'}}$ cannot be regarded as reliable even though their nominal standard deviations are not extremely large. The effects of correlation between $J_{\mathrm{HH'HH'}}$ and j_{H} in this kind of experiment have been commented upon previously.[13] (The negative value of j_{C} is within one standard deviation of zero and thus does not cause similar difficulty in interpretation.)

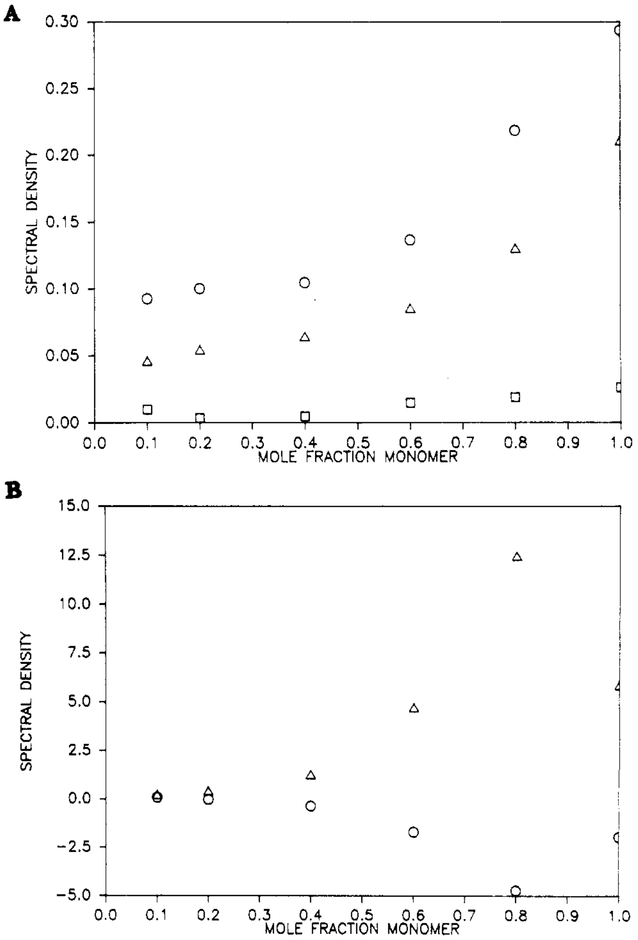

Figure 1. Dipolar and random field methylene spectral densities plotted versus mole fraction monomer: (A) ○, J_{CHCH}; △, $J_{\mathrm{CHHH'}}$; □, $J_{\mathrm{CHCH'}}$; (B) ○, $J_{\mathrm{HH'HH'}}$; △, j_{H}.

The relaxation of the spins in the methine region of the CBD chain was also characterized. It was assumed that the methine ^{13}CH could be described as an isolated AX spin system and that the relaxation of the two methine protons could be described as an A$_2$ spin system. Using methods described previously[9] and analogous to those already described for the methylene relaxation, it was possible to characterize two dipolar spectral densities, J_{CHCH} and $J_{\mathrm{HH'HH'}}$, and two random field terms, j_{C} and j_{H}, for the alkene portion of the molecule. These results are given in Table II (and Figure 2).

The four dipolar spectral densities which describe the relaxation of a methylene group are directly related to corresponding time correlation functions, but these (especially the cross-correlation functions) are not easily interpretable. It has recently been shown that the observed spectral densities can be reexpressed in terms of four autocorrelated Cartesian spectral densities, which are in turn simply related to four correlation times.[22] These model independent transformations are extremely useful in that

Table II
Methine Spectral Densities from the Relaxation of Poly(*cis*-1,4-butadiene)

	mol % monomer					
	10	20	40	60	80	100
J_{CHCH}	0.056 ± 0.001	0.064 ± 0.002	0.089 ± 0.004	0.099 ± 0.003	0.151 ± 0.006	0.211 ± 0.004
$J_{\mathrm{HH'HH'}}$	0.006 ± 0.003	0.022 ± 0.005	0.06 ± 0.04	0.094 ± 0.007	0.154 ± 0.014	
j_{C}	0.103 ± 0.004	0.107 ± 0.008	0.15 ± 0.05	0.203 ± 0.010	0.32 ± 0.02	0.657 ± 0.012
j_{H}	0.138 ± 0.007	0.139 ± 0.013	0.12 ± 0.11	0.214 ± 0.018	0.33 ± 0.04	0.47 ± 0.02

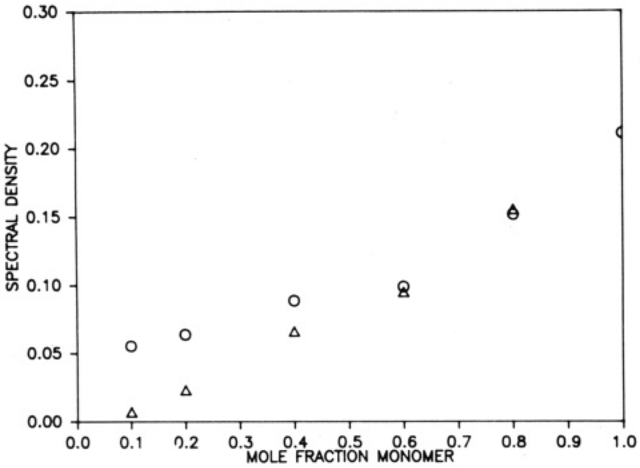

Figure 2. Dipolar methine spectral densities plotted versus mole fraction monomer: ○, J_{CHCH}; △, $J_{\mathrm{HH'HH'}}$.

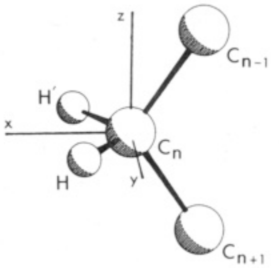

Figure 3. Orientation of the Cartesian axis system in the molecular frame.

the difficulty of interpreting cross-correlation functions is removed and the results are presented in the Cartesian axis system common to most statistical mechanical treatments of chain dynamics. In the transformation to this basis no biases or assumptions are introduced about the dynamic behavior of the molecule as encountered in using diffusional dynamical models.

If we define the methylene group to lie in the xy plane with the x axis bisecting the HCH angle (see Figure 3), we find for the zero frequency or extreme narrowing spectral densities:

$$J_{yy} = K_{\mathrm{HH'HH'}}J_{\mathrm{HH'HH'}}$$

$$J_{zz} = \{0.5K_{\mathrm{CHCH}}(J_{\mathrm{CHCH}} + J_{\mathrm{CHCH'}}) + (\alpha^2 - \beta^2)K_{\mathrm{HH'HH'}}J_{\mathrm{HH'HH'}} + 2(\alpha^2 - \beta^2)K_{\mathrm{CHHH'}}J_{\mathrm{CHHH'}}\}/\alpha^4$$

$$J_{xx} = \{0.5K_{\mathrm{CHCH}}(J_{\mathrm{CHCH}} + J_{\mathrm{CHCH'}}) + \beta^4K_{\mathrm{HH'HH'}}J_{\mathrm{HH'HH'}} - 2\beta^2K_{\mathrm{CHHH'}}J_{\mathrm{CHHH'}}\}/\alpha^4$$

$$J_{xy} = K_{\mathrm{CHCH}}(J_{\mathrm{CHCH}} - J_{\mathrm{CHCH'}})/8\alpha^2\beta^2$$

where $\alpha = \cos(\theta/2)$, $\beta = \sin(\theta/2)$, θ is the HCH angle, and $K_{ijkl} = r_{ij}{}^3r_{kl}{}^3/\gamma_i\gamma_j\gamma_k\gamma_l h^2$. r_{ij} is the internuclear distance between i and j and γ_i is the magnetogyric ratio of nuclei i.

The correlation times associated with reorientational motion are the zero frequency parts of the normalized correlation functions associated with a particular vector or tensor in the molecule. Given the Cartesian spectral densities, the correlation times are

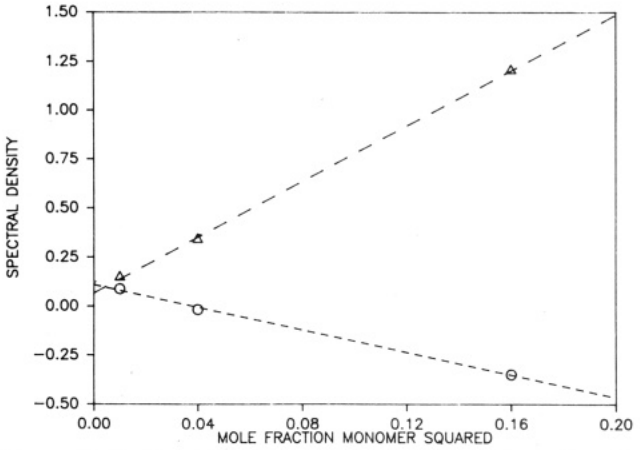

Figure 4. Scaling of HH′ dependent spectral densities with mole fraction of monomer squared: ○, $J_{\mathrm{HH'HH'}}$; △, j_{H}.

$$\tau_q = J_q/T_q$$

with the normalization constants T_q being

$$T_q = \begin{cases} 2/3 & q = xx,\ yy,\ zz \\ 1/2 & q = xy,\ xz,\ yz \\ 2 & q = xx\text{–}yy,\ xx\text{–}zz,\ yy\text{–}zz \end{cases}$$

The Cartesian correlation functions describe the reorientation of geometrical constructs having the shape of d orbitals. Thus τ_{xx}, τ_{yy}, and τ_{zz} are the correlation times for the motion of a d_0 construct fixed along the x, y, and z axes, respectively, while τ_{xy} is the correlation time of a clover leaf basis of the d_{xy} or $\mathrm{d}_{x^2-y^2}$ form. As with d orbitals, τ_{xx-yy} is linearly dependent upon τ_{xx}, τ_{yy}, and τ_{zz} and so a degree of arbitrariness exists in our choice of basis. Rotational correlation functions exist for xz and yz constructs, but for a methylene group whose geometry is defined as above it is not possible to determine these specific power densities experimentally from the spin relaxation data because of the effective symmetry and orientation of the spin system.

In the present instance, however, there is no reliable estimate of one of the dipolar spectral densities. This prevents the use of the transformation to four Cartesian spectral densities as described above. Furthermore, the three remaining dipolar spectral densities can be converted to the Cartesian form only through use of a simplifying assumption about the nature of the dynamics.

It is possible to obtain reasonable estimates of all four spectral densities by extrapolating the data to infinite dilution. This is done by assuming that the random field spectral densities are due to pairwise intermolecular interactions and therefore should scale with the square of the concentration of monomer. The magnitude of $J_{\mathrm{HH'HH'}}$ given by the fit is assumed to be correlated with j_{H} and is therefore expected to scale similarly. The other dipolar spectral densities are assumed to scale linearly with con-

Table III
Spectral Densities Extrapolated to Infinite Dilution

	methylene	methine
J_{CHCH}	0.090 ± 0.006	0.043 ± 0.003
$J_{CHCH'}$	0.010 ± 0.003	
$J_{HH'HH'}$	0.108 ± 0.015	0.004 ± 0.003
$J_{CHHH'}$	0.040 ± 0.004	
j_C	−0.017 ± 0.020	0.097 ± 0.004
j_H	0.067 ± 0.009	0.133 ± 0.007

Table IV
Cartesian Correlation Times[a] Calculated from Methylene Dipolar Spectral Densities Extrapolated to Infinite Dilution

τ_{xx}	75 ± 19	τ_{zz}	55 ± 6
τ_{yy}	23 ± 2	τ_{xy}	11 ± 1

[a] In picoseconds.

centration. At concentrations less than 50 mol % monomer these assumptions seem to hold very well, as shown in Figure 4. The extrapolated values of the spectral densities are given in Table III. Also given in Table III are values for the methine spectral densities similarly extrapolated to infinite dilution.

The transformation to Cartesian correlation times requires that the geometry of the spin system be well known. The existing X-ray diffraction studies of CBD are inadequate for our purposes.[23] There are few structural studies of analogues of CBD which do define the geometry of the methylene group adequately. Those that give some information suggest that the structure is unperturbed from that of the methylene in small alkanes.[24,25] We shall adopt values from electron diffraction studies of propane through heptane: HCH angle = 108.5°, r_{CH} = 1.12 Å.[26] The results of the transformation of the dipolar spectral densities extrapolated to infinite dilution into Cartesian correlation times given this geometry are listed in Table IV.

IV. Discussion

Over the past 10 years poly(*cis*-1,4-butadiene) has been a frequent subject of investigations with the purpose of understanding the dynamics of entangled polymer chains.[27-34] Many of these studies have focused on transverse spin relaxation processes in an effort to look at slow motions of the polymer. Others have included longitudinal spin relaxation studies and attempted to enhance understanding of fast local motions in the chain. The general picture emerging from all of these studies is one where the motions of the CBD chain are divided into two different regimes: (1) motions on a time scale slower than 10^{-3} s, corresponding to slow movement of large portions of the chain; and (2) motions on a time scale of 10^{-9} s or shorter which correspond to local motions of the chain between entanglement points. This general picture agrees with that arising from viscoelastic studies. Both approaches characterize the length between entanglements as about 200 monomer units.[30,35] Because local motions depend largely on the size of this "submolecule", overall molecular weight dependence of the local motions is not expected for chains long enough to be highly entangled.

Previous efforts to distinguish the details of the rapid motions have been limited. It was recognized at an early stage that the relaxation processes were nonexponential and required a distribution of correlation times or anisotropic motion to explain them.[27] A recent solid-state NMR study by English[33] considers these models and others and concludes that the observed behavior is due to anisotropic motion. One study[29] has shown that trends in ^{13}C T_1's with temperature can be more easily explained by models invoking local conformational transitions than by librational motions. Time scales of the local motions were shown to be on the order of 10 ps.

Table V
Motional Anisotropies

	τ_{zz}	τ_{yy}	τ_{xy}
5-nonane (exptl, 313 K)	2.2	1	0.38
11-heneicosane (exptl, 313 K)	2.3	1	0.45
CBD (exptl, 293 K)	2.4	1	0.48
polyethylene κ_0^{-1}	4.6	1	
κ_1^{-1} (calcd, 330 K)	2.2	1	

In this study multiplet relaxation of a scalar coupled spin system, $^{13}CH_2$, has been used to approach the same questions. Estimates of four dipolar spectral densities characterizing this one spin system have been obtained by extrapolating our data to infinite dilution. These can then be converted to Cartesian correlation times which are relatively simple to interpret and to compare to other results and calculations.

The rationale behind our extrapolation procedure should be noted. At high CBD concentrations the high-spin densities make resolution of the directly bonded dipolar contributions difficult. Interactions with protons on either neighboring methylenes and methines (intramolecular) or neighboring chains (intermolecular) can effect the behavior of the $^{13}CH_2$ spin system. These interactions are expressed in the magnitude of the random field spectral densities. As noted above, extraction of the dipolar and random field terms is correlated, and when either is very large, it can distort the magnitude of the other. If the relevant interactions are intermolecular, it is expected that the random field spectral densities will scale with the square of the monomer concentration. The dipolar spectral densities, because of their correlation with the random field terms, will scale similarly. Intramolecular interactions should cause less dramatic changes with concentration, as the changes would be due to alterations in rotational time scales and chain packing rather than directly to concentration. It has been shown that the data obtained at less than 50 mol % monomer extrapolates linearly to infinite dilution versus the square of the monomer concentration. This is strong support for the interpretation that the large random field terms are due to intermolecular effects, and this study has been completed under that assumption.

The results thus obtained are in good agreement with the previous studies outlined above. Correlation times range from 11 to 75 ps. Those correlation times which directly reflect reorientation about a single axis (τ_{xx}, τ_{yy}, and τ_{zz}) show an anisotropy of a factor of 3 or 4.

It is now possible to compare the dynamics of the CBD chain to the dynamics of other chain molecules in some detail. In Table V the measured anisotropies of motion of CBD are listed. Also listed are the anisotropies, measured or calculated from simulations, available for other chain molecules. The anisotropies for nonane and heneicosane were measured by using techniques similar to those described in this paper.[18] Motional anisotropies for polyethylene are calculated from a simulation of the dynamics by Weber and Helfand.[36] As τ_{xx} is not well-determined by the approach described here, it is not included in this comparison.

The similarities in the anisotropies of the smaller alkanes and CBD are striking. It should be emphasized that this is a result which is not forced by the experimental methodology. Other systems studied by these methods have exhibited a wide range of distinctive dynamical behavior. Nonetheless, it is not at all clear whether the similarities in the anisotropies reflect fundamental similarities in the

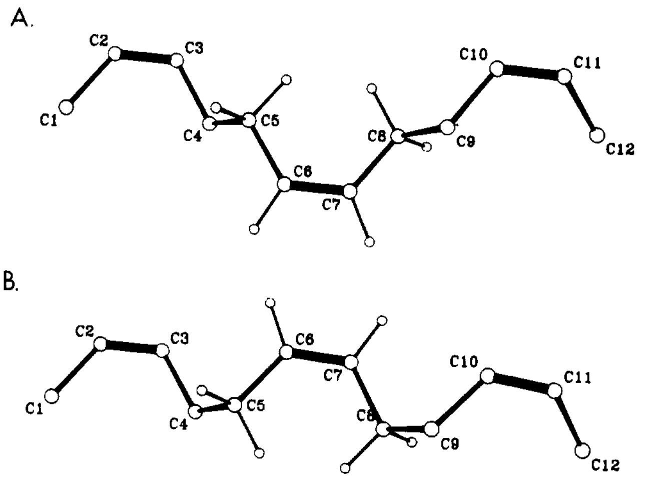

Figure 5. Conformations of CBD. Hydrogens are indicated only on the middle of the three monomers portrayed: (A) CBD with trans methylene–methylene bonds; (B) CBD with gauche methylene–methylene bonds.

dynamics of these chains because of the dissimilar chain length and structure. More interesting is the comparison of the CBD data with the polyethylene calculation. Weber and Helfand identify κ_0 with conformational transitions about a single bond, while κ_1 is a faster rate associated with cranklike correlated pair transitions. The experimental ratio of τ_{zz} to τ_{yy} for CBD is similar to that they calculate for κ_1. This would suggest that in CBD, despite the dissimilar chain structure, the spin relaxation is dominated by cranklike pair transitions of the polymer chain.

It is straightforward to propose a mechanism for such a motion in CBD. Theoretical studies of the energy of the CBD chain as a function of bond torsional angles show that there is a series of similar energy minima for the chain with the methylene–methylene torsional angle (C4–C5 or C8–C9, see Figure 5) either trans (180°) or gauche (±60°) and the neighboring methylene–methine torsional angles either ±120°.[37,38] If one examines a three-monomer segment, it can be seen that a transition from a 120°, 180°, −120°, 0°, −120°, 180°, 120° conformation (for bonds C3–C4 through C9–C10 as shown in Figure 5) to a 120°, 180°, −120°, 0°, −120°, 180°, 120° conformation describes a cranklike rotation where the outer double bonds (C2–C3 and C10–C11) are essentially unmoved. The first conformation described is that which is crystallographically observed.[23]

The objection to such a model for the motion is obvious, in that it requires a four-bond transition. This may not be such a difficulty as it first may appear, given that the rotational barriers around the methylene–methine bonds are calculated to be quite low, about 1 kcal/mol. It has also been suggested that the apparent activation energies for multiple-bond motions in polymers are more comparable to the activation energy for rotation about one bond rather than the sum of all the bonds involved.[39] Finally, such a motion does not reorient the ethylinic H–H vector. Thus one would expect the methine $J_{\mathrm{HH'HH'}}$ to be very small. This is indeed what is observed ($J_{\mathrm{HH'HH'}} = 0.004$). Further condiseration of analytical models of such a process will be considered in a separate paper.

This study has shown that it is possible by extrapolating to infinite dilution to obtain four dipolar spectral densities and thus four Cartesian correlation times describing the reorientation of a methylene group in CBD. The results, especially when considered in light of the methine proton relaxation, suggest that the dominant motion in the spin relaxation process is a cranklike rotation. A similar suggestion has recently been made for polybutadiene melts studied by fluorescence anisotropy decay.[32] The similarity of this motion to that seen in simulations of polymethylene chains is striking and suggests that it may be characteristic of freely jointed linear polymer chains.

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