Anisotropy of Local Dynamics of Polyethylene

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ABSTRACT: The anisotropy of the local dynamics of polyethylene in dilute biphenyl solution at 401 K has been studied by coupled spin relaxation methods. Three second-rank correlation times, including those for vectors parallel (τ_{zz}) and perpendicular ($\tau_{\perp}$) to the local chord axis, are determined. τ_{zz} is proportionately larger than those measured in previous studies of polymers in solution, and ratios of correlation times involving τ_{zz} are larger as well. Since only polyethylene of the polymers studied by this method prefers *trans* conformers at every torsion, it is suggested that the large anisotropy observed in the dynamics is associated with this conformational preference. The ratio of τ_{zz} to $\tau_{\perp}$ is 7.5, which is within the range of values calculated in recent simulations of polyethylene melts.

Introduction

In this paper we report the anisotropy of the local dynamics of polyethylene (PE) in dilute solution as measured by NMR coupled spin relaxation methods. The local dynamics of polymer chains are thought to have an important influence on the macroscopic properties of polymer systems, including such technologically important properties as elasticity, phase transition temperatures, and solution and melt viscosities.[1,2] In recent years polymer local dynamics have been studied largely by computer simulation, with polyethylene receiving special attention.[3−7] While many of the results of these simulations have agreed qualitatively, others do not, including the anisotropy of the local dynamics. The results reported here are the first experimental measurements of the anisotropy of the local dynamics of polyethylene.

Orientational relaxation in polymers is commonly conceptualized as occurring on three time scales: a very rapid relaxation due to librational motion about the current conformation (rotational isomeric state), a somewhat slower relaxation due to transitions between conformations, and finally slower relaxations associated with loss of orientational memory of larger portions of the polymer chain. The time scales of the latter processes clearly change dramatically as the environment of a polymer changes from dissolved in solution, to a melt, and to a glass. The two faster processes are commonly characterized as "local dynamics." A topic of current research and debate is the relative importance and amount of change in these processes as a function of the polymer environment.

Computer simulations of the polymer dynamics generate a trajectory of the atomic coordinates over some hundreds of picoseconds. Analysis of the local dynamics is commonly accomplished, on the one hand, by identifying discrete events like torsional transitions or the degree of torsional "spreading" between transitions and alternatively by calculating P_1 or P_2 autocorrelation functions associated with various orientational or conformational properties. These might include the torsion angle itself, the rotational isomeric state, or unit vectors attached to a local frame of reference. A frequently encountered example is the CH bond vector P_2 autocorrelation function,

$$\mathrm{ACF}(t) = \langle P_2(\hat{u}(0)\hat{u}(t))\rangle = \frac{\langle 3\cos^2\theta(t) - 1\rangle}{2} \quad (1)$$

where P_2 is the second Legendre polynomial, $u(t)$ is a unit vector pointing in the direction of the CH bond at time t, and $\theta(t)$ is the angle between the vector orientations at times 0 and t. The time integral of this autocorrelation function is commonly referred to as a correlation time, τ_c, and is related to the ^{13}C T_1 spin relaxation time. Thus, unlike many quantities calculated from simulated trajectories, this characteristic of the local dynamics is directly related to an experimental observable.

Less commonly examined, but more informative about the nature of the local dynamics, are correlation times associated with unit vectors related to the local symmetry of the polymer chain. These are illustrated in Figure 1. The z axis is parallel to the local chain axis and is often called the chord vector (from the chord between C_{n-1} and C_{n+1}). The x axis, or bisector, bisects the CCC angle, or equivalently the HCH angle. The y axis, or out-of-plane vector, is perpendicular to x and z and is parallel to the HH vector. Recent computer simulations of polyethylene dynamics show that the correlation time for z-axis reorientation is significantly longer than the other two; that is, the local dynamics are anisotropic.[3−7]

Spin relaxation studies, which take advantage of the multiple interactions among several scalar coupled spins, for example $^{13}CH_2$, can measure all three of these correlation times.[8,9] In isotropic solutions the ^{13}C spin−lattice relaxation time of a pair of dipolar coupled spins, ^{13}CH, is given by

$$\frac{1}{T_1} = \frac{1}{3}J_{\mathrm{CHCH}}(\omega_H - \omega_C) + J_{\mathrm{CHCH}}(\omega_C) + 2J_{\mathrm{CHCH}}(\omega_H + \omega_C) \quad (2)$$

where the spectral densities, $J_{\mathrm{CHCH}}(\omega)$, are proportional to the Fourier transform of the CH autocorrelation function given in eq 1:

$$J_{\mathrm{CHCH}}(\omega) = \frac{3}{10}\frac{\gamma_C^2\gamma_H^2\hbar^2}{r_{\mathrm{CH}}^6}\int_0^\infty \mathrm{ACF}(t)e^{i\omega t}\,dt \quad (3)$$

where γ is the gyromagnetic ratio of the appropriate

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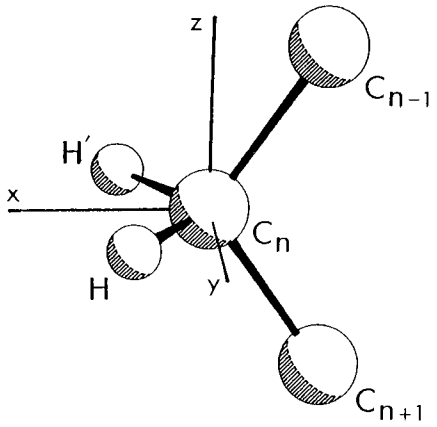

Figure 1. Orientation of the Cartesian axis system in the molecular frame.

nucleus and r_{CH} is the internuclear distance.[9] In the limit of extreme narrowing, $\omega\tau_c \ll 1$, the spectral densities become frequency independent and $1/T_1$ is directly proportional to τ_c. For a methylene or methyl group with two or three identical CH interactions, the common practice has been to regard them as independent and the resulting ^{13}C relaxation rate, $1/T_1$, then scales with the number of attached hydrogens. However, for three or more spins a complete description of the relaxation also includes cross-correlation terms between pairs of dipolar vectors, such as the two different CH vectors in a methylene group.[11−13] The traditional approach has been to regard these as either small or unimportant. Additionally, if the ^1H spins are decoupled to enhance ^{13}C sensitivity, the ^{13}C spin will almost always relax with an "effective" single-exponential recovery law as the multiple-exponential relaxation behavior of the coupled spins is obscured with the collapse of the proton-induced multiplet under decoupling.[10] Study of the fully coupled multiplets provides significant additional information. For a methylene group, four independent spectral densities are required to describe the relaxation even in the extreme narrowing limit. These can be used to calculate the three correlation times described above, plus a fourth one describing the reorientation of something looking like a d_{xy} orbital.[8]

Coupled spin relaxation methods have been used to study local dynamics in small-chain molecules,[14,15] in biomolecules,[16−20] and in polymers in solution.[21−23] Careful application of these methods requires a completely isolated spin system. In polymers this is often not convenient, due to hydrogens on adjacent carbons. A study of the isotopomers of [5-^{13}C]nonane has shown that under these conditions three correlation times can be reliably extracted if the assumption is made that the correlation times for reorientation of *x* and *y* axes are the same.[24] Both coupled spin relaxation results and computer simulations suggest that this is a reasonable assumption.[3,4,14,15]

This paper reports the results of coupled spin relaxation experiments on polyethylene in dilute biphenyl solution at 401 K, which are Θ conditions.[25] The results can be compared directly to earlier Brownian dynamics simulations of polyethylene[3,5] and are interesting in relation to recent molecular dynamics simulations of polyethylene melts.[4,7] While there is considerable evidence that polymer chain conformations under Θ conditions are the same as in the melt,[26] it would be desirable to study polyethylene melts directly both because of their technological importance and for comparison to the most recent simulations. This is difficult, however, because the "extreme narrowing" condition is not met in melts and interchain spin interactions may introduce further difficulties.

Experimental Section

Linear polyethylene (MW = 52 000; M_w/M_n = 2.9) was obtained from Polysciences (Warrington, PA). Deuterated biphenyl (99% D) was obtained from Cambridge Isotope Laboratories (Woburn, MA). Both materials were used without further purification. The sample was made by dissolving 0.0305 g of PE in 3.0956 g of biphenyl at 401 K. The sample was subjected to five freeze−pump−thaw cycles and sealed under vacuum in a 10 mm NMR tube.

Spectra were acquired on a Bruker AC300 NMR spectrometer operating at a ^{13}C frequency of 75.5 MHz. The temperature for all runs was 401 ± 1 K. Spectral widths were set to 2000 Hz for ^1H soft-pulse experiments and 1000 Hz for all hard-pulse experiments. For each spectrum, 548 scans of 8192 data points were acquired. FIDs were baseline corrected and then zero filled to 16 384 data points. A total of 8 Hz of line broadening was applied before Fourier transformation.

A single ^{13}C multiplet is observed at 34.6 ppm. The carbon−hydrogen coupling constant, J_{CH}, is 126 Hz. The root mean square signal-to-noise ratio for the central line of the fully relaxed multiplet is approximately 120:1.

Spin relaxation measurements were made after four different perturbations of the coupled $^{13}CH_2$ spin system. These were as follows: (1) a ^{13}C 180° pulse inverting the ^{13}C triplet; (2) a ^1H 180° pulse inverting the ^1H doublet; (3) a low-power ^1H pulse inverting only the upfield line of the ^1H doublet;[27] (4) a *J* pulse preparation on the ^1H magnetization which inverts the outer lines of the ^{13}C triplet.[28] In each experiment the initial perturbation was followed by a variable delay and a 90° ^{13}C sampling pulse. Twenty delay times were used for each experiment, ranging from 0.008 to 18 s. Delays were randomly ordered to reduce systematic errors. The longest delay was at least 10 times the nominal T_1 of the sample.

Peak amplitudes of the ^{13}C triplet were obtained after application of a linear baseline correction over a 500 Hz region centered on the ^{13}C multiplet. Data were analyzed using a multiparameter fitting routine as described previously.[24] In addition to spectral densities, variables included pulse efficiencies, equilibrium intensities, and scaling factors compensating for line width differences and instrumental artifacts.

Results

Instead of characterizing the behavior of individual resonance lines, it is convenient to analyze the data in terms of "magnetization modes", which are linear combinations of line intensities.[9,11,13] Three magnetization modes of the $^{13}CH_2$ spin system can be obtained from observation of the ^{13}C multiplet: (1) $^a\nu_C$, the total ^{13}C magnetization; (2) $^a\nu_{+-+}$, the difference between the inner and outer line intensities of the ^{13}C triplet; (3) $^s\nu_{+0-}$, the difference between the intensities of the two outer lines of the ^{13}C triplet. Figures 2−5 show the relaxation curves obtained. The equilibrium NOE was also measured and a value of 2.9 ± 0.2 obtained. This indicates that within experimental error the extreme narrowing condition is met in this study.

The time evolution of the magnetization modes is governed by a Redfield-type relaxation matrix whose elements are combinations of spectral densities arising from all relaxation mechanisms active in the sample.[9,11,13] For this study, spectral densities included in the fit include four frequency-independent spectral densities describing the dipolar relaxation of a methylene group ($^{13}CH_2$) in the limit of extreme narrowing (J_{CHCH},

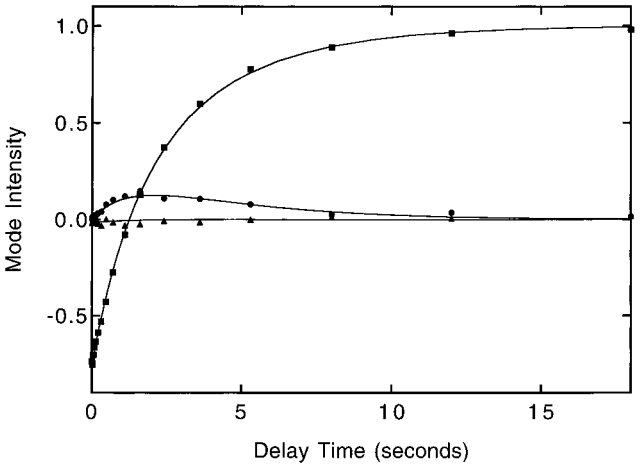

Figure 2. Magnetization mode intensities for PE after ^{13}C inversion. Intensity units are defined by setting ${}^{a}\nu_C(\infty)$ to unity. Experimental values for ${}^{a}\nu_C$ (■); experimental values for ${}^{a}\nu_{+-+}$ (●); experimental values for ${}^{s}\nu_{+0-}$ (▲). Solid lines are calculated from fitted parameters.

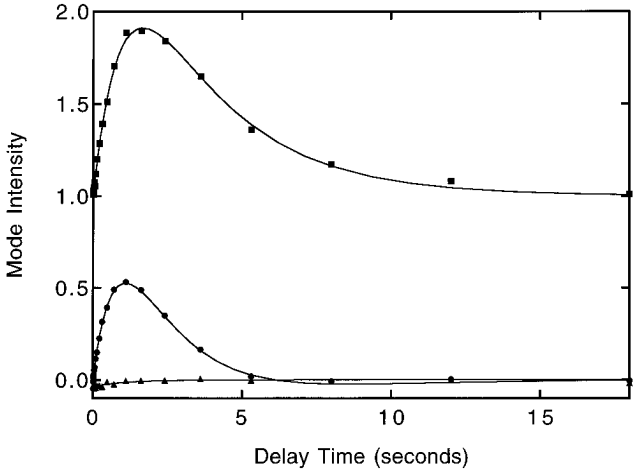

Figure 3. Magnetization mode intensities for PE after ^{1}H inversion. Intensity units and symbols are as defined in Figure 2.

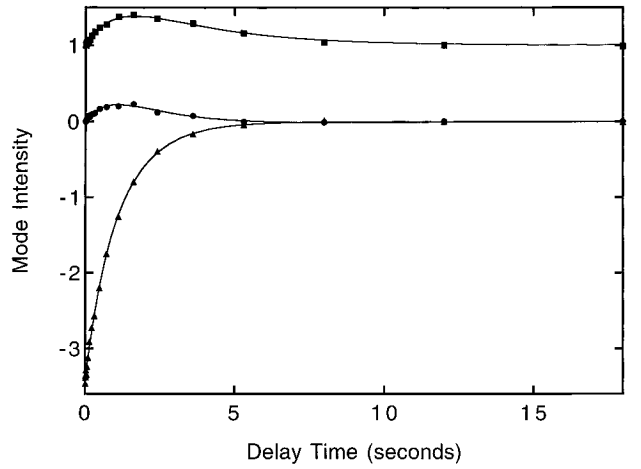

Figure 4. Magnetization mode intensities for PE after selective inversion of one line of the ^{1}H doublet. Intensity units and symbols are as defined in Figure 2.

$J_{HH'HH'}$, $J_{CHCH'}$, and $J_{CHHH'}$ where pairs of subscripts specify a dipolar interaction). Random field spectral densities are also included to account for other relaxation mechanisms operating in the sample, primarily remote dipolar interactions. For the methylene spin system, a complete set of random field spectral densities

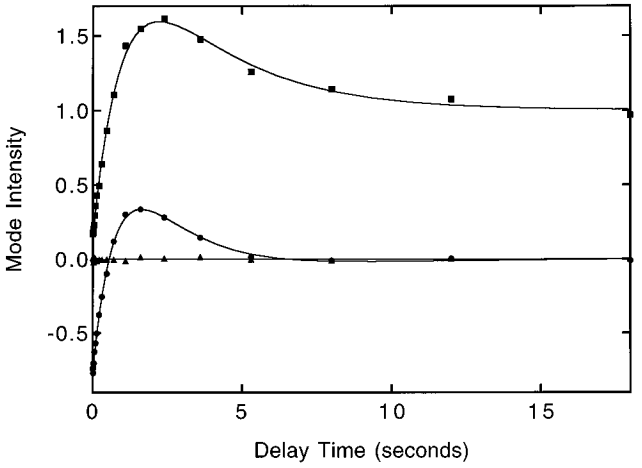

Figure 5. Magnetization mode intensities for PE after *J* pulse preparation of the ^{1}H spins, resulting in ^{1}H inversion and inversion of the outer lines of the ^{13}C multiplet. Intensity units and symbols are as defined in Figure 2.

Table 1. Polyethylene Spectral Densities (s^{-1})

J_{CHCH}	0.0741 ± 0.0019	j_C	[0][a]
$J_{HH'HH'}$	0.044 ± 0.007	j_H	0.140 ± 0.013
$J_{CHCH'}$	0.051 ± 0.006	$j_{HH'}$	0.07 ± 0.03
$J_{CHHH'}$	0.0520 ± 0.0018		

[a] Brackets indicate value that was fixed during the fit.

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 ($j_{HH'}$). At high fields or in a more anisotropic electronic environment caused by insertion of a heteroatom into the polymer chain, cross-correlation between chemical shift anisotropy (CSA) and dipolar relaxation mechanisms can be significant.[19,30] Where appropriate, this requires inclusion of four more spectral densities in the fit. These terms are negligible in this study and not reported.

Rigorous characterization of longer range dipolar interactions as random fields requires that both the rotational and translational motions of the interacting spins be independent.[31,32] This independence of motion is not satisfied for protons bonded to carbons adjacent to the methylene group of interest. A study of isotopomers of [5-^{13}C]nonane has shown that inclusion of random field terms in the relaxation matrix is not enough to allow accurate measurement of all four dipolar spectral densities in the presence of protons on neighboring carbons. However, that study showed that as long as the random field term j_C is held equal to zero in the fitting procedure, then J_{CHCH}, $J_{CHCH'}$, and $J_{CHHH'}$ may be reliably evaluated. $J_{HH'HH'}$ remains strongly correlated to j_H.[24] In the current study j_C is not distinguishable from zero even if fit freely. Even so, the results reported conform to this practice. Final fitted values of the spectral densities are reported in Table 1. Uncertainties reported are standard errors.

The three dipolar spectral densities that have been reliably evaluated can be reexpressed in terms of three second-rank autocorrelation times ($\tau_\perp = \tau_{xx} = \tau_{yy}$, τ_{zz}, and τ_{xy}). The transformation to Cartesian correlation times requires that the geometry of the spin system be known.[8] We shall adopt values from electron diffraction studies of small alkanes: 108.5° for the HCH angle and 1.12 Å for the CH bond length.[33] The Cartesian correlation times calculated using these parameters are given in Table 2.

Table 2. Cartesian Correlation Times (ps)

$\tau_\perp = 6.4 \pm 2.2$
$\tau_{zz} = 48 \pm 3$
$\tau_{xy} = 3.1 \pm 0.8$

Table 3. Motional Anisotropies from NMR Experiments

	$\tau_{zz}/\tau_\perp$	τ_{zz}/τ_{xy}	$\tau_\perp/\tau_{xy}$
PE	7.5	16	2.1
C11-heneicosane[a]	2.1	4.8	2.3
poly(*cis*-1,4-butadiene)[b]	2.4	5.0	2.1
poly(oxymethylene)[c]	1.6	2.6	1.6
poly(ethylene oxide)[d]	2.7	2.6	1.0
C_α-poly(tetramethylene oxide)[d]	3.0	6.2	2.0
C_β-poly(tetramethylene oxide)[d]	3.0	3.0	1.0

[a] From ref 14. [b] From ref 21. [c] From ref 22. [d] From ref 23.

Discussion

As described in the Introduction, one approach to characterizing the local dynamics of a polymer chain is to evaluate the correlation times associated with different axes fixed to a local frame of reference, for instance, a given methylene group in polyethylene. Using the coupled spin relaxation of the $^{13}CH_2$ group, we have evaluated the P_2 autocorrelation times for the *z* axis or chord vector (τ_{zz}), for a vector perpendicular to the *z* axis ($\tau_\perp$), and for something resembling a d_{xy} orbital (τ_{xy}). These times, as given in Table 2, are consistent with the time scales of tens of picoseconds usually observed for polymers in solution.

Of more interest for purposes of comparison to other polymers are the ratios of these correlation times, which give the anisotropy of the local motion. These are given in Table 3, along with the ratios previously found for other polymers in solution[21−23] and also for a smaller hydrocarbon.[14] The anisotropies for polyethylene that involve τ_{zz} are strikingly larger than any measured previously.

The reasons for the large anisotropies observed for polyethylene in dilute biphenyl solution as compared to other polymers in solution are not immediately apparent. When comparisons are made to the other studies of polymer solutions, the following differences may be significant: (1) The temperature used in the present study, 401 K, is significantly higher. (2) The solvent in the present study, biphenyl, is much larger and more viscous (even at the elevated temperature). (3) Polyethylene is the only polymer among those studied whose equilibrium chain configuration is dominated at every torsion by *trans* conformers. An exception to the first two points is the study of poly(oxymethylene) in phenol which was done at temperatures as high as 387 K, at which point the viscosity of phenol still exceeds the viscosity of biphenyl at 401 K by a factor of 1.5.[34]

Large anisotropies could occur either because of relatively slow *z* axis reorientation or relatively rapid reorientation perpendicular to that axis. Comparison of the correlation times measured here to those measured for poly(oxymethylene) at a slightly lower temperature and more viscous solvent shows that $\tau_\perp$ and τ_{xy} are shorter by a factor of 2, while τ_{zz} is longer by factor of 3. If barriers to conformational transitions were identical in these two systems, a decrease of a factor of 2 in the correlation times seems consistent with the differences in conditions. In fact, recent estimates of the barriers to torsional motions in poly(oxymethylene)[35] and polyethylene[7] indicate that poly(oxymethylene) has the higher barriers, which would lead one to expect even slower correlation times relative to polyethylene. This suggests that the large anisotropies occur because of a longer τ_{zz} than expected. Furthermore, this is true even after considering differences in temperature, viscosity, and rotational barriers, leading to the conclusion that the large motional anisotropies observed may be linked to polyethylene's unique (among this group of polymers) equilibrium chain configuration.

Table 4. Characteristic Times and Anisotropies from Simulations

	$\tau_\perp$(ps)	τ_{zz}(ps)	$\tau_{zz}/\tau_\perp$
Correlation Times			
C5-nonane, 353 K[a] (united atom BD)	4.1	11	2.7
infinite phantom chain, 425 K[b] (united atom BD)	32	112	3.5
C_{44}, 400 K[c] (explicit atom MD)	19	76	4.0
1/*e* Relaxation Times			
infinite phantom chain, 425 K[b] (united atom BD)	12	35	3.0
C_{44}, 400 K[c] (explicit atom MD)	3.0	17	5.7
infinite chain, 443 K[d] (united atom MD)	0.94	8.7	9.3

[a] Reference 14. [b] Estimated from parameters reported in ref 3. [c] Estimated from parameters reported in ref 7. [d] Reference 4.

Some support for this suggestion comes from analysis of computer simulations of polymer dynamics. Several simulations have reported results that make possible estimation of the anisotropy of the local dynamics for polyethylene or shorter hydrocarbons. These include united atom Brownian dynamics (BD) studies of the central carbon in nonane[14] and of an infinite polymethylene phantom chain,[3,5] a united atom molecular dynamics (MD) study of an infinite polymethylene chain in a melt,[4] and an explicit atom molecular dynamics study of a C_{44} melt.[7] Since it is not possible to estimate correlation times from all of these studies, both correlation times and 1/*e* relaxation times estimated from these simulations are summarized in Table 4. While correlation times are the quantities measured by NMR experiments, it may be useful when comparing melt simulations to solution experiments to examine 1/*e* relaxation times since these do not depend as strongly on the long time tails of the correlation functions, which are presumably absent in solution. This presumption is supported by the observation here of a full NOE, which implies that the spectral densities are frequency independent. This could not be true if the correlation function has a long time tail.

All of the simulations show some anisotropy in the local dynamics. The results of the nonane simulations are consistent with directly comparable NMR measurements.[14] For studies of polyethylene, like systems from which the correlation times can be estimated, the anisotropy or ratio of correlation times falls in the range 2.7−4.0, values that are smaller than the value of 7.5 reported here. With the exception of the Brownian dynamics study of the infinite phantom chain, the ratios of 1/*e* relaxation times are larger and bracket the value measured here. Normally, it would be expected that the results of a Brownian dynamics simulation would show better agreement with observed solution dynamics than a melt simulation. This is not the case here. A possible reason is that removing intrachain van der Waals interactions, which allows the chain to overlap itself (the "phantom chain"), has a larger effect on the simulation of local dynamics than previously anticipated. As well as the molecular dynamics simulation of a polyethylene melt using a full set of potentials, Takeuchi and Roe reported the results of a simulation with the van der

Waals terms set to zero.[4] The ratio of the P_2 1/*e* relaxation times τ_{zz} to $\tau_\perp$ decreases to 1.6, much lower than observed, or than calculated for the melt using a full potential, or even than calculated from the Brownian dynamics simulations. Some of the differences in the calculated anisotropy with and without the van der Waals potentials must be due to the differences in interchain interactions, as Takeuchi and Roe suggested. However, the results reported here when examined in the context of all of these simulations suggest that longer range intrachain interactions may impose as large a constraint on local dynamics as chain connectivity, even in solution.

The similarity of the ratio of 1/*e* relaxation times in the melt simulations and the ratio of correlation times measured here suggests that the short time local dynamics of the melt and of the solution may be sufficiently similar that closer analysis of the melt simulations can be helpful in understanding the origin of this substantial anisotropy. Previous analysis of these simulations has led to suggestions that reorientation in the plane perpendicular to the *z* axis is characteristic of the strictly local motions, while *z* axis or chord vector reorientation is associated with larger scale reorientation of the polymer chain.[4] This would be uniquely true of polyethylene among the polymers mentioned here because only polyethylene has a predominantly *trans* chain configuration, which places the chord vector parallel to the local chain axis. Polymers with torsions whose populations are predominantly *gauche* or *anticlinal* tend to adopt configurations in which the chord axis is not aligned with the chain axis and might not be expected to be dynamically unique. This conclusion is reinforced not only by the lower anisotropy observed for other polymer solutions but also by the fact that a simulation of polyisoprene melts also show smaller ratios of P_2 1/*e* relaxation times,[36] indicating that even in the constrained environment of a melt large anisotropies like that seen here may be particularly associated with the polyethylene system.

In this paper we have reported the results of coupled spin relaxation experiments on polyethylene in dilute biphenyl solution at 401 K. Second-rank correlation times of vectors fixed to a local frame of reference are obtained from these measurements. The anisotropy of the local dynamics thus expressed is larger than any observed before for polymers in solution. Comparison of this result to those previously obtained for other polymers in solution and to simulations of polyethylene dynamics suggests that the origin of the large anisotropy is slow reorientation of the *z* (chord) axis and that this may be characteristic of polyethylene dynamics in particular.

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