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Chain Dynamics of Extended Polymers: Poly(hexyl isocyanate) and Poly(benzyl glutamate)

Donald B. DuPré* and Honghui Wang

Department of Chemistry, University of Louisville, Louisville, Kentucky 40292

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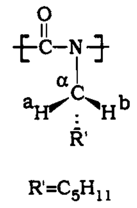
ABSTRACT: New data on the spin–lattice and spin–spin relaxation times and nuclear Overhauser enhancements of carbon atoms in or near the backbone of the extended-chain polymer poly(hexyl isocyanate) (PHIC) and similar literature data on the more rigid poly(benzyl L-glutamate) (PBLG) are analyzed in terms of the elastic filament model of Barkley and Zimm (*J. Chem. Phys.* **1979**, *70*, 2992) and Schurr et al. (*Chem. Phys.* **1984**, *84*, 71). Known values or estimates of the persistence length, the friction factor for azimuthal rotation of monomeric level segments, and the transverse rotational diffusion constant of the chain enter into the model as fixed molecular parameters, whereas the torsional elastic constant per segment is treated as adjustable for data-fitting purposes. ^{13}C NMR data for PHIC were taken on 300- and 500-MHz instruments, whereas those of PBLG were obtained on 100- and 300-MHz instruments.

Introduction

The dynamics of segmental motion in macromolecular chains may be monitored on the nanosecond time scale by the relaxation of ^{13}C nuclei located on or near the polymer backbone. Spin–lattice and spin–spin relaxation times, T_1 and T_2, respectively, and nuclear Overhauser enhancements, NOE, are experimentally accessible quantities sensitive to such motion, which are now available at high NMR frequencies (proton frequencies 300, 500, and 600 MHz). These parameters are directly related to the spectral density, $J(\omega)$, of the modes of fluctuation of the polymer chain. $J(\omega)$ in turn can be related through a Fourier transform to the time correlation function of relaxing bond vectors containing the magnetic dipoles.

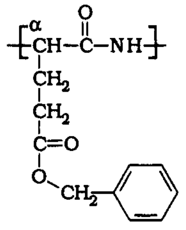
We present here new data on T_1, T_2, and NOE obtained at 300 and 500 MHz for the extended-chain polymer poly(hexyl isocyanate) (PHIC). Solutions of the polymer were studied in two solvents, $CDCl_3$ and toluene, at concentrations well below the onset of liquid crystal formation. PHIC is a helical polymer, held into place by steric interactions of the side chains with backbone carbonyl groups.[1–4] The twisting and bending motions of such a flexible, though elongated, chain have been treated theoretically by the elastic filament model of Barkley and Zimm,[5] improved more recently by Schurr et al.[6–9] Our data will be interpreted in terms of these models with known values of the persistence length of PHIC and estimates of the friction factor for azimuthal rotation of segments (perhaps several monomers in a helical turn) of the polymer about the long axis of the chain and the transverse rotational diffusion constant. The torsional elastic constant per segment remains as a data-fitting parameter, in line with other uses of the theory to account for fluorescence polarization anisotropy (FPA) of other polymers (e.g., DNA fragments[9]).

The theory will also be used to discuss data of Budd et al.[10] on ^{13}C NMR relaxation spectrometry of the more rigid polymer, poly(benzyl L-glutamate) (PBLG). The structures of the repeating unit of both polymers of this study are shown below:



R'=C_5H_{11}

PHIC



PBLG

Materials

Poly(hexyl isocyanate) (PHIC) was synthesized from hexyl isocyanate by polymerization in anhydrous dimethylformamide (DMF) at −58 °C with NaCN as the initiator.[11] The reaction was terminated by addition of methanol. By controlling the concentration of initiator, we were able to make PHIC with different molecular weights. The polymer was filtered, washed with methanol, and vacuum dried. Fractionation was accomplished by precipitation in CCl_4 with methanol as the nonsolvent. Nine fractions were thus obtained. In this work, we utilized one of the lower molecular weight samples which offered the best NMR resolution. This sample had a $\bar{M}_w$ = 33 900 and polydispersity $\bar{M}_w/\bar{M}_n \leq 1.10$ as determined by dielectric dispersion methods.[12,13]

^{13}C T_1, T_2, and NOE Measurements

^{13}C NMR spectra were obtained for 6% (w/v) PHIC solutions in $CDCl_3$ and toluene on Varian XL-300 and Bruker AMX-500 spectrometers operating at 300 and 500 MHz, respectively. A total sample of 180 mg was used in a 10-mm tube in the 300-MHz spectrometer, whereas only 60 mg could be accommodated in 5-mm tubes in the 500-MHz instrument. A standard saturation-recovery pulse sequence was used to determine spin–lattice relaxation times, with the delay time set to at least 5–6 times the measured T_1. The temperature was maintained at 30 °C during all measurements. A typical spectrum of PHIC in $CDCl_3$ is shown in Figure 1, along with peak assignments.[14,15] A complete listing of relaxation parameters for PHIC in both solvents is found in Table I. Spin–spin relaxation times were estimated from spectral line widths $\Delta\upsilon_{1/2}$ using $T_2 = 1/\pi\Delta\upsilon_{1/2}$, with an error of as much as 50%. NOE was determined from resonance intensities (peak heights) with and without proton decoupling. The estimated error for NOE is about ±0.1–0.2. Carbon atoms are labeled C0 for the carbonyl carbon in the backbone of PHIC and C1 through C6 outward along the hexyl side chain. C1 is thus the α-carbon.

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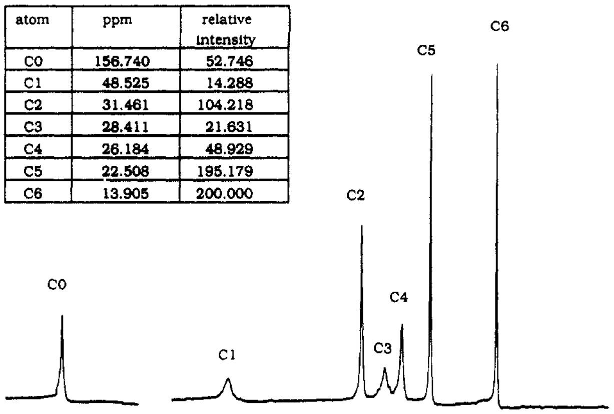

atom	ppm	relative intensity
C0	156.740	52.746
C1	48.525	14.288
C2	31.461	104.218
C3	28.411	21.631
C4	26.184	48.929
C5	22.508	195.179
C6	13.905	200.000

Figure 1. A typical 300-MHz ^{13}C NMR spectrum of PHIC with a table of peak assignments.

Table I
Experimental Values of T_1, T_2, and NOE for PHIC ($\bar{M}_w = 3.39 \times 10^4$, $\bar{M}_w/\bar{M}_n \leq 1.10$)[a]

	300 MHz			500 MHz		
atom	T_1 (s)	NOE	T_2 (ms)	T_1 (s)	NOE	T_2 (ms)
			CDCl$_3$ as Solvent			
C0	2.52 (0.13)	1.23	20	1.91 (0.13)	1.02	13
C1	0.145 (0.017)	1.59	5	0.290 (0.034)	1.13	5
C2	0.887 (0.049)	2.47	30	1.05 (0.03)	2.49	57
C3	0.191 (0.019)	1.77	7	0.586 (0.070)	1.57	7
C4	0.388 (0.012)	2.16	14	0.570 (0.018)	2.12	21
C5	1.57 (0.03)	2.68	60	1.77 (0.08)	2.71	130
C6	2.16 (0.09)	2.67	76	2.59 (0.07)	2.64	220
			Toluene as Solvent			
C0	2.36 (0.11)	1.23	18	1.89 (0.20)	1.06	11
C1	0.100 (0.031)	1.63	5	0.342 (0.13)		3
C2	0.908 (0.047)	2.63	26	1.01 (0.01)	2.71	32
C3	0.178 (0.026)	1.94	9	0.35 (0.14)	1.80	4
C4	0.410 (0.044)	2.46	13	0.637 (0.023)	2.68	20
C5	1.20 (0.08)	2.84	48	1.61 (0.04)	2.80	76
C6	2.32 (0.10)	2.76	86	2.61 (0.15)	2.79	110

[a] Error estimates for T_1 are in parenthesis. Errors for NOE range from ±0.1 to ±0.2. Errors for T_2 can be as high as 50%.

Theoretical Interpretation and Discussion of Results

The dynamic and equilibrium properties of extended-chain polymers have been discussed in terms of a wormlike chain model with contour length L and a characteristic persistence length P. Under low resolution, the twisting, tumbling, and bending motion of such a chain may be modeled in terms of an elastic filament, segmented into a series of connected disks of the size of a helical turn in molecules such as DNA, PBLG, and PHIC. If a ^{13}C–^{1}H internuclear bond makes a fixed angle ϵ with respect to the helical axis, the time correlation function for the fluctuations of this bond may be written[6–8] as

$$C(t) = [P_2(\cos\epsilon)]^2 B_0(t) + 3(\sin^2\epsilon)(\cos^2\epsilon) B_1(t)\, T_1(t) + (3/4)(\sin^4\epsilon) B_2(t)\, T_2(t) \quad (1)$$

where P_2 is the second Legendre polynomial and $B_n(t)$ and $T_n(t)$ are the (assumed separable) bending and twisting correlation functions, respectively, of the segmented filament. $T_n(t)$ is related to $\langle \Delta_\parallel(t)^2 \rangle$, the mean-square angular displacement of the subunit disk about the helical symmetry axis at time t, through[7,8]

$$T_n(t) = \langle \exp[-(n^2/2)\langle \Delta_\parallel(t)^2 \rangle] \rangle_R \quad (2)$$

where the outer angular brackets with a subscript R indicate the average over all disks in a representative chain. Similarly, for bending/tumbling[6–8]

$$B_n(t) = \left\langle \exp\left[-\frac{6-n^2}{2}\langle \Delta_\perp(t)^2 \rangle\right] \right\rangle_R \quad (3)$$

where $\langle \Delta_\perp(t)^2 \rangle$ is the time dependence of the mean-square displacement of the central axis of the disk transverse to the helix.

A general formula for $T_n(t)$ has been derived by Allison and Schurr.[6] The filament that represents the polymer chain is set up to contain an odd number, $N + 1$, of subunit disks each of height h and radius b, connected to one another by Hookean torsional springs with force constant α and azimuthal friction factor $\gamma = 4\pi\eta b^2 h$. η is the viscosity of the solvent in which the polymer is embedded. In terms of these parameters the twisting correlation function was found to be[6]

$$T_n(t) = \frac{\exp[-n^2 k_B T t/(N+1)\gamma]}{N+1} \sum_{m=1}^{N+1} \exp\left(-n^2 \sum_{j=2}^{N+1} d_j^{\,2} Q_{mj}^{\,2} (1 - e^{t/\tau_j})\right) \quad (4)$$

where

$$\tau_j = \gamma/4\alpha \sin^2[(j-1)\pi/2(N+1)] \quad (5)$$

and

$$d_j^{\,2} = k_B T/4\alpha \sin^2[(j-1)\pi/2(N+1)] \quad (6)$$

are the relaxation time and mean-squared amplitude of the jth normal mode of the torsion ($j \geq 2$), respectively, and

$$Q_{mj} = \left(\frac{2}{N+1}\right)^{1/2} \cos\left[\left(m - \frac{1}{2}\right)(j-1)\pi/(N+1)\right] \quad (7)$$

is the transformation matrix that diagonalizes the force constant matrix. Note when $t = 0$, $T_n(0) = 1.0$. Equation 4 has also been approximated by a sequence of computationally simpler formulas,[7] where $T_n(t)$ is divided into time zones whose boundaries depend on the exact values of certain of the relaxation times τ_j. In what follows below, however, we calculate the entire sum in several loops on a supercomputer.

A mathematical form for the bending/tumbling correlation function is more problematical. Barkley and Zimm[5] have presented a functional form for $B_n(t)$ for the central segment of a filament, based on the higher normal modes of a long and weakly bending rod. The result in our notation is equivalent to

$$B_n(t) = \exp[-(6-n^2)D_\perp t]\, D_n(\infty) \times \exp\left[(6-n^2)\left(\frac{4}{\pi}\right)^2 \frac{L}{2P} \sum_{m,\mathrm{even}}^{\infty} \frac{\exp(-t/\tau_m^{\,\mathrm{b}})}{(2m+1)^2}\right] \quad (8)$$

where the relaxation times are given by

$$1/\tau_m^{\,\mathrm{b}} = \frac{P k_B T}{4\pi\eta} \kappa_m^{\,4} \left[K_0(\kappa_m b) + \frac{\kappa_m b}{2} K_1(\kappa_m b)\right] \quad (9)$$

with $\kappa_m = (2m+1)\pi/2L$, and K_0 and K_1 as modified Bessel functions. For long times, $B_n(t)$ decays exponentially and is controlled by the rotational diffusion $D_\perp$ perpendicular to the helical axis. $D_\perp$ is related to L and b and may be calculated through an equation such as[16]

$$D_\perp = \frac{3k_B T}{\pi\eta L^3}\left[\ln\left(\frac{L}{b}\right) - 0.5\right] \quad (10)$$

In the Barkley–Zimm[5] (BZ) development, the amplitude

Table II
T_1, T_2, and NOE Data for PBLG in DMF at 60 °C[a]

	ω_H = 100 MHz				ω_H = 300 MHz		
	α ((kg m^2)/s^2)	T_1 (ms)	T_2 (ms)	NOE	T_1 (ms)	T_2 (ms)	NOE
Sample 1: $\bar{M}_w$ = 35 000, L = 240 Å, $D_\perp = 1.42 \times 10^6$ s^{-1}, $\tau_2 = 9.6 \times 10^{-9}$ s, $\tau_2^b = 1.8 \times 10^{-9}$ s							
exptl results		75 ± 8	20.7		320 ± 16	19.0	1.2 ± 0.1
WS model	1.0×10^{-19}	58.3	4.27	1.48	252	4.95	1.45
	2.6×10^{-19}	70.7	3.20	1.42	340	3.72	1.42
	5.0×10^{-19}	82.0	2.73	1.39	420	3.19	1.40
	1.0×10^{-18}	96.2	2.41	1.37	523	2.81	1.39
BZ model	3.0×10^{-19}	66.5	2.70	1.41	326	3.16	1.41
Sample 2: $\bar{M}_w$ = 81 000, L = 560 Å, $D_\perp = 1.50 \times 10^5$ s^{-1}, $\tau_2 = 2.2 \times 10^{-8}$ s, $\tau_2^b = 5.3 \times 10^{-8}$ s							
exptl results		147 × 10		1.1 ± 0.1	505 ± 25		1.5 ± 0.1
WS model	2.6×10^{-19}	91.2	1.69	1.46	413	2.89	1.44
	6.0×10^{-19}	118	1.30	1.43	562	2.32	1.43
BZ model	1.0×10^{-18}	115	0.86	1.42	561	1.59	1.43

[a] Fixed parameters: b = 9.0 Å, h = 1.5 Å, P = 800 Å, ϵ = 62.5°, M_0 = 218, T = 333 K, η = 0.006 21 P.

of this uniform tumbling mode is given by

$$D_n(\infty) = D_n^{BZ}(\infty) = \exp\left[-(6-n^2)\left(\frac{4}{\pi}\right)^2 \frac{L}{2P} \sum_{m,\text{even}}^{\infty} \frac{1}{(2m+1)^2}\right] = \exp\left[-(6-n^2)\left(\frac{4}{\pi}\right)^2 \frac{L}{2P}(0.07483)\right] \quad (11)$$

a result that has been criticized by Wu et al.[9] (WS) as an overestimate, as well as applying only to the central disk in the filament. A correction has been offered by these researchers,[9] which also includes an averaging over all disks:

$$D_n^{WS}(\infty) = Z_n^{-1/2} \exp(-Z_n/3)(\pi^{1/2}/2) \operatorname{erf}(Z_n^{1/2}) \quad (12)$$

where $Z_n = (6 - n^2)L/4P$. The complete time correlation function for bending is taken as eq 8 with eq 12 substituted for $D_n(\infty)$ even though $B_n(0)$ fails to reach 1.0. These functions have been used successfully in the analysis of FPA data on short DNA restriction fragments.[9] In that work, the torsional constant α and friction factor γ were taken as adjustable parameters.

In application of this theory to NMR relaxation spectrometry, we must also calculate the spectral density $J(\omega)$ through the Fourier transform:[17,18]

$$J(\omega) = 2\int_0^\infty C(t) \cos(\omega t)\, dt \quad (13)$$

For dipolar relaxation[17,18]

$$1/n_b T_1 = c[J(\omega_H - \omega_C) + 3J(\omega_C) + 6J(\omega_H + \omega_C)] \quad (14)$$

$$1/n_b T_2 = (c/2)[4J(0) + J(\omega_H - \omega_C) + 3J(\omega_C) + 6J(\omega_H) + 6J(\omega_H + \omega_C)] \quad (15)$$

$$\text{NOE} = 1 + \frac{\gamma_H[6J(\omega_H + \omega_C) - J(\omega_H - \omega_C)]}{\gamma_C[J(\omega_H - \omega_C) + 3J(\omega_C) + 6J(\omega_H + \omega_C)]} \quad (16)$$

where $c = \hbar^2\gamma_H{}^2\gamma_C{}^2/20r_{CH}{}^6 = 1.78 \times 10^9$ s^{-2}, with γ_H and γ_C the gyromagnetic ratios of the hydrogen and carbon nuclei, respectively, r_{CH} the carbon–hydrogen bond length, and n_b the number of such bonds to the carbon atom.

Complete correlation functions were calculated on an IBM 3090-600 SuperComputer located at the University of Kentucky. The Fourier transform of eq 13 was obtained with the fast Fourier transform subroutine available in *Numerical Recipes, The Art of Scientific Computing.*[19] To perform the discrete transform, a time interval Δt and number of increments (2^n) in the time domain must be selected. Using a simple exponential decay function for $C(t)$, we found that 2^{17} = 131 072 gives satisfactory computational results when $\Delta t = 1/2000(\omega_H + \omega_C)$ and τ is in the range 1.0×10^{-11} to 5.0×10^{-8} s. Δt and 2^n were so fixed in subsequent calculations unless otherwise stated.

Table III
T_1, T_2, and NOE Data for PBLG in DMF at 60 °C[a]

2^n	T_1 (ms)	T_2 (ms)	NOE
exptl	320 ± 16	19.0	1.2 ± 0.1
16 384	348	11.4	1.40
65 536	347	4.82	1.42
131 072	340	3.72	1.42

[a] Fixed parameters: b = 9.0 Å, h = 1.5 Å, P = 800 Å, ϵ = 62.5°, M_0 = 218, T = 333 K, η = 0.006 21 P. Sample 1: $\bar{M}_w$ = 35 000, L = 240 Å, $D_\perp = 1.42 \times 10^6$ s^{-1}. WS model: $\alpha = 2.6 \times 10^{-19}$ (kg m^2)/s^2. ω_H = 300 MHz.

We first applied the model to available literature data on T_1, T_2, and NOE for poly(benzyl L-glutamate) (PBLG). Budd et al.[10] measured these relaxation parameters at 60 °C for the α-carbon located in the backbone of this helical polymer for two different molecular weight samples at two NMR frequencies (100 and 300 MHz). Their data are reproduced in Table II along with the best fits we obtained with the models explored here. The azimuthal friction factor $\gamma = 4\pi\eta b^2 h$ was calculated for this polymer using h = 1.5 Å and b = 9 Å, with η = 0.006 21 P for the solvent (DMF). The contour length of the polymer was determined from $L = (\bar{M}_w/\bar{M}_0)h$, where the monomer residue molecular weight M_0 = 218. $D_\perp$ is calculated from eq 10 to be 1.42×10^6 s^{-1} for the 35 000 molecular weight polymer and 1.50×10^5 s^{-1} for the 81 000 molecular weight sample. (A more recent expression[20] for the transverse diffusional constant results in somewhat smaller values for $D_\perp$. Calculation based on this version of $D_\perp$ would result in somewhat different values of the adjustable parameter α.) Measured values of the persistence length for PBLG range from 700 to 1500 Å.[21-23] For the purposes of these calculations, we take P = 800 Å for PBLG. (The use of a rigid rod expression for $D_\perp$ for the higher molecular weight sample of PBLG may be suspect as the length of the chains of this polymer is 70% of the presumed persistence length.) ϵ was taken to be 62.5° as found from coordinates from X-ray data.[10,24] The remaining parameter, α, was treated as adjustable and was varied to obtain the best fit to available data. The results shown in Table II labeled WS model use eq 12 for $D_n(\infty)$, whereas BZ refers to eq 11. The best value of $\alpha = 2.6 \times 10^{-19}$ (kg m^2)/s^2 was obtained from data on the 35 000 molecular weight polymer at both 100 and 300 MHz using the WS version of the theory. This value of α compares well with that obtained by Wu et al.[9] in their analysis, with the same theory, of FPA data on short DNA fragments. The same value of $\alpha = 2.6 \times 10^{-19}$ (kg m^2)/s^2 was used in the first

Table IV
T_1 and NOE Data for PHIC in $CDCl_3$ at 30 °C[a]

α ((kg m^2)/s^2)	$T_1{}^a$ (ms)	$T_1{}^b$ (ms)	T_1(calcd) (ms)	T_1(exptl) (ms)	NOE^a	NOE^b	NOE(calcd)	NOE(exptl)
				ω_H = 300 MHz				
1.0×10^{-20}	190	228	104		1.76	1.67	1.73	
5.0×10^{-20}	253	323	142	145 ± 17	1.52	1.51	1.52	1.59 ± 0.2
6.0×10^{-20}	265	339	149		1.51	1.50	1.51	
				ω_H = 500 MHz				
1.0×10^{-20}	314	391	174		1.65	1.60	1.63	
5.0×10^{-20}	479	621	270	290 ± 34	1.50	1.49	1.50	1.13 ± 0.1
6.0×10^{-20}	507	658	286		1.48	1.47	1.48	

[a] Fixed parameters: $\bar{M}_w = 33\,900$, $L = 530$ Å, $P = 230$ Å, $T = 30$ °C, $b = 8$ Å, $\eta = 0.005\,14$ P, $h = 1.98$ Å, $D_\perp = 1.386 \times 10^5$ s^{-1}, $M_0 = 127$, $\epsilon^a = 81.3°$, $\epsilon^b = 118.6°$. $\tau_2 = 9.9 \times 10^{-8}$ s. $\tau_2{}^b = 1.4 \times 10^{-7}$ s.

Table V
T_1 and NOE Data for PHIC in Toluene at 30 °C[a]

α ((kg m^2)/s^2)	$T_1{}^a$ (ms)	$T_1{}^b$ (ms)	T_1(calcd) (ms)	T_1(exptl) (ms)	NOE^a	NOE^b	NOE(calcd)	NOE(exptl)
				ω_H = 300 MHz				
1.0×10^{-20}	171	197	91.5		1.75	1.68	1.72	
5.0×10^{-20}	230	287	128	100 ± 30	1.52	1.50	1.51	1.63 ± 0.2
8.0×10^{-20}	261	329	146		1.48	1.48	1.48	
				ω_H = 500 MHz				
1.0×10^{-20}	283	342	155		1.64	1.60	1.62	
5.0×10^{-20}	437	554	244	342 ± 130	1.50	1.49	1.50	
8.0×10^{-20}	510	649	286		1.47	1.46	1.47	

[a] Fixed parameters: $\bar{M}_w = 33\,900$, $L = 530$ Å, $P = 350$ Å, $T = 30$ °C, $b = 8$ Å, $\eta = 0.005\,26$ P, $h = 1.98$ Å, $D_\perp = 1.354 \times 10^5$ s^{-1}, $M_0 = 127$, $\epsilon^a = 81.3°$, $\epsilon^b = 118.6°$. $\tau_2 = 1.2 \times 10^{-7}$ s. $\tau_2{}^b = 9.1 \times 10^{-8}$ s.

entry for the NMR calculations for the 81 000 molecular weight sample of PBLG. Although the torsional friction factor should be independent of molecular weight, at least for these large polymers, we find that α must be adjusted to 6.0×10^{-19} (kg m^2)/s^2 for sample 2 to achieve as good a fit of the data as that obtained for sample 1. Wu et al.[9] also found that a higher value for α was necessary for longer DNA fragments. The BZ version of the elastic filament model was also used to fit the NMR relaxation data for PBLG. Our calculations show that both models can reach the same results with different values of the parameter α: cf. Table II, with the BZ formulas generally requiring higher values of α. This also is similar to comparative results in the work of Wu et al.[9] Table III shows the sensitivity of the calculations for T_1, T_2 and NOE on the number of divisions of the time domain in the fast Fourier transform part of the computation. Little change is found in calculated values of T_1 and NOE as 2^n, and the calculation time increases. Experimental values of T_1 and NOE thus may be accounted for with reasonable parameters in these two models of polymer chain dynamics. The corresponding (and less accurately known) T_2 values, however, are about 5 times too low. The values of the calculated, longest torsional and bending relaxation times, τ_2 and $\tau_2{}^b$, respectively, are also listed in Table II.

In the NMR relaxation study of PHIC, we chose the α-C feature for analysis as this carbon is near the polymer beackbone and relaxes largely by a dipolar process in coupling with the H^a and H^b hydrogens labeled in the numbering scheme shown above. The relaxation of the carbonyl carbon in the backbone is complicated by chemical shift anisotropy for which values of the main chemical shift tensor elements are not now available. A recent NMR relaxation study of poly((*R*,*S*)-3,7-dimethyl-1-octene) and poly((*R*,*S*)-3-methyloctene) shows that the side chain C–H bond nearest the backbone in these polymers is stiffly attached to the main chain with internal order parameters $S^2 > 0.9$.[25] By analogy, we might reasonably assume that the α-C–H^{a,b} bonds of PHIC are rigidly attached to the backbone and follow its bending and twisting motion. From molecular modeling, we have determined that $\epsilon = 81.3°$ for the C–H^a bond and $\epsilon = 118.6°$ for the C–H^b bond when PHIC is in the helical state [eight residues in three turns 2]. In the calculations that follow, the helical cross-section radius of PHIC is taken as $b = 8$ Å and the rise of the helix per monomer unit as $h = 1.98$ Å, according to X-ray data.[26] The persistence length of PHIC has been measured as $P = 230$ Å in $CHCl_3$ and $P = 350$ Å in toluene.[13,27] According to eq 1, the $C(t)$ is a function of the angle ϵ. Therefore, each α-C–H bond will make a different contribution to the relaxation parameters. If the values of $T_1{}^a$ and $T_1{}^b$, etc., are not too different, we may calculate effective values as

$$\frac{1}{T_1} = \frac{1}{T_1{}^a} + \frac{1}{T_1{}^b} \tag{17}$$

$$\frac{1}{T_2} = \frac{1}{T_2{}^a} + \frac{1}{T_2{}^b} \tag{18}$$

$$\text{NOE} \cong (\text{NOE}^a + \text{NOE}^b)/2 \tag{19}$$

which can be compared with experiment. The results of calculations in the WS model are presented in Tables IV and V for PHIC in $CDCl_3$ and toluene at ω_H = 300 and 500 MHz. A value of $\alpha = 6.0 \times 10^{-20}$ (kg m^2)/s^2 ($CDCl_3$) and $\alpha = 5.0 \times 10^{-20}$ (kg m^2)/s^2 (toluene) is seen to account for experimental T_1 and NOE values of this polymer with the above-stated molecular parameters. Calculated values of the longest torsional and bending relaxation time, τ_2 and $\tau_2{}^b$, respectively, are also listed. Experimental values have greater error in toluene due to strong solvent peaks.

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