

Articles

A Study on Local Segmental Motions of Methylene Chain in Poly(Butylene Terephthalate) in Solution Phase

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Temperature dependent data of ^{13}C spin-lattice relaxation times and NOE factors for methylene carbons at 50.3 MHz and 125.5 MHz have been used to probe the local chain dynamics of poly(butylene terephthalate) (PBT) in solution phase. The interpretation of the relaxation data for methylene chain carbons in PBT was attempted on the basis of several proposed motional models, among which the DLM model was found to be superior. Analysis based on the DLM model indicated that the motion of the OCH_2 groups was more restricted compared with the central methylene carbon, which is consistent with conclusions from solid state experiments reported by other investigators. Librational amplitudes of terminal and central carbon of PBT were estimated to be 29.84° and 32.01° , respectively.

Introduction

Nuclear magnetic resonance spectroscopy has been used to gain insight into the details of local segmental motions in many polymers at the molecular level.¹⁻⁵ In particular, ^{13}C relaxation times (T_1 , T_2) and the NOE factor sensitive to the reorientation of a carbon-proton bond in a polymer chain can provide helpful information on local chain dynamics.⁶⁻⁹ However, extracting the relevant information on molecular motions from the NMR data is not an easy matter because it requires detailed knowledge of the relevant local modes of motion related with the intramolecular barrier to transition and energies.¹⁰⁻¹²

Several idealized theoretical models have been proposed to interpret the experimental data for polymers obtained in solution and bulk phase. As pointed out by Helfand and Skolnick,¹³ local polymer dynamics can be described in terms of orientational auto-correlation function, which takes into consideration of the specific character of the polymer backbone. They show that the three or four-bond crankshaft-type transition, *gauche* migration, pair *gauche* production, and internal rotation of the side group of hydrocarbon chain molecules can all contribute to the local dynamics of polymers in solution and bulk phase. However, Monnerie *et al.*⁹ have shown that anomalous deviation of the ratio $T_1(\text{CH})/T_1(\text{CH}_2)$ from the expected value of 2 and an unusually high minimum T_1 value cannot be explained based only on the Helfand's motional framework. They suggested the existence of an additional kind of fast anisotropic motion of small

amplitude corresponding with the so-called libration of internuclear CH vectors which is usually 100 times as fast as segmental motions.

A complete understanding of the local dynamics of polymers is a challenging problem. In this respect, the local motion of poly(butylene terephthalate), hereafter referred to as PBT, has been an interesting subject for many researchers in that the alkyl chain portion of PBT can undergo ideal three-bond-type motion, whereas terephthalate groups behave like anchors. So PBT serves as a good exemplary molecule for which various theoretical models can be tested. Kitamaru analyzed the local motion of the methylene sequence in PBT based on the three-bond motion, concluding that the central methylene carbons are more mobile than the terminal methylene carbons.¹⁴ Deuterium NMR spectroscopy studies in the solid state also reveal different motional patterns of these two different methylene carbon atoms. Jelinski *et al.*^{15,16} observed two different deuterium NMR spectra of PBT, which indicates the predominant mechanism is the three-bond motion like the pair *gauche* production in PBT polymer. Through the reproduction of chemical shift parameters and relaxation data they also confirmed the same motional information on PBT. Monnerie *et al.*¹⁷ studied the dynamics of the aryl-aliphatic polyester in solution *via* proton and carbon-13 relaxation at several fields of different strength. They have described the solution state dynamics of polymers in terms of several independent correlation times. Data on the barriers to rotation about the O-CH_2 and $\text{CH}_2\text{-CH}_2$ bond were also obtained. And they compared their results with Helfand's suggested motional model. Despite the efforts of many investigators the motional mechanism of PBT in dilute solution state is seldom reported because of experimental difficulties. In the present study, we report the carbon-13 relaxation and NOE data for methylene carbon-13's in PBT dissolved in trifluoroacetic acid measured at 50.3 and 125.5

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MHz. We tested several proposed models to understand the motional dynamics of methylene moieties in PBT and found that the Dejean-Laupretre-Monnerie (DLM) model produce the best fit with the experimental relaxation data.

Theory

Dipolar interactions between a carbon-13 and directly-bonded protons are usually the main source to the relaxation process of the former in dilute polymer solution. The spin-lattice relaxation time (T_1) and NOE factor (η) of the ^{13}C nucleus in a CH_2 group are given by^{6,18}

$$\frac{1}{T_1} = \frac{K}{10} [J_0(\omega_H - \omega_C) + 3J_1(\omega_C) + 6J_2(\omega_H + \omega_C)]$$

$$\eta = \frac{\gamma_H}{\gamma_C} \left[\frac{6J_2(\omega_H + \omega_C) - J_0(\omega_H - \omega_C)}{J_0(\omega_H - \omega_C) + 3J_1(\omega_C) + 6J_2(\omega_H + \omega_C)} \right] \quad (1)$$

$$\text{with } K = \left(\frac{\mu_0 \gamma_H \gamma_C \hbar}{4\pi r_{\text{CH}}^3} \right)^2,$$

where γ_H and γ_C are the magnetogyric ratios of the proton and carbon nucleus, respectively, ω_H and ω_C their respective Larmor frequencies, μ_0 the vacuum magnetic permeability ($=4\pi \times 10^{-7} \text{ H m}^{-1}$), and r_{CH} the C-H internuclear distance. $J_m(\omega)$ is the spectral density function related to the time correlation function, $G_m(t)$, as follows:

$$J_m(\omega) = 2\text{Re} \int_0^\infty G_m(t) e^{-i\omega t} dt, \quad (2)$$

where Re indicates the real part of the complex Fourier transform of Eq. (2).

If the molecular rotation could be described on the basis of isotropic rotational diffusion, then the correlation function would be expressed by a single exponential decaying function with a rotational correlation time, τ_c . But in polymer molecules the molecular rotation is not very well described by the isotropic diffusion model.

Hall and Helfand's expression for spectral density based on a conformational jump model for a polymer chain can be written as¹⁹

$$G(t) = \exp(-t/\tau_1) \exp(-t/\tau_2) I_0(t/\tau_1), \quad (3)$$

where I_0 is a modified Bessel function of the zeroth order, τ_1 is the correlation time associated with correlated jumps responsible for orientation diffusion along the chain, and τ_2 corresponds to damping, which consists either of nonpropagative specific motions or of distortions of the chain with respect to its most stable local conformations. The corresponding spectral density is given as follows:

$$J_m(\omega) = \frac{\cos(\rho/2)}{(\alpha^2 + \beta^2)^{1/4}} \quad (4)$$

where

$$\alpha = \tau_2^{-2} + 2\tau_1^{-1}\tau_2^{-1} - \omega^2 \quad \beta = -2\omega(\tau_1^{-1} + \tau_2^{-1}) \quad \text{and} \quad \tan \rho = \frac{\beta}{\alpha}.$$

Recent investigations have revealed the presence of additional mode of motions much faster than the orientational diffusion process along the chain, which is the so-called librational motion.²⁰ This motion occurring within the dihedral potential well can be incorporated into the correlation function if we assume that the two kinds of motions are mutually independent. In this case, the correlation function and spectral density take the following forms:²¹

$$G(t) = (1 - A) \exp(-t/\tau_1) \exp(-t/\tau_2) I_0(t/\tau_1) + A \exp(-t/\tau_0) \exp(-t/\tau_1) \exp(-t/\tau_2) I_0(t/\tau_1), \quad (5)$$

where τ_0 is the correlation time associated with the librational motion, θ is defined as a cone of half-angle, the axis of CH vector is the rest position of the CH bond and

$$1 - A = \left[\frac{(\cos \theta - \cos^3 \theta)}{2(1 - \cos \theta)} \right]^2. \quad (6)$$

Assuming that τ_0 is much shorter than τ_1 and τ_2 , the spectral density can be written as

$$J_m(\omega) = (1 - A) \frac{\cos(\rho/2)}{(\alpha^2 + \beta^2)^{1/4}} + \frac{A}{1 + \omega^2 \tau_0^2} \quad (7)$$

It has been shown by earlier investigators that the depth of the T_1 minimum is highly dependent on the amplitude of the libration mode, which was confirmed in the present study as well.

Experimental Section

PBT [poly(butylene terephthalate)] was purchased from Aldrich Chemical Co., Inc. and used without further purification. A 5% (w/v) solution of PBT in trifluoroacetic acid (TFA, m.p. = -15.4 °C, b.p. = 72.4 °C) was prepared and placed in a 5 mm NMR tube, which was degassed by repeating the standard freeze-pump-thaw cycle five times and then sealed under vacuum ($\leq 10^{-5}$ torr).

All the T_1 measurements were performed on Varian VXR-200S and UNITY500 NMR spectrometers operating, respectively, at 50.3 and 125.5 MHz for ^{13}C under the condition of broadband proton decoupling at several temperatures ranging from 263 to 308 K. The standard inversion recovery pulse sequence was used for these measurements with the delay time set to be longer than five times the longest T_1 values to ensure the full recovery of equilibrium magnetization before the application of the next pulse sequence. The width of the 90° pulse used was found to be 16.5 μsec at 50.3 MHz and 10 μsec at 125.5 MHz, respectively. The NOE factor for C_5 was measured at 50.3 MHz as a function of temperature (263-308 K) by employing a typical gated decoupling pulse sequence.

Results and Discussion

T_1 values for methylene carbons measured at 50.3 MHz and 125.1 MHz as a function of temperature are listed in Table 1 along with the NOE data obtained at 50.3 MHz. The

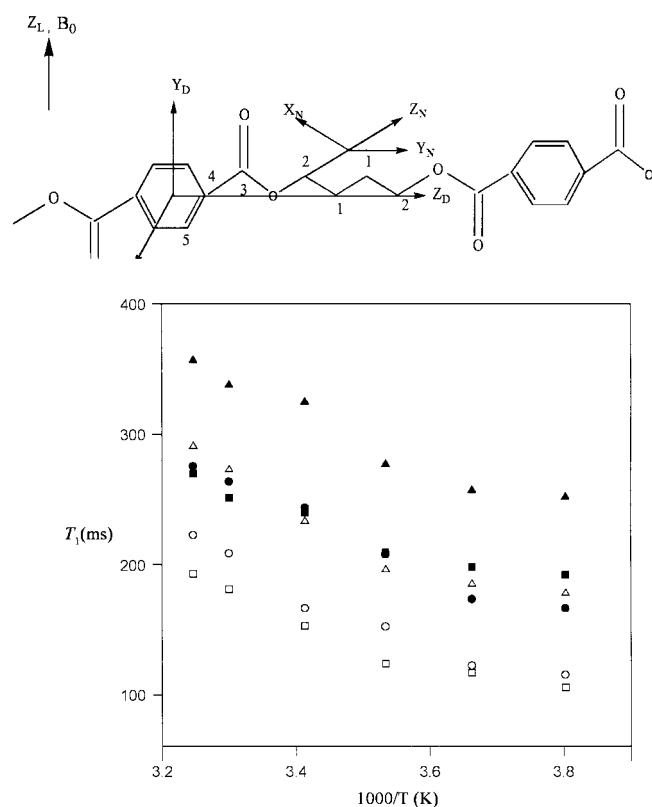


Figure 1. Coordinate System Used for Calculation of Dynamic Parameters (upper) and Experimental T_1 values at 50.3 MHz (open symbol) and 125.5 MHz (filled symbol): (○ : C-1), (□ : C-2), and (△ : C-5) (lower)

observed T_1 data are also graphically presented in Figure 1. From Figure 1 we can see that T_1 is longer at higher magnetic field, which indicates that the extreme narrowing condition is not valid for our system. However, T_1 increases as temperature rises, which means that $\omega_0\tau_c$ is still smaller than unity over the observed temperature range.

It is evident that different T_1 values for the two carbon-13's indicate different motional behaviors of the two methylene moieties. Earlier studies have shown that segmental motions of a polymer chain in dilute solution are too complicated to be described by the single correlation time model. But we have investigated how well it reproduces the experimental data, because this model can give a crude but useful picture of molecular motions. A significant discrepancy between the experimental and theoretical data is observed over the entire temperature range. The calculated T_1 values at ^{13}C 50.3 MHz are longer than the experimental ones, but the trend reverses at 125.5 MHz, indicating that the motion of PBT cannot be described by this simple model.

With this in mind the Helfand-Hall (HH) model, which was adequate for explaining the local dynamics in time resolved optical experiments, was examined to check its validity for the motion of PBT. To obtain the best fit, we adjusted two parameters τ_1 and τ_2 , which are related to the bond diffusion and damping rate, respectively. The short dashed lines in Figures 2 and 3 denote the calculated values

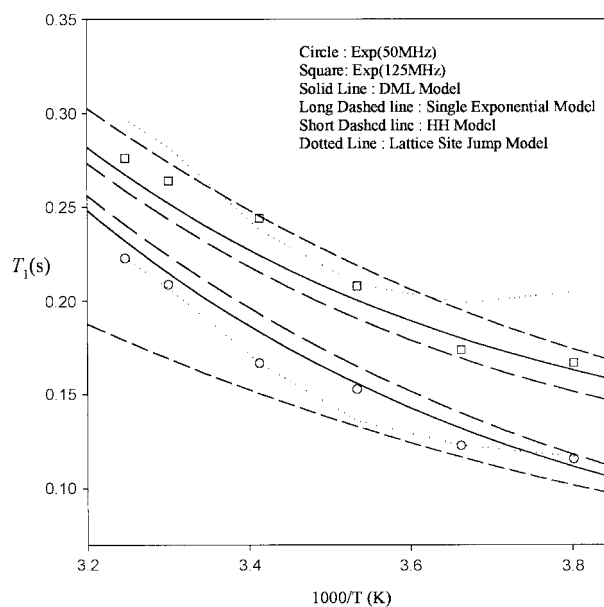


Figure 2. T_1 Data Reproduced by Several Motional Models for C-1 Carbon.

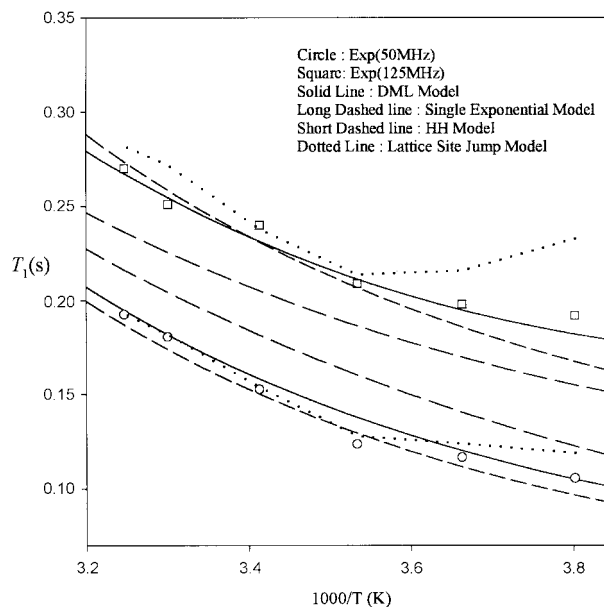


Figure 3. T_1 Data Reproduced by Several Motional Models for C-2 Carbon.

using Eq. (3). We can see that the T_1 values of C-2 and C-1 carbon give poorer fit at low temperature and at high temperature, respectively. This fact reflects that, although the HH model is sufficient to describe the general trend of the relaxation process in several polymers, such as polyethylene, polyethyleneoxide, etc., it does not provide satisfactory results in the case of PBT.

Studies on a series of polyesters show that the relaxation parameters for all carbons in a terephthalate unit are independent of the methylene chain length.²² On this basis it may be presumed that the large terephthalate group flanked on both sides by two methylene chains can be looked upon as

the local chain center for chain motion occurring inside the methylene chains. It has been reported¹⁵ that the local motions of the methylene group in PBT usually occur in such a way that three bond motions become independent of terephthaloyl residues. In line with this, we assumed that the corresponding relaxation process might be interpreted on the basis of these local conformational transitions in repeating units of PBT plus the overall rotation of their local center. Since the length of the methylene chain is relatively short, only a limited number of the conformational transitions can arise. We could treat the problem on the basis of a model developed by our laboratory in which transitions are assumed to take place through jump among the sterically allowed conformations. In this model the spectral density of carbon-proton dipolar interaction can be expressed as follows:^{23,24}

$$J_{\text{CH}}(\omega) = \frac{1}{5} \xi_{\text{CH}}^2 \sum_{a,n} \frac{6D_{\perp} + a^2(D_{\parallel} - D_{\perp}) + \lambda_n}{(6D_{\perp} + a^2(D_{\parallel} - D_{\perp}) + \lambda_n)^2 + \omega^2} \left| \sum_{b,q} D_{a,b}^{(2)}(\Omega_N^D) X_q^{(0)} X_q^{(n)} Y_{2,b}(\Omega_{\text{CH}}^N(q)) \right|^2, \quad (8)$$

Table 1. Experimental relaxation data

Temp (K)	50.3 MHz (C-1)		50.3 MHz (C-2)		125.5 MHz (C-1)	125.5 MHz (C-2)
	T_1	NOE	T_1	NOE	T_1	T_1
263	0.116	1.32	0.106	1.28	0.167	0.192
273	0.123	1.40	0.117	1.38	0.174	0.198
283	0.153	1.47	0.124	1.39	0.208	0.209
293	0.167	1.62	0.153	1.54	0.244	0.240
303	0.209	1.74	0.181	1.60	0.264	0.251
308	0.223	1.75	0.193	1.62	0.276	0.270

Table 2. Significant conformations and the direction of C-C and C-H bonds in the tetrahedral lattice coordinates

Conformation	C-C Bond Conformation					C-C Bond Direction					C-H Bond Direction			
	O-C2	C2-C1	C1-C1	C1-C2	C2-O	O-C2	C2-C1	C1-C1	C1-C2	C2-O	C2	C1	C1	C2
1	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>a</i>	<i>c'</i>	<i>a</i>	<i>c'</i>	<i>a</i>	<i>b'</i>	<i>b</i>	<i>b'</i>	<i>b</i>
2	<i>g</i> ⁺	<i>t</i>	<i>g</i> ⁻	<i>t</i>	<i>t</i>	<i>a</i>	<i>d'</i>	<i>a</i>	<i>c'</i>	<i>a</i>	<i>c'</i>	<i>c</i>	<i>b'</i>	<i>b</i>
3	<i>g</i> ⁻	<i>t</i>	<i>g</i> ⁺	<i>t</i>	<i>t</i>	<i>a</i>	<i>b'</i>	<i>a</i>	<i>c'</i>	<i>a</i>	<i>d'</i>	<i>d</i>	<i>b'</i>	<i>b</i>
4	<i>t</i>	<i>g</i> ⁺	<i>t</i>	<i>g</i> ⁻	<i>t</i>	<i>a</i>	<i>c'</i>	<i>b</i>	<i>c'</i>	<i>a</i>	<i>b'</i>	<i>d</i>	<i>d'</i>	<i>b</i>
5	<i>g</i> ⁺	<i>g</i> ⁻	<i>t</i>	<i>g</i> ⁺	<i>t</i>	<i>a</i>	<i>c'</i>	<i>d</i>	<i>c'</i>	<i>a</i>	<i>b'</i>	<i>a</i>	<i>d'</i>	<i>b</i>
6	<i>t</i>	<i>t</i>	<i>g</i> ⁺	<i>t</i>	<i>g</i> ⁻	<i>a</i>	<i>c'</i>	<i>a</i>	<i>d'</i>	<i>a</i>	<i>b'</i>	<i>b</i>	<i>c'</i>	<i>c</i>
7	<i>t</i>	<i>t</i>	<i>g</i> ⁻	<i>t</i>	<i>g</i> ⁺	<i>a</i>	<i>c'</i>	<i>a</i>	<i>b'</i>	<i>a</i>	<i>b'</i>	<i>b</i>	<i>d'</i>	<i>d</i>
8	<i>t</i>	<i>t</i>	<i>g</i> ⁺	<i>t</i>	<i>t</i>	<i>a</i>	<i>c'</i>	<i>a</i>	<i>d'</i>	<i>a</i>	<i>b'</i>	<i>b</i>	<i>c'</i>	<i>c</i>
9	<i>g</i> ⁺	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>a</i>	<i>d'</i>	<i>a</i>	<i>d'</i>	<i>a</i>	<i>c'</i>	<i>c</i>	<i>c'</i>	<i>c</i>
10	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>g</i> ⁺	<i>a</i>	<i>c'</i>	<i>a</i>	<i>c'</i>	<i>a</i>	<i>b'</i>	<i>b</i>	<i>b'</i>	<i>b</i>
11	<i>t</i>	<i>t</i>	<i>g</i> ⁻	<i>t</i>	<i>t</i>	<i>a</i>	<i>c'</i>	<i>a</i>	<i>b'</i>	<i>a</i>	<i>b'</i>	<i>b</i>	<i>d'</i>	<i>d</i>
12	<i>g</i> ⁻	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>a</i>	<i>b'</i>	<i>a</i>	<i>b'</i>	<i>a</i>	<i>d'</i>	<i>d</i>	<i>d'</i>	<i>d</i>
13	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>g</i> ⁻	<i>a</i>	<i>c'</i>	<i>a</i>	<i>c'</i>	<i>a</i>	<i>b'</i>	<i>b</i>	<i>b'</i>	<i>b</i>
14	<i>t</i>	<i>g</i> ⁺	<i>t</i>	<i>t</i>	<i>t</i>	<i>a</i>	<i>c'</i>	<i>b</i>	<i>c'</i>	<i>b</i>	<i>b'</i>	<i>d</i>	<i>d'</i>	<i>d</i>
15	<i>t</i>	<i>t</i>	<i>t</i>	<i>g</i> ⁺	<i>t</i>	<i>a</i>	<i>c'</i>	<i>a</i>	<i>c'</i>	<i>b</i>	<i>b'</i>	<i>b</i>	<i>b'</i>	<i>d</i>
16	<i>t</i>	<i>g</i> ⁻	<i>t</i>	<i>t</i>	<i>t</i>	<i>a</i>	<i>c'</i>	<i>d</i>	<i>c'</i>	<i>d</i>	<i>b'</i>	<i>a</i>	<i>d'</i>	<i>a</i>
17	<i>t</i>	<i>t</i>	<i>t</i>	<i>g</i> ⁻	<i>t</i>	<i>a</i>	<i>c'</i>	<i>a</i>	<i>c'</i>	<i>d</i>	<i>b'</i>	<i>b</i>	<i>b'</i>	<i>a</i>

where the symbols have their usual meanings.

The sterically allowed lattice sites and corresponding transition constants are tabulated in Table 2. Using Eq. (1) and Eq. (8), we can construct the temperature dependence of T_1 values, assuming that the diffusion frame is fixed on the phenyl ring in terephthalate unit. The rate constants for conformational transition are defined as follows

$$\begin{aligned} tttgt \rightarrow tgttt \text{ (gauche migration)} &: k_0 \\ ttgtt \rightarrow gtttt \text{ (gauche migration)} &: k_1 \\ ttttt \rightarrow tgtgt \text{ (pair gauche annihilation)} &: k_2 \\ ttttt \rightarrow gtgtt \text{ (pair gauche annihilation)} &: k_3 \end{aligned} \quad (9)$$

All conformations considered in this calculation are listed in Table 2. Since the two rate constants, for example, between pair *gauche* annihilation and pair *gauche* creation involved in a conformational interconversion are connected as a forward-reverse pair, determination of the one leads to evaluation of the other. The reverse rate constants are simply deduced from the relation

$$k_f/k_r = \exp(\Delta E/RT), \quad (10)$$

where ΔE is the energy difference between two conformations involved in the transition.

In the present study, the ΔE was set to be 1 kcal/mol and the obtained data are given in Table 3, which are also graphically presented as dotted lines in Figures 2 through 3. From these data we can see that the calculated T_1 values are in good agreement with the observed ones at high temperatures. But a significant discrepancy arises as the temperature decreases. Although there are many factors responsible for this discrepancy, such as insufficient experimental T_1 data, difficulty in choosing diffusion origin, etc., it seems necessary that to obtain more faithful reproduction of the relax-

Table 3. Calculated rate constants for conformational transitions in PBT*

Temp (K)	k_0	k_1	k_2	k_3	D_Z	D_X
263	0.60	1.09	1.04	1.35	1.66	0.049
273	0.54	1.03	1.58	1.37	1.78	0.093
283	1.59	1.28	3.61	1.53	1.91	0.118
293	2.50	1.60	4.80	1.87	2.54	0.170
303	3.67	2.23	4.32	2.42	3.41	0.209
308	4.63	2.31	7.45	2.58	3.65	0.245

E_a (Kcal/mol) 7.23 3.58 6.54 2.92 3.02 7.16

(*unit: $10^9/s$)

Table 4. Relaxation parameters obtained from DLM model

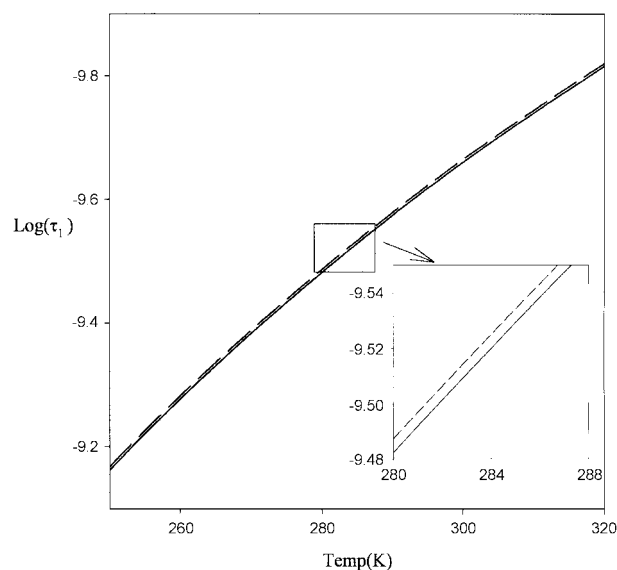
Temp (K)	τ_1^* C-1(C-2)	50.3 MHz		50.3 MHz		125.5 MHz		125.5 MHz	
		(C-1)		(C-2)		(C-1)		(C-2)	
		T_1 Cal	NOE	T_1 Cal	NOE	T_1 Cal	NOE	T_1 Cal	NOE
263	4.83(4.90)	0.110	1.31	0.105	1.30	0.189	0.182		
273	3.81(3.85)	0.126	1.37	0.120	1.36	0.203	0.195		
283	3.05(3.09)	0.145	1.44	0.138	1.44	0.221	0.212		
293	2.49(2.51)	0.167	1.59	0.158	1.52	0.243	0.231		
303	2.05(2.07)	0.192	1.67	0.182	1.60	0.267	0.254		
308	1.87(1.89)	0.206	1.70	0.195	1.65	0.281	0.267		

E_a 25.55(25.68)

(KJ/mole)

(* 10^{-10} s)

ation rate over the entire temperature range covering lower temperatures an additional motional mode must be taken into consideration. The T_1 minimum can be seen near 263 K, which suggests additional evidence for the existence of librational motion. So we turned our attention to the Dejean-Laupretre-Monnerie (DLM) model, where small scale librational motions with amplitudes of 30° - 50° and frequencies of 10^{11} Hz are considered. Using the DLM expression [Eq. (7)], we could explain the T_1 behaviors at both carbons over the observed temperature range in a satisfactory manner assuming $\tau_2/\tau_1 = 3.0$ along with $\tau_1/\tau_0 = 52.9$ for 1-carbon and $\tau_1/\tau_0 \gg 100$ for 2-carbon, which is shown in Figures 2 and 3 as solid lines. The factor A for two carbons produce librational amplitude 32.01° and 29.84° for 1- and 2-carbon, respectively. This result is consistent with previous reports that indicate that the central methylene carbon (1-carbon) is more mobile than the terminal methylene carbon (2-carbon) in solution phase as well as in the solid state.^{14,25} This difference in amplitude and frequency also accounts for a major source of the difference in the crystallization rate between PBT and PET.²⁶ The temperature depen-

**Figure 4.** Correlation Times Calculated from the DLM Model: Solid Line (C-1 Carbon), Dashed Line (C-2 Carbon).

dence of the correlation time, τ_1 , obtained from the DLM model is shown in Figure 4. Within the experimental error, τ_1 value, fitted at two carbons, appears to follow an Arrhenius relationship, yielding an apparent activation energy of 25.61 ± 0.05 kJ/mol, which is slightly greater than that for the one bond rotation in small chain molecules.¹⁵ This activation energy is understandable if we consider that the local backbone motion of PBT can be classified as Helfand type II motion.

Conclusions

Reorientational motions of the backbone carbon-proton internuclear vector in PBT can be grouped into two categories in solution state. One is thermally activated conformational transition between potential wells. The other is small-scale librational motion within the potential well. As has been observed in solid state experiments, we have confirmed that the motion of terminal methylene carbon is relatively more restricted than that of central methylene carbon in solution as well. When both three-bond motion (*gauche* migration and pair *gauche* creation and annihilation) and librational motion considered together, the temperature dependence of the relaxation rate can be explained in a satisfactory manner, giving the useful dynamical information on the local dynamics of methylene chains in PBT.

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Table 5. Dynamic parameters obtained from DLM model

Parameters	τ_2/τ_1	τ_1/τ_0	τ_1/τ_0	A	θ	A	θ
		(1-carbon)	(2-carbon)	(1-carbon)	(1-carbon)	(2-carbon)	(2-carbon)
	3.0	52.9	8625	0.386	32.01°	0.344	29.84°

References

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