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Effect of Internal Librational Motions on the Carbon-13 Nuclear Magnetic Resonance Relaxation Times of Poly(β-hydroxybutyrate) in Tetrachloroethane Solution

In a recent paper[1] we reported a detailed analysis of carbon-13 magnetic relaxation of poly(β-hydroxybutyrate) (PHB) in 1,1,2,2-tetrachloroethane solvent.

The chain local motion of PHB was described by using the Jones and Stockmayer (JS) and Hall, Weber, and Helfand (HWH) models. Nevertheless, the $T_{1,\mathrm{CH}}/T_{1,\mathrm{CH_2}}$ ratio of the backbone carbons in the temperature range of this study was found to be 1.69 ± 0.04 for measurements at 200 MHz and 1.67 ± 0.03 for the 300-MHz experiments.

These experimental values are different from the approximate value of 2, which is expected from the number of protons directly bonded to each of considered carbons. No other relaxation source from remote protons (e.g., methyl protons) can account for this discrepancy.[1] This observation indicates that the local motions are not identical for the internuclear vectors associated with the CH and CH_2 carbons.

Recently, Dejean de la Batie, Lauprêtre, and Monnerie[2] (DLM) considered an additional motion superimposed on the HWH model that contributes to a partial orientation of the CH vectors with a characteristic correlation time that differs from the correlation times for orientation diffusion along the chain. This motion, which must be faster and thus more local than the orientation diffusion process along the chain, has been attributed to molecular librations of limited extent of the CH vectors about their equilibrium conformation and corresponds to oscillations inside a potential well. Such a librational motion has been described by Howarth[3] in terms of a random anisotropic fast reorientation of the CH vector inside a cone of half-angle, θ, the axis of which is the rest position of the CH bond.

Accordingly, the DLM model describes the local chain motions in terms of two independent kinds of motions: (i) a diffusional process along the chain which occurs via conformational transitions and (ii) bond librations. The composite orientation autocorrelation function of the DLM model is given in ref 2, and its Fourier transformation yields the reduced spectral density

$$J(\omega) = (1-a)/(\alpha + i\beta)^{1/2} + a\tau_2/(1+\omega^2\tau_2^{\,2})$$

with

$$1 - a = [(\cos\theta - \cos^3\theta)/2(1-\cos\theta)]^2$$
$$\alpha = \tau_0^{-2} + 2\tau_0^{-1}\tau_1^{-1} - \omega^2$$
$$\beta = -2\omega(\tau_0^{-1} + \tau_2^{-1})$$

τ_0 and τ_1 are the correlation times in the HWH model[4] describing single conformational transitions and cooperative or correlated motions, respectively, and τ_2 is the correlation time associated with the librational motion in the Howarth description.[3]

$(T_1)^{-1}$ can then be written as

$$\frac{1}{T_1} = (1-a)\frac{\hbar^2\gamma_C^{\,2}\gamma_H^{\,2}}{10}\frac{1}{r_{\mathrm{CH}}^{\,6}}[J_{\mathrm{HH}}(\omega_H - \omega_C) + 3J_{\mathrm{HH}}(\omega_C) + 6J_{\mathrm{HH}}(\omega_H + \omega_C)] + a\frac{\hbar^2\gamma_C^{\,2}\gamma_H^{\,2}}{10}\frac{1}{r_{\mathrm{CH}}^{\,6}}[J_0(\omega_H - \omega_C) + 3J_0(\omega_C) + 6J_0(\omega_H + \omega_C)]$$

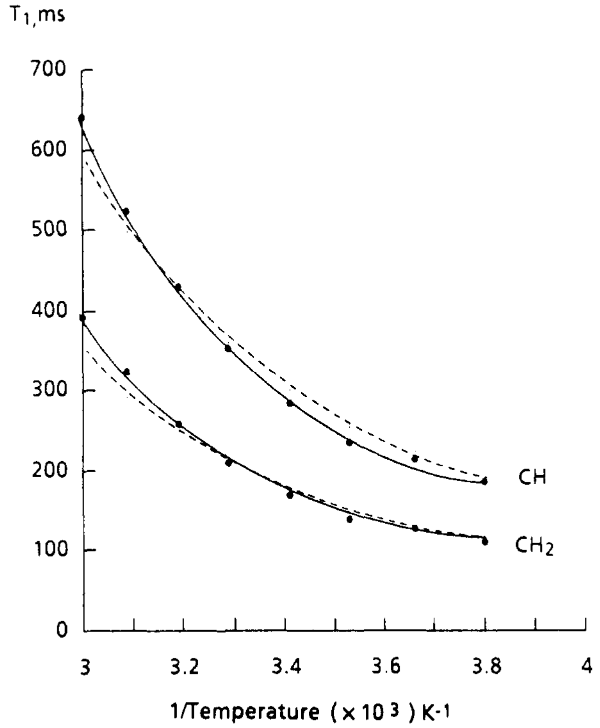

Figure 1. Plot of ^{13}C spin–lattice relaxation times, T_1 (ms), versus reciprocal temperature for PHB in TCE-d_2 at 300 MHz. DLM model: solid lines, experimental values; dashed lines, calculated values.

The best fit of the T_1 data is plotted in Figures 1 and 2 for the CH and CH_2 carbons, respectively. The fitting has been performed as described in ref 2 and corresponds to $\tau_0/\tau_1 = 3$ and $\tau_1/\tau_2 = 200$. Agreement between experimental and calculated values is very good. It should be noted that the τ_1/τ_2 ratio cannot be accurately determined and that good agreement between theory and experiment is obtained in so far as $200 \le \tau_1/\tau_2 \le 500$.

The simulated values for the angle θ defined in ref 3 is 22° for the CH carbon and 29° for the CH_2 carbon. The different values of θ explain the fact that the $T_{1,\mathrm{CH}}/T_{1,\mathrm{CH_2}}$ ratio is not approximately equal to 2, and they support the conclusion that the internuclear vectors at two carbon sites do not experience exactly the same local dynamics. The greater θ value for the CH_2 carbon indicates a lesser steric hindrance to the librational motion of the corresponding CH vector relative to that in the CH carbon for which the presence of an adjacent methyl group restricts the amplitude of the local libration. This observation is in accord with earlier findings in other polymeric systems.[2,5]

Another feature of the calculation using the DLM function over the whole temperature range under study refers to the assumption that the angle θ and the parameter a should be practically independent of temperature as was shown in ref 2 and confirmed in the present study for the PHB system.

Table I is a compilation of the τ_1 values derived from fitting the experimental relaxation data with the DLM motional model. These values plotted as a function of $1/T$ show a linear correlation ($r = 0.9998$) with $1/T$ in the frequency and temperature range under study. The slope of the line leads to an apparent activation energy of 19.5 kJ/mol, which is close to the value of 22 kJ/mol calculated by using the HWH model alone.[1] The true

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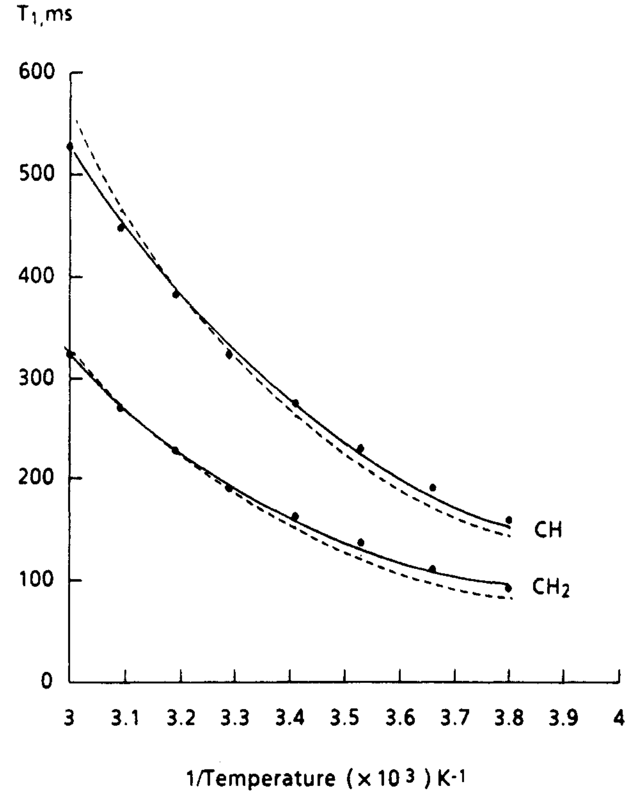

Figure 2. Plot of ^{13}C spin–lattice times, T_1 (ms), versus reciprocal temperature for PHB in TCE-d_2 at 200 MHz. DLM model: solid lines, experimental values; dashed lines, calculated values.

activation energy, E^*, of the conformational transitions associated with the τ_1 correlation time can be estimated through the formula[1]

$$E^* = E_a - \Delta H_\eta$$

where ΔH_η is the activation energy for the solvent viscosity. In the case of TCE, this value has been found to be ca. 12 kJ/mol, and therefore $E^* = 7.5$ kJ/mol, which corresponds to the type 2 chain local motion according to Helfand's terminology.[6]

Numerical Calculations. The fitting of the experimental data to the DLM function and the calculated correlation times and other parameters in the model were achieved by using the MOLDYN program,[7] modified to include the DLM motional model. Initially, the T_1 values and NOEs for the CH group at both field strengths and at -10 °C were used as an input, and the best fits for correlation time τ_1 and angle θ were calculated while the correlation time ratios τ_0/τ_1 and τ_1/τ_2 were varied stepwise by 1 and 20 units, respectively. The best fit was obtained by using a Simplex routine to vary the parameters until the sum of squares of deviations of the calculated relaxation times and NOEs from the observed data was a minimum. Values for the sum of squares of the order of 0.01–0.001 were observed in the present calculations, reflecting a good fit. In subsequent calculations for the CH group over the whole temperature range, the parameters τ_0/τ_1, τ_1/τ_2, and θ obtained at -10 °C were kept constant, while the τ_1 correlation time was varied. Calculation of the T_1 values and NOEs for the CH_2 group was done by using the values of τ_1, τ_0/τ_1, and τ_1/τ_0 parameters obtained for the CH group at a given temperature and the value of angle θ calculated from the experimental data of the CH_2 carbon at -10 °C.

Table I
Calculated T_1 (in ms), NOE, and τ_1 for the Backbone Carbons of PHB in TCE-d_2 Using the DLM Model[a]

temp, °C	200 MHz		300 MHz		
	CH	CH_2	CH	CH_2	$\tau_1 \times 10^{-10}$
-10	153 (2.23)	89 (2.23)	194 (2.01)	113 (2.02)	6.30
0	182 (2.40)	107 (2.40)	223 (2.20)	130 (2.20)	4.45
10	214 (2.53)	125 (2.53)	254 (2.33)	148 (2.33)	3.39
20	261 (2.66)	153 (2.66)	301 (2.48)	176 (2.48)	2.50
30	320 (2.76)	187 (2.76)	359 (2.61)	210 (2.61)	1.89
40	387 (2.83)	227 (2.83)	424 (2.74)	248 (2.71)	1.49
50	465 (2.88)	272 (2.88)	499 (2.78)	292 (2.78)	1.20
60	560 (2.91)	328 (2.91)	591 (2.84)	345 (2.84)	0.97
					$r = 0.9998$ $E_a = 19.5$ kJ/mol $\tau_\infty = 8.4 \times 10^{-14}$ s

[a] $\tau_0/\tau_1 = 3$; $\tau_1/\tau_2 = 200$.

References and Notes

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