

Nuclear spin—lattice relaxation and molecular motions in isotactic poly(but-1-ene) and (but-1-ene)—propylene copolymers in solution

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^{13}C spin—lattice relaxation times have been measured at 25.15 MHz on poly(but-1-ene) and (but-1-ene)—propylene copolymers, as a function of molecular weight and concentration in 1,2,4-trichlorobenzene, and over the 50°–150°C temperature range. Maximum nuclear Overhauser enhancement was observed for all carbons. Independence of T_1 from molecular weight and bulk sample viscosity for solutions less concentrated than 50% w/v, indicates that relaxation is dominated by local conformational rearrangements rather than by overall tumbling of the macromolecule. Relaxation studies on copolymers show that this segmental motion affects only short sequences of the chain. No influence of stereochemical configurations is observed. Relaxation data for backbone carbons was interpreted in terms of a single τ isotropic motional model. Internal rotations of side CH_2 and CH_3 groups were analysed using the two and three correlation times Woessner models, and show little dependence on an eventual anisotropy of chain motion. Similar temperature dependence (18–21 kJ/mol) is observed for chain and side carbons, and even if internal reorientation of side CH_3 groups is much more rapid, it appears interlinked with segmental motion.

INTRODUCTION

^{13}C n.m.r. spin—lattice relaxation measurement is now a widely used method of approaching molecular motions in small molecules as well as in polymers. In the latter case, motional frequencies are lower and ^{13}C relaxation times are short. Most generally governed by dipolar interactions with directly bonded protons¹, ^{13}C relaxation results from fluctuating reorientation of the ^{13}C — ^1H vectors. Observed independence of the T_1 values with molecular weight ($\geq 10^4$), shows that the local conformational rearrangements, which are associated with segmental motion, are often the dominant process^{2,3}.

Assuming a purely ^{13}C — ^1H dipolar relaxation mechanism, the spin—lattice relaxation time T_1 and the nuclear Overhauser enhancement are given by the well-known expressions⁴:

$$\frac{1}{T_1} = \frac{1}{10} \hbar^2 \gamma_C^2 \gamma_H^2 r^{-6} [J(\omega_H + \omega_C) + 3J(\omega_C) + 6J(\omega_H + \omega_C)] \quad (1)$$

$$\text{NOE} = \frac{\gamma_H}{\gamma_C} \frac{6J(\omega_H + \omega_C) - J(\omega_H - \omega_C)}{J(\omega_H - \omega_C) + 3J(\omega_C) + 6J(\omega_H + \omega_C)} \quad (2)$$

where ω_H and ω_C are the ^1H and ^{13}C resonance frequencies, r is the internuclear vector, and $J(\omega)$ is the spectral density function defined by:

$$J(\omega) = \frac{1}{2} \int_{-\infty}^{+\infty} G(\tau) e^{i\omega\tau} d\tau$$

Here $G(\tau)$ is the normalized second order spherical harmonic autocorrelation function. The simplest approximate description of $J(\omega)$ is to assume an isotropic rotation of the internuclear vector. In this case, $J(\omega)$ can be written as:

$$J(\omega) = \frac{\tau_{\text{ch}}}{1 + \omega^2 \tau_{\text{ch}}^2}$$

where τ_{ch} is the rotational correlation time.

Although an isotropic rotation is a rather unrealistic model of segmental motions in polymers, it quite well describes the relaxation data reported for a variety of flexible macromolecules in moderately viscous solutions, such as polypropylene⁵, polyisobutene^{6,7}, poly(propylene oxide)⁷ and poly(styrene peroxide)⁸. In the case of viscous polymer solutions, or less flexible polymers undergoing slow motions, the extreme narrowing condition is no more fulfilled and the single exponential description of the relaxation is usually inconsistent with both experimental spin—lattice relaxation times and nuclear Overhauser enhancements. Then the motional anisotropy may be accounted for by using different models such as the rotational diffusion of a symmetrical ellipsoid^{9,10}, a broad distribution of correlation times¹¹, or more elaborated interpretations of backbone rearrangements^{12–14}.

Table 1 ¹³C relaxation parameters of isotactic poly(but-1-ene)^a observed at 25.15 MHz as a 15% (w/v) solution in 1,2,4 trichlorobenzene. T₁ (sec) ± 10%; (NOE ± 10%)

Temperature (°C)	T ₁ backbone		T ₁ side group	
	CH ₂	CH	CH ₂	CH ₃
50	0.09 (2.9)	0.18 (2.8)	0.12 (2.8)	1.1 (2.9)
60	0.12	0.24	0.16	1.5
70	0.16	0.29	0.19	1.7
80	0.19	0.37	0.25	2.0
100	0.26 (2.9)	0.49 (2.8)	0.33 (2.8)	3.0 (2.8)
150	0.53	1.0	0.70	5.3
50 ^b	0.09	0.18	0.13	1.0

^a Crude polymers with an isotactic triad content 0.84 ≤ |mm| ≤ 0.96

^b Observation at 15.08 MHz

Overall motion of side groups, undergoing internal rotation about the axis of the linkage with the main chain is necessarily more complex to analyse. The simplest case to be considered is the relaxation of a rotating symmetrical group attached to a framework undergoing isotropic rotation. The model was mathematically formulated by Woessner¹⁵. Another commonly used method consists of considering the overall motion of side carbon as isotropic and separating the corresponding effective correlation time into its segmental and internal contributions through the approximate expression¹⁶:

$$(\tau_{\text{eff}})^{-1} = (\tau_{\text{ch}})^{-1} + (\tau_L)^{-1} \quad (3)$$

Separate determination of τ_{ch} from chain ¹³C relaxation times leads to an estimate of τ_L

We have determined ¹³C relaxation parameters for isotactic poly(but-1-ene) and (but-1-ene)-propylene copolymers in solution, and applied some of the above models to the analysis of the chain and side-group motions. Preliminary results were previously communicated¹⁷ and we intend to develop here a more complete interpretation. Relaxation data on the same polymer were recently reported by Bovey et al.¹⁸ and their conclusions will be considered together with ours in the present paper.

EXPERIMENTAL

Materials

Isotactic poly(but-1-ene) samples (0.80 ≤ |mm| < 0.96) and random butene-propylene copolymers were provided by CdF Chimie. Atactic fractions of homopolymers were obtained by extraction with refluxing CH₂Cl₂¹⁹.

N.m.r. analysis

The 25.15 MHz C.m.r. spectra were recorded on a Jeol PFT 100 instrument. FID were stored in 8K computer locations using a spectral width of 1 kHz. Spin-lattice relaxation times were measured by using the standard inversion recovery [π - t - (π/2)] technique, with repetition times between pulse sequences greater than five times the longest T₁ of considered nuclei. Values were derived from plots of ln(I_∞ - I_t) vs. t. In all cases a proper linearity was observed and the T₁ values are within an estimated maximum error of ±10%. Amplitudes were determined from peak heights for the isotactic samples and from resolved peaks areas for the atactic samples.

Nuclear Overhauser enhancements were measured using a gate decoupling technique. Unless specified conditions

applied, observations were performed on solutions in 1,2,4-trichlorobenzene (TCB) - benzene-d₆ mixtures (3/1, v/v) in order to provide the deuterium lock. The lock signal appeared stable enough to ensure (even at 100°C) the 100-1000 scans required for each value of the delay time. A 5 mm inner tube containing benzene-d₆ was used for measurements at 150°C. Samples were not degassed.

The 15.08 MHz spectra were recorded on a Brücker WP60 FT spectrometer, using similar conditions.

RESULTS AND DISCUSSION

Relaxation data and influence of temperature, concentration and molecular weight

Spin-lattice relaxation times of chain and side carbons of isotactic poly(but-1-ene) were measured on 15% (w/v) solutions in TCB, from 50° to 150°C and the values are collected in Table 1. At 25.15 MHz, the theoretical maximum value of the nuclear Overhauser enhancement was closely approached for all carbons at 50° and 100°C. Identical values of T₁ were obtained for an observation frequency of 15.08 MHz. Both results indicate that, over the observed temperature range, the extreme narrowing condition is fulfilled.

The effect of polymer concentration was studied at 150°C from dilute solution (15% w/v) to bulk polymer in the melt. In Figure 1 it appears that T₁ becomes independent of the overall viscosity of the medium for solvent to monomer molar ratio R higher than 0.8, i.e. for solutions ≤ 50% w/v. NOE values are also close to the maximum expected for bulk polymer and the most concentrated solutions.

It is also evident, from Table 2, that the spin-lattice relaxation times of the three observed carbons are independent of molecular weight over the wide range studied.

¹³C relaxation data of random (but-1-ene)-propylene copolymers over a wide range of propylene contents are shown in Figure 2. Analysis of the samples from C.m.r. spectra is possible as the methine carbons of PP, PB and BB dyads appear fairly well separated²⁰. Quantitative measurement of peak intensities thus allow the separate determination of average lengths of polybutene and polypropylene sequences in the copolymer, and more particularly the pro-

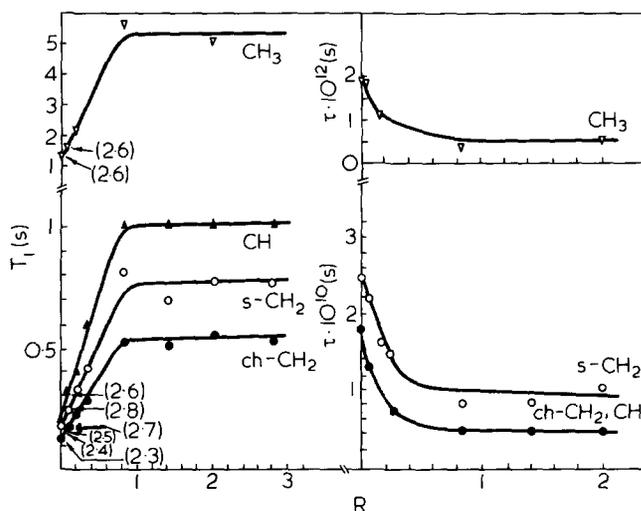


Figure 1 ¹³C relaxation data of poly(but-1-ene) at 150°C. Variation with concentration in 1,2,4-trichlorobenzene. R = solvent to monomer molar ratio. Values in brackets are referred to NOE for polymer in the melt and for the highest concentration: Δ, CH₃; ▲, CH; ○, s-CH₂; ●, ch-CH₂

Table 2 Independence of T₁ with molecular weight (15% w/v solutions in TCB, at 100°C)

\bar{M}_n^*	$\frac{\bar{M}_w}{\bar{M}_n}$	T ₁ (sec) ± 10%		
		CH ₂ chain	CH	CH ₂ side
203 000	4.4	0.27	0.51	0.37
79 900	8.7	0.25	0.45	0.32
35 450	11.0	0.24	0.50	0.32
26 200	11.7	0.25	0.47	0.34
9 500	6.5	0.26	0.52	0.35

* Samples with isotactic triad content 0.80 ≤ |mm| ≤ 0.96

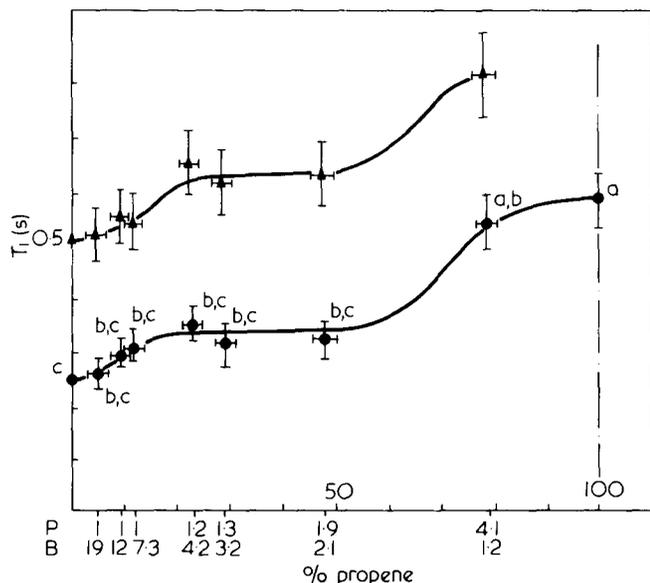
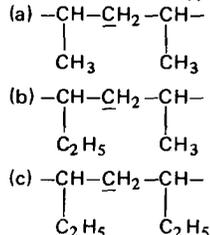


Figure 2 ¹³C spin-lattice relaxation times of chain carbons in random copolymers (but-1-ene)-propene, as observed at 100°C on 15% w/v solutions in TCB-C₆D₆: ▲, CH (butene unit); ●, ch-CH₂ of (a), (b) and (c) types



P and B are the respective average lengths of propene and butene sequences in the copolymers, as determined by c.m.r. analysis

portions of isolated P units, isolated PP dyads and larger polypropylene sequences²¹.

It may be seen in Figure 2 that the three copolymers with lowest propylene contents contain only isolated P units, and that the spin-lattice relaxation times of chain carbons do not increase significantly until the polybutene sequences become shorter than 20 units. A plateau is reached for intermediate compositions (20–80 to 60–40 P–B%) corresponding to very short sequences of each monomer, and it is remarkable that, for the highest propylene contents T₁ of chain carbons become close to those of homopolypropylene when propylene sequences are longer than about 4 units.

The above set of results (independence of T₁ from molecular weight and on concentration for R ≥ 0.8) strongly indicates that, at the considered temperatures, relaxation is dependent on local reorientation of the backbone rather than on overall diffusional tumbling of the macromolecule. Furthermore, data on copolymers might also support that

the sequential motions which are efficient in carbon relaxation affect only short sequences of the chain.

Comparison of relaxation data for poly(but-1-ene) samples of different stereoregularities does not exhibit any influence of tacticity on spin-lattice relaxation times. Results collected in Table 3 concern crude polymers, their atactic soluble fractions and their highly isotactic insoluble fractions¹⁹. For atactic samples, no significant difference was observed between the T₁ of (i) and (h + s) configurations of the chain methine.

Examination of the whole data shows that the spin-lattice relaxation times of the chain carbons are inversely proportional to the number of bonded hydrogen atoms. Further comparison with values of T₁ for side methylene and methyl carbons is no more valid as, in addition to segmental motions, each of these groups experiences its own internal rotation.

It must be noted that our T₁ values are about 30% higher than those recently reported by Bovey et al.¹⁸ for the same polymer at 22.62 and 90.52 MHz in pentachloroethane solution. As the extreme narrowing condition is fulfilled this discrepancy cannot be explained by a lower observation frequency and most probably, results from the difference in local viscosity behaviour with the two solvents respectively used²². Motions appear more rapid in TCB than in pentachloroethane.

Motional analysis of chain carbon relaxation data

It appears from the previous sections that a simplified single τ approach of the segmental rotation might be consistent with our relaxation results. The linear decrease of lnT₁ with (temperature)⁻¹ indicates that, in the examined temperature range, we are far away from the minimum on the left wing of the T₁ vs. τ plot in the range of short correlation times, under extreme narrowing condition. We are in a domain of segmental mobility where any mathematical model may fit with experimental results, and our relaxation data were interpreted in terms of a single τ_{ch} description of segmental reorientation. Values of correlation times versus temperature are collected in Table 4.

The Arrhenius plot (Figure 3) is fairly linear and an activation energy of 19 kJ/mol may be deduced for the segmental motion. This value is in agreement with those observed for polyethylene and polypropylene (Table 4), owing to the higher conformational barrier expected for poly(but-1-ene). Bovey et al.¹⁸ used simultaneously the isotropic model and

Table 3 Spin-lattice relaxation times for poly(but-1-ene) samples of various tacticities (15% w/v solutions in TCB, 100°C)

mm% ± 3	CH ₂ chain	T ₁ (sec) ± 10%	
		CH	
		(mm)	(mr) + (rr)
33*	0.28	0.52	0.49
36*	0.29	0.53	0.51
39*	0.26	0.50	0.46
70	0.26	0.49	—
81	0.25	0.47	—
86	0.24	0.46	—
90	0.26	0.52	—
96	0.28	0.52	—

* Soluble fractions obtained from extraction with refluxing CH₂Cl₂

Table 4 Correlation times for backbone motion and internal rotation of side methylene group, assuming an isotropic segmental reorientation of the main chain

Temperature (°C)	$\tau_{ch} \times 10^{10}$ (sec)	$\tau_L \times 10^{10}$ (sec)	
		Woessner model	Approximate relation
50	2.3	5.8	5.3
60	1.7	4.7	4.2
70	1.4	3.8	3.5
80	1.1	3.0	2.5
100	0.85	2.2	1.9
		PP 0.38 *	
		PE 0.18	
150	0.4	0.9	0.8
$E_a \pm 10\%$ (kJ/mol)	19		21
	PP 14 *		
	PE 10		

r_{C-H} for methylene and methine²³: 0.107 nm

θ_{CCH} : 109°28'

* Values extrapolated for polyethylene and polypropylene in 25% (w/v) solution in o-dichlorobenzene from results of Inoue et al.⁵

the two correlation times diamond lattice model of Valeur¹³. Above 40°C the first model satisfactorily fits experimental T_1 but cannot account for the deviating NOE values for which a better agreement was observed using the second model, particularly at high field strength. At lower temperature neither model fits simultaneously experimental T_1 and NOE. Values of τ_{ch} derived from the isotropic model appear closely comparable to those of the more rapid mode (τ_D) derived from the diamond lattice model, and this last description of backbone motion was preferred. Under our conditions (frequency, temperature, solvent), observed NOE values are maximum within experimental error, and even if a significant anisotropy of chain motion is necessarily more realistic, the isotropic description through an average single τ_{ch} , which only reflects the most rapid short range segmental reorientations efficient in relaxation, remains acceptable.

Motional analysis of side methylene relaxation data

Our approach to side group methylene motion was built on two reasonable and simplifying assumptions. First, the overall motion of side methylene is independent of the rapid rotation of borne methyl group. Second, the internal reorientation of s-CH₂ (τ_L) is an isotropic rotation about the CH-CH₂ axis occurring through random jumps between three conformational equilibrium positions at $2\pi/3$ rd. As the backbone motion (τ_{ch}) was considered isotropic, overall motion of s-CH₂ may be described by the Woessner model¹⁵. The spectral density only depends on the overall diffusion coefficient R_1 and on a constant R equal to 3/2 of the total rate of jumping of the side carbon from any of its three equilibrium positions¹⁵. The expression of $J(\omega)$ simplifies to:

$$J(\omega) = A \frac{\tau_{ch}}{1 + \omega^2 \tau_{ch}^2} + B \frac{\tau_0}{1 + \omega^2 \tau_0^2}$$

where

$$A = \frac{1}{4} (3 \cos^2 \theta - 1)^2$$

$$B = \frac{3}{4} \sin^2 \theta (1 + 3 \cos^2 \theta)$$

$$\tau_0^{-1} = \tau_{ch}^{-1} + \tau_L^{-1}$$

with

$$\tau_{ch} = \frac{1}{6R_1}$$

and

$$\tau_L = \frac{1}{R}$$

θ is the angle between the reorienting C-H vector and the internal rotation axis.

Using at each temperature the value of τ_{ch} reported in the previous section, we computed the theoretical T_1 corresponding to a wide range of τ_L . Matching values of theoretical and experimental T_1 leads to the appropriate τ_L which are collected in Table 4. It appears that the internal rate of rotation of s-CH₂ is of the same order of magnitude as the chain reorientation one. In this case the approximate expression of Doddrell (equation 3) becomes valid and leads, as may be seen in Table 4, to close values of τ_L . An activation energy of 21 kJ/mol (Figure 3) is observed which might mean, as the conformational barrier for the side CH₂

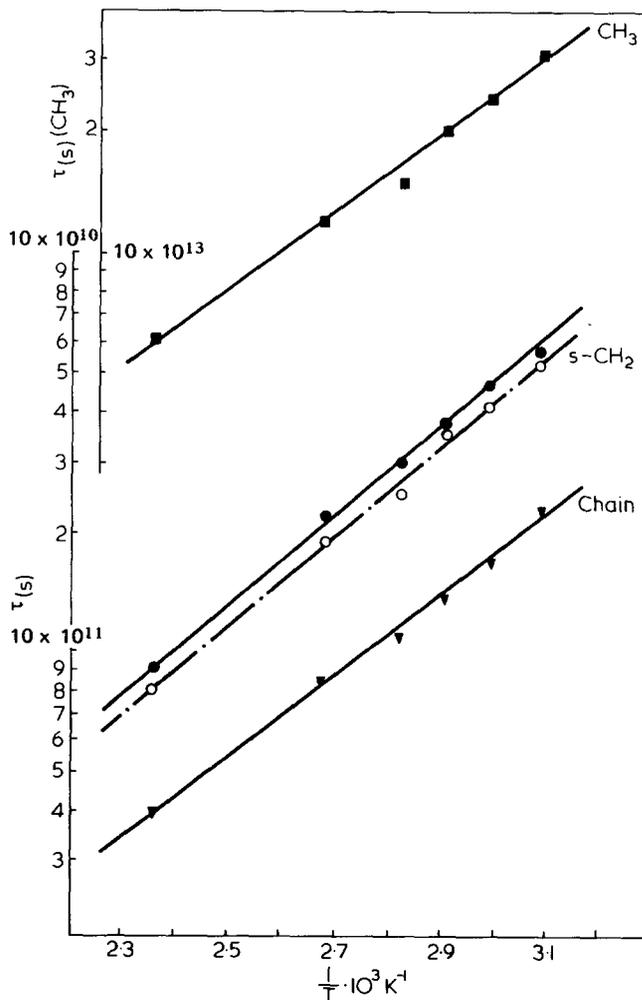


Figure 3 Semilogarithmic plots of τ vs. $1/T$ for the backbone motion (\blacktriangle) and internal motions of side methylene (\bullet , Woessner's model; \circ , approximate relation) and methyl (\blacksquare) groups

approaches that of the chain, that freedom of conformational jumps is strongly dependent on the mobility of adjacent segments of the chain. Such an effect has been reported by Heatley⁷ to explain the hindrance of methyl rotation in polyisobutene and was supported by parallel increases in correlation times for backbone and side methyl motions when increasing concentration. It may be seen in *Figure 1* that a similar behaviour is observed in our case.

It was nevertheless important to test the influence of an eventual anisotropy of chain motion upon the correlation times derived for the rotation of side methylene. First, anisotropy of main chain motion was accounted for by the symmetrical ellipsoid description through its more general expression of spectral density⁹, defined with the following three correlation times and three parameters *A*, *B*, *C*:

$$J(\omega) = \frac{A\tau_A}{1 + \omega^2\tau_A^2} + \frac{B\tau_B}{1 + \omega^2\tau_B^2} + \frac{C\tau_C}{1 + \omega^2\tau_C^2} \quad (5)$$

$$A = \frac{1}{4} (3 \cos^2 \Delta - 1)^2 \quad \tau_A^{-1} = 6R_2$$

$$B = 3 \sin^2 \Delta \cos^2 \Delta \quad \tau_B^{-1} = R_1 + 5R_2$$

$$C = \frac{3}{4} \sin^4 \Delta \quad \tau_C^{-1} = 4R_1 + 2R_2$$

where *R*₁, *R*₂ are the rotational diffusion constants about major and minor axes, and Δ, the angle between the internuclear C–H vector of chain methine and the symmetry axis of the ellipsoid. Anisotropic models were chosen by computing theoretical *T*₁ over wide ranges of Δ (0 to 2π), of *R*₁/*R*₂ (1 to 50) and for values of τ_C of the same order of magnitude as that found for isotropic τ_{ch} at 60°C (from ~ τ_{ch}/3 to τ_{ch}). Sets of parameters leading to matching values of experimental and theoretical chain *T*₁ were selected to cover a large scale of anisotropy, and corresponding values of τ_A, τ_B are collected in *Table 5*.

Second, the s-CH₂ group was supposed attached to this symmetrical ellipsoid, and to undergo isotropic rotation through conformational jumps about an axis fixed with respect to the symmetry axis of the ellipsoid.

The model has been proposed and discussed in detail by Woessner²⁴ and leads to the following expression of spectral density:

$$J(\omega) = \frac{A\tau_A}{1 + \omega^2\tau_A^2} + \frac{A'\tau_{A'}}{1 + \omega^2\tau_{A'}^2} + \frac{B\tau_B}{1 + \omega^2\tau_B^2} + \frac{B'\tau_{B'}}{1 + \omega^2\tau_{B'}^2} + \frac{C\tau_C}{1 + \omega^2\tau_C^2} + \frac{C'\tau_{C'}}{1 + \omega^2\tau_{C'}^2} \quad (6)$$

where τ_A, τ_B, τ_C describe the anisotropic chain motion and τ_L the internal rotation of side methylene group.

$$\tau_{A'}^{-1} = \tau_A^{-1} + \tau_L^{-1}$$

$$\tau_{B'}^{-1} = \tau_B^{-1} + \tau_L^{-1}$$

$$\tau_{C'}^{-1} = \tau_C^{-1} + \tau_L^{-1}$$

with

$$A = \frac{1}{16} (1 - 3 \cos^2 \alpha)^2 (1 - 3 \cos^2 \theta)^2$$

$$A' = \frac{9}{32} (\sin^2 2\alpha \sin^2 2\theta + \sin^4 \alpha \sin^4 \theta)$$

$$B = \frac{3}{16} \sin^2 2\alpha (3 \cos^2 \theta - 1)^2$$

$$B' = \frac{3}{8} \left[(\cos^2 2\alpha + \cos^2 \alpha) \sin^2 2\theta + (\sin^2 \alpha + \frac{1}{4} \sin^2 2\alpha) \sin^4 \theta \right]$$

$$C = \frac{3}{16} \sin^4 \alpha (3 \cos^2 \theta - 1)^2$$

$$C' = \frac{3}{8} (\sin^2 \alpha + \frac{1}{4} \sin^2 2\alpha) \sin^2 2\theta + \frac{3}{32} \left[(1 + \cos^2 \alpha)^2 + 4 \cos^2 \alpha \right] \sin^4 \theta$$

θ is the constant angle between the internuclear C–H vector of s-CH₂ and the axis of internal rotation of this group (θ = 109° 28'), and α, which is the angle between the axis of internal rotation and the symmetry axis of the ellipsoid, is then equal to (109° 28' - Δ).

Again computation with the different sets of τ_A, τ_B, τ_C over a wide range of τ_L led to matching values of theoretical and experimental *T*₁ of side methylene. Corresponding values of τ_L were extracted, and it may be observed on some examples collected in *Table 5* that τ_L is nearly insensitive to anisotropy of chain motion. Such attempts clearly remain questionable and they only might indicate that the use of a single τ description of chain motion may lead in this particular case to a correct order of magnitude of the correlation time derived, through the Woessner model, for side -CH₂ internal rotation.

Motional analysis of methyl relaxation data

Motional analysis of side CH₃ was performed in a very similar way. This group was considered to experience its own isotropic internal rotation (τ_G) around the CH₂-CH₃ bond, and the anisotropic motion of s-CH₂ itself described by a two correlation times Woessner's model (segmental isotropic τ_{ch} + internal rotation τ_L). In this case τ_A of equation (6) represents the single correlation time τ_{ch} of the chain motion whereas τ_B and τ_C are equal to τ₀ defined as:

Table 5 Examples of arbitrary anisotropic description of chain motion and influence on side methylene internal correlation time at 60°C

<i>R</i> ₁ / <i>R</i> ₂	cos ² Δ	τ _C × 10 ¹⁰ (sec)	τ _B × 10 ¹⁰ (sec)	τ _A × 10 ¹⁰ (sec)	τ _L × 10 ¹⁰ (sec)
1 (isotropic)	—	1.70	1.70	1.70	4.7
2	0.4	1.36	1.95	2.3	4.4
3	0.05	1.25	2.3	3.1	4.4
8	0.5	0.75	2.0	4.3	4.4
10	0.15	0.86	2.4	6.0	3.2
50	0.4	0.50	1.8	17.0	3.4

(*R*₁/*R*₂, Δ, τ_C are chosen parameters — see text)

Table 6 Correlation times for internal rotation of side methyl group. $E_a \pm 10\% = 18$ kJ/mol

T (°)	$\tau_G \times 10^{12}$ (sec)
50	3.1
60	2.4
70	2.0
80	1.5
100	1.2 (7.5)*
150	0.6

r_{C-H} in CH_3 : 1.10Å r_{C-H} in CH_2 : 1.02Å

* Value calculated for isotactic polypropylene from T_1 measurements of Inoue⁵ and by using the Woessner's two correlation times model (equation 4)

$$\tau_0^{-1} = \tau_{ch}^{-1} + \tau_L^{-1}$$

Assuming that the CCC angle of $CH-CH_2-CH_3$ bonds is roughly equal to the CCH angle in CH_3 group ($\alpha \sim \theta = 110^\circ 22'$)²³ and owing to fulfilment of extreme narrowing condition, expression (6) for the spectral density function simplifies and leads to the theoretical T_1 :

$$\frac{1}{T_1(CH_3)} = 3h^2\gamma_H^2\gamma_C^2 r^{-6}(A''\tau_{ch} + B''\tau_0 + C''\tau_1 + D''\tau_2) \quad (7)$$

where

$$\tau_0^{-1} = \tau_{ch}^{-1} + \tau_L^{-1}$$

$$\tau_1^{-1} = \tau_{ch}^{-1} + \tau_L^{-1} + \tau_G^{-1}$$

$$\tau_2^{-1} = \tau_{ch}^{-1} + \tau_G^{-1}$$

$$A'' = \frac{1}{16} (1 - 3 \cos^2\theta)^4$$

$$B'' = \frac{3}{16} (1 - 3 \cos^2\theta)^2 (\sin^2 2\theta + \sin^4\theta)$$

$$C'' = \frac{3}{8} \left[\sin^4\theta \left(2 - \frac{3}{4} \sin^4\theta \right) + \sin^2 2\theta \left(2 - \frac{3}{4} \sin^2 2\theta \right) \right]$$

$$D'' = \frac{9}{32} (\sin^4 2\theta + \sin^8\theta)$$

Correlation times τ_G of methyl group internal rotation were deduced after introduction of the previous τ_{ch} and τ_L values in expression (7) and computation of the theoretical T_1 (Table 6).

A corresponding activation energy of 18 kJ/mol is obtained, close to that found for segmental reorientation. The simultaneous increase of τ_G , τ_L and τ_{ch} for highest polymer concentrations at 150°C (Figure 1) might indicate that internal motion of the methyl group is dependent on chain motion.

In fact, internal rotation of side methyl appears much faster than the sequential reorientation, and the difference between τ_{ch} and τ_G clearly reflects the large gap observed

between the respective T_1 of chain and methyl carbons (see Table 1). It may be noted that, owing to the low value of τ_G , the terms $A''\tau_{ch}$ and $B''\tau_0$ in equation (7) predominate and the above model is used close to its boundary conditions. Thus confidence in values of τ_G must be limited to their order of magnitude and their temperature dependence. Nevertheless it may be concluded that methyl rotation in polybutene is more rapid than in polypropylene. Difference between T_1 is significant, and in order to compare the corresponding correlation times, we exploited the relaxation data of Inoue⁵ on polypropylene in solution at 100°C by using Woessner's model (equation 4). Values obtained (Table 6) for the respective rates agree with the higher freedom which is expected for the side methyl rotation in polybutene as this group is linked to a methylene and thus is less sterically crowded. Noting that the observed segmental mobility of polypropylene is higher than that of poly(but-1-ene), the large and unexpected difference between rates of segmental reorientation and internal rotation of side methyl in polybutene, may appear reasonable. Furthermore, the rapid increase in mobility along side aliphatic branches in polymers has been previously pointed out. Levy²⁵ reported a factor of 30 between correlation times of backbone motion and terminal methyl rotation in side butyl chains of poly(butyl methacrylate) observed at 35°C on 25% w/v solution in tetrachlorethylene. It remains however obscure why the rapid rotation of methyl group in poly(but-1-ene) is so strongly dependent on motion about chain bonds and why the barrier associated to this rotation is higher than that observed in polypropylene⁵ and in poly(propylene oxide)⁷. A possible explanation might be the effect on methyl rotation of the intramolecular packing of side groups, depending itself on segmental motion of the chain. This assumption was formulated by Hirai²⁶ to account for the difference in mobilities observed for the terminal methyl group of long side chains (C-18) and shorter (C-4) in poly(alkyl methacrylates).

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