Macromolecules **1983**, *16*, 415–420

(7) Jelinski, L. W.; Dumais, J. J.; Engel, A. K. *Macromolecules*, preceding paper in this issue.
(8) Jelinski, L. W.; Schilling, F. C.; Bovey, F. A. *Macromolecules* **1981**, *14*, 581.
(9) Jelinski, L. W. *Macromolecules* **1981**, *14*, 1341.
(10) Wolfe, J. R., Jr. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1978**, *19*(1), 5.
(11) Steger, T. R.; Schaefer, J.; Stejskal, E. O.; McKay, R. A. *Macromolecules* **1980**, *13*, 1127.
(12) Becker, E. D. "Higher Resolution NMR", 2nd ed.; Academic Press: New York, 1980; pp 232–237.
(13) Werbelow, L. G.; Grant, D. M. *J. Chem. Phys.* **1975**, *63*, 4742.
(14) Opella, S. J.; Nelson, D. J.; Jardetzky, O. *J. Chem. Phys.* **1976**, *64*, 2533.
(15) VanderHart, D. L.; Garroway, A. N. *J. Chem. Phys.* **1979**, *71*, 2773 and references cited.
(16) Schaefer, J.; Sefcik, M. D.; Stejskal, E. O.; McKay, R. A. *Macromolecules*, submitted.
(17) Lyerla, J. R., Jr.; Horikawa, T. T. *J. Phys. Chem.* **1976**, *80*, 1106.
(18) Mantsch, H. H.; Saito, H.; Smith, I. C. P. In *Prog. Nucl. Magn. Reson. Spectrosc.* **1977**, *11*, 211–271.
(19) Schaefer, J.; Natusch, D. F. S. *Macromolecules* **1972**, *5*, 416.
(20) Allerhand, A.; Doddrell, D.; Komoroski, R. *J. Chem. Phys.* **1971**, *55*, 189.
(21) Schaefer, J. *Macromolecules* **1972**, *5*, 427.
(22) Schaefer, J. *Macromolecules* **1973**, *6*, 882.
(23) See, for example: Dechter, J. J.; Axelson, D. E.; Dekmezian, A.; Glotin, M.; Mandelkern, L. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 641.
(24) See, for example: Lyerla, J. R., Jr.; Levy, G. C. In "Topics in Carbon-13 NMR"; Levy, G. C., Ed.; Wiley: New York, 1974.
(25) Jelinski, L. W.; Dumais, J. J.; Watnick, P. I.; Bass, S. V.; Shepherd, L. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 3285.
(26) Komoroski, R. A. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 45.
(27) Menick, Z. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 2173.
(28) Alter, U.; Bonart, R. *Colloid Polym. Sci.* **1976**, *254*, 348.
(29) Riande, E. *Eur. Polym. J.* **1978**, *14*, 885.
(30) Yokouchi, M.; Sakakibara, Y.; Chatani, Y.; Tadokoro, H.; Tanaka, T.; Yoda, K. *Macromolecules* **1976**, *9*, 266.
(31) Desborough, J.; Hall, I. H. *Polymer* **1977**, *18*, 825.
(32) Hall, I. H.; Pass, M. G. *Polymer* **1976**, *17*, 807.
(33) Stach, W.; Holland-Moritz, K. *J. Mol. Struct.* **1980**, *60*, 49.
(34) Tashiro, K.; Nakai, Y.; Kobayashi, M.; Tadokoro, H. *Macromolecules* **1980**, *13*, 137.
(35) Wunderlich, B. J. *J. Chem. Phys.* **1962**, *37*, 2429.
(36) Comments by T. F. Schatzki following paper by: Reding, F. P.; Faucher, J. A.; Whitman, R. D. *J. Polym. Sci.* **1962**, *57*, 483.
(37) Schatzki, T. F. *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.* **1965**, *6*(2), 646.
(38) Rosenke, K.; Sillescu, H.; Spiess, H. W. *Polymer* **1980**, *21*, 757.
(39) Jelinski, L. W.; Dumais, J. J.; Engel, A. K. *Macromolecules* **1983**, *16*, 492.

Dynamics of Macromolecular Chains in Solution. Nuclear Magnetic Relaxation of Aryl–Aliphatic Polyesters

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ABSTRACT: Proton and carbon-13 NMR relaxation data at several field strengths have been determined as a function of temperature for two aryl–aliphatic polyesters differing by the length of the aliphatic segment separating neighboring terphenyl groups. The solution-state motional dynamics of these two polymers can be interpreted in terms of four correlation times: τ_0, τ_{ir}, θ, and ρ. The correlation time for overall isotropic reorientation of the terphenyl moiety is τ_0, τ_{ir} is the internal correlation time for phenylene ring rotation, θ describes the mean correlation time for isotropic reorientation of the aliphatic groups and is found to be equal to τ_0 for the methylene carbon next to the carboxyl unit, and ρ is the mean correlation time for the diffusive processes that relax the aliphatic subchain. According to the terminology of Helfand, results thus obtained show that these ρ processes are fast type 1 or type 2 short-range motions, whereas θ modes are much slower type 3 long-range motions. Moreover, type 2 motions are more likely in the longer aliphatic subchain whereas mainly crankshaft motions or three-bond jumps occur in the shorter one.

Over the past few years, a considerable amount of work has aimed at interpreting relaxation measurements on polymers in solution in terms of local chain motions. Several conformational jump models[1-3] have been proposed and lead to autocorrelation functions that have proved most powerful for accounting for fluorescence depolarization,[4] dielectric relaxation,[5] and nuclear spin relaxation[2,3,6-10] data. Extensive tests of these descriptions of the segmental motion of polymers have been performed by making use of, for example, carbon-13 NMR at two field strengths,[6] by investigating coupled relaxation between nonequivalent protons in vinyl polymers by three different experiments[8] probing both high- and low-frequency portions of the spectral density, and by carrying out proton spin–lattice relaxation time determinations over the observation frequency range 5–100 MHz,[10] thus extending the dynamic range over 5–200 MHz.

However, in spite of the success of these conformational jump models in representing these important sets of data obtained on a number of polymers in solution,[11] very little information is available on the detailed elementary molecular processes responsible for the segmental main-chain motion. Electron spin resonance experiments on spin-labeled polymers have pointed out the very local nature of the fastest modes: Measurements carried out on poly(ethylene oxide) have shown that about one monomer unit may be considered as involved in the ESR relaxation process.[12] The same study in the case of polystyrene leads to one to five monomer units, depending on the experimental conditions.[13] Even these short-range motions have not been yet identified. Certain modes of motion such as the Schatzki crankshaft[14] or the three-bond motion[15] have been proposed. The important point is that they involve two barrier crossings. Using Brownian dynamics simulations, Helfand has described other types of localized processes requiring only slightly more than one barrier height separating the trans and gauche state.[16] From an exper-

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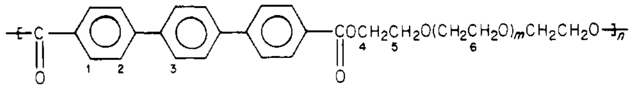
imental point of view, measured activation energies are often of the order of one energy barrier. Liao, Okamoto, and Morawetz have ruled out the possibility of crankshaft motions by comparing the temperature dependence of excimer fluorescence intensity in a polymer and in a small-molecule analogue.[17] However, there exist contradictory conclusions.[18]

Therefore, in order to gain deeper insight into the precise nature of the localized motional modes of polymers in solution, it appeared of interest to study the nuclear magnetic relaxation of polyesters of general formula



$m = 2$, polymer A
$m = 8$, polymer B

These polymers have large terphenyl groups, which may act as anchors for the rapid short-range processes affecting the aliphatic part of the molecule. Besides, the variable length of this aliphatic subchain may contribute to the identification of some elementary modes. It is also noticeable that the number of monomer units is large enough, at least for $m = 8$, to approach the dynamic behavior of a poly(ethylene oxide) chain.

Experimental Section

The polyesters were prepared by B. Fayolle at the Centre de Recherches des Carrières de Rhône-Poulenc, Saint-Fons, France. They were synthesized by reaction of di-*n*-propyl *p*-terphenyl-4,4″-dicarboxylate with the appropriate diol, as described elsewhere.[19,20] Inherent viscosities [$\eta_{\mathrm{inh}} = \ln(\eta_{\mathrm{rel}})/C$] were determined at 25 °C and for a polymer concentration C of 0.6 g/100 mL of solution in dichloroacetic acid. They strongly supported high molecular weights (0.6 dL·g^{-1} for $m = 2$ and 0.69 dL·g^{-1} for $m = 8$).

NMR experiments were carried out on 10% (w/v) deuteriochloroform solutions of these polymers. Solutions were carefully degassed and the tubes were sealed under vacuum.

The 20-MHz ^{13}C and 80-MHz ^{1}H NMR spectra were recorded on a Varian Associates CFT-20 spectrometer. The 25.15-MHz ^{13}C NMR spectra were obtained on a Jeol PS100 apparatus and the 62.9-MHz ^{13}C spectra on a Bruker WP250 spectrometer. Spin–lattice relaxation times T_1 were measured by using the standard inversion–recovery [π–t–$\pi/2$] technique, with repetition times between pulse sequences greater than 5 times the longest T_1 of the considered nuclei. Due to the very long relaxation times of nonprotonated carbons and required number of about 1000 transients, relaxation parameters were determined for the protonated carbons only. T_1 values were derived from plots of ln ($I(\infty) - I(t)$) vs. t. In all cases a proper linearity was observed.

Nuclear Overhauser enhancements (NOE) were measured by using a gate decoupling technique. Each reported T_1 or NOE value was an average of 2–3 separate determinations and is within an estimated maximum error of ±10%.

Theoretical Background

With the assumption of a purely ^{13}C–^{1}H dipolar relaxation mechanism, the spin–lattice relaxation time T_1 and the nuclear Overhauser enhancement (NOE) obtained from a ^{13}C experiment are given by the well-known expressions[21]

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

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

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

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

Here, $G(\tau)$ is the normalized second-order spherical harmonic autocorrelation function.

In the same way, by assuming a purely ^{1}H–^{1}H dipolar relaxation mechanism between proton pairs, the spin–lattice relaxation time T_1 obtained from a proton experiment is[22]

$$\frac{1}{T_1} = \frac{3}{10}\gamma_H^4\hbar^2 r^{-6}[J(\omega_H) + 4J(2\omega_H)] \quad (3)$$

For an isotropic rotation of the internuclear vector, $J(\omega)$ can be written as

$$J(\omega) = \tau_R/(1 + \omega^2\tau_R^2) \quad (4)$$

where τ_R is the rotational correlation time.

The segmental motion of a polymer chain in solution is usually too complicated to be described by such a simple picture. Among the various motional models used to represent relaxation data, conformational jump models have been found to account well for fluorescence depolarization,[4] dielectric relaxation,[5] and nuclear spin relaxation data for polymers in solution.[2,3,6–10] Three different expressions have been derived for the corresponding autocorrelation function.[1–3] They all lead to similar decrease of $G(t)$ vs. t in the time range of interest. As in the present state of the experimental technique there appears no means to distinguish between these three theoretical descriptions of main-chain polymer relaxation, we will restrict our study to the use of the diamond lattice motional model of Valeur, Jarry, Gêny, and Monnerie (VJGM)[1] as a basis for qualitative interpretation of experimental results. In this case, the description of the motion requires two correlation times ρ and θ. In the original treatment ρ characterized the three-bond process in an ideal diamond lattice, and θ reflected either isotropic modes of subchains or discrepancies from the ideal lattice. At the present time, it is clear that the orientation autocorrelation function derived by these authors does not depend on the precise description of local motions. Indeed the most important feature comes from the resulting effect of these motions on chain bond orientation. From this point of view, two classes of motions must be considered:

The first class corresponds to any process leading to a diffusion of chain orientation along the chain (three-bond motions and crankshaft motions belong to this class). These modes are described by a harmonic mean correlation time ρ.

The second class deals with processes resulting in a loss of orientation without implying any conformational transitions of neighbor bonds (overall rotation, valence angle, and internal rotation angle fluctuations belong to this class). These processes are characterized by a harmonic mean correlation time θ.

$J(\omega)$ is written

$$J(\omega) = \theta\{1 + (\theta/2\rho)^{1/2}[1 + (1 + \omega^2\theta^2)^{1/2}]^{1/2}\}/\{1 + \omega^2\theta^2 + 1/2\theta(1 + \omega^2\theta^2)^{1/2} + (2\theta/\rho)^{1/2}(1 + \omega^2\theta^2)^{1/2}[1 + (1 + \omega^2\theta^2)^{1/2}]^{1/2}\} \quad (5)$$

Results and Discussion

1. Motional Analysis of Aromatic Nuclei Relaxation Data. Proton Spin–Lattice Relaxation Times. The proton spectrum of the terphenyl groups of polyesters A and B presents three peaks. In a 180°–t–90° spin–lattice

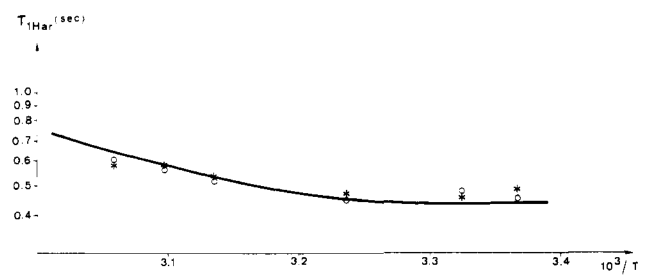


Figure 1. Proton spin-lattice relaxation times $T_{1H_{ar}}$ of aromatic protons of polyesters A and B in $CDCl_3$ solution as a function of temperature T at 80 MHz: (○) polyester A; (*) polyester B.

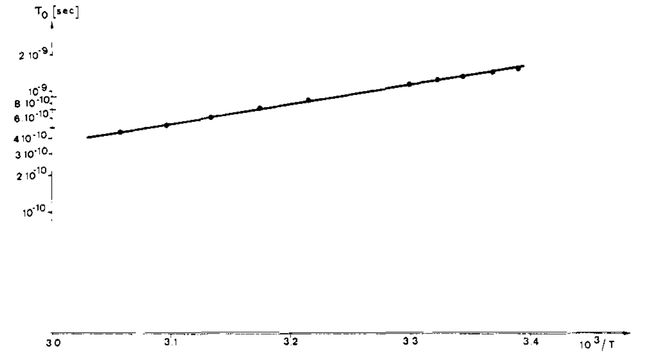
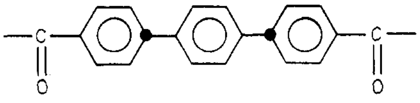
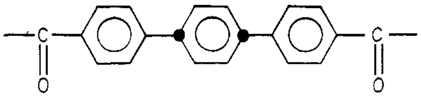
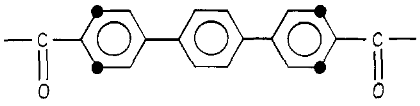
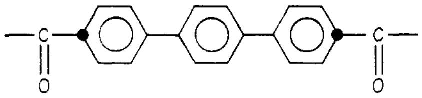
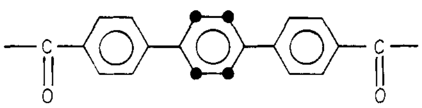
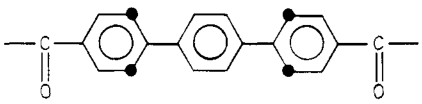
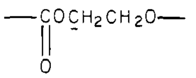
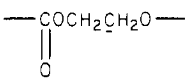
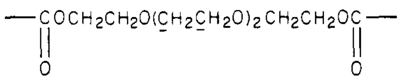


Figure 2. Isotropic diffusional rotational correlation times τ_0 calculated from data reported in Figure 1.

experiment at 80 MHz, each of these lines has an exponential decrease as a function of interval t, which is characterized by the same spin-lattice relaxation time $T_{1H_{ar}}$. No cross-correlation effect is apparent in the purely exponential decay of the magnetization. Moreover, the observation that any aromatic proton, whatever its location on the terphenyl group, has the same relaxation time $T_{1H_{ar}}$, corroborates the fact that spin-lattice relaxation of these nuclei is dominated by dipolar interaction between pairs of protons bonded to adjacent aromatic carbons. In such a case, the proton-proton internuclear vector is parallel to the long symmetry axis of the terphenyl group and is not sensitive to any internal rotation of the phenyl rings about this axis. Therefore the simplest assumption to interpret the relaxation times $T_{1H_{ar}}$ in terms of motion is to use an isotropic diffusional rotational model for the reorientation of these internuclear vectors. This assumption is supported by the dependence of $T_{1H_{ar}}$ as a function of temperature (Figure 1), which shows the characteristic features of a Bloembergen, Purcell, and Pound (BPP) curve.[23] The isotropic correlation times τ_0 deduced from the BPP formula[23] using an internuclear distance of 2.45 Å are shown in Figure 2. The value of $T_{1H_{ar}}$ at the minimum of the curve calculated from this internuclear distance of 2.45 Å is 0.45 s, in agreement with the experimental determination. Polymers A and B present identical behavior as a function of temperature. There is no dependence of $T_{1H_{ar}}$ and τ_0 upon the length of the aliphatic chain. The τ_0 variation on temperature for the two polyesters is characterized by an activation energy of 7.5 kcal/mol.

Nuclear Overhauser Enhancements and Spin-Lattice Relaxation Times of Carbon-13 Atoms. The ^{13}C spectrum of polyester A in $CDCl_3$ solution is shown in Figure 3. ^{13}C chemical shifts are summarized in Table I. Peak assignments of aromatic carbons are based upon the use of empirical parameters for the calculation of chemical shifts in substituted benzenes[24] and are supported by relative peak intensities and spin-lattice relaxation times T_{1C}. In particular, assignments of carbons C_2 and C_3 rely on the fact that the C_2 spin-lattice relaxation time T_{1C} is equal to C_1 T_{1C}, whereas C_3 T_{1C} is longer. Similar results are obtained for polymer B.

Table I
^{13}C Peak Assignments of Polymer A in $CDCl_3$ Solution

^{13}C peak assignment	δ_C, ppm ($(CH_3)_4Si$)
C=O	166.2
	144.7
	139.5
	130.2
	129.0
	127.6
	126.7
 $-\underset{\underset{\text{O}}{\Vert}}{\text{C}}\text{O}\underline{\text{C}}\text{H}_2\text{CH}_2\text{O}-$	64.1
 $-\underset{\underset{\text{O}}{\Vert}}{\text{C}}\text{OCH}_2\underline{\text{C}}\text{H}_2\text{O}-$	69.2
 $-\underset{\underset{\text{O}}{\Vert}}{\text{C}}\text{OCH}_2\text{CH}_2\text{O}(\underline{\text{C}}\text{H}_2\underline{\text{C}}\text{H}_2\text{O})_2\text{CH}_2\text{CH}_2\text{O}\underset{\underset{\text{O}}{\Vert}}{\text{C}}-$	70.6

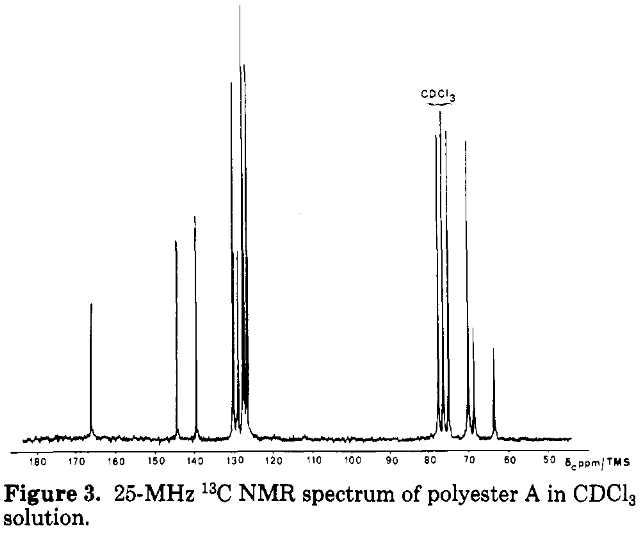


Figure 3. 25-MHz ^{13}C NMR spectrum of polyester A in $CDCl_3$ solution.

Spin-lattice relaxation times T_{1C} and nuclear Overhauser enhancements (NOE) measured at 20, 25, and 63 MHz for the aromatic C_1, C_2, and C_3 carbons of polyesters A and B at 27 °C are listed in Table II. All these results can be analyzed in terms of motion using the isotropic diffusional correlation time τ_0, derived from proton experiments at 80 MHz, and a stochastic diffusion of each of the phenyl rings about the long axis of the terphenyl

Table II
Experimental and Calculated Parameters Describing Relaxation Data of Aromatic Nuclei of Polyesters A and B in $CDCl_3$ Solution at 27 °C

carbon and proton line		80 MHz H_1 T_{1ar}, s	20 MHz ^{13}C T_1, s	25 MHz ^{13}C T_1, s	25 MHz NOE	63 MHz ^{13}C T_1, s	63 MHz NOE
			Polyester A (m = 2)				
3	exptl	0.45	0.70	0.72	2.7	0.74	3.0
	calcd	0.45	0.72	0.72	3.0	0.73	3.0
	best fit correl times			$\tau_0 = 1.3 \times 10^{-9}$ s $\tau_{ir} = 6.8 \times 10^{-11}$ s			
1, 2	exptl	0.45	0.42	0.44	2.7	0.46	3.0
	calcd	0.45	0.42	0.43	3.0	0.44	2.9
	best fit correl times			$\tau_0 = 1.3 \times 10^{-9}$ s $\tau_{ir} = 1.2 \times 10^{-10}$ s			
			Polyester B (m = 8)				
3	exptl	0.45	0.70	0.80	2.7	0.82	3.0
	calcd	0.45	0.72	0.81	3.0	0.82	3.0
	best fit correl times			$\tau_0 = 1.3 \times 10^{-9}$ s $\tau_{ir} = 6 \times 10^{-11}$ s			
1, 2	exptl	0.45	0.50	0.52	2.7	0.50	3.0
	calcd	0.45	0.50	0.52	3.0	0.51	3.0
	best fit correl times			$\tau_0 = 1.3 \times 10^{-9}$ s $\tau_{ir} = 1 \times 10^{-10}$ s			

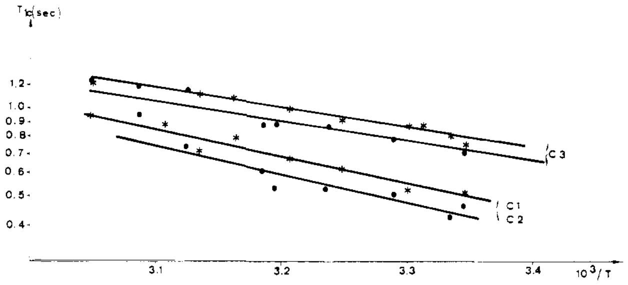


Figure 4. ^{13}C spin–lattice relaxation times of carbons C_1 and C_2 (outer rings) and C_3 (inner ring) of polyesters A and B as a function of temperature T at 25 MHz: (●) polyester A; (*) polyester B.

group described by a correlation time τ_{ir}, as formulated by Woessner.[25] The best fit parameters are given in Table II. The agreement between experimental and calculated data is very good. The internal rotations of the phenyl rings are slightly faster in polymer B (m = 8) than in polymer A (m = 2). For each polymer, the rate of rotation is greater for the central ring than for the outer ones. This result is in good agreement with X-ray and neutron diffraction studies of p-terphenyl crystals,[26] which have demonstrated that the central ring oscillates more strongly about the long axis of the molecule than do the two end rings. The rates of the thermal librations thus observed are generally consistent with potential energy functions calculated for rotation about the symmetry axes of the molecule.[26]

The dependence on temperature of the spin–lattice relaxation times T_{1C} of the aromatic C_1, C_2, and C_3 carbons at 25 MHz is plotted in Figure 4. The nuclear Overhauser enhancement measured on these nuclei at 25 MHz is maximum over the range of temperature of interest. As well as the 27 °C data, these variable-temperature data are well represented by the isotropic τ_0 process, the values of which are given in Figure 2, and internal phenyl ring reorientation τ_{ir}. The activation energies for the latter motion are summarized in Table III. Within experimental error, the same values are obtained for the two polymers. There is no dependence of the activation energy of the inner and outer ring rotations about the long axis of the terphenyl group upon the length of the aliphatic part of the polyester chain. Such a result has been observed by Komoroski,[27] who has shown that in a series of terephthalic acid polyesters the relaxation parameters of all carbons in the terephthalate groups are independent of the length of the separating alkyl chain. The same conclusion has been reached by conformational energy calculations on model molecules of polymers A and B.[28] The 5 kcal/mol energy barrier determined for the internal rotation of the outer ring is in close agreement with the 4.8 kcal/mol value derived from conformational energy calculations, assuming independent rotation of each of the three rings of the terphenyl unit.[28] In the same way, the 3.0–3.5 kcal/mol experimental activation energy for the internal inner ring rotation about the long axis of the terphenyl moiety is consistent with the 3.8 kcal/mol barrier height calculated under the same assumptions.[28]

Table III
Apparent Activation Energy[a] for Individual Carbons of Polyesters A and B

polymer	carbon $C_{1,2}$[b]	C_3[b]	C_6[c]
polyester A (m = 2)	5.0 ± 0.5	3.5 ± 0.5	7.0 ± 0.5
polyester B (m = 8)	4.8 ± 0.5	3.0 ± 0.5	4.0 ± 0.5

[a] kcal/mol. [b] Calculated from variation of τ_{ir}. [c] Calculated from variation of ρ.

2. Motional Analysis of Aliphatic Carbon Relaxation Data. The aliphatic part of the spectrum of polyesters A and B presents three well-resolved peaks as shown in Figure 3. The two high-field ones (C_4 and C_5) are to be assigned to the methylene carbons of the oxyethylene unit next to the terphenyl ring. The third line (C_6) groups all the methylene carbons of the central oxyethylene units. Data obtained at 27 °C for the three experimental frequencies are summarized in Table IV. As shown in the table, these results, both spin–lattice relaxation times T_{1C} and nuclear Overhauser enhancements, are well represented with the VJGM model.[1] The length of the aliphatic C–H bond is taken as 1.1 Å. The isotropic diffusional correlation time θ, deduced from C_4 relaxation data, is equal to τ_0 derived from proton experiments, indicating that the terphenyl, the two carboxyl groups, and the methylene units next to them reorient as a whole in the

Table IV
Comparison between Experimental and Calculated Parameters from the Diamond Lattice Motional Model for Aliphatic Lines of Polyesters A and B in $CDCl_3$ Solution at 27 °C

		polyester A (m = 2)					polyester B (m = 8)				
		20 MHz	25 MHz		63 MHz		20 MHz	25 MHz		63 MHz	
line		T_{1C}, s	T_{1C}, s	NOE	T_{1C}, s	NOE	T_{1C}, s	T_{1C}, s	NOE	T_{1C}, s	NOE
C_4	exptl	0.15	0.19	2.7	0.28	2.3	0.20	0.21	2.7	0.34	2.3
	calcd	0.18	0.19	2.7	0.27	2.3	0.21	0.22	2.7	0.31	2.4
	diamond lattice parameters	$\theta = 1.3 \times 10^{-9}$; $\rho = 2.4 \times 10^{-11}$ s					$\theta = 1.3 \times 10^{-9}$; $\rho = 1.7 \times 10^{-11}$ s				
C_5	exptl	0.17	0.20	2.7	0.35	2.3	0.25	0.25	2.7	0.33	2.3
	calcd	0.20	0.21	2.7	0.29	2.4	0.23	0.24	2.7	0.33	2.4
	diamond lattice parameters	$\theta = 1.2 \times 10^{-9}$; $\rho = 2 \times 10^{-11}$ s					$\theta = 1.2 \times 10^{-9}$; $\rho = 1.5 \times 10^{-11}$ s				
C_6	exptl	0.56	0.55	2.7	0.70	2.4	0.70	0.68	2.7	0.80	2.4
	calcd	0.51	0.54	2.8	0.70	2.5	0.64	0.66	2.8	0.83	2.5
	diamond lattice parameters	$\theta = 1.1 \times 10^{-9}$; $\rho = 2.8 \times 10^{-12}$ s					$\theta = 9 \times 10^{-10}$; $\rho = 2.1 \times 10^{-12}$ s				

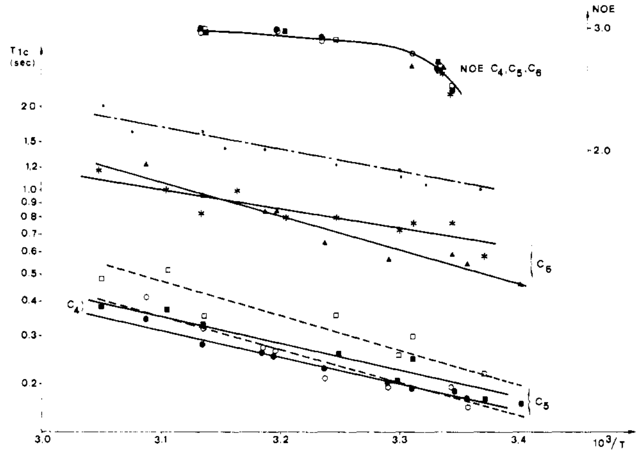


Figure 5. ^{13}C spin-lattice relaxation times and nuclear Overhauser enhancements of carbons C_4 (●, ■), C_5 (○, □), and C_6 (▲, *) of polyesters A and B, respectively, as a function of temperature T at 25 MHz. (•, ★) ^{13}C spin-lattice relaxation times of poly(ethylene oxide) at 20 and 25 MHz.

θ process. This correlation time θ is slightly shorter for the C_5–H and C_6–H internuclear vectors. The influence of the length of the aliphatic subchain is only visible for the central oxyethylene units. Similarly, the diffusive process characterized by correlation time ρ is faster for the central aliphatic methylene carbons than for those next to the terphenyl moiety. Moreover, this diffusive process is strongly dependent on the number of oxyethylene monomers. Comparable results were obtained on the methylene carbons of poly(butylene terephthalate) and poly(hexamethylene terephthalate),[27] for which it was noted that the average correlation time $\bar{\tau}$ necessary to explain the data decreases with increasing distance from the aromatic units and that, in addition, $\bar{\tau}$ for a methylene carbon in a given position decreases with increasing chain length. Moreover, it might be expected that the increasing T_1 observed for the C_6 line of polyester B would be accompanied not only by shorter correlation times ρ, as noted above, but also by a narrower distribution of rotational modes. From the six sets of ρ and θ values given in Table IV as well as from results reported on poly(butylene terephthalate) and poly(hexamethylene terephthalate),[27] this does not appear to be the case: Though decreasing from C_4 to C_6, θ remains of the same order of magnitude for all the aliphatic carbons of the two polyesters.

The dependence on temperature of T_{1C} relaxation times and nuclear Overhauser enhancements for lines C_4, C_5, and C_6 at 25 MHz is plotted in Figure 5. As for room-temperature experiments, the influence of the chain length is clearly visible for the central units. The θ and ρ correlation times deduced from measurements on peak C_6 are plotted in Figure 6. The apparent activation energies for the ρ process decrease from polyester A (m = 2) to polyester B (m = 8). The longer the subchain, the smaller the apparent activation energy.

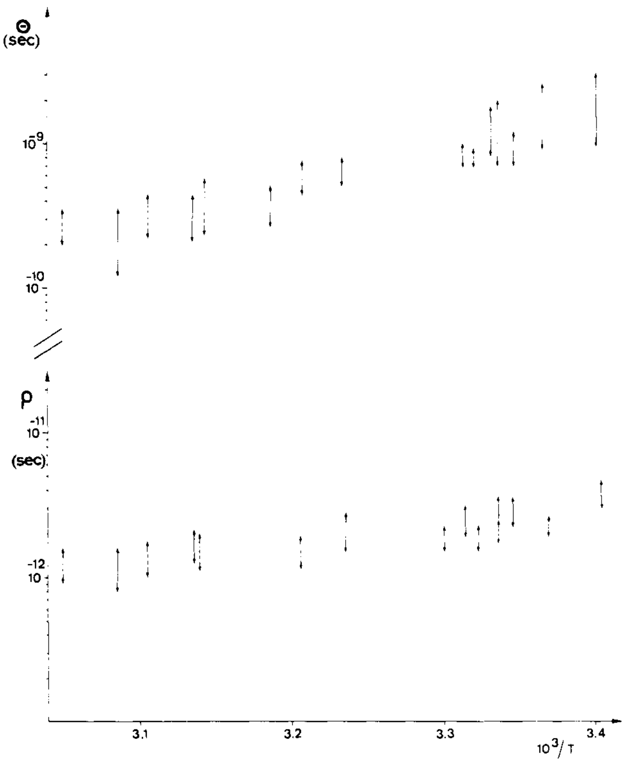


Figure 6. ρ and θ correlation times calculated from formulas 1, 2, and 5 and data reported in Figure 5 for line C_6: (—) polyester A; (---) polyester B.

It is of interest to discuss these results in terms of Helfand's classification of polymer motions.[29] Type 1 modes of motion (generally called crankshafts) such as the Schatzki crankshaft[14] or the three-bond motion,[15] leave the tails in the same position at the start and end of the transition. Because the chain ends are not involved, these motions are particularly favorable. However, such motions require two barrier crossings or the passage through some fairly high energy intermediate state.[16] In type 2 processes, on the other hand, the chain ends are translated relative to each other by the motion, but the angular orientation of the two is unaffected. This second type of motion has been recently extensively studied.[16,30,31] The activation energy has been shown to be slightly more than the barrier separating the trans and gauche state.[16] Therefore the type 2 motions may very well be responsible for many relaxation data in which the activation energy is comparable to the barrier height between the trans and gauche state. Finally, type 3 processes change the angular orientation of the chain ends, and the necessity for large-scale rearrangement of solvent by the chain ends is expected to result in high barriers. It is noticeable that type 1 motions clearly result in an orientation diffusion process described by ρ correlation time. As regards type 2 motions, Brownian dynamics simulations[16] have shown that the rate of motion depends on the conformations of the neighbors of the transforming bond. A significant number of conformational transitions are involved in correlated processes with the second neighbors. Thus these type 2 motions induce a diffusion of bond orientation along the chain, characterized by ρ correlation time.

Let us now consider results obtained on carbons C_3, C_4, and C_5 of polyesters A and B. C_4–H and C_5–H internuclear vectors are relaxed by both ρ and θ processes. On the other hand, the overall reorientation of the phenyl group (the internal rotation of the ring is not of interest in the present discussion) is characterized by the τ_0 correlation time only. Moreover, τ_0 is equal to θ calculated for carbon C_4 next to the terphenyl and carboxyl group moiety. These points clearly show that the motions which are described by the ρ correlation time are fast type 1 or type 2 short-range motions which leave the carboxyl unit unrotated. On the contrary, the fact that C_3 and C_4 relaxation times and nuclear Overhauser effects are represented by the same θ (or τ_0) correlation time leads to the conclusion that the θ process affecting the C_4–H internuclear vector, which is much slower than the ρ one, is a type 3 long-range motion. Indeed it is characterized by a high activation energy of 7.5 kcal/mol.

Another interesting point is the comparison of the activation energies obtained for the ρ process in polyesters A ($m = 2$) and B ($m = 8$) for the C_6 line (Table IV): The smaller activation energy is observed for the longer aliphatic subchain. This observation may also be interpreted in terms of Helfand's analysis of elementary motions:[29] C–H internuclear vectors located in the middle of the aliphatic subchain are involved in rotations about C–C and C–O bonds. From spectroscopic data and conformational analysis[32-34] the barrier for internal rotation about typical CH_2–CH_2 bonds is known to be slightly over 3 kcal/mol. The barrier to rotation about a CH_2–O bond is of the order of 2.5 kcal/mol. Assuming that the observed activation energy E_a can be written as[12,29,35,36]

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

where ΔH_η is the activation energy for the solvent viscosity ($\Delta H_\eta \simeq 1.4$ kcal/mol for $CDCl_3$ in the temperature range 15–40 °C) and E^* is the potential barrier for the motion of interest, results reported in Table IV lead to $E^* \simeq 5.6$ kcal/mol for $m = 2$ and $E^* \simeq 2.6$ kcal/mol for $m = 8$. Comparison of these data with rotational barriers cited above shows that experimental activation energies E^* for ρ processes in aliphatic subchains are of the order of one barrier crossing for $m = 8$ and of two barrier crossings for $m = 2$. Keeping in mind that, in the terminology of Helfand, type 1 motions require two barrier crossings and type 2 motions slightly more than one, we note that this result indicates that type 2 motions are more likely in long aliphatic subchains where the localization mode involving distortions of the neighboring degrees of freedom can happen, whereas mainly type 1 motions, i.e., crankshafts or three-bond jumps, occur in shorter flexible segments terminated by fixed chain ends. It is also noticeable that in polyester B, the temperature dependence of T_{1C} for line C_6 is very close to that of the methylene carbons of poly(ethylene oxide) as shown in Figure 5. This result points out the fact that the behavior of the central aliphatic carbons of polyester B approaches that of poly(ethylene oxide) carbons and therefore type 2 motions may be expected in this polymer, too.

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Registry No. Polymer A, 70548-66-2; polymer B, 84304-04-1; dipropyl *p*-terphenyl-4,4″-dicarboxylate–tetraethylene glycol copolymer, 70554-91-5; decaethylene glycol–dipropyl *p*-terphenyl-4,4″-dicarboxylate copolymer, 84304-05-2.

References and Notes

(1) Valeur, B.; Jarry, J. P.; Gény, F.; Monnerie, L. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 667, 2251.
(2) Jones, A. A.; Stockmayer, W. H. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 847.
(3) Bendler, J. T.; Yaris, R. *Macromolecules* **1978**, *11*, 650.
(4) Valeur, B.; Monnerie, L. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 29.
(5) Gény, F.; Monnerie, L. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 1.
(6) Lauprêtre, F.; Noël, C.; Monnerie, L. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 2127.
(7) Heatley, F.; Begum, A. *Polymer* **1976**, *17*, 399.
(8) Heatley, F.; Cox, M. *Polymer* **1977**, *18*, 225.
(9) Heatley, F.; Begum, A.; Cox, M. *Polymer* **1977**, *18*, 637.
(10) Jones, A. A.; Robinson, G. L.; Gerr, F. E.; Bisceglia, M.; Shostak, S. L.; Lubianez, R. P. *Macromolecules* **1980**, *13*, 95.
(11) Heatley, F. *Prog. NMR Spectrosc.* **1979**, *13*, 47.
(12) Friedrich, C.; Lauprêtre, F.; Noël, C.; Monnerie, L. *Macromolecules* **1980**, *13*, 1625.
(13) Friedrich, C.; Lauprêtre, F.; Noël, C.; Monnerie, L. *Macromolecules* **1981**, *14*, 1119.
(14) Schatzki, T. F. *J. Polym. Sci.* **1962**, *57*, 496. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1965**, *6*, 646.
(15) Monnerie, L.; Geny, F. *J. Chim. Phys. Phys.-Chim. Biol.* **1969**, *66*, 1691.
(16) Helfand, E.; Wasserman, Z. R.; Weber, T. A. *Macromolecules* **1980**, *13*, 526.
(17) Liao, T. P.; Okamoto, Y.; Morawetz, H. *Macromolecules* **1979**, *12*, 535.
(18) Cochran, M. A.; Dunbar, L. H.; North, A. M.; Pethrick, R. A. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 215.
(19) Meurisse, P.; Noël, C.; Monnerie, L.; Fayolle, B. *Br. Polym. J.* **1980**, *12*, 163.
(20) Bosio, L.; Fayolle, B.; Friedrich, C.; Lauprêtre, F.; Meurisse, P.; Noël, C.; Virlet, J. *Liq. Cryst. Ordered Fluids* **1983**, *4*.
(21) Allerhand, A.; Doddrell, D.; Komoroski, R. J. *J. Chem. Phys.* **1971**, *55*, 189.
(22) Abragam, A. "Principles of Nuclear Magnetism"; Oxford University Press: London, 1961.
(23) Bloembergen, N.; Purcell, E. M.; Pound, R. V. *Phys. Rev.* **1948**, *73*, 679.
(24) Wehrli, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden and Son Ltd.: London, 1976; p 47.
(25) Woessner, D. E. *J. Chem. Phys.* **1962**, *36*, 1.
(26) Rietveld, H. M.; Maslen, E. N.; Clews, C. J. B. *Acta Crystallogr., Sect. B* **1970**, *26*, 693.
(27) Komoroski, R. A. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 45.
(28) Meurisse, P. Thèse de 3ème cycle, Paris, 1982.
(29) Helfand, E. *J. Chem. Phys.* **1971**, *54*, 4651.
(30) Helfand, E.; Wasserman, Z. R.; Weber, T. A.; Skolnick, J.; Runnels, J. H. *J. Chem. Phys.* **1981**, *75*, 4441.
(31) Skolnick, J.; Helfand, E. *J. Chem. Phys.* **1980**, *72*, 5489.
(32) Herzberg, G. "Infrared and Raman Spectra"; Van Nostrand-Reinhold: New York, 1945.
(33) Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrisson, G. A. "Conformational Analysis"; Interscience: New York, 1967.
(34) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Interscience: New York, 1969.
(35) Kramers, H. A. *Physica* **1940**, *7*, 284.
(36) Mashimo, S. *Macromolecules* **1976**, *9*, 91.