^{13}C n.m.r. investigation of the local dynamics of aryl-aliphatic polyesters in solution

Anne Gérard, Françoise Lauprêtre* and Lucien Monnerie
Laboratoire de Physico-Chimie Structurale et Macromoléculaire associé au CNRS, ESPCI, 10 rue Vauquelin, 75231 Paris Cedex 05, France
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The local motions of aryl-aliphatic polyesters based on ethylene glycol and hydroxybenzoic acid or isophthalic acid were investigated in chloroform and trifluoroacetic acid/dichloromethane solutions using ^{13}C n.m.r. Measurements of the ^{13}C spin–lattice relaxation times have indicated the existence of hydrogen-bonding interactions between the carboxyl groups of the polymers and the solvent in the trifluoroacetic acid/dichloromethane mixture. Interpretation of the ^{13}C spin–lattice relaxation times in terms of segmental main-chain motions was carried out using the Dejean–Lauprêtre–Monnerie orientation autocorrelation function. The internal motions of the aromatic rings have been described in terms of jumps between two equilibrium positions for the hydroxybenzoic rings and by stochastic jump processes for the isophthalic rings. The energy barriers determined for these motions have been compared with those measured in related systems or estimated from conformational energy calculations.

(Keywords: polyesters; ^{13}C n.m.r.; local mobility)

INTRODUCTION

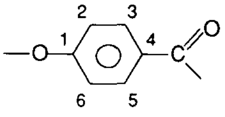
The aromatic copolyester (A) based on hydroxybenzoic acid (HBA), hydroquinone (HQ) and isophthalic acid (IA) in equal amounts has attractive mechanical properties arising from the existence of a nematic phase which favours the orientation of the chain axis along the stretching or flow directions. However, below the glass transition temperature, secondary transitions occur, which induce a loss in the mechanical properties[1]. Since these secondary relaxations are known to originate from local motions, the identification and characterization of the different motional processes that may occur in this thermotropic polymer are of major interest for the understanding of its mechanical behaviour.

The local dynamics of polymers can be investigated by a number of spectroscopic techniques. Among these techniques nuclear magnetic resonance (n.m.r.) has proven to be a very powerful tool since its selectivity allows a detailed analysis of the motions of the different parts of the polymer chain. The different n.m.r. parameters, spin–lattice relaxation time T_1, spin–spin relaxation time T_2, nuclear Overhauser enhancement, or line shape in exchange study, provide information on very rapid processes or on much slower ones. In a polymer solution, the ^{13}C spin–lattice relaxation time and nuclear Overhauser enhancement are of particular interest in the study of the fast local motions of the chain and the internal modes of the rings.

The local dynamics of a given molecule are ruled by both intramolecular constraints and intermolecular interactions. In a dilute polymer solution, the dominant interactions are usually of intramolecular nature. The intermolecular interactions are established between the solvent and the polymer and their strength depends on the solvent used in the experiment. In bulk polymers, both intramolecular and intermolecular polymer–polymer interactions should be taken into account. In order to study the influence of these two factors, high-resolution ^{13}C n.m.r. experiments have been carried out both in solution and in the solid state. The bulk study has been performed using high-resolution solid-state ^{13}C n.m.r. and the results have been reported in a previous paper[2]. The present paper deals with the investigation of local motions by high-resolution ^{13}C n.m.r. experiments in solution.

When determined by a ^{13}C–^1H dipolar relaxation mechanism, the ^{13}C spin–lattice relaxation times reflect the reorientation of the ^{13}C–^1H vectors. The data interpretation is straightforward for protonated carbons for which the ^{13}C–^1H vector of interest is the C–H bond. However, in the thermotropic copolyester (A) based on the three following units in equal proportions:

Unit I



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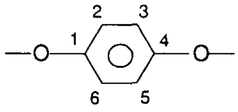

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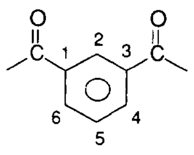

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*To whom correspondence should be addressed

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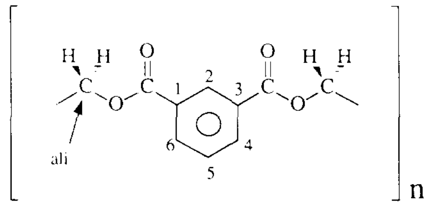
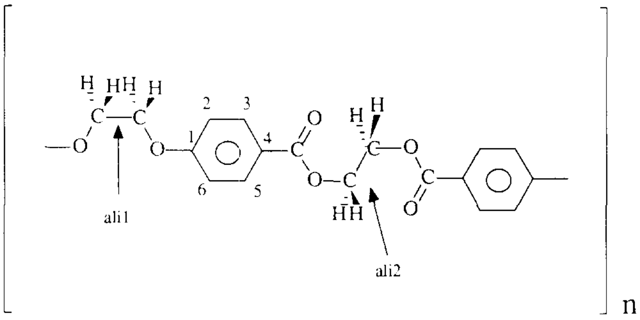
all the C–H bonds simultaneously undergo two types of motions, that is, segmental motions of the main chain involving a small number of monomer units, and internal motions of the phenyl rings whose nature depends on the relative positions of the substituents. Therefore, in order to characterize each of these motional processes independently, we have first investigated two aryl-aliphatic polyesters:

polyethylene isophthalate (PEI), based on ethylene glycol and IA:



and poly[1-(methyleneoxy)phenylene-4-(carbonyloxyethylene)-1-(oxycarbonyl)phenylene-4-(oxymethylene)] (PHB), containing ethylene and hydroxybenzoic units:



In these polymers, the methylene carbons are involved in the segmental chain motion only, whereas the aromatic carbons undergo both main-chain and ring-internal motions. Therefore, the contributions of each type of motion to the relaxation can be determined independently and characterized in terms of correlation times and activation energies.

Another difficulty exists in the study of HBA-, HQ- and IA-based copolyesters. In the absence of aliphatic units, the copolyesters are insoluble in most organic solvents. The only solvent known for polymer A is a 70% dichloromethane/30% trifluoroacetic acid mixture. However, hydrogen-bonding interactions may occur between the trifluoroacetic acid molecule and the carboxylic groups of the polymer. Therefore the local dynamics of the aryl-aliphatic PEI polymer has been first investigated in chloroform, where such interactions do not occur. In a second step, experiments were carried out in the 70% dichloromethane/30% trifluoroacetic acid mixture for the three polymers A, PEI and PHB. The analysis of the local dynamics of PEI and PHB will be discussed in this paper; results obtained for polymer A will appear in a subsequent paper.

EXPERIMENTAL

The polyesters A, PEI and PHB were synthesized at ICI Co., Wilton Centre, UK.

The solvents used were either $CDCl_3$ or a 70% dichloromethane/30% trifluoroacetic acid mixture (CD_2Cl_2/CF_3COOH). The polymer concentrations were 0.1 g cm^{-3}. The n.m.r. tubes were sealed to avoid solvent evaporation.

^{13}C n.m.r. spectra, at 22.6 and 50.3 MHz, were recorded on a Bruker WH90 and a Bruker AC200 spectrometer, respectively, using proton noise decoupling. ^{13}C spin–lattice relaxation times, T_1, were measured using the standard (180°, t, 90°) pulse sequence, with repetition times between pulse sequences greater than five times the longest T_1 of the considered nuclei. T_1 values were determined from exponential regression of the ^{13}C magnetization as a function of t. Nuclear Overhauser enhancements (NOE) were obtained from:

$$\mathrm{NOE} = R - 1 \qquad (1)$$

where R is the ratio of the line areas recorded in the presence or in the absence of proton decoupling during the repetition time. In the gated experiment, the repetition time was of the order of 10 times the longest T_1 of the considered nuclei, that is, long enough to avoid the build-up of NOE due to decoupling during acquisition. The INEPT (Insensitive Nuclei Enhanced by Polarization Transfer) sequence was used to discriminate between the protonated and unprotonated carbons[3].

THEORETICAL BACKGROUND

With the assumption of a purely ^{13}C–^{1}H dipolar relaxation mechanism, the spin–lattice relaxation time, T_1, obtained from a ^{13}C experiment under proton decoupling conditions is given by the well-known expression[4]:

$$\frac{1}{nT_1} = \frac{1}{10}\frac{\gamma_C^2\gamma_H^2\hbar^2}{r_{CH}^6}\left[J(\omega_H-\omega_C)+3J(\omega_C)+6J(\omega_H+\omega_C)\right] \qquad (2)$$

where n is the number of protons directly bonded to the carbon of interest, ω_H and ω_C are the ^1H and ^{13}C resonance frequencies respectively, r_{CH} is the internuclear distance, and $J(\omega)$ is the spectral density function defined by:

$$J(\omega) = \frac{1}{2}\int_{-\infty}^{+\infty} G(t)\,e^{i\omega t}\,dt \qquad (3)$$

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

Under the above assumption of a purely ^{13}C–^{1}H dipolar relaxation mechanism, the NOE is written as:

$$\mathrm{NOE} = \frac{\gamma_H}{\gamma_C}\,\frac{6J(\omega_H+\omega_C)-J(\omega_H-\omega_C)}{J(\omega_H-\omega_C)+3J(\omega_C)+6J(\omega_H+\omega_C)} \qquad (4)$$

and therefore:

$$\frac{\mathrm{NOE}}{nT_1} = \frac{\hbar^2\gamma_C\gamma_H^3}{10r_{CH}^6}\left[6J(\omega_H+\omega_C)-J(\omega_H-\omega_C)\right] \qquad (5)$$

Among the other relaxation mechanisms that may induce the ^{13}C spin–lattice relaxation, mechanisms based on spin-rotation, chemical shift anisotropy or dipolar interactions with nuclei other than protons, affect only the transition probability at the frequency ω_C[5–7]. When these mechanisms are active, the spin–lattice relaxation time, T_1, and the denominator in the NOE expression are modified in a similar way. On the contrary, equation (5), which depends only on the $J(\omega_H+\omega_C)$ and $J(\omega_H-\omega_C)$ spectral densities, is unchanged. Therefore, whenever several relaxation mechanisms contribute to the spin–lattice relaxation, and no scalar relaxation occurs, information on the reorientation of the ^{13}C–^{1}H vectors can be obtained from the NOE/nT_1 ratio, which depends on the dipolar interaction only. (In the polymers considered, the $^{13}C-^{1}H$ scalar coupling, J, is of the order of 170 Hz. The minimum relaxation time associated with the scalar relaxation mechanism is: $(\omega_H-\omega_C)/\pi^2J^2=3000$ s for $(\omega_H-\omega_C)\tau=1$, which makes its contribution to the T_1 relaxation negligible.)

In polymers, local motions are too complicated to be described by a simple isotropic rotation. Fluorescence depolarization experiments[8,9], which permit the direct observation of the orientation autocorrelation function, have clearly shown the non-exponential nature of $G(t)$. Different expressions have been proposed for the orientation autocorrelation function[8,10,11]. During the last few years, the Dejean–Lauprêtre–Monnerie (DLM) expression has proven a most useful representation of a large number of relaxation data obtained from polymers in solution or bulk polymers at temperatures well above their glass transition temperature[12–15]. This expression is based on a damped diffusion of bond orientation along the chain sequence and independent bond librations.

The DLM orientation autocorrelation function is written as:

$$G(t)=(1-a)\exp(-t/\tau_2)\exp(-t/\tau_1)I_0(t/\tau_1)$$
$$+a\exp(-t/\tau_0)\exp(-t/\tau_2)\exp(-t/\tau_1)I_0(t/\tau_1) \qquad (6)$$

where

$$1-a=[(\cos\theta-\cos^3\theta)/2(1-\cos\theta)]^2 \qquad (7)$$

τ_1 is the correlation time associated with the segmental motions responsible for the bond orientation diffusion along the chain sequence; τ_2 describes the damping of this diffusion. The libration has been described by an anisotropic reorientation occurring inside a cone of half-angle θ with a characteristic correlation time τ_0.

The influence of the τ_1/τ_0 ratio on the spin–lattice relaxation time is not observed for τ_1 values shorter than 3×10^{-8} s. Only spin–lattice relaxation time measurements in the long correlation time regime permit the determination of this ratio. The τ_2/τ_1 value can be obtained from the ratio of relaxation times measured at the same temperature and at two different frequencies. As the height of the T_1 minimum is proportional to $1/(1-a)$, the libration amplitude θ can be directly derived from the minimum T_1 value[12].

Different models can be used to describe the ring motions[16]. The expression of the orientation autocorrelation function depends on the type of internal motion considered. For a jump between two equilibrium positions, $G(t)$ is written as:

$$G(t)=(A+C)+B\,e^{-t/\tau_i} \qquad (8)$$

whereas, for a jump between three equilibrium positions:

$$G(t)=A+(B+C)\,e^{-t/\tau_i} \qquad (9)$$

and for a stochastic process:

$$G(t)=A+B\,e^{-t/\tau_i}+C\,e^{-4t/\tau_i} \qquad (10)$$

where

$$A=(3\cos^2\alpha-1)^2/4$$
$$B=[3\sin^2(2\alpha)]/4$$
$$C=(3\sin^4\alpha)/4 \qquad (11)$$

α is the angle between the rotation axis and the internuclear vector C–H and τ_i is the internal correlation time.

For independent motions of the chain and rings, the orientation autocorrelation function is the direct product of the corresponding orientation autocorrelation functions.

RESULTS AND DISCUSSION

^{13}C n.m.r. spectra and hydrogen bonding interactions

Figures 1 and *2* show the proton-decoupled ^{13}C n.m.r. spectra of the PEI and PHB polymers recorded at 25°C at the experimental frequency of 50.3 MHz. The line assignment and the spin–lattice relaxation times of the different carbons at 25°C are also indicated. The assignment of the aromatic resonances is based on empirical additivity rules for the aromatic ring carbons[17]. It is also confirmed by INEPT spectra, which discriminate the unprotonated from the protonated carbons.

As seen in the spectra, the PEI and PHB carboxyl carbon lines are broader in CF_3COOH/CD_2Cl_2 solution than in $CDCl_3$ solution. The CF_3COOH carbon lines are also broad. In $CDCl_3$ solution, the line assignment of the PEI carbons is corroborated by the values of the ^{13}C spin–lattice relaxation times: at 25°C and 50 MHz, the unprotonated carbons have relatively long relaxation times (higher than 1 s). The protonated aromatic carbons have much shorter relaxation times which range from 0.26 to 0.40 s. These relaxation times are approximately

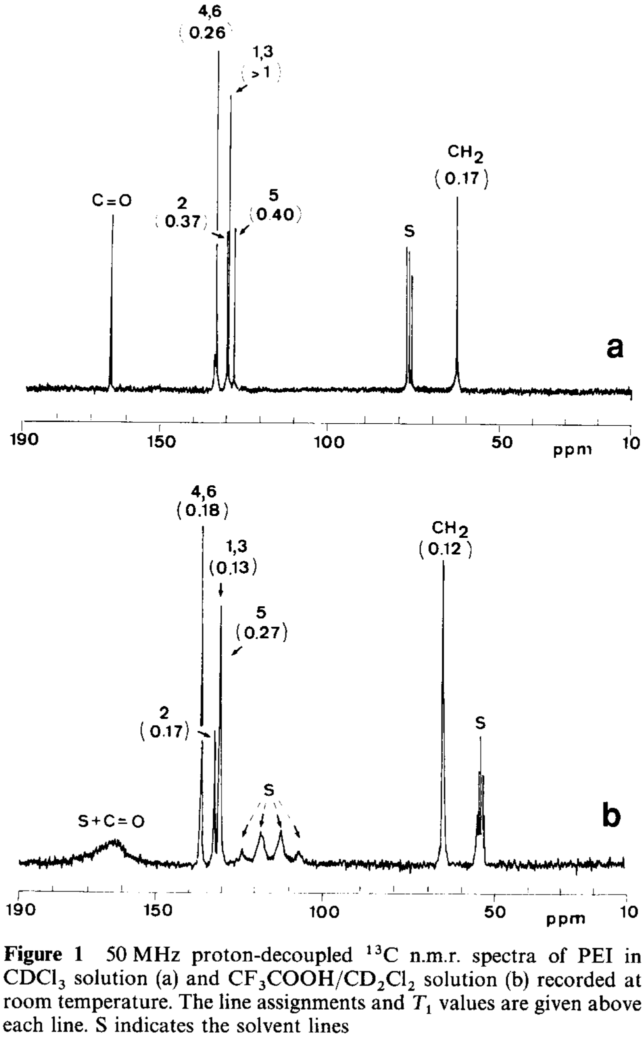


Figure 1 50 MHz proton-decoupled ^{13}C n.m.r. spectra of PEI in $CDCl_3$ solution (a) and CF_3COOH/CD_2Cl_2 solution (b) recorded at room temperature. The line assignments and T_1 values are given above each line. S indicates the solvent lines

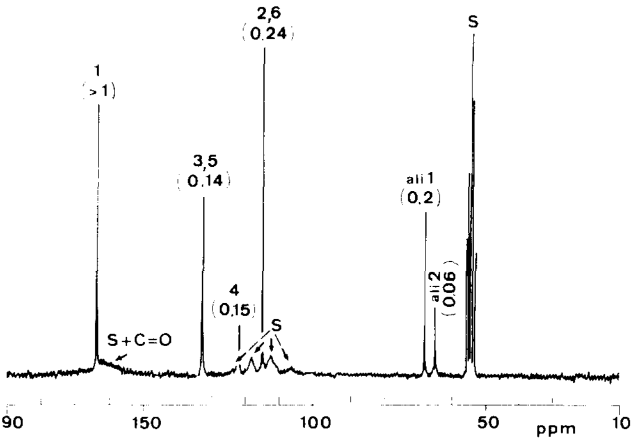


Figure 2 50 MHz proton-decoupled ^{13}C n.m.r. spectra of PHB in CF_3COOH/CD_2Cl_2 solution recorded at room temperature. The line assignments and T_1 values are given above each line. S indicates the solvent lines

twice those of the methylene carbons. The NOE are equal to 1.7, close to the theoretical maximum of 2. As will be described in more detail in the next section, these results can be explained in terms of a pure ^{13}C–^1H dipolar relaxation mechanism.

In CF_3COOH/CD_2Cl_2 solution, the unprotonated carbons of PEI and PHB have, in contrast, short relaxation times of 0.13 and 0.15 s, respectively, and NOE (~ 0.8) that are too small to be described in terms of a unique intramolecular dipolar relaxation mechanism. The spin–lattice relaxation times of the two magnetically unequivalent aromatic carbon pairs (2,6 and 3,5) in the *para*-substituted PHB polymer are different, although the corresponding C–H vectors are expected to undergo identical segmental and ring motions with the same value of the angle α for the internal ring process. All these observations are an indication of the existence of a second relaxation mechanism which is specific to the CF_3COOH/CD_2Cl_2 solution. They are corroborated by the widening of the CF_3COOH line in the ^1H n.m.r. spectra and the unusually small values of the spin–lattice relaxation times (0.015 s at 25°C and 200 MHz) of the aromatic protons in an *ortho* position with respect to the carboxyl group and the aliphatic protons[18].

The above results can be interpreted in terms of hydrogen-bonding interactions between the CF_3COOH molecule and some of the polymer atoms. A detailed analysis of these phenomena will be given in a subsequent paper. On the one hand, the temperature dependence of the linewidths of the polymer carboxyl carbon indicates the existence of a site exchange between a bonded and a non-bonded state. In this case, the atoms involved in hydrogen bonding are the polymer carboxyl carbon and the acid proton of the CF_3COOH molecule. On the other hand, the very short ^1H spin–lattice relaxation times of the aromatic protons in *ortho* position with respect to the carboxyl group are consistent with a H---F distance of the order of about 1.6 Å, that is, of the order of the H---F hydrogen-bond length. Indeed, the respective geometries of the PHB and CF_3COOH molecule allow the coexistence of two types of hydrogen bonds: the first involves the PHB C=O group and the CF_3COOH acid proton; the second is established between the aromatic protons in *ortho* position with respect to the carboxyl group and the solvent fluorine atoms.

Spin–lattice relaxation analysis of PEI in $CDCl_3$ solution

The spin–lattice relaxation times of the different carbons have been measured at the experimental ^{13}C resonance frequencies of 22 and 50 MHz in the temperature range of 230–320 K. Variations in nT_1 as a function of temperature are shown in *Figure 3* for the aliphatic carbons. As discussed in the previous section, for PEI in $CDCl_3$ solution, there is no experimental indication of an interaction between the polymer and the solvent, and the nT_1 values can be interpreted in terms of a unique ^{13}C–^1H dipolar relaxation mechanism.

Chain dynamics. As described in the Introduction, the dipolar contribution to the spin–lattice relaxation times of the aliphatic carbons reflects the local chain dynamics.

Values of nT_1 reported in *Figure 3* decrease with decreasing temperature. The shape of the nT_1 curve in the low-temperature range indicates that, at 230 K, nT_1 approaches its minimum value, and that the observed motions therefore have a frequency of the order of the Larmor frequency. This result is supported by the temperature variation of the relaxation times of the aliphatic protons for which the curve minimum is clearly reached at low temperature[18]. It must be noticed that, in the low-temperature region where nT_1 approaches its minimum, the 22 MHz nT_1 values are substantially higher than the 0.040 s nT_1 minimum calculated from an isotropic model. They are also higher than the 0.050 s

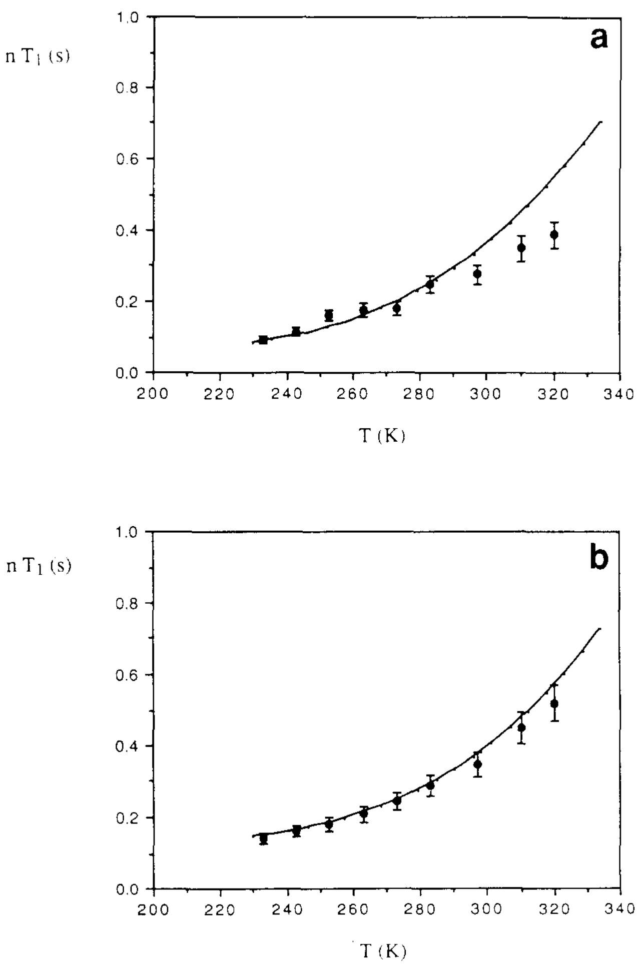


Figure 3 Temperature dependence of the experimental (●) and calculated (—) ^{13}C spin–lattice relaxation times, $2T_1$, of the CH_2 carbons of PEI in $CDCl_3$ solution at 22 MHz (a) and 50 MHz (b)

nT_1 minimum derived from a damped diffusion of bond orientation in the absence of librations ($a = 0$ in equation (6)). These discrepancies between experimental and calculated values indicate that both the isotropic model and the damped diffusion of bond orientation in the absence of librations are inadequate for the representation of the nT_1 data. Therefore, following the approach described in reference 12, nT_1 values shown in *Figure 3* were analysed in terms of a damped diffusion of bond orientation along the chain sequence and independent bond librations using the DLM orientation autocorrelation function. The values of the internuclear distances, r_{CH}, used in the calculations were taken as 1.09 ± 0.005 Å and 1.084 ± 0.005 Å for the methylene and aromatic carbons, respectively[19]. In the region of the nT_1 minimum, the dependence of the nT_1 values on the τ_1/τ_0 ratio is very weak. Therefore, the τ_1/τ_0 ratio was taken arbitrarily as 200, which is a value commonly encountered in linear polymers. The ratio of the relaxation times determined at the two frequencies (22 and 50 MHz) is consistent with a τ_2/τ_1 ratio of the order of 1. It indicates a strong damping of the bond orientation diffusion along the chain. Since the minimum of the nT_1 curve is almost reached at low temperature, a libration angle of 35° was derived from the nT_1 value at 230 K. This value is in good agreement with libration angles determined for methylene carbons in other polymers: between 35° and 40°, depending on the steric hindrance at the considered site[12–15].

Using the above set of θ, τ_1/τ_0 and τ_2/τ_1 parameters, the correlation time τ_1, which reproduces the experimental value of nT_1 at each temperature and frequency, was determined. The variation of the τ_1 values thus obtained, as a function of the reciprocal of temperature, is given in *Figure 4*. It follows an Arrhenius-type law:

$$\tau_1 = \tau_1^0 \exp(E/RT) \qquad (12)$$

with $\tau_1^0 = 5 \times 10^{-13}$ and $E = 4$ kcal mol^{-1}.

Experimental and calculated nT_1 values are compared in *Figure 3*. At low temperature, the agreement is very good. However, at the highest temperatures investigated, the 22 MHz data are not as well represented as the 50 MHz data. This discrepancy is due to the difference between the nT_1 values at the two experimental frequencies, which unexpectedly increases with increasing temperature.

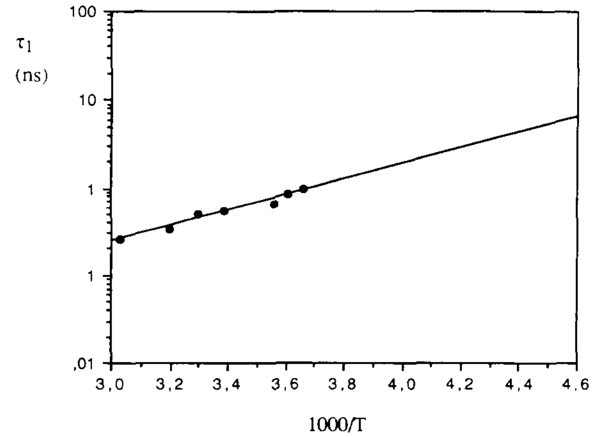


Figure 4 Plot of τ_1 *versus* $1000/T$ for the aliphatic carbons of PEI in $CDCl_3$ solution. T (K) is the absolute temperature

The activation energy, E, determined from the τ_1 variation as a function of $1/T$, has been interpreted in terms of Kramers theory[20] for the diffusion of a particle over a potential barrier. This theory has been applied to conformational transitions in polymer chains by Helfand[21]. According to this theory, the correlation time associated with a motional mode involving the crossing of an energy barrier E^* can be written as:

$$\tau \approx \eta C \exp(E^*/RT) \qquad (13)$$

where η is the solvent viscosity and C is a molecular constant. The activation energy of the motion can then be estimated from:

$$E^* = E - E_\eta \qquad (14)$$

where E_η is the activation energy for the solvent viscosity.

For chloroform, $E_\eta = 1.7$ kcal mol^{-1} in the considered temperature range and, therefore, the activation energy associated with the segmental motion of the PEI chain is $E^* = 2.3$ kcal mol^{-1}. E^* is of the order of the energy barriers determined in poly(vinyl methyl ether)[12] and other aryl-aliphatic copolyesters[22].

Meta-*substituted ring motion.* T_1 variations as a function of temperature are shown in *Figures 5* and *6* for the aromatic 2,5 and 4,6 carbon pairs, respectively. To interpret these T_1 values, one has to take into account both the segmental dynamics and the internal ring

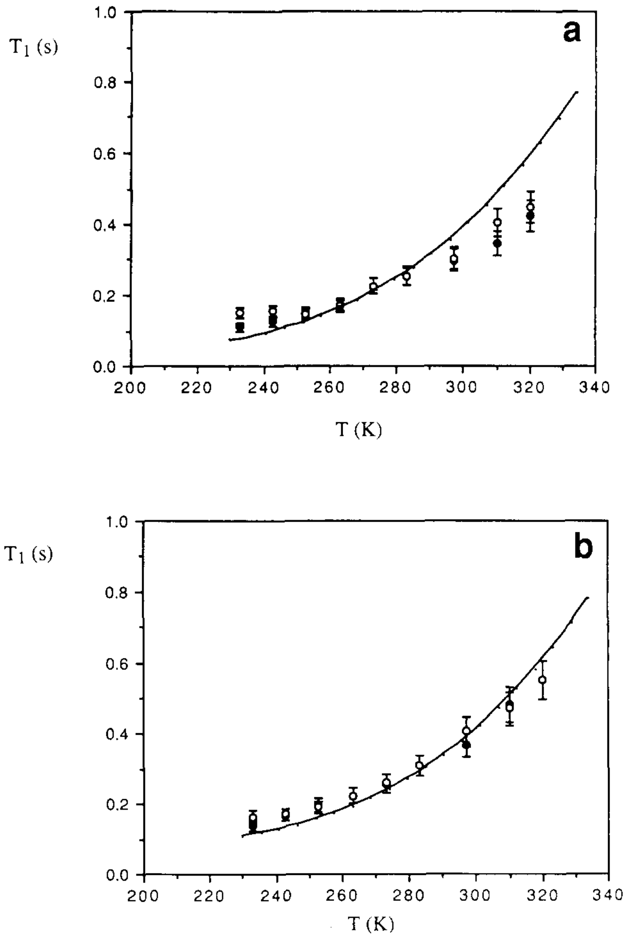


Figure 5 Temperature dependence of the experimental ^{13}C spin–lattice relaxation times, T_1, of carbons 2 (●) and 5 (○) of PEI in $CDCl_3$ solution at 22 MHz (a) and 50 MHz (b). The full line represents calculated values

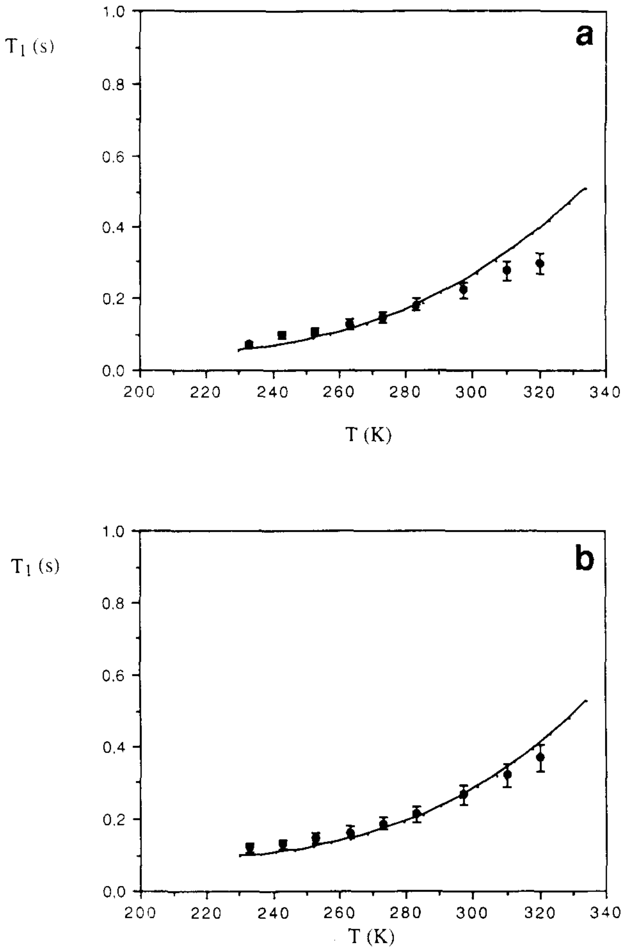
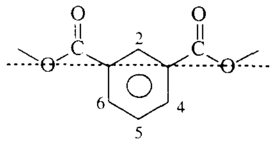
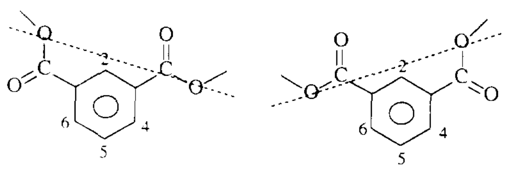


Figure 6 Temperature dependence of the experimental (●) and calculated (—) ^{13}C spin–lattice relaxation times T_1 of the carbons 4,6 of PEI in $CDCl_3$ solution at 22 MHz (a) and 50 MHz (b)

motions in which the PEI rings are involved. In the following, we will assume that the methylene and ring carbons undergo exactly the same segmental dynamics in terms of τ_1 and τ_2. Regarding the internal ring motion, different motional models have been considered in relation to molecular models. The observation of molecular models shows that the motion of a *meta*-substituted ring is likely to occur about an axis joining two oxygen atoms. Three axes have to be considered according to the *trans* or *cis* conformations of the carboxyl groups with respect to the ring:



cis conformation



trans conformations

It should be noted that, whatever the geometry—*cis* or *trans*—of the unit considered, no motion of the ring can occur without a motion of the chain. Besides, chain motions induce changes in the relative position of the C=O groups and therefore they induce a rapid exchange between the above conformations with a time constant of the order of τ_1. As a first approximation, we have assumed that the ring motion occurs around an average axis which is identical to the oxygen–oxygen axis in the *cis* conformation and that this motion is not correlated with the chain dynamics. To describe this ring process, two different motional models can be chosen, that is, either jumps between three equilibrium positions (equation (9)) or stochastic jumps (equation (10)). In the following analysis, we have used the more likely motional model of stochastic jumps.

The fit of the 22 and 50 MHz spin–lattice relaxation times (*Figures 5* and *6*) associated with carbons 2 ($T_1(2)$), 5 ($T_1(5)$) and 4,6 ($T_1(4,6)$) permits the determination of the libration amplitude of the aromatic C–H vectors and the correlation times of the internal ring motion, τ_i. A libration angle of 17° for the aromatic C–H vectors has been derived from the T_1 values at the lowest temperature. This value, which is smaller than the value determined for CH_2 groups (35°), is in agreement with the larger steric hindrance experienced by the aromatic carbons. The best fit of the $(T_1(2))/(T_1(4,6))$ and $(T_1(5))/(T_1(4,6))$ ratio has indicated that τ_i/τ_1 is of the order of 1.5. *Figures 5* and *6* show the comparison of the experimental and calculated values of the T_1 associated with carbons 2,5 and 4,6, respectively, as a function of temperature. The overall agreement is very good, except for the high temperature 22 MHz nT_1. For these data, the quality of the fit is similar to that observed in *Figure 3* for the nT_1 of the aliphatic carbons. The differences in the T_1 values, as a function of the carbon position on the ring, are well reproduced by the model used.

Spin–lattice relaxation analysis of PEI in CF_3COOH/CD_2Cl_2 solution

As discussed in a previous section, the comparison of the T_1 values measured for the different PEI carbons in CF_3COOH/CD_2Cl_2 solution indicates the existence of hydrogen-bonding interactions. Moreover, the carbons do not relax under a unique intramolecular ^{13}C–^{1}H dipolar mechanism. Therefore, to analyse the dynamics we have used the ratio NOE/nT_1, which is determined by the ^{13}C–^{1}H dipolar interaction only.

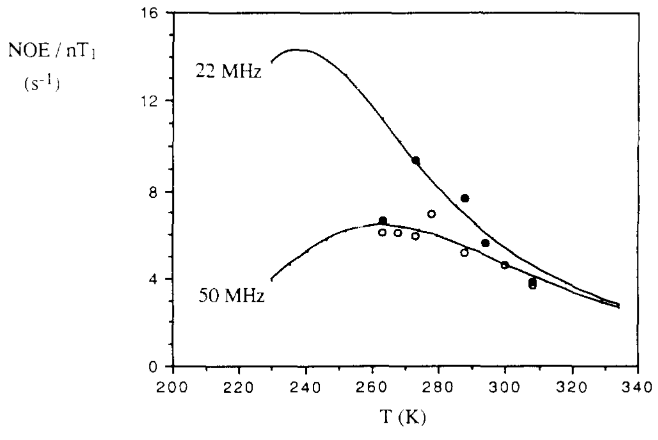


Figure 7 Temperature variation of experimental and calculated (—) NOE/2T_1 ratios for the aliphatic carbons of PEI in CF_3COOH/CD_2Cl_2 solution at 22 MHz (●) and 50 MHz (○)

Chain dynamics. Figure 7 shows the comparison of the experimental NOE/nT_1 for the aliphatic carbons and the values calculated using the τ_2/τ_1, τ_1/τ_0 and θ parameters determined from the study of PEI dynamics in $CDCl_3$ solution. The τ_1 values used to fit the data obey an Arrhenius equation similar to equation (12), with $\tau_1^0 = 5.3 \times 10^{-13}$ and $E = 4$ kcal mol^{-1}.

The good agreement between the experimental and calculated values displayed in *Figure 7* indicates that, within the accuracy of the experiments, the chain dynamics can be described by the same τ_2/τ_1, τ_1/τ_0 and θ values in both $CDCl_3$ and CF_3COOH/CD_2Cl_2 solutions. Only the segmental dynamics is slightly slower in CF_3COOH/CD_2Cl_2 than in $CDCl_3$.

Meta-*substituted ring motion. Figure 8* shows the experimental NOE/T_1 values measured for the aromatic carbons in CF_3COOH/CD_2Cl_2 solution and the calculated values using the dynamics parameters τ_2/τ_1, τ_1/τ_0, θ and τ_i/τ_1 determined for the ring dynamics of PEI in $CDCl_3$. Both calculated and experimental values have a parallel temperature dependence. However, the calculated values are higher than the experimental ones. The fit can be improved either by increasing the libration angle from 17° to 30° or decreasing the ratio τ_i/τ_1 from 1.5 to 1. The change in the nature of the solvent is expected to induce a change in the rate of motion rather than a noticeable increase in the libration amplitude. Calculated values obtained with τ_i/τ_1 equal to 1 are represented in *Figure 8*. They show good agreement with the experimental results.

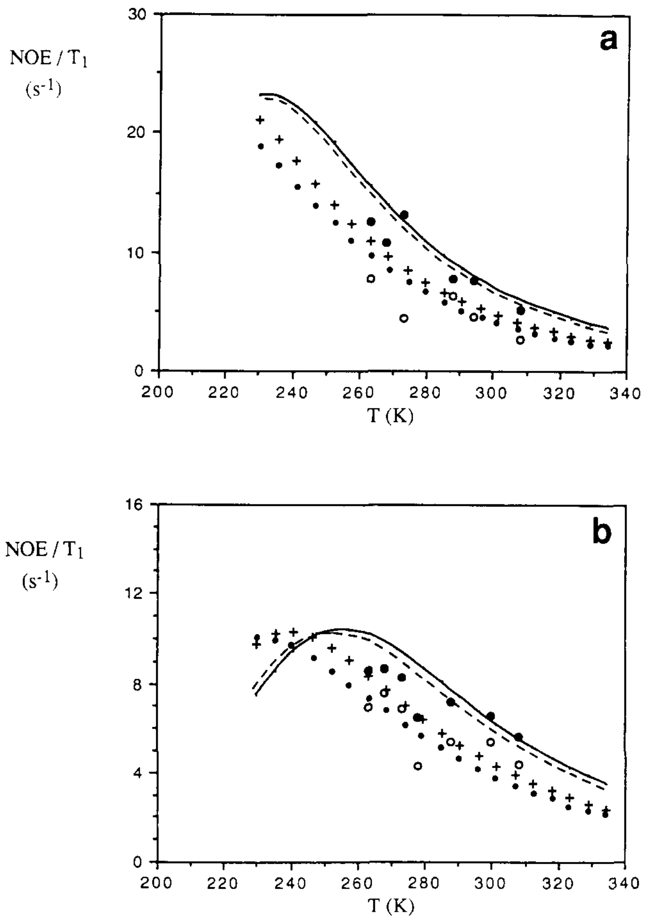


Figure 8 Temperature dependences of the NOE/T_1 ratios for PEI in CF_3COOH/CD_2Cl_2 solution. (a) 22 MHz experiments: calculated values assuming $\tau_i/\tau_1 = 1.5$ (—) and $\tau_i/\tau_1 = 1$ (– – –) and experimental values (●) for carbons 4,6; calculated values assuming $\tau_i/\tau_1 = 1.5$ (+) and $\tau_i/\tau_1 = 1$ (. . .) and experimental values (○) for carbon 2. (b) 50 MHz experiments: calculated values assuming $\tau_i/\tau_1 = 1.5$ (—) and $\tau_i/\tau_1 = 1$ (– – –) and experimental values (●) for carbons 4,6; calculated values assuming $\tau_i/\tau_1 = 1.5$ (+) and $\tau_i/\tau_1 = 1$ (. . .) and experimental values (○) for carbon 2

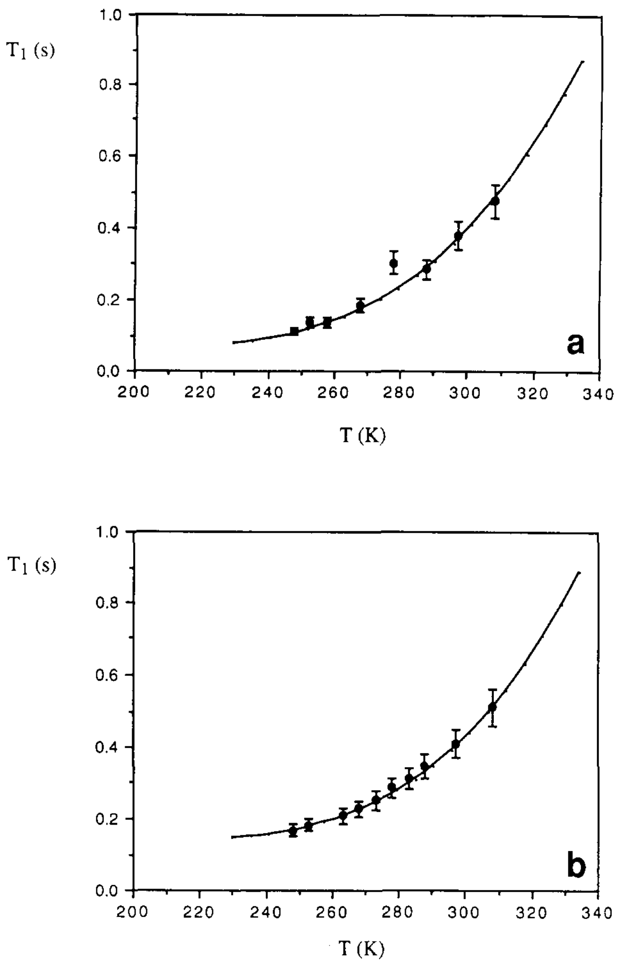


Figure 9 Temperature dependence of the experimental (●) and calculated (—) ^{13}C spin–lattice relaxation times, T_1, of the ali1 carbons of PHB in CF_3COOH/CD_2Cl_2 solution at 22 MHz (a) and 50 MHz (b)

Spin–lattice relaxation analysis of PHB in CF_3COOH/CD_2Cl_2 solution

Chain dynamics. The PHB polymer has two magnetically unequivalent aliphatic carbons denoted ali1 and ali2. The temperature dependence of the spin–lattice relaxation times at the two experimental frequencies is given in *Figure 9* for the ali1 carbons. At high temperature, their NOE (*Figure 10*) are of the order of 1.7, close to the theoretical maximum of 2. This is evidence of a ^{13}C–^1H dipolar relaxation mechanism and is in agreement with the fact that the ali1 carbons are situated quite far from the carboxylic groups and fluorine carbons involved in the ^{13}C–^{19}F intermolecular interactions. As shown in *Figure 9*, the accessible temperature range is quite small and the minimum of the T_1 curve is not reached. Consequently, the DLM model parameters cannot be precisely determined for this polymer. However, the T_1 values reported for PHB in CF_3COOH/CD_2Cl_2 and for PEI in $CDCl_3$ show quite similar temperature dependences and absolute values. Therefore, the τ_1 values

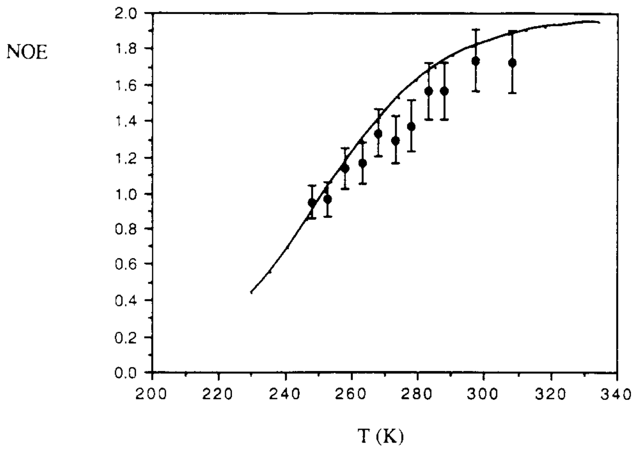


Figure 10 Temperature dependence of the experimental (●) and calculated (—) nuclear Overhauser effect (NOE) for the ali1 carbons of PHB in CF_3COOH/CD_2Cl_2 solution at 50 MHz

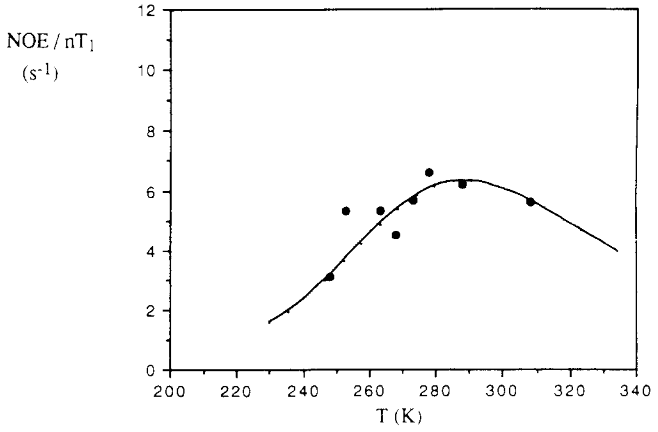


Figure 11 Temperature dependence of the experimental (●) and calculated (—) $NOE/2T_1$ ratio for the ali2 carbons of PHB in CF_3COOH/CD_2Cl_2 solution at 50 MHz

that represent the PHB relaxation data at each temperature have been calculated using the τ_2/τ_1, τ_1/τ_0 and θ parameters determined for PEI in $CDCl_3$. The variation of τ_1 as a function of $1/T$ is an exponential function similar to equation (12) with: $\tau_1^0 = 1.4 \times 10^{-14}$ and $E = 4.7$ kcal mol^{-1}. The temperature dependence of the viscosity of the CF_3COOH/CD_2Cl_2 mixture permits the experimental determination of the activation energy E_η. E_η is equal to 1.6 kcal mol^{-1} and therefore, E^* is 3.1 kcal mol^{-1}.

The agreement between experimental and calculated T_1 and NOE values is shown at the two experimental frequencies in *Figures 9* and *10*, respectively. The data fit is good over the whole temperature range, which, *a posteriori*, supports the assumptions used in the data analysis. In contrast with results observed on PEI, the 22 and 50 MHz T_1 values of PHB tend to merge at high temperature, which is well represented by the motional model considered.

The NOE of the ali2 carbons is of the order of 0.8, much smaller than the value measured for the ali1 carbons. Besides, the ali2 carbons are closer to the sites of the ^{13}C–^{19}F interactions. Therefore, the spin–lattice relaxation mechanism is not likely to be based purely on ^{13}C–^{1}H interactions and the analysis of the relaxation data of the ali2 carbons has not been performed in terms of T_1 but in terms of NOE/nT_1. The NOE/nT_1 ratios determined at 50 MHz are reported in *Figure 11*. Their interpretation has been carried out using the same τ_2/τ_1, τ_1/τ_0 and θ parameters as those used for the ali1 carbons. The agreement between experimental data and calculations is illustrated in *Figure 11*. Values of τ_1 used for the ali2 carbons are twice those used for the ali1 carbons, leading to the conclusion that the segmental dynamics, in terms of the τ_1 correlation time, is two times slower for the ali2 carbons than for the ali1 carbons. This result indicates that the $-O-CH_2-CH_2-O-$ sequence has more motional freedom than the $COO-CH_2-CH_2-OOC-$ unit whose local dynamics is slowed down by the polymer–solvent interactions.

Para-*substituted ring motion.* As indicated in a previous section, the observed difference in the spin–lattice relaxation times of the 2,6 and 3,5 aromatic carbon pairs of PHB (*Figure 2*) indicates the contribution to the relaxation of a second mechanism favoured by the presence of hydrogen-bonding interactions with the CF_3COOH molecules. Experimental NOE/T_1 ratios are reported in *Figure 12*. Data corresponding to the two carbon pairs are identical within experimental error. This is in agreement with the fact that the C–H vectors,

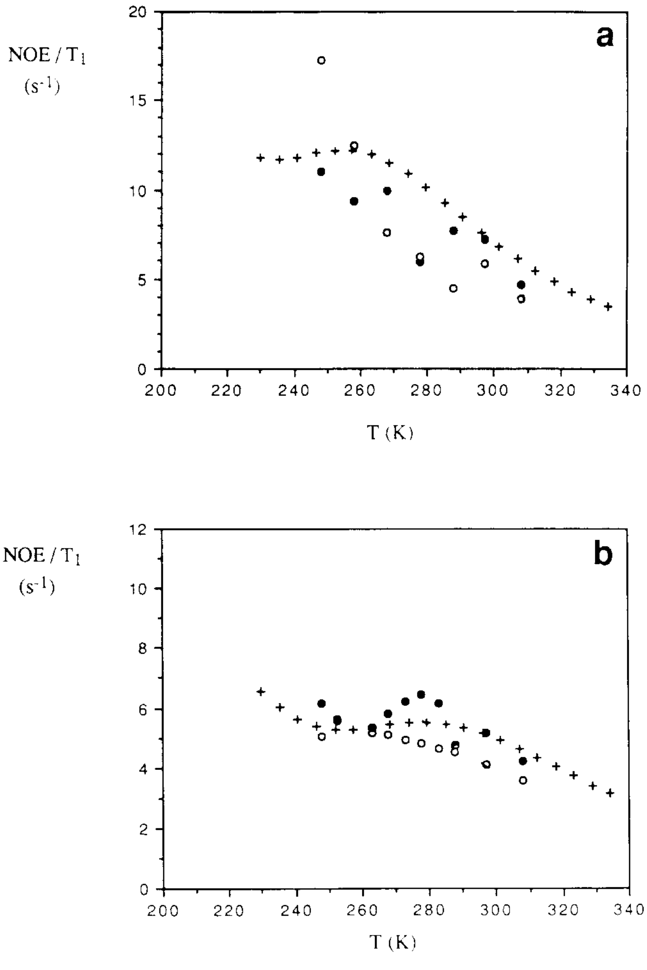


Figure 12 Temperature dependence of the experimental and calculated (+) NOE/T_1 ratio for the aromatic carbons of PHB in CF_3COOH/CD_2Cl_2 solution at 22 MHz (a) and 50 MHz (b). ●, Carbons 3,5, experimental; ○, carbons 2,6, experimental

associated with carbons 2, 6, 3 and 5, share the same local dynamics, that is, segmental chain motions plus internal ring motions about the symmetry axis of the ring.

The segmental motions of the aromatic rings can be described using the results obtained either on the ali1 or ali2 aliphatic carbons. However, as indicated above, the ali1 carbons have more motional freedom than the ali2 carbons whose local dynamics are slowed down by polymer–solvent interactions. As the local dynamics of the rings is also expected to be slowed down by these interactions, the τ_1 values chosen to interpret the NOE/T_1 ratios have been taken from the relaxation data of the ali2 carbons.

The internal motions of the *para*-substituted rings have been described in terms of jumps between two equilibrium positions using equation (8). The libration parameter has been taken as 17°, identical to the value determined for the PEI ring carbons.

Using the above set of parameters, the best fit of the NOE/nT_1 ratios has been obtained from a τ_i/τ_1 ratio of 0.04. The agreement between experimental and calculated data is illustrated in *Figure 12*. Although the sensitivity of the experiments to the τ_i process is not sufficient for an accurate determination of the energy barrier associated with the internal ring motion, experimental results are consistent with an activation energy for the internal ring motion of the same order of magnitude ($E^* = 3.1$ kcal mol^{-1}) as the energy associated with the τ_1 segmental chain motions. Such a result may be compared with calculated E^* values for the rotation of a methylbenzoate ring, which range from 2 to 6 kcal mol^{-1}. Our experiments are consistent with the value of 2.9 and 2.6 kcal mol^{-1} derived by Meurisse *et al.*[23] and Coulter and Windle[24], respectively. However, they disagree with the value of 6.7 kcal mol^{-1} found by Bicerano and Clark[25,26].

CONCLUSION

The analysis of the 22 MHz and 50 MHz ^{13}C spin–lattice relaxations in the PEI and PHB polymers in solution has pointed out the existence of several motional modes. On the whole, the segmental chain motions are well represented by the DLM orientation autocorrelation function. The parameters used for the data fit are comparable with those determined in other polymer systems[12–15], except for the τ_2/τ_1 ratio, whose rather small value indicates a strong damping of the bond orientation diffusion along the chain sequence. This result is possibly related to the presence of phenyl rings inside the main chain.

The internal motions of the *meta*-substituted ring are well described by stochastic jump processes, whereas results obtained on *para*-substituted rings are consistent with a motional model of jumps between two equilibrium positions.

The energy barriers thus determined are of the order of magnitude of those obtained for related molecules, either from experimental techniques or from conformational energy calculations.

In a further paper, this analysis will be extended to the study of the local dynamics of the copolymer A which is based on isophthalic acid, hydroxybenzoic acid and hydroquinone units in equal proportions and does not contain any aliphatic units.

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