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^{13}C n.m.r. investigation of the local dynamics of an aromatic copolyester in solution

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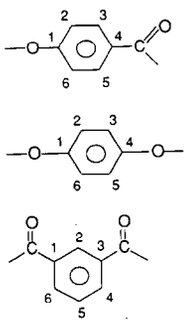
The local motions of an aromatic copolyester made from hydroquinone, hydroxybenzoic acid and isophthalic acid were investigated in trifluoroacetic acid/dichloromethane solution using ^{13}C n.m.r. The interpretation of the ^{13}C spin-lattice relaxation times was based on results previously obtained on aryl–aliphatic copolyesters obtained from ethylene glycol and hydroxybenzoic acid or isophthalic acid. It was carried out in terms of relatively slow segmental main-chain motions and faster internal motions of the aromatic rings. The segmental main-chain motions were represented by the Dejean–Lauprêtre–Monnerie orientation autocorrelation function. In agreement with the poor mobility of the aromatic copolyester, there is not any noticeable libration of the phenyl rings. The internal motions of the aromatic rings were described in terms of jumps between two equilibrium positions for the *para*-substituted phenyl rings and by stochastic jump processes for the isophthalic rings.

(Keywords: aromatic copolyester; ^{13}C n.m.r.; local motions)

INTRODUCTION

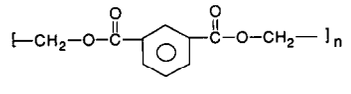
The present paper deals with the investigation of the local dynamics in solution of an aromatic copolyester (A) made from hydroxybenzoic acid (HBA), hydroquinone (HQ) and isophthalic acid (IA) in equal amounts. The technique used involves measurement of the ^{13}C spin-lattice relaxation times, T_1, which are of particular interest in the study of fast motions. Indeed, when determined by a $^{13}C-^{1}H$ dipolar relaxation mechanism, the ^{13}C spin-lattice relaxation times reflect the reorientation of the $^{13}C-^{1}H$ vectors in the hundreds of MHz range. Data interpretation is straightforward for protonated carbons for which the $^{13}C-^{1}H$ vector to be considered is the C–H bond.

However, in the thermotropic copolyester A based on the following three units in equal proportions:



two major difficulties arise. The first results from the poor solubility of copolyester A. Its only solvent known is a 70% dichloromethane/30% trifluoroacetic acid mixture. However, in such a solvent, hydrogen-bonding interactions may occur between the trifluoroacetic acid molecule and the carboxylic groups of the polymer and induce additional relaxation mechanisms. These non-intramolecular relaxation mechanisms are not directly related to the local dynamics of the chain. The second problem comes from the specific structure of copolyester A. Examination of its chemical formula shows that, in such a molecule, all the C–H bonds are likely to undergo two types of motions simultaneously, i.e. 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. One possible way to separate these two motional contributions in copolyester A would be to study the spin-lattice relaxation of the protons of the *para*-substituted units, which is not affected by the internal ring motions. However, due to proximity effects, the proton spin-lattice relaxation is still more sensitive to solvent-induced relaxation than the ^{13}C relaxation. Indeed, determinations of ^{1}H spin-lattice relaxation times have shown that the experimental values are too short to be determined by $^{1}H-^{1}H$ dipolar relaxation only[1].

To clarify the difficulties mentioned above, we previously investigated two aryl–aliphatic polyesters based on ethylene glycol and isophthalic acid or hydroxybenzoic acid[2], i.e. poly(ethylene isophthalate) (PEI):



and the following polymer (PHB) containing ethylene

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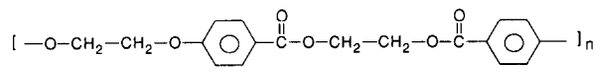
and hydroxybenzoic units:



The PEI polymer is soluble in chloroform and in the 70% dichloromethane/30% trifluoroacetic acid mixture. Therefore, comparison of n.m.r. results obtained from both solutions permitted the study of any eventual polymer–solvent interactions. Additionally, in the PEI and PHB compounds, 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 were determined independently, represented by suitable orientation autocorrelation functions and characterized in terms of correlation times and activation energies[2].

EXPERIMENTAL

The synthesis of copolyester A was performed by Drs W. A. McDonald and N. Clough of the ICI Company.

The solvent used was a 70% dichloromethane/30% trifluoroacetic acid mixture (CD_2Cl_2/CF_3COOH). The polymer concentration was 0.1 g cm^{-3}. The n.m.r. tube was 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 carbon-13 magnetization as a function of the time interval, t. Nuclear Overhauser enhancements (NOE) were obtained from:

$$\mathrm{NOE} = R - 1 \tag{1}$$

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, i.e. long enough to avoid the build-up of NOE due to decoupling during acquisition. The INEPT 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]:

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

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

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

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 nuclear Overhauser enhancement is written as:

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

In the PEI and PHB copolyesters[2], the segmental chain motion was well represented by the orientation autocorrelation function proposed by Dejean, Lauprêtre and Monnerie (DLM), which is based on a damped diffusion of bond orientation along the chain sequence and independent bond librations[5]:

$$G(t) = (1 - a)\exp(-t/\tau_2)\exp(-t/\tau_1)I_0(t/\tau_1) + a\exp(-t/\tau_0)\exp(-t/\tau_2)\exp(-t/\tau_1)I_0(t/\tau_1) \tag{5}$$

where I_0 is the modified Bessel function of order 0, and

$$1 - a = [(\cos\Theta - \cos^3\Theta)/2(1 - \cos\Theta)]^2 \tag{6}$$

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

The internal motions of the *para*-substituted rings were represented by jumps between two equilibrium positions[6]:

$$G(t) = (A + C) + Be^{-t/\tau_i} \tag{7}$$

whereas, for the *meta*-substituted rings, a stochastic process[6] was found to be relevant:

$$G(t) = A + Be^{-t/\tau_i} + Ce^{-4t/\tau_i} \tag{8}$$

where

$$A = (3\cos^2\alpha - 1)^2/4 \qquad B = 3\sin^2(2\alpha)/4 \qquad C = 3\sin^4\alpha/4 \tag{9}$$

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

Assuming that the motions of the chain and rings occur independently, the resultant orientation autocorrelation function is the direct product of the corresponding orientation autocorrelation functions.

RESULTS AND DISCUSSION

Figure 1 shows the aromatic carbon resonances of a proton-decoupled ^{13}C n.m.r. spectrum of copolyester A, recorded at 25°C at the experimental frequency of 50 MHz under quantitative conditions. The line assignment is also indicated. The assignment of the aromatic resonances corresponding to carbons belonging to HBA and HQ units is based on empirical additivity rules for the aromatic ring carbons[7] and comparison with model compounds such as 1,4-acetoxybenzoate,

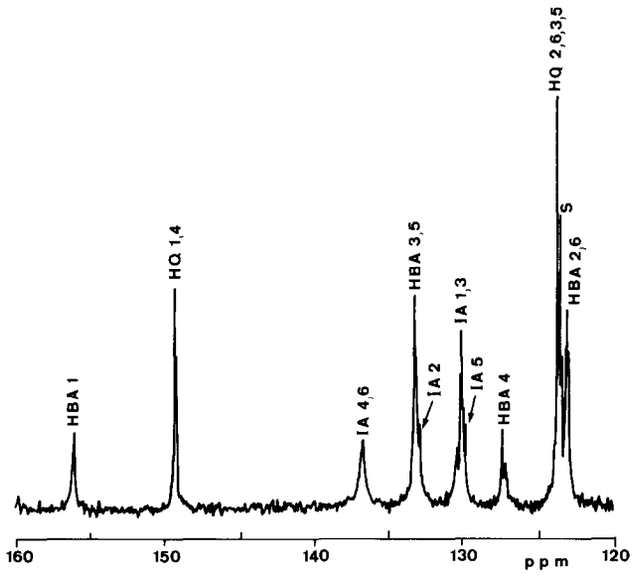


Figure 1 Aromatic carbon resonances of a proton-decoupled ^{13}C n.m.r. spectrum of copolyester A, recorded at 25°C at the experimental frequency of 50 MHz under quantitative conditions

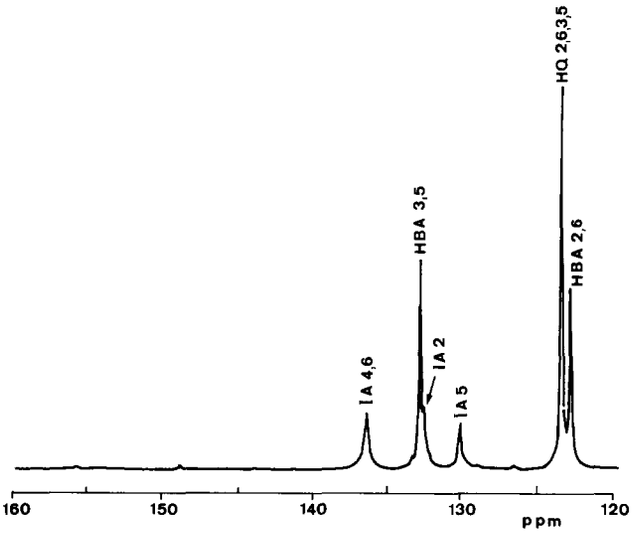


Figure 2 INEPT spectrum of copolyester A, recorded at 25°C at the experimental frequency of 50 MHz

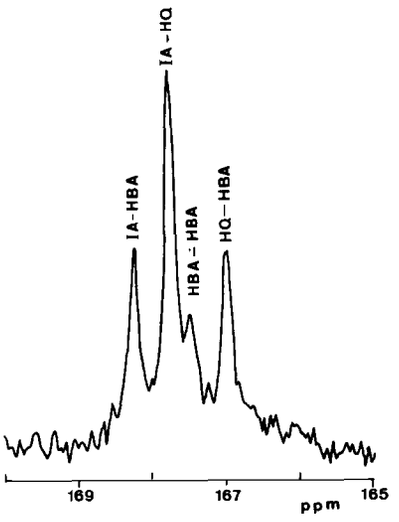
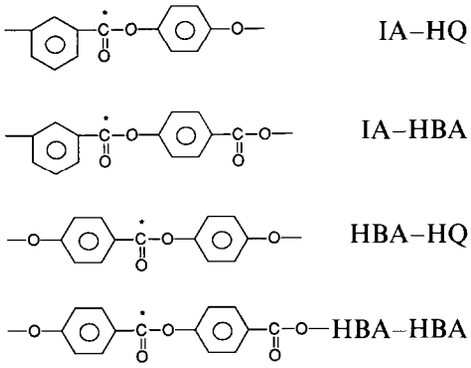


Figure 3 Carboxyl carbon resonances of copolyester A

diacetoxybenzene and dimethylisophthalate[1]. This is confirmed by the INEPT spectrum (*Figure 2*), which discriminates the unprotonated carbons from the protonated ones.

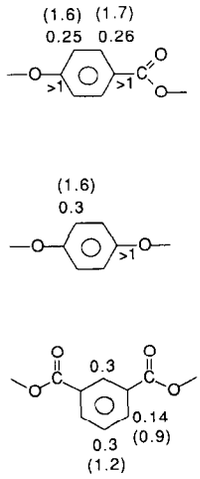
As shown by comparison of the line intensities in the ^{13}C n.m.r. spectrum obtained under quantitative conditions and the INEPT spectrum, carbons 2 and 5 of the isophthalic acid unit resonate as high-field shoulders of the 133 and 130 ppm lines, respectively. This assignment was also checked by analysing the quantitative ^{13}C n.m.r. spectrum of a copolyester built from HBA, HQ and IA units in different proportions.

In *Figure 3* are plotted the resonances assigned to the carboxyl carbons of copolyester A. The existence of four lines indicates that copolyester A is not a block copolymer based on HBA and HQ–IA sequences. It is in agreement with a statistical microstructure containing the following segments:



where C* is the considered carbon. Taking into account the fact that the HBA, HQ and IA units are in equal amounts, the amounts of carboxyl groups in the above segments are in the proportion 4 : 2 : 2 : 1, respectively. These numbers are in agreement with the relative intensities of the carboxyl carbon lines and lead to the line assignment given in *Figure 3*. The statistical character of copolyester A is supported by the observation of a single glass transition temperature by d.s.c.[8].

The spin-lattice relaxation times T_1 (s) and nuclear Overhauser enhancements (in parenthesis) of the carbons of copolyester A, determined at room temperature and 50 MHz, are summarized below:



In the *para*-substituted units, the nuclear Overhauser enhancements are of the order of 1.6–1.7, not far from

their theoretical maximum. The unprotonated carbons have relatively long relaxation times (> 1 s). The protonated aromatic carbons have much shorter relaxation times which range from 0.25 to 0.30 s. In addition, the lines assigned to carbons 3, 5 and 2, 6 of the hydroxybenzoic acid units have identical spin-lattice relaxation times, as expected for carbons located on *para*-substituted rings that share the same local motions. In the isophthalic units, carbons 2 and 5, that share identical motions, have identical spin-lattice relaxation times. This behaviour is in agreement with results expected for a purely $^{13}C-^{1}H$ dipolar relaxation mechanism. Moreover, it corroborates the line assignment of the ^{13}C n.m.r. spectrum of copolyester A.

These results are in sharp contrast with those obtained for PEI and PHB in CF_3COOH/CD_2Cl_2 solution. As described in ref. 2, the unprotonated carbons of PEI and PHB had relaxation times of 0.13 and 0.15 s, respectively, that were 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 were different, although the corresponding C–H vectors were expected to undergo identical segmental and ring motions. These observations, which indicate the existence of a second relaxation mechanism specific to the CF_3COOH/CD_2Cl_2 solution, were corroborated by the widening of the CF_3COOH line in the ^{1}H 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.

On the contrary, the ^{13}C spin-lattice relaxation behaviour of copolyester A is very close to results observed for PEI in $CDCl_3$ solution: in this solvent, at room temperature and 50 MHz, the unprotonated polymer carbons had relatively long relaxation times (> 1 s). The protonated aromatic carbons had much shorter relaxation times which ranged from 0.26 to 0.40 s. The nuclear Overhauser enhancements were equal to 1.7, close to the theoretical maximum of 2. In this solvent, which has no specific interaction with the polymer, the nT_1 values were in agreement with the existence of a unique $^{13}C-^{1}H$ dipolar relaxation mechanism[2].

The close similarity in the ^{13}C relaxation behaviour of PEI in $CDCl_3$ solution and copolyester A in CF_3COOH/CD_2Cl_2 solution is a clear indication of the absence of noticeable interactions between the polymer and the CF_3COOH molecule. Therefore, in the following, the nT_1 values of copolyester A will be interpreted in terms of a unique $^{13}C-^{1}H$ dipolar relaxation mechanism.

As indicated in the Introduction, all the protonated carbons of copolyester A are simultaneously involved in internal ring motions and segmental chain motions. To interpret the spin-lattice relaxation of copolyester A in terms of two motional contributions, the first related to the segmental chain motions and the second associated with the internal ring motions, we will base our analysis on the motional analogy that probably exists for the isophthalic unit in the PEI polymer and copolyester A in CF_3COOH/CD_2Cl_2 solution. For PEI[2], the segmental chain motion was described in terms of a damped diffusion of orientations along the chain sequence and independent librations using the DLM orientation autocorrelation function. The internal modes of the *meta*-substituted ring were represented by stochastic jumps. Results obtained[2] showed that, within the experimental accuracy, the correlation time for the internal ring process, τ_i, was equal to the segmental correlation time, τ_1, and to the damping term, τ_2. Therefore, in the following, we will interpret the relaxation characteristics of the isophthalic units of copolyester A, using the DLM orientation autocorrelation function for modelling the chain motion and stochastic jumps for the isophthalic internal ring motion. As a starting point, the ratios of the different correlation times, τ_i/τ_1 and τ_2/τ_1, will be taken to be equal to unity.

Interpretation of spin-lattice relaxation data under the assumption $\tau_1 = \tau_i$

Local dynamics of the isophthalic units. In the isophthalic units of copolyester A, the only T_1 relaxation times that can be accurately determined are those associated with carbons 4 and 6 at 50 MHz. The accuracy of the 22 MHz measurements for these carbons is quite poor. Moreover, lines corresponding to carbons 2 and 5 overlap with lines corresponding to carbons 3 and 5 of the hydroxybenzoic acid units and 1 and 3 of the isophthalic units, respectively. The 50 MHz T_1 variation as a function of temperature is shown in *Figure 4* for carbons 4 and 6. It shows a very broad minimum centred around 263 K. Use of the DLM orientation autocorrelation function permits evaluation of the amplitude of the libration, Θ, for carbons 4 and 6. Under the assumptions $\tau_i = \tau_1$ and $\tau_2 = \tau_1$, the a parameter derived from the 0.15 s value of the T_1 minimum is $a = 0.3$, corresponding to a libration amplitude Θ of 28°. The temperature dependence of the segmental correlation times τ_1, that lead to the best fit of the 50 MHz data reported in *Figure 4*, is shown in *Figure 5*. It follows an Arrhenius-type law:

$$\tau_1 = \tau_1^0 \exp(E/RT) \qquad (10)$$

with $\tau_1^0 = 4.6 \times 10^{-15}$ s and $E = 7.4$ kcal mol^{-1}.

Experimental and calculated values of T_1 are

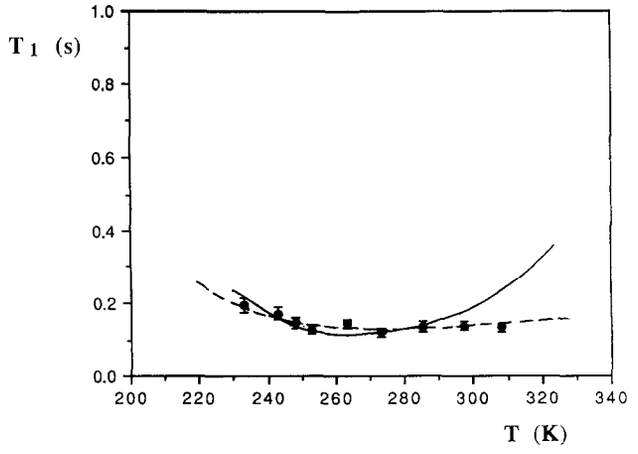


Figure 4 T_1 variation at 50 MHz as a function of temperature for carbons 4, 6 of the isophthalic acid units: experimental data (●), and best fits calculated using $\tau_1 = \tau_i$ (——) and $\tau_1 = 1000\tau_i$ (– – –)

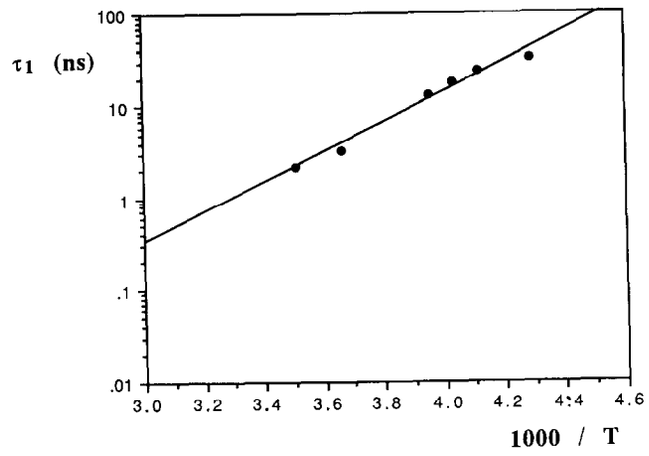


Figure 5 Temperature dependence of the segmental correlation times τ_1, derived from results reported in *Figure 4* using the assumption $\tau_1 = \tau_i$

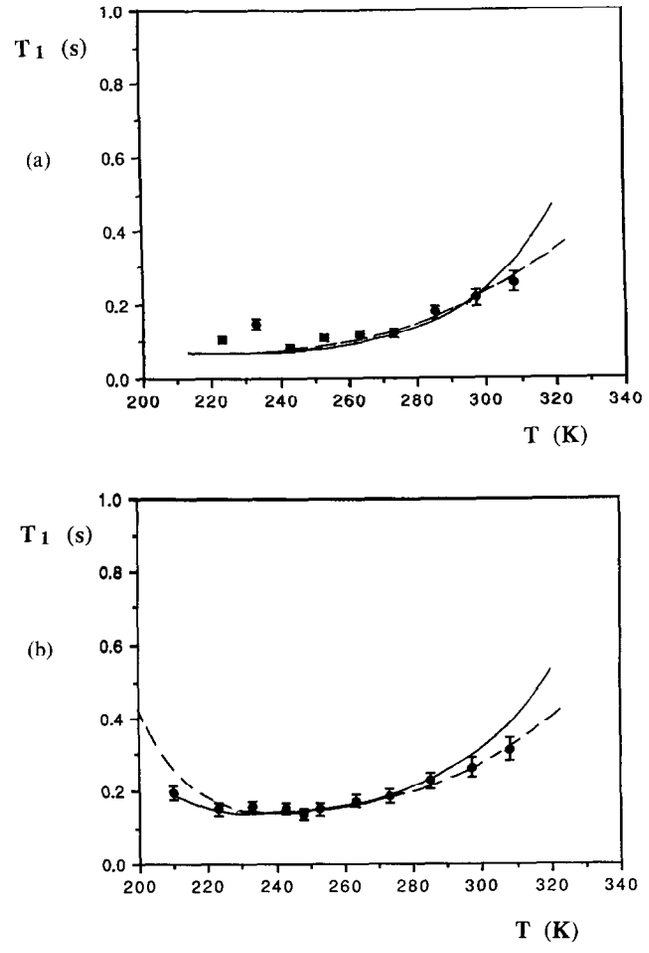


Figure 6 T_1 variations at 22 MHz (a) and 50 MHz (b) as a function of temperature for the protonated carbons of the hydroxybenzoic acid units: experimental data (●), and best fits calculated using $\tau_1 = \tau_i$ (——) and $\tau_1 = 1000\tau_i$ (– – –)

compared in *Figure 4*. The agreement is quite good except for the broadness of the T_1 minimum at high temperatures. The nuclear Overhauser enhancement determined at room temperature is 0.9, in agreement with the calculated value of 0.95.

The activation energy E determined from the τ_1 variation as a function of $1/T$ has been interpreted in

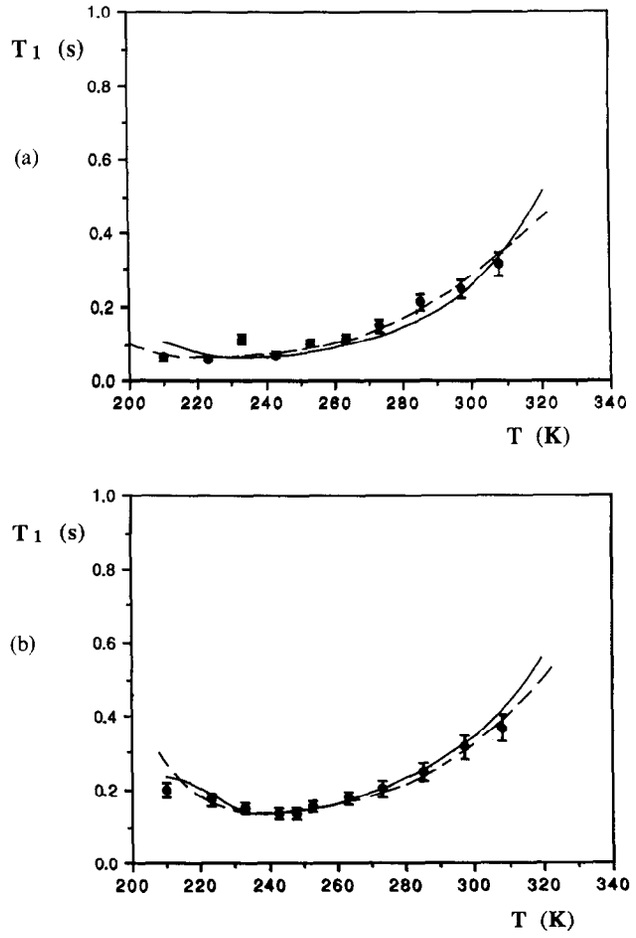


Figure 7 T_1 variations at 22 MHz (a) and 50 MHz (b) as a function of temperature for the protonated carbons of the hydroquinone units: experimental data (●), and best fits calculated using $\tau_1 = \tau_i$ (——) and $\tau_1 = 1000\tau_i$ (– – –)

terms of Kramers theory[9] for the diffusion of a particle over a potential barrier. This theory has been applied to conformational transitions in polymer chains by Helfand[10]. According to this theory, the correlation time associated with a motional mode involving the crossing of an energy barrier E^* can be written as:

$$\tau \approx \eta C \exp(E^*/RT) \qquad (11)$$

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

$$E^* = E - E_\eta \qquad (12)$$

where E_η is the activation energy for the solvent viscosity.

For CF_3COOH/CD_2Cl_2, $E_\eta = 1.6\,\text{kcal mol}^{-1}$ in the considered temperature range and, therefore, the activation energy associated with the segmental motion of the A chain is $E^* = 5.8\,\text{kcal mol}^{-1}$.

Local dynamics of the hydroxybenzoic acid and hydroquinone units. Variations of T_1 at 22 and 50 MHz as a function of temperature are shown in *Figures 6* and *7* for the protonated carbons of the hydroxybenzoic acid and hydroquinone units, respectively. For both units, the 50 MHz T_1 minimum is observed around 248 K, very close to the T_1 minimum assigned to the main-chain motion exhibited by the isophthalic units.

T_1 data for the *para*-substituted ring carbons were interpreted using the DLM orientation autocorrelation function for the segmental motion and jumps between two positions for the internal ring motion. The τ_1, τ_2 and τ_0 correlation times and the a parameter, which characterize the segmental chain motion, were taken from the study of the isophthalic unit. The values of the correlation times τ_i for the internal ring motions, that lead to the best fit of the data shown in *Figures 6* and *7*, are displayed in *Figure 8* for the hydroxybenzoic and hydroquinone rings. They obey an Arrhenius-type law, $\tau_i = \tau_i^0 \exp(E/RT)$, with $\tau_i^0 = 4.9 \times 10^{-17}$ s, $E = 8.2$ kcal mol^{-1} and $E^* = 6.6$ kcal mol^{-1} for the hydroxybenzoic ring; and $\tau_i^0 = 1.3 \times 10^{-19}$ s, $E = 11.3$ kcal mol^{-1} and $E^* = 9.7$ kcal mol^{-1} for the hydroquinone ring.

Comparison of experimental and calculated values at the two n.m.r. frequencies is shown in *Figures 6* and *7*. The overall agreement is quite good, which indicates that the combination of the DLM orientation autocorrelation function and internal ring motions under the assumption $\tau_1 = \tau_i$ enables the whole set of spin-lattice relaxation data obtained for copolyester A to be accounted for. However, several points must be considered:

1. The very broad minimum observed for the T_1 of carbons 4 and 6 of the isophthalic units (*Figure 4*) is not entirely represented by the motional model considered.
2. The libration amplitude Θ for the ring carbons is 28°, much higher than the value of 17° determined for the libration amplitude in the PEI and PHB polyesters investigated earlier[2]. This result is quite unexpected since the steric hindrance at the site of the aromatic carbons is larger in the absence of aliphatic group spacers between the phenyl rings.
3. As shown in *Table 1*, the activation energies E^* derived

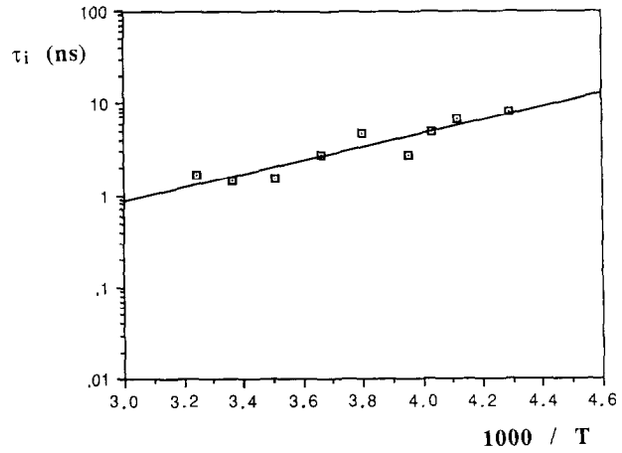


Figure 9 Temperature dependence of the segmental correlation times τ_1, derived from results reported in *Figure 4* using the assumption $\tau_1 = 1000\tau_i$

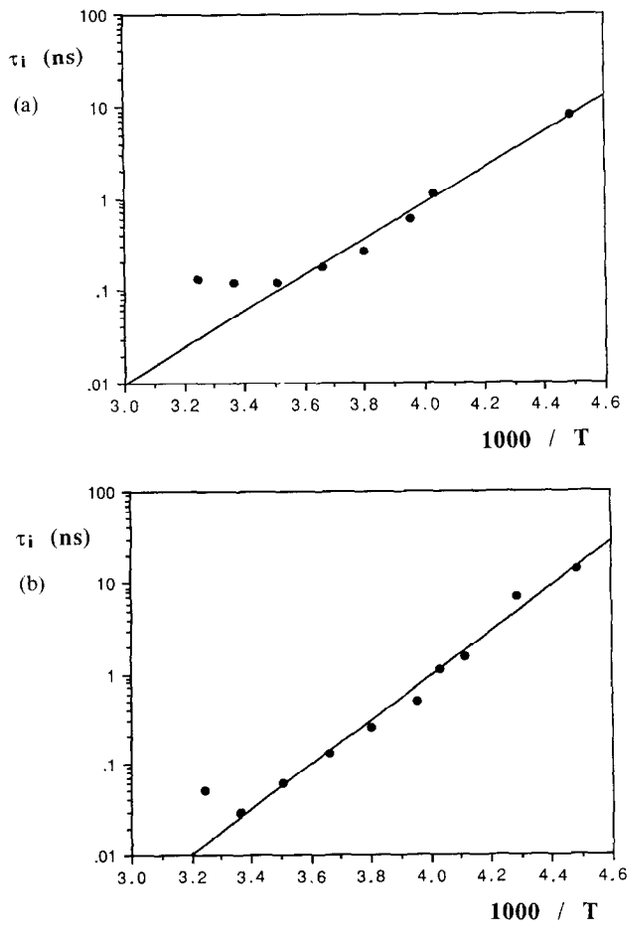


Figure 8 Temperature dependence of the correlation times τ_i, derived from T_1 variations as a function of temperature for the protonated carbons of the hydroxybenzoic acid units (a) and hydroquinone units (b), using the assumption $\tau_1 = \tau_i$

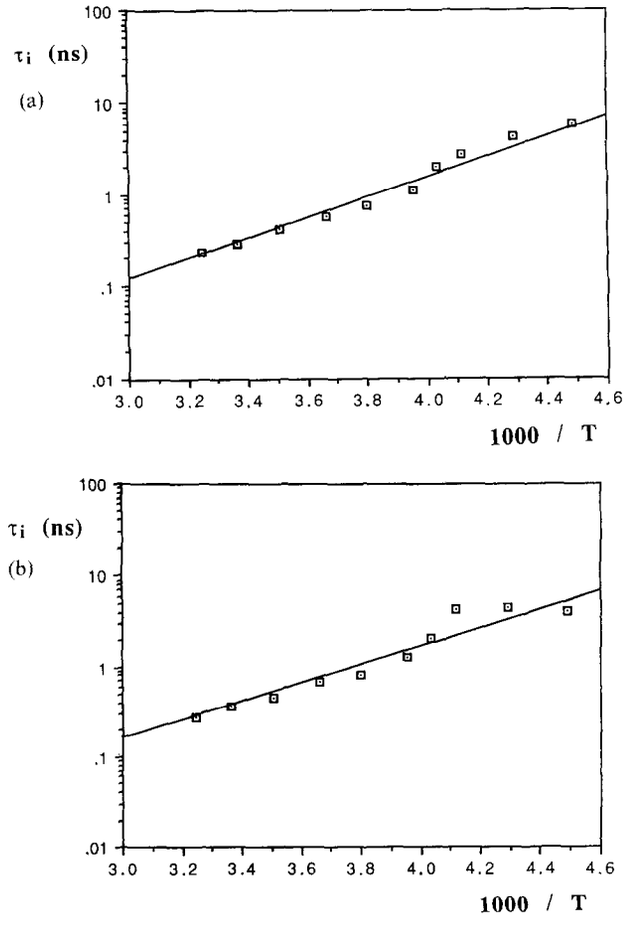
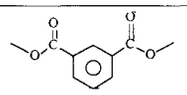
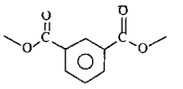
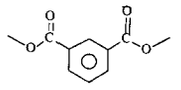
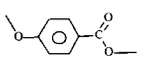
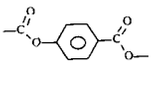
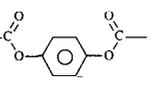


Figure 10 Temperature dependence of the correlation times τ_i, derived from T_1 variations as a function of temperature for the protonated carbons of the hydroxybenzoic acid units (a) and hydroquinone units (b), using the assumption $\tau_1 = 1000\tau_i$

Table 1 Fit parameters for the PEI, PHB and A polyesters

Chemical unit (polymer, solvent)	τ_1/τ_0	τ_1/τ_i	a	Θ (°)	E^* (kcal mol^{-1})	τ_i^0 (s)
	200	1	0.12	17	2.3	7.5×10^{-13}
(PEI, $CDCl_3$)						
	200	1	0.12	17	2.4	5×10^{-13}
(PEI, CD_2Cl_2/CF_3COOH)						
	200	1 1000	0.3 0	28 0	5.8 1.7	4.6×10^{-15} 5.4×10^{-12}
(A, CD_2Cl_2/CF_3COOH)						
	200	1	0.12	17	3.1	1.1×10^{-14}
(PHB, CD_2Cl_2/CF_3COOH)						
	200	1 1000	0.3 0	28 0	6.6 3.1	4.9×10^{-17} 1.4×10^{-13}
(A, CD_2Cl_2/CF_3COOH)						
	200	1 1000	0.3 0	28 0	9.7 3.4	1.3×10^{-19} 5.8×10^{-14}
(A, CD_2Cl_2/CF_3COOH)						

from the above calculations are much higher than those determined in PEI and PHB polyesters for similar internal ring motions[2].

It must also be observed that the fast local chain dynamics mainly originates from conformational jumps. However, in copolyester A, due to the absence of aliphatic spacers, the only groups involved in conformational jumps are the carboxyl carbons whose motions mostly induce a translation rather than a reorientation of the aromatic C–H vectors. Therefore, in copolyester A, the chain motions should be very slow compared with the internal ring motions. In the following, we will use the assumption $\tau_1 = 1000\tau_i$ to interpret results obtained on the isophthalic unit.

Interpretation of spin-lattice relaxation data under the assumption $\tau_l = 1000\tau_i$

Local dynamics of the isophthalic units. Under the assumptions $1000\tau_i = \tau_1$ and $\tau_2/\tau_1 = 1$, the interpretation of the T_1 minimum observed for carbons 4 and 6 leads to the conclusion that the a parameter is equal to zero. No libration occurs for the isophthalic acid C–H vectors.

The segmental correlation times τ_1 that fit the data reported in *Figure 4* are shown in *Figure 9*. They obey the equation $\tau_1 = \tau_1^0 \exp(E/RT)$, with $\tau_1^0 = 5.4 \times 10^{-12}$ s, $E = 3.3$ kcal mol^{-1} and $E^* = 1.7$ kcal mol^{-1}.

Comparison of experimental and calculated data is shown in *Figure 4*. The broad shape of the T_1 minimum is well represented under the assumption $1000\tau_i = \tau_1$. The calculated nuclear Overhauser enhancement is 0.7, comparable to the measured value (0.9) within the limits of experimental accuracy.

Local dynamics of the hydroxybenzoic acid and hydroquinone units. Using the parameters derived for the chain motion from the study of the isophthalic ring, the correlation times τ_i that lead to the best fit of the data reported in *Figures 6* and *7* are shown in *Figure 10*. They obey the Arrhenius-type equations with the following parameters: $\tau_i^0 = 1.4 \times 10^{-13}$ s, $E = 4.7$ kcal mol^{-1} and $E^* = 3.1$ kcal mol^{-1} for the hydroxybenzoic acid unit; and $\tau_i^0 = 5.8 \times 10^{-14}$ s, $E = 5.0$ kcal mol^{-1} and $E^* = 3.4$ kcal mol^{-1} for the hydroquinone unit.

The comparison between experimental and calculated values is shown in *Figures 6* and *7*. The agreement is quite good. As shown in *Table 1*, the activation energies E^* thus determined for the internal ring motions are of the same order of magnitude as those determined for the internal motions of the same units in the PEI and PHB polyesters previously studied[2].

CONCLUSION

The above analysis, assuming relatively slow chain motions, leads to a quite satisfying representation of spin-lattice relaxation data obtained for copolyester A in solution, in terms of a segmental chain motion using the DLM orientation autocorrelation function and specific ring internal reorientations. The discrepancies observed using the first assumption, $\tau_i = \tau_1$, are eliminated and the data fit is quite good over the whole temperature range.

In agreement with the poor mobility of copolyester A, there does not occur any noticeable libration of the phenyl rings. The activation energies determined for the internal dynamics of the *para*-substituted rings are very close to those obtained for similar internal motions in the PEI and PHB polyesters previously studied. Furthermore, they do not depend on the exact nature of the ring considered: hydroxybenzoic acid and hydroquinone rings share quite similar internal dynamics. Since, in copolyester A, many of the hydroxybenzoic acid units have a hydroquinone ring as nearest neighbour, this similarity in behaviour may indicate the existence of correlations between the motions of the two rings.

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