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^{13}C and ^{1}H nuclear magnetic resonance relaxation of poly(ethylene terephthalate), poly(ethylene isophthalate) and their copolyester in solution: a molecular motion study

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^{13}C nuclear magnetic resonance spin–lattice relaxation times (T_1) and nuclear Overhauser enhancement factors ^{13}C{^{1}H} (*NOEf*) have been measured on solutions of poly(ethylene terephthalate) (PET), poly(ethylene isophthalate) (PEI) and poly(ethylene isophthalate-*co*-terephthalate) (PEIT) in d$_2$-tetrachloroethane. The T_1 and *NOEf* values are well described by a $\log X^2$ distribution of correlation times, while the isotropic model appears to be inadequate. The average correlation times (τ_0) and the distribution parameters (p) of carbons and protons show features that are explained by invoking rotations and/or oscillations of terephthalic and isophthalic rings around the C1–C4 axis.

(Keywords: n.m.r. relaxation; molecular motion; PEIT copolyester)

INTRODUCTION

The analysis of ^{13}C and ^{1}H n.m.r. relaxation processes in solution has been widely used as a tool to characterize the segmental chain motions of polymers. Especially, in the 1970s and 1980s, many works dealing with the motional behaviour of some of the most important polymers, such as, for example, polystyrene (PS)[1,2,5], poly(methyl methacrylate) (PMMA)Σ[3–5] and poly(phenylene oxide) (PPO)[5], were published.

Despite their well recognized industrial importance, aromatic polyesters did not attract the same attention, and, to our knowledge, few studies dealing with the macromolecular dynamics of such compounds in solution have appeared up to now.

Komorowsky[6], reporting on relaxation behaviour in solution of terephthalic acid polyesters with aliphatic dialcohols, focused his attention on the effects of the alkyl chain length on the backbone mobility, while considering terephthalic rings as centres of restricted mobility.

Later Lauprêtre *et al.*[7], while studying in solution terphenyl diacid polyesters with aliphatic segments of various lengths, showed the presence of aromatic ring rotation superimposed on the overall isotropic reorientation of the macromolecular chain. However, this approach is rather specific, as polymeric systems rarely fit models based on overall isotropic reorientation.

Jelinsky *et al.*[8,9] addressed molecular motion by solid-state ^{13}C n.m.r. in copolymers having terephthalic rings interleaved by butylene ether or poly(tetramethylene) ether units (Hytrel), and concluded that aromatic rings undergo 180° flips.

Very recently, Lauprêtre *et al.*[10] came out with a study dealing with ^{13}C relaxation times of polyesters such as poly(ethylene isophthalate) (PEI) and PHB, which contains alternating units of ethylene and hydroxybenzoic acid. A detailed motional analysis has been performed by using the DLM (Dejean–Lauprêtre–Monnerie) autocorrelation function, which accounts for the experimental features reported herein.

In recent years we have been interested in studying poly(ethylene terephthalate) (PET), poly(ethylene isophthalate) (PEI), their copolyester poly(ethylene isophthalate-*co*-terephthalate) (PEIT) and similar aromatic polyesters. We have considered different aspects such as: analysis of sequence distribution[11], or, more recently, conformational analysis based on the measurement of ^{1}H–^{1}H nuclear Overhauser enhancement (NOE) effects between different aromatic rings[12].

In the present work we have extended our investigation to a careful analysis of the ^{13}C and ^{1}H T_1 spin–lattice relaxation times of PET (**1**), PEI (**2**) and PEIT (**3**), whose structures are reported in *Figure 1*.

These relaxation data, together with the ^{13}C NOE effects, have formed an experimental basis to give an insight into local and segmental motions of macromolecular chains in these kinds of copolyesters.

To support our conclusions, the dynamic behaviour of these polymers has been compared with that of a related small molecule, the cyclic dimer of isophthalic acid with ethylene glycol (DIMIS, **4**).

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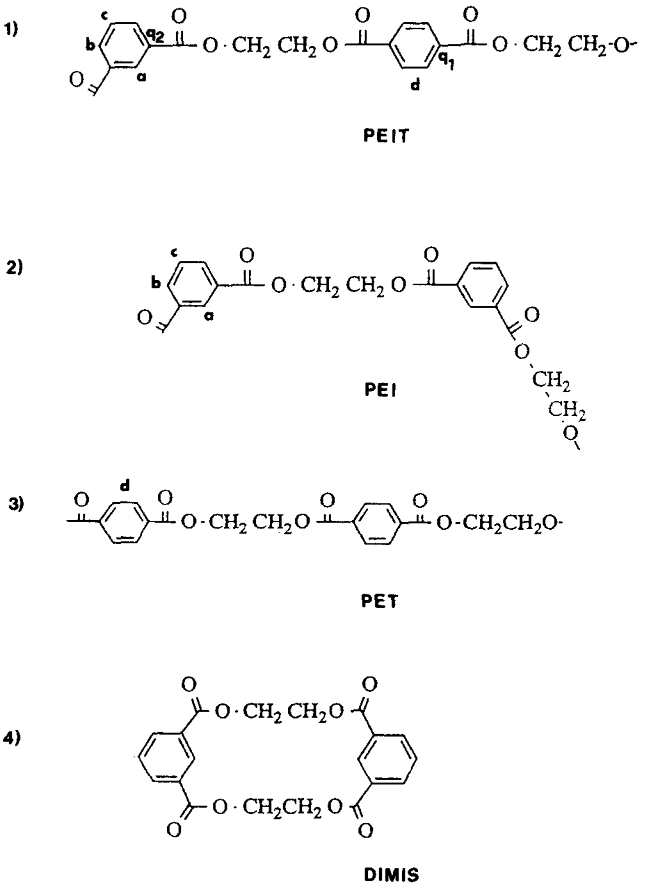

Figure 1 Chemical structure of the four samples: (**1**) poly(ethylene isophthalate-*co*-terephthalate), PEIT; (**2**) poly(ethylene isophthalate), PEI; (**3**) poly(ethylene terephthalate), PET; (**4**) DIMIS

EXPERIMENTAL

The synthesis of the compounds studied in this work was already described in a previous paper[12].

N.m.r. experiments were carried on solutions of polymers (≈5% w/v) in deuterated 1,1,2,2-tetrachloroethane ($C_2D_2Cl_4$). 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) (10% v/v) was added to the solutions to increase the solubility.

Solutions were carefully degassed and the tubes were sealed under vacuum.

All the n.m.r. measurements were recorded on a Varian VXR 300 spectrometer, operating at 300 MHz for ^{1}H and 75.4 MHz for ^{13}C.

In order to measure the ^{13}C{^{1}H} nuclear Overhauser enhancement factors (*NOEf*), ^{13}C n.m.r. spectra with and without proton decoupling before the acquisition step (gated decoupling technique) were run at 70°C and with a delay time between scans of 10 s. The *NOEf* were then calculated by comparing the signal intensities in these two sets of spectra. Each *NOEf* value is an average of two different determinations.

The ^{13}C T_1 spin–lattice relaxation times at 70°C were measured by using the standard inversion–recovery pulse sequence with a repetition time between scans longer than five times the longest T_1, and with eight values of τ (recovery time) ranging from 0.1 to 6 s. A total of 768 transients were accumulated for each τ.

The ^{1}H T_1 spin–lattice relaxation times were always measured at 70°C with the above sequence. Ten τ values were used, ranging from 0.1 to 8 s, with a relaxation delay of 8 s.

Table 1 ^{13}C chemical shifts at 70°C

	δ (ppm)			
Carbon	PET	PEI	PEIT	DIMIS
C=O	162.7	162.4	162.1	162.0
C_b		130.4	130.3	130.8
C_{q1}	129.8		129.9	
C_a		127.0	127.1	126.7
C_{q2}		126.3	126.4	126.4
C_d	125.9		125.9	
C_c		125.1	125.1	125.4
CH_2	59.4	59.3	59.3	59.1

RESULTS

^{13}C n.m.r. spectra

The ^{13}C n.m.r. spectra of the four samples, run at 70°C, are reported in *Figure 2* (only the aromatic region and the CO signals are shown).

Carbon signals are labelled according to the chemical structures reported in *Figure 1* and their chemical shifts are reported in *Table 1*.

The assignment of the signals was performed by comparing the four spectra. Protonated carbons C_a, C_b, C_c and C_d and the two quaternary carbons, C_{q1} and C_{q2}, fall in the region between 124 and 132 ppm.

The C=O signals are found around 162 ppm and those of CH_2 groups around 60 ppm.

A splitting of the terephthalic ring quaternary carbon into three resonances is observed in the spectra of PEIT (*Figure 3*). This clearly arises from the triad sequence distribution of the terephthalic (T) and isophthalic (I) units (TTT, TTI and ITT, ITI).

In fact, as already observed[13], the quaternary carbons are usually more sensitive than the other aromatic carbons to the effects of through-space (and through-bond) interactions between neighbouring units. This observation complies with our previous findings in which, by means of ^{1}H–^{1}H NOE experiments[12], through-space interactions between adjacent aromatic rings were proved to occur in PEIT.

Very small differences are observed among the chemical shifts of the CH_2 groups of the four samples, while more evident differences among the δ(C=O) are found. Besides, in PEIT, CH_2 and C=O signals are split into doublets, corresponding to terephthalic–ethylenic and isophthalic–ethylenic bonds.

^{13}C T$_1$ relaxation times

The ^{13}C relaxation times of the four samples, measured at 70°C in d$_2$-tetrachloroethane/HFIP, are reported in *Table 2*.

Assuming a pure dipolar relaxation mechanism, the ^{13}C relaxation times can be expressed according to the well known equation[14]:

$$\frac{1}{T_1} = \frac{N}{10}\frac{g_H^2 g_C^2 \hbar^2}{R_{CH}^6}[J(\omega_H - \omega_C) + 3J(\omega_C) + 6J(\omega_H + \omega_C)] \tag{1}$$

where N is the number of attached protons, R_{CH} is the C–H bond distance, g_H and g_C are the proton and

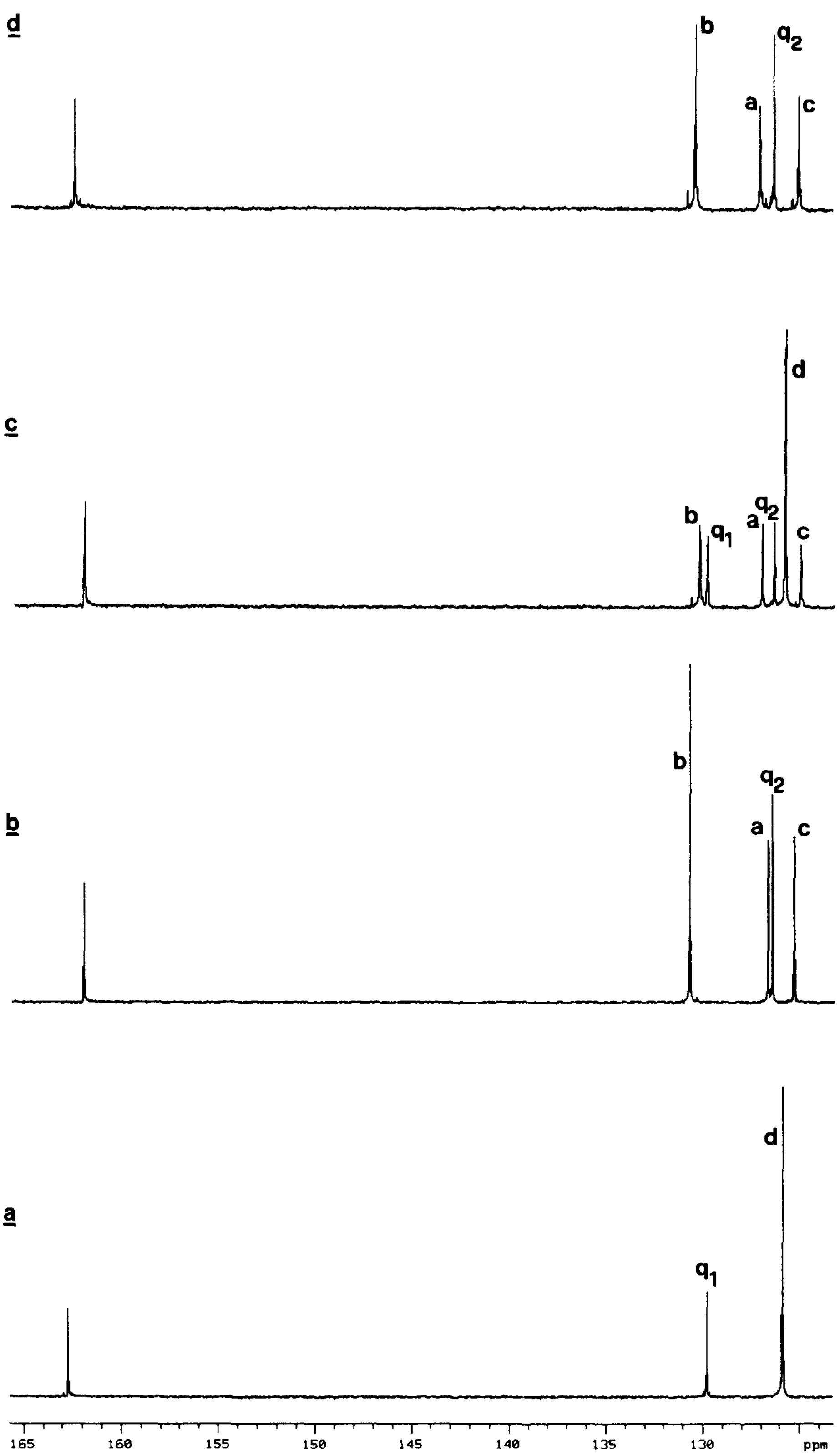

Figure 2 ^{13}C n.m.r. spectra of the four samples: (a) PET, (b) PEI, (c) PEIT and (4) DIMIS at 70°C in $C_2D_2Cl_4$ + HFIP (10%). The aliphatic region is not shown in the spectra

carbon gyromagnetic ratios respectively, ω_H and ω_C are the ^{1}H and ^{13}C resonance frequencies, and $J(\omega)$ is the spectral density function.

Since the dominant dipolar relaxation for protonated carbons involves only directly attached protons, a fixed value of 1.084 Å can be assumed for R_{CH}.

For isotropic molecular motions, the correlation times τ_c can be calculated from experimental T_1 values, according to the following expression of the spectral density function:

$$J(\omega) = \frac{\tau_c}{1 + \omega^2 \tau_c^2} \qquad (2)$$

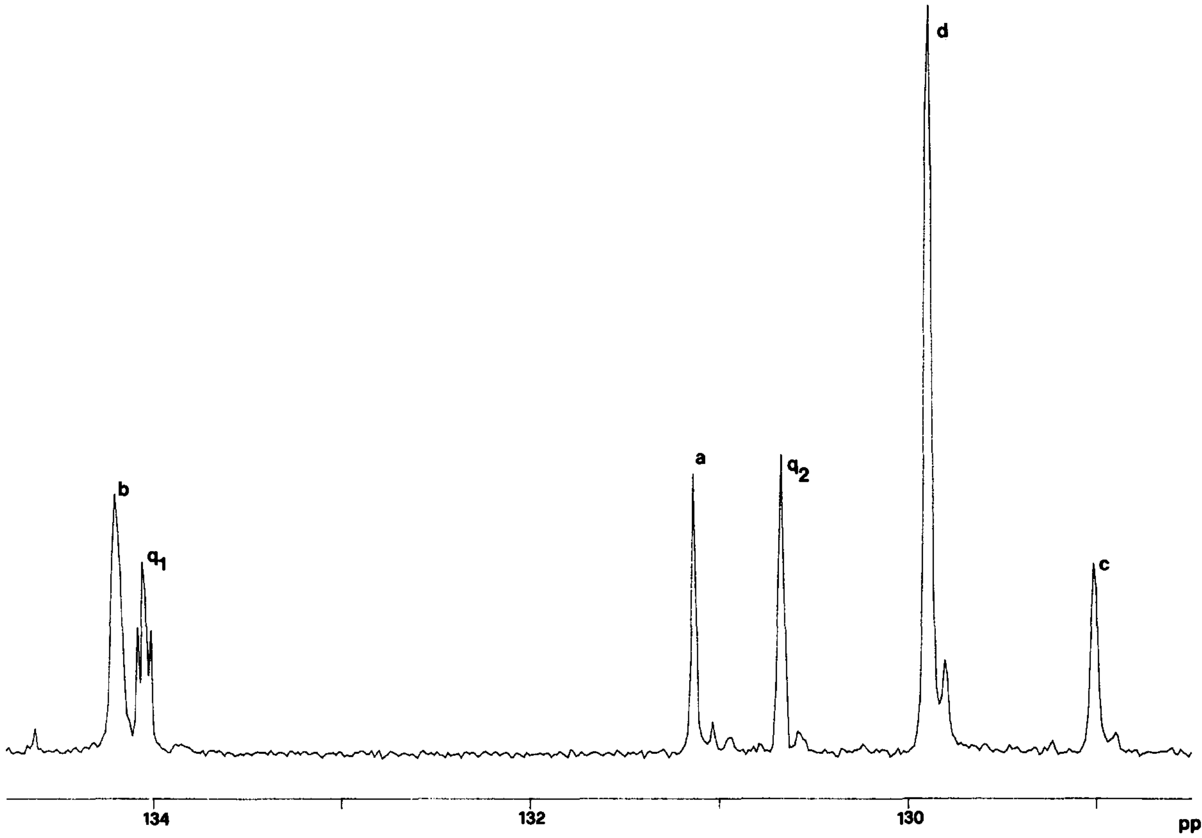

Figure 3 Enlarged area (from 135 to 129 ppm) of the ^{13}C n.m.r. spectrum of PEIT: the splitting of the quaternary carbon of the terephthalic ring (q1) is clearly visible

Table 2 T_1 (^{13}C) relaxation times at 70°C

	T_1 (s)			
Carbon	PET	PEI	PEIT	DIMIS
C_b		0.35	0.35	0.70
C_a		0.47	0.50	0.78
C_d	0.57		0.54	
C_c		0.50	0.53	0.86
CH_2	0.20	0.23	0.21	0.45

From the τ_c values thus obtained (*Table 3*) it comes out that, as already reported for PET[6], $\omega\tau_c \ll 1$ always, so that the 'extreme narrowing condition' at this temperature still holds. This result is not unusual for polymers, despite the quite high molecular weights.

In fact, for this class of compounds, segmental mobility and internal rotation are considered very efficient relaxation sources for the backbone carbons, while because of the high molecular weights, the overall reorientation is much slower and its contribution to the relaxation of the backbone carbons can be neglected[14,21,22].

The range of values covered by the isotropic τ_c is $(8-12) \times 10^{-11}$ s, and is almost the same for the three polymers.

The increase observed in the nT_1 values of some of the aromatic carbons in comparison with those of the glycolic CH_2 (see *Table 2*) can be ascribed to the contribution of anisotropic internal rotations and/or oscillations of the aromatic groups, as widely confirmed in many cases through solid-state and solution-state investigations[7,8].

Therefore, for the aromatic carbons, the assumption to deal with isotropic motions is unlikely to be true. Thus, the τ_c values reported in *Table 3* have only a qualitative meaning and should be considered 'effective' correlation times.

In DIMIS all T_1 are longer, as expected for the much smaller dimensions of this structure, and there are no significant differences between the T_1 values of the aromatic and aliphatic carbons, owing to the fact that the contribution of the overall tumbling to the relaxation is now preponderant.

NOEf

On the same samples also the *NOEf* at 70°C have been measured. As generally reported, the *NOEf* are expressed according to the following equation:

$$NOEf = \frac{g_H}{g_C} \frac{6J(\omega_H + \omega_C) - J(\omega_H - \omega_C)}{J(\omega_H - \omega_C) + 3J(\omega_C) + 6J(\omega_H + \omega_C)} \quad (3)$$

where g_H, g_C and $J(\omega)$ have their previous meanings.

If, as already shown, the 'extreme narrowing condition' holds, the *NOEf*, calculated as $(S_d - S_0)/S_0$, where S_d and S_0 are the intensity of the observed carbon signals with and without proton decoupling respectively, should approximate the maximum value of 2. As can be seen in *Table 4*, only DIMIS follows this behaviour, while in all three polymers the maximum value of *NOEf* is never reached.

This fact indicates that these polymers cannot be properly described by a single correlation-time model, and that the use of a distribution of correlation times is more appropriate.

Table 3 Correlation times derived from equations (1) and (2)

	PET			PEIT			PEI			DIMIS		
Carbon	τ_c	$\omega\tau_c$	$\omega^2\tau_c^2$	τ_c	$\omega\tau_c$	$\omega^2\tau_c^2$	τ_c	$\omega\tau_c$	$\omega^2\tau_c^2$	τ_c	$\omega\tau_c$	$\omega^2\tau_c^2$
Cb				1.38E−10	0.0654	0.0043	1.38E−10	0.065	0.0043	6.56E−11	0.031	0.0010
C_a				9.33E−11	0.0442	0.0020	9.97E−11	0.047	0.0022	5.87E−11	0.028	0.0008
C_d	8.13E−11	0.039	0.0015	8.60E−11	0.0408	0.0017						
C_c				8.77E−11	0.0416	0.0017	9.33E−11	0.044	0.0020	5.31E−11	0.025	0.0006
CH_2	1.19E−10	0.056	0.0032	1.13E−10	0.0534	0.0029	1.02E−10	0.048	0.0023	5.07E−11	0.024	0.0006

Table 4. Nuclear Overhauser enhancement factors $^{13}C\{^1H\}$ at 70°C

	NOEf			
Carbon	PET	PEI	PEIT	DIMIS
C_b		1.39	1.19	1.92
C_a		1.42	1.56	1.90
C_d	1.48		1.41	
C_c		1.40	1.52	1.89
CH_2	1.34	1.47	1.28	1.80

Table 5 Distribution parameters derived from $T_1(^{13}C)$ and *NOEf* at 70°C for each carbon

	PET		PEIT		PEI		DIMIS	
Carbon	p	$\tau_0 \times 10^{11}$	p	$\tau_0 \times 10^{11}$	p	$\tau_0 \times 10^{11}$	p	$\tau_0 \times 10^{11}$
C_b			7	1.71	13	2.35	55	2.12
C_a			15	1.47	12	1.31	44	1.70
C_d	13	1.01	17	1.41				
C_c			20	1.63	11	1.09	39	1.43
CH_2	10	1.58	16	1.95	14	1.53	39	1.37

These relatively small *NOEf* values could also originate from intermolecular interactions with solvent and in particular with HFIP, added to the solutions in order to increase polymer solubility.

Very recently Lauprêtre proved for two polymers[10], PEI and PHB, the existence of specific interactions with the solvent mixture trifluoroacetic acid/dichloromethane. These interactions lead to a lowering of the experimental *NOEf* and to a shortening of the $T_1(^{13}C)$ relaxation times of the unprotonated carbons, which become quite similar to those of the protonated ones (around 0.15 s), while in $CDCl_3$ the unprotonated carbons exhibit much longer relaxation times (>1 s) than the protonated ones. This was explained by the presence of a second relaxation mechanism, hydrogen-bonding interactions between the CF_3COOH molecule and the polymer leading to site exchange between bonded and non-bonded states.

In order to verify if this was also our case, the $T_1(^{13}C)$ relaxation times of PEI were measured in $C_2D_2Cl_4$ only and in the mixture $C_2D_2Cl_4$/HFIP 10/1, always at 70°C. No significant differences were observed between the two sets of values, for the protonated as well as for the unprotonated carbons (i.e. $T_1(C{=}O)$ is 7.8 s in the absence of HFIP and 5.6 in its presence). The $T_1(^1H)$ relaxation times again are almost equal in the two situations and the C=O signal is relatively narrow in the two ^{13}C spectra. It is clear that in our case the main relaxation mechanism is the dipolar intramolecular one in both solutions. Our opinion is that the alcoholic OH of HFIP is not so clearly involved in hydrogen bonding as the carboxylic OH of CF_3COOH, so that the interactions with solvent are less important.

Therefore, in order to account for the behaviour of the T_1 relaxation times and of the experimental *NOEf*, it should be more correct to interpret these results in terms of a distribution of motions of the main chain and of the local groups, a distribution that should enclose also motions described by longer correlation times, probably modulated by cooperative actions between units[15].

Now the question of which model to employ arises: models based on the details of the motional mechanism such as the DLM model[10,16–19] do not account for the low *NOEf* observed, while the more traditional $\log X^2$ distribution model reported by Schaefer[15], although allowing only a qualitative description of the local motions, is more coherent with our experimental findings.

The $\log X^2$ distribution model reported by Schaefer[15] was therefore employed. Accordingly, the spectral density function, appearing in the T_1 and *NOEf* equations, is expressed in terms of a correlation-time distribution described by two parameters, p (width of the distribution) and τ_0 (mean correlation time of the distribution), that are optimized in order to match the experimental data. A third parameter, b, is usually kept constant and equal to 1000. The values found for p and τ_0 for each carbon in polymers **1**, **2** and **3** and in DIMIS **4** are reported in *Table 5*. The adopted model can be considered reliable if approximately the same width parameter is found for all the carbons, so that the whole structure can be described by the same kind of distribution.

Actually, the calculated values of p are spread out in a quite narrow range, going from 10 to 20 for all carbons except C_b, which, as discussed later, always follows a different behaviour.

Inside this range, the best p value was chosen as the one that gives predicted *NOEf* and T_1 closest to the experimental ones for all the carbons of the same structure. The obtained values are $p = 12$ for PET, $p = 15$ for PEIT, $p = 12$ for PEI and $p = 40$ for DIMIS.

By using these p values, the average correlation times (τ_0) have been recalculated for each compound and reported in *Table 6*. From this table, it comes out that the C_b carbons exhibit the longest τ_0 and that the glycolic CH_2 undergo slower motions than the aromatic carbons. Besides, the p parameter is much higher for DIMIS and this means that a narrower distribution function characterizes this molecule, whose behaviour can be approximately described by a single isotropic τ_c model.

Table 6 Average τ_0, $T_1(^{13}C)$ and *NOEf* derived from $\log X^2$ distribution model

	PET $p = 12$			PEIT $p = 15$			PEI $p = 12$			DIMIS $p = 40$		
Carbon	$\tau_0 \times 10^{11}$	T_1	*NOEf*	$\tau_0 \times 10^{11}$	T_1	*NOEf*	$\tau_0 \times 10^{11}$	T_1	*NOEf*	$\tau_0 \times 10^{11}$	T_1	*NOEf*
C_b				2.59	0.35	1.44	2.25	0.35	1.37	1.82	0.70	1.87
C_a				1.43	0.50	1.52	1.32	0.47	1.42	1.62	0.78	1.88
C_d	0.95	0.57	1.46	1.27	0.54	1.53						
C_c				1.30	0.53	1.53	1.20	0.50	1.43	1.46	0.86	1.89
CH_2	1.76	0.20	1.39	1.89	0.21	1.48	1.37	0.23	1.42	1.39	0.45	1.90

Table 7 $T_1(^1H)$ relaxation times at 70°C

	T_1 (s)			
Carbon	PET	PEIT	PEI	DIMIS
H_a		5.87	6.07	5.95
H_b		2.23	2.19	3.24
H_d	1.90	1.95		
H_c		1.29	1.30	2.32
CH_2	0.33	0.38	0.38	0.52

Table 8 Experimental $T_1(^1H)$ compared with the $T_1(^1H)$ values obtained with the p value and the average τ_0 derived from the $\log X^2$ distribution model

	p	τ_0 (s)	R_{HH} (Å)	T_1 (theor.)	T_1 (expt.)
PET					
$C{-}H_d$	12	0.95×10^{-11}	2.45	4.80	1.90
CH_2	12	1.76×10^{-11}	1.66	0.34	0.33
PEIT					
$C{-}H_b$	15	2.59×10^{-11}	2.45	2.99	2.23
$C{-}H_d$	15	1.27×10^{-11}	2.45	4.30	1.95
$C{-}H_c$	15	1.30×10^{-11}	2.45	2.12	1.29
CH_2	15	1.89×10^{-11}	1.66	0.34	0.38
PEI					
$C{-}H_b$	12	2.25×10^{-11}	2.45	3.19	2.19
$C{-}H_c$	12	1.20×10^{-11}	2.45	2.13	1.30
CH_2	12	1.37×10^{-11}	1.66	0.39	0.38

^1H T_1 relaxation times

Also in the case of proton–proton nuclear pairs a purely dipolar relaxation mechanism[14] can be assumed, and therefore the T_1 spin–lattice relaxation times can be expressed in the following way:

$$\frac{1}{T_1} = \frac{3}{10}\frac{g_H^4\hbar^2}{R_{HH}^6}[J(\omega_H) + 4J(2\omega_H)] \qquad (4)$$

For isotropic motions, the spectral density function $J(\omega_H)$ is given by (2), where ω_H is the proton frequency in rad s^{-1}. The $T_1(^1H)$ values, measured at 70°C, are reported in *Table 7*.

In the case of proton relaxation times, the calculation of the correlation times is limited to those systems where R_{HH} are fixed and well defined.

H_b, H_d and H_c protons of the aromatic rings and the geminal protons of the aliphatic CH_2 satisfy these requirements, as they relax mainly through each other and their distances are well known (2.45 Å for *ortho* aromatic protons and 1.66 Å for geminal protons).

To check the validity of the model adopted to describe the motional behaviour of these samples, predicted proton relaxation times have been calculated by using the values of τ_0 and p found for carbons on the basis of the $\log X^2$ distribution. In the case of CH_2 groups, there is a close agreement between theoretical and experimental results (see *Table 8*), thus confirming the validity of the asymmetric distribution model and of the width parameters assumed for each polymer. Aromatic protons show instead larger predicted values and this difference becomes particularly anomalous in the case of H_d.

CONCLUSIONS

DIMIS can be used as a starting model for a final discussion: in this sample short correlation times ($\omega\tau_c \ll 1$) and a narrow distribution ($NOEf = 2$) are observed, which comply with values expected for a small molecule.

The behaviour of the three polymers is quite different. T_1 values fall in the motional narrowing region, but are mismatched with respect to *NOEf* values. In order to account for *NOEf* values less than 2, a distribution entailing long correlation times is invoked.

Differences in τ_0 and p inside the same aromatic ring and between the ethylenic groups and the aromatic ones might arise from additional rotation and/or oscillation of the aromatic groups around the C1–C4 axis.

Flips of 180° in terephthalic groups are widely accepted, as supported by studies performed by means of ^{13}C n.m.r.[9] and deuteron n.m.r.[20] in solid samples. For this process an activation energy of 5.9 kcal mol^{-1} has been found[20]. In solution such motions are likely to be easier.

The minor value of τ_0 found for C_d with respect to CH_2 in PET and in PEIT indicates a greater modulation of the $C{-}H_d$ coupling. The same τ_0 values give for CH_2 a predicted $T_1(^1H)$ close to the experimental one, and a much higher one for H_d (see *Table 8*). These results are in agreement with the fact that the terephthalic ring is undergoing significant jumps or rotations around the C1–C4 axis. In fact under such anisotropic motion the $C{-}H_d$ vector, having an angle of 60° with respect to the rotation axis, contributes to the modulation of the dipolar interaction and decreases the overall correlation time of the relative carbon. On the other hand no contribution to the relaxation of the protons H_d comes from this motion, as the $H_d{-}H_d$ dipolar vector is parallel to the rotation axis[7]; thus a T_1 shorter than the one predicted on the basis of the carbon average correlation time and p parameter is found.

The isophthalic ring in PEIT shows odd features as C_b carbon has a behaviour different from the other aromatic carbons: its *NOEf* value is less than the others (1.2). As

*NOEf*s are more affected than T_1 by lower-frequency motions, this fact determines the larger distribution or the longer τ_0 (if we use the average p value of the whole structure) characterizing C_b.

In our opinion, this behaviour can be explained by assuming that oscillations around the C1–C4 axis are operative also in the isophthalic ring, where C1 is the carbon bounded to the C=O and C4 coincides with C_b. During these oscillations only half of the C_b-H_b vectors are involved, the other half being colinear with the axis of motion. As a consequence, the oscillatory motions are less effective in relaxing C_b and the contribution coming from slower segmental reorientation motions becomes more important, leading to a broader distribution of τ_c.

A kind of rotational motion giving rise to the same effects has been proposed in ref. 10 for the isophthalic ring having the C=O groups in a *trans* conformation and the rotational axis joining the oxygen atoms almost colinear with the vectors C4–H or C6–H.

Also in PEI the average τ_0 of C_b is always longer than that of the other aromatic carbons, because of the orientation of the C_b–H vector with respect to the axis of oscillation, but its distribution width is narrower than in PEIT. We suggest that in PEI segmental reorientation motions are faster, and thus the corresponding τ_c values are closer to those characteristic of the oscillatory motions.

In a previous work[12] we have demonstrated that interactions between adjacent aromatic rings occur in PEIT. Now we suspect that these interactions can play a significant role in slowing the rate of the segmental reorientations of this polymer.

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