Investigation of the molecular mobility in a ternary copolyester in the liquid crystalline and isotropic states by means of deuteron n.m.r.*

C. Spies and H. G. Zachmann†
Institut für Technische und Makromolekulare Chemie, University of Hamburg, Bundesstr. 45, D-20146 Hamburg, Germany

Selectively deuterated ternary copolyesters of poly(ethylene terephthalate) (PET), poly(ethylenenaphthalene-2,6-dicarboxylate) (PEN) and poly(*p*-hydroxybenzoic acid) (PHBA) showing the molar composition 35:35:30 were synthesized. In these copolyesters the liquid crystalline state, as well as the isotropic state, can be frozen in by quenching the material from different temperatures. In this way it is possible to compare the molecular mobility in both states. By means of dynamic mechanical analysis it was shown in previous investigations that the glass transition temperature, T_g, of the liquid crystalline state is about 35°C lower than that of the isotropic state. The molecular mobility of the ethylene groups and of the phenylene rings below and above T_g in both the liquid crystalline and the isotropic state is now investigated by means of deuteron n.m.r. It is shown that the *trans–gauche* jumps of the CH_2 groups in the elongated chains in the liquid crystalline state can occur at lower temperatures than in the coiled chains in the isotropic state. As a consequence, the fraction of flipping phenylene rings in the liquid crystalline state is larger than in the isotropic state, when compared at the same temperature.

(Keywords: molecular mobility; copolyester; deuteron n.m.r.)

INTRODUCTION

Deuteron n.m.r. is a powerful tool for investigating molecular mobility in polymers[1–4]. For example, previous investigations[5] have shown that in poly(ethylene terephthalate) (PET), flipping of the phenylene rings (180° jumps about the *para* axis) begins well below the glass transition temperature, T_g, at much lower temperatures than the *trans–gauche* jumps of the ethylene groups. In contrast, the motion of the naphthalene ring in poly(ethylenenaphthalene-2,6-dicarboxylate) (PEN) only occurs in conjunction with the motion of the ethylene groups[6]. In poly(*p*-hydroxybenzoic acid) (PHBA) the development of flipping of the phenylene rings in the orthorhombic crystal lattice is related to a change of the crystal modification into a pseudo-hexagonal lattice[7]. Allen and Ward[8] have shown that in liquid crystalline (LC) aromatic copolyesters, with increasing temperature the flipping of the phenylene rings goes over into unrestricted rotational motion. However, in PET, isotropic motion develops[5,8,9].

In continuation of these investigations, it seems interesting to compare the mobility in the LC state with the mobility in the amorphous isotropic state in more detail, including the motion of ethylene groups. Most suitable for such a comparison is a material in which both the LC and the isotropic amorphous states can be frozen in by different thermal treatments. In previous investigations[10], we have shown that the ternary copolyester PEN-*co*-PET-*co*-PHBA (35:35:30) is such a material. At thermal equilibrium, this copolyester is in the LC state up to about 160°C, where it starts to become gradually isotropic. At 290°C it is completely isotropic. If quenched from this temperature to room temperature, the isotropic state is frozen in, and can only be transformed into the LC state by reheating the sample to about 100°C. The glass transition temperature of the isotropic state, T_{gi}, is 95°C, while that of the material in the LC state, T_{gLC}, is only 60°C. Some preliminary deuteron n.m.r. investigations have shown[11] that in the LC phase the majority of the ethylene groups are in the *trans* conformation, and that *trans–gauche* jumps are already starting to occur at room temperature. In the isotropic state, on the other hand, only about 50% of the ethylene groups are in the *trans* conformation, and jumps do not occur to a similar extent below 86°C.

In the current paper we present a more detailed investigation of the molecular motion in the isotropic and LC state of the ternary copolyester PEN-*co*-PET-*co*-PHBA (35:35:30) by means of deuteron n.m.r. The mobility of the ethylene groups, of the phenylene rings in the PET, and of the phenylene rings in PHBA, are studied separately using materials in which only one kind of the three different atomic groups is deuterated.

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* Presented at 'Polymer Science and Technology—a conference to mark the 65th birthday of Professor Ian Ward FRS', 21–23 April 1993, University of Leeds, UK

† To whom correspondence should be addressed

0032-3861/94/18/3816–11

Table 1 Thermal treatment and designation of the differently heated samples

		Designation		
Thermal treatment	Symbol	Ethylene groups deuterated	Phenylene ring in PET deut.	Phenylene ring in PHBA deut.
70 s melt-pressed at 290°C, quenched to 0°C	i (isotropic)	Ed_8-i	PET-Phd_4-i	PHBA-Phd_4-i
70 s melt-pressed at 290°C, quenched to 0°C, 2 min annealed at 135°C, quenched to 0°C	LC (liquid crystalline)	Ed_8-LC	PET-Phd_4-LC	PHBA-Phd_4-LC
70 s melt-pressed at 290°C, quenched to 0°C, 2 h annealed at 180°C	c (crystallized)	Ed_8-c	PET-Phd_4-c	PHBA-Phd_4-c

Table 2 Intrinsic viscosity in hexafluoroisopropanol, [η], apparent molecular weight, M_w, degree of crystallinity, x_c, as measured by WAXS, and density, ρ, of the different samples

Sample	[η]	M_w ($g\,mol^{-1}$)	x_c	ρ ($g\,cm^{-3}$)
Ed_8-i	0.5447	22 200		1.3743
Ed_8-LC				1.4006
Ed_8-c			0.04	1.4038
PET-Phd_4-i	0.4819	18 600		1.3567
PET-Phd_4-LC				1.3900
PET-Phd_4-c			0.07	1.3921
PHBA-Phd_4-i	0.4892	19 000		1.3534
PHBA-Phd_4-LC				1.3845
PHBA-Phd_4-c			0.06	1.3933

EXPERIMENTAL

Three different copolyesters were synthesized: one in which the ethylene groups were deuterated (PEN-Ed_4-*co*-PET-Ed_4-*co*-PHBA), one in which the phenylene ring in the PET was deuterated (PEN-*co*-PET-Phd_4-*co*-PHBA) and one in which the phenylene ring in the PHBA was deuterated (PEN-*co*-PET-*co*-PHBA-Phd_4). The molar ratio of the three components was 35:35:30 in each of the three polymers. In the following, the three different materials will be called Ed_8, PET-Phd_4 and PHBA-Phd_4, respectively.

The selectively deuterated copolyesters were synthesized as described in previous publications: the syntheses of the deuterated monomers are described in ref. 12, and those of PEN and PET in refs 13 and 14, respectively. The ternary copolyester was obtained by transesterification of PEN, PET and *p*-acetoxybenzoic acid followed by condensation[13,15].

From the synthesized materials, films with a thickness of 230 μm were obtained by melt-pressing at 290°C for 70 s *in vacuo* followed by quenching in ice water. As these samples were mainly isotropic they will be designated by 'i' (see *Table 1*). Some of these films were annealed for 2 min at 135°C and quenched again. As these samples became mainly liquid crystalline they will be designated by 'LC'. Finally, some of the amorphous films were annealed for 2 h at 180°C. As these films became partially crystalline they will be designated by 'c'. The different pretreatments are summarized in *Table 1*.

To characterize the material, the intrinsic viscosity, [η], of the isotropic samples was measured in hexafluoroisopropanol. The values obtained are shown in *Table 2*.

From the values of [η] an apparent molecular weight was calculated using the relationship $[\eta]=KM_w^{\alpha}$, with $K=5.20\times10^{-4}\,dl\,g^{-1}$ and $\alpha=0.695$, which is valid for PET[16].

Wide angle X-ray scattering (WAXS) measurements were performed by means of a Siemens D-500 diffractometer in transmission mode. For the dynamic mechanical analysis (d.m.a.), a DMA-983 instrument from DuPont (now Thermal Analysis Instruments) was used. The densities were measured in graded density columns filled with hexane/tetrachloromethane.

The deuteron n.m.r. investigations were performed on a Bruker MSL 300 FT NMR spectrometer. The n.m.r. spectra were measured by the solid echo method. First, a progressional saturation pulse sequence consisting of 10 90° x pulses was applied, which completely destroyed all magnetization in the sample. After a waiting time, τ_w, a solid echo pulse sequence followed, consisting of a 45° x and a 45° y pulse separated by a time $\tau_1=23\,\mu s$. The duration of the 45° pulse was about 3 μs. The n.m.r. spectra were obtained by Fourier transformation of the echo signal observed after the last of the pulses. In each measurement, about 2×10^3 spectra had to be accumulated in the case of the ethylene group deuterated sample and about 5×10^3 measurements when the phenylene rings were deuterated, in order to account for the mole percentage of each component.

In order to measure the longitudinal relaxation curve, the waiting time τ_w was varied and the maximum intensity of the echo, M_z, was determined as a function of τ_w (saturation recovery).

RESULTS

WAXS, d.m.a. and density measurements

The two upper curves in *Figure 1* show the WAXS scattering diagrams obtained from a quenched sample Ed_8-i and from a sample annealed for 2 min at 135°C after quenching (Ed_8-LC). These samples show no crystalline reflections. The halo of the annealed sample is a little narrower than that of the unannealed sample. The other curves are the scattering curves of the samples Ed_8-c, PET-Phd_4-c and PHBA-Phd_4-c, which were annealed for 2 h at 180°C. The crystal reflections of PEN as a consequence of the annealing processes can be clearly recognized. There is also clear evidence for crystal reflections of PET, designated by T in *Figure 1*.

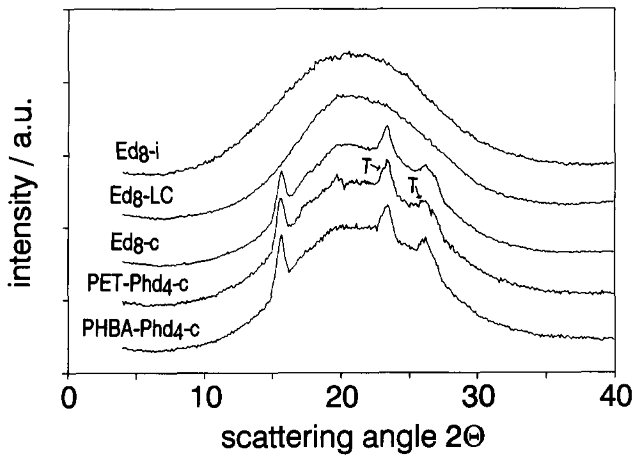

Figure 1 WAXS diagrams of the different samples investigated

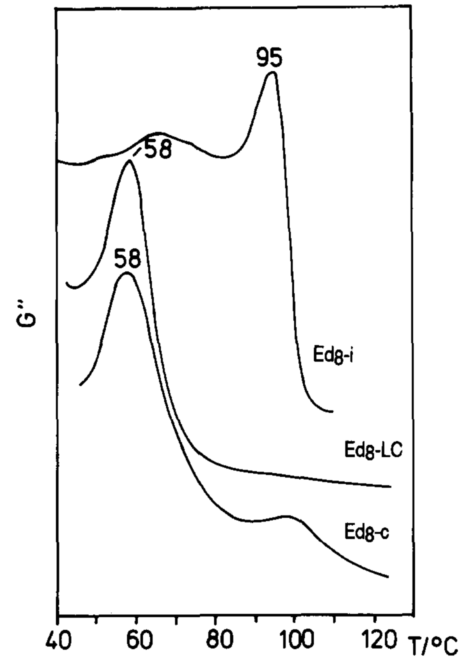

Figure 2 Loss modulus G'' as a function of temperature for the ethylene deuterated sample after quenching from 290°C (Ed_8-i), after annealing for 2 min at 135°C (Ed_8-LC) and after annealing for 2 h at 180°C (Ed_8-c)

Figure 2 shows the loss modulus, G'', as a function of temperature for the ethylene deuterated quenched sample Ed_8-i and for the same sample after annealing for 2 min at 135°C, Ed_8-LC. The main peak of the quenched sample is at 95°C, which corresponds to the isotropic state, while in the annealed sample Ed_8-LC the peak at 58°C prevails, indicating that the material is mainly liquid crystalline[17,18]. In the quenched sample Ed_8-i there is also a broad maximum at 65°C which, however, is not related to liquid crystallinity but corresponds to the β^* maximum in PEN[10]. *Figure 2* also presents the loss curve of the crystallized sample Ed_8-c. The small peak at 95°C is evidence that a small part of the material has been transformed into the isotropic state as a consequence of annealing at 180°C.

The densities of the samples are given in *Table 2*. The density of the sample in which the ethylene groups are deuterated increases from 1.3743 to 1.4006 g cm^{-3} when the isotropic state is transformed into the LC state. The corresponding density values of the samples in which the phenylene rings are deuterated are smaller, because the fraction of protons replaced by deuterons is smaller.

Longitudinal relaxation

Figure 3 shows the relative longitudinal magnetization $M_z(\tau_w)/M_0$ as a function of the logarithm of the waiting time τ_w for some of the measurements. The symbols represent the measured values, and the curves were obtained by best fitting of a superposition of exponential functions according to the equation

$$M_z(\tau_w)=M_0\left(1-\sum_{j=1}^{n} x_j\exp[-\tau_w/T_1^{(j)}]\right) \qquad (1)$$

For the samples crystallized at 180°C, a superposition of four exponential curves had to be assumed in order to

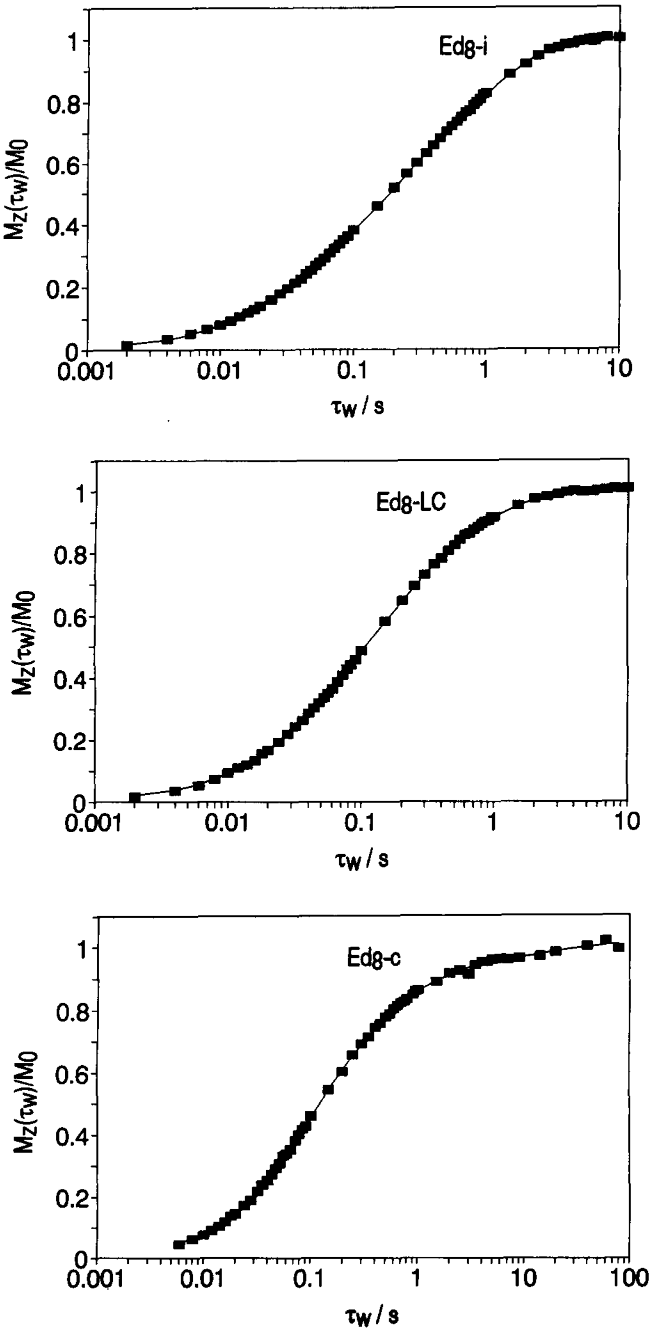

Figure 3 Relative longitudinal magnetization $M_z(\tau_w)/M_0$ as a function of the logarithm of the waiting time τ_w for the three samples of *Figure 2* measured at 22°C (symbols) and fitted by curves calculated using equation (1) and the values of *Table 3*

Table 3 Relaxation times, $T_1^{(j)}$, and fractions, x_j, of the different exponential components of the longitudinal relaxation curve at 22°C

Sample	$T_1^{(1)}$ (s)	x_1	$T_1^{(2)}$ (s)	x_2	$T_1^{(3)}$ (s)	x_3	$T_1^{(4)}$ (s)	x_4
Ed$_8$-i			1.23 ±0.03	0.39 ±0.01	0.20 0.01	0.41 0.01	0.031 ±0.001	0.20 ±0.01
Ed$_8$-LC			1.02 ±0.06	0.22 ±0.01	0.21 ±0.01	0.46 ±0.01	0.044 ±0.001	0.32 ±0.01
Ed$_8$-c	20 ±8	0.06 ±0.01	1.54 ±0.41	0.15 ±0.02	0.27 ±0.03	0.41 ±0.02	0.057 ±0.003	0.38 ±0.03
PHBA-Phd$_4$-i			1.34 ±0.13	0.56 ±0.05	0.26 ±0.04	0.38 ±0.05	0.017 ±0.006	0.07 ±0.01
PHBA-Phd$_4$-LC			0.81 ±0.06	0.70 ±0.05	0.12 ±0.05	0.18 ±0.04	0.004 ±0.007	0.12 ±0.02
PHBA-Phd$_4$-c			1.73 ±0.12	0.47 ±0.02	0.26 ±0.03	0.35 ±0.02	0.024 ±0.003	0.18 ±0.01
PET-Phd$_4$-i			1.10 ±0.05	0.66 ±0.03	0.24 ±0.05	0.22 ±0.03	0.023 ±0.003	0.11 ±0.01
PET-Phd$_4$-LC			1.08 ±0.06	0.64 ±0.03	0.19 ±0.04	0.27 ±0.03	0.024 ±0.007	0.09 ±0.02
PET-Phd$_4$-c	10 ±3	0.13 ±0.01	0.70 ±0.04	0.66 ±0.02	0.10 ±0.04	0.15 ±0.02	0.018 ±0.009	0.06 ±0.03

Table 4 Relaxation times, $T_1^{(j)}$, and fraction, x_j, of the exponential components of the longitudinal relaxation curves at elevated temperatures

Sample	Temp. (°C)	$T_1^{(1)}$ (s)	x_1	$T_1^{(2)}$ (s)	x_2	$T_1^{(3)}$ (s)	x_3	$T_1^{(4)}$ (s)	x_4
Ed$_8$-i	86			0.40 ±0.02	0.30 ±0.02	0.064 ±0.005	0.52 ±0.02	0.010 ±0.001	0.18 ±0.02
Ed$_8$-i	108	4.8 ±0.3	0.19 ±0.01	0.27 ±0.05	0.10 ±0.01	0.024 ±0.0003	0.71 ±0.01		
Ed$_8$-LC	108	5.0 ±0.8	0.15 ±0.01	0.28 ±0.07	0.11 ±0.01	0.025 ±0.0006	0.74 ±0.01		

obtain good agreement between the measured and calculated curves. For all other samples, three exponentials were sufficient.

Table 3 represents the fractions x_j and the relaxation times $T_1^{(j)}$ of the different components for the samples measured at room temperature. In the case of crystalline samples, as discussed in previous publications[5,6,19], the component with the longest relaxation time is related to the crystalline phase. This component is designated by the index 1. The components arising from the amorphous regions are designated by the indices 2, 3 and 4, respectively. As a consequence, in the case of the non-crystalline samples the index 1 does not appear.

This separation into three or four exponential curves does not necessarily mean that there are exactly three or four components present. Rather, we assume that there exists, at least in the amorphous regions, a continuous spectrum of relaxation times T_1 and that the separation into discrete relaxation times is simply a method to characterize this distribution (see the Discussion).

A comparison of the results in *Table 3* for the different samples shows that a slight shift to shorter values of T_1 takes place when the sample is transformed from the isotropic into the LC phase. This means that the mobility of the chains in the LC state is higher than in the isotropic state. This is true for all three kinds of atomic groups. The decrease of T_1 is largest for the phenylene rings in the PHBA units.

When the material is crystallized, a new component with a large relaxation time appears in the case of the samples in which the phenylene rings in the PET or the ethylene groups are deuterated. This component is related to the crystals. Such a slowly relaxing component does not appear in the material in which the phenylene rings of the PHBA units are deuterated. This indicates, as expected, that these rings are not built into the crystals. The fraction x_1 of rigid ethylene groups and rigid phenylene rings given in *Table 3* (0.06 and 0.13, respectively) are both larger than the crystalline fraction x_c as determined by WAXS, which is shown in *Table 2* (0.04 and 0.07, respectively). This is due to the fact that x_1 refers to the amount of ethylene group or phenylene rings, respectively, whereas x_c is related to the total material.

It is worthwhile noting that the largest relaxation time in the amorphous regions changes by a factor of 10 when the material crystallizes, whereas a factor of less than two applies when the material goes over into the frozen-in LC state. Furthermore, the relaxation times decrease during the latter transition while increasing as a consequence of crystallization, although the density increases in both cases.

Table 4 represents some results obtained at higher temperatures. One can see that the relaxation times generally decrease with increasing temperature owing to the increase of chain mobility. When the measurement is performed at 108°C, the component x_1 with the long relaxation time appears, thus indicating that some crystallization has occurred during the measurements at this high temperature. This was confirmed by means of

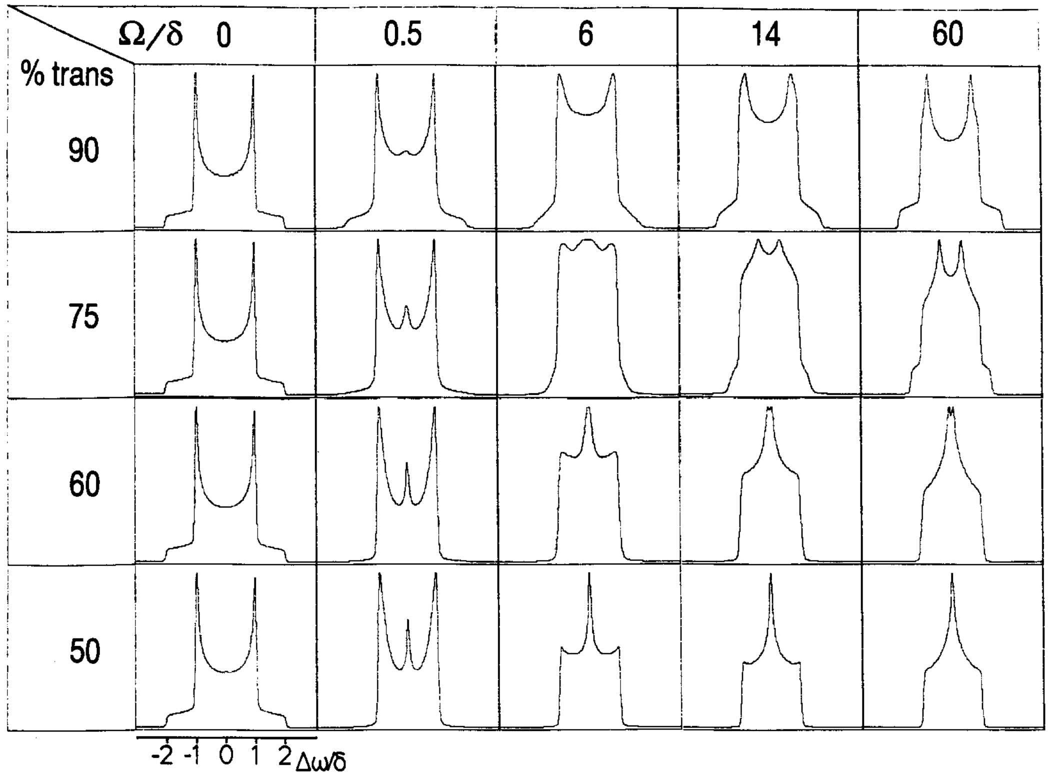

Figure 4 Calculated spectra for ethylene groups performing *trans–gauche* jumps for some values of the jump frequency Ω assuming four different values for the fraction of groups in *trans* conformations

WAXS measurements. At this high temperature the relaxation time $T_1^{(4)}$ became so small that it was not possible to obtain a significant separation of components 3 and 4. Therefore, component 3 contains both of these contributions.

Spectra of the ethylene deuterated samples Ed_8

For the interpretation of these spectra it is necessary to determine the influence of *trans–gauche* jumps of the ethylene groups on the shape of the spectra. The shapes of these spectra are not only dependent upon the jump rate, Ω, but also on the fraction of *trans* conformations present in the chains. In addition, the time τ_1 between the 45° x pulse and the 45° y pulse (see Experimental section) is of influence. Using the method described in an earlier publication[7], we have calculated the spectra for different values of Ω and as a function of the fraction of *trans* conformations assuming that, as in the experiments, $\tau_1 = 23\,\mu$s.

The results are shown in *Figure 4*. If 90% of the groups are in the *trans* conformation, the main result of the jumps is a decrease in the distance between the two peaks. The higher the jump frequency Ω (which is given in units of $\delta = 2\pi \times 59$ kHz, where δ is half the splitting of the two maxima in the Pake diagram), the smaller the distance. In addition, at intermediate values of Ω, a small central peak appears, which vanishes in the fast motion limit ($\Omega/\delta = 60$).

When the percentage of the groups in *trans* conformation decreases, the central peak becomes more pronounced and the distance between the two peaks gradually becomes smaller. At 50% *trans* conformation the central peak dominates and the two other peaks gradually disappear with increasing values of Ω.

The measurements of the spectra were performed using different values of the waiting time τ_w. In the case of small values, only the highly mobile parts of the molecules contribute to the spectra. When longer waiting times are used, the less mobile parts are also contributing.

The upper row in *Figure 5* shows the n.m.r. spectra of the sample with deuterated ethylene groups in the LC state (sample Ed_8-LC) measured at different temperatures up to 90°C, using a waiting time $\tau_w = 0.05$ s. At this comparatively short waiting time, the fast relaxing components are the main contributors to the spectra. The fractions of material from each component y_j contributing to the spectra and the fraction of total material $u_i = y_j x_j$ belonging to the component j and contributing to the spectra are shown in *Table 5*. Pake-like spectra are observed. However, the distance between the peaks is a little smaller than in the Pake diagram and decreases with increasing temperature. This is indicated more clearly in *Figure 6*, where the distance is plotted as a function of temperature. In addition, the intensity of the spectra between the two peaks is higher than in the Pake diagram. These differences can be explained if one assumes that 90% of the ethylene groups are in the *trans* conformation and that *trans–gauche* jumps occur with a frequency Ω which becomes larger with increasing temperature. The lower row in *Figure 5* illustrates the corresponding calculated spectra, in which the jump frequencies Ω were chosen in such a way that a best fit between the measured and the calculated spectra was obtained. It can be seen that excellent agreement was obtained.

Figure 7 shows the measured spectra at higher temperatures. At 103°C the intensity of the two original peaks becomes smaller and a second doublet (b,b) with a smaller distance between the two peaks appears. Such a doublet can be explained either by the onset of free rotation of the CH_2 groups or by *trans–gauche* jumps under the assumption that 75% of the groups are in the

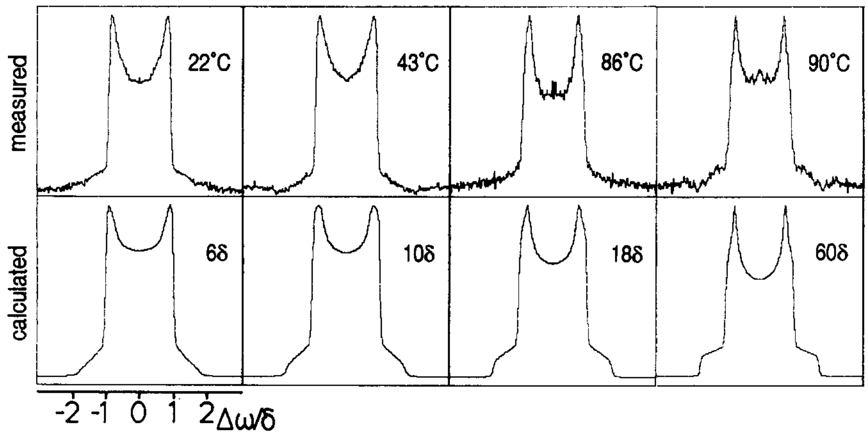

Figure 5 Spectra of the ethylene deuterated sample in the liquid crystalline state (Ed_8-LC) measured at different temperatures with a waiting time $\tau_w = 0.05$ s (upper row) and corresponding calculated spectra assuming *trans–gauche* jumps with a frequency Ω indicated at each spectrum and a *trans* population of 90% (lower row)

Table 5 Fraction (%) y_j of component j contributing to the spectrum and fraction (%) $u_j = x_j y_j$ of total material belonging to component j and contributing to the spectra obtained at different waiting times, τ_w

Sample	Temp. (°C)	τ_w (s)	y_1	y_2	y_3	y_4	u_1	u_2	u_3	u_4
Ed_8-LC	22	0.05	–	5	21	68	–	1	10	22
Ed_8-LC	108	0.05	1	16	86		0	2	64	
Ed_8-LC	22	5	–	99	100	100	–	22	46	32
Ed_8-LC	108	5	63	100	100		9	11	74	
Ed_8-LC	22	5;0.5	–	61	9	0	–	13	4	0
Ed_8-LC	108	0.5;0.05	9	67	14		1	7	10	
Ed_8-i	22	0.05	–	4	22	80	–	2	9	16
Ed_8-i	86	0.05	–	12	54	99	–	4	28	18
Ed_8-i	108	0.05	1	17	88		0	2	62	
Ed_8-i	22	5	–	98	100	100	–	38	41	20
Ed_8-i	86	5	–	100	100	100	–	30	52	18
Ed_8-i	108	5	66	100	100		12	10	71	
Ed_8-i	22	5;0.5	–	65	8	0	–	25	3	0
Ed_8-i	86	0.5;0.05	–	60	46	1	–	18	24	0
Ed_8-i	108	0.5;0.05	9	67	12		2	7	9	

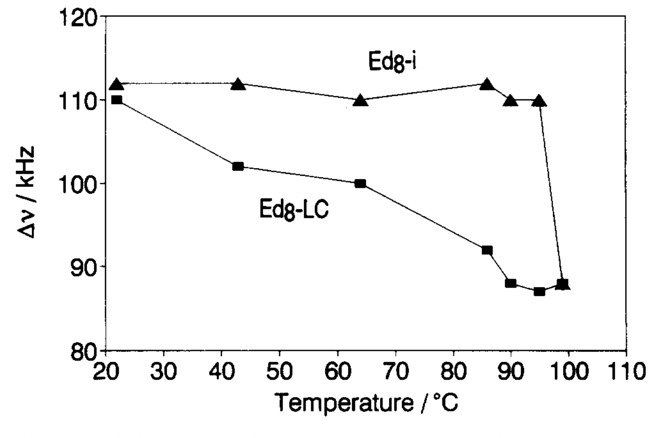

Figure 6 Splitting, $\Delta\nu$, of the dominant double peak of the ethylene deuterated samples Ed_8-i (▲) and Ed_8-LC (■) as a function of temperature

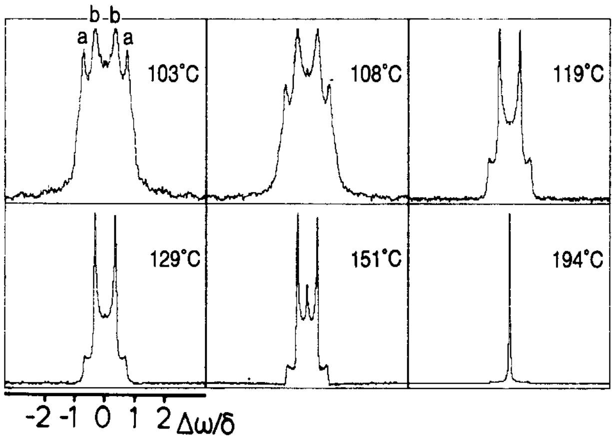

Figure 7 Spectra of the ethylene deuterated sample in the liquid crystalline state (Ed_8-LC) measured at different temperatures with a waiting time $\tau_w = 0.05$ s

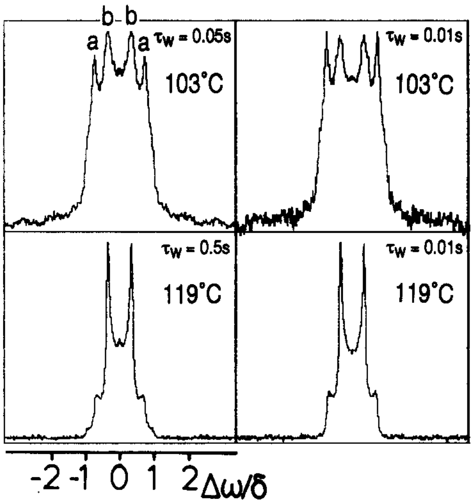

Figure 8 Spectra of the ethylene deuterated sample in the liquid crystalline state (Ed_8-LC) measured at 103 and 119°C with two different waiting times τ_w

trans conformation. In principle, the shape of the spectrum outside of this doublet is different for these two kinds of motion (compare spectra in *Figure 4*, 75% *trans*, with spectrum at 119°C in *Figure 8*). However, because of the superposition with the original doublet (a,a), one cannot determine which of the two possible assignments is correct. At 119°C, a spectrum with the typical shape of the spectrum of unrestricted rotating ethylene groups is obtained. At 151°C, a central peak, indicating the onset of isotropic motion, appears. At 194°C, the motion is completely isotropic.

In order to obtain more information concerning the assignment of the spectrum obtained at 103°C, we have also measured this spectrum with a shorter waiting time, $\tau_w = 0.01$ s. As can be seen in *Figure 8*, the relative intensity of the doublet b,b is smaller than when $\tau_w = 0.05$ s. From this it is concluded that the doublet b,b arises from the motion of ethylene groups with 75% *trans* population (see the Discussion). In contrast, the spectrum measured at 119°C remains unaffected when τ_w is decreased.

Let us next consider the spectra arising from the less mobile parts of the chains. *Figure 9* shows the spectra obtained with the relatively long waiting time $\tau_w = 5$ s. In this case all three components completely (at room temperature) or almost completely (at 108°C, see *Table 5*) contribute to the spectra which, as a consequence, become quite complicated. For example, at 86°C, we see a double peak with a large distance (1,1) corresponding to rigid groups or to *trans–gauche* jumps with a population of 75% *trans*, a double peak with a somewhat smaller distance (2,2) corresponding to *trans–gauche* jumps with a population of 90% *trans*, and a central peak (3) which can be attributed to *trans–gauche* jumps with a population of 75% *trans*. Thus, the complicated shape of the spectra is a consequence of the fact that chains with a great variety of mobilities are contributing to the spectra.

In order to obtain spectra arising only from less mobile chains, differences of the spectra measured with $\tau_w = 5$ s and $\tau_w = 0.5$ s (at room temperature and at 43°C) and with $\tau_w = 0.5$ s and $\tau_w = 0.05$ s (at higher temperatures) were calculated. The values of τ_w were chosen in such a way that a small fraction of the chains in the crystals and a large fraction of the less mobile parts of the chains in the non-crystalline regions are contributing to the spectra. The fractions of the different components contributing to the spectra under these conditions are also shown in *Table 5*. The difference spectra are designated by $\tau_w = (5$ s; 0.5 s) and $\tau_w = (5$ s; 0.05 s), respectively. The spectra obtained in this way are represented in *Figure 10* (upper row) and *Figure 11*. Up to 90°C, the spectra can be explained by assuming *trans–gauche* jumps with a population of 75% *trans*. The jumping rate Ω increases with increasing temperature. In contrast to the results obtained with $\tau_w = 0.05$ s (see *Figure 5*), no indication of jumps with a population of 90% *trans* is observed. This is due to the fact that, according to *Table 5*, the spectra in *Figure 10* do not contain any contribution of component 4, which prevails in the spectra of *Figure 5*. The spectra at 95°C and at the higher temperatures shown in *Figure 11* cannot simply be explained by *trans–gauche* jumps with 75% *trans* population. Here we have to assume additional small contributions of rigid ethylene groups and of jumps with 50% *trans* population, as a consequence of crystallization of the sample and of the presence of a small amount of isotropic material, respectively. At higher temperatures the spectrum of freely rotating ethylene is observed.

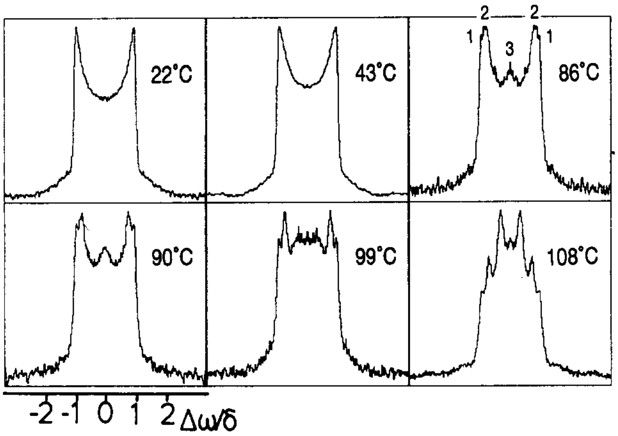

Figure 9 Spectra of the ethylene deuterated sample in the liquid crystalline state (Ed$_8$-LC) measured at different temperatures with a waiting time $\tau_w = 5$ s

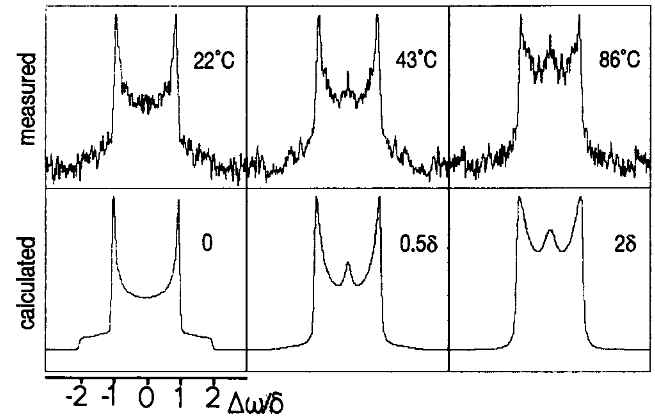

Figure 10 Upper row: difference spectra of the ethylene deuterated sample in the liquid crystalline state (Ed$_8$-LC) measured with $\tau_w = 5$ s and $\tau_w = 0.5$ s (at 22°C and 43°C) and with $\tau_w = 0.5$ s and $\tau_w = 0.05$ s (at higher temperatures). Lower row: corresponding calculated spectra assuming *trans–gauche* jumps with a frequency Ω as indicated and a *trans* population of 75%

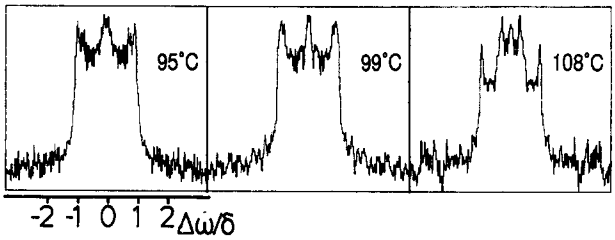

Figure 11 Difference spectra of the ethylene deuterated sample in the liquid crystalline state (Ed$_8$-LC) measured with $\tau_w = 0.5$ s and $\tau_w = 0.05$ s

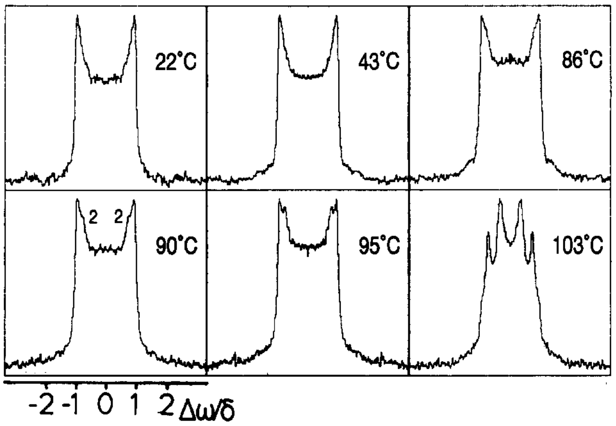

Figure 12 Spectra of the ethylene deuterated sample in the isotropic state (Ed$_8$-i) measured at different temperatures with the waiting time $\tau_w = 0.05$ s

Let us now consider the results obtained from the isotropic sample. *Figure 12* shows the spectra of the sample Ed$_8$-i measured with a waiting time $\tau_w = 0.05$ s at different temperatures. In contrast to the LC sample, no indication of *trans–gauche* jumps can be observed at room temperature or at 43°C. This was also indicated in

Figure 6, where the distance between the peaks, $\Delta\nu$, was plotted as a function of temperature. The background between the peaks is higher and $\Delta\nu$ a little lower than in the case of a Pake diagram. We have found that at $-93°C$ $\Delta\nu = 118$ kHz, and at room temperature $\Delta\nu = 112$ kHz. According to Hirschinger *et al.*[3], both deviations from the Pake diagram can be attributed to librations. At 86 and 90°C, the spectrum is still dominated by a Pake-like diagram with elevated background; however, in addition a doublet (2,2) with somewhat smaller $\Delta\nu$ appears. This is attributed to the fact that the sample starts to be transformed into the LC state. Therefore a small part of the chains has about 90% of the ethylene groups in the *trans* conformation and performs *trans–gauche* jumps. This is even more pronounced at 95°C. At higher temperatures, the spectra of the initially isotropic sample are exactly the same as those of the LC sample shown in *Figure 7*, because the sample has been completely transformed into the LC state. Therefore only the spectrum at 103°C is shown.

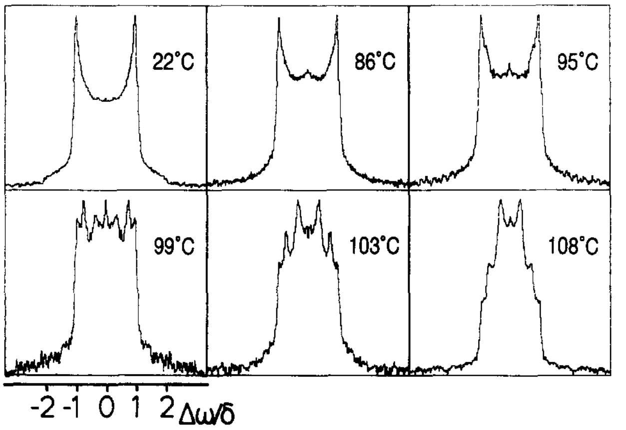

Figure 13 Spectra of the ethylene deuterated sample in the isotropic state (Ed$_8$-i) measured at different temperatures with the waiting time $\tau_w = 5$ s

Figure 13 represents the spectra obtained with a waiting time $\tau_w = 5$ s, which indicate a superposition of different motions as with the spectra in *Figure 9*. The upper row of *Figure 14* shows the differences between the spectra with $\tau_w = 5$ s and $\tau_w = 0.5$ s (at 22 and 43°C) and with $\tau_w = 0.5$ s and $\tau_w = 0.05$ s (at higher temperatures). These spectra can be explained by assuming *trans–gauche* jumps with a population of 50% *trans*. The lower row of *Figure 14* shows the calculated spectra and the frequency Ω that had to be assumed to obtain the best fit. The calculated and the measured spectra agree very well.

Spectra of the phenylene deuterated samples PET-Phd$_4$ and PHBA-Phd$_4$

Figure 15 shows the spectra, measured at different temperatures, of the samples in which the phenylene rings in the PET were deuterated (PET-Phd$_4$). The waiting

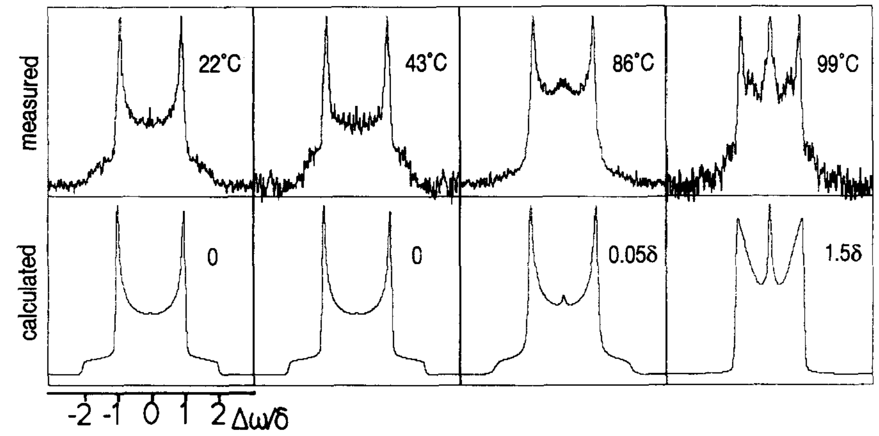

Figure 14 Upper row: difference spectra of the ethylene deuterated sample in the isotropic state (Ed$_8$-i) measured with $\tau_w = 5$ s and $\tau_w = 0.5$ s (22°C and 43°C) and $\tau_w = 0.5$ s and $\tau_w = 0.05$ s (at higher temperatures). Lower row: corresponding calculated spectra assuming *trans–gauche* jumps with a frequency Ω as indicated and a *trans* population of 50%

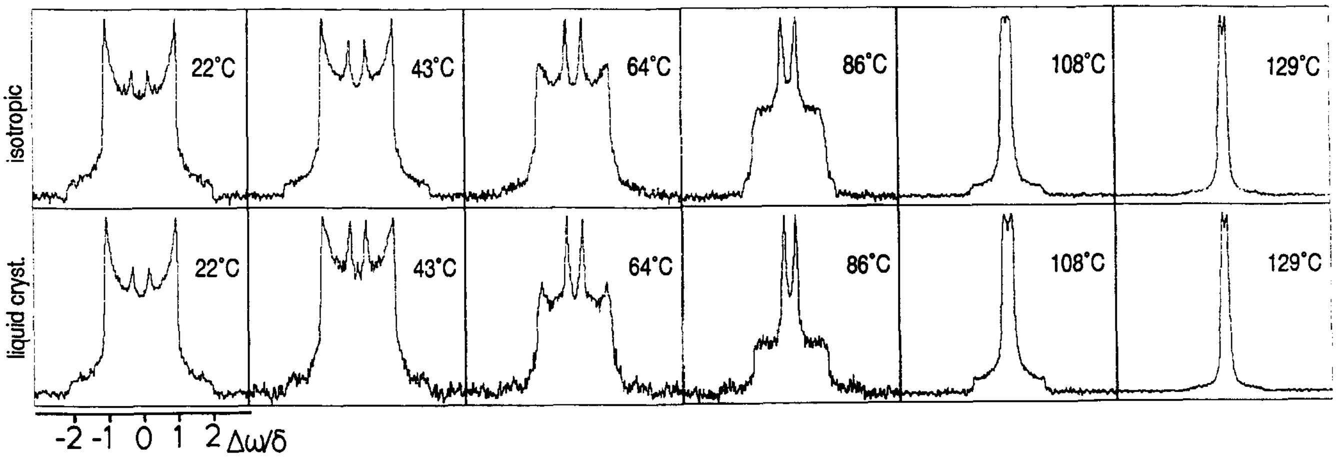

Figure 15 Spectra of the sample in which the phenylene rings in the PET units were deuterated (PET-Phd$_4$), measured at different temperatures with $\tau_w = 5$ s. Upper row, isotropic sample; lower row, liquid crystalline sample

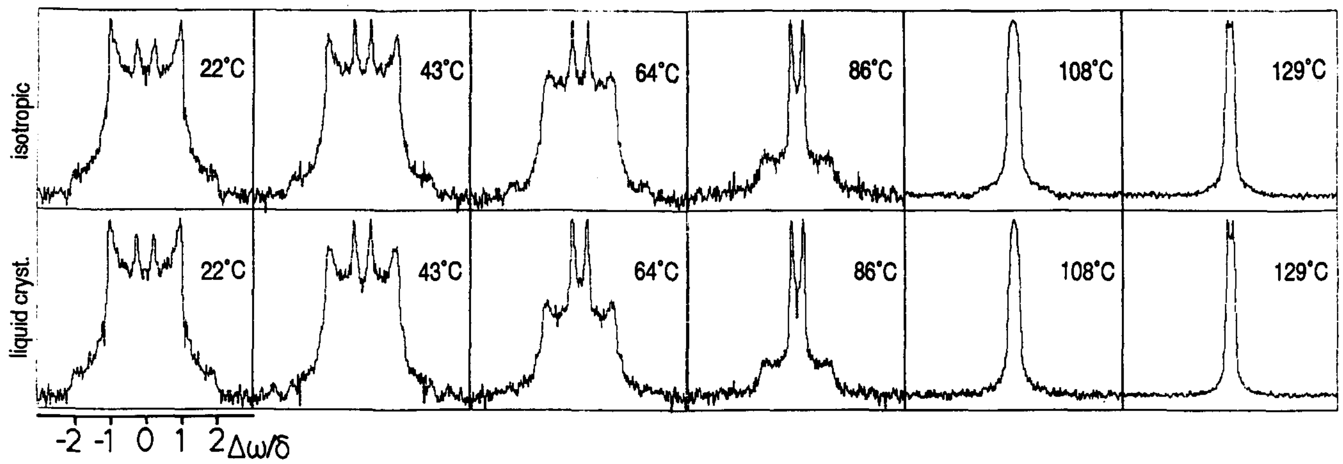

Figure 16 Spectra of the sample in which the phenylene rings in the PHBA units were deuterated (PHBA-Phd$_4$), measured at different temperatures with $\tau_w = 5$ s. Upper row, isotropic sample; lower row, liquid crystalline sample

time τ_w was 5 s. The spectra of the isotropic sample (upper row) are compared to those of the LC sample (lower row). *Figure 16* shows the corresponding results for the material in which the phenylene ring in the PHBA was deuterated (PHBA-Phd$_4$).

At lower temperatures all spectra can be explained as a superposition of rigid phenylene groups and groups performing 180° jumps (flipping) in the fast motion limit. Above about 60°C, an increasing fraction of groups gradually seems to perform unrestricted rotation. With increasing temperature, the fraction of the quickly moving rings increases. This increase is slightly larger for the rings in the PHBA units than for those in PET units, reflecting a somewhat higher mobility in the PHBA units. In both units, there is a significant difference between the motion in the isotropic state and that in the LC state at about 60°C. Here, the fraction of flipping rings in the LC state is larger than in the isotropic state.

DISCUSSION

Relaxation time spectrum

In the evaluation of the longitudinal relaxation curves we have assumed that there exists a spectrum of several distinct relaxation times T_1. For the non-crystalline regions, it seems more appropriate to assume a continuous distribution of relaxation times. Such a distribution of T_1 values is a consequence of a distribution of correlation times τ_c which reflects a non-uniform distribution of the free volume.

In fact, the measured longitudinal relaxation curves can be fitted very well assuming a logarithmic normal distribution of relaxation times, as has been proposed previously, for example by Rössler *et al.*[20]. *Figure 17* illustrates the result for one of the measured curves (symbols) and the fitted curve (line) obtained by assuming the distribution of correlation times τ_c given by

$$p(\ln\tau_c)=\frac{\beta}{\pi^{1/2}}\exp[-\beta^2(\ln\tau_c-\ln\tau_{c0})^2] \qquad (2)$$

and using the equation of Solomon[21] with the constants valid for deuterons[20]

$$\frac{1}{T_1}=\frac{3\pi^2}{10}C^2\left(\frac{\tau_c}{1+\omega^2\tau_c^2}+\frac{4\tau_c}{1+4\omega^2\tau_c^2}\right) \qquad (3)$$

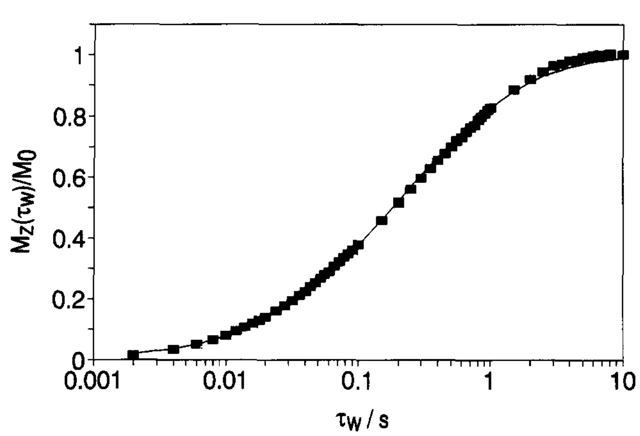

Figure 17 Relative longitudinal magnetization $M_z(\tau_w)/M_0$ as a function of the logarithm of the waiting time τ_w for the sample Ed$_8$-i measured at 22°C (symbols) and fitted curve calculated assuming the continuous distribution of waiting times given by equations (2) and (3)

with $\tau_{c0} = 2.04 \times 10^{-5}$ s and $\beta = 0.486\,\mathrm{s}^{-1}$. The value of T_1 corresponding to τ_{c0} is $T_1^0 = 0.24$ s. The values for the $T_1^{(j)}$ and x_j for this sample in *Table 3* can be considered as parameters describing the continuous distribution.

Relation between T_1 *and* trans *population in the LC state*

As shown in *Figure 5*, after a short waiting time the spectra of the ethylene groups up to 86°C can be interpreted by assuming *trans–gauche* jumps with a population of 90% *trans* conformation, whereas, as shown in *Figure 10*, a population of about 75% *trans* has to be assumed to reproduce the difference spectra obtained by subtracting the spectra measured with a shorter waiting time τ_w from those measured with a longer τ_w. This shows that the longitudinal relaxation time of the chains with a larger fraction of *trans* groups is longer. The reason for this effect is obviously the higher jump frequency in the parts of chains with high *trans* population. For example, at 43°C we have found $\Omega = 10\delta$ when 90% of the groups are in *trans* conformation (*Figure 5*), while $\Omega = 0.5\delta$ when 75% of the groups show this conformation (*Figure 10*).

This result is also important for the interpretation of the spectra measured with $\tau_w = 0.05$ s at 103°C (*Figure 7*). As stated in the Results section, the doublet with the smaller peak distance can arise either from unrestricted rotation of the ethylene groups or from *trans–gauche* jumps with a population of about 75% *trans* conformations. Because the relative intensity of this doublet is decreased when τ_w decreases from 0.05 to 0.01 s (*Figure 8*), we can conclude that this doublet arises from jumps in parts of the chains showing 75% *trans* conformations. If the doublet were due to unrestricted rotation, one would expect that the intensity would remain unchanged, as shown for the spectra at 119°C in *Figure 8*, or even increase. One possible explanation is that, at 103°C the relaxation times T_1 have decreased so much that such *trans–gauche* jumps, which become visible at 46°C only at larger τ_w values, can already be observed at $\tau_w = 0.05$ s. Another possibility is that the fraction of *trans* conformation is reduced with increasing temperature, as has been observed by Müller *et al.*[22] for other LC polymers.

We wish to stress that it is only an approximation when we speak of 90% or 75% *trans* conformations. Actually there will be a more or less continuous distribution of such populations. The single value of the population given is just an average of part of the population, the influence of which dominates in the measurement considered. This becomes evident when one tries to fit the spectra measured at 103 and 108°C by assuming *trans–gauche* jumps. If only two populations with distinct values of *trans* conformations (90% and 75%) are assumed, it is not possible to obtain complete agreement between the measured and calculated spectra. In order to obtain complete agreement, a continuous spectrum of populations has to be assumed.

It is worthwhile noting that there is no general correlation between the relaxation time T_1 and the fraction of *trans* conformations. Such a correlation was only found if the sample was in the frozen-in LC state. In the glassy isotropic state there exist almost the same short relaxation times T_1 (see *Table 3*) without corresponding *trans–gauche* jumps.

Comparison of the mobility in the isotropic and LC state

Let us first discuss the spectrum of longitudinal relaxation times represented in *Table 3*. In the frozen-in LC state, the values of the relaxation times T_1 are smaller than in the frozen-in isotropic state. For example, the corresponding values of $T_1^{(2)}$ of the ethylene groups are 1.02 and 1.23 s, respectively. Generally, however, the difference is only about 20% or less. Only in the case of the phenylene rings in the PHBA units does one observe a decrease of about 50% from 1.34 to 0.81 s. According to *Table 2*, the density increases by approximately 2%.

It is interesting to compare these differences with the changes in T_1 and density occurring during crystallization. Here, an increase of T_1 by roughly 1500% is observed (for example from 1.23 s in $\mathrm{Ed_8}$-i to 20 s in $\mathrm{Ed_8}$-c). The density of the crystals is about 10% larger than that of the amorphous material in both PET and PEN. Despite the fact that in both transitions (isotropic–LC and isotropic–crystalline) the density increases, the relaxation time T_1 in one case becomes smaller and in the other case becomes larger. This result reflects the high mobility of the chains in the LC state. Obviously, stretching of the chains without obtaining a high degree of crystalline order increases the chain mobility so strongly that even the reduction in free volume is compensated.

From an analysis of the shapes of the spectra one can deduce the kinds of molecular mobility that occur in the frozen-in states: *trans–gauche* jumps of ethylene groups and flipping of the phenylene rings. While in the LC state the *trans–gauche* jumps are already evident at room temperature, in the isotropic state these jumps do not occur below 86°C.

Why can these jumps start at such low temperatures in the case of the LC sample despite the higher density? Our results show that the ethylene groups that start to jump below 86°C belong mainly to those parts of the chains showing about 90% *trans* conformations, which corresponds to almost completely extended chains. Those parts of the chains in which the *trans* population is smaller, for example 75%, only become mobile at higher temperatures. There also exists some mobility at 43 and 90°C, but with a comparatively small jumping rate (0.5δ and 2δ, respectively). As there are no parts of chains with a *trans* population of 90% in the isotropic material, the *trans–gauche* jumps can only be observed at higher temperatures.

In contrast to the ethylene groups, the flipping of the phenylene rings starts at lower temperatures in both states. However, at temperatures where *trans–gauche* jumps occur in the LC state, i.e. at 64 and 86°C, the fraction of flipping rings is larger.

In summary, we can say that both the longitudinal relaxation times and the shapes of the spectra show that the chain mobility in the frozen-in LC state is higher than in the frozen-in isotropic state. As a consequence of this, the glass transition of the LC state is lower than that of the isotropic state.

Above the glass transition, T_g, the situation is completely different. Unfortunately, it was not possible to perform measurements in the isotropic state above T_g on the samples investigated in this paper, because the isotropic samples were immediately transformed into the LC state. However, measurements in PET have shown[5] that a narrow single line is obtained in isotropic samples, reflecting the isotropic motion of the chain segments. In the LC state, above T_g, only unrestricted rotation of the chains is possible, resulting in a doublet. Thus, above the T_g, the mobility of the chains in the LC phase is more restricted than in the isotropic phase. This has also been pointed out by Allen and Ward[8].

What is the T_g *of an LC phase?*

In the isotropic phase, T_g is defined as the temperature at which 'segmental motion' starts, i.e. where the chains become able to change their conformations. Above this temperature, rubber elasticity can be observed and crystallization can take place. It is also generally assumed that the frequency dependence of T_g is governed by the Fulcher–Vogl equation.

In the LC state, by definition, larger changes of chain conformations cannot take place because the chains have to remain almost extended. The mobility of the chains is restricted to rotation and translational motion. However, as has been pointed out, for example by Wunderlich and Grebowicz[23], these motions can also be frozen in, so that one can speak of a 'liquid crystalline glass'. Obviously, in our copolyester these motions are frozen in at 58°C, where a peak of the loss modulus G'' and a step in the d.s.c. curve are observed. It is a matter of definition whether one refers to this temperature as the glass transition temperature or not. We think that it is justifiable to consider it as T_g for the following reasons:

(i) one observes a peak in G'' and a step in the d.s.c. curve corresponding to the peak and step in the isotropic state; (ii) the material crystallizes above this temperature while no crystallization takes place below it.

CONCLUSIONS

In the LC state, besides the almost elongated parts of chains in which about 90% of the ethylene groups are in the *trans* conformation, there also exist less elongated parts showing a much smaller fraction of *trans* conformation (about 75%).

Near T_g, at the same temperature, the frequency of the *trans–gauche* jumps in the elongated parts of the chains is much larger than the frequency in the less elongated chains.

As a consequence of the higher mobility of the ethylene groups in the elongated chains, the fraction of flipping phenylene rings is larger.

In the isotropic state, where the fraction of ethylene groups in *trans* conformation is only about 50%, the motion of the ethylene groups starts at higher temperatures than in the LC state.

The lower T_g value of the LC state seems to be related to our result that *trans–gauche* jumps of the ethylene groups can be performed more easily in the almost elongated parts of the chains.

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