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Characterization of a main-chain semiflexible liquid crystalline polymer: degree of orientational order

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Selectively deuterated liquid crystalline copolyesters of 4,4′-dihydroxy, α,α'-dimethylbenzalazine were investigated by proton and deuterium n.m.r. N.m.r. spectra were recorded over a wide temperature range: from 100°C (50 to 60°C below the solid to nematic phase transition, T_m) to 255°C which is well above the isotropic–nematic phase transition. The main-chain liquid crystalline polymer does not align in the n.m.r. magnetic field below $T_m + 20°C$, where T_m represents the melting temperature measured by differential scanning calorimetry. However, from the splitting $\Delta\nu$ between the peaks in the powder pattern we conclude that the sample is composed of randomly oriented domains. Within these domains the same type of molecular motion occurs as in the monodomain nematic phase at $T > T_m + 20°C$. Above $T_m + 20°C$ the ^2H n.m.r. spectra show the existence of doublets which are characteristic of an aligned monodomain nematic phase.

High degrees of orientational order, S_{zz}, measured by both proton and deuterium n.m.r. are practically independent of sample thermal history. Values of S_{zz} at the nematic to isotropic phase transition and the order parameters of the flexible units are consistent with data reported for other polymers of similar chemical structure.

(Keywords: orientational order; liquid crystalline polymers; main-chain semiflexible LCPs)

INTRODUCTION

The phase transition from a completely disordered (isotropic) to a partially ordered (liquid crystalline) system which can be induced by either a temperature change (thermotropic liquid crystals) or in solution (lyotropic liquid crystals) has stimulated a considerable amount of theoretical work.

Early models developed by Onsager[1] and Flory[2,3] for molecules having rigid rod like structures emphasized the role of anisotropic repulsive forces: the asymmetry of molecular shape and the constraint that the molecules cannot overlap are considered as the dominant features responsible for the appearance of liquid crystallinity. A first order transition is predicted with increasing concentration and/or axial ratio. Attractive forces or solvent interactions are not required to account for the formation of a liquid crystalline (LC) phase.

An alternative approach was developed by Maier and Saupe[4] for monomeric liquid crystals (LCs). The physical basis for the appearance of liquid crystallinity is now ascribed to anisotropic attractive forces (London dispersion forces). A first order transition is predicted with an order parameter S_{zz} which jumps from 0 to 0.429 at the isotropic to nematic transition, T_{N-I}.

Liquid crystalline behaviour has been assessed for a number of semiflexible polymers whose repeat unit is constituted of a rigid core and one or more flexible spacers[5–8] (main-chain semiflexible LCPs). The low melting temperatures obtained by inserting flexible spacers into the polymer main-chain allow stable LCP melts to be formed at processable temperatures.

Semiflexible liquid crystalline polymers (LCPs) exhibit much higher enthalpy and entropy changes (by factors of 5 to 10) compared to the corresponding monomeric LCs[9]. At the same time, the degree of orientational order appears to be higher for the polymers than for the monomeric counterpart[10]. Both findings suggest the existence of strong correlations between the rigid segments of the same chain even for relatively long flexible units and highlight the important role of the flexible spacer in the stabilization of the mesophase. That the flexible spacer actively participates in the ordering process is also demonstrated by the pronounced odd–even effect in which oscillations of the transition temperatures and entropy changes have been observed

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as the number of $-CH_2-$ groups alternates between odd and even[5]. As discussed by Abe[11], orientational correlations between two successive cores are strongly dependent on the odd–even character of the spacer units. Even numbered methylene sequences allow consecutive mesogenic units to align parallel to the ordering direction whereas a similar alignment is unfavoured for odd sequences. Hence, the higher entropy changes determined for semiflexible LCPs with an even number of $-CH_2-$ units can be explained by a higher contribution from conformational changes at the transition.

Although theories solely based on anisotropic repulsive forces and anisotropic attractive forces were found suitable to describe the liquid crystalline properties of rigid rod like polymers and thermotropic monomeric liquid crystals, respectively, the same theories cannot be directly applied to polymer chains having some degree of flexibility either in solution or in the melt. Several attempts have been made to incorporate the inherent flexibility of the polymer chains into the ordering of the liquid crystalline phase, treating the polymer chain as a continuous elastic curve i.e. a worm-like chain[12–15].

The new feature of semiflexible LCPs is given by the conformational changes that accompany the isotropic to nematic phase transition. At T_{N-I}, the polymer chains are predicted to undergo a change from a random coil to highly extended structures. A number of studies have been performed to elucidate the conformational properties of semiflexible polymers forming nematic phases. The overall conformation of semiflexible LCPs has been investigated by small angle neutron scattering (SANS)[16–19] although the results obtained so far are only preliminary ones. On a local scale, n.m.r. has proved extremely useful in providing information on the conformation and ordering of the flexible units in dimer[20–21] and polymer liquid crystals[22–28].

Here we present a detailed n.m.r. study of a main-chain semiflexible liquid crystalline polyester over a wide temperature range from 100 to 255°C. The polymer conformation has been recently investigated by SANS[16] whereas in this work we concentrate on the local order of the mesogenic units and the local conformation of the methylene sequences in the flexible spacers. We will show that the LCP is characterized by a high degree of orientational order, higher than previously measured for polymers having similar structures and by highly extended conformations of the flexible spacers which are consistent with the large persistence length measured by SANS.

This work is part of a more extensive study of main-chain semiflexible LCPs which includes the investigation of the polymer chain conformation and the local dynamics. A complete characterization of the mesophase and the degree of orientational order is particularly relevant for our present study of the anisotropic molecular motion.

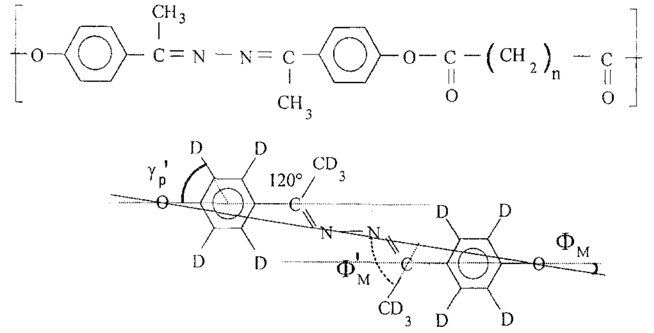

Figure 1 Chemical structure and angle notation for n.m.r. measurements of copolyesters of 4,4′-dihydroxy, α,α'-dimethyl benzalazine

Table 1 Weight average molecular weights and transition temperatures of the polymers investigated

Sample	η_{inh} (dl g^{-1})	M_w (g mol^{-1})	T_m (°C)^a	T_{N-I} (°C)^a
flD-LCP	0.44	8600	151	236
mD-LCP	0.63	14800	162	250
D-LCP	0.55	12000	162	250

^{a} Measured from differential scanning calorimetry on first heating (heating rate: 20°C min^{-1})

EXPERIMENTAL

Materials

The main-chain LCPs investigated in this work were synthesized as described in ref. 29. The structure of the LCP, a copolyester of 4,4′-dihydroxy, α,α'-dimethylbenzalazine, is shown in *Figure 1*. Two flexible units with eight and ten methylene groups are randomly inserted into the polymer main-chain in the same weight percentage. Selectively deuterated polymers were used for n.m.r. experiments: (a) completely deuterated in the flexible linkages with $n = 8$ and $n = 10$ methylene units (flD-LCP), (b) deuterated in the mesogenic unit, both in the aromatic ring and in the methyl groups (mD-LCP) and (c) fully deuterated (D-LCP). The characteristics of the polymers are reported in *Table 1*. The inherent viscosities were measured in chloroform solutions at a polymer concentration of 0.5 g dl^{-1} and $T = 25$°C. The weight average molecular weights, M_w, were calculated using the relationship between the intrinsic viscosity and M_w reported in ref. 29:

$$[\eta] = 9.6 \times 10^{-4} M_w^{0.68}. \qquad (1)$$

Values of intrinsic viscosity $[\eta]$, to be used in equation (1) were calculated from the inherent viscosity by considering its concentration dependence in $CHCl_3$ solutions in the range between 0.5 and 1.5 g dl^{-1}.

The polymers exhibit a glass transition at 25°C[29]. The solid to nematic and the nematic to isotropic transition temperatures measured by differential scanning calorimetry (d.s.c.) are reported in *Table 1* for flD-LCP, mD-LCP and D-LCP.

N.m.r. measurements

Samples were prepared in 5 mm diameter tubes by melting the powder (~200 mg) at temperatures below the nematic to isotropic transition ($T \sim 190$°C) in the absence of a magnetic field. The procedure usually required a few melting–solidification cycles.

Proton and deuterium n.m.r. experiments were performed on a Bruker MSL-200 spectrometer equipped with a temperature control unit. The spectrometer was operated at 200 MHz for proton n.m.r. (^{1}H n.m.r.) and 30.7 MHz for deuterium n.m.r. (^{2}H n.m.r.). ^{2}H n.m.r. measurements were carried out using a quadrupole-echo sequence[30]. A delay time between 90° pulses of 25 μs was usually used with a 90° pulse length of 3.4 μs. 512 free induction decays (FID) were accumulated with recycle times of 100 ms for the polymer mD-LCP and 800 ms for the polymer flD-LCP. Proton n.m.r. spectra were recorded using a simple $\pi/2$-FID sequence with recycle delay of 3 s. Averaging of 32 FID was used.

Measurements were performed on heating above the solid–nematic transition and on cooling from the isotropic liquid phase allowing for 10 to 15 min equilibration at each temperature. No sensible variations were detected for longer annealing times.

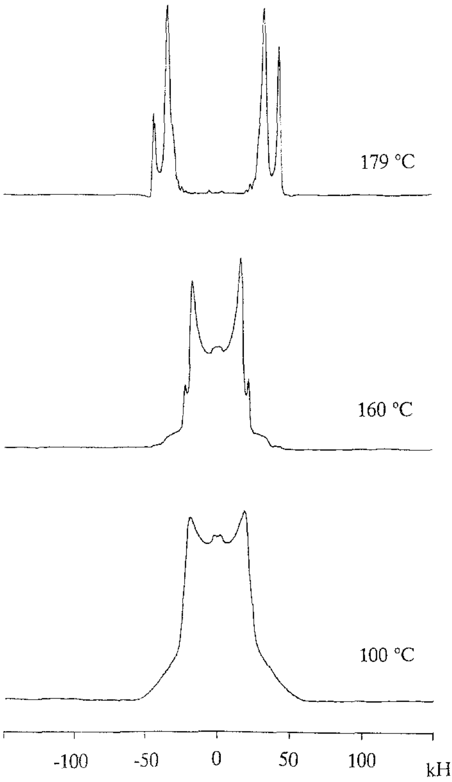

Figure 2 Deuterium n.m.r. spectra of the main-chain LCP deuterated in the flexible spacers (flD-LCP) at 100, 160 and 179°C, on heating from the solid phase

RESULTS

Measurements below the solid–nematic phase transition

Examples of ^{2}H n.m.r. spectra recorded at 100, 160 and 180°C on heating from the solid phase are reported in *Figures 2* and *3* for the LCP deuterated in the flexible (flD-LCP) and in the mesogenic units (mD-LCP), respectively. The ^{2}H n.m.r. spectra below the solid to nematic transition can be qualitatively described as due to the superposition of a 'powder' pattern and a broad central component.

The quadrupolar splitting for a C–D bond oriented at an angle θ with respect to the magnetic field is given by the following expression[31,32]:

$$\Delta\nu = \tfrac{3}{2}\chi\left(\frac{3\cos^2\theta - 1}{2}\right) \tag{2}$$

if the asymmetry parameter is neglected. In the absence of molecular motion and a preferred direction of orientation, the angle θ can take any value between 0 and 180°. For each orientation θ, a symmetric splitting is observed and, by summing up all contributions, the characteristic powder pattern, the so-called Pake spectrum, is generated. The splitting between the two peaks in the powder pattern corresponds to nuclear sites oriented at $\Theta = 90$°C with respect to the magnetic field. In the absence of molecular motion, the quadrupolar coupling constant, $\chi = e^2qQ/\mathrm{h}$ (where e is the elementary charge, Q is the quadrupole moment of the nucleus, q is the electric field gradient and h is Planck's constant) can be determined from equation (2)[33].

The quadrupolar splittings between the peaks corresponding to 90° orientation with respect to the magnetic field are reported in *Tables 2* and *3* as a function of temperature below $T_{\mathrm{N-I}}$ for the polymer flD-LCP and mD-LCP. For flD-LCP, $\Delta\nu$ amounts to 36 ± 1 kHz, in the temperature range from 100°C to 140°C (*Table 2*). The polymer deuterated in the mesogenic unit, mD-LCP, gave similar spectra with a frequency splitting between the peaks of 8.9 ± 0.1 kHz in the temperature range from 100°C to 160°C (*Table 3*). For both polymers, the measured frequency splittings are considerably reduced

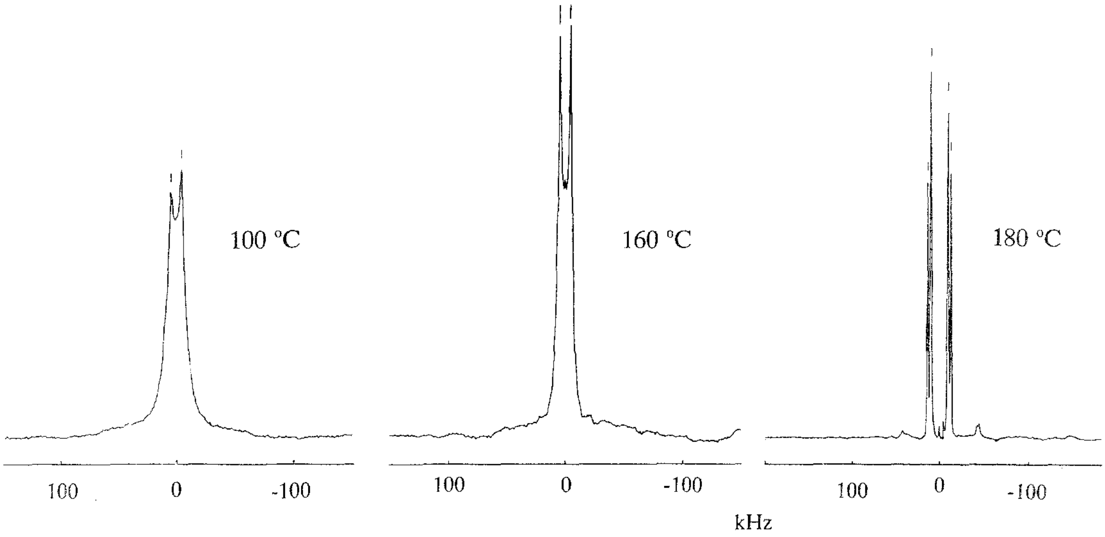

Figure 3 Deuterium n.m.r. spectra of the main-chain LCP deuterated in the mesogen (mD-LCP) at 100, 160 (after 45 min) and 180°C (after 15 min) on heating from above $T_{\mathrm{N-I}}$

Table 2 Quadrupolar splittings as a function of temperature for the polymer flD-LCP, deuterated in the flexible spacers

T (°C)	$\Delta\nu_1$ (kHz)	$\Delta\nu_2$ (kHz)
100	37.9	
140	36.02	44.91
150	34.6	44.21
160	33.99	43.77
170	68.58	88.40

Table 3 Quadrupolar splittings as a function of temperature for the polymer mD-LCP, deuterated in the mesogenic units

T (°C)	$\Delta\nu_1$ (kHz)	$\Delta\nu_2$ (kHz)
100	8.84	
140	8.99	
150	8.99	
160	8.93	
170	8.87	12.46
180	19.76	26.50

compared to the static values which correspond to 140 kHz, considering a quadrupolar constant of 187 kHz[34] for deuterons in the aromatic ring and to 130 kHz taking $\chi = 174$ kHz for deuterons in the aliphatic spacer[27,35].

The line shape just below the transition to the nematic phase contains subtle details of the chemical structure. In the temperature range from 140°C to 160°C the ^{2}H n.m.r. spectra of the sample flD-LCP can be described by the superposition of two powder patterns (*Figure 2*). The quadrupolar splittings between the peaks amount to $\Delta\nu_1 = 35 \pm 1$ kHz and $\Delta\nu_2 = 44.5 \pm 0.5$ kHz. It is interesting to note that these values are approximately half the frequency splittings between the doublets observed just above the transition to the nematic phase ($T = 165$°C) (see *Table 2*). The outer doublet is assigned to the α-methylene and the inner doublet to the other $-CH_2-$ groups in the flexible spacers, in accordance with previous studies of similar LCPs[22,23]. The ratio between the areas of the peaks confirms this assignment.

The polymer deuterated in the mesogen showed a double powder pattern only at $T > 165$°C (*Figure 3*). The quadrupolar splittings between the peaks amount to 8.9 ± 0.1 kHz and 12.5 ± 0.5 kHz, only a few kHz less than half the quadrupole splittings between doublets at 180°C (*Table 3*). The ratio between the area of the inner and outer doublets is 4 : 3, as expected between ring deuterons and methyl groups, respectively: the inner doublet is assigned to the deuterons in the aromatic ring and the outer doublet to the methyl groups.

The sample flD-LCP aligns in the magnetic field at 170°C, 16 degrees above the melting peak measured by d.s.c.; no alignment is observed below 165°C even for long annealing times. Similarly, the d.s.c. T_m of mD-LCP occurs at 162°C but the LCP does not align in the magnetic field below 175°C. Above 175°C for mD-LCP and 165°C for flD-LCP, the typical n.m.r. spectra of nematic monodomain structures are detected.

Both polymers exhibit a biphasic region in the temperature range from 225°C to 255°C (*Figure 4*). The intensity of the central peak increases with increasing temperature, until the phase appears completely isotropic at 255°C. On cooling from the isotropic liquid phase, a central isotropic peak and quadrupolar doublets were observed over the entire temperature range investigated (down to 130°C, on cooling). Low cooling rates or long annealing times did not seem to alter the extent of the biphase. Examples of ^{2}H n.m.r. spectra recorded on cooling from the isotropic liquid phase are shown in *Figure 4* for the LCP deuterated in the mesogen.

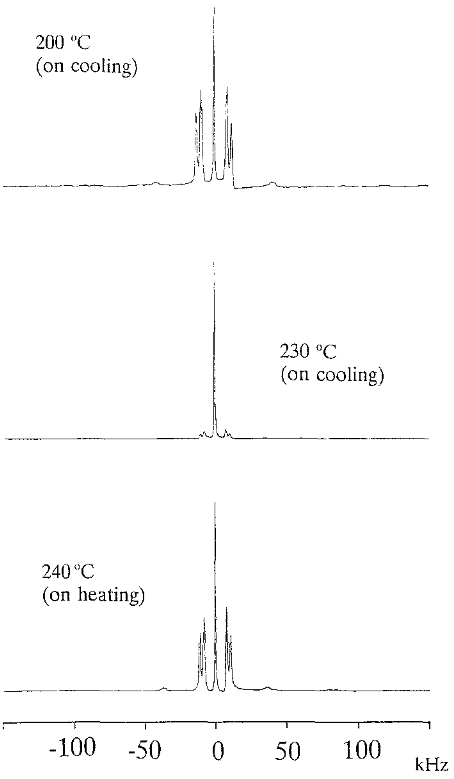

Figure 4 Deuterium n.m.r. spectra of the LCP deuterated in the mesogen (mD-LCP) on heating above the solid to nematic phase transition and on cooling from the isotropic liquid phase

The ^{2}H n.m.r. spectra of the copolyester indicate that the splitting $\Delta\nu$ is considerably reduced compared to the static values predicted for aromatic and aliphatic deuterons [see equation (2)], due to molecular motion. Because the measurements were performed well above the polymer glass transition temperature such a result is not unexpected. However, what is more surprising is that the same type of molecular motion appears to be involved below and above the transition to the nematic phase. The frequency splittings between the peaks in the powder pattern above 100°C are very close to half the quadrupolar splittings measured in the nematic phase. For $\theta = 90°$ the angular term in equation (2) reduces to $-1/2$. Hence the powder pattern observed at the lowest temperatures can be explained by considering that the sample is composed of randomly oriented microdomains where the same type of molecular motion as in the monodomain nematic phase takes place. A study of molecular motion close to the solid to nematic transition is currently under way and it will be the subject of a future publication.

The presence of a central isotropic component observed on cooling from the isotropic phase for our copolyester seems to be rather peculiar. The experimental results reported so far in the literature clearly indicate that the mesophase behaviour of semiflexible main-chain polyesters is strongly dependent on the system investigated. Biphasic regions which extend only over a few degrees[22] or in the entire temperature range[27] have been reported. In addition, polydispersity and more recently 'polyflexibility', i.e. a distribution of chains having different persistence lengths, have been invoked to explain the breadth of the biphasic region[36,37].

Orientational order of the mesogens

Proton n.m.r. measurements of orientational order of the mesogenic core were reported by us in a previous publication[38]. Here we describe in detail the ^{2}H n.m.r. order parameters measured on heating and cooling on the LCP deuterated in the mesogenic units (mD-LCP).

By assuming that the mesogenic units orient about the long molecular axis and that the phenyl rings rotate about the *para*-axis, the quadrupolar splitting of the C–D bonds in the aromatic ring can be expressed as:

$$\Delta\nu_Q^{ar} = 280.5\,\mathrm{kHz}\,S_{zz}\left(\frac{3\cos^2\gamma'_P - 1}{2}\right)\left(\frac{3\cos^2\Phi'_M - 1}{2}\right) \tag{3}$$

where S_{zz} represents the orientational order of the long molecular axis with respect to the nematic director. (χ was considered equal to 187 kHz.) The angle γ'_P in equation (3) which indicates the orientation of the C–D bond with respect to the *para*-axis (*Figure 1*) was estimated from the ratio between the dipole and quadrupole splittings determined from ^{1}H n.m.r. and ^{2}H n.m.r., respectively, at constant S_{zz}[40,41]. Averaging between values at various temperatures gave $\gamma'_P = 51.8°$ or 57.7° (corresponding to solutions on each side of the 'magic angle'). The latter value represents the most probable result, closest to the typical bond angle (60°). Comparable values were obtained in the study of *p*-azoxyanisole by Rowell *et al.* (57.5°)[40] and by Visintainer *et al.* (58.1°)[41].

The quadrupole splitting arising from the methyl groups can be expressed by the following equation:

$$\Delta\nu_Q^{CD_3} = 261\,\mathrm{kHz}\,S_{zz}\left(\frac{3\cos^2\Phi'_M - 1}{2}\right)\left(\frac{3\cos^2\sigma - 1}{2}\right) \tag{4}$$

considering $\chi = 174$ kHz. The angle C_α–C–D (σ) accounts for the rotation of the methyl groups and it was here assumed to be equal to the tetrahedrahal angle (109.5°)[40,41]. Φ'_M describes the orientation of the rotation axis with respect to the molecular axis (*Figure 1*). It was calculated from the ratio between the quadrupolar frequency splittings given by equation (4) and the dipolar splittings[39]. The average value amounts to 42.49° or 66.94°. If $\Phi'_M = 66.94°$ and the angle C_{ar}–C_α–D(D$_3$) is 120°[42], the angle between the molecular axis and the *para*-axis is estimated to be 6.9° which is consistent with values calculated from valence angles and bond lengths[42,43] assuming the molecular axis corresponds to a line connecting the oxygen atoms at each end of the mesogenic unit. A value of 67.01° for Φ'_M was also determined from the ratio between the quadrupolar splittings of the aromatic rings and the methyl groups.

The orientational order of the long molecular axis with respect to the nematic director, S_{zz}, calculated from ^{2}H n.m.r. spectra using equations (3) and (4), is plotted in *Figure 5* as a function of the reduced temperature, T/T_{N-I}, for both heating and cooling runs. The nematic to isotropic transition temperature, T_{N-I}, was evaluated from the maximum of the endotherm peak measured by d.s.c. during the first heating. Supercooling effects are here neglected but if a lower value of T_{N-I} is considered as shown by the small supercooling effect detected by d.s.c. on first cooling, then the temperature dependence of all data superimposes. Also shown in *Figure 5* are the proton n.m.r. data of flD-LCP. The comparison shows good agreement between the order parameters of flD-LCP and mD-LCP obtained from the dipolar and quadrupolar splittings.

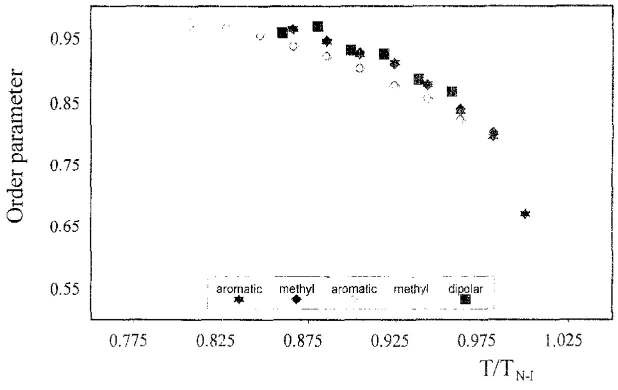

Figure 5 Order parameter S_{zz} from ^{2}H n.m.r. measurements on mD-LCP as a function of reduced temperature T/T_{N-I} from the aromatic deuterons (★, ○) and the methyl group (◆, ◇). Data (★, ◆) refer to the heating run whereas (○, ◇) to the cooling run. Comparison between S_{zz} determined from the dipolar splittings of flD-LCP (■) is also shown

The copolyester investigated in the present work exhibits a high degree of orientational order which reaches a maximum of 0.965, on heating, at the solid to nematic transition corresponding to a reduced temperature $T/T_{NI} = 0.880$ and an even higher value on cooling below the isotropic to nematic phase transition (0.975 at $T/T_{NI} = 0.828$).

High degrees of orientational order have been reported for other main-chain thermotropic LCPs forming nematic phases although these are lower than S_{zz} measured by us. For example, an order parameter of 0.84 was measured for a polyester of 2,2′-dimethyl-4,4′-azoxybenzene[44] at the solid to nematic phase transition ($T/T_{NI} = 0.880$) and S_{zz} equal to 0.9 was reported for a similar compound[45]. Theoretically, high degrees of orientational order (order parameter between 0.90 and 0.98) have been predicted from conformational analysis carried out by Abe[11] on several semiflexible LCPs.

The orientational order decreases with increasing temperature with a minimum at the nematic–isotropic transition of 0.67 as evaluated from the quadrupole splitting of the ring deuterons of mD-LCP at temperatures within the biphasic region. As shown in *Figure 5*, the order parameter decreases in the biphasic range which is in contrast with data reported for other LCPs of similar structure[22]. In other cases a single quadrupolar doublet was observed[27].

The order parameter at the nematic to isotropic transition measured here is in good agreement with n.m.r. order parameters for other main-chain semiflexible LCPs. This supports observations made by several authors that although the Maier and Saupe theory is well adapted to the description of mesophases formed by

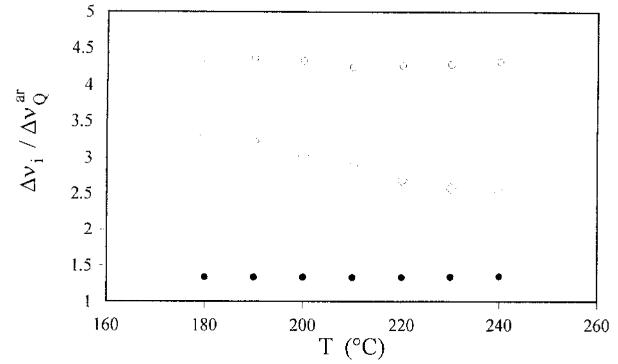

Figure 6 Ratios $\Delta\nu_i/\Delta\nu_Q^{ar}$ as a function of temperature for (○) α-CD_2, (◇) internal CD_2 and (●) methyl groups

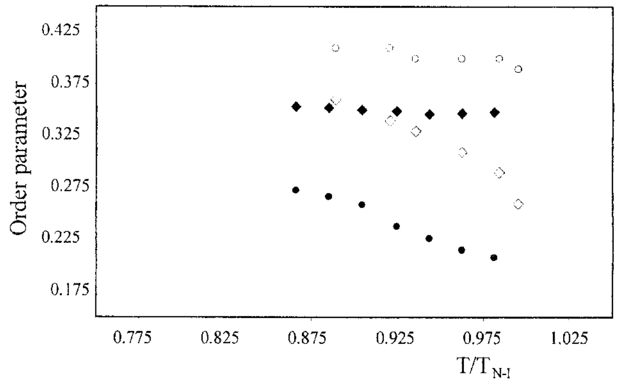

Figure 8 $\langle P_2(\cos\beta)\rangle$ of D-LCP *versus* reduced temperature for (◆) α and (●) and internal-CD_2 and comparison with data from ref. 22 ((○) α-CD_2 and (◇) internal CD_2)

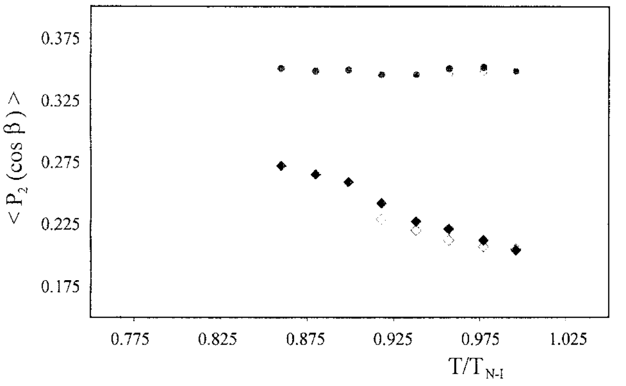

Figure 7 $\langle P_2(\cos\beta)\rangle$ as a function of reduced temperature from measurements on flD-LCP: (○, ●) α-CD_2 and (◇, ◆) internal-CD_2 on heating (●, ◆) and on cooling (○, ◇)

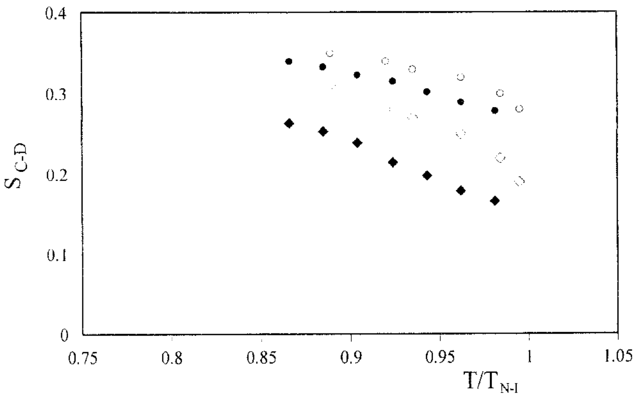

Figure 9 Order parameter of the C–D bonds *versus* reduced temperature for (●) α-CD_2 and (◆) internal CD_2 and comparison with data from ref. 22 ((○) α-CD_2 and (◇) internal CD_2)

small nematogens, it is not suitable to model the LC behaviour in polymeric systems. In other words, theories solely based on attraction forces cannot describe the high order parameters which have been measured experimentally on LCPs. On the other hand, theoretical treatments which emphasize the effect of steric repulsions are successful in accounting for high order parameters[25]. The Ronca and Yoon theory[15] predicts, for example, order parameters ranging between 0.4 and 0.7 (at the nematic to isotropic transition) for cutoff axial ratio x_c between 0 and 4.45. In contrast, order parameters lower than 0.43 are predicted by the treatment developed by ten Bosch *et al.*[13,14]. Similarly, the theory of Warner[12] leads to an order parameter at the nematic to isotropic transition equal to 0.356, in the limit of long chains.

In general, order parameters ranging between 0.4 and 0.7 at $T/T_{NI} = 1$ have been reported for main-chain LCPs of different structures. It has been shown, by conformational analysis that the length of the flexible spacer is relevant in determining the mesophasic behaviour[25]. Polymers containing odd numbers of $-CH_2-$ units in the flexible spacer give rise to lower S_{zz}.

Order of the flexible spacers

The ^{2}H n.m.r. spectra of the polymer deuterated in the flexible alkyl chains show two distinct quadrupole doublets at temperatures above T_m (*Figure 2*). As already discussed, the outer doublet has been assigned to the α-methylenes which are more influenced by the constraints of the nematic environment whereas the inner doublet is assigned to the remaining $-CH_2-$ in the alkyl chains.

Similar spectra were obtained for a polyester of similar chemical structure deuterated in the flexible linkage by Samulski *et al.*[22] and for a dimer including *p*-azoxyanisole as the mesogenic unit by Martins *et al.*[23].

The resolution between different positions in the flexible spacer is thus lower than observed for terminal alkyl chains in LCs. A doublet for each $-CD_2-$ group in the alkyl chain is observed in monomeric LCs[45]. This fact can be attributed to the constraint imposed on the possible conformations of the flexible chains by the two mesogenic units attached at each end.

The ratios $\Delta\nu_i/\Delta\nu_Q^{ar}$ of the measured quadrupole splitting of the α-CD_2, the internal-CD_2 and the methyl groups with respect to the quadrupole splitting of C–D bonds in the aromatic ring ($\Delta\nu_Q^{ar}$) are plotted in *Figure 6* as a function of temperature. By assuming that the orientational order is the same at a given temperature for both flD-LCP and mD-LCP, the ratio $\Delta\nu_i/\Delta\nu_Q^{ar}$ may be considered to be independent of the order parameter S_{zz}. This is confirmed by the constant values of $\Delta\nu_i/\Delta\nu_Q^{ar}$ observed for α-methylene and $-CD_3$.

The ratio $\Delta\nu_i/\Delta\nu_Q^{ar}$ calculated for the internal methylene units shows a clear temperature dependence in the mesophase range which may be attributed to conformational changes (*Figure 6*). In particular, the decrease of $\Delta\nu_i/\Delta\nu_Q^{ar}$ with increasing temperature reflects an increasing mobility of internal $-CD_2-$. Similar behaviour was observed for dimers and polymers of similar chemical structure.

The parameter $\langle P_2(\cos\beta)\rangle$ indicating the conformational order of the flexible spacer can be calculated from the following equation:

$$\Delta\nu = \tfrac{3}{2}\chi\left(\frac{3\cos^2\theta_o - 1}{2}\right)S_{zz}\left\langle\frac{3\cos^2\beta - 1}{2}\right\rangle$$
$$= \tfrac{3}{2}\chi\left(\frac{3\cos^2\theta_o - 1}{2}\right)S_{zz}\langle P_2(\cos\beta)\rangle$$

where $\chi = 174\,\mathrm{kHz}$. The order parameter S_{zz} was derived from the ^{2}H n.m.r. spectra of mD-LCP. Data collected on heating through the solid to nematic transition and on cooling from the isotropic phase are plotted in *Figure 7*.

Experiments were also carried out on a polymer deuterated in the flexible units and in the mesogen (D-LCP). The parameters $\langle P_2(\cos\beta)\rangle$ and S_{zz} can be determined in this case in the same experimental conditions and are plotted in *Figure 8*. There is excellent agreement between values of $\langle P_2(\cos\beta)\rangle$ determined on flD-LCP and D-LCP, as expected considering the small difference between the molecular weight of the two polymers. The data reported in ref. 22 for a polyester of *p*-azoxyanisole are also plotted in *Figure 8*. The temperature dependence for the α- and internal CD_2 in our polymer and in polyesters of *p*-azoxyanisole is qualitatively the same although values of $\langle P_2(\cos\beta)\rangle$ are lower for the polymer investigated in this work. This could be attributed to differences between the orientational order parameters of the two polymers. In order to eliminate the effect of the orientational order parameter S_{zz}, the order of the C–D bonds, $S_{C-D} = S_{zz}\langle P_2(\cos\beta)\rangle$, was calculated. Data are compared with values calculated from ref. 22 in *Figure 9*. Agreement between the data is in this case closer, in particular for the α-CD_2.

The temperature dependence of $\langle P_2(\cos\beta)\rangle$ indicates that restrictions in the mobility of the internal methylene occur with decreasing temperature. However, conformational changes seem to be rather small, at least in the range of molecular weights investigated.

CONCLUSIONS

We have presented a detailed characterization of a nematic liquid crystalline polymer by ^{2}Hn.m.r. and ^{1}H n.m.r. Partially deuterated LCPs were studied in a wide temperature range and the orientational order of the mesogens and the flexible spacers were both determined. N.m.r. measurements were performed below and above T_m. For all polymers investigated, a monodomain nematic structure was only observed from about 20°C above T_m. However, a detailed analysis of the ^{2}H n.m.r. powder patterns indicated that, within a domain below this temperature, the type of molecular motions and degrees of orientational order were the same as those measured just above $T_m + 20°C$ when the doublets characteristic of an aligned monodomain structure are observed.

The LCP has degrees of orientational order which are high not only compared to values relative to LLCs but also with respect to data reported for similar main-chain LCPs. Order parameters at the nematic to isotropic phase transition are consistent with data reported for polymers of similar structure and seem to confirm the effect of steric repulsions in the stabilization of the liquid crystalline behaviour. Analysis of ^{2}H-n.m.r. spectra of the polymer deuterated in the flexible spacer is consistent with data reported for polyesters of 2,2′-dimethyl-4,4′-dihydroxyazoxybenzene.

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