2 H NMR Study of a Deuterium Labelled Ferroelectric Liquid-Crystalline Polysiloxane

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²H NMR STUDY OF A DEUTERIUM LABELLED FERROELECTRIC LIQUID-CRYSTALLINE POLYSILOXANE

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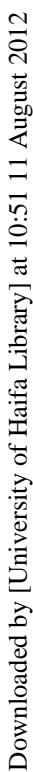degli Studi di Pisa, via Risorgimento 35, 56126 Pisa, Italy*

We investigated by ²H NMR spectroscopy a ferroelectric liquid crystalline polysiloxane (poly11EB1M7-d₂) derived from the mesogen (+)(S) 4-[4′-(1-methylheptyloxy)]biphenyl 4-(10-undecenyloxy)benzoate-d₂ (11EB1M7-d₂). The labelling on the phenyl fragment allowed us to study the orientational order of such unit. From the analysis of the deuterium lineshapes we could also determine the effect of the magnetic field on the mesogen alignment and the ferroelectric helix distortion. In particular, deuterium spectra showed a contribution due to aligned mesogens in addition to a "Pake-like" one. This was accounted for by considering isotropic distribution of helices, with possible helix distorsion.

INTRODUCTION

The interest in ferroelectric liquid crystals, including liquid-crystalline polymers [1], has grown because of their potential applications in optical and electrooptical devices. In order to fully understand the molecular properties of the high molar mass liquid crystals, one should better comprehend the peculiar differences between liquid crystal monomers and polymers. In fact, in the latter systems one typically notes an increase in the mesophase thermal stability, that is much higher clearing temperatures T_c and wider extensions of the mesophase range from T_g, the glass transition temperature, to T_c, with respect to the corresponding monomers. Additionally, an increase in the order degree usually takes place going from low to high molar mass liquid crystals, smectic mesophases being usually favoured rather than the nematic one. Another important effect of the

FIGURE 1 Reaction scheme for the preparation of polysiloxane poly 11 EB1M7-d_2.

polymerization of liquid crystal monomers is the reduced mesophase polymorphism: in fact in liquid crystal polymers only few cases of mesophase sequences are known, normally not including chiral subphases such as the antiferroelectric and ferrielectric. Finally, the mesophase order can be quenched by the formation of gels, elastomers and densely crosslinked networks.

NMR spectroscopy has proved to be very valuable in the study of side-group liquid crystalline polymers [2], including ^{2}H NMR of perdeuterated or selectively deuterated liquid crystals [3]. We are interested in understanding the structure, dynamics and order in ferroelectric liquid crystal monomers and polymers, and their inter-relationships, by ^{2}H NMR spectroscopy. In this work we investigate the structure and orientational order of a polysiloxane (poly11EB1M7-d_2) containing a selectively deuterated mesogenic side group (11EB1M7-d_2) (Fig. 1).

EXPERIMENTAL

Synthesis of Polysiloxane Poly11EB1M7-d_2

The monomer $(+)$-(S) 4-[4′-(1-methylheptyloxy)]biphenyl 4-(10-undecenyloxy)benzoate-d_2(11EB1M7-d_2) was synthesized following a general procedure [4]. Full details will be given elsewhere. The synthetic procedure for the preparation of polysiloxane poly11EB1M7-d_2 is sketched in Figure 1.

1.00 g (1.8 mmol) of 11EB1M7-d_2 and 0.10 g (1.6 mmol r.u.) of poly-(hydrogenmethyl siloxane) were dissolved in 50 ml of dry toluene under

nitrogen atmosphere. 0.8 ml of 2% xylene solution of Pt(*endo*-dicyclo-pentadiene dichloride) (PtDCPDDCl) catalyst was added and the solution was stirred at 50°C for 150 h. The solution was poured into a large excess of methanol and the coagulated polymer was purified by repeated precipitations from chloroform solution into diethyl ether, giving 280 mg of poly11EB1M7-d_2 (26% yield). $[\alpha]^{20}_D = 3.6$(CHCl$_3$).

^{1}H NMR (CDCl$_3$): $\delta = 8.1$ (2H, m), 7.6-7.4 (4H, m),7.2 (2H, m), 6.9 (2H, m), 4.4 (1H, m), 3.9 (2H, t), 2.0-0.9 (34H, m), 0.5 and 0.1 (5H, 2 m).

IR (film on KBr) $\bar{v}$ (cm^{-1}): 1728 ($\bar{v}$ C=O), 1606, 1494 and 1468 ($\bar{v}$ C=C aromatic), 1260 ($\bar{v}$ Ar-C(=O)O), 1128-1000 ($\bar{v}$ SiO).

Characterization

The structure of poly11EB1M7-d_2 was confirmed by elemental analysis, IR (Nicolet Magna 750 FT-IR spectrophotometer) and ^{1}H NMR (Varian VXR 300 spectrometer).

Molecular masses and dispersity ratios of the polymer were determined by SEC with a Perkin-Elmer 2/2 chromatograph equipped with Shodex A802/S and A803/S columns and a Perkin-Elmer LC75 UV detector. CHCl$_3$ was used as solvent (1 mL min^{-1}, 25°C) with polystyrene calibration.

The transition temperatures were determined by a Mettler TA4000 differential scanning calorimeter (rate 10°C/min) on samples that had been annealed by cooling from the isotropic liquid. They were also verified by visual observation of the birefringent textures with a Reichert Polyvar polarizing optical microscope.

The ²H NMR spectra were recorded using a Varian VXR-300 spectrometer, working at 46.04 MHz for deuterium. The sample was macroscopically aligned within the magnet by slow cooling from the isotropic into the smectic C* phase (Fig. 2, spectra on the left). The thermal equilibration was checked by slowing repeating the heating and cooling procedure and by recording spectra at 140°C every one hour during a day. The spectra which have been finally analyzed were recorded every ten degrees from 140 to 110°C and every two degrees from 108 to 50°C (± 0.2°C). We also performed ²H NMR measurements at various temperatures after cooling the polymer from the isotropic phase into the SmC* outside the magnetic field (Fig. 2, spectra on the right).

RESULTS AND DISCUSSION

The transition temperatures of poly11EB1M7-d_2 are summarized in Table 1 together with those of the non-deuterated sample poly11EB1M7 [4] for comparison. Both polymers formed a SmC* phase (tilt angle of 45° [5]) with an underlying SmF* phase.
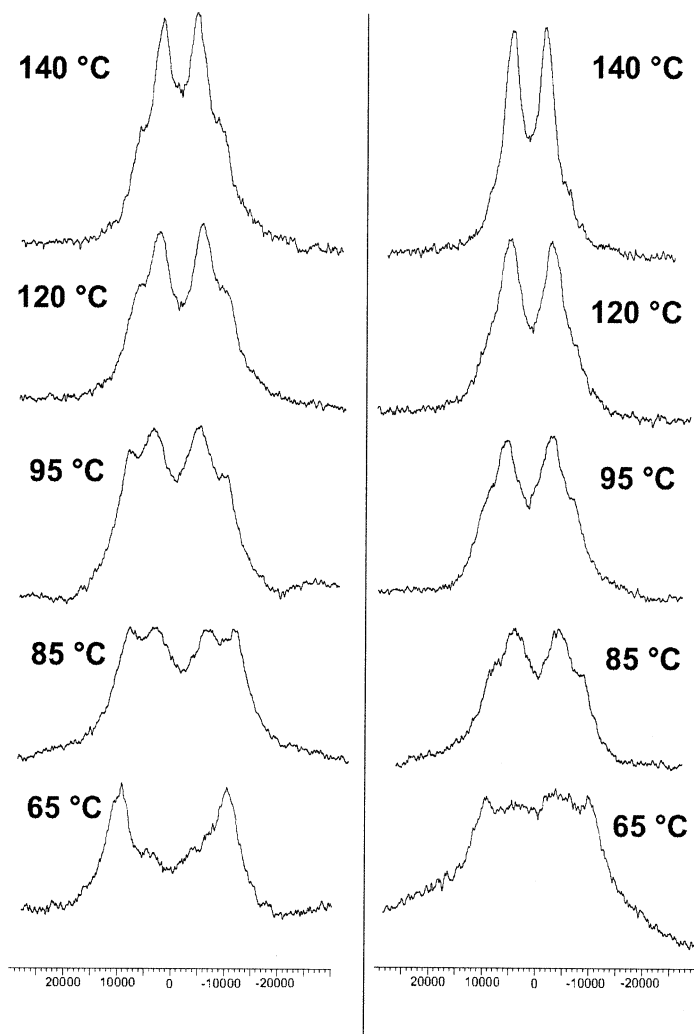
FIGURE 2 ^{2}H NMR spectra for poly 11EB1M7-d_2 as function of temperature on cooling from the isotropic phase within (left) or outside (right) the magnetic field.

TABLE 1   Molar Masses and Phase Transition Temperatures of Polysiloxanes

Sample	M_w (g/mol)	M_w/M_n	T_g (°C)	$T_{SmF*-SmC*}$ (°C)	T_i (°C)
poly11EB1M7 [4]	32000	1.8	39	70	169
poly11EB1M7-d_2	29000	1.9	41	57	161

Left column of Figure 2 shows ²H NMR spectra of poly11EB1M7-d_2 recorded on cooling the sample from the isotropic phase in the magnetic field as already described. At high temperatures one notes complex line-shapes which are clearly due to a distribution of molecular director orientations, but not typical isotropic "Pake spectra". Below 95°C, the intensity of the internal peaks progressively decreases until the external quadrupolar doublet dominates. This behaviour suggests that, as already observed for other polymers [6], the spectra could result from the super-imposition of an external doublet, ascribable to a fraction of the sample with the molecular director parallel to the magnetic field, and a broad band ascribable to the unoriented fraction of the sample. With decreasing tem-perature, the amount of the unoriented component decreases.

Right column of Figure 2 shows ²H NMR spectra of poly11EB1M7-d_2 recorded on cooling the sample from the isotropic phase outside the magnetic field.

In this case the smectic domains could not be oriented by the magnetic field and the lineshape of the recorded spectra is ascribable to the super-imposition of the patterns due to smectic C* helices with randomly dis-tributed axes ("Pake-like distribution"). In fact the spectra on the right are very similar to the left ones, except for the external portions where the intensity is much reduced.

In Figure 3 there are reported the inner (squares) and outer (circles) quadrupolar splittings, as a function of temperature, obtained by cooling the sample in (full symbols) and outside (open symbols) the magnetic field, respectively. The trends of the data obtained by the two different proce-dures are in good agreement.

The assignment of the external doublet to the mesogenic fragments averagely aligned to the magnetic field is supported by the comparison of its quadrupolar splitting with the one of the monomer 11EB1M7-d_2 [7] in its smectic A and unwounded smectic C* phases. The splittings of the polymer and monomer are quite similar. The evaluation of the order parameter S_{zz} relative to the *para* axis of the deuterated ring can be done by the following equation [8]:

$$\Delta v_q = \frac{3}{2} q_{aa} \left[S_{zz} \left(c^2 - \frac{1}{2}s^2 - \frac{1}{6}\eta c^2 + \frac{1}{3}\eta s^2 + \frac{1}{6}\eta \right) + \Delta \left(\frac{1}{2}s^2 + \frac{1}{6}\eta c^2 + \frac{1}{6}\eta \right) \right]$$

(1)

with $q_{aa} = 185$ kHz, $\eta = 0.04$, $\Delta = 0$ [9]. The parameters "c" and "s" stand for cos ϕ and sin ϕ where ϕ is the angle between the C-D bond and the phenyl *para* axis which is fixed to 60°.

As one can see in Figure 3, the local order parameter computed from the greater splittings ranges from 0.45 to 0.70 with decreasing temperature.
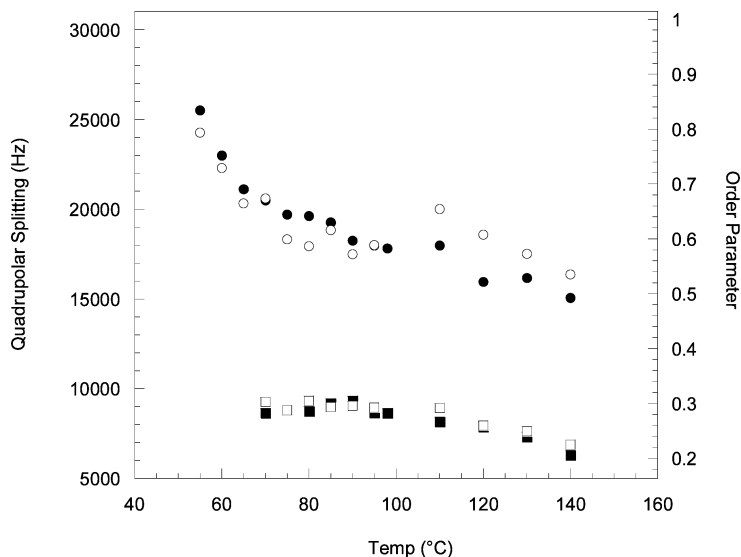
FIGURE 3 Experimental quadrupolar splitting and order parameter as function of temperature (circles and squares indicate outer and inner splittings, respectively; full and empty symbols refer to the spectra obtained by cooling the sample in and out the magnetic field, respectively).

These values are ascribable to portions of the sample where the local director is parallel to the magnetic field.

In order to better clarify the orientational behaviour of our sample in the magnetic field we computed the lineshape corresponding to different models. First, we assumed an isotropic distribution for the axes of undeformed smectic helices, with various values of the tilt angle θ between the molecular director and the normal to the smectic layers. Some of the computed spectra are reported in Figure 4.

As evident from the simulation, the tilt angle θ of the SmC* phase heavily influences the expected lineshape. The "Pake-like spectra" for the SmC* phase with a tilt angle different from 0 (Figs. 4b–4d) are very different from the "Pake spectrum" due to an isotropic distribution of molecular directors (Fig. 4a). The only computed lineshape that resembles the experimental ones corresponds to $\theta = 45°$, and we know that X-ray measurements yield a tilt angle of just 45° for this SmC* phase [5]. In particular, the spectra recorded at 95°C–85°C, after cooling the sample outside the magnetic field, seem to fairly fit our simple model.

As a second step, at least two effects are expected to be essential for explaining the experimental lineshapes at various temperatures:
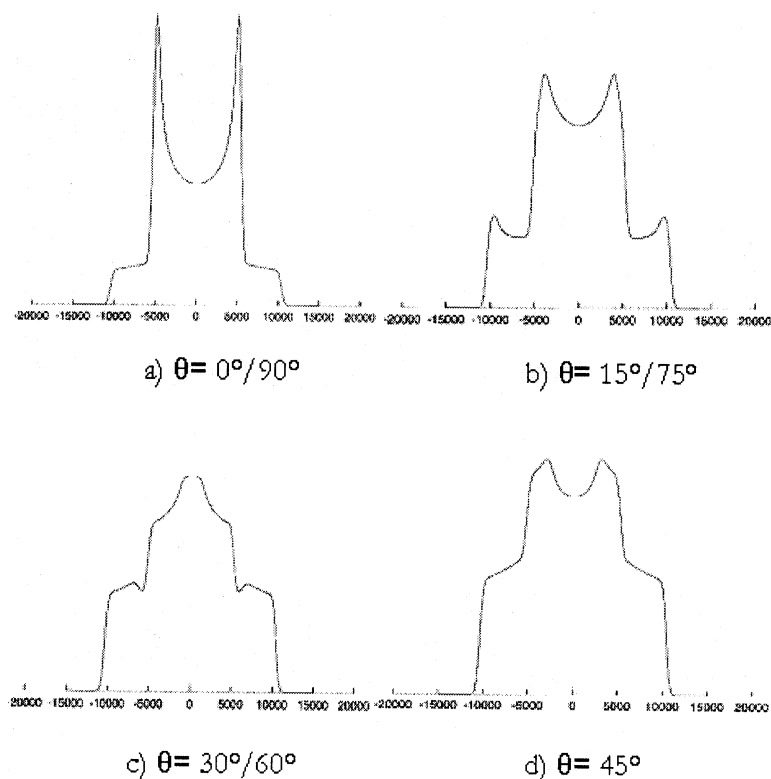
FIGURE 4 Simulated spectra for isotropic distribution of undeformed chiral helices, with various tilt angles. The local order parameter is fixed to 0.6 and the linewidth, for the single Gaussian component, is fixed to 700 Hz. The molecular motions of exchange between the domains with different orientations to the magnetic field are assumed to be frozen.

(i) translational diffusion along the helical axis, certainly more important at high temperatures; (ii) helix deformation by the magnetic field due to the diamagnetic coupling [10,11]. We have taken into account the latter effect.

It is well known that the magnetic field can induce a deformation of the director phase profile $\Phi(z)$ (Fig. 5): the fraction of the helix for which the angle between the molecular director and the magnetic field is the smallest increases. For example, considering the function $\Phi(z)$ in the case of a smectic helix perpendicular to the magnetic field, with $\theta = 90°$, which would be equivalent to a cholesteric phase, the deformation provides a 2π-soliton lattice [10] (see phase profiles in Fig. 6).

A possible analytical expression describing the functions shown in Figure 6 is given by the following equation:
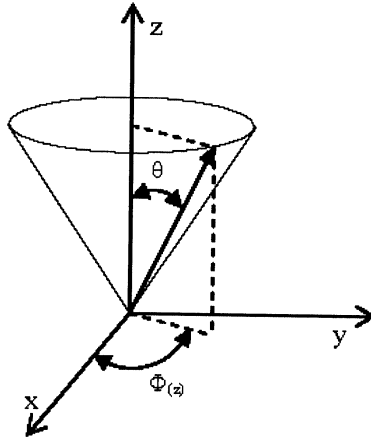
D. Catalano et al.

FIGURE 5 Schematic picture of the orientation of the local director with respect to the smectic layer frame: z is the helix axis direction, x-y is the layer plane, θ is the tilt angle, and Φ(z) is the director phase angle.
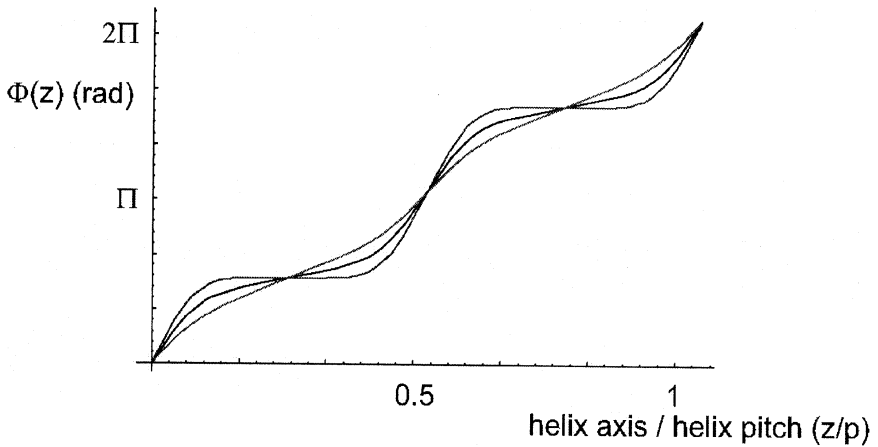

FIGURE 6 The distortion of the director phase profile Φ(z) of a ferroelectric liquid crystal in the external magnetic field. The distortion effect increases with the increasing of the oscillation amplitude.

$$\varphi(z) = z + a\big[\sin(2z) + 1/4 \cdot \sin(4z) + 1/45 \cdot \sin(6z)\big] \qquad (2)$$

where a is an empirical parameter increasing with increasing distortion, ranging from 0 to 3/4. The effect of the distortion of the phase profile can be taken into account starting from Eq. (2) and computing different
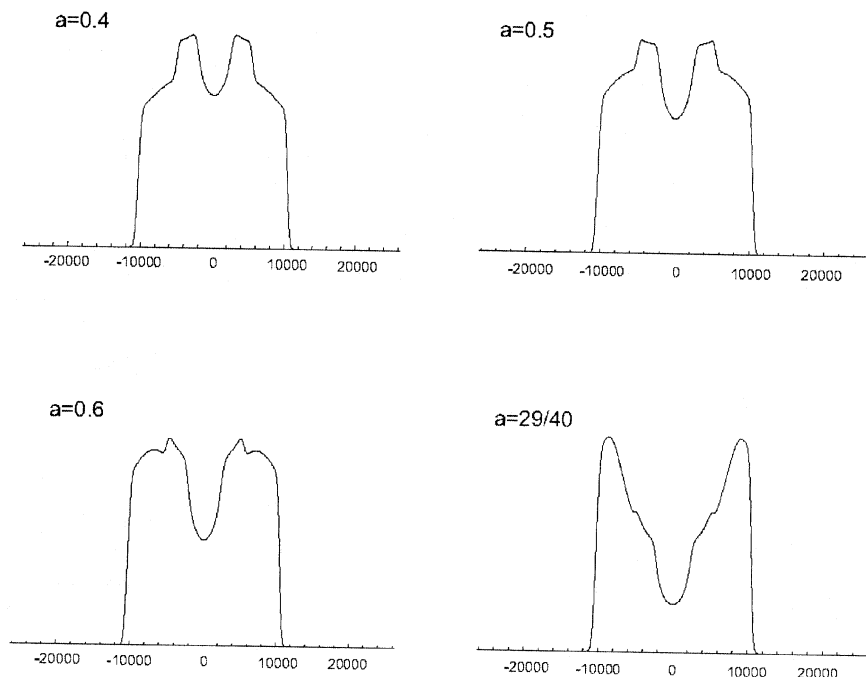
FIGURE 7 Simulated spectra for isotropic distribution of deformed chiral helices, with tilt angle of 45° and different deformation degree. The local order parameter is fixed to 0.6 and the linewidth, for the single Gaussian component, is fixed to 700 Hz. The molecular motions of exchange between the domains with different orientations to the magnetic field are assumed to be frozen.

weights for different orientations of the local director with respect to the magnetic field. Some of the spectra computed with the helix deformation are shown in Figure 7.

By comparing the simulated spectra with the experimental ones we observe that our rough model can outline the features and changes of the spectra recorded from 95 to 65°C for the sample slowly cooled in the magnetic field (Fig. 2, left column). Therefore, the magnetic distortion effect seems to be essential at low temperatures and to increase with decreasing temperature.

CONCLUSIONS

The ²H NMR spectra obtained by cooling the sample in the magnetic field revealed the coexistence of SmC* layers with the molecular director

parallel to the magnetic field, prevailing at low temperature, with a "Pake-like" distribution of helices. This has been explained by the distortion effect of the magnetic field on the helix phase profile. The simulation of spectral patterns obtained by cooling the sample outside the magnetic field ("Pake-like" spectra) confirms the value of $45°$ for the SmC* phase tilt angle.

REFERENCES

[1] Galli, G. (2001). In: *Advanced Functional Molecules and Polymers*, Nalwa, H. S. (Ed.), Overseas Publishers Association: Singapore, Vol. I, 271.

[2] Boeffel, C. & Spiess, H. (1989). In: *Liquid Crystal Polymers*, McArdle, C. B. (Ed.), Blackie: Glasgow.

[3] Mazzalupo, R., Ranieri, G., Catalano, D., Galli, G., & Veracini, C. A. (1995). *Liq. Cryst.*, *19*, 367.

[4] Ragnoli, M. (1999) *Thesis*, Università di Pisa, Italy.

[5] Gallot, B. private communication.

[6] Chiezzi, L., Fodor-Csorba, K., Galli, G., Gallot, B., Pizzanelli, S., & Veracini, C. A. (2001). *Mol. Cryst. Liq. Cryst.*, *372*, 69.

[7] Catalano, D., Chiezzi, L., Domenici, V., Fodor-Csorba, K., & Veracini, C. A. *Liq. Cryst., unpublished*.

[8] Veracini, C. A. (1985). In: *NMR of Liquid Crystals, Nato ASI Series C*, Emsley, J. W. (Ed.), Reidel: Dordrecht, Vol. 141, 99.

[9] Catalano, D., Cavazza, M., Chiezzi, L., Geppi, M., & Veracini, C. A. (2000). *Liq. Cryst.*, *27*, 621.

[10] Musevic, I., Blinc, R., & Zeks, B. (1995). *The Physics of Ferroelectric and Antiferro-electric Liquid Crystals*, World Scientific: Singapore.

[11] Zalar, B., Gregorivic, A., Simsic, M., Zidaznek, A., Blinc, R., Keast, S., & Neubert, M. (1998). *Phys. Rev. Lett.*, *80*, 4458.