Partially Deuterated Liquid Crystal Polymers: Structure and Orientational Order by X-ray Diffraction and 2 H NMR

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Abstract The structure, magnetic alignment and orientational order of polysiloxane liquid crystal copolymers were investigated by X-ray diffraction and ^{2}H NMR spectroscopy. The copolymers incorporated significant amounts of non-mesogenic counits, and the influence of the composition on their properties was studied. The deuterium spectra were analyzed in terms of ordered and Pake disordered components.

Keywords chiral liquid crystal polymer, orientational order, deuterium NMR

INTRODUCTION

Smectic chiral polymers giving rise to ferroelectric and anti-ferroelectric phases are materials of interest because of their potential application in electrooptical devices that are light and robust and can be filmed and processed in various shapes [1].

We are interested in studying the structure and dynamics of smectic polymers exhibiting ferroelectric and electroclinic properties. Deuterium labelling at specific sites of the repeat unit of liquid crystal polymers provides a unique tool for investigations by ^{2}H NMR spectroscopy [2, 6]. In a previous paper, we reported on the different orientation behaviors in the magnetic field of two partially deuterated polysiloxane copolymers [3]. This difference was ascribed to the disturbing effects of the non-mesogenic units on the mesophase ordering.

In order to clarify the question of different magnetic field induced orientational orders and to assess the effect of composition in liquid crystal copolymers, we decided to reinvestigate by ^{2}H NMR those samples (polymers I and II) and other copolymers (polymers III and IV) in which the content of non-mesogenic units was enriched to a significant proportion. Their structures were also studied by X-ray diffraction.

EXPERIMENTAL

Synthesis

Chiral monomers 1 and 2 were prepared as previously described [3].

Polysiloxanes I-IV were prepared following a similar procedure which is described here in detail for polysiloxane III: 0.3 g (0.6 mmol) of 1 and 0.08 g (1.2 mmol) of poly(hydrogenmethyl) siloxane 4 were dissolved in 50 ml of dry toluene under nitrogen atmosphere. 0.04 ml of a 2.5% xylene solution of platinum (divinyltetramethyl disiloxane) was added and the solution was stirred at 40 °C for 96 h. 0.08 ml (0.6 mmol) of 1-hexene 3 was then added and the solution was let to react for an additional 12 h at room temperature. The solution was poured into a

large excess of methanol and the coagulated polymer was purified by repeated precipitations from diethyl ether solution into n-hexane, giving 0.35 g (41% yield) of III.

^{1}H-NMR (CDCl$_3$) δ (ppm): 0.1 and 0.5 (2m, 12H, SiCH$_2$ + SiCH$_3$), 0.9-1.9 (m, 37H, aliphatic), 4.0-4.2 (2m, 4H, OCH$_2$ + COOCH$_2$), 6.9 (m, 0.35H, aromatic), 7.2 (m, 2H, aromatic), 8.1 (m, 3.5H, aromatic).

Characterization

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

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

X-ray diffraction experiments were performed on powder samples with a pinhole camera under vacuum, with Ni-filtered Cu beam (λ= 1.54 Å) and equipped with a device for recording the diffraction patterns between 20 and 250 °C with the accuracy of 1 °C. Several exposures were taken so as to measure the strongest and the weakest reflections. Intensities of the reflections were measured with a laboratory built microdensitometer. Experimental amplitudes of diffraction of the different orders of reflection on the smectic layers were corrected for the Lorentz polarization factor and normalized so that the strongest one had an amplitude of one. The corrected amplitudes for polymer I were: a_1 = 1 and a_2 = 0.47 for the S_{C1} phase, and a_1 = 1 and a_2 = 0.43 for the S_{A1} phase.

RESULTS

Polymers I-IV were synthesized following the procedure outlined in Figure 1. Their relative compositions (x and y) were varied in order to

dilute differently the mesogenic side chains by non-mesogenic hexyl units (Table 1).
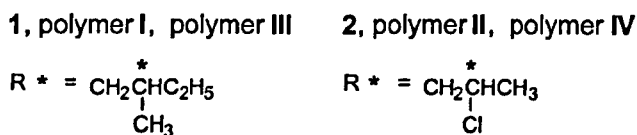

FIGURE 1.   Reaction scheme for the synthesis of polymers **I-IV**.

The phase transition temperatures of the polymers are summarized in Table 1.

TABLE 1.   Phase transition temperatures of polymers **I-IV**.

Polymer	x	Transition temperatures (in °C)						
I	28	g	-17	S_C	80	S_A	113	i
II	29	g	-10			S_A	163	i
III	18	g	-21	S_C	65	S_A	100	i
IV	19	g	-9			S_A	148	i

The structures of their mesophases were investigated by X-ray diffraction on powder samples. Typical results are described here for polymers **I** and **II**. In each case the X-ray diagrams obtained between room temperature and isotropization temperature, exhibited in the low-angle domain two sharp reflections that could be indexed as the $00l$ reflections of a layered smectic structure of periodicity d, and in the wide-angle domain a diffuse band characteristic of a disordered smectic (A or C) (Figure 2).
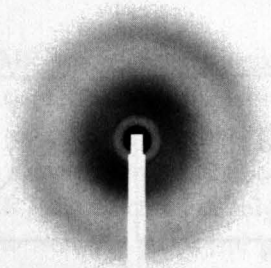

FIGURE 2. X-ray diffraction pattern of polymer **I** in the SmC phase (T = 24 °C)

The comparison between the thickness d of the smectic layers and the length L of the fully extended repeat unit as measured on CPK models allowed us to determine the type A or C of the smectic phases. For the low temperature mesophase of polymer **I** $d = 36.0$ Å was shorter than $L = 37.4$ Å. Therefore, the mesophase was of the tilted smectic S_{C1} type, the tilt angle evaluated being 16°. For the high temperature mesophase of polymer **I** $d = 37.7$ Å was slightly longer than L, and the structure was of the perpendicular S_{A1} type. The mesophase of polymer **II** was of the S_{A1} type ($d = 36.0$ Å, $L = 35.0$ Å). In any case, d remained constant within all domain of stability of each mesophase.

In order to gain further information on the structure of the mesophases we deduced the electron density profiles $\rho(z)$ along the smectic layer normal from the respective intensities of the low-angle reflections [4,5]. As the X-ray diagrams exhibited two low-angle reflections we could

draw the four corresponding electron density profiles (Figure 3). The average electron densities of the different parts of the repeat unit of polymer I were: 7.8 e/Å for the main chain, 6.4 e/Å for the spacer, 9.8 e/Å for the mesogen and 7.8 e/Å for the tail substituent. Therefore, to be consistent with an S_{C1} or S_{A1} structure, the electron density profile should present a central maximum for the mesogens, flanked by minima for the spacers and secondary maxima for the main chains. Such an electron density profile was obtained by the combination of signs – and + (Figure 3b).
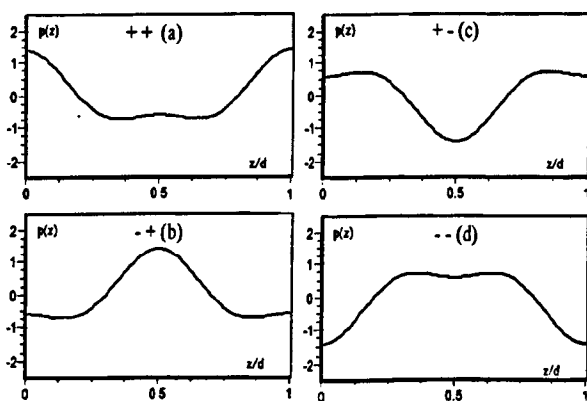
FIGURE 3.   Calculated electron density profiles for polymer I in SmA phase

The deuterium spectra were recorded by cooling from the isotropic phase and allowing for temperature equilibration with a suitable pre-acquisition delay. In the spectra of polymer II we observed a dependence of the magnetic alignment on the thermal history of the sample; a slight dependence of the alignment was observed for polymer I as well. The spectra for polymers I and II, recorded with different experimental conditions and cooling rates are shown in Figures 4 and 5.
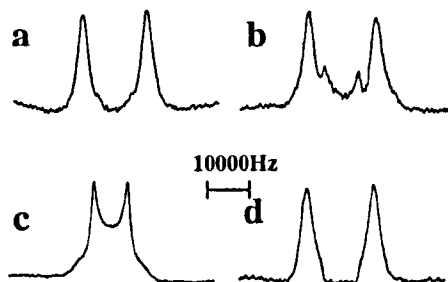
FIGURE 4   a) ^{2}H-NMR spectrum of polymer I with a high order (T=80°C), obtained.by quenching the sample from the isotropic phase. b) ^{2}H-NMR spectrum of polymer I with a lower order (T=80°C), obtained by cooling the sample from the isotropic phase in steps of 1°C every 3 min. c) ^{2}H-NMR Pake spectrum of polymer I at 80°C obtained by heating the sample to isotropic phase and letting it cool out of the magnet. d) ^{2}H-NMR spectrum of polymer I (T=80°C), obtained from the difference of b and c, where c is 9% of a.
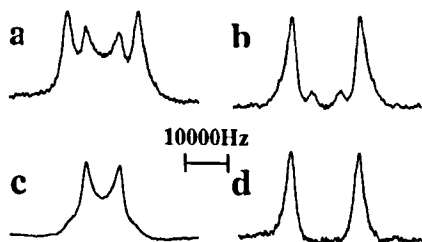

FIGURE 5.   a) ^{2}H-NMR spectrum of polymer II with a low order (T=70°C), obtained by quenching the sample from the isotropic phase. b) ^{2}H-NMR spectrum of polymer II with an almost full orientation (T=70°C), obtained by cooling the sample from the isotropic phase in steps of 3°C every 3 min. c) ^{2}H-NMR Pake spectrum of polymer II at 70°C obtained by heating the sample to isotropic phase and letting it cool out of the magnet. d) ^{2}H-NMR spectrum of polymer II (T=70°C), obtained from the difference of a and c, where c is 20% of a.

One can see that the ^{2}H spectrum of polymer **II** obtained by quenching the sample from the isotropic phase had a greater contribution of disorder (20% of the intensity was due to a Pake spectrum) than the spectrum obtained on slow cooling (10% of disorder). The ^{2}H spectra of polymer **II** showed a much lower contribution from the unaligned polymer: what is puzzling in this case is that the spectra obtained by slow cooling do show an amount of disordered polymer slightly higher (about 10%) than those obtained by quenching the sample to 80°C from the isotropic phase (about 5-6%).

The spectra of polymers **III** and **IV** did not show dependence on the cooling rate and always the broad quadrupolar doublet, typical of an oriented polymer samples, was obtained with either a slow cooling or a quenching of the sample from the isotropic phase.

From the ^{2}H spectra the order parameters of the aromatic core of the mesogenic side groups could be evaluated. The quadrupolar splittings can be expressed in terms of local order by Eq. 1:

$$\Delta v_q = \frac{3}{2} q \left[S_{aa} + \frac{\eta}{3} (S_{cc} - S_{bb}) \right] \tag{1}$$

where q, the quadrupolar coupling constant is 185 KHz and η, the asymmetry parameter, is 0.04 [6]. The a axis of the local reference frame, where the electric field tensor is diagonal, coincides with the C-D bond direction, and the b axis is perpendicular to the aromatic ring plane. To this purpose the ordered part of the spectra, separated by the disordered one by means of spectral subtraction, can be utilized. The deuteria 2 and 6, as well as 3 and 5, are equivalent because of the rotation of the phenyl moiety. In addition, in spite of the possible small inequivalence of adjacent deuteria 2,3 and 5,6, they can not be distinguished on the basis of the quadrupolar splitting because of the broad linewidth. So the spectra give just one quadrupolar splitting relative to the four deuteria.

Figures 6 and 7 show the trend of the order parameter S_{zz} defined in a molecular frame where the z axis is parallel to the long molecular axis.

The trends are reported as a function of the temperature. The relation between S_{ZZ} and Δv_q is given by the Eq. (2) which is derived from (1) by transforming the local reference frame into the molecular one.

$$\Delta v_q = \frac{3}{2}q[S_{zz}\left(\cos^2\theta - \frac{1}{2}\sin^2\theta - \frac{1}{6}\eta\cos^2\theta + \frac{1}{3}\eta\sin^2\theta + \frac{1}{6}\eta\right) +$$
$$+ \Delta\left(\frac{1}{2}\sin^2\theta + \frac{1}{6}\eta\cos^2\theta + \frac{1}{6}\eta\right)]$$

(2)

θ, the angle between the long molecular axis and the C-D bond direction, has been set to 60°. S_{XX}-S_{YY} has been assumed to be the same as that of the monomers, reported in a previous work [3].
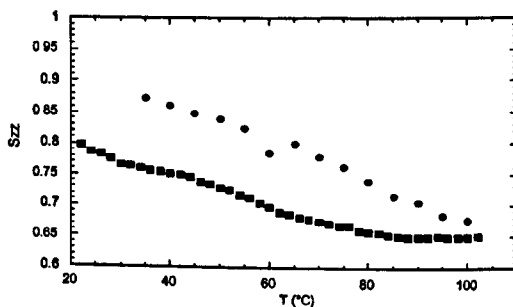

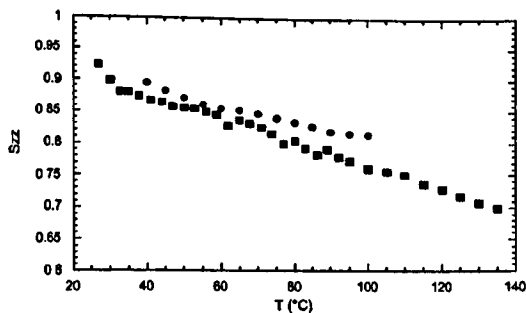FIGURE 6. Temperature dependence of the principal order parameters for polymer I (■) and polymer III (●).

FIGURE 7. Temperature dependence of the principal order parameters for polymer II (■) and polymer IV (●).

The order parameter of the core of the mesogenic units was the same for of polymers **II** and **IV** and showed a monotonic behaviour as a function of temperature confirming for these materials the existence of one smectic A phase as shown by X-ray measurements. The difference in the trends of the similar order parameters in the case of polymers **II** and **IV** revealed that two phases formed on changing temperature: the phase transition of polymer **I** could be more easily located around 70-75 °C, in agreement with X-ray results. In polymer **III** the larger percentage of non-mesogenic moieties with respect to polymer **I** (50 mol% with respect to 20 mol%) produced a sizeable decrease of order in all the temperature range. This is in contrast with the insensibility of polymer **II** to concentration of hexyls groups in the copolymer.

DISCUSSION

First we would like to contrast the behaviour of polymers **I** and **II** to put in evidence the effect of the difference in molecular structure of the lateral mesogenic units, then we will consider the effect of increasing non-mesogenic 1-hexyl lateral units.

The 2-chloropropyl substituents favor the stability of the smectic A phase more than 2-metylbutyl substituents: the latter seem to impart either greater flexibility or different mesomorphic organization, and consequently lower stability, to the mesomorphic range. This is consistent with the much higher clearing temperature of polymer **II**, namely 163 °C vs. 113 °C and with a higher degree of orientational order of the lateral mesogenic groups of this polymer. Also in agreement with this, a good alignment of polymer **II** is achieved only when using a slow cooling rate from the isotropic phase while the magnetic alignment is much easier for polymer **I**. To this respect it is surprising that the alignment of polymer **I** obtained by fast cooling is even slightly better than that obtained on slow cooling.

It is not easy, however, to rationalize the differences between these two polymers: it is not clear if these are due to a different flexibility of the

substituents (the 2-chlorobutyl group is more bulky and more rigid than 2-methylbutyl), or if the different polarity of the monomers could induce a different organization within the two polymers.

In polymers III and IV the substantial presence of non-mesogenic moieties (50 mol%) eliminates the difference between the two substituents as far as alignment in the magnetic field is concerned. However, the 2-methylbutyl polymer, as a consequence of the increase of hexyl unities suffers a major decrease of the orientational order, whereas the 2-chloropropyl polymer undergoes only a minor perturbation.

Lastly we would point out that no effect of the monomers chirality seems to affect the deuterium spectra, at least from what the aligned spectra is concerned; this means that also in the smectic C phase, magnetic field aligns the mesogenic unities and the chiral helix is unwound.

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