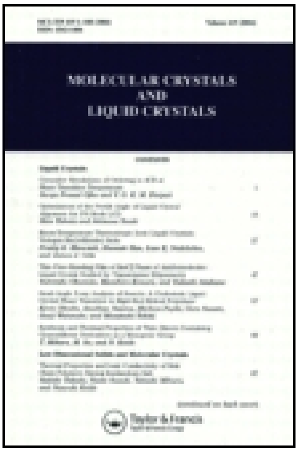

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Profiles of Backbone Distribution of Different Side-Chain Liquid-Crystal Polymers in the Smectic Phase

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PROFILES OF BACKBONE DISTRIBUTION OF DIFFERENT SIDE-CHAIN LIQUID-CRYSTAL POLYMERS IN THE SMECTIC PHASE

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Abstract: The measurements of the smectic reflection intensities of side-chain liquid-crystal polymers give access, after inverse Fourier transform, to the profile of coherent scattering length density along the normal to the layers. We give here three backbone density profiles associated to three liquid-crystal polymers: two polymethacrylates and one polyacrylate differing only by the nature of the backbone or by the mesogen extremity. It is shown that the backbones are always confined between the mesogen layers, and could be even localized right in the middle of the mesogen layer. In addition, this study demonstrates that small modifications of the liquid-crystal polymer formula are sufficient to induce very different backbone density profiles.

INTRODUCTION

The structure of the multilayer of long range one-dimensional order as the smectic A phase of side-chain liquid-crystalline polymers is very few described when it comes out the question to know where the polymer backbone is localized inside a smectic layer.

The foremost measurements carried out in this sense, were realized by X-Ray diffraction[1-3]. By using the properties of the inverse Fourier transform on the smectic reflections intensities, the electronic density associated to the layer profile was given. The presence of the polymer backbone inside the layer was identified by an additional increase of electronic density on both sides of the mesogen zones. In contrast to X-Ray diffraction, the use of neutron scattering associated to the isotopic labelling technique, allows the extraction of the signal corresponding to the polymer backbone alone. This method was first employed by Ohm et al[4] on a smectic liquid crystal polymer powder. Backbone distribution profile and profile of distribution of the hard cores were given. It was for the first time proved by this way that the backbone density is higher apart from the hard core zones. However, the drawback of measurements on unoriented polymers is the lack of accuracy and the difficulty to identify smectic reflections from smectic fluctuations or other diffuse scattering.

The same principle is applied now to three oriented liquid-crystal polymers called PMA-OC4H9, PMA-OCH3 and PA-OCH3 respectively. The two first one are liquid-crystal polymethacrylates differing only by the mesogen extremity which is -OC4H9 in the case of PMA-OC4H9 and -OCH3 for PMA-OCH3. The third one is a polyacrylate PA-OCH3 possessing the same side-chain mesogen as the polymethacrylate PMA-OCH3. Table 1 displays the detailed formula of each polymer and its characteristics (polymerization degree and polydispersity).

Contrary to X-Ray, neutron patterns obtained with labelled polymers and with corresponding unlabelled ones are different, demonstrating that the polymer backbone is not uniformely distributed in the smectic layer. The smectic reflection intensities will be measured in order to determine the structure factor of each isotopic species. The profiles of coherent scattering length associated to each labelled species will be then deduce and finally from the difference between labelled and corresponding unlabelled polymer, the backbone profile will be draw.

These three polymers present the same polymorphism: isotropic phase, nematic phase, monolayer smectic phase (SA_1) and finally the glassy state appear successively by decreasing the temperature. In the smectic phase, it has been demonstrated by Small-Angle Neutron Scattering[5] that the average conformation of the backbone of these polymers is an oblate shape. The polymer backbone is then mostly oriented perpendicular to the direction of the mesogens.

EXPERIMENTAL PART

Three couples of samples corresponding to:
- PMA(H)-OC4H9 and its labelled counter part: PMA(D)-OC4H9,
- PMA(D)-OCH3 and the 1:1 mixture of labelled and unlabelled polymers PMA(H)-OCH3/PMA(D)-OCH3,
- PA(H)-OCH3 and the 1:1 mixture of labelled and unlabelled polymers PA(H)-OCH3/PA(D)-OCH3, were prepared. These samples were placed in quartz disc-like cells of 17 mm diameter and 1 mm thickness. Each disc-like cell was set in an oven itself placed between the poles of a magnet (1.4 T). The sample is then heated up to the isotropic phase and then slowly cooled down to the SA_1 phase in the presence of the magnetic field. We present here only the results obtained at low temperature in the SA_1 phase after alignment.

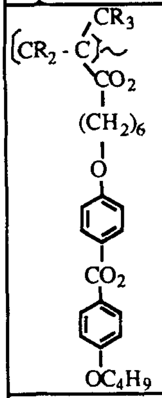
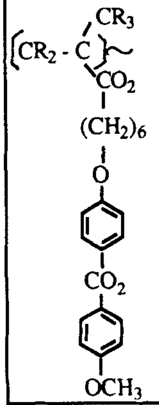
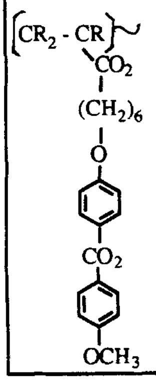
Chemical formulas of the repetitive unit	Names	Polymerization Degrees and Polydipersity
	PMA(H)-OC4H9 when R=H PMA(D)-OC4H9 when R=D	DP_H= 257 000, I_H=2.2 DP_D= 355 000, I_D=4.4
	PMA(H)-OCH3 when R=H PMA(D)-OCH3 when R=D	DP_H= 354 000, I_H=2.7 DP_D= 289 000, I_D=2.7
	PA(H)-OCH3 when R=H PA(D)-OCH3 when R=D	DP_H= 27 000, I_H=2.6 DP_D= 41 000, I_D=2.

TABLE 1: List of the chemical formulas and characteristics of each polymer (determined by Gel Permeation Chromatography/ Light Scattering on line in collaboration with C. Strazielle at the I.C.S. Strasbourg).

The study versus temperature has been carried out in the case of PMA(R)-OC4H9 which was investigated very carrefully using a three-axis spectrometer. This work is described in the reference 6.

The two other polymers (PMA(R)-OCH3, PA(R)-OCH3) were studied at low temperature after alignment, using the two-dimensional neutron multidetector PAXY of the Lab. Léon Brillouin. The disc-like cell, placed on the trajectory of the incident neutrons, was rotated around its vertical axis in order to find the position of Bragg reflection of the smectic layers. The smectic reflection intensities were evaluated by integrating the area corresponding to each reflection and substracting the background noise equivalent to this surface. The table 2 gives the different intensities reported to the respective background noise and corrected of the Lorentz factor versus angle.

Polymer / reflections	001	002	003
PMA(H)-OC4H9	7.6	0.4	0.12
PMA(D)-OC4H9	0.6	negligible	1.4
PMA(D)-OCH3	4.3	negligible	negligible
mixture H/D PMA(R)-OCH3	negligible	negligible	negligible
PA(H)-OCH3	4.0	negligible	negligible
mixture H/D PA(R)-OCH3	0.2	7.5	negligible

TABLE 2.: Comparative table of the different smectic reflection intensities obtained by neutron diffraction given in percentage relative to the integrated background noise.

It is also interesting to compare the results of this table with X-Ray diffraction data[3,5]. Since hydrogen and deuterium are similar from an electronic point of view, the diffraction patterns of hydrogenated and deuterated polymers are effectively identical by X-Ray scattering. This underlines that the labelling doesn't affect the microscopic organization in the smectic layers (at the scale of X-Ray).

As for the differences presented by the three types of polymers, the X-Ray measurements show three smectic reflections (001, 002, 003) of decreasing intensity in the case of PMA-OC4H9, only one smectic reflection in the case of PMA-OCH3 and two smectic reflections (001 and 002) in the case of PA-OCH3. For this last polymer, it is important to notice that by X-Ray, the intensity of the 002 reflection is weaker than the 001 and that the inverse establishment can be made on the neutron pattern of the isotopic mixture of PA(H)-OCH3/PA(D)-OCH3.

PRINCIPE AND DETERMINATION OF THE BACKBONE DENSITY PROFILES

The first step of this method consists to determine the coherent scattering profile of each polymer labelled and unlabelled using Fourier inverse transform properties. This method is explained in details in references such as reference 3 for X-Ray or references 4 or 7 for neutron studies.

The oriented smectic phase is, following the axis z of the director, a periodic modulated medium. It can be then described by a Fourier series. This Fourier series gives in the reciprocal space, a series of i delta peaks which are actually the different smectic reflections. The intensities of these smectic reflections are proportional to the square of the amplitude of each term F_i of the Fourier series. As a result, the measurement of the different integrated intensities of each smectic reflection F_i^2, provides the absolute value of each term of the Fourier series. To find the sign before each term, all the combinations of sign are tried and compared to a theoretical profile of coherent scattering length of each polymer. Only one combination is physically valid and can be written:

- for the unlabelled polymer: $\Psi_H(z)= \Psi_{0H} + \sum_i (F_{iH}^{bk} + F_{iH}^{sc}) \cos (\frac{2\pi}{d}.i.z)$

-for the polymer labelled on the backbone: $\Psi_D(z)= \Psi_{0D} + \sum_i (F_{iD}^{bk} + F_{iH}^{sc}) \cos (\frac{2\pi}{d}.i.z)$

- for the mixture of labelled and unlabelled polymers:

$$\Psi_{HD}(z)= 1/2\ (\Psi_{0H} + \Psi_{0D}) + \sum_i (1/2(F_{iH}^{bk} + F_{iD}^{bk}) + F_{iH}^{sc}) \cos (\frac{2\pi}{d}.i.z)$$

where $\Psi_R(z)$ represents the density of coherent scattering length associated to each species (R=H or D), F_{iR}^{bk} is the partial structure factor associated to the backbone, F_{iR}^{sc} the partial structure factor of the side-chain, and d the layer thickness.

Using the numerical values of the table 2, the different functions $\Psi_H(z)$, $\Psi_D(z)$, $\Psi_{H/D}(z)$ are determined and are compared to the associated theoretical models of profile of coherent scattering density. These theoretical profiles are built on the assumption that each element of the repetitive unit of the liquid-crystal polymer can be represented by a square-function. The length associated to each element is the supposed length of the element in the smectic layer and the calculated hight is proportional to the density of coherent scattering length of this element. These theoretical profiles are symmetrical since it is supposed that there is no preferential orientation of the mesogens in the layers (up or down).

The second step of this method is the substraction of the experimental profile of labelled polymer from the profile of the unlabelled polymer in order to keep only the term associated to the backbone alone. Indeed, the functions $\Psi_D(z) - \Psi_H(z)$ and $\Psi_{HD}(z) - \Psi_H(z)$ correspond exclusively to the backbone structure factor:

$$\Psi_D(z) - \Psi_H(z) = (\Psi_{0D} - \Psi_{0H}) + \sum_i (F^{bk}_{iD} - F^{bk}_{iH}) \cos (\frac{2\pi}{d}.i.z)$$

$$\Psi_{HD}(z) - \Psi_H(z) = 1/2(\Psi_D(z) - \Psi_H(z))$$

Application to the three different polymers:

Since the structure factors of polymers of different chemical formulas cannot be compared, only the variation relative to the medium of the backbone density is given for the three considered polymers:

$$\Delta\Psi(z) = (\Psi_D(z) - \Psi_H(z)) - (\Psi_{0D} - \Psi_{0H}) = \sum_i (F^{bk}_{iD} - F^{bk}_{iH}) \cos (\frac{2\pi}{d}.i.z)$$

This procedure allows a qualitative comparison of the different profiles presented by the three polymers.

First polymer: PMA(R)-OC4H9

Fig.1 displays the experimental profiles (Fig.1b) of the unlabelled PMA(H)-OC4H9 and of the labelled polymer PMA(D)-OC4H9 which fits the best with the respective theoretical model (Fig.1.a). The study[7] versus temperature was also very usefull to determine the right signs of the functions $\Psi_{H,D}(z)$, since at high temperature this function was simply a sin wave. The substraction of the two preceding profiles gives the figure 1.c. We check that Fig.1c corresponds to the best solution since all other combinations of sign implies a decrease of the backbone density at the extremities of the mesogen layer.

Following Fig.1c, the backbone of PMA-OC4H9 is largely excluded from the mesogen zones. Two shoulders on each side of the region of deep exclusion, should correspond to intermediate regions where the backbone is less affected by the exclusion and could be associated to the softer regions which are spacer and extremities of mesogen.

Second polymer: PMA(R)-OCH3:

PMA(R)-OCH3 presents by X-Ray as well by neutron diffraction, only one smectic reflection which is of weak intensity and can be seen on the two-dimensional multidetector only with the labelled polymer PMA(D)-OCH3. On figure 2.b, the experimental profiles

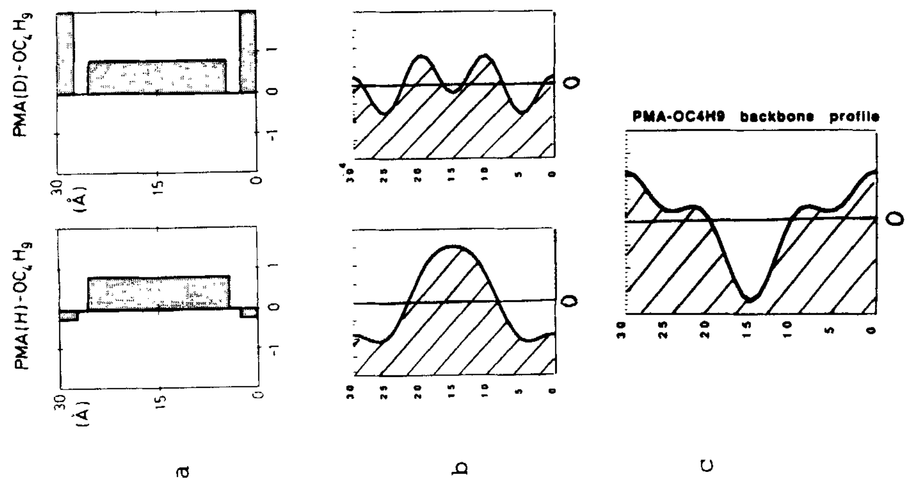


FIGURE 1

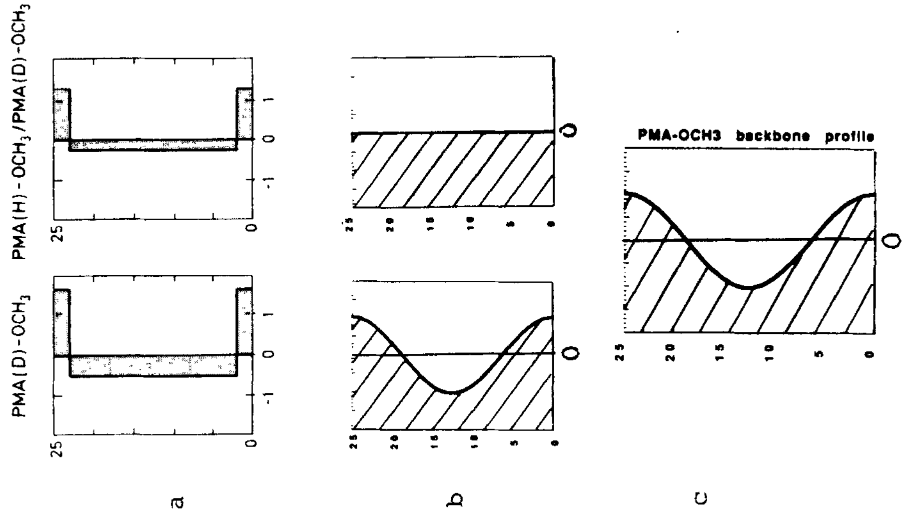


FIGURE 2

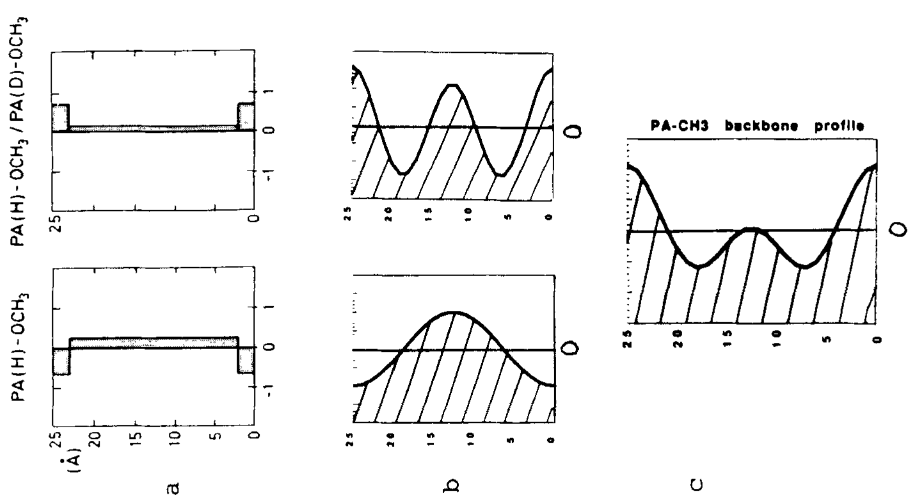


FIGURE 3

Variation relative to the medium of the density of coherent scattering length of coherent scattering length of the deuterated polymer PMA(D)-OCH3 and of the mixture, are compared to the theoretical calculations (Fig.2.a). The fact that no smectic reflection was detected in the case of the mixture, can be partly explained by the loss of contrast due to the mixture (Fig.2 a), but also and certainly mainly due to a very low smectic order parameter (already discussed in the reference 8). By substraction, the profile obtained is a simple sin function $\Delta\Psi(z) \approx \cos(\frac{2\pi}{25}.z)$ which is the signature of a very soft modulated backbone segregation (Fig.2.c).

Third polymer: PA(R)-OCH3:

The theoretical models calculated for the unlabelled polyacrylate PA(H)-OCH3 and for the mixture of labelled and unlabelled polymers, are displayed on Fig.3.a, whereas the experimental results which best fits with these models are shown on Fig.3.b. It is remarkable to notice that the intensity of the 002 smectic reflection is much stronger than the 001, in the case of the mixture PA(H)-OCH3/PA(D)-OCH3 (Fig.4). This surprising observation gives a result which doesn't fit anymore with a simple theoretical model of backbone confined between mesogen layers since it leads to the conclusion that there is a segregation of the polymer backbone not only between the mesogens, but also in a zone right in the middle of the mesogen zone (Fig.3.c). This astonishing result can be obtained only in the case where the second order is of much higher intensity than the first one which is apparently extremely rare.

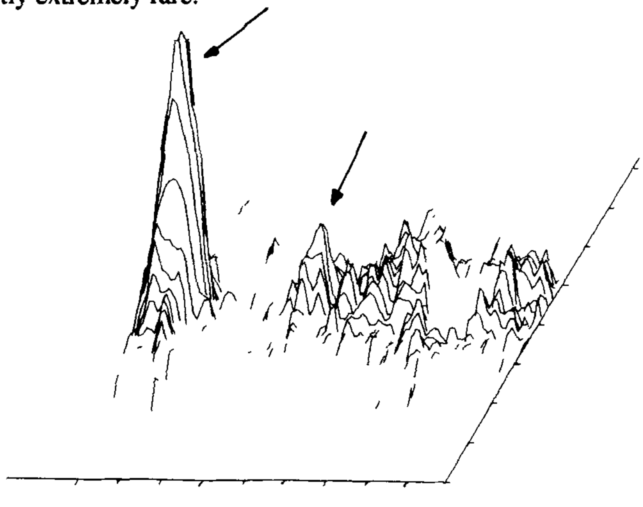


FIGURE 4: Neutron diffraction pattern of the mixture PA(H)-OCH3/PA(D)-OCH3 oriented in the smectic phase. The director axis is horizontal. The two arrows indicate the 001 and 002 smectic reflections.

DISCUSSION

The three polymers choosen for this study have close chemical formulas. PMA(R)-OC4H9 differs from PMA(R)-OCH3 by the nature of the extremity, whereas PMA(R)-OCH3 differs from PA(R)-OCH3 by the chemical nature of the backbone. By examining the backbone density profiles of these three polymers, a common feature is revealed: the maximum of backbone density at each side of the layer confirms a segregation of the backbones in sublayers which are mostly squeezed between adjacent layers. However, although these polymers are few different, the weak modifications are sufficient to induce large differences in the profile of backbone distribution (Fig.1c, 2c, 3c). PMA(R)-OC4H9 presents a deep and clear separation between the hard core zones and the backbone zones whereas the density of backbones of PMA(R)-OCH3 is only relatively weaker in the middle of the mesogen layer. Since the only difference between these two polymers is the length of the mesogen extremity, we have shown here how the length of the alkyl extremity can reinforce the segregation effect of the backbones. The effect of the backbone nature was underlined by the comparison of PMA(R)-OCH3 and PA(R)-OCH3. The profiles are strongly different and the absence of the methyl group of the polyacrylate chain corresponds to a decrease of the rigidity of the chain. The polyacrylate chain is then more sensitive to the mesogen arrangement and can explain why PA(R)-OCH3 is more confined than the polymethacrylate counter part. Moreover PA(R)-OCH3 shows in addition an increase of the backbone density right in the middle of the mesogen layer. This surprising result could be understood using symmetry arguments since the hard core and the spacer have the same length. However, this assumption has to be confirmed using a sample containing polymers deuterated on the backbone instead of a mixture or by using another labelling (for example on the mesogen extremity). Such studies are under investigation.

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