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Direct observation of the main-chain conformation of a combined liquid-crystal polymer

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The conformation of the main-chain (backbone) of a combined main-chain/side-chain liquid crystalline polymer has been qualitatively determined by small angle neutron scattering in the oriented nematic, the smectic A and the smectic C phases. The polymer backbone presents only a weak anisotropy, of prolate shape, in the nematic and the smectic C phases. A stronger reorientation of the backbones in the direction of the applied magnetic field is measured for the S_A phase. However, this anisotropy remains small compared to the stretching of a main-chain liquid crystal polymer and the smectic structure results apparently from side-chain ordering. On the other hand, hydrodynamic measurements show that the combined polymer, in solvent, is as flexible as a polystyrene chain. This result is compatible with an explanation for the weak observed anisotropy.

1. Introduction

Side-chain liquid crystal (LC) polymers and main-chain LC polymers have been intensively studied for more than 10 years. About the conformation of these polymers in the bulk, only a few studies have been realized, probably because these measurements require access to the heavy equipment of Neutron Facilities.

The conformation of the backbone of side-chain polymers has now been established in each liquid crystal phase [1]. When the polymer presents successively the nematic phase and the smectic phase, the polymer backbone adopts in the first phase a slightly oblate shape, which becomes more pronounced when passing into the smectic phase. That means that the backbone is not oriented in the direction of the mesogenic side-chains, but remains more or less perpendicular to the director. For cases where just a nematic phase exists, it has been found [2] that the backbone tends to be aligned in the same direction as the liquid crystal moieties. However in the latter case, the alignment is weak compared with that obtained in the case of main-chain LC polymers.

Recently, neutron measurements [3] have demonstrated that main-chain LC polymers are mostly completely elongated in the direction of the nematic field. The orientational order parameter associated with these cylinder-like polymers reaches values of $P_2 \approx 0{\cdot}97$ (P_2 has the same meaning as the nematic order parameter S). When the main-chain LC polymers are long, they bend themselves, forming local hairpins in order to keep the liquid crystal moieties in the direction of the nematic field.

For combined LC polymers, the mesogenic groups are both in the main-chain and in the side-chain. The question arises as to whether they behave more like side-chain or main-chain LC polymers (see figure 1). Also, does the smectic layer thickness correspond in most cases to the length of the side-chain part [4] and is the drastic change in mechanical properties related to a change of backbone conformation [5]?

We use here the technique of small angle neutron scattering (SANS) on mixtures in the bulk of a fully hydrogenous combined LC polymer with a combined LC polymer deuterated in the main-chain. This method allows

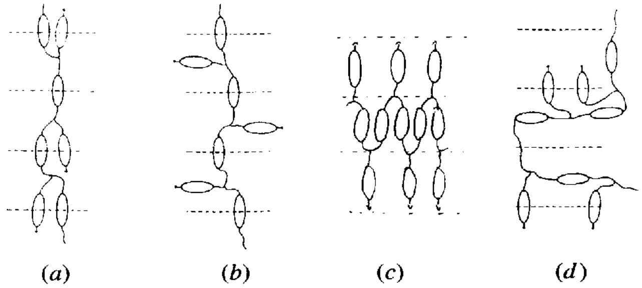
(*a*) (*b*) (*c*) (*d*)

Figure 1. Schematic representation of combined liquid crystal polymers. Four main-chain versus side-chain orientations are proposed here. The dotted lines represent the smectic layers.

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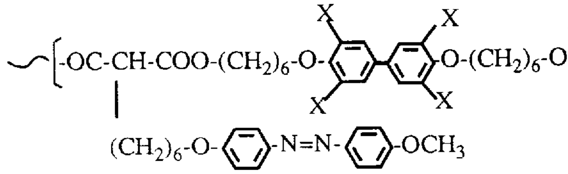
the determination of the averaged conformation of one backbone in the melt in each liquid crystal phase.

2. Experimental

The combined LC polymer chosen for this study is the following polyester, widely studied by Reck [4(*b*)].



where X is either H or D.

This side-chain/main-chain polyester presents the following succession of phases on decreasing the temperature:

$$\text{I } 153°\text{C N } 136°\text{C S}_\text{A} \text{ } 130°\text{C S}_\text{C} \text{ } 109°\text{C}$$

These temperatures are available for both polymer-hydrogenous or deuterated.

This polymer is a rare combined liquid crystal polymer which possesses a nematic phase, in addition to the smectic phases. This former phase, of low viscosity, is very important since it enables the monodomain orientation with a magnetic field.

The SANS measurements are carried out with disc-like cell samples of 15 mm diameter and 1 mm thickness. These samples are placed in an oven between the poles of a magnet of 1·4 T. They are heated until the nematic phase is reached and the temperature is then slowly decreased from this phase to the S_C phase from the magnetic field. The spectrometer PAXY at LLB (Orphée Reactor, Saclay) is adjusted to a wavelength of $\lambda = 10$ Å and a distance between sample and multidetector of 3·1 m. The range of the corresponding scattering vector ($Q = 4\pi/\lambda \sin(\theta/2)$ where θ is the scattering angle) is then $7{\cdot}5 \times 10^{-3} < Q < 0{\cdot}065$ Å^{-1}.

In the Guinier domain where $QR_g \leq 1$, the intensity $S(\mathbf{Q})$ scattered by a sample containing half of each of the hydrogenous and deuterated polymers can be written [6]

$$S^{-1}(\mathbf{Q}) = S^{-1}(0)(1 + Q_\parallel^2 R_\parallel^2 + Q_\perp^2 R_\perp^2),$$

where $R_\parallel$ and $R_\perp$ are the partial components of the radius of gyration ($R_g^2 = R_\parallel^2 + 2R_\perp^2$), respectively, in the directions parallel and perpendicular to the applied magnetic field.

Since the polymer is only partly deuterated (4 sites) and the length of the chain is rather small ($M_W \approx 22\,000$), the resulting intensity at small angles is weak and the signal $S(Q)$ is then difficult to extract. The background level was evaluated by extrapolating the intensity at large q-values at each temperature and was then extracted from the measured intensity. This procedure avoids the problem of subtraction of the background of a reference sample containing an assumed identical number of scatterers. The values of $R_\parallel$ and $R_\perp$ are then determined by a two-dimensional fit of the scattering plane.

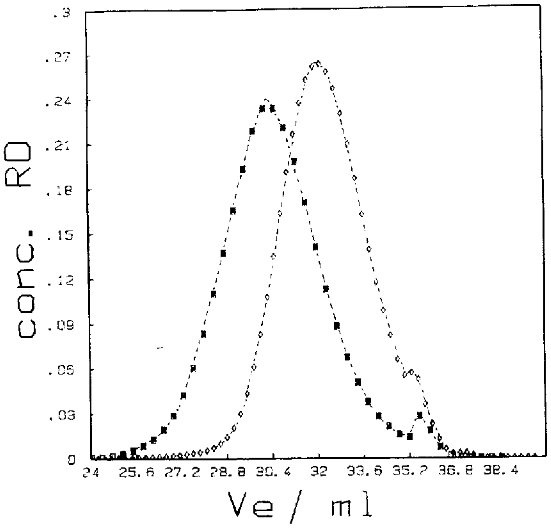


Figure 2. Chromatogram of concentration measured as a function of elution volume (by SEC-LS on line) for the two combined polymers: (■) before the neutron experiment, (PE initial, $V_e = 30{\cdot}3$) and (□) after the neutron experiment (PE final, $V_e = 32{\cdot}1$).

Diffraction measurements were carried out simultaneously with the SANS experiments, simply by reducing the wavelength to 5·3 Å and the distance (sample–multidetector) to 1·2 m. The scattering vector range corresponding to these conditions ($0{\cdot}04 < Q < 0{\cdot}31$ Å^{-1}) allows the observation of the first Bragg order in the smectic phase. In this way, we can check the nature of the phase (N, S_A or S_C).

The molecular weight was determined by size exclusion chromatography—light scattering (SEC-LC) on line on the mixture (1 : 1 by weight) of hydrogenous and deuterated combined LC polymers before and after the neutron experiments. The weight average molecular weight, M_W, decreases from the initial state to the final state (after thermal treatment during the neutron experiment) to reach finally the value of 22 000 with a polydispersity index of 2·4.

No change in polydispersity, or in the shape of the mass distribution is observed as it is shown in figure 2. One observes only a shift of the chromatogram to the range of higher elution volumes. The chains are simply cut.

More surprising is the similarity between the hydrodynamic behaviour of the combined polymer and the polystyrene (PS) chains. The viscosity law for the PS (determined using a THF solution on the initial sample in the 10^4–10^5 molecular weight range) [7] is η (ml/g) $= 1{\cdot}4 \times 10^{-2} M^{0{\cdot}70}$. For the combined polymer, one obtains a rather similar result: η (ml/g) $=$

$2{\cdot}2 \times 10^{-2} M^{0{\cdot}69}$. This astonishing result reveals the high flexibility in solution of the combined polymer.

3. Results and interpretations

SANS measurements give the polymer backbone anisotropy in each liquid crystal phase (N, S_A, S_C). The extrapolated value of the intensity at the origin $S(0)$ remains constant with temperature indicating that the modified molecular weight has been reached as soon as the experiment starts. From the temperature study, the following features can be raised:

(i) In the nematic phase, the signal for small angle neutron scattering detected in the plane of the multidetector presents a slight anisotropy. This anisotropy is an elongation of the central scattering in the direction perpendicular to the magnetic field. This corresponds, in real space, to a prolate conformation of the main-chain in the nematic phase. The radii of gyration correspond to $R_\parallel = 48 \pm 5$ Å and $R_\perp = 32 \pm 5$ Å in the nematic temperature range from 153°C down to 137°C. The anisotropy ratio $\rho = R_\parallel/R_\perp$ can be estimated as equal to $1{\cdot}5 \pm 0{\cdot}2$. The backbone is therefore weakly oriented in the direction of the magnetic field, which is in deep contrast to nematic main-chain LC polymers which are very strongly stretched, with $\rho = R_\parallel/R_\perp = 7$–$8$ [3].

(ii) For the smectic phase, the multidetector show a strongly elongated central scattering (see figure 3). Such a shape in reciprocal space indicates that the main-chains are more strongly oriented in the direction of the magnetic field. In the direction parallel to the magnetic field, $R_\parallel$ is estimated to be 106 ± 10 Å, whereas in the opposite direction, $R_\perp = 30 \pm 5$ Å. By decreasing the wavelength and the distance, we measured the smectic layer thickness $d = 21{\cdot}6 \pm 0{\cdot}1$ Å, which corresponds to the length of the mesogenic side-chain in its most extended form and proves that the smectic phase is of the S_{A_1} type. An estimation of the mosaic spread obtained via a rocking curve gives 6° (HWHM).

(iii) By following the layer thickness as a function of temperature (see figure 4), we can monitor the appearance of the smectic C phase. The initial value of 21·6 Å obtained in the smectic A phase decreases and stabilizes at 20·75 Å from 108°C. This difference in layer thickness corresponds to a tilting of 16° of the mesogenic groups, which is in good agreement with X-ray data [4 (*a*)]. Simultaneously, there is a transverse broadening of the 001 Bragg reflection on passing into the smectic C phase, without any splitting of the peak from the S_A phase (see figure 5). Since there is no additional intensity in the regions corresponding to the tilt angle, we can consider that the smectic C layers are, on average, perpendicular to the magnetic field and as a result, that the liquid crystal moieties are tilted in the layers. This assumption is checked by

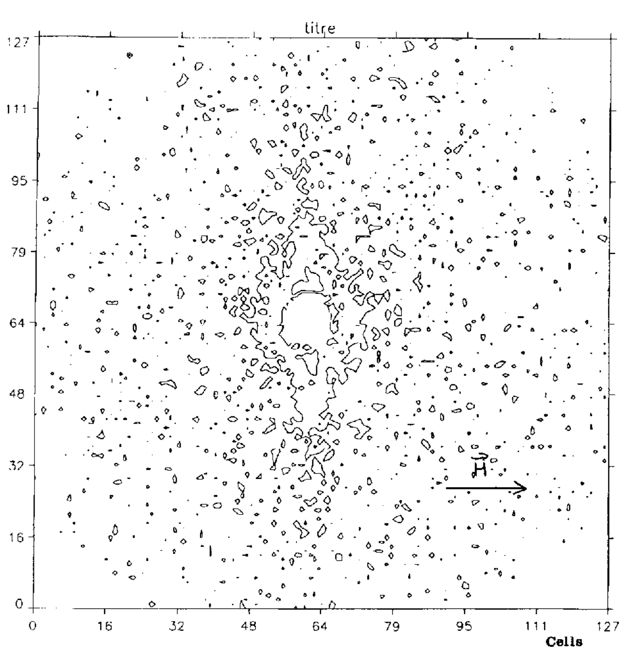


Figure 3. Transverse section of the intensity scattered by the main-chain part of the combined LC polymers in the smectic A phase. The experimental conditions were $\lambda = 10$ Å, $d = 3{\cdot}1$ m. The continuous lines represent the lines of iso-intensity. The white area in the centre is due to the beam trap. The closer the lines of equal intensity are to the centre, the higher is the intensity. The applied magnetic field is horizontal.

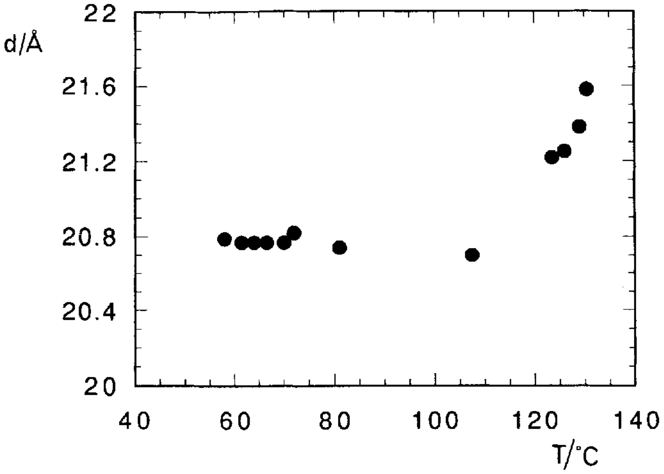


Figure 4. Variation of the layer thickness of the combined LC polymers in the smectic A and the smectic C phases with temperature.

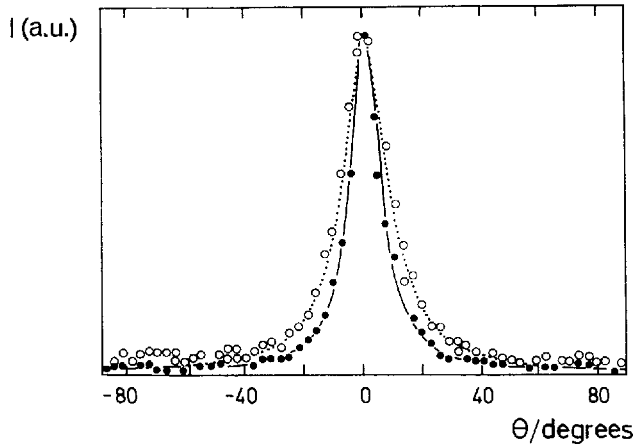


Figure 5. Variation of the intensity of the 001 Bragg peak at constant scattering vector versus Θ, the gap in degrees from the meridian. The dashed line corresponds to the profile in the smectic C phase, and the continuous line to the profile of the 001 reflection in the smectic A phase.

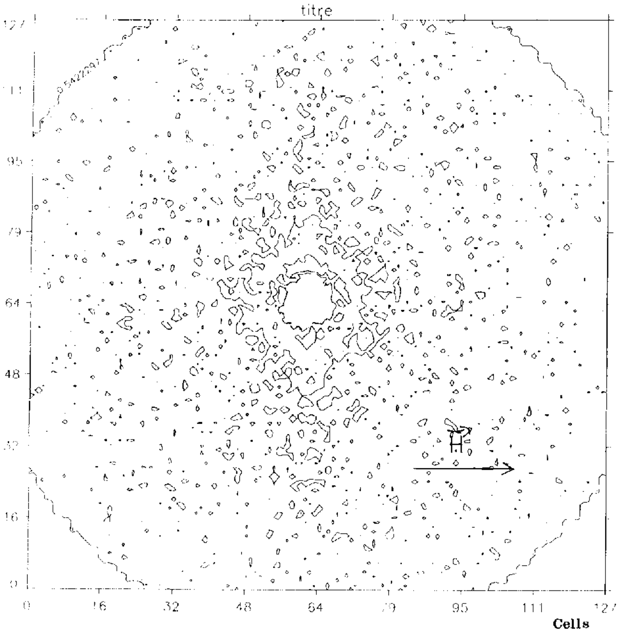


Figure 6. Same as for figure 3, but this time the scattering is obtained in the S_C phase.

removing the magnetic field just before the S_A–S_C transition. An identical profile is indeed found for the 001 Bragg reflection with and without the magnetic field.

The scattering at small angles detected in the plane of the multidetector for the S_C phase shows a slight anisotropy (see figure 6) corresponding to the following main-chain dimensions: $R_{\perp} = 60 \pm 5$ Å and $R_{\parallel} = 27 \pm 5$ Å. The anisotropy is of the same type but of lower amplitude than that obtained in the smectic A phase. The polymer backbone is no longer oriented strongly perpendicular to the smectic layers, but is also spread over other directions of which the principal direction is mostly parallel to the magnetic field. The decrease in $R_{\parallel}$ compared to the value for the smectic A phase is too great to be interpreted only by a tilting of the backbones equivalent to that of the mesogenic groups ($\Theta = 16°$). (Indeed, the application of the calculation explained in [8(*a*)] to the reorientation of rod-like backbones shows that the parallel dimension, $R_{\parallel}$, is practically unaffected by such a tilt angle on passing from the S_{A1} to the S_C phase.) It can be concluded therefore that the backbones are more randomly oriented in the S_C phase than in the S_{A1} phase.

4. Discussion and conclusions

From the SANS study, we have demonstrated that the backbone of the combined LC polymers is always, more or less and depending on the phase, oriented in the direction of the magnetic field (prolate shape). However, the low rate of anisotropy in the nematic and the smectic C phases suggests the following comments:

(i) In the nematic phase, the polymer backbones have a slightly prolate shape compared to main-chain liquid crystal polymers, and corresponding to 50 per cent of deformation. This means that the main-chains are more or less randomly distributed along an axis of reference given by the magnitude field. The spread can be explained by the flexibility of the combined polymer as revealed by on line GPC-light scattering. In these conditions, the nematic order is mostly established by the side-chain mesogenic groups, and corresponds rather to figure 1 (*d*).

(ii) The smectic layer thickness ($d = 22$ Å) confirms that the lateral mesogenic groups impose the smectic order, as suggested for the nematic phase by the wide distribution of backbone orientation. However, in the smectic A phase, the backbones are better aligned in the direction of the magnetic field. In this phase, the behaviour of the combined LC polymers has several similarities to that of main-chain polymers [3]. However, it is far from clear that the main-chain mesogenic groups associate to form the smectic layers (see figure 1 (*a*)); and [4(*a*)], since in this case, we should find $R_{\perp} \gg R_{\parallel}$.

(iii) Finally, in the S_C phase, the polymer backbone loses partly its orientation perpendicular to the smectic layers. Because of the symmetry of the S_C phase, the situation is more complex. Nevertheless, the small anisotropy of the polymer backbones and their high flexibility allows one to say that there are more backbones randomly distributed than in the smectic A phase, as previously observed in the higher temperature nematic phase. From this viewpoint, it seems that the structure of the smectic C phase is also built upon the arrangement of the side-chain liquid crystal moieties.

Finally, in order to compare this liquid crystal polymer with its homologues having different lengths of main-chain spacer, we make the following remarks. Following Diele *et al.* [4 (*a*)], it clearly appears that the smectic layer thickness is equivalent to the length of the lateral mesogenic group when the main-chain spacer is long enough—$(CH_2)_6$. This can be understood in terms of a loss of the mesomorphic properties of the main-chain mesogen system. In contrast, when the main-chain spacer is shorter, the resulting smectic layer thickness is not a commensurable value of either of the mesogenic units. It could be of interest to know if the backbone adopts other conformations in such a situation.

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