



Experiment title: A new class of liquid crystal polymers based on bent-core megonic units: an X-ray diffraction study.

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SC-3348

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Report:

Summary of the experiment

The experiment consisted in a systematic SAXS/WAXS investigation of a novel main-chain thermotropic liquid crystal (LC) polymer based on a bent-core (*banana*-shaped) monomeric unit. Aligned monodomain samples were obtained by means of a static magnetic field \mathbf{B} ($B = 1$ T) and investigated at different temperatures across the nematic range. In this way, for the first time we got evidence of a (skewed) cybotactic nematic phase in a bent-core LC polymer [1]. This finding makes our material a promising candidate for the search of a ferroelectric nematic phase.

Motivation and description of the experiment

In the recent past, we used X-ray diffraction and other complementary techniques to study the structural and electro-optical properties of an asymmetric bent-core LC based on an oxadiazole moiety, namely 3,5-bis-{4-[4-(n-nonyloxy)benzoyloxy]phenyl}-1,2,4-oxadiazole [2]. Surprisingly, we found the nematic phase of this compound to exhibit a ferroelectric response to low frequency electric fields. This result was extremely interesting because the existence of a ferroelectric nematic phase, although theoretically anticipated [3], has never been experimentally demonstrated in thermotropic LCs. In our compound this property originates from the cooperative alignment of nanometer-sized polar and biaxial *cybotactic groups*, i.e. clusters of molecules characterized by short-range smectic-like positional order [4,5]. Experimentally, the existence of cybotactic order in aligned LC samples is evidenced by a characteristic *four-spot pattern* in small-angle XRD measurements; on the contrary, the SAXS pattern generated by (aligned) conventional nematics consists in two crescents placed along the alignment direction.

Starting from these results, in this experiment we investigated the structural properties of the polymeric counterpart of the above-mentioned compound. The underlying idea is that a polymerized sequence of

banana units would maximize the dipole correlations, thus leading to a larger ferroelectric response. Moreover, the mechanical constraints imposed by a polymeric network could result in a glassy phase, useful to freeze ferroelectric (and possibly biaxial) order at lower temperatures (compared to those found in the low molar weight counterpart), with obvious benefits for applications.

The structure of the investigated thermotropic LC polymer is shown in Fig. 1: it consists in a main-chain sequence of asymmetric oxadiazole-based bent mesogenic units, regularly spaced by long ($n = 9$) alkoxy chains. The compound was polymerized starting from sufficiently large concentration of monomer, in order to obtain a significant molar mass (in the range between 20000 and 40000). The material was placed in glass capillaries (1 mm diameter), mounted in a special temperature controlled (± 0.1 °C) hot stage. This sample holder, made by the ESRF staff and already used for several past experiments at ID02 and BM16 beamlines [2,4,5], allows insertion of a static magnetic field \mathbf{B} ($B = 1$ T) perpendicular to the incident X-ray beam. The magnetic field is necessary to obtain monodomain samples with the molecular director \mathbf{n} aligned along the field (in fact, our compounds exhibits a positive diamagnetic anisotropy). Both SAXS and WAXS measurements were performed. The former were carried out using a Pilatus 1M detector (981 x 1043 pixels) placed at $l = 1286$ mm from the sample (a vacuum chamber was placed between sample and detector to reduce air scattering); for the latter we used a FReLoN 2000 CCD camera (2048x2048 pixels) and a sample-to-detector distance $l = 200$ mm; in both cases the X-ray radiation wavelength was $\lambda = 1.033$ Å (12 keV). Each SAXS measurement was repeated with the detector slightly displaced, to get rid of the detector blind areas by two image recombination. Measurements were carried out at different temperatures, during repeated heating and cooling cycles. In fact, it is well known that the thermodynamic properties of polymeric compounds can strongly depend on the thermal history of the sample.

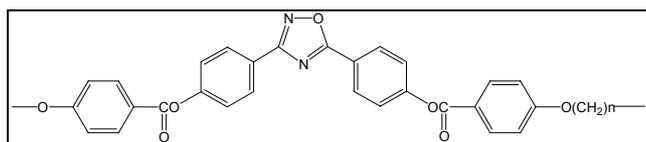


Fig. 1

Fig. 1 The chemical structure of the main-chain polymer **I**.

Fig. 2 SAXS patterns of **I** at different temperatures under an aligning (horizontal) \mathbf{B} -field: 180 °C (a); 200 °C (b); 210 °C (c); 220 °C (d); 230 °C (e); 240 °C (f); 250 °C (g); 260 °C (h).

Fig. 3 WAXS patterns of **I** at different temperatures under an aligning (horizontal) \mathbf{B} -field: 230 °C (a); 190 °C (b); 150 °C (c); 110 °C (d); 30 °C (e).

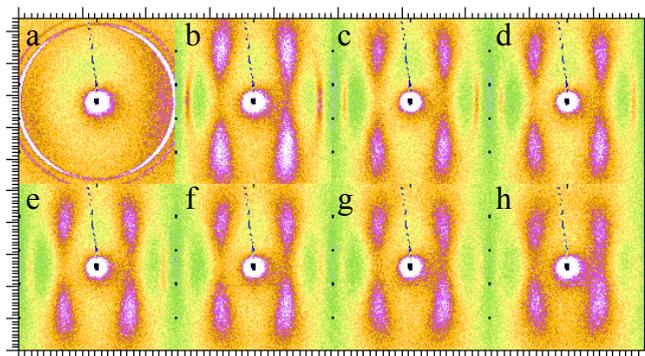


Fig. 2

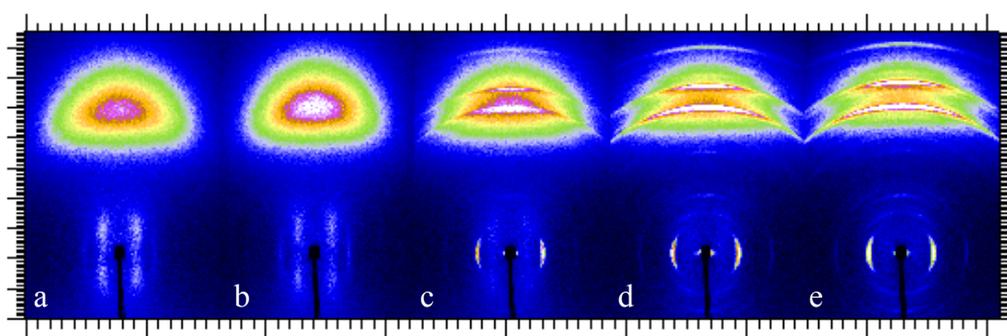


Fig. 3

Results

We first performed SAXS measurements. When heating the sample under magnetic field, we could observe a clear transition from the crystalline (Fig. 2a) to the aligned nematic phase (Fig. 2b) at about 190 °C. The nematic phase was characterized by a strong four-spot pattern, a well-known signature of cybotactic order in bent-core nematics [2,4,5]. The maxima of the four spots correspond to a q -vector $q = 0.314$ Å⁻¹, i.e. a d -spacing $d = 20.0$ Å; the angle β made by the four spots with the aligning directions is $\sim 58.5^\circ$. Within the cybotactic model the d -spacing represents the periodicity of the smectic layers formed by the polymerized mesogenic units, while β indicates the tilt angle of the mesogenes' long axis (aligned by \mathbf{B}) and the normal to the smectic layers. As a consequence, dividing the d by the cosine of β provides a estimate of the length L of

the monomer units: using the values above, we obtain $L = 38.3 \text{ \AA}$, in good agreement with molecular simulation predictions [4].

The cybotactic nematic pattern persisted up to $260 \text{ }^\circ\text{C}$ (Fig. 2c-h), showing only a slight evolution with temperature; we could not reach the clearing point, where such changes are expected to be more evident [5], because of the thermal degradation of the samples at higher temperatures.

The SAXS pattern of the polymer also showed some significant difference with respect to its low molar weight counterpart. In particular, besides the four spots, two strong crescents orthogonal to the meridian are clearly visible along the alignment direction. These crescents, which are stronger at lower temperatures and almost fade away at higher temperatures, correspond to a q -vector $q = 0.335 \text{ \AA}^{-1}$, i.e. a d -spacing $d = 18.8 \text{ \AA}$, a value about half the calculated monomer length. They were not observed in the low molecular weight equivalent of our polymer; however similar features have been found in other bent-core liquid crystals, although much weaker [4], as well as in other polymeric compounds [6]. We are still working on the exact interpretation of these patterns (e.g. they could represent the second order of a diffraction signal whose first order is hidden by the partially superimposed four-spot pattern). However, a generally accepted idea is that they originate from the tendency of the molecules to align in chains parallel to \mathbf{n} , a tendency clearly much favoured in main-chain polymers.

Finally we performed WAXS measurements. Figure 3 shows a typical sequence acquired while cooling the sample from the nematic phase. In Fig. 3a-b the sample is still in the cybotactic nematic phase: the four-spot pattern and the pair of crescents discussed above are clearly visible in the small q region, while two large lobes are symmetrically placed along the equatorial direction in the large q region [note that only the upper lobe is visible in Fig.3a-e because of the off-centered detector position]. The d -spacing associated to these lobes ($\sim 4.5 \text{ \AA}$) reflects the lateral dimension of the polymer chains. When cooling the sample, the first signs of crystallization were observed at $\sim 150 \text{ }^\circ\text{C}$ (Fig. 3c), $40 \text{ }^\circ\text{C}$ below the transition temperature measured in the heating cycle. However the crystallization temperature was strongly dependent on the thermal history of the sample and in a few cases we could observe no sign of crystallization down to room temperature; even when crystallization occurred, we always observed the simultaneous persistence of the nematic signal, as shown in Fig. 3c-e.

In other words *the polymeric compound shows a cybotactic nematic phase* which is thermodynamically stable at high temperature and apparently tends to become metastable at temperatures approaching the room temperature. This encouraging result has been recently corroborated by first repolarization current measurements, showing an unequivocal ferroelectric response to low frequency electric fields. Further electrical and electro-optical investigations are ongoing.

References

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