

SYNCHROTRON STUDY OF THE PHASE BEHAVIOUR IN  
LIQUID CRYSTALLINE POLYMERS

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**Introduction**

The phase behaviour of liquid crystal polymers, LCPs, is usually rather complicated, and many of these materials exhibit polymorphism and/or polyomesomorphism. A combination of DSC and X-ray diffraction techniques is a very useful tool for the study of the phase behaviour. Moreover, taking advantage of the extremely high intensity of synchrotron radiation, very short acquisition times can be used, so that the corresponding experiments can be performed under real time conditions, and temperature programs similar to those employed in DSC can be imposed to the samples.

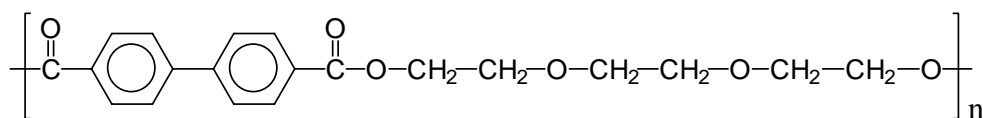
Three scattering regions of interest are found in LCPs, characterized by different ranges of the scattering vector,  $s = 1/d = 2 \sin\theta / \lambda$

A) The region at higher angles, with a typical  $s$ -range between 1 and 4  $\text{nm}^{-1}$ , designated as wide-angle X-ray scattering, WAXS, region, where the scattering from the amorphous phase, as well as from the smectic and crystalline domains, can be observed. The crystal phase and the quasi-crystalline smectic crystals exhibit relatively narrow peaks in the WAXS patterns, overlapped to the amorphous halo. The diffuse scattering in this interval arises either from the fully amorphous regions or/and to the diffraction from low-ordered smectic domains in the direction perpendicular to the molecular axes.

B) A middle-angle X-ray scattering (MAXS) region, covering, approximately, the  $s$  range between 0.2 and 1  $\text{nm}^{-1}$ . The mesogenic layer spacing peaks are typically observed in this region.

C) The small-angle X-ray scattering (SAXS) region, with  $s$  values below 0.2  $\text{nm}^{-1}$ . The crystalline or quasi-crystalline long periods, as well as different parameters derived from the correlation function are obtained from this region.

In previous works (1-5) we have analyzed several main-chain thermotropic liquid crystalline polymers, finding that the biphenyl mesogenic unit leads to the obtainment of different kinds of smectic mesophases, the nature of the spacer being of capital importance for the phase behaviour. For those polymers incorporating all-methylene spacers, a rapid transformation of the LC phase into a three-dimensional crystal structure has been found (6). In contrast, when oxygen atoms are included in the spacers, that transformation is greatly inhibited in such a way that the mesophase is stable at room temperature for a considerable time. This is the case of poly(triethylene glycol *p,p'*-bibenzoate), PTEB, with the following chemical structure:



Some details of the thermotropic behaviour of this polymer have been already reported (7,8).

Additional aspects of the phase behaviour of PTEB are studied here, by performing simultaneous SAXS/MAXS/WAXS experiments, trying to get a deeper understanding of the nature and structural characteristics of the phases involved.

## Experimental

A film of PTEB was prepared by melting in a Collin press at 150 °C for 5 min, followed by fast cooling to room temperature. The sample, named as PTEB-RT, was held at room temperature for more than one year prior to the analyses.

Differential scanning calorimetric measurements were carried out with a Perkin-Elmer DSC7 calorimeter, connected to a cooling system.

Simultaneous SAXS/MAXS/WAXS experiments have been performed on the Spanish CRG BM16 beamline at ESRF, at a fixed wavelength of 0.098 nm. A MARCCD detector, placed at around 200 cm from the sample, and off beam, was able to cover both the SAXS and MAXS regions (from around 40 to 1.25 nm), while the Princeton detector was used for the WAXS region. A Linkam THMS600 stage was used for controlling the temperature. A scanning rate of 8 °C was employed. The scattering patterns were collected in time frames of 15 s, so that we have a temperature resolution of 2 °C between frames. Crystalline iPP and silver behenate samples were used for the calibration of the WAXS and MAXS/SAXS detectors, respectively.

## Results

The thermal behaviour of the PTEB-RT sample was studied first by differential scanning calorimetry. The DSC melting curve, recorded at a scanning rate of 8 °C/min, is shown in figure 1. Besides a barely visible glass transition at around 20 °C, an initial endotherm centred at 55 °C is observed, followed by a cold crystallization at around 65 °C and two more endotherms at 102 and 115 °C.

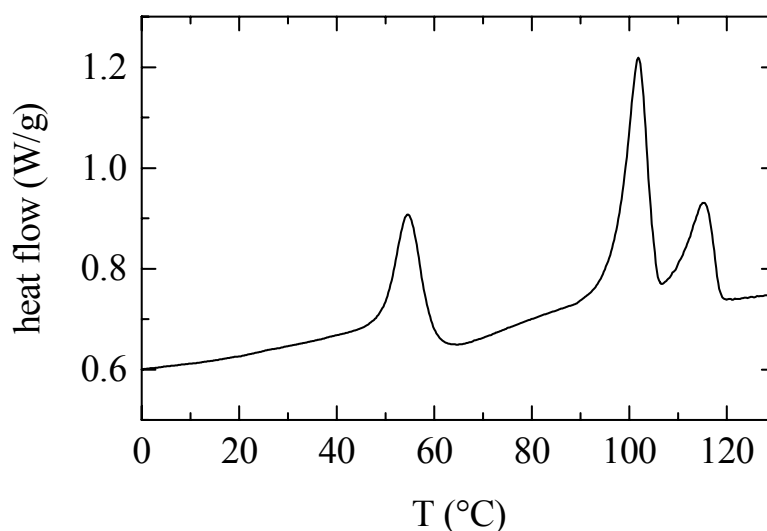


Fig. 1: DSC melting curve, at 8 °C/min, of the PTEB-RT sample.

The nature of the phases involved and the phase transitions were analyzed by performing

simultaneous SAXS/MAXS/WAXS diffraction experiments at variable-temperature. The diffraction profiles corresponding to a melting experiment, at 8 °C/min, are shown in figure 2.

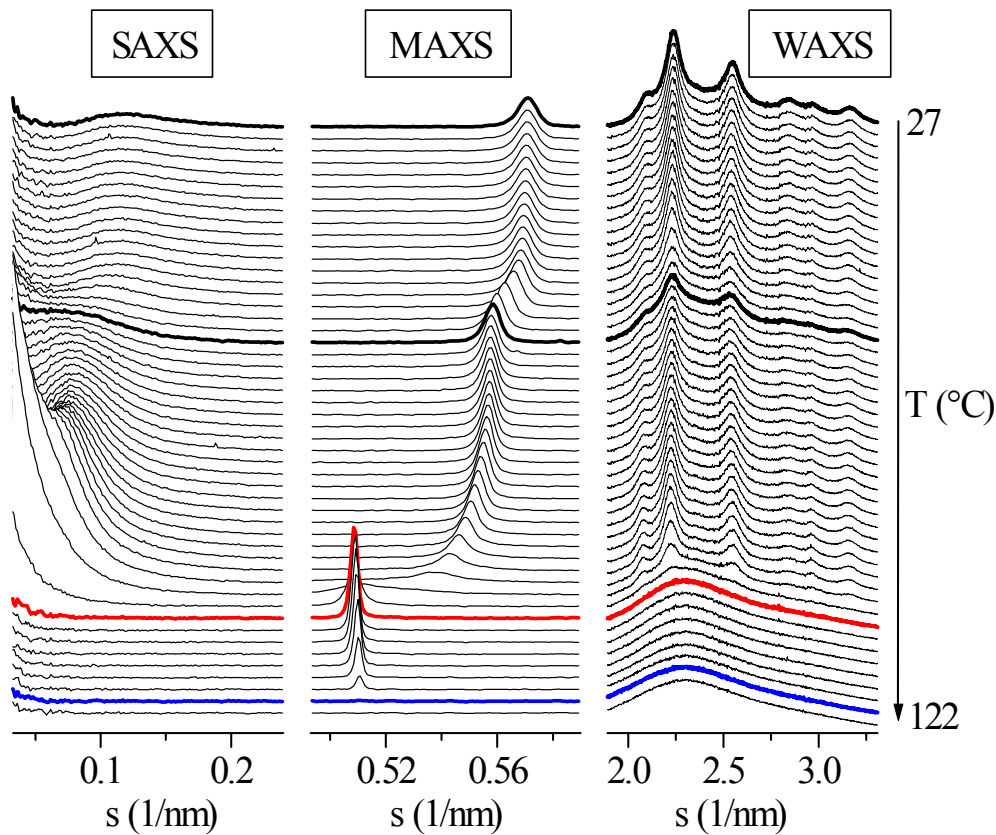


Fig. 2: SAXS (left), MAXS (middle) and WAXS (right) profiles for sample PTEB-RT in a melting experiment.

It follows from these experiments that the sample exhibits a crystalline phase at low temperature, and that the cold crystallization observed in the DSC melting curve leads to the same crystalline phase. This recrystallization is characterized by a slightly different MAXS spacing and a better perfection of crystallites, as deduced from the SAXS diffractograms. On the other hand, this crystalline structure is transformed into a smectic phase (most probably a SmA mesophase) at around 102 °C, which later on undergoes the isotropization centred at 115 °C.

All these facts are better observed in figure 3, where the temperature variation of different structural parameters deduced from the diffractograms in figure 2 are compared with the DSC melting curve. Thus, the recrystallization is characterized by a significant increase of the long spacing, of the SAXS invariant and of the MAXS spacing. Moreover, the position and intensity of the main WAXS peak (peak 2 at around 0.448 nm,  $s = 2.23 \text{ nm}^{-1}$ ) are also sensitive to this recrystallization. On the other hand, the transformation into the smectic mesophase involves, obviously, the disappearance of the long spacing and of the crystalline WAXS peaks, while the MAXS spacing experiences a rather important increase (from around 1.8 to 2.0 nm). Finally, the isotropization is attained at higher temperatures and the MAXS peak corresponding to the smectic layer spacing disappears completely at around 119 °C.

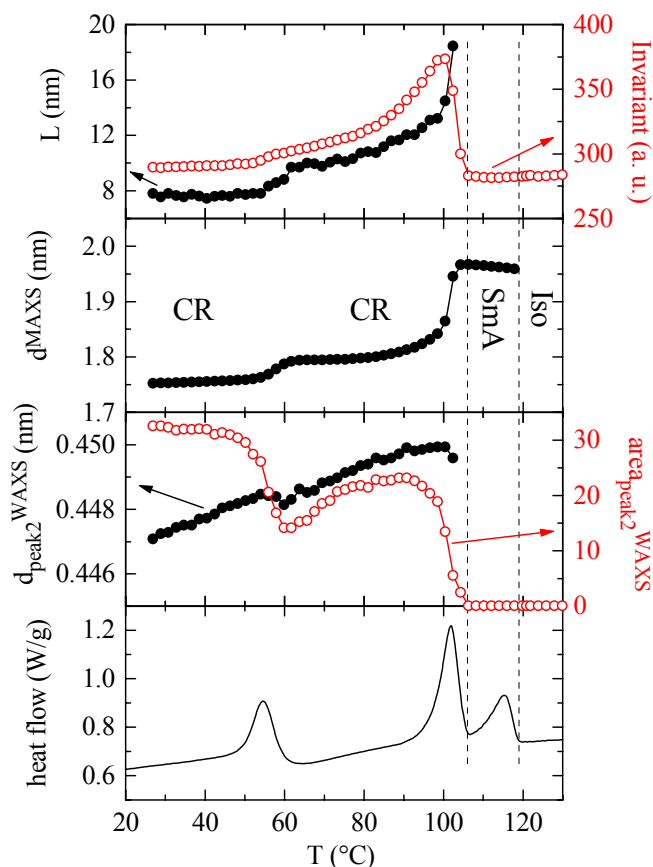


Fig. 3: Temperature variation of different parameters for sample PTEB-RT, obtained from the diffractograms in figure 2, and compared with the DSC melting curve.

### Acknowledgements

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