Phase transitions in a liquid-crystalline biphenyl derivative

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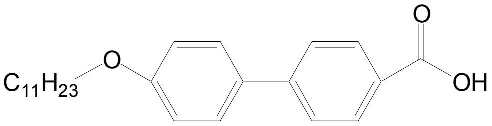
Biphenyl derivatives have been extensively studied [1] because of their application in liquid crystal displays. Moreover, liquid crystalline polymers (LCPs) with mesogenic side chains have attracted special interest because of the possible applications in the fields of non-linear optics, optical storage and electro-optic displays [2]. It is known that the mesogens must be connected to the polymer backbone via a sufficiently flexible spacer in order to decouple, at least partially, the motions of the polymer main chain from that of the side-chains, enabling the mesogens to exhibit the anisotropic liquid crystalline state. Most of the side-chain LCPs described in the literature have been constructed by attaching mesogenic units to a polymeric backbone through polymethylene spacers (more flexible oxyalkyl spacers are sometimes used). In such case, it is expected that the polymer will display a phase behaviour rather similar to that found in the monomer [3].

We report here a synchrotron study of the phase transitions in a liquid crystalline monomer with a biphenyl unit and with a functionalisation suitable to be inserted as side chain in appropriate polymeric skeletons. The chemical structure of the biphenyl derivative is the following:



The thermal behaviour was studied first by differential scanning calorimetry. The DSC melting curve, recorded at a scanning rate of 20°C/min, is shown in figure 1.

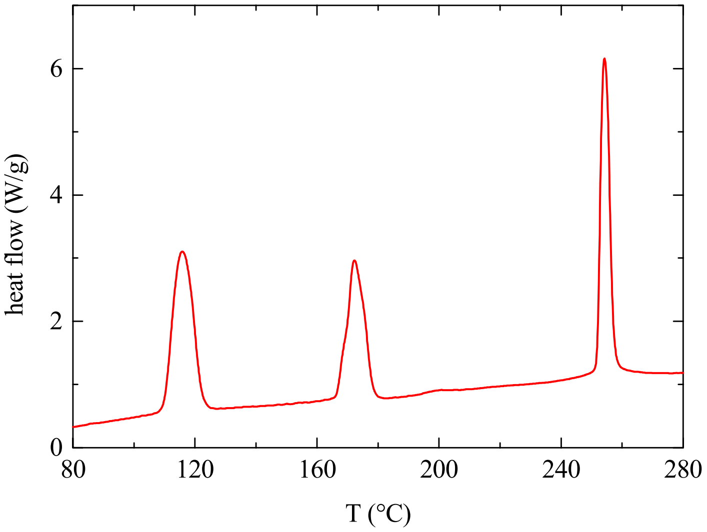


Figure 1: DSC melting curve of the biphenyl derivative.

Four endothermic peaks are observed (one of them of very small intensity) centred at 115.8, 172.2, 200.5 and 254.2 °C, with an enthalpy of 63.5, 45.2, 1.6 and 55.5 J/g, respectively.

The nature of the phases involved was analysed by performing simultaneous MAXS/WAXS diffraction experiments at variable-temperature in the soft-condensed matter beamline A2 at Hasylab, acquiring data with a MAR-CCD detector, located at 169 mm from the sample. The diffraction profiles corresponding to a melting experiment similar to that used in the DSC are shown in figure 2. At low temperatures, no peak is observed in the MAXS region, but several diffractions appear in the WAXS diffractogram. These characteristics, together with the textures obtained by optical microscopy, support the presence of a three-dimensional crystal structure. When the temperature reaches the value of around 116 °C, a clear MAXS peak, centred at 3.47 nm and with several orders, is beginning to appear, and the WAXS diffractogram shows important changes. This is attributed to the formation, totally completed at 128 °C, of a highly ordered smectic mesophase, probably a SmE mesophase. At around 180 °C, the MAXS peak decreases very much in intensity, and the WAXS profile is now completely different, since a single relatively broad halo is obtained, indicating the formation of a smectic mesophase of lower order. Since the WAXS halo is not very broad, a smectic mesophase of intermediate order seems to be present. These features are typical of a mesophase with disordered hexagonal packing within the smectic layers (probably a SmB mesophase). On further increasing of the temperature, and at around 200 °C, the MAXS peak intensity increases again, while the WAXS halo is now considerably wider and amorphous-like. This is interpreted as the formation of a low-ordered SmA mesophase, coinciding with the small endotherm observed in the DSC curve. Finally, above 262 °C the isotropization of this mesophase is obtained.

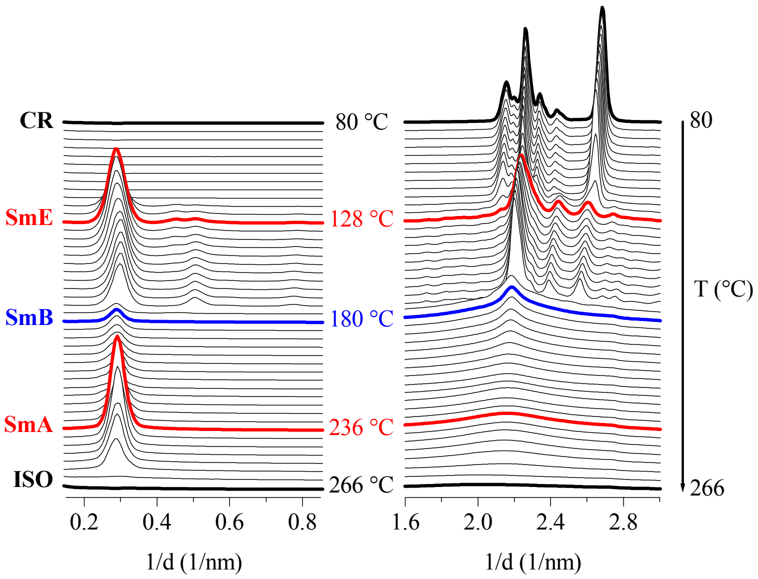


Figure 2: MAXS (left) and WAXS (right) profiles for the biphenyl derivative in a melting experiment.

Considering that the length of the molecule in its all-trans conformation is calculated to be 2.58 nm, the MAXS spacing value of 3.47 nm seems to indicate the presence of dimeric acid species, through intermolecular hydrogen bonds between the carboxylic acids. In such case, intercalated and/or tilted structures may be involved.

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