

Kinetically induced intermolecular association: unusual enthalpy changes in the nematic phase of a novel dimeric liquid-crystalline molecule†

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Received (in Cambridge, UK) 20th May 2002, Accepted 5th August 2002

First published as an Advance Article on the web 15th August 2002

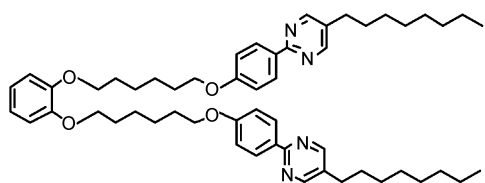
A novel dimeric liquid-crystalline molecule in which two mesogenic groups are connected *via* catechol was found to have smectic-like layer ordering in the nematic phase, and unusual enthalpy changes were observed in the nematic phase on heating from the monotropic smectic C phase.

The driving force of mesophase formation is a fundamental topic in the investigation of molecular assembly systems. A primary factor in thermotropic liquid crystal phases is the gross molecular shape of a compound.^{1,2} Recently microsegregation and molecular topology have attracted much attention as novel self-organizing systems.^{1,3} In addition to structural studies, molecular motion is also important to understand the microscopic behaviour of liquid-crystalline molecules. Our ¹³C NMR study reveals that (1) cooperative motion for the core parts contributes to the orientational order of the molecules in each layer and (2) inter-layer permeation of tails causes correlation between cores in adjacent layers.⁴

In the present study, we have designed a compound in which two liquid-crystalline molecules are connected *via* catechol. Strong correlation of rotation around the long axis of each mesogenic group is expected. On the other hand, U-shaped dimeric liquid crystals have been investigated by several research groups.^{5–8} Attard and Douglass reported property–structure correlations of the dimeric liquid crystals derived from phthalic acid, providing important understanding about the U-shaped liquid crystal system.⁸

Preparation of the compound, 1,2-bis{6-[4-(5-octylpyrimidine-2-yl)phenoxy]hexyloxy}benzene (**BOPPHB**), was obtained from two successive alkylations. 5-Octyl-2-(4-hydroxyphenyl)pyrimidine was treated with 1,6-dibromohexane in the presence of potassium carbonate and then catechol was alkylated with the obtained 5-octyl-2-[4-(6-bromohexyl)phenyl]pyrimidine. Purification of the material was carried out using column chromatography and then recrystallization from ethanol. The purity was determined to be 99.9% by HPLC analysis. The structure was elucidated by IR and ¹H NMR studies.

The transition temperatures determined by optical microscopy were Iso Liq 83.3 °C N 43.4 °C SmC on cooling and the melting point was 76.0 °C. Transition temperatures for the corresponding monomeric molecule, 5-octyl-2-(4-hydroxyphenyl)pyrimidine (**8-PYP-6O**), were Iso Liq 64.0 °C N 56.0 °C SmA 45.0 °C SmC. A phase diagram between **BOPPHB** and **8-PYP-6O** is shown in Fig. 1. The N phase of **BOPPHB** was



† Electronic supplementary information (ESI) available: photomicrographs of the nematic phase formed by **BOPPHB** on cooling, X-ray diffraction patterns and DSC thermograms. See <http://www.rsc.org/suppdata/cc/b2/b204901p/>

miscible with that of **8-PYP-6O**. The SmA phase of **8-PYP-6O** was found to disappear as the percentage of **8-PYP-6O** rose above 40 wt.%.

In a photomicrograph of **BOPPHB** in the N phase at 50 °C director fluctuation was observed in the homogeneous alignment, on the other hand, the texture of the homeotropic alignment was found to become slight white, indicating that the director tilts (Fig. S1, ESI†). By conoscopic observations of a homeotropic aligned sample of **BOPPHB** in the nematic phase, the interference pattern of the conoscopic texture changed to be split with decreasing temperature, suggesting that the nematic phase has biaxiality.⁹ Further investigations will be necessary to prove the biaxiality. In the small angle region of the X-ray diffraction profile in the N phase, a peak around $2\theta = 3.2^\circ$ became sharp with decreasing temperature, indicating the formation of smectic-like layer structure in the nematic phase (Fig. S2, ESI†). Such a sharp peak was not detected in the N phase of the corresponding monomeric molecule **8-PYP-6O**. A XRD profile at 41 °C in the SmC phase gives a layer spacing of $d = 29 \text{ \AA}$, whereas the length of **BOPPHB** is estimated to be 31 Å from a MM2 model.

DSC measurements were carried out at a scanning rate of 5 °C min⁻¹ for both cooling and heating cycles, and the results are shown in Fig. 2. Fig. 2(c) shows a thermogram on heating from crystal to isotropic liquid and then cooling from isotropic liquid. Fig. 2(a) shows a thermogram on cooling from Iso Liq to N and then heating from N to Iso Liq. The transition behaviour in Fig. 2(a) did not depend on the rate of cooling and heating. Cooling from Iso Liq and holding the sample at 55 °C in the N phase for 1 h and then heating to Iso Liq, a reversible profile between the cooling and heating processes was obtained. Fig. 2(b) shows a thermogram observed on cooling from Iso Liq to SmC and then heating from the monotropic SmC to Iso Liq. Marked hysteresis in DSC thermograms between the cooling and heating processes was observed. In the heating process the SmC to N transition peak at 44.2 °C (0.23 kJ mol⁻¹) was detected reversibly, however three new peaks at 66.4 °C (6.2 kJ mol⁻¹), 71.3 °C (0.43 kJ mol⁻¹) and 77.0 °C (0.33 kJ mol⁻¹) were observed. Then the N-I transition at 84.3 °C (2.5 kJ mol⁻¹) was detected.

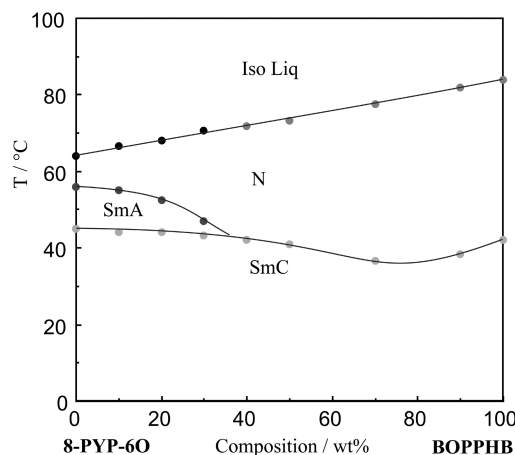


Fig. 1 Binary phase diagram for **BOPPHB** with **8-PYP-6O**.

The locations and intensity of the new peaks are reproducible within experimental errors, not only with a given sample, but also with another sample (Fig. S3, ESI†) The transition enthalpies for the three new peaks decreased as the scanning rate was increased, but the transition temperatures did not depend on the rate. In order to assess the reversibility, the phase behaviour on cooling from a temperature between two of the new peaks was investigated (Fig. 3). On cooling the sample from 73.7 °C or 69.6 °C at a scanning rate of 5 °C min⁻¹, no

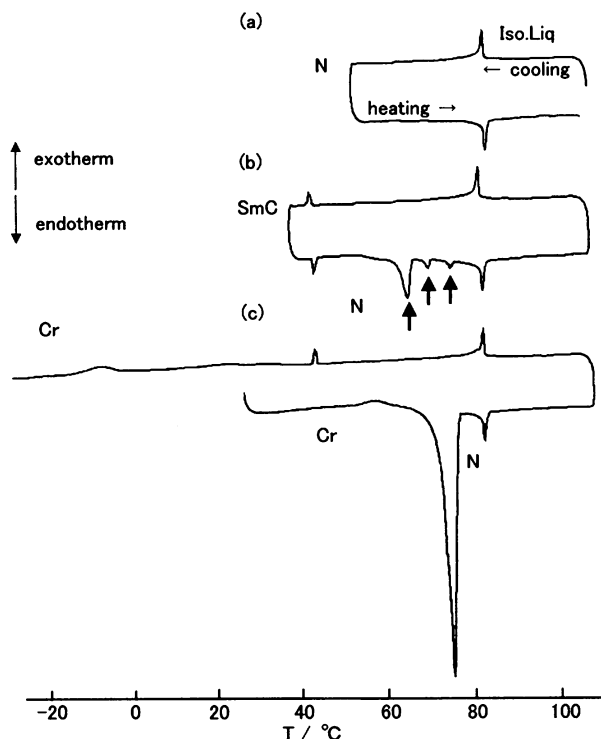


Fig. 2 DSC thermograms for **BOPPHB**. The rate of cooling and heating was 5 °C min⁻¹. (a) Cooling from Iso.Liq to the N phase and then heating from the N phase to Iso.Liq. (b) Cooling from Iso.Liq to the SmC phase and then heating from the SmC phase to Iso.Liq. (c) Heating from the Cr phase to Iso.Liq and then cooling from Iso.Liq to the Cr phase.

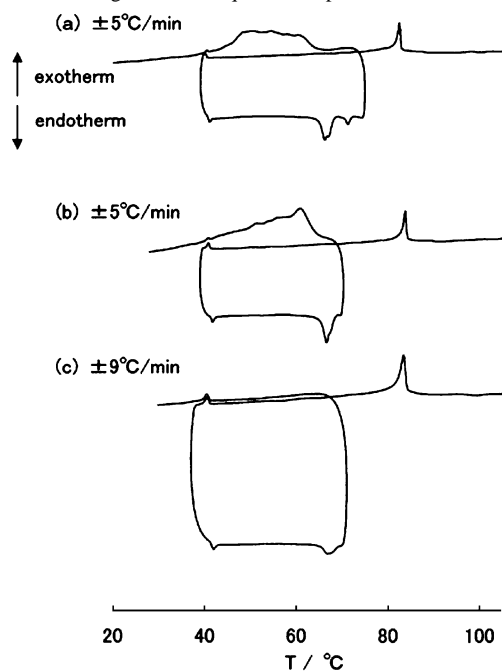


Fig. 3 DSC thermograms of **BOPPHB** on cooling from a temperature between two of the new peaks. (a) On cooling from 73.7 °C at a scanning rate of 5 °C min⁻¹. (b) On cooling from 69.6 °C at a scanning rate of 5 °C min⁻¹. (c) On cooling from 69.6 °C at a scanning rate of 9 °C min⁻¹.

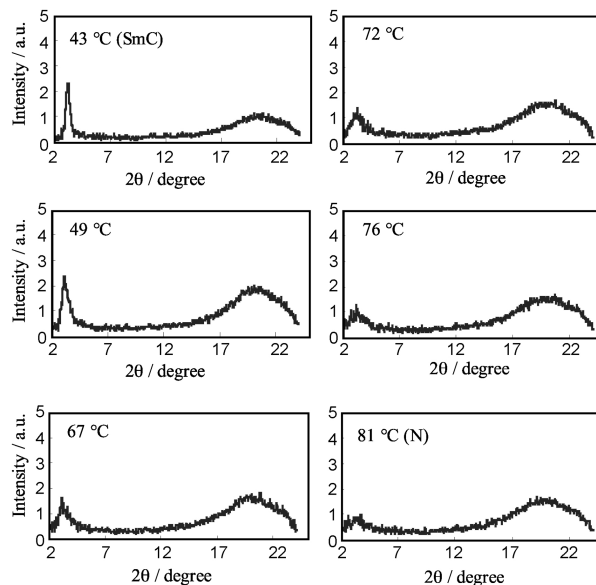


Fig. 4 X-Ray diffraction patterns for **BOPPHB** on heating from the monotropic SmC phase.

reversible exothermic peak was detected in the corresponding temperature range. However, a large and broad exothermic peak due to crystallization appeared in both the cooling cycles. To avoid the crystallization, the measurements were carried out at a scanning rate of 9 °C min⁻¹. On cooling from 69.6 °C, no peak apart from the N–SmC transition was detected. Thus, the new phase transitions that appeared on heating from the monotropic SmC phase were found to be irreversible.

X-Ray diffraction measurements were performed on heating from the monotropic SmC phase to the Iso.Liq (Fig. 4). The intensity of a sharp peak around $2\theta = 3.1^\circ$ in the small angle region of the diffraction profile decreased on heating from 49 °C to 67 °C, indicating disappearance of the smectic-like ordering. The birefringence of the optical texture in the homeotropic region of the sample decreased markedly on heating from 46 °C to 68 °C. Further heating decreased the birefringence gradually. These results suggest that a cluster with layer ordering decomposes at the new phase transition with the largest enthalpy change.

We have found unusual hysteresis in thermal behaviour of a novel U-shaped dimeric liquid crystal compound derived from catechol. On heating from the monotropic SmC phase three new phase transitions appeared. The kinetically induced transitions were found to be irreversible. In a following full paper we will report property–structure correlations of the U-shaped dimeric system and characterization of the new phase transitions.

We thank Drs Isa Nishiyama, Jun Yamamoto and Hiroshi Yokoyama of Yokoyama Nano-structured Liquid Crystal Project for XRD measurements.

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