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Liquid Crystals

Publication details, including instructions for authors and subscription information:

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Online publication date: 06 August 2010

To cite this Article He, Lei(1999) 'Influence of cooling rate on the phase transitions of ferroelectric liquid crystals, MBOPDOB and MBOPDoOB', *Liquid Crystals*, 26: 1, 63 – 67

To link to this Article: DOI: 10.1080/026782999205551

URL: <http://dx.doi.org/10.1080/026782999205551>

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Influence of cooling rate on the phase transitions of ferroelectric liquid crystals, MBOPDOB and MBOPDoOB

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(Received 15 May 1998; in final form 10 August 1998; accepted 24 August 1998)

The phase transitions of ferroelectric liquid crystals (FLCs), *D*-4-(2-methylbutyloxy)phenyl 4-decyloxybenzoate (MBOPDOB) and *D*-4-(2-methylbutyloxy)phenyl 4-dodecyloxybenzoate (MBOPDoOB), were investigated by means of differential scanning calorimetry (DSC) and polarizing microscopy. The DSC and polarizing microscopy results show that MBOPDOB and MBOPDoOB exhibit different phase transition sequences on slow cooling, whereas they have the same sequence under rapid cooling. In MBOPDoOB, we also observed a quench-induced metastable phase that differs from the normal crystal phase formed by slow cooling. The textures corresponding to the two crystal phases were observed using a polarizing microscope. X-ray diffraction (XRD) was also used to study the quench-induced phase. The influence of the alkoxy chain length on the molecular interactions in FLCs is discussed.

1. Introduction

The advent of a bistable, fast switching electro-optical light-valve based on the properties of ferroelectric liquid crystals (FLCs) has aroused considerable interest in the synthesis of optically active smectic liquid crystal materials [1]. General guidelines have been established for the synthesis of FLC materials and the primary requirement is for materials to exhibit tilted chiral smectic phases such as SmC^* , SmI^* , and SmF^* [2–5]. Figure 1 shows a general structure of FLC mesogens which consist of at least two rigid aromatic groups (marked A and B) coupled by central linking groups (-X-). *R* and *R'* may be alkyl, alkoxy or nitro groups, etc.

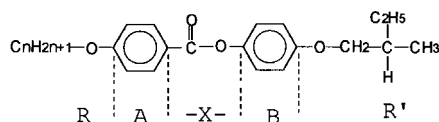


Figure 1. The most general molecular structure of an FLC material. A and B denote rigid aromatic benzene rings; -X- denotes the central linking group; *R* and *R'* denote the terminal chains, and *R'* contains an asymmetric atom acting as the chiral centre.

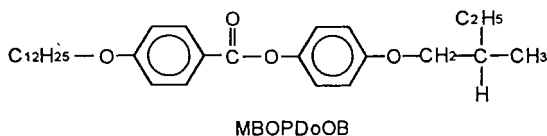
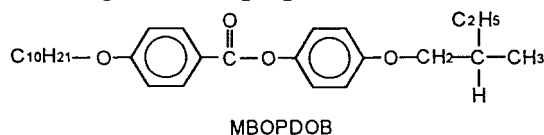
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In addition, either *R* or *R'* should have strong terminal lateral dipoles and contain an asymmetric atom acting as a chiral centre giving the asymmetry necessary for ferroelectric properties.

The length of the terminal chains appears to be an important factor in phase formation in these materials. In mesogenic esters, the dominant alkoxy chain usually has at least eight carbon atoms and the other chain must be more than four units long before tilted phases can be observed [6, 7]. For an FLC mesogen, if we retain the structure of the core and the tail which contains a chiral centre, and increase the length of the other alkyl chain, the material often shows a phase transition sequence with more mesophases. If the length is further increased, the lowest temperature mesophase which has the highest symmetry may vanish. This phenomenon has been observed for *S*-4-(2-methylbutyl)phenyl 4-*n*-alkoxybiphenyl-4'-carboxylates, *R*-1-methylpropyl 4-*n*-alkanoyloxybiphenyl-4'-carboxylates, *S*-2-methylbutyl 4-*n*-alkanoyloxybiphenyl-4'-carboxylates and *S*-3, 7-dimethyloctyl 4-*n*-alkanoyloxybiphenyl-4'-carboxylates, etc. [8, 9].

In this paper, we study two optically active esters, both (+)-4-(2-methylbutyloxy)phenyl 4-alkyloxybenzoates,

MBOPDOB and MBOPDoOB. The molecular formulae of these compounds are [10],



The temperature dependence of the spontaneous polarization and the tilt angle in the SmC* phase of these FLC materials have been extensively investigated [10, 11]. In this paper, the study will focus on the phase transitions for these FLC materials under different cooling rates.

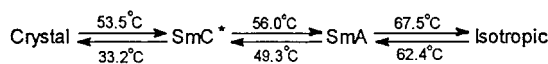
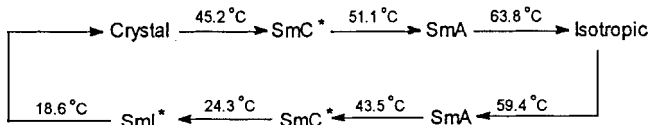
2. Experimental

The liquid crystal cell which contains the sample is made of two flat glass plates, separated by 25 μm mylar spacers. The cell was placed in a hot stage in a Leitz polarizing microscope (ORTHOPLAN-POL). The accuracy in the temperature measurements is better than 0.05 $^{\circ}\text{C}$. The FLC sample was drawn into the cell by capillarity in the isotropic liquid phase.

In the DSC measurements, powder samples of MBOPDOB and MBOPDoOB were placed in hermetically sealed aluminium containers in a dry atmosphere. The heating and cooling curves were recorded by a Perkin-Elmer DSC7 differential scanning calorimeter. XRD measurements were performed using a Rigaku X-ray diffractometer (Cu-K α_1) at room temperature (20 $^{\circ}\text{C}$).

3. Results and discussion

Using DSC and polarizing microscopic techniques, the following phase transitions were observed for MBOPDOB and MBOPDoOB:



Figures 2(a) and 2(b) show the thermographs of MBOPDOB and MBOPDoOB, respectively, during

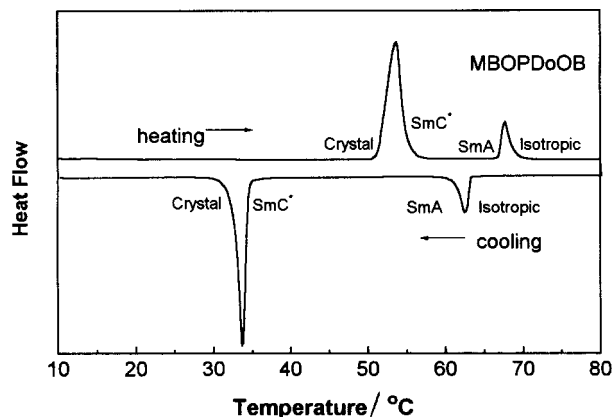
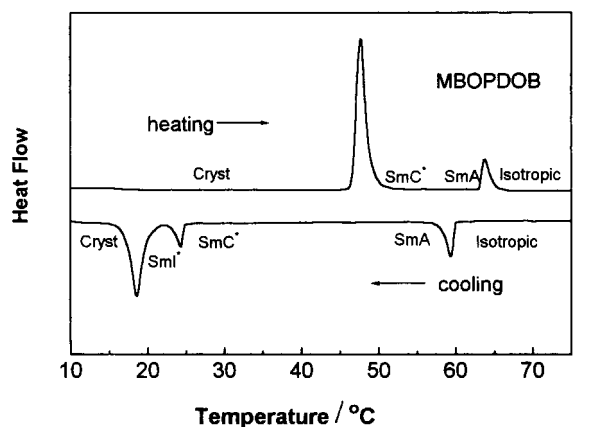


Figure 2. DSC scans of MBOPDOB (a) and MBOPDoOB (b) at 1 $^{\circ}\text{C min}^{-1}$ heating and cooling rates.

both heating and cooling at a rate of 1 $^{\circ}\text{C min}^{-1}$. As usual, the transitions with the largest enthalpy in these cycles are the melting transitions of the crystal phase. The clearing point transition, to and from the isotropic liquid, is always first order in nature. In MBOPDOB and MBOPDoOB, the latent heat for the SmC*–SmA endotherm is too small to be observed, implying a very weak first order or second order transition. It should be pointed out that not all previously observed SmA–SmC* transitions in FLCs are second order. DSC measurements on the FLC 4-(3-methyl-2-chlorobutanoyloxy)-4'-heptyloxybiphenyl (A7) and a high resolution X-ray study on the FLC 4-(3-methyl-2-chloropentanoyloxy)-4'-heptyloxybiphenyl (C7) both indicated the first order nature of the transitions [12, 13]. The reason why the SmA–SmC* transition in the FLC materials MBOPDOB and MBOPDoOB is second order is thought to be due to the position of the COO group giving rise to the transverse dipole moment in the molecule. Because the COO group is located between

two benzene rings, the intermolecular dipole–dipole interaction is weak and may change continuously near the SmA–SmC* transition [11]. Figure 2 shows clearly that MBOPDOB and MBOPDoOB have different phase transition sequences on cooling, although they exhibit the same sequence on heating. When MBOPDOB is cooled, the SmC* phase transformation to the SmI* phase occurs before crystallization, while for MBOPDoOB, the SmC* phase changes to the solid phase directly. The SmC*–SmI* transition is weakly first order and the SmI*–crystal transition is first order for MBOPDOB. This means that due to the shorter alkyl chain, the crystalline solid appears at a lower temperature for MBOPDOB and this makes the monotropic SmI* phase accessible on cooling.

Well-aligned planar textures were observed for the SmA and SmC* phases using slow cooling rates (3°C h^{-1}) for both MBOPDOB and MBOPDoOB. In the SmA phase, the samples show a fan-like texture. Further cooling results in parallel stripe patterns which are characteristic of the SmC* phase, in addition to the fan-like texture [14,15]. The distance between two adjacent stripes gives the helical pitch of the SmC* phase [16]. Figure 3(a) illustrates the texture of the SmI* phase in MBOPDOB, and 3(b) shows the pattern of the solid phase in MBOPDoOB as observed by polarizing microscopy.

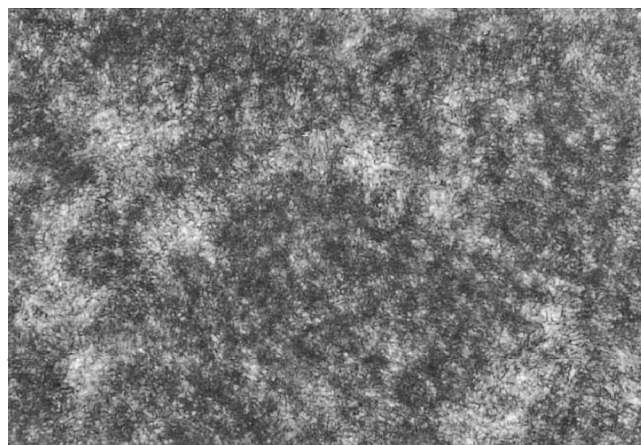
When an MBOPDoOB sample is cooled naturally from the isotropic phase, at a cooling rate estimated to be greater than $15^{\circ}\text{C min}^{-1}$, we obtain a new texture at room temperature. This texture is shown in figure 3(c) and it obviously differs from the texture of the normal crystal phase formed by slow cooling, shown in figure 3(b). The texture does not change even when the sample is cooled to about -10°C by putting it into a refrigerator. But when the sample is heated to 35°C at which it is still in the solid phase, the texture turns to that shown in figure 3(b); this transition is not reversible within the solid phase region at any cooling rate. The texture shown in figure 3(c) corresponds to a metastable crystal phase induced by quenching. For convenience, we denote the normal crystal phase as Cr1 and the metastable phase as Cr2.

XRD measurements of the Cr1 and Cr2 phases were performed using a RigaRu X-ray diffractometer ($\text{Cu-K}\alpha_1$) at room temperature (20°C). The powder sample of Cr2

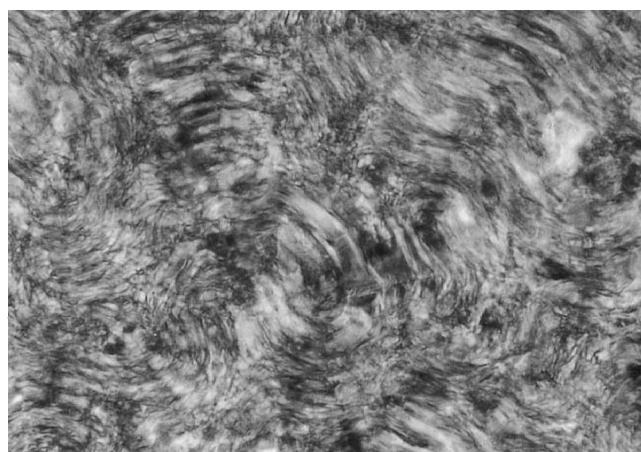
was prepared by heating MBOPDoOB to the isotropic phase followed by cooling at a set rate of $20^{\circ}\text{C min}^{-1}$. The diffraction patterns of the two phases are given in



(a)



(b)



(c)

Figure 3. (a) The texture of the SmI* phase of MBOPDOB. (b) The texture of the stable solid phase of MBOPDoOB at 20°C , formed by slow cooling at 3°C h^{-1} . (c) The texture of the metastable solid phase of MBOPDoOB at 20°C , induced by quenching at $20^{\circ}\text{C min}^{-1}$. The photographs were taken with crossed polarizers and $40\times$ magnification.

figure 4. As these phases are obtained from the smectic phase, they retain the layer structure of the original smectic phase. Using the X-ray diffraction pattern shown in figure 4, the layer thickness can be calculated from the positions of the peaks indexed $(0, 0, l)$, using the Bragg equation [17]:

$$2d \sin \theta = K \lambda$$

where d is the layer thickness, θ the diffraction angle, K the order of diffraction and λ the wavelength of the X-rays. For a Cu target the wavelength λ of the K_{α_1} line is 1.5406 Å. Most of the diffraction peaks shown in figure 4 can be indexed as $(0, 0, l)$, and the calculated layer thicknesses are 29.9 and 30.8 Å for Cr1 and Cr2, respectively. The difference in thickness is mostly due to the change in the molecular tilt angle within the layer. In the Cr1, there are three peaks, denoted by "*", which indicate the interlayer and intralayer long range positional order. Two of these peaks disappear in Cr2, and only the peak at around 20° is retained. Considering the broad background in curve (b) in the diffraction region $2\theta = 16^\circ \sim 25^\circ$, the Cr2 phase shows some characteristics of a two-dimensional liquid. The sharp peak around 20° , just like the higher angle peak in the X-ray diffraction pattern of SmI*, indicates that quasi-long range positional order within the plane still exists. Therefore, although the diffraction results prove that the Cr2 phase is a crystalline phase, the structure is similar to that of the SmI* phase, a layer structure with in-plane quasi-long range positional order.

The DSC thermographs of MBOPDoOB are shown in figure 5. Run 1 is the heating curve of the crystalline material at a rate of $10^\circ\text{C min}^{-1}$. On heating, the

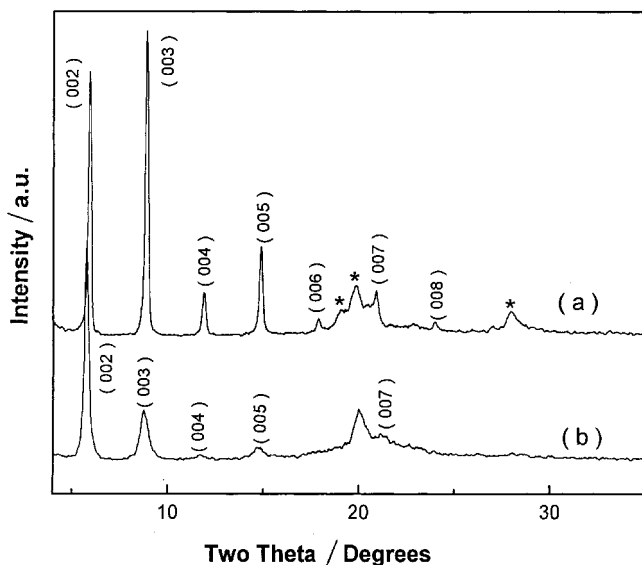


Figure 4. X-ray diffraction patterns of (a) the Cr1 phase and (b) the Cr2 phase of MBOPDoOB, at room temperature.

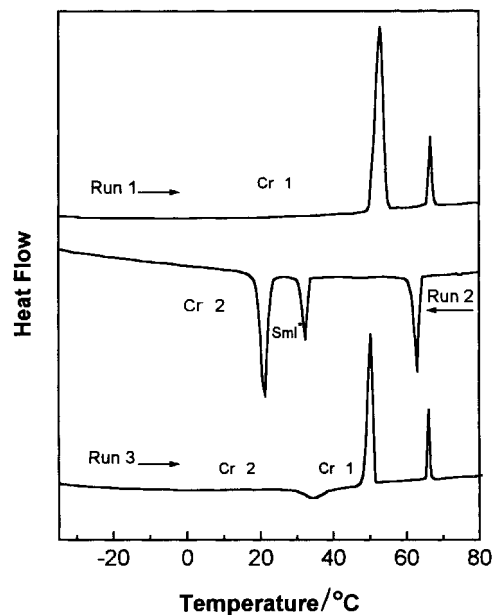


Figure 5. DSC scans for MBOPDoOB at different heating and cooling rates. Run 1: heating at $10^\circ\text{C min}^{-1}$; Run 2: cooling at $20^\circ\text{C min}^{-1}$; Run 3: subsequent heating at 5°C min^{-1} .

transition temperatures and phase sequence are consistent with those at 1°C min^{-1} , shown in figure 2 (b). But a new transition sequence was observed at a high cooling rate of $20^\circ\text{C min}^{-1}$, as shown in Run 2 of figure 5. Two exothermic peaks at 32.5 and 21.4°C were recorded, indicating that the SmC*–crystal phase transition occurs in two steps. We propose a SmI* phase between the SmC* and the crystal phase. Compared with the DSC results of MBOPDOB, the DSC cooling curve shown in figure 2 (a) is very similar to the curve for MBOPDoOB at high cooling rate and the texture of the Cr2 phase of MBOPDoOB is somewhat similar to the texture of the SmI* phase of MBOPDOB (figure 3). However, in MBOPDOB, the monotropic SmI* phase is readily obtained and does not need to be induced by rapid cooling. The X-ray measurements also prove that the structure of Cr2 is very similar to that of the SmI* phase, and it looks therefore as if the Cr2 phase is virtually a quenched SmI* phase.

Run 3 in figure 5 shows the heating curve of the Cr2 phase at 5°C min^{-1} . At 34.7°C the Cr2 phase is transformed into Cr1 via a broad exothermic transition. On further heating, Run 3 repeats the corresponding part of Run 1 in figure 5, showing that the phase above 34.7°C is indeed Cr1. This result is also supported by the polarizing microscopy observation that the texture of Cr2 changes to that of Cr1 when the sample is heated. The DSC curves also show that the transition from Cr2 to Cr1 is not a glass transition. Commonly the glass transition shows a baseline jump in the DSC curve.

XRD results also show that Cr2 is a crystal phase (figure 4). Since Cr2 is transformed into Cr1 by an exothermic transition, Cr2 has a higher internal energy than the Cr1 phase, indicating that Cr2 is metastable.

4. Conclusions

We have studied the phase transitions of MBOPDOB and MBOPDoOB. When cooled slowly, the SmC* phase transforms to the crystal phase directly for MBOPDoOB, whereas a monotropic SmI* phase exists between the two phases for MBOPDOB. The longer tail of MBOPDoOB appears to enhance the molecular interactions, making it easier to crystallize. Unlike slow cooling, in which the molecules of liquids have enough time to adjust their rotational, positional and orientational order between two thermodynamically stable states, quenching is a highly non-equilibrium process and some intermediate state may be frozen into the final state. The observation of the quench-induced SmI* phase in MBOPDoOB indicates that the changes within a layer have shorter relaxation times than those between layers for the SmC*-crystal transition. During the quenching of MBOPDoOB, in the supercooled SmC* phase, the degree of ordering within the layers increases rapidly and the hexagonal structure forms in the layer. However the molecules do not have enough time to rearrange their positions along the direction normal to the layers, readjusting the layers and forming a three dimensionally ordered crystal. So the sample forms the SmI* phase instead. On further cooling, the SmI* phase transforms to the metastable crystal phase, Cr2.

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