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A. Jakli[a]; I. Janossy[a]; A. Vajda[a]
[a] Research Institute for Solid State Physics and Optics,

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Polymorphic crystalline forms of 8OCB

A. JÁKLI*, I. JÁNOSSY and A. VAJDA
Research Institute for Solid State Physics and Optics, H-1525 Budapest,
P.O. Box 49, Hungary

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For most alkoxycyanobiphenyls (3OCB, 5OCB, 6OCB, 7OCB and 9OCB) it has been observed that slow or delayed cooling gave rise to a lower melting crystalline polymorphic form which then slowly converted into the higher melting stable crystalline structure. Although under slow evaporation from a solvent, polymorphic crystalline structures were observed also for 8OCB, a polymorphism on cooling like that in other *n*OCBs has not previously been reported. We have now observed that 8OCB also shows polymorphism, which brings it into line with the other homologues. On keeping the material between 35 and 38°C after it was cooled from above the melting point of the stable crystal form (55°C), regular platelets grow usually from one point and fill the whole sample. The texture is stable for weeks at room temperature. Upon heating it shows a melting point at 50°C, i.e. 5 degrees below the stable crystalline melting point. It is interesting that all platelets are non-symmetric and have the same handedness.

1. Introduction

Polymorphic crystalline forms result from a subtle balance of intermolecular interactions. In order to obtain precise information about the molecular interactions, attempts have been made to find relationships between crystalline and mesophase structures (as a review see [1]). For these studies, 4-cyano-4′-alkylbiphenyls (*n*CB) or 4-cyano-4′-alkoxylbiphenyls (*n*OCB) [2] are the most suitable materials because of their simple molecular structures and their practical importance. X-ray diffraction studies [3] showed that the mesophases have interdigitated structures with overlapping of their core regions due to the strong dipole moment of the CN group.

For most alkoxycyanobiphenyls (3OCB, 5OCB, 6OCB, 7OCB and 9OCB) it was observed that slow or delayed cooling gave rise to a lower melting crystalline polymorphic form, which then slowly converted into the higher melting stable crystalline structure [4]. For 8OCB polymorphism has been reported up to now only during slow evaporation of solvents from acetone–water or diethyl ether–methanol solutions [5]. In this case four different crystalline phases were found [6]: square-plate, parallelepiped and needle crystal forms which are metastable, and the most stable crystalline phase that can be found in commercial powder specimens. The square-plate crystals are unstable even at −20°C, whereas the needle crystals may retain transparency at room temperature for several months. Similar crystal structures were also found in 6CB and 7CB [7].

2. Experimental results

A relaxed sample of 8OCB has a powder-type crystal form, which shows a grainy texture in thin films. A regular crystal texture of a 10 μm thick film between crossed polarizers is shown in figure 1.

We have observed that on slow cooling, 8OCB does show polymorphism, which brings it into line with the other homologues. Thermostatting the material between 35 and 38°C after it was cooled from above the melting point of the stable crystal form (55°C), regular platelets grow, usually from one point, and fill the whole sample. A typical growing domain is shown in figure 2. The shape of the platelets resembles the periodic array of lamellae when growth is fast enough in non-faceted systems of binary eutectics [8]. The final texture is transparent and contains uniform platelets of about 300 μm width (figure 3). The extinction direction of the platelets is parallel to the edge of the growing domain, i.e. it makes an angle of about 45° with the side edges which are parallel to the growth direction. It is interesting that all platelets are non-symmetric and have the same handedness (see figure 2). In repeated growth processes, left and right handedness was found with the same probability, but in *each* growth process only one handedness was found.

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*Author for correspondence; e-mail: jakli@lci.kent.edu; present address: Liquid Crystal Institute, Kent State University, Kent, OH 44242, USA.

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Figure 1. Texture of the most stable, regular crystal form of a 10 μm thick film of 8OCB.

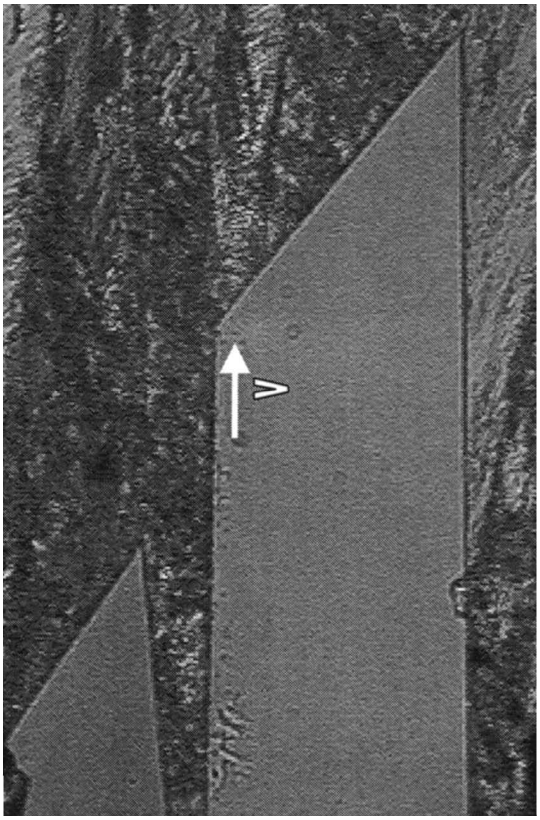

Figure 2. Metastable platelet-type crystal growing at 37°C in the SmA phase of 8OCB.

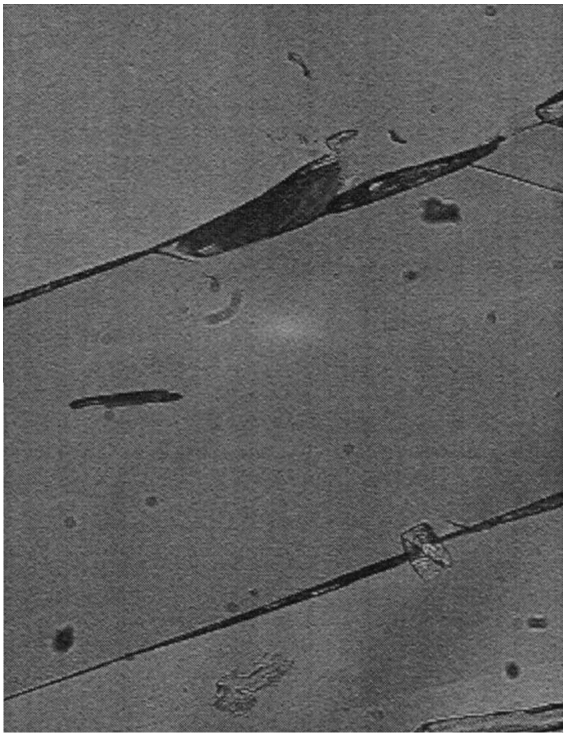

Figure 3. Typical texture of the metastable platelet-type crystal formed by 8OCB at 37°C.

When this crystalline phase is heated, the SmA phase now appears at 50°C, whereas on heating from the stable crystalline state of a commercial sample, the SmA phase was found only at 55°C. The texture consisting of the uniform platelets is metastable: after a few weeks the stable crystalline texture nucleates and invades the whole sample very slowly.

In some cases the growth of platelets and the regular powder-crystalline forms start to form simultaneously and coexistence of the two polymorphic forms is observed. In a heating cycle, the area covered by the platelets is first transformed at 50°C into the SmA phase, and then the powder-crystal form also expands into this area.

In figure 4 we show various DSC curves at a heating rate of 2°C $\min^{-1}$. Figure 4 (*a*) represents the situation when a relaxed sample was heated for the first time. This is the most stable crystal, which melts at 55°C. Figure 4 (*b*) shows the melting of the pure platelet-type crystal (see figure 3). It melts at 50°C, i.e. 5°C below the stable crystal form. Interestingly the transition enthalpy is larger for the platelet type crystal form than for the powder specimen. Figure 4 (*c*) shows the temperature dependence of the heat current in a sample that was previously cooled to 28°C from the isotropic state. It contains both the stable powder-like crystal and the platelet-type crystal. The exothermic peak appearing between the melting point of the platelets and the melting

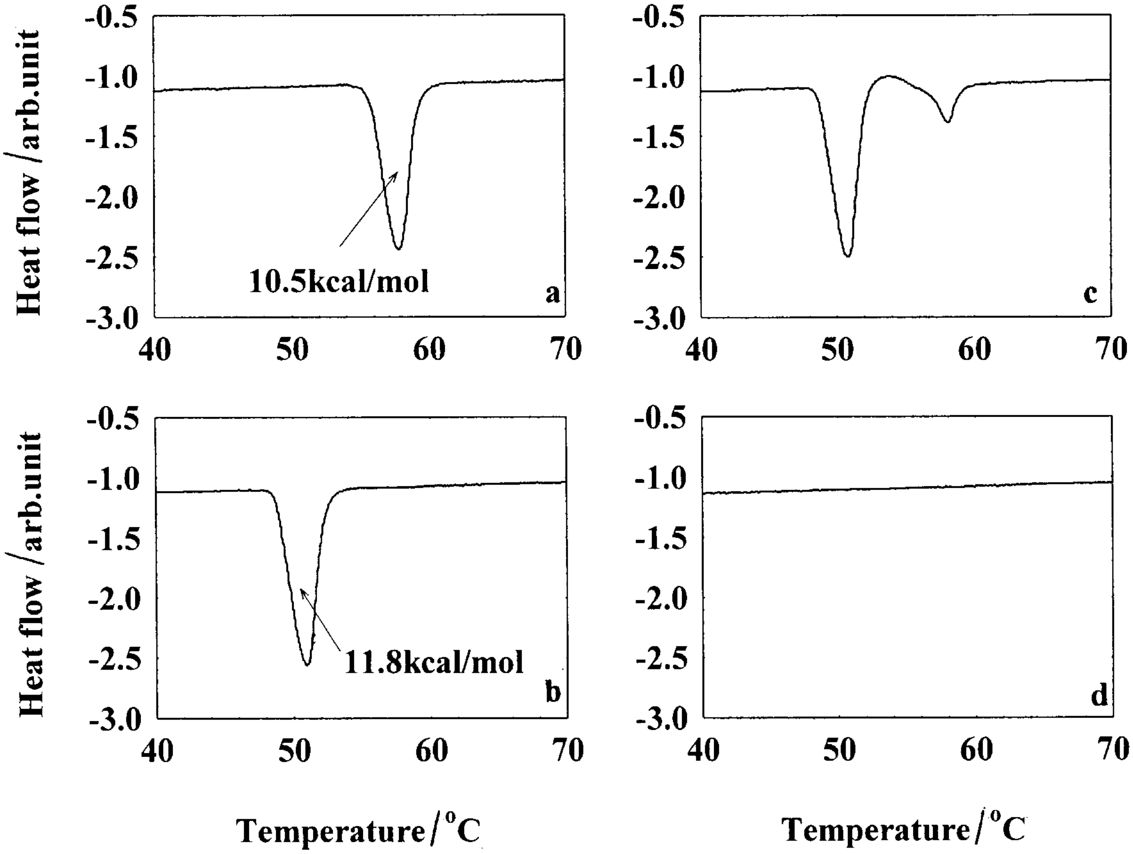

Figure 4. DSC curves on heating at a rate of 2°C min^{-1}. (*a*) Relaxed sample on first heating; (*b*) pure platelet-type crystal; (*c*) sample that was previously cooled to 28°C from the isotropic state; (*d*) heating curve of a supercooled sample of SmA phase. The SmA–I transition would not occur until a higher temperature.

of the powder is due to growth of powder crystal that is already present. Figure 4(*d*) represents the heating curve of a supercooled SmA phase, formed when the cooling rate was fast enough to avoid crystallization. As can be seen, there is no phase transition in this case.

3. Discussion

The melting behaviour of the platelet-type crystals observed in the present experiments strongly resembles that of the 'needle' crystals observed in the evaporation process [6]. For this reason we assume that the metastable crystal formed on slow cooling has the same structure as that of the 'needle' crystals. By X-ray measurements it was shown by Hori *et al.* [9] that the 'needle' crystal has a smectic-like structure composed of bilayers with a two-dimensional infinite network of closely arranged CN groups. The crystal has a triclinic symmetry. It is important (see figure 5) that the planes of the rings of the biphenyl moieties are not coplanar, but make an angle with each other (38.2° for molecules *A* and 38.9° for molecules *B* [9]). In addition the molecules have no head-to-tail symmetry (one benzene ring is attached to an alkoxy chain, the other to a CN group). This means that the stable molecular conformation has no mirror symmetry. The molecules *A* and *B* can be transferred to *A'* and *B'* by pure rotation, i.e. they have the same handedness. Although the mirror images of the molecular conformations shown in figure 5 must have the same energy, a growing crystal domain contains only molecules with the same handedness to assure the closest packing. From observation, the domains tend to nucleate at one common point, explaining why we observed growing domains of the same handedness.

Parity breaking and left–right asymmetric propagating patterns are known in lamellar eutectics [8] and in some liquid crystals [10], but there it was related to the speed of the directional solidification through a new mechanism for wavelength selection [11]. The origin of the present symmetry breaking is therefore distinct from that of the previous examples in [8, 10].

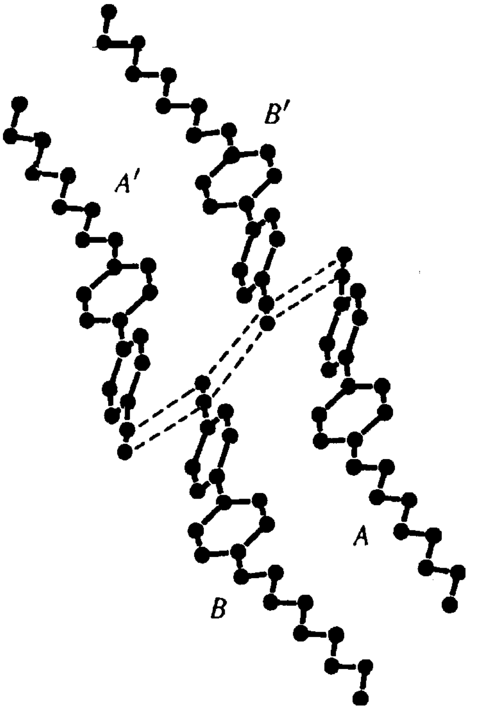

Figure 5. Structure of the 'needle crystals' formed by evaporation as determined by X-ray studies [9]. Since the needle crystals have the same melting point as the 'platelet-type crystal' formed on cooling at temperatures between 35 and 38°C, we assume that they have the same structures.

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