Structure of a B_6-like phase formed from bent-core liquid crystals determined by microbeam x-ray diffraction

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We studied the structure of the B_x phase formed from the short terminal homolog, 1,3-(4-bromobenzene) bis[4-(4-*n*-butoxyphenylliminomethyl)benzoate] (4Br-P-4-O-PIMB), by focusing a microbeam of x ray on the well-developed fan-shaped texture. From the highly oriented x-ray patterns detected at the two states of DC-ON and DC-OFF, the B_x structure was definitely illustrated. It is a kind of frustrated one similar to the B_1 phase: the molecules lie perpendicularly to the layer, and the frustration takes place perpendicularly to the bent direction. Unlike in the B_1 phase, however, the size of the resulting antidomain is not definite, but fluctuates from position to position as observed in the B_6 phase.

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Liquid crystalline (LC) phases of bent-shaped molecules have evoked considerable interests in recent years, in particular due to their exotic packing symmetry. These molecules form the ferroelectric LCs [1–4], and simultaneously chiral LCs by breaking mirror symmetry [2,5–9] in spite of an absence of a chiral carbon. So far, seven kinds of banana phases, the B_1–B_7 phases, have been widely found and studied in many interesting reports [10]. Among these, the B_2 phase is of particular interest and the most studied because it is chiral and switchable in electric fields, and the electrooptic effects can be exploited to characterize the chiral and polar structures and dynamics.

The B_1 phase with the frustrated structure is also interesting, which was reported by Watanabe *et al.* [6,11], for the short terminal chain homolog in the classic banana-shaped molecules, bis[4-(4-*n*-butoxyphenylliminomethyl)benzoate] (P-*n*-O-PIMB). This phase can be distinguished from x-ray diffraction pattern. In the highly oriented sample, the meridional layer reflection is accompanied by four point (off-meridional) reflections. The spacing of the first meridional reflection corresponds to half a molecular length. These reflections are assigned to (002) and (101) reflections attributable to the two-dimensional rectangular lattice. Such a characteristic x-ray diffraction pattern is reminiscent of the frustrated smectic phases where the smectic layers display an unusual density modulation along the layer [12,13]. The density modulation can be explained to result from the antidomain structure such that the conventional layered structure is constructed in a small domain, but the molecules in the adjacent domain slide halfway along the layer normal after the 180° rotation around their molecular long axes. Although there are two possible directions of layer modulation parallel and perpendicular to the bent direction as shown in Figs. 1(a) and 1(b) [11,12], the latter structure of Fig. 1(b) has been proved for the B_1 phase [13–15,18]. Such an antidomain structure is considered to result from the two-dimensional escape from the spontaneous polarization [12,16,17,19]. Commonly, the periodic amplitude along the layer (or the size of antidomain) ranges around 40–100 Å [11,14,19,21,22].

The B_6 phase recently discovered [23–28] would be related to the B_1 phase. It is formed from the short terminal homolog of banana molecules as well. Sometimes, the B_6 phase is followed by the B_1 phase on cooling. The transition enthalpy between B_1 and B_6 is negligibly small (less than 0.2 kJ mol^{-1}), which suggests only subtle modifications of the molecular arrangement. B_6 shows only a layer reflection with a spacing corresponding to half a molecular length which corresponds to (002) reflection. Thus, it has been speculated to be an intercalated smectic phase in which the molecules change their bent direction oppositely in the short range either without an order or with quite a lower order [3,23,24]. Following these, a number of studies on the mesomorphic properties of the B_6 phase and B_6-B_1 transition behavior have been reported [20,26–28]. So far all the researchers have accepted the model structure of Fig. 1(c) with the intercalated structure along the bend direction, which was proposed by Shen *et al.* [22]. However, from the analogy of the B_1 structure, quasimodulated structure perpendicular to

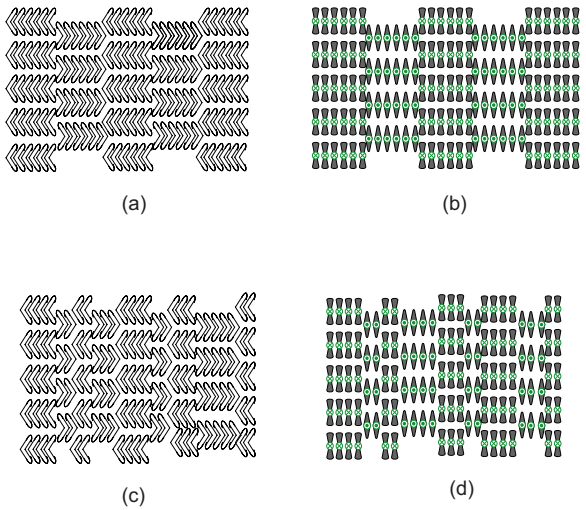

FIG. 1. (Color online) Schematic illustration of the two possible packing structures of B_1 phase [(a) and (b)] and B_6 phase [(c) and (d)]. The model of (b) has been identified for the B_1 phase. In this study, the model of (d) was proved for the B_x phase.

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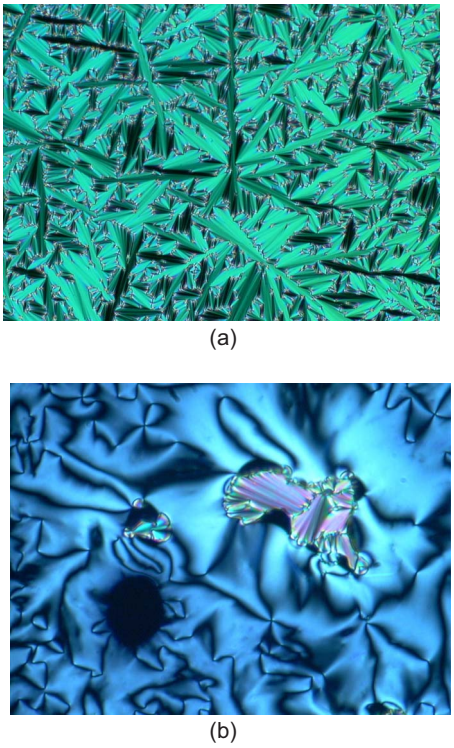
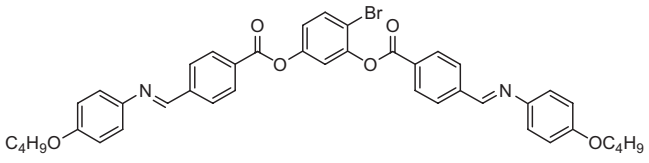


FIG. 2. (Color online) Polarized optical micrographs in the B_x phase of 4Br-P-4-O-PIMB; (a) for homogeneous fan-shaped texture and (b) homeotropic texture prepared by shearing between glasses.

the bend direction [Fig. 1(d)] is also possible and has to be examined.

In our previous studies [29,30], we found that the interesting phase related to the B_6 phase is formed in the short terminal homolog, 1,3-(4-bromobenzene) bis 4-(4-*n*-butoxyphenylliminomethyl)benzoate (so-called 4Br-P-n-PIMB) with the following formula:



Iso 139.9°C B_x 100.3°C X_3

Iso 139.9 ° C B_x 100.3 ° C X_3

This material shows the transition of Iso-B_x-X_3. Here, the X_3 phase is the solid phase characterized by having the extremely large lattice [29] and the noticeable phase is the B_x phase observed in the highest mesophase temperature region. When the B_x phase is aligned homogeneously, it shows the fan-shaped texture in the microscope observation [see Fig. 2(a)]. The homeotropically aligned sample still exhibits the high birefringent domain including the Schlieren texture in Fig. 2(b). Thus, the B_x phase should possess the biaxial nature as well as one-dimensionally positional order such as layer order. By conventional x-ray method, however, it does not show any sharp layer reflection, but only the broad reflection with a spacing of 4.4 Å [29]. As far as the x-ray data is concerned, thus, the phase is similar to a nematic liquid crystal. In this Brief Report, we studied the structure of this B_x phase in detail using the microbeam synchrotron radiation (SR) x-ray experiment, and found that it is identical with the intercalated B_6 structure, but different from that so far speculated with respect to the direction of the frustration.

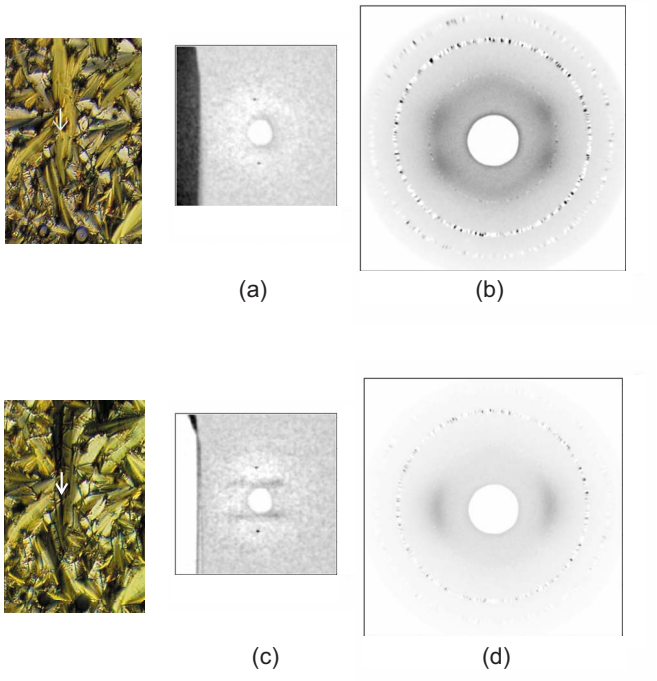


FIG. 3. (Color online) Microbeam x-ray patterns taken by focusing on the fan-shaped texture domain of the B_x phase. The white arrows on the micrographs indicate the location of beam incidence. (a) and (b) show the patterns in the small-angle and wide-angle regions at the DC-OFF state. The patterns (c) and (d) are observed on applying a dc voltage parallel to the beam incidence direction (75 V for 25 μm cell).

The microbeam SR x-ray experiment was performed at the Photon Factory on the beamline 4A (Tsukuba, Japan). The beam size was roughly 3×4 μm^2, and the energy was 14 keV ($\lambda=0.88$ Å). The x-ray diffraction profile was recorded using a two-dimensional charge-coupled device (CCD) as an area detector.

The sample for a microbeam x-ray measurement was prepared by using a sandwich-type glass cell coated with indium-tin-oxide (ITO) electrodes. Figure 3(a) shows the x-ray pattern in a small-angle region taken by the irradiation on a single domain of fan-shaped texture. One can find the clear layer reflection with a spacing of 18.1 Å although the exposure time to obtain the current intensity of the layer reflection was needed ten times as long as that of the conventional smectic phase. The intensity is thus weak, but it is fairly sharp. The correlation length estimated with the aid of the Scherrer equation [31] is around 300 Å so that there is a well-developed layer order in the B_x phase. Thus, the extremely small intensity that could not be detected by means of a common laboratory-scaled x-ray might be attributable to the enormously small value of structure factor at this 2θ

region. The spacing of reflection, 18.1 Å, is nearly equal to half a length of molecule. The observed reflection is hence indexed with (002) and the lack of (001) reflection suggests the frustrated phase such as B_1 phase. Figure 3(b) shows the corresponding wide-angle profile. It can be found that the broad outer reflections with a spacing of 4.4 Å are split above and below the equator. This indicates that the bent-shaped molecules are laterally packed into a layer with a liquidlike nature, but with a biaxiality in which a bent direction is parallel to the cell substrate.

When an external dc voltage was applied perpendicularly to the cell substrate, the fan-shaped texture is invariably observed, but a birefringence is significantly changed. On this transformation, no switching current is observed, showing that the response to an external field is not due to the spontaneous polarization, but the dielectric anisotropy. On the other hand, the microbeam x-ray pattern shows a distinct change as shown in Figs. 3(c) and 3(d). In the small-angle diffraction pattern of Fig. 3(c), the (002) reflection is still observed as two spots, but is newly followed by the diffuse scatterings at a height ($1/36$ Å^{-1}) of the first layer line. Further, a significant change can be seen in the wide-angle pattern of Fig. 3(d). The four broad outer reflections observed at the DC-OFF state is altered to the two broad ones located just on the equator, i.e., in a direction perpendicular to (002) reflection. Thus, we know that the molecules are now aligned with the bent direction perpendicular to the cell substrate.

These characteristic diffraction patterns observed at the DC-OFF and DC-ON states are definitely indicative of the structure of the B_6 phase, which has so far been speculated in the literature [20,23–28]. The molecules lie perpendicular to the layer since twice the d-spacing of (002), 36.2 Å, corresponds to the calculated molecular length of 36.8 Å. The significant difference between the B_x and B_1 phases is observed in the profile of (101) reflection; it is sharp in the B_1 phase, while broad in the B_x phase. This means that the size of antidomain is not definite in the B_x phase, but fluctuates from the position to position. The diffraction characteristics are clear from the different electron density distributions shown in Fig. 4. The maximum position of the diffuse scattering along the first layer line corresponds to 23 Å, giving the average lattice size of $a=30$ Å. Hence, the three or four molecules on an average are included in each antidomain. This number is fairly smaller than that reported in the B_1 phase. From the small-angle and wide-angle x-ray patterns of Figs. 3(c) and 3(d) at the DC-ON state, we know that the direction of the intercalated structure is perpendicular to the bent plane as illustrated in Fig. 1(d). This is similar to that in the B_1 phase [13–15,18], but different from the model structure of the B_6 phase in Fig. 1(c), which has been speculated [22].

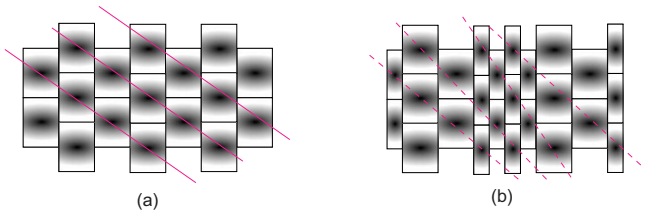


FIG. 4. (Color online) Electron density distribution in (a) B_1 and (b) B_x phases.

In summary, we clarified the structure of the unknown B_x phase in the short terminal homologue, 4Br-P-4-O-PIMB, by focusing a microbeam of x ray on the well-developed fan-shaped texture. From the highly oriented x-ray patterns detected at the two states of DC-ON and DC-OFF, the unknown B_x phase is found to have the similar frustrated structure as the B_6 phase. The molecules lie perpendicularly to the layer, and the frustration takes place perpendicularly to the bent direction similarly as in the B_1 phase. Unlike in the B_1 phase, however, the size of the resulting antidomain is not definite, but fluctuates from position to position.

It is likely that the B_x phase is assigned to the B_6 phase, but its properties are very special and different from those of typical B_6 phases. The layer reflection of (002) is very weak, whereas it is strong in typical B_6 phases. It seems to be relatively easy to obtain a homeotropic Schlieren texture in the present B_x phase, whereas in many of the B_6 phases it is not possible to get a homeotropic alignment, i.e., a fan texture is observed under all conditions. Therefore, the assignment of the B_x phase to the B_6 phase should be carefully examined. The study is now in progress to clarify why the size of antidomain in the B_x phase fluctuates and whether the fluctuation takes place in a statistic or dynamic manner.

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