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Analysis of the intralayer molecular orientation in the B1 phase of a bent-core liquid crystal molecule using X-ray microbeam

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アキラル屈曲型液晶の B1 相構造に関して、X 線マイクロビームでその配向解析を行った。結果、これまで提案されていた 2 つの構造のうち、 $Col(pm2,m)$ の対称性を持つ屈曲面に垂直な面内に 2 次元周期構造を有することがわかった。

Achiral bent-core liquid crystals are very interesting from a viewpoint of "chirality" which appears in an "achiral" molecular system [1], and have been investigated experimentally and theoretically by many researchers. The bent-core molecules exhibit specific mesogenic phases, B1~B8, different from those in rod-like molecules. The determination of the structure in each phase is crucial but difficult, because of difficulties in obtaining large uniform domains. The B1 phase was found in P-6-O-PIMB (Fig. 1(a))[2]. A two-dimensional (2D) modulated structure ($Col(p2mg)$) was proposed for the phase, as shown in Fig. 1(b), based on macroscopic x-ray diffraction. On the other hand, another 2D structure ($Col(pm2,m)$) shown in Fig. 1(c) has been very recently proposed in the other compound [3].

In order to determine precisely the molecular orientation in the B1 phase, X-ray micro-beam-diffraction measurements were carried out on BL-4A. The relation between the layer structure and the intralayer molecular orientation was discussed. The sample used was P-6-O-PIMB (see Fig. 1(a)), and was sandwiched between two 80- μm -thick glass plates coated with an ITO electrode. The cell gap was 29 μm . We could obtain relatively large uniform B1 domains, as shown in Fig. 2(a), by gradually cooling from the isotropic liquid. The X-ray energy was 14 keV and the beam size was $3 \times 4 \mu\text{m}^2$ [4]. A CCD camera with an image intensifier was used as a 2D detector.

Figure 2(b) shows the 2D X-ray profiles at small and wide angles before applying an electric field. At small angles, only one pair of (002) spots was observed. The corresponding spacing (19.3 Å) is almost equivalent to half of the molecular length. At wide angles, four diffuse peaks were observed symmetrically with respect to (002) spots, and the angle between them, $\Delta\theta(36.7^\circ)$ is close to a supplementary angle of the molecular bending angle $\alpha(=132.3^\circ)$ (see Fig. 1(a)). Figure 2(f) shows the 2D X-ray profiles at small and wide angles, obtained from the same irradiated spot under the application of a DC electric field. At small angles, additional two pairs of spots corresponding to 29.1 Å appear symmetrically with respect to the (002) spots. At the wide angles, the diffuse-scattering pattern also changes to two peaks. This pattern arises from the 2D modulated structure, and the additional spots correspond to (101). Considering that the powder x-ray diffraction results exhibit (002) and (101) diffraction peaks regardless of the field application [2,3], we concluded that this change of diffraction pattern is not caused by the structure change, but by the layer (or molecular) orientation change. Our result indicates that, without an electric field, molecules align with their molecular bending plane parallel to the glass substrate as shown in Fig. 2(d). At this stage, the modulated plane is normal to the substrate, so that the (101) peaks are not observed due to the mismatch of Bragg condition. When the electric field is applied, the molecular bending plane reorients to be normal to the substrate due to the dielectric anisotropy, and the modulated plane becomes parallel to the substrate as shown in Fig. 2(h), resulting in the emergence of the (101) peaks. This layer structure is just the same as that in Fig. 1(c), whose group symmetry is $pm2,m$. Hence it is necessary to reexamine the structure of the B1 ($Col(p2mg)$) phase of other compounds.

The orientational order parameter S of the mesogenic part of each side wing was estimated from each diffuse-scattering peak as shown in Figs. 2(c) and (g), based on the Maier-Saupe mean-field theory. S is 0.78 and 0.65 before and after applying the field. These values are comparable to that in the SmA phase, suggesting that the molecules align with a high orientational order.

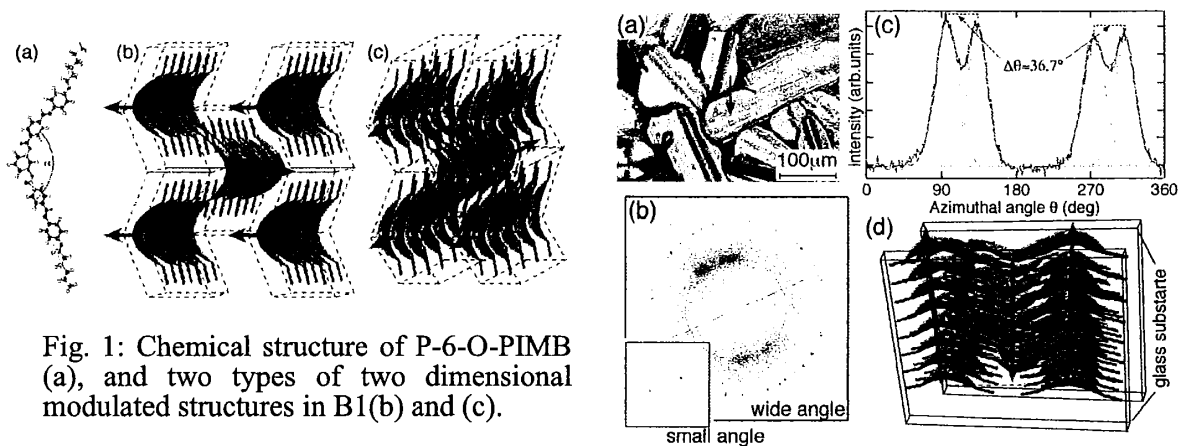


Fig. 1: Chemical structure of P-6-O-PIMB (a), and two types of two dimensional modulated structures in B1(b) and (c).

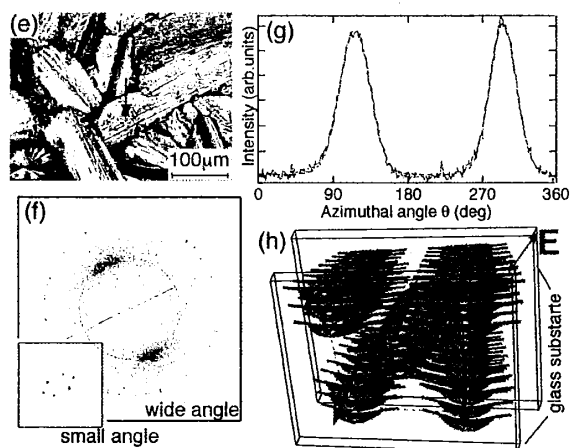


Fig. 2: (a) Microphotograph showing an irradiated position (red arrow) of P-6-O-PIMB before a DC field application. (b) 2D small-angle and corresponding wide-angle X-ray profiles. A dot-and-dash line indicates the layer normal direction. (c) The intensity profiles as a function of equatorial arc along a dotted circle in (b). A dotted line is a fitted curve using Gaussian function. (d) Molecular orientation of the B1 phase before applying the field. (e) Microphotograph showing an irradiated position (red arrow) of P-6-O-PIMB during the DC field ($3.1 \text{ V}/\mu\text{m}$) application. (f) 2D small-angle and corresponding wide-angle X-ray profiles during the DC field. (g) The intensity profiles as a function of equatorial arc along a dotted circle in (f). A dotted line is a fitted curve using a Gaussian function. (h) Molecular orientation of the B1 phase during the field application.

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