SYNCHROTRON X-RAY MICROBEAM CHARACTERIZATION OF SMECTIC A LIQUID CRYSTALS UNDER ELECTRIC FIELD

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ABSTRACT

When an electric field is applied to chiral smectic A (SmA) liquid crystals, a tilt is induced in the director of orthogonal SmA liquid crystals (electroclinic effect). The layer shrinkage due to the tilted smectic arrangement is mitigated by local layer deformation. This paper presents detailed measurements of the local layer spacing under the electroclinic effect of the chiral SmA phase in a surface-stabilized liquid crystal cell, performed using time-resolved synchrotron X-ray microbeam diffraction with a high-resolution CCD X-ray detector. It is shown that the layer spacing variation corresponds well to the applied electric field and the horizontal chevron angle. Further, techniques for the simultaneous measurement of layer deflection and molecular orientation are discussed.

INTRODUCTION

The electroclinic effect (Garoff and Meyer, 1977) induces a tilt in the director of orthogonal smectic A (SmA) liquid crystals near the SmA–chiral smectic C (SmC\textsuperscript{#}) phase transition under the application of an electric field. This phenomenon has attracted considerable attention for understanding the electro-optical behavior of pre-transition phenomena in liquid crystals (Lagerwall, 1999; Williams \textit{et al}., 1991). A study of the dynamics of the layer structure as well as the molecular orientation is important in understanding the electro-optical behavior of a surface-stabilized liquid crystal cell. One of the characteristic features of the layer structure is the formation of the so-called chevron layer due to the shrinkage in the layer spacing induced by molecular tilt under an electric field (Shao \textit{et al}., 1991; Rieker \textit{et al}., 1987; Selinger \textit{et al}., 2000). A striped texture along the layer normal usually appears in connection with the chevron structure when observed under a polarizing optical microscope. Recently, the static and dynamic local layer structures in the electroclinic effect have been analyzed in detail by time resolved X-ray microdiffraction using synchrotron X-rays (Iida \textit{et al}., 2005). As the applied field increased, the layer structure of the electroclinic liquid crystal changed from the bookshelf to the compound chevron, and
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subsequently, it changed to the horizontal chevron (Fig.1).

The direct result of the electroclinic effect is the molecular tilt in relation to the layer normal along with layer shrinkage, while the layer deformation (such as the formation of the chevron layer structure) is induced by the interaction between molecules and the alignment film of the surface-stabilized cell. A previous study has reported the relation between the molecular orientation and the layer deformation (Iida et al., 2010). In addition, although we carried out the preliminary layer spacing measurement during the electric field application (Iida et al., 2005), the precision of the measurement was not satisfactory.

In the present study, the layer spacing dependence on the applied electric field is measured in order to examine the direct effect of the applied electric field with sufficient accuracy. The layer spacing dependence and its relation to the layer structure is also discussed. Furthermore, the techniques for the simultaneous measurement of the layer spacing, layer deformation and the molecular orientation were tested preliminarily in order to overcome the change in the layer response characteristic under prolonged electric field application (Iida et al., 2005).

EXPERIMENTAL

The sample and the cell alignment condition are the same as previous experiments (Iida et al., 2010). A ferroelectric liquid crystal sample was TK-C101 (Chisso) (Takanishi et al., 1996) and was sandwiched between ITO-coated glass plates (80 μm thick) with

Fig.1 Schematic drawing of layer structures of the smectic liquid crystal in the surface stabilized cell. Coordinates and rotation axes are also shown. X-rays are incident along Z axis. δ and γ are the layer deflection angles.
polyimide alignment films. The phase sequence is isotropic (80°C) N* (70°C) SmA (56°C) SmC*. The experiments were performed in the SmA phase at 0.5°C to 1.0°C above the phase transition temperature. The cell gap was about 7 μm.

The X-ray experimental conditions are briefly described. The synchrotron X-ray micro-diffraction experiments were carried out on beam-line 4A at the Photon Factory. A combination of a double multilayer monochromator and Kirkpatrick–Baez mirrors was used for X-ray optics. The beam size was slightly less than 5 × 5 μm² and the angular divergence of the incident beam was approximately 0.7 mrad in the horizontal direction. The X-rays were incident on the sample normal to the cell surface. The rubbing direction was set to horizontal.

For the layer diffraction measurement, the incident X-ray energy used was 9.5 keV. We used an image–intensified CCD X-ray camera (Hamamatsu C4880-50) with a pixel size of 23.4 μm; this size is approximately 5 times smaller than the pixel size used in the previous measurement (Iida et al., 2010). The X-ray detector was placed 175cm away from the sample. Fig.2(a) shows a section of the Debye ring obtained from the sample without the alignment process (powder pattern); this ring was used as a reference to correct the layer spacing variation.

Several experimental arrangements were tested for the simultaneous measurement of the layer deformation, molecular orientation and the layer spacing. These are described in the following section.
LAYER SPACING VARIATION DUE TO ELECTROCLINIC EFFECT

The time resolved measurement of the electroclinic liquid crystal was carried out in the quasi-static mode using a triangular waveform electric field (10 Hz, ±25 V). The diffraction data within a certain measurement time were summed and stored separately. In the present case, one cycle of the triangular field was divided into 24 subdivisions so that the time resolution was 4.17 ms (voltage resolution was 4.17 V).

Fig.3(a) shows the $\omega$–angular intensity distribution obtained in the time integration mode, in which the integrated intensity of the layer diffraction peak during the electric field application was measured as a function of the sample position across the striped texture (Y), i.e., normal to the rubbing direction and parallel to the layer (see Fig.1). The peaks at near $\omega = 0^\circ$ (central peak) and $\omega = \pm 5^\circ$ (side peak) are due to the horizontal chevron and vertical chevron, respectively. It is seen that the compound chevron is realized from the alternate intensity variation between the central and the side peaks, and its periodicity is approximately 10 $\mu$m. Fig.2(b) shows an example of the time resolved reflection pattern obtained at $\omega = 0^\circ$ for an applied field between 20.8 V and 25 V. Two separate diffraction spots are due to the horizontal chevron. The time resolved $\chi$–angular distribution obtained at $\omega = 0^\circ$ and Y =
9 \( \mu \text{m} \) as a function of time (applied electric field) for a half cycle of the triangular wave form is shown in Fig.3(b). The chevron angle depends on the applied field. Since the beam divergence due to the focused microbeam was large (0.7 mrad), the center of mass for each diffraction pattern was calculated, and the geometrical deformation of the diffraction pattern was corrected using the reference data (Fig.2(a)). Fig.4 shows the relative layer spacing variation \( \Delta d/d_0 \), where \( d_0 \) denotes the layer spacing without an electric field, and \( \Delta d \) represents the change in the layer spacing from \( d_0 \), as a function of time (applied field) during a half cycle of the applied field. The molecular tilt is proportional to the magnitude of the applied field. In addition, the layer spacing deduced from the horizontal chevron angle \( (\Delta d/d - \gamma^2/2) \) is shown. The layer spacing changes during the field application: further it corresponds to the chevron angle. The previously reported preliminary results (Iida et al., 2005) were thus clearly confirmed.

**SIMULTANEOUS MEASUREMENT OF LOW- AND WIDE-ANGLE SCATTERING**

As shown in our previous paper (Iida et al., 2005), the chevron formation depends on the history of the applied electric field; prolonged application of the electric field changes the bookshelf to the compound chevron and subsequently to the horizontal chevron. This layer structure change is due to the interaction between the electroclinic effect and the anchoring effect at the alignment interface. A simultaneous measurement of the molecular orientation and the layer orientation (chevron angle) or the layer spacing is much preferable to sequential measurements in order to characterize the electroclinic effect quantitatively, since the sequential measurements may lead to analysis of different layer structures. The molecular orientation can be obtained by means of wide angle halo scattering with a detector placed near the sample, while the layer structure is measured by means of a low–angle Bragg reflection with a high resolution detector set at a distance from the sample. Two types of simultaneous time resolved measurement systems are preliminarily examined in the study.

When a 6–in. image–intensified X-ray CCD camera was used for recording the full halo
pattern, the resolution for the low–angle layer diffraction was poor. A method to improve the low–angle scattering resolution is to move the camera downstream and record the layer diffraction and the halo pattern by using incident X-rays of the fundamental energy and those of higher harmonics, respectively (dual energy technique). This arrangement can be realized, because a conventional Si (111) double crystal monochromator has third and higher harmonics. The halo pattern appears perpendicular to the layer diffraction, consequently, each scattering does not overlap. Since the double multilayer monochromator was used in the present experiment, the second harmonic appeared. Fig.5(a) shows the overlapped diffraction pattern of the halo and the layer diffraction in the vertical and horizontal directions, respectively. The fundamental energy value for the layer diffraction was 8 keV and an absorber was inserted to reduce the incident X-ray intensity in order to avoid radiation damage of the liquid crystal sample. Though the second harmonic is weak due to the low critical energy of the Photon Factory 2.5 GeV ring (4 keV), two sets of scattering appear separately. If this technique is used at the higher critical energy beamline (e.g., the wiggler beamline or a beamline on the high energy third generation ring), the intensity of the higher harmonics is much stronger than the one shown in Fig.5(a). The resolution for the low–angle scattering can be greatly improved in this case. This technique is used for obtaining the layer scattering and the halo scattering simultaneously with one detector and can be easily extended to the time resolved measurement.

If another two–dimensional (2D) detector is placed near the sample to obtain the halo pattern in addition to the present experimental arrangement, two scattering are obtained simultaneously with different detectors. A simultaneous time resolved measurement can be realized by applying the same gate signal to both detectors. Fig.5(b) shows one halo pattern obtained by a compact pixel array detector (PILATUS 100K, Dectris) placed 18cm away from the sample. The layer diffraction was obtained simultaneously with a high resolution CCD, in a manner similar to the one obtained in Fig.2(b). Due to the high signal to noise ratio of the pixel array detector, no background subtraction was required in order to obtain the pattern.
shown in Fig. 5(b). The simultaneous time resolved measurement with this scheme is now underway.

In summary, the layer spacing in the electroclinic effect of the chiral smectic A phase in the surface stabilized cell near the phase transition temperature has been measured in detail using the time resolved synchrotron X-ray microbeam diffraction technique with a high resolution CCD X-ray camera. The layer spacing change during the field application well corresponds to the chevron angle. Further, techniques which measure the layer deflection and the molecular orientation simultaneously have been examined.

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