**E–T** phase diagrams with EFIB contours and RXRS in Se-containing chiral smectic LC mixtures frustrating between ferro- and antiferro-electricity

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In the binary mixture system of AS657–MHPOCBC, we have drawn **E–T** phase diagrams with EFIB (Electric-Field-Induced Birefringence) contours and found several temperature- and electric-field-induced subphases. Some of their approximate flat (planar) superlattice structures are successfully determined by using RXRS (Resonant X-Ray Scattering) intensity data. Thus we can appreciate the appropriateness of Emelyanenko-Osipov’s LRILIs (Long-Range InterLayer Interactions) to calculate the non-planar structures.

**Keywords:** E–T phase diagram, RXRS, Se containing compound, MHPOCBC, MHPOOCBC

1. Introduction

The frustration together with LRILIs may cause the temperature-induced sequence of phase transitions, producing a variety of optically biaxial polar subphases between the two main phases, SmC A and SmC* [1]. Biaxial subphases have non-planar superlattice structures with microscopic short-pitch, highly distorted helical director arrangements in their unit cells [2-4]. We have insisted on the appropriateness of specifying the biaxial subphases, which emerge sequentially in the temperature-induced transition, by the relative ratio of ferroelectric [F] and antiferroelectric [A] orderings in the superlattice structure unit cell, i.e. \( q_T = [F]/([A] + [F]) \). The subphases with 3- and 4-layer superlattice structures, 1/3 and 1/2, were well established by resonant X-ray scattering (RXRS).

Additional subphases, 1/4, 2/5, and 3/5, have been reported to exist by performing careful electro-optical investigations [1]. Their superlattice structures have, however, not been studied systematically by RXRS, except for two special cases [5,6]; because of the difficulties in performing RXRS as well as a lack of appropriate materials. Here we show by some preliminary investigations that two binary mixture systems, MHPOCBC–AS567 and AS657–MHPOOCBC, the structural formula of which are given in Fig. 1, are useful for systematic RXRS after pinpointing the composition and temperature for a particular subphase by drawing the **E–T** phase diagram with EFIB contours. Notice that RXRS and EFIB are thoroughly complementary for studying subphase details.

Figure 1: Structures of the relevant compounds [1,7]. The (S)-moieties are used in the present experiments.

2. Experiment

Homeotropically aligned 25-µm-thick cells were prepared to measure EFIB using a photoelastic modulator (PEM) set-up. The cell was constructed using a bottom glass plate with two indium tin oxide (ITO) electrodes separated by a distance of 180 µm and a top normal glass plate set apart from the bottom one by a 25-µm-PET spacer. The two ITO electrodes on the bottom glass plate were used for applying an in-plane electric field for measuring EFIB. Homeotropic alignment in a cell was achieved by coating Dow Corning 9-6346 silane coupling agent and by curing at a temperature of 120 °C for 30 min. The cell was heated and filled with a sample mixture in the isotropic phase and cooled slowly to SmA. The cell was in a temperature-controlled hot stage, where the temporal fluctuation is regulated within an accuracy of 0.01 °C or better but the spatial uniformity throughout the aperture of 1 mmϕ is about 0.1 °C. The homeotropic alignment was confirmed by examining the cell under the polarizing microscope.
3. Results and discussion

Figure 2 illustrates the $E$–$T$ phase diagrams of (a) pure AS657 and (b) an MHPOCBC binary mixture containing 90 wt.% AS657. In addition to the ordinary subphases, 1/3 and 1/2, two other subphases are observed in both (a) and (b). By referring to the systematic investigations in the MHPOCBC–MHPOOCBC binary mixture system [1], we can identify these two subphases as $qT=1/4$ and $2/5$, respectively. In fact, the emergence of the antiferroelectric 1/4 subphase with the 8-layer unit cell is confirmed by RXRS in the AS657 90 wt.% mixture, the planar structure of which is not in contradiction to the non-planar structure predicted theoretically [8,9].

The other ferrielectric subphase identified as 2/5 in Fig. 2 (a) and (b) is also studied by RXRS to find its 10-layer periodicity, although further details are not clarified yet. The phenomenological Landau model predicts that the 2/5 subphase is antiferroelectric but not ferrielectric [8]. The partially molecular model in its prototypical form, on the other hand, can stabilize the ferrielectric 2/5 subphase, although it also predicts the stabilization of 3/7 subphase with the 7-layer unit cell [9]. In the MHPOCBC–MHPOOCBC binary mixture system, the emergence of the subphase(s) between 1/3 and 1/2 is not so clear as in Fig. 2.

Applying an electric field stabilizes another ferrielectric subphase as seen in Fig. 2 (a), which may stably emerge even at zero field in a binary AS657–MHPOOCBC mixture as anticipated from the previous systematic studies of the MHPOCBC–MHPOOCBC binary mixture system [1]. This ferrielectric subphase must be specified by 3/5 or 2/3. By taking account of superlattice structures consisting of up to 10 smectic layers, the prototypical partially molecular model predicts ferrielectric 3/5 and 2/3 subphases with 10- and 6-layer unit cells, respectively, although these subphases exist only for extremely restricted parameter values [9]. In order to study the biaxial subphase that emerge close to the optically uniaxial Sm$C^*_A$ subphase, we need to extend the partially molecular model by taking account of the frustration among the three main phases, Sm$C^*_A$, Sm$C^*$, and SmA. Takanishi et al. observed the ferrielectric 2/3 subphase in a Br-containing compound by RXRS [6].

Systematically investigating the two binary mixture systems, MHPOCBC–AS657 and AS657–MHPOOCBC, first by drawing $E$–$T$ phase diagram and then by measuring RXRS under an applied electric field must prove the appropriateness of the extended partially molecular model in the near future.

References