Molecular orientation behavior of chiral nematic liquid crystals based on the presence of blue phases using polarized microscopic FT-IR spectroscopy

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Study on molecular orientation behavior of highly twisted chiral nematic liquid crystals (N’LCs) expressing blue phases (BPs) is important for developing new devices. This study examines the change of molecular orientation of N’LCs due to the presence of BPs. Polarized microscopic FT-IR spectroscopy was used to study the in- and out-of-plane molecular orientations of N’LCs that undergo a phase transition involving BPs. The band intensity ratio of CN to CH2 stretching modes (CN/CH2) in the IR spectra was used to determine the orientation of N’ LC molecules. The measured spectra indicated that the helical axis of N’LC molecules was perpendicular to the substrate before heating and inclined on the substrate after cooling the sample which has phase transition from BP I to chiral nematic (N’). The N’ LC molecule in the cell of rubbed orientation film exhibited the in-plane anisotropy after a heating-cooling ramp only in samples that passed through BP I. These results indicate that the changes of molecular orientation of N’ LC by phase transition are affected by BP I.

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1. Introduction

Chiral nematic liquid crystals (N’LCs) that exhibit the blue phases (BPs) have been attracting considerable attention as fast-response materials for next-generation liquid crystal displays (LCDs) [1]. BPs were first observed by Reinitzer in 1888 in samples of cholesterol benzoate upon cooling; however, it was not until the work of Armitag et al. in 1975 that BPs were shown to be stable, distinct and thermodynamic phases of liquid crystals (LCs) [2]. BPs occur within a small temperature range (1–2 K) at the boundary of the chiral nematic (N’) and isotropic phases of N’LCs. While molecules of N’LC are oriented uniformly in directions perpendicular to the helical axis, the molecules are rotated with respect to one another along the helical axis. In contrast, LC molecules in BPs produce a biaxial helical structure. This configuration is referred to as a “double-twist cylinder.” The double-twist cylinder structure of LC molecule and defects called disclination [3] form three-dimensional structure in lattice of BPs. These cylinders are fitted to form lattice into a three-dimensional structure. However, they have not been fill the full space without defects [4]. BPs have been subdivided into three different according to the temperature at which the phase transition occurs, BP I, BP II and BP III [5]. BP I and BP II have cubic symmetry, whereas BP III has the same symmetry as the isotropic phase. Specifically, BP I and BP II form body-centered and simple-cubic lattices, respectively.

BPs with these characteristics has been examined for use in LCDs. In Kikuchi et al. [6], cross-linked polymer networks were selectively concentrated in disclination lines to stabilize the lattice structure of BPs across a larger temperature range. The dependence of the temperature range of BPs on alkyl or alkoxy chain length has been investigated by the LC molecules that exhibit the nematic (N) phase [7,8]. The structure of cholesteric liquid crystal expressing BPs has been studied by Bragg diffraction using visible and near-ultraviolet lights as well as electron microscopy [9,10]. In contrast, while change in the CH stretching mode in N’LC by the phase transition has been studied by IR and Raman spectra [11,12], change in molecular orientation have not been studied for N’LC phase transitions that involve BPs. The phase transition behavior of ferroelectric LCs, wherein the molecular orientation and conformation indicate ferroelectricity or antiferroelectricity, has been characterized using parallel and perpendicular bands with respect to the molecular axis in IR spectroscopy [13–16]. It is important to understand the changes of molecular orientation of N’LCs undergo
during phase transitions that involve BPs. These orientation behaviors are essential for producing high quality LCDs.

Previous studies on the orientation of LC molecules have analyzed the IR band intensity of each functional group in the LC molecule [17,18]. In this study, polarized microscopic FT-IR spectroscopy has been applied to the study of in- and out-of-plane changes in the molecular orientation of NLCs that undergoes phase transitions through BPs. The purpose of this study is 1) to elucidate the changes in molecular orientation of NLCs that expresses BPs during phase transitions, and 2) to prove the effect of BPs in molecular orientation change of NLCs.

2. Experimental

The base NLC materials were mixture of 5CB, 6CB, 5OCB and 7OCB (Tokyo Chemical Industry Co., Ltd, 98.0%); and ISO(6OBA)2 (Midori Kagaku Co., Ltd, 97.0%) was used as a chiral dopant. The chemical structures of the materials are shown in Fig. 1. Two different mixtures of the NLCs were used (on a weight basis): Mixture-1 (5CB/6CB/5OCB/7OCB = 3/2/4/1) and Mixture-2 (5CB/6CB/5OCB/7OCB = 2/1/5/2). ISO(6OBA)2 was doped into the NLC mixtures at 5, 6, 7, 8 and 9 wt%. The parallel-orientation cell was assembled using CaF2 substrates coated with a thin film of polyvinyl alcohol (PVA); substrates were rubbed 0, 1 or 30 times to induce in-plane orientation of the LCs. The NLC samples were sandwiched into the substrates with 14-μm-thick polystyrene films as spacers on either side.

The polarized infrared spectroscopy measurements of NLC samples in the cell were carried out by an FT-IR spectrometer (Perkin Elmer, Spectrum One) equipped with a microscope unit. The temperature was controlled with a hot-stage (Mettler, FP82HT) in the range between 35.0 and 42.0 °C using 0.3 °C steps. The band height from the baseline of each peak in IR spectra was used for analysis of the orientation of NLC molecule.

3. Results and discussion

3.1. Determining NLC phase transition using textured micrographs

Each phase of the NLC in Mixture-1 (7% chiral dopant) is clearly shown in the polarized micrographs in Fig. 2. The following phase transition sequences were observed in Mixture-1 (7% chiral dopant): upon heating BP III at 39.8 °C and isotropic phase at 41.0 °C, and upon cooling BP III at 40.8 °C, BP II at 40.2 °C, BP I at 39.8 °C and the N* phase at 38.0 °C. The BPs expressed during the phase transition were determined from the platelet textures: red, green and blue in BP I; light-blue with a dark background in BP II [3,4,6,19]; and dark-bluish in BP III [20]. The following phase transition sequences were observed in Mixture-2 (7% chiral dopant): upon heating BP III at 47.2 °C and the isotropic phase at 49.0 °C, and upon cooling BP III at 49.0 °C, BP II at 48.4 °C, BP I at 47.6 °C and the N* phase at 46.0 °C. The phase transition temperatures are different for each mixture, while the phase transition sequence is the same. Thus, it was elucidated that the phase transition sequences have not been influenced by the component ratio of base NLCs in this range. In contrast, the NLC comprising 5–6% chiral dopant exhibits no BPs and that with 8–9% exhibits only BP III on cooling. Table 1 shows the phase transition sequence of each
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