Noble Orientation Change with Temperature in Nematic Liquid Crystalline Mixtures

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Unusual alignment phenomena were observed for nematic liquid crystalline mixtures with a dopant having a cyclohexane asymmetric frame. The liquid crystalline molecules changed from being homeogeneously aligned with the glass plates to being homeotropically aligned perpendicular to the glass plates. We report the conditions for the phenomena and discuss the results.

The molecular orientation of nematic liquid crystals is an important topic for a variety of science and technological applications. Kimura and Nakano have reported the theoretical basis of molecular alignment for various conditions.[1,2] In particular, they calculated the surface tension of nematic liquid crystals on a hard flat wall and predicted that the possible orientation phase transitions on the wall were either from a discontinuous planar to a normal transition or from a continuous planar to a tilted transition as the temperature was decreased.[3] Birecki reported the temperature dependences of molecularly aligned cyanobiphenyls on a hard flat wall coated with fluorocarbon polymer.[4] In heptyloxycyanobiphenyl (7OCB) and octyloxycyanobiphenyl (8OCB) systems, the molecular alignment was parallel to the surface at high temperatures, but changed to a normal orientation with decreasing temperature. Zhou and co-workers reported the control of anchoring of nematic liquid crystals at polymer surfaces.[5,6] Control was obtained by variation of the alkyl side chains of polyacrylates.

Also of great interest in the field of liquid crystals is the application of chirality. Chiral nematic (cholesteric) liquid crystals having a macro helical structure are currently used in liquid crystal display (LCD) devices. Generally the chiral nematic materials consist of achiral host mixtures of nematic liquid crystals, and a chiral dopant with a large helical twisting power (HTP). The helical structure of the chiral nematic liquid crystals is induced by the interaction between the host liquid crystalline molecules and the chiral dopants. We have reported many chiral dopants for nematic liquid crystals.[7–9] New chiral dopants were synthesized using optically active *trans*-1,2-cyclohexanedicarboxylic anhydride, and their HTP values were evaluated. Subsequently, we have found that the liquid crystalline mixture shows an unusual change in alignment in the nematic phase. In this paper, we report on this change in alignment of the liquid crystalline mixture.

The new chiral dopant, (1*R*,2*R*)-bis{4-(5-decyl-2-pyrimidinyl)phenoxymethyl}cyclohexane (1^*) was synthesized from (1*R*,2*R*)-cyclohexanedicarboxylic anhydride in the usual way.[10] The optical purity of 1^* was over 99 ee%.

The HTP value of 1^* was evaluated in the host nematic mixture (MERCK LTD., ZLI-1132) using Cano's cell (HTP = $5.0\,\mu m^{-1}$). The chiral dopant (1^*) did not show any mesophases, so the mixture of 1^* (10 wt %) and 5-heptyl-2-{4-(4-pentylphenyl)phenyl}pyrimidine (BP57)[11] (90 wt %) was investigated (Figure 1). The mixture was sandwiched between glass plates (MATSUNAMI GLASS IND., LTD.), which had only been washed with acetone and were not coated, and was observed with a polarized microscope. The mixture showed several mesophases, namely, nematic, smectic A, and unidentified smectic X phases.[12]

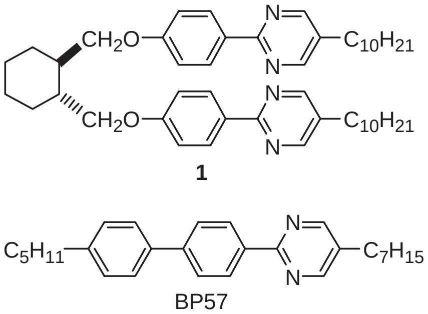

Figure 1. Structures of **1** and BP57.

In the nematic phase, schlieren texture and marble texture were observed at the high-temperature range. This means that the molecular orientation is homogeneously aligned with the glass plates. However, a pseudo-isotropic texture was observed at the low-temperature range. Conoscopic observation of the pseudo-isotropic texture showed that the phase had homeotropic alignment, namely, the director was oriented perpendicular to the glass plates. Therefore, in the nematic phase the molecular orientation changed from homogeneous to homeotropic alignment with decreasing temperature (Figure 2).

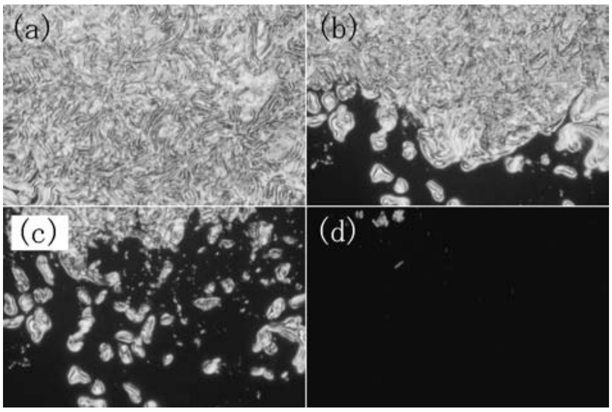

Figure 2. Photomicrographs of the liquid crystalline phase of the mixture. (a) 140 °C, (b) 120 °C, (c) 110 °C, (d) 105 °C.

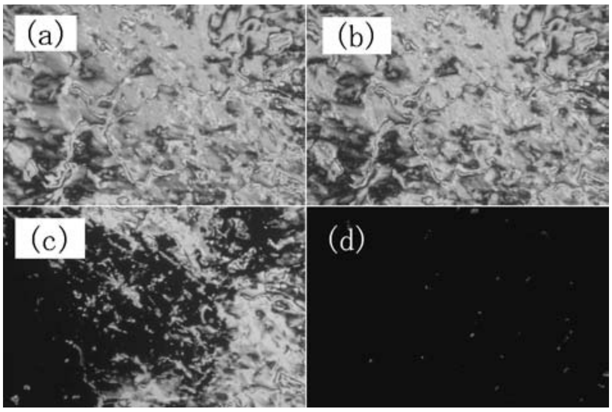

Figure 3. Photomicrographs of the liquid crystalline phase of the racemic mixture. (a) 140 °C, (b) 120 °C, (c) 110 °C, (d) 105 °C.

Generally, the orientation of liquid crystalline molecules is influenced by certain materials such as surface active agents. Elemental analysis of **1*** confirmed its purity was very high. In addition, the orientation change was a reversible phenomenon meaning that other species were probably not playing a role in the orientation. With increasing temperature, the texture of the nematic phase changed from pseudo-isotropic to a schlieren texture. Therefore, it is considered that **1*** did not contain a surface active agent.

Chiral nematic phases usually exhibit a texture of oily streaks under planar anchoring conditions, while under homeotropic anchoring conditions they exhibit fingerprint textures. The observed textures of the chiral nematic mixture suggest that the helical pitch of the mixture is relatively long.

In order to investigate the effect of chirality on the phenomena, a mixture of racemic **1** (10 wt %) and BP57 (90 wt %) was also prepared and observed. The racemic mixture showed a similar orientation change in the nematic phase (Figure 3). This means that the orientation change is independent of the helical structure of the liquid crystals.

Based on this result, it is likely that this phenomenon is a result of the molecular structure of **1**, which is extremely different from that of typical liquid crystals. Many liquid crystalline molecules have rod like structures, that is, they are calamitic. On the other hand, bent-core liquid crystals have shown some interesting liquid crystalline properties.[13] The bent-core molecules show chirality and ferroelectricity despite being achiral.

Yoshizawa and co-workers reported on the synthesis and electrooptic properties of a noble U-shaped liquid crystalline molecule.[14] The U-shaped system effectively reduced the threshold voltage for LCD devices.

The unusual alignment phenomenon must be on the glass surface, so compound **1** probably plays an important role on the surface. The attractive dispersion forces and core–core repulsions of **1** are probably similar as those of rod-like molecules, while the excluded volume effects of **1** must be different. However, Kimura concluded that the nematic molecules align planar at high-temperatures because of the excluded volume effect, but tend to orient normally to the surface at low-temperatures by the attractive energy effect.[3] The structure of **1** is strongly bent and is twisted by the cyclohexane moiety. Therefore, the excluded volume effect of **1** may be small and the attractive energy effect of **1** may be relatively large. Alternatively, a conformational change of **1** could occur on the surface, namely the phenylpyrimidine moieties of **1** could be oriented perpendicular to the surface with decreasing temperature.

In another experiment, the mixture was sandwiched between glass plates coated with polyimide and was rubbed to give homogeneous alignment (E.H.C. CO., LTD.). The mixture was homogeneously aligned and an orientation change did not occur. This result shows that the strength of the phenomenon is weaker than the surface anchoring force.

In conclusion, a mixture of **1** and BP57 showed a noble orientation change on non-treated glass plates regardless of the optical purity of **1**. This phenomenon is probably induced by noble interaction between the host liquid crystalline molecules and **1**, in addition to an interaction between the surface of the glass plates and **1**, which is also important. Other combinations of host liquid crystals and surface conditions should be further investigated.

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10 Analyses: (1*R*,2*R*)-bis{4-(5-decyl-2-pyrimidinyl)phenoxymethyl}cyclohexane: ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.87 (t, $J = 6.80$ Hz, 6H, CH$_3$), 1.18–1.43 (m, 32H, CH$_2$, CH$_2$CC*), 1.57–1.68 (m, 4H, OCH$_2$), 1.77–1.99 (m, 6H, C*H, CH$_2$C*), 2.59 (t, $J = 7.53$ Hz, 4H, ArCH$_2$), 4.97–4.13 (m, 4H, CH$_2$O), 6.95 (d, $J = 9.18$ Hz, 4H, Ar), 8.32 (d, $J = 9.21$ Hz, 4H, Ar), 8.56 (s, 4H, Ar). Anal. Found: C, 78.84; H, 9.36; N, 7.60%. Calcd. For $C_{48}H_{68}N_4O_2$: C, 78.64; H, 9.35; N, 7.64; O, 4.36%. MS $m/z = 732$ [M$^+$]. $[\alpha]_D$ +47° (*c* 1.0, CHCl$_3$). mp 130.5–131.0 °C.
11 Phase transition temperatures on cooling: Iso 163 N 120 SmA 109 SmC 39 Cr.
12 Phase transition temperatures on cooling: Iso 149 N* 107 SmA 46 SmX 38 Cr.
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