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Liquid Crystal Oligomers Exhibiting a Blue Phase

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Liquid crystal blue phases have a fluid lattice whose structure is stabilized by cubic defects. Blue phases, which are classified as BPIII, BPII and BPI observed on cooling, exist over a small temperature range (ca. 1 K) between isotropic and chiral nematic phases. Recently, we reported electro-optical switching with a response time of the order of 10^{-2} s for the BPIII exhibited by a polar chiral T-shaped compound. We describe molecular design of a liquid crystal stabilizing a blue phase III, and discuss electro-optical switching in the blue phase.

Keywords Blue phase; chirality; display; liquid crystal

1. Introduction

Blue phases are potentially useful for application as fast light modulators or tunable photonic crystals. They are classifiable as blue phase I (BPI), blue phase II (BPII), or blue phase III (BPIII) depending on their double-twist-cylinder packing structure [1,2]. The BPI packing structure is a body-centered cubic structure; that of BPII is a simple cubic structure [3,4]. Theoretical investigations have revealed that BPIII and the isotropic phase have identical symmetry [5]. It can be expected that BPIII consists of double twist cylinders with arbitrary orientation [1,6,7]. Blue phases are normally found in a very narrow (*ca.* 1 K) temperature range between the isotropic liquid and a chiral nematic (N^*) phase of sufficiently short pitch. Electric field effects in blue phases have been investigated [1]. The applied field can cause three distinct transformations: local reorientation of the molecules, distortion of the lattice (electrostriction), and phase transition to lower symmetry phases [8–14]. However, their narrow temperature range is a daunting obstacle to their application. Kikuchi *et al.* reported fast electro-optical switching for a polymer-stabilized blue phase I [15,16]. Switching with the speed of 10^{-4} s is attributed to the local reorientation of molecules by an electro-optic Kerr effect. Coles *et al.* reported that eutectic mixtures of three homologues of symmetric dimer doped with a small quantity of a highly twisting chiral additive show BPI of a very wide temperature range; moreover, the BPI shows a wide color range of reflected color in 10^{-2} s by applied electric fields because of electrostriction [17]. On the other hand, an electric-field-induced

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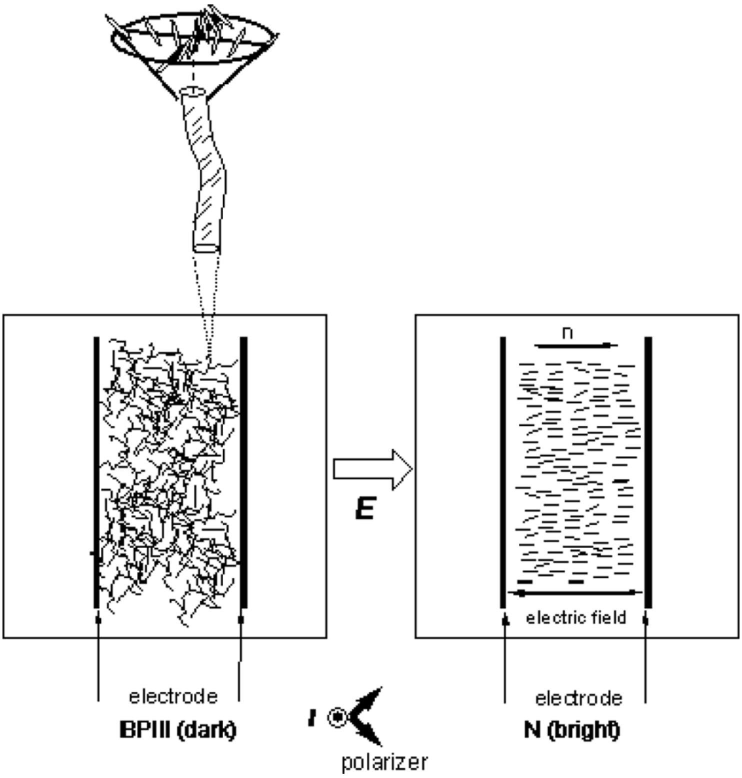


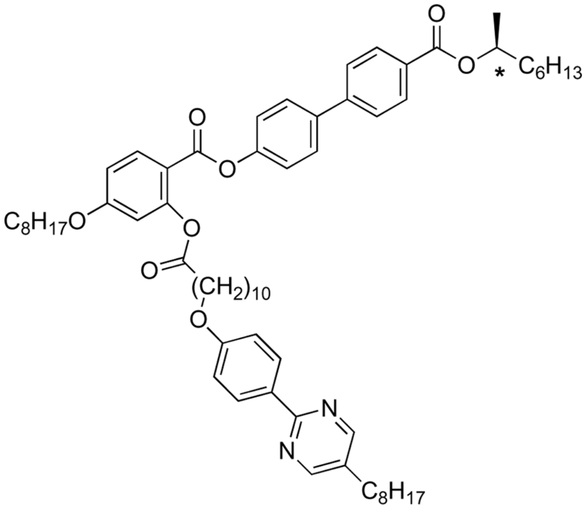
Figure 1. Molecular organization model for the electric-field-induced phase transition between BPIII and N phases.

phase transition in BPI and BPII necessitates higher applied voltages and shows slow switching of more than a few seconds.

Recently, we reported an electric-field-induced phase transition between BPIII and N phases of a chiral T-shaped liquid crystal as shown in Figure 1 [18]. Actually, BPIII has a twisted nematic order that exists microscopically, although it appears to be macroscopically isotropic. Furthermore, BPIII has no periodic defects. Therefore, a well black state is obtainable without surface treatment. Then a homogeneous bright state is achieved in the electric-field-induced N phase. On the other hand, the BPIII was found to be induced in some binary mixtures of T-shaped nematic liquid crystal and a conventional chiral compound [19]. We describe molecular design of a liquid crystal stabilizing a blue phase III, and discuss electro-optical switching in the blue phase.

2. Chiral T-Shaped System

We designed T-shaped chiral compound **1** [20]. The molecular structure and transition temperatures are shown in Figure 2. The T-shaped compound exhibited BPIII with a relatively wide temperature range on cooling. Theoretical work suggests that biaxaility plays an important role in the blue phases [2]. However, the biaxiality in most chiral nematic liquid crystals is slight, and as a result the double twist structure cannot exist in a wide temperature range. The T-shaped system is thought to

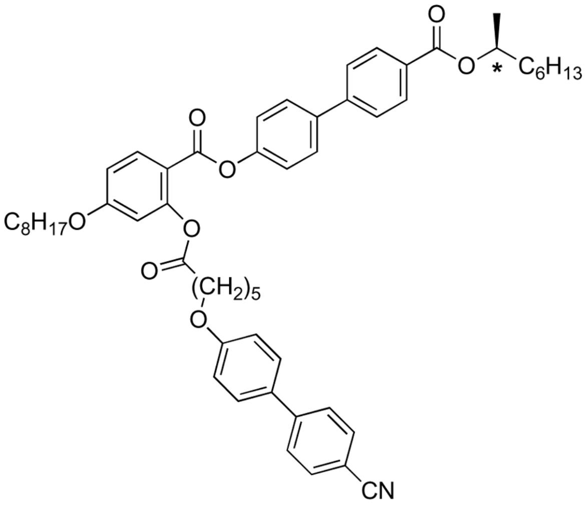


1: Cr 63 [N* 15 BP 28] Iso

Figure 2. Molecular structure and transition temperatures (°C) of compound **1**.

have two origins of twisting power: the chiral center and a twisted conformation of the two mesogenic moieties *via* intramolecular chirality transfer, which can induce biaxial helix to stabilize the double twist cylinders.

Then, we introduced a polar group into the chiral T-shaped system in order to couple the molecule with an electric field. The polar T-shaped chiral compound **2** showed BPIII and N* phases on cooling as shown in Figure 3. We investigated electro-optical effects in the BPIII of compound **2** [18]. Optical transmittance as a function of the AC field at a frequency of 10 Hz was observed for a sample in



2: Cry 63 [N* 15 BP 28] Iso

Figure 3. Molecular structure and transition temperatures (°C) of compound **2**.

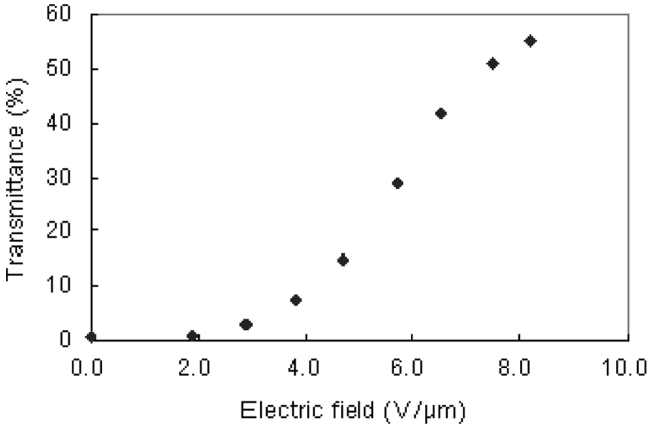


Figure 4. Optical transmittance of compound **2** as a function of an AC field at a frequency of 10 Hz at 47°C. The cell gap was 10 μm. (Reprinted with permission from ref. 18. Copyright 2007 Wiley-VCH Verlag GmbH & Co. KGaA.).

the region between the comb-type interdigitated electrodes under crossed polarizers. The distance between electrodes was 10 μm. Figure 4 shows the voltage-transmittance curve at 47°C.

A dark state with the transmittance of 0.85% is obtainable in the BPIII that is macroscopically isotropic. The change in transmittance as a function of an AC field is attributed to an electric-field-induced phase transition between BPIII and N phases. Figure 5 shows the temperature dependence of response times for the rise and decay processes with an AC field of 8.2 V/μm at 10 Hz. The rise time ($t_{0\text{–}90}$) does not depend on the temperature, indicating that the rise process occurs cooperatively. However, the decay time ($t_{100\text{–}10}$) lengthens with decreasing temperature. The increase of the decay time with decreasing temperature is explainable by temperature dependence of the rotational viscosity [18].

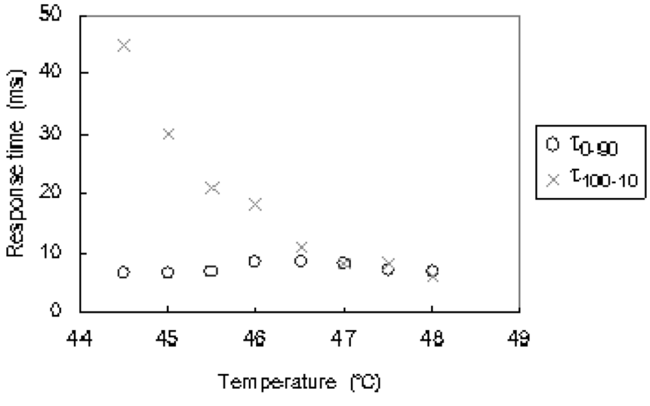


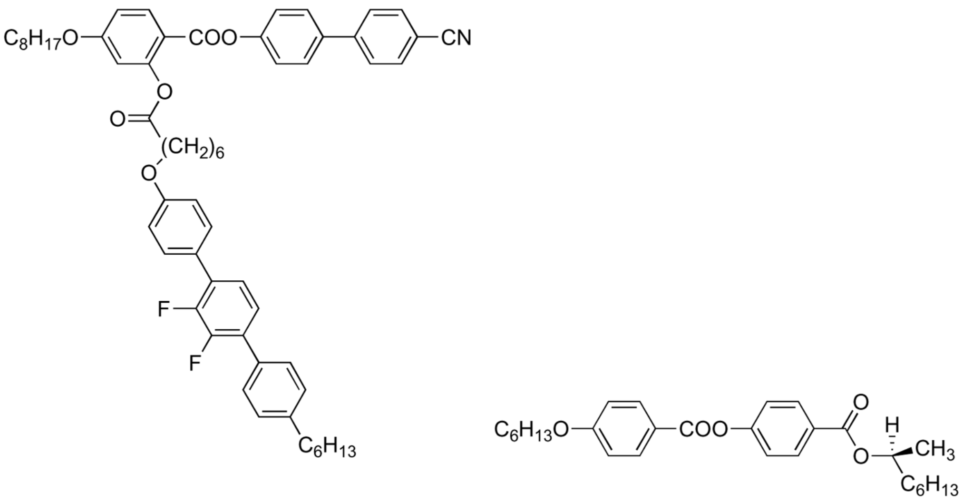
Figure 5. Temperature dependence of response times for the rise and decay processes of compound **2** with an AC field of 8.2 V/μm. The cell gap was 10 μm. (Reprinted with permission from Ref. [18]. Copyright 2007 Wiley-VCH Verlag GmbH & Co. KGaA.).

3. A Binary System of a T-Shaped Nematic Liquid Crystal and a Chiral Compound

Actually, BPIII has a twisted nematic order that exists microscopically, although it appears to be macroscopically isotropic. Furthermore, BPIII has no periodic defects. Therefore, a well black state is obtainable without surface treatment. Then a homogeneous bright state is achieved in the electric-field-induced N phase. However, some problems remain for application of this technology to display devices, i.e., broadening of the temperature range, reduction of the driving voltage, and improvement of the response speed. We have designed a binary system of a host nematic liquid crystal and a chiral compound for developing practical blue phase materials. Recently, we found that blue phases are induced in binary mixtures of compound **3** and a chiral smectic liquid crystal (**S811**) [19]. Molecular structures and transition temperatures of compound **3** and **S811** are presented in Figure 6. Figure 7 shows the binary phase diagram between **S811** and compound **3**. For mixtures containing 30–60 wt% of **S811**, blue phases were observed.

A binary mixture of compound **3** (40 wt%) and **S811** (60 wt%) showed the following phase sequence: isotropic liquid 36°C BPIII 28°C N*; the melting temperature was 44°C. We investigated electro-optical effects in the BPIII [21]. Figure 8 portrays the voltage-transmittance curve at 33°C. The transmittance without an electric field was 0.9%. The transmittance increased concomitantly with the increase of the electric field. With an applied field of 13 V/μm, the transmittance is 85%. The voltage-transmittance curve of the binary mixture is almost identical as that of chiral T-shaped compound **2**.

Subsequently, we investigated the response speed of the electric-field-induced phase transition between BPIII and N phases. Figure 9 depicts the temperature dependences of response times for the rise and decay processes with an AC field of 13 V/μm at 10 Hz. The respective rise and decay times at 35°C are 1.6 ms and



3: Cry 71 N 150 Iso

S811: Cry 41 [SmA 22] Iso

Figure 6. Molecular structures and transition temperatures (°C) of host nematic compound **3** and chiral smectic liquid crystal **S811**.

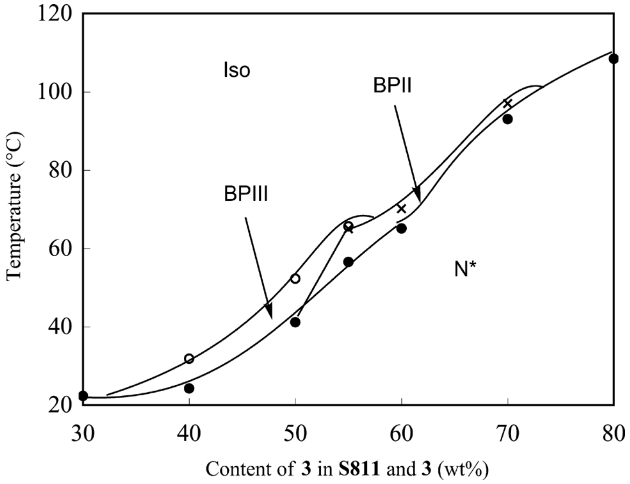


Figure 7. Binary phase diagram between **S811** and compound **3** on cooling.

3.9 ms. They do not depend on the temperature, except near the BPIII-to-N* phase transition. With respect to the response times in the BPIII of chiral T-shaped compound **2**, the rise time does not depend on the temperature, although the decay time lengthens with decreasing temperature. A marked difference exists in the decay process between the binary system and the chiral T-shaped compound. Slowing of the N-to-BPIII transition process of the T-shaped chiral liquid crystal with decreasing temperature is a critical problem for improving the response speed. The separation between chirality and an oligomeric structure can produce the temperature-independent decay process.

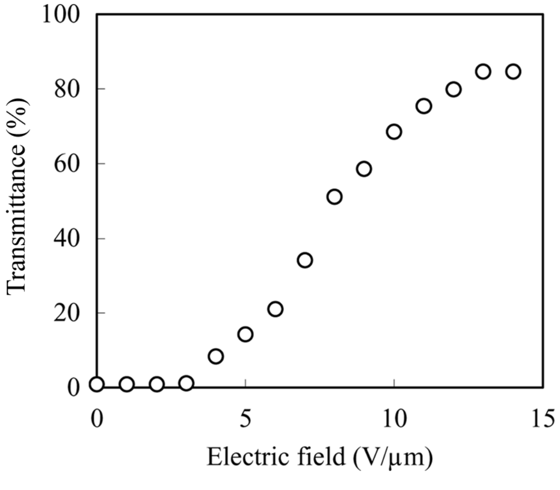


Figure 8. Optical transmittance of a mixture of compound **3** (40 wt%) and **S811** (60 wt%) in the BPIII as a function of an AC field at a frequency of 10 Hz at 33°C. The cell gap was 12 μm. (Reprinted with permission from ref. 21. Copyright 2008 Institute of Pure and Applied Physics.)

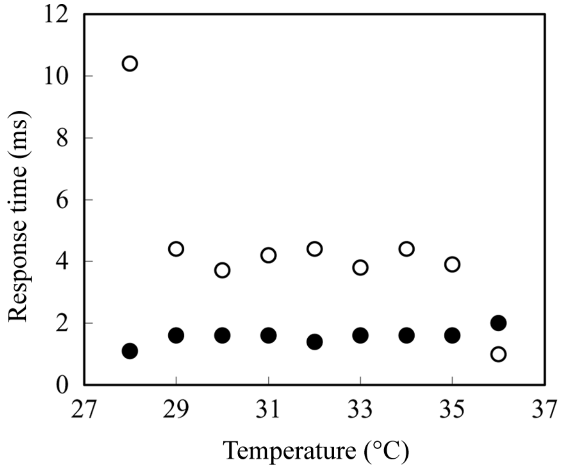


Figure 9. Temperature dependence of response times for rise and decay processes of a mixture of compound **3** (40 wt%) and **S811** (60 wt%) in the BPIII with an AC field of 13 V/μm at a frequency of 10 Hz. The cell gap was 12 μm. Closed circles represent the rise times; open circles denote the decay times. (Reprinted with permission from ref. 21. Copyright 2008 Institute of Pure and Applied Physics.)

4. Summary

We have designed liquid crystal oligomers stabilizing BPIII. The electo-optical switching in the BPIII is attributed to an electric-field-induced phase transition between BPIII and N phases. A well black state is obtainable in the BPIII without surface treatment and a homogeneous bright state has been achieved in the electric-field-induced N phase. There is no marked difference in the BPIII-to-N transition behavior between the T-shaped chiral liquid crystal and the binary system. However, the decay time of the N-to-BPIII transition of the binary system does not depend on the temperature, although that of the T-shaped chiral liquid crystal lengthens with temperature. Switching speed of the electric-field-induced BPIII-to-N transition depends on magnitude of dielectric anisotropy of a liquid-crystalline material, on the other hand, the chirality is thought to play an important role in the N-to-BPIII process.

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