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## Liquid crystalline amorphous blue phase and its large electrooptical Kerr effect

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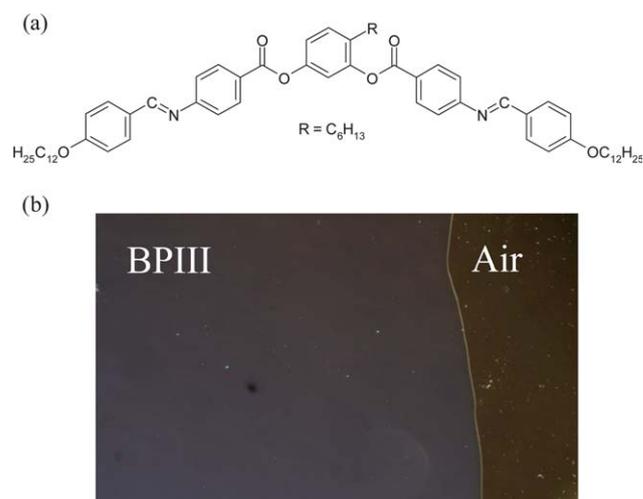
**An amorphous blue phase III with low and wide thermal range (~20 °C) including room temperature is induced by doping a bent-core nematic with a strong chiral material. We confirm that the electrooptical response is due to the Kerr effect, with the Kerr constant being up to two orders of magnitude larger than conventional Kerr materials such as nitrobenzene.**

Blue phases (BPs) are thermodynamically stable mesophases that appear between the isotropic (Iso) and the helical cholesteric (Ch) phases. Although they have no birefringence, they can show colorful selective reflection which is due to Bragg reflection of circularly polarized visible light. The molecules organize into double-twist cylinders and depending on how the cylinders assemble themselves in space, there can be 3 different types; BPI and BPII are characterized by the body-centered cubic and simple cubic structures, respectively, while BPIII is believed to be amorphous by most observations to date.<sup>1</sup> For many years, BPs used to be only of academic interest since their available temperature range was limited in one Kelvin or less.<sup>2,3</sup> Nevertheless, some efforts to expand it have been successfully made<sup>4-7</sup> and thereby BPs have drawn the attention of researchers again from the standpoint of practical applications. Recently Karatairi *et al.* doped some chiral liquid crystals (LCs) with surface-functionalized CdSe nanoparticles and succeeded in expanding the temperature range of BPIII over nearly 20 K, although the concentration of nanoparticles was still quite high.<sup>8</sup> On the other hand, Iwamochi *et al.* synthesized a T-shaped compound that exhibited BPIII with a temperature range of about 30 K including room temperature, but the switching in this system was considerably slow.<sup>9</sup>

Meanwhile, recently we have also shown an amorphous BP over a wide temperature range by simply doping achiral bent-core (BC) nematics (Ns) (BCNs) with a few percentages of a certain chiral dopant. This effect is seemingly general for all bent-core molecules.<sup>10</sup>

The low bend/splay elastic ratio of bent-core molecules<sup>11</sup> might account for the wide stability of the BP, as suggested by a theoretical study several years ago.<sup>12</sup> In addition, similar to T-shaped molecules,<sup>6,9</sup> only BPIII was stabilized in our study and such phenomenon was explained by the broad-temperature range smectic nano-clusters that inhibit the development of long-range order of the double twisted helical structures of BPI or BPII.<sup>13-16</sup> In this communication, we demonstrate a material with BPIII which covers room temperature and can be switched between dark and bright states with an electric field. For the first time, the electrooptical switching in BPIII is also confirmed to be due to the Kerr effect<sup>17</sup> with a large Kerr constant (up to two orders of magnitude larger than conventional Kerr materials, such as nitrobenzene). This promises unprecedented optoelectronic and photonic applications making use of amorphous BP.

We have studied a mixture made by doping a BCN LC with 3.9 wt% the same high twisting power chiral dopant BDH1281 (Merck Chemicals) used in ref. 5 and 10. Fig. 1a depicts the molecular structure of the host BCN (compound M12). The detailed synthetic scheme has been reported elsewhere.<sup>18</sup> M12 exhibits monotropic nematic (N) phase at 45 °C upon cooling from the isotropic fluid as



**Fig. 1** (a) Molecular structure of compound M12 used in the experiments; (b) texture of the BPIII mixture (left) observed at 25 °C under a polarizing optical microscope. This view is slightly brighter than in the air region.

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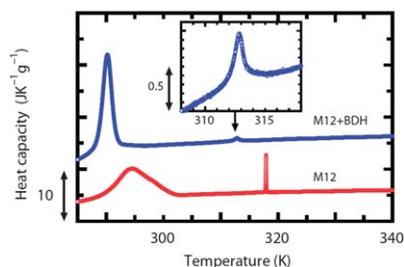
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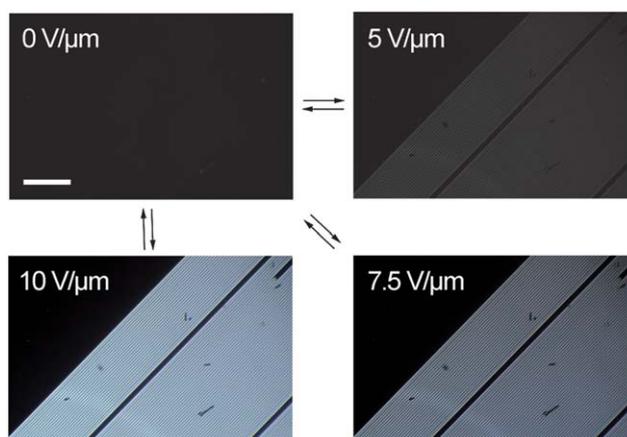
observed under a polarizing microscope, and can be easily super-cooled to room temperature. Attaching a flexible alkyl chain in the central core is thought to facilitate the N phase at low temperature. The doped mixture embedded between two cover slides was completely heated to Iso phase ( $\sim 85^\circ\text{C}$ ) first and then cooled down to the N phase at a rate of  $0.5^\circ\text{C min}^{-1}$ . It was hard to recognize any phase transition since the texture remained very dark. However, if an exposure time is long enough, a uniform bluish domain can be clearly observed, as shown in Fig. 1b. Neither platelet textures featuring BPI and BPII phases, nor oily streak textures characteristic of the Ch phase emerged before a very slow crystallization that started at  $22^\circ\text{C}$ . This indicates that the phase is BPIII, as we have also observed in other 3 BCNs used as host compounds earlier.<sup>10</sup>

BPIII is usually difficult to observe visually, since the selective reflection moves into the ultraviolet region. Moreover, although the Iso-BPIII transition is of the first-order type, it is known that the transition from BPIII to BPII/BPI, or BPIII to Ch (if any) is associated with a very small enthalpy change. Hence, high-resolution calorimetry is needed,<sup>8,19</sup> by which the temperature range of BPIII can be measured. In the present study, a high-resolution heat-flux differential scanning calorimetry (DSC) was performed. The calorimetry (heat capacity) data (cooling rate of  $0.1^\circ\text{C min}^{-1}$ ) taken from the pure M12 compound and that doped with 3.9 wt% BDH1281 are shown in Fig. 2. Both the Iso-BPIII and the BPIII-crystal transition temperatures were decreased by about  $5^\circ\text{C}$  than of the nematic phase of the undoped material. In addition, the enthalpy of the Iso-BPIII transition became much smaller than of the Iso-N transition of the pure M12. It must be emphasized that the first-order Iso-BPIII transition may terminate in a critical point and vanish at some very high chirality,<sup>20</sup> so that the transition we observed here could be yet supercritical. The situation is analogous to the liquid–gas transition, which also ends at a liquid–gas critical point as discussed in some theoretical works.<sup>21</sup> Similar to liquid and gas, the Iso and BPIII phases have the same symmetry. It is also worth noting that Fig. 2 gives no indication of the existence of BPI/BPII or Ch phase below BPIII, which is consistent with the textural observations.

We next investigated the electrooptical performance of the BPIII mixture using a  $10\ \mu\text{m}$  thick cell with ITO (indium tin oxide) comb-type electrodes on one of the two substrates. Fig. 3 shows some electrooptical switching behaviors under a rectangular field (1 kHz), in which the electrodes make an angle of  $45^\circ$  with crossed polarizers. The bright state could be readily switched on and off by an electric field; with the same field, the brightness increased with decreasing temperature. This is because of the larger Kerr constant at lower temperatures as discussed later. The response time ranged from several to several tens of milliseconds, which was similar to that in



**Fig. 2** Calorimetry data for the pure M12 compound and the mixture M12 + BDH 3.9 wt%. The inset shows the enlarged peak of the Iso-BPIII transition.



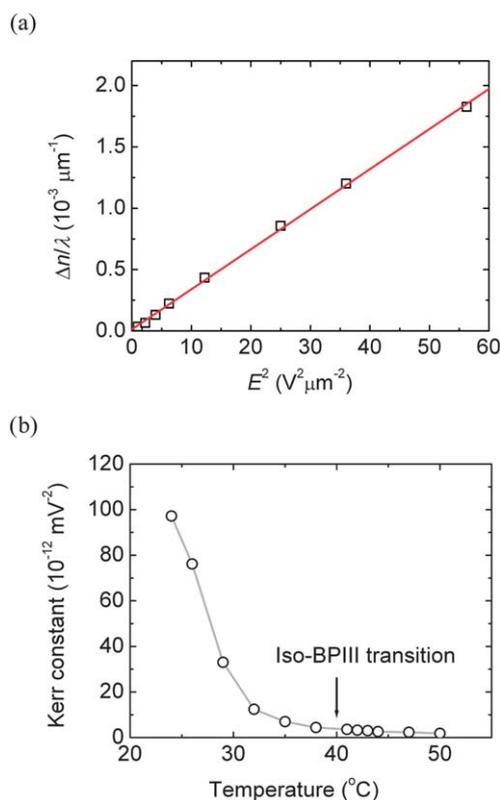
**Fig. 3** Electrooptical switching under various field strengths (rectangular, 1 kHz) in the BPIII mixture at  $23.5^\circ\text{C}$ . The electrodes are  $10\ \mu\text{m}$  apart and tiny dark rods are glass spacers. The forward and backward arrows indicate the application and removal of fields, respectively. Note that the upper left corner and two straight lines' region in each photo have no electrodes, so that no switching occurs. Scale bar is  $200\ \mu\text{m}$  long. Polarizers are vertical and horizontal.

a previous BPIII phase made of another bent-core compound.<sup>10</sup> Such a slow response is mainly caused by the high viscosity of the material since the Kerr switching normally should be much faster.<sup>22</sup>

Kerr effect is a third-order nonlinear optical or a second-order electrooptical effect in which an optically isotropic medium can show an induced birefringence  $\Delta n$  due to the reorientation of polar molecules by an external field  $E$ .<sup>17</sup> The Kerr effect is expressed by

$$\Delta n = \lambda K E^2, \quad (1)$$

where  $\lambda$  is the probe wavelength of the light and  $K$  is the Kerr constant. In practice, the same comb-electrode cell mentioned above was applied with various voltages (up to  $200\ V_{\text{pp}}$ ) and the induced retardation  $\Delta n d$  was measured using a phase modulation technique with the help of a helium–neon laser ( $\lambda = 632.8\ \text{nm}$ ), a photoelastic modulator (ORC, PEM-112), and a lock-in amplifier (Signal Recovery, 7265). Fig. 4a shows typical data at  $29^\circ\text{C}$ . The strong linear relation between  $\Delta n/\lambda$  and  $E^2$  indicates that the switching behavior is due to the Kerr effect described by eqn (1). The Kerr constant is calculated from the slope of the plot and the temperature dependence of that is shown in Fig. 4b. The Kerr constant increases with decreasing temperature and it is extraordinarily large at low temperatures, reaching a value of  $10^{-10}\ \text{mV}^{-2}$ , although it is only in a few  $10^{-12}\ \text{mV}^{-2}$  range in the Iso phase of a pure bent-core mesogen as observed by Dhara *et al.*<sup>23</sup> According to a preliminary measurement conducted previously by us, the effective thickness where the in plane field acts on the surface of the electrodes<sup>24,25</sup> was found to be about  $2\ \mu\text{m}$  for the same design of cell.<sup>23</sup> Hence the genuine Kerr constant probably is 5 times larger than the measured one, approximately  $5 \times 10^{-10}\ \text{mV}^{-2}$ , which is about 250 times larger than nitrobenzene which is known to have a very large Kerr constant ( $K = 2.4 \times 10^{-12}\ \text{mV}^{-2}$  at  $\lambda = 589.3\ \text{nm}$ ).<sup>26</sup> This value is comparable with that in a polymer-stabilized BP.<sup>27</sup> So far, the electrooptical study on BPIII is quite rare. Kitzerow *et al.* have reported that BPIII (with negative dielectric anisotropy  $\Delta\epsilon < 0$ ) can show a sharper reflection peak upon applying an electric field, and even transits to an unknown “BPE”



**Fig. 4** (a) Variation of induced birefringence with square of an applied electric field at 29 °C. The solid line is the best fit to eqn (1); (b) temperature dependence of the Kerr constant showing a continuous change at the Iso-BPIII transition (40 °C). The line is a guide to the eye.

under a sufficiently high field of  $\sim 6 \text{ V } \mu\text{m}^{-1}$ .<sup>28</sup> In contrast, our BPIII material showed no reflection even with a field as high as  $10 \text{ V } \mu\text{m}^{-1}$ , indicating that the electric field cannot enhance the ordering in this case. This supports the existence of nano-smectic clusters that randomize and inhibit any periodic cubic structure to develop, as proposed.<sup>10</sup>

In a conventional NLC, a relatively large Kerr effect can be observed just above the N-Iso transition temperature ( $T_{\text{NI}}$ ) due to the existence of short-range nematic-like order which persists over the coherence length  $\xi$  that is larger than the molecular length. According to Landau-de Gennes theory, when the temperature approaches the critical temperature  $T^*$  (typically,  $T_{\text{NI}} - T^* \approx 1 \text{ K}$ ),  $\xi$  tends to diverge.<sup>29</sup> However, an amorphous BPIII possesses only local order, and in the present mixture the BPIII phase is in a supercritical state (or at least, very near the critical point). For this reason the divergence of  $\xi$  is suppressed and thus one cannot see the discontinuity at the Iso-BPIII transition (at 40 °C) as shown in Fig. 4b (albeit  $\xi$  can grow larger as the temperature decreases). The light scattering intensity also shows no discontinuity at the Iso-BPIII transition in a highly chiral LC.<sup>20a</sup>

In summary, we have demonstrated a BPIII material over a wide temperature range near the room temperature. It can be switched from an optically isotropic (dark) to an anisotropic (bright) state by external fields. Our study also unambiguously shows that the Kerr effect is responsible for such electrooptical switching, and it is found that the Kerr constant becomes extraordinarily large at lower temperatures. Although a modified design of a bent-core molecule with low viscosity is still required to enhance the switching speed, we

believe the present study will open up a new possibility of optoelectronic and photonic applications making use of amorphous BPIII.

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