Phase Destruction upon Photopolymerization of Cholesteric Liquid Crystal Blue Phases with Mono- and Diacrylate Constituents

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We report an anomalous destruction of cholesteric blue phases I and II upon photopolymerizing a liquid crystal mixture composed of mono- and diacrylate monomers. The platelet texture characteristic of the blue phase collapsed when the sample was irradiated by a weak UV light source, while usual freezing of both blue phases I and II was obtained upon photopolymerization by a stronger light source. The phase destruction seems to be reflecting the robustness of the cubic lattice structure against external purterbations.

Liquid crystals (LCs) are categorized into a number of different phases, depending on the molecular ordering.[1] In materials with chiral constituents, the cholesteric (Ch) phase is exhibited where the LC director assumes a helical configuration along a single helical axis. In materials with a stronger chirality, cholesteric blue phases (BPs) with a three-dimensional periodic structure are exhibited. In BPs, the "double twist cylinder" in which the molecules twist in all 360-degree directions becomes the fundamental building block of the periodic lattice, and they are further categorized into BPI, -II, or -III, depending on the symmetry of the lattice structure. A schematic of the molecular orientation in the body-centered-cubic BPI and the simple-cubic BPII are shown in Figure 1 (BPIII is thought to be amorphous).

As can be seen from Figure 1, the double twist cylinders cannot fill the whole three-dimensional space and so disclination lines coexist in the cubic lattice. Because of these defects, the BP normally appears over a narrow temperature range between the cholesteric phase and the isotropic phase. Although numerous electrooptic investigations have been performed in hope of finding possible applications, the major drawback of these systems had been the narrow existing temperature range, and recent research had focused on finding chemical and physical approaches to increase the appearing temperature range.[2–5] However, for certain applications such as lasers, photopolymerizing the BPs is an easy solution since although molecular motion is inhibited by fixation, stable performance can be achieved owing to the increased mechanical and chemical stability.

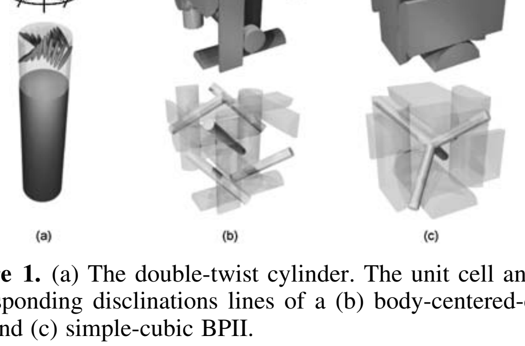

Figure 1. (a) The double-twist cylinder. The unit cell and the corresponding disclinations lines of a (b) body-centered-cubic BPI and (c) simple-cubic BPII.

In this paper, we report the observation of the destruction of the BP texture upon photopolymerization. The first report on photopolymerizable BPs was made using a mixture of chiral and nonchiral diacrylates and succeeded in polymerizing the material by irradiating a weak ultraviolet (UV) light ($\approx$10 mW/cm^2) for a few seconds.[6] We show that in the material used in our study composed of chiral monoacrylates and nonchiral diacrylates, the platelet texture of the BP is destroyed upon photopolymerizing the material using a weak UV light.

The photopolymerizable ChLC mixture provided by Merck [Merck: RMS03-010] was mixed with a photoinitiator [Ciba: Irgacure 819] to extend the reacting wavelength to $\lambda <$ 430 nm. The mixture had a right-handed helix and positive anisotropy and exhibited the following phase sequence: ChLC 74.7 °C BPI 75.9 °C BPII 76.6 °C Iso. The sample was infiltrated in a sandwich cell with a cell gap of approximately 6 µm and photopolymerized at various temperatures, under various UV light intensities.

Figure 2a shows the BPI and -II textures of the sample observed under a polarizing optical microscope (POM). When the sample was irradiated by a weak UV light source ($\approx$10 mW/cm^2 at $\lambda <$ 390 nm for 10 s), the platelet texture of the BP disappeared upon polymerization. The circular region shown in the center of Figure 2b is the region in which light was irradiated; a sandy texture with a small optical birefringence is observed instead of the platelet texture. The sandy texture was not uniaxial and did not disappear even when the sample was raised to above the clearing point, confirming that the material was polymerized; in fact, the resultant texture was similar to that observed when the material was polymerized in the isotropic phase, as shown in Figure 2c. The reflectance spectrum of the sample measured between crossed nicols shown in Figure 2d also confirms the similarity between the two textures. From these observations, we believe that the lattice structure of the BP became unstable as it polymerized and resulted in a collapsed lattice structure without any noticeable periodicity. The destruction of the phase was observed only in the BP, and usual stabilization of the helix was observed when the material was photopolymerized using a weak UV light in the Ch phase.

Upon irradiating the sample with a stronger UV light, usual freezing of the BP was observed. Figure 3a shows the platelet texture preserved in the photopolymerized material after the whole sample was irradiated by light with intensity $\approx$750 mW/cm^2 at $\lambda = 365$ nm for 2 s. The reflectance spectra of BPI and II

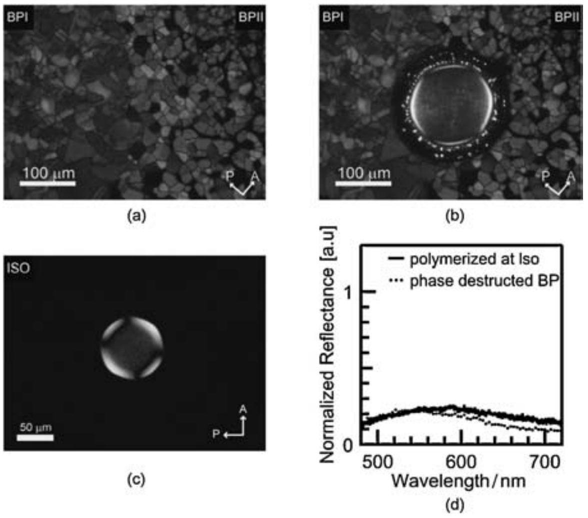

Figure 2. (a) POM images of BPI and -II exhibited by the sample. (b) Destruction of the phase observed upon photopolymerization by a weak UV source (round area in center, $I \approx 10\,\mathrm{mW/cm^2}$ at $\lambda < 390\,\mathrm{nm}$ for 10 s). (c) Texture of the sample photopolymerized in the isotropic phase. (d) Reflectance spectrum of the sample polymerized in the isotropic phase and the phase destructed BP.

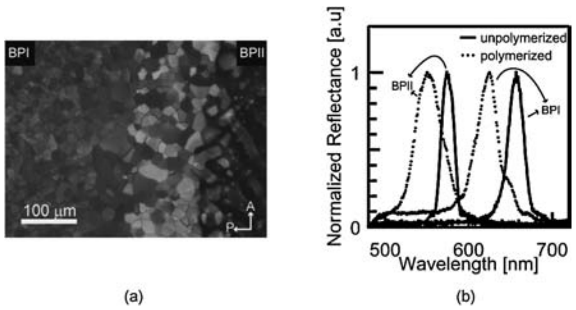

Figure 3. (a) Freezing of the platelet texture observed upon irradiating the sample with a strong UV source ($I \approx 750\,\mathrm{mW/cm^2}$ at $\lambda = 365\,\mathrm{nm}$ for 2 s). (b) Reflectance spectrum of the sample at BPI and BPII before and after polymerization.

measured before and after photopolymerization are shown in Figure 3b. The spectra were measured under crossed nicoles at red and green domains of BPI and -II, respectively. The selective reflection peak of the platelets shifted toward the shorter wavelength region after polymerization, due to shrinking commonly observed in photopolymerizable LC materials. It should be noted, however, that as well as the shortening of the selective reflection peak, broadening of the peak and an increase in the birefringence were observed in the wavelength region outside the reflection peak. The Q-factor of each peak calculated by $\lambda_{\mathrm{peak}}/\Delta\lambda$ decreases from 30 (BPI) and 31.9 (BPII) before polymerization to 20.2 (BPI) and 13.6 (BPII) after polymerization. We, therefore, believe that photopolymerization of the material causes a decrease in the order parameter, and whether the platelet texture is macroscopically preserved or not is determined by the number of photons entering the material over a certain short period of time in which photopolymerization takes place. This instability could be caused by the change in the elastic constants upon polymerization or a change in the local chirality as a result of the slow polymerization process; using the same material, we have previously reported an increase in the local chirality in the vicinity of the polymerized region as a result of the concentration gradient formed by the large difference in the reactivities of the comprising monomers.[7] On the other hand, usual freezing has been observed in diacrylate-only BPs,[6] and there is a theoretical study claiming that the cubic lattices of BPs become unstable in the high-chirality regime.[8] However, in order to understand the physical and chemical mechanism of the observed phenomena, a systematic study investigating the kind of materials that exhibit phase destruction should be undertaken.

Finally, we investigated the threshold energy required to photopolymerize the BP textures for a 6 µm thick cell. Interestingly, the power densities required to freeze BPI and -II were different. For a UV irradiation time of 1 s, BPI required $\approx 65\,\mathrm{mW/cm^2}$, whereas BPII required a smaller intensity of $\approx 31\,\mathrm{mW/cm^2}$. For a particular UV intensity above the threshold ($I \approx 98\,\mathrm{mW/cm^2}$ at $\lambda = 365\,\mathrm{nm}$), a certain dose ($3.1\,\mathrm{mJ/cm^2}$) was required to freeze the platelet texture, but the threshold energy was the same for BPI and -II. Following the presented arguments, the threshold energy of photopolymerization seems to be reflecting the robustness of the lattice structure of BPs against external perturbations, and interestingly suggests that BPI, which is thermodynamically more stable than BPII, is less immune to perturbations. Whether this feature is universal in BP-exhibiting LCs requires further investigation.

In conclusion, we reported the destruction of the BP lattice structure upon photopolymerizing a material composed of acrylates with different reactivities. For UV light at $\lambda = 365\,\mathrm{nm}$, intensities above 65 and $31\,\mathrm{mW/cm^2}$ were required to freeze the molecular order of BPI and -II, respectively. Further investigation of the origin of the observed phenomenon may lead to the discovery of a new property of this very fascinating liquid crystalline phase.

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