Disappearance of Reflection Color by Photopolymerization of Lyotropic Cholesteric Liquid Crystals from Cellulose Derivatives

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In this communication, we report on the disappearance of reflection color by photopolymerization of an acrylate monomer in lyotropic cholesteric liquid crystals from a cellulose derivative for color image applications. When a hydroxypropyl cellulose (HPC) derivative possessing propionyl side chains (HPC-Pr) was homogeneously dissolved in a liquid monomer of 4-hydroxybutyl acrylate (4HBA), we obtained lyotropic cholesteric liquid crystals (HPC-Pr_4HBA) with a Bragg reflection peak in the visible wavelength range. Such reflection wavelength was controllable by not only temperature, but also concentration of HPC-Pr in 4HBA. We found that Bragg reflection peak of lyotropic HPC-Pr_4HBA mixture disappears by photopolymerization of 4HBA, thereby leading to the fabrication of a photolithographic color image. This report provides promising clues to fabricate intriguing photonic devices adopted with cellulose derivatives by utilizing such Bragg reflection characteristics.

Keywords: Cellulose, Cholesteric liquid crystals, Lyotropic liquid crystals, Bragg reflection, Photopolymerization, Color image

1. Introduction

Cellulose is derived from β-glucose units, which are straightly polymerized through glycosidic bonds, and is the most abundant polymer on Earth. Such cellulose and its derivatives are known to be one of environmentally-friendly and safe natural polymers. This is because we find cellulose as the main chemical component in natural biomass of cotton, wood, and dried hemp. Furthermore, cellulose derivatives are commercially available as synthetic products of rayon and cellophane.

The cellulose derivatives are known to form cholesteric liquid crystal (CLC) phase with light reflection characteristics in both thermotropic and lyotropic manners by chemical modification of the side chains of cellulose [1-10]. In such CLC phase, the chiral (optically active) molecules self-organize the periodic helicoidal structures consisting of nematic liquid crystalline layers due to the intrinsic twisting force of chiral molecules. By sandwiching the CLC material between a pair of substrates with homogeneous anchoring surfaces, the helical axis of CLC is well-aligned to the orthogonal direction of the substrate surface in spontaneous way. In the CLC cells, one of the most interesting optical property is selective Bragg reflection of light due to their helical molecular structures. For instance, when a linearly polarized light propagates into the CLC with right-handed molecular sense along the helical axis, right- and left-handed circularly polarized light are reflected and transmitted, respectively. The maximum wavelength of Bragg reflection (λ) peak is numerically expressed as

\[ \lambda = np \]  

where \( p \) denotes the helical pitch length and \( n \) is the average refractive index of the CLCs [11-13]. The helical pitch length of \( p \) can be tuned by temperature, electric field, and so on, thereby resulting the on-demand control of reflection colors by such external stimuli.

In this context, crosslinkable CLC materials have been the subject of long-standing attention for technological applications such as reflection...
displays, full-color recording media, reflectors, and so forth [14-17]. Hitherto, significant progress in the research area of cellulose CLCs has established a wide variety of methodologies to fabricate the solid-state films with reflection colors by crosslinking reaction. In this Communication, we have developed lyotropic cellulose CLC materials by mixing a hydroxypropyl cellulose (HPC) derivative possessing propionyl side chains (HPC-Pr) in a liquid monomer of 4-hydroxybutyl acrylate (4HBA). As will be seen below, we successfully fabricated a photolithographic color image by utilizing the photoinduced disappearance of reflection color in lyotropic CLC materials.

2. Experimental

2.1. Materials

Figure 1 shows the chemical structures of a hydroxypropyl cellulose (HPC) derivative possessing propionyl side chains (HPC-Pr) and 4-hydroxybutyl acrylate (4HBA). In order to synthesize HPC-Pr, we used commercially available HPC (Wako Pure Chemical Industries, Ltd.; Hydroxypropyl Cellulose 2.0~2.9) as the starting material. Before the HPC-Pr synthesis, when we analyzed $^1$H-NMR spectrum of this pristine HPC in CDCl$_3$, the number of moles of chemically combined propylene oxide per anhydroglucose units (molar substitution; MS) was found to be 4.0 [18]. Therefore, the MS value denotes the sum of $x$ and $y$, as depicted in Fig. 1 (a).

HPC-Pr was synthesized by esterification of HPC with propionyl chloride according to a conventional procedure in our previous report [19]. We adopted 4HBA (Tokyo Chemical Industry Co., Ltd.) and 2-hydroxy-2-methylpropiophenone (HMPP; Tokyo Chemical Industry Co., Ltd.) as liquid monomer and photopolymerization initiator, respectively. The lyotropic CLC materials (HPC-Pr_4HBA) were prepared by dissolving homogeneously HPC-Pr in 4HBA at various concentrations between 72 wt% and 84 wt%, followed by addition of HMPP at 0.06 wt% in the mixture to generate the photopolymerization of an acryloyl group in 4HBA.

2.2. Fabrication of CLC Cells

A thin film of poly(vinyl alcohol) (PVA) as CLC alignment layer was prepared by spin-coating of its aqueous 2.0 wt % solution on a glass substrate. After drying at 100 °C for 1 h, the PVA film surface was uniaxially rubbed for fabrication of well-aligned CLC cells. The HPC-Pr_4HBA mixture was placed between a pair of the glass substrates covered with rubbed PVA films. The thickness of HPC-Pr_4HBA was adjusted using PTFE spacer with ca. 200 µm thickness. The well-aligned CLC cells were obtained by shearing thermotropic HPC-Pr or lyotropic HPC-Pr_4HBA mixtures at appropriate temperatures.

2.3. Physical Measurements

Transmission spectral properties of the CLC cells were studied by using a compact spectrometer (Ocean Optics, USB2000+) equipped with an optical fiber. The CLC cell of HPC-Pr or HPC-Pr_4HBA mixture settled on a hot stage (Mettler Toledo, HS82) was illuminated with white light from a tungsten halogen light source. The collinearly transmitted light from CLC cell was collected through a pair of achromatic doublet lenses, and focused onto the entrance of an optical fiber connected with a spectrometer.

In order to generate the photopolymerization of 4HBA in the lyotropic HPC-Pr_4HBA mixture, the CLC cell was irradiated with UV light from the surface normal. Photoirradiation was performed using a 150 W Hg-Xe lamp (San-ei Electric MFG. Co., UV Supercure-230S).

3. Results and discussion

3.1. Synthesis of HPC-Pr

After the HPC-Pr synthesis, we compared with FT-IR spectra before and after esterification of HPC with propionyl chloride. Before esterification, pristine HPC showed a strong and broad band in a
range from 3000 cm\(^{-1}\) to 3600 cm\(^{-1}\) originating from O–H stretching vibration of the terminal OH groups of HPC. In contrast, when esterification of HPC was carried out by using propionyl chloride, we observed the drastic changes in FT-IR spectroscopic shape before and after the esterification. In the FT-IR spectrum of HPC-Pr, O–H stretching vibration completely disappeared, whereas a sharp band of C=O stretching vibration was clearly observed at ca. 1700 cm\(^{-1}\). This result implies that almost all OH groups of HPC are esterified by propionyl chloride to be HPC-Pr. This is supported by \(^1\)H-NMR spectral measurement. Taking account of the MS value of HPC, as mentioned above, we numerically evaluated the esterification degree of propionyl side chains (PrE) from \(^1\)H-NMR spectrum of HPC-Pr \([19,20]\). As evident from Fig. 1 (a), the theoretically maximum value of PrE corresponds to 3.0. Because the monomer unit of HPC has three OH groups at the terminal points. In the \(^1\)H-NMR spectrum of HPC-Pr, we estimated the PrE value of approximately 3.0, suggesting that the terminal OH groups of HPC are fully esterified by propionyl chloride.

3.2. Reflection properties of thermotropic HPC-Pr

It was found that HPC-Pr shows thermotropic CLC properties with visible Bragg reflection. We measured transmission spectra of a CLC cell of HPC-Pr upon heating process, as shown in Fig. 2. When the CLC cell was heated at 90 °C, we could observe Bragg reflection with violet color, whose peak appeared at ca. 395 nm in the transmission spectrum. Upon elevating the temperature over 90 °C, the reflection wavelength was shifted to longer wavelength in continuous way. As prolonged heating treatment, the reflection peak reached 560 nm at 120 °C due to the thermally induced expansion of the helical pitch length of CLC \([13]\). As heated at 120 °C, the reflection peak of HPC-Pr was broadened rather than those heated below 115 °C. It is plausible that the molecular helical structure of HPC-Pr slightly deteriorates by heating at high temperature such as 120 °C. As heating over 120 °C, the reflection peak disappeared owing to thermally induced phase transition from CLC to isotropic phase. Subsequently, when the temperature of CLC cell was lowered to 90 °C, the reflection peak was reversibly shifted from 560 nm to the initial wavelength of 395 nm.

3.3. Reflection properties of lyotropic HPC-Pr_4HBA mixtures

As stated in the preceding section, thermotropic HPC-Pr exhibited a reflection peak in the wavelength range from 395 nm to 560 nm upon sweeping the temperature from 90 °C to 120 °C. From a technological viewpoint, it is a serious obstacle to induce visible reflection in the CLC cell of HPC-Pr by elevating to high temperature such as 90 °C or more. Moreover, this thermotropic CLC of HPC-Pr could not cover Bragg reflection peak in the full visible-wavelength range.

On the other hand, when HPC-Pr was completely dissolved in 4HBA to prepare lyotropic CLCs, visible Bragg reflection could be observed for the mixture of HPC-Pr_4HBA even at room temperature. Such reflection colors of blue, green, and red were controllable by the concentration of HPC-Pr in 4HBA, as given in Fig. 3 (a). For instance, as mixing at 72 wt% of HPC-Pr in 4HBA, this mixture showed red reflection color corresponding to ca. 700 nm at room temperature. By considering the reflection properties of thermotropic HPC-Pr, as shown in Fig. 2, it can be inferred that the helical pitch length of CLC increases by dissolving HPC in 4HBA.

When HPC-Pr was completely dissolved in 4HBA at 84 wt%, the CLC cell of lyotropic HPC-Pr_4HBA mixture showed Bragg reflection with violet color at ambient temperature. The reflection peak was located at ca. 420 nm. Subsequently, we pursued the transmission spectral changes of this CLC cell of HPC-Pr_4HBA upon heating process. The experimental result is shown in Fig. 3 (b). Although HPC-Pr_4HBA was a lyotropic CLC material, we found that the HPC-Pr_4HBA mixture also shows the thermally induced changes in the reflection wavelength in a similar fashion of thermotropic CLCs. Although this
CLC cell of HPC-Pr_4HBA exhibited a reflection peak at ca. 420 nm room temperature, the reflection peak was shifted to longer wavelength as elevating the temperature to 90 °C. It should be stressed that such reflection wavelength shift is fully covered in the visible wavelength range from 420 nm to 690 nm. As compared with Figs. 2 and 3, the thermally induced shift range of reflection peak in lyotropic HPC-Pr_4HBA mixture was obviously wider than that in pristine thermotropic HPC-Pr. More importantly, Bragg reflection peak of HPC-Pr_4HBA was not broadened even when this lyotropic material was heated at 90 °C. This experimental fact indicates that this lyotropic HPC-Pr_4HBA mixture has thermal stability in the molecular helical structure as heated up to 90 °C.

Figure 3 compiled the temperature dependence of Bragg reflection peak wavelengths of lyotropic HPC-Pr_4HBA mixtures which were prepared at the concentrations of HPC-Pr in 4HBA in the high concentration range from 72 wt% to 84 wt%. Although the reflection peak wavelength of HPC-Pr_4HBA mixture observed at room temperature was determined by the concentration of HPC-Pr in 4HBA, each CLC cell showed similar shift ratio of reflection peak wavelength by heating process. In this way, our finding enables the on-demand control of the reflection peak by simply dissolving thermotropic cellulose CLCs in a wide variety of liquid monomers.

3.4. Disappearance of Reflection Color by Photopolymerization of 4HBA

As shown in Fig. 1, a liquid monomer of 4HBA has an acryloyl group. This situation motivated us to demonstrate the photopolymerization of 4HBA in the lyotropic HPC-Pr_4HBA mixture doped with HMPP by irradiation with UV light.

For this purpose, we fabricated a CLC cell of a lyotropic HPC-Pr_4HBA mixture which was prepared at 72 wt% of HPC-Pr in 4HBA, followed by addition of HMPP at 0.06 wt% in the mixture. When the CLC cell was irradiated with UV light of a 600 mJ cm$^{-2}$ dose through a photomask, we could observe a color image in the CLC cell according to
In order to obtain the further information in reflection characteristics before and after irradiation with UV light, we measured the transmission spectra of UV-irradiated and non-irradiated area in this photopatterned CLC cell. The experimental spectra are shown in Fig. 4 (b). As expected, Bragg reflection peak was observed at ca. 700 nm for non-irradiated area. However, such reflection peak thoroughly disappeared in UV-irradiated area of this photopatterned CLC cell. Concurrently, it turned out found that the base line in transmission spectra decreases from ca. 100% to ca. 90%. This probably happened from phase separation of HPC-Pr and photopolymerized 4HBA by irradiation with UV light, thereby leading to light scattering. Although such photolithographic color image in this CLC cell was not stable for a long time, the photopolymerized lyotropic cellulose CLC mixtures with permanent stability would be realized by improving the present methodology for full-color imaging.

4. Conclusion

In this report, we have found the disappearance of Bragg reflection peak by photopolymerization of a liquid acrylate monomer in a lyotropic CLC prepared from a cellulose derivative. As compared with thermotropic CLCs, the lyotropic CLCs have technically important advantages to control the reflection peak by not only temperature, but also concentration of acrylate monomer in the lyotropic CLCs. The photoinduced disappearance of reflection peak allows us to inscribe a color image in the lyotropic CLC, probably due to the phase separation, by irradiation with UV light through a photomask. The present report includes promising guidelines for the rational design and fabrication of versatile photonic devices based on cellulose materials [12,21-24].

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