Preparation of the Color Films from Cellulose Derivatives in a Diacrylate Liquid

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In this study, we fabricated the multi-colored films of lyotropic cholesteric liquid crystals (CLCs) prepared from a hydroxypropyl cellulose (HPC) derivative by photopolymerization of a diacrylate liquid monomer for color image applications. When a hydroxypropyl cellulose derivative tethering propionyl side chains (HPC-PrE) was completely dissolved in a liquid monomer of 1,4-bis(acryloyloxy)butane (BAOB) to prepare lyotropic CLC (HPC-PrE_BAOB), we could observe Bragg reflection in the visible wavelength range at room temperature. Photopolymerization of BAOB in the lyotropic CLC mixture gave rise to fabrication of robust solid-state CLC films with reflection colors. Furthermore, we found that the reflection wavelength is tunable by controlling the light intensity of irradiation UV light, thereby enabling the facile fabrication of multi-colored films by the photolithographic technique. The present report opens promising ways to design and produce intriguing photonic devices by utilizing the environmentally-friendly and safe natural polymer of cellulose.

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

1. Introduction

Paints enable not only to protect the outermost surface on objects, but also to give them aesthetic appearance. Therefore, they are widely used in industrial products such as commercial buildings, furniture, cars, and so on. However, volatile organic compounds (VOCs) emitted from the conventional color paints are harmful to human health and environment. Due to the ever-increasing regulations concerning the toxic substances in recent years, we should develop the environment- and human-friendly materials for alternative painting method [1,2].

In this context, numerous efforts have been made on the syntheses and fabrications of color materials derived from cellulose [3–10]. Cellulose is the most abundant natural polymer on the Earth, and therefore is one of low-cost biomasses with safety and low-risk for both human and global environment. From the ancient civilization, we have widely used it in the wooden buildings, clothes, books, food additives, and so on [11–13]. Nowadays, cellulose derivatives are well-known to form cholesteric liquid crystal (CLC) phase by chemical modification of the side chains [14–17]. In the CLC phase, the chiral molecules are self-assembled into the periodic helicoidal structure, thereby leading to the emergence of unique optical property of selective light reflection, which is the so-called Bragg reflection. The maximum wavelength of the selective reflection ($\lambda$) is numerically expressed as the following formula:

$$\lambda = np$$  (1)

where $p$ means the helical pitch length, and $n$ is the average refractive index of CLC materials [18]. Therefore, the low-molecular weight CLCs can be applied to photonic devices such as reflection displays, full-color recording media, and so forth.

Very recently, we have reported the fabrication of lyotropic CLC materials by mixing a hydroxypropyl
cellulose (HPC) derivative possessing propionyl side chains (HPC-PrE) in a liquid monomer of 4-hydroxybutyl acrylate (4HBA) [8]. By using this lyotropic CLC mixture, we have successfully demonstrated the photolithographic color imaging by utilizing the photoinduced disappearance of reflection color in lyotropic CLC mixture through the phase separation between HPC-PrE and photopolymerized 4HBA. However, the color image is not stable for a long time. Because the fluidity and volatility of lyotropic CLC mixture remain in the non-irradiated area due to the existence of non-polymerized 4HBA monomer. Therefore, this strategy is not suitable for the practical applications.

In order to overcome these issues, we attempted herein to fabricate the color films of lyotropic CLCs of HPC-PrE by using 1,4-bis(acryloyloxy)butane (BAOB) with two acryloyl groups at the termini instead of 4HBA with solely one acryloyl group at the terminus. As a result, the multi-colored CLC films could be prepared without photoinduced disappearance of reflection color even after the polymerization of BAOB.

2. Experimental

2.1. Materials

Figure 1 shows the chemical structures of a hydroxypropyl cellulose (HPC) derivative possessing propionyl side chains (HPC-PrE) and 1,4-bis(acryloyloxy)butane (BAOB). In order to synthesize HPC-PrE, we used commercially available HPC (Wako Pure Chemical Industries, Ltd.; Hydroxypropyl Cellulose 2.0–2.9; weight average molecular weight; \( M_w = 2.8 \times 10^4 \)) as the starting material. When we measured \(^1\H\text{H}-\text{NMR}\) spectrum of a solution of pristine HPC in CDCl\(_3\), the number of moles of chemically combined propylene oxide per anhydroglucose units, i.e., molar substitution (MS) value, was estimated to be 4.0 according to a previous report [19]. As a result, the MS value means the sum of \( x, y \) and \( z \), as depicted in Fig. 1 (a).

HPC-PrE was synthesized by esterification of pristine HPC with propionyl chloride according to our previous report [20]. We adopted BAOB (Tokyo Chemical Industry Co., Ltd.) and 2-hydroxy-2-methylpropiophenone (HMPP; Tokyo Chemical Industry Co., Ltd.) as liquid acrylate monomer and photopolymerization initiator, respectively. The lyotropic CLC mixtures (HPC-PrE_BAOB) were prepared by completely dissolving HPC-PrE in BAOB at various concentrations between 72 wt% and 80 wt%, followed by addition of HMPP at 3 wt% in the mixture to proceed the photopolymerization of terminal acryloyl groups of BAOB.

2.2. Fabrication and photopolymerization of CLC cells

We prepared a rubbed alignment layer of poly(vinyl alcohol) (PVA) on a glass substrate according to our previous reports [8,20]. The HPC-PrE_BAOB mixture was placed between a pair of the glass substrates covered with rubbed PVA films. The CLC cell gap was adjusted by using polytetrafluoroethylene film spacers with the thickness of ca. 200 \( \mu \text{m} \).

In order to generate photopolymerization in the HPC-PrE_BAOB mixture, irradiation with UV light was performed by a 150 W Hg-Xe lamp (San-ei Electric Mfg. Co., UV Supercure-203S) with a long-pass filter (Toshiba, UV-35). The light intensity was measured by a photodiode sensor (Ophir, PD300-UV) equipped with a PC interface (Ophir, Smart Head to USB Interface).

3. Results and discussion

3.1. Synthesis of HPC-PrE

We compared with FT-IR spectra before and after esterification of HPC with propionyl chloride. After the esterification, we observed completely disappearance of a broad band in a range from 3000
cm\(^{-1}\) to 3600 cm\(^{-1}\) attributed to O-H stretching vibration of the terminal OH groups of HPC, and clearly appearance of a sharp band around 1700 cm\(^{-1}\) due to C=O stretching vibration of HPC-PrE. This result indicates that almost all OH groups of HPC are esterified by propionyl chloride. In addition, we numerically evaluated the esterification degree of propionyl side chains (PrE) from the \(^1\)H-NMR spectrum of HPC-PrE. Consequently, we calculated the PrE value of ca. 3.0 [20]. As can be seen in Fig. 1 (a), the theoretically maximum value of PrE corresponds to 3.0. Therefore, we found that the synthesized HPC-PrE is fully esterified by propionyl chloride, as also evidenced by the FT-IR spectral results.

3.2. Reflection properties of lyotropic HPC-PrE_BAOB mixtures

Figure 2 (a) shows the transmission and reflection spectra of lyotropic CLC mixtures of HPC-PrE_BAOB with different concentrations of HPC-PrE. It was found that the Bragg reflection wavelength can be controlled by concentration of HPC-PrE in the lyotropic CLC mixture. For example, as mixing at 80 wt% of HPC-PrE, this lyotropic CLC mixture showed blue reflection color, corresponding to ca. 490 nm at room temperature. The Bragg reflection wavelength of HPC-PrE_BAOB shifted to longer wavelength as decreasing the concentration of HPC-PrE. In this way, we prepared easily the CLC cells with not only blue reflection color, but also green and red reflection colors, as seen in the inset of Fig. 2 (a). This probably happened due to the decrease of helical twisting power of periodic helicoidal CLC or the expansion of helical pitch length of CLC as the BAOB content is increased.

Figure 2 (b) shows the changes in transmission spectrum of a CLC cell of lyotropic HPC-PrE_BAOB mixture, prepared at 76 wt% of HPC-PrE, upon heating process from 30 °C to 70 °C. At 30 °C, Bragg reflection as green color appeared at ca. 570 nm. When temperature of the CLC cell was elevated over 30 °C, the reflection wavelength shifted to longer wavelength in continuous way due to the thermally induced expansion of helical pitch length of HPC-PrE_BAOB. As heated at 70 °C, the Bragg reflection reached ca. 750 nm. We found that the reflection band is gradually broadened as heating from 30 °C to 70 °C. This probably happened from the increasing in thermodynamic molecular motion of HPC-PrE at higher temperatures. As prolonged heating over 70 °C, the reflection peak thoroughly disappeared, implying that the HPC-PrE mixture is changed from CLC phase to isotropic by heating.

In addition, we evaluated systematically the temperature dependences of reflection peak...
wavelengths of lyotropic HPC-PrE_BAOB mixtures, which were prepared at the concentrations of HPC-PrE in the range between 72 wt% and 80 wt%. The profiles are shown in Fig. 2 (c). Although the initial reflection wavelength was different from each HPC-PrE_BAOB, all of the mixtures showed the similar shift ratio of reflection wavelength as a function of the temperature. Moreover, we found that as decreasing the content ratio of HPC-PrE, i.e., increasing the content ratio of BAOB, the isotropic phase transition temperature is lowered.

However, considering the practical applications for color imaging, it is a serious disadvantage that the reflection colors are changed by the temperature. Thus, in the following section, we attempted to prepare the solid-state CLC films of HPC-PrE with Bragg reflection properties by photopolymerization between acryloyl groups in BAOB, which are stable regardless of external temperature changes.

3.3. Patterning of reflection color by photopolymerization of BAOB

As shown in Fig. 1 (b), a liquid monomer of BAOB has two acryloyl moieties at its terminal positions. This enables us to proceed the photopolymerization of BAOB in the lyotropic CLC mixture of HPC-PrE_BAOB doped with a photopolymerization initiator of HMPP by irradiation with UV light.

With this view, we fabricated CLC cells of lyotropic HPC-PrE_BAOB mixtures which were prepared at 76 wt% of HPC-PrE in BAOB, followed by addition of HMPP at 1 wt%, 3 wt%, and 5 wt% in the mixtures, respectively. When we measured transmission spectra of CLC cells, the reflection peak shifted to longer wavelength as the introduction amount of HMPP in the mixtures increased [solid curves in Fig. 3 (a)]. This is attributed to the expansion in helical pitch length of CLC mixture by addition of HMPP.

Subsequently, the CLC cells were irradiated with UV light of an energy of 100 mJ cm\(^{-2}\). At this time, the light intensity was set at 80 mW cm\(^{-2}\). As a result, we could observe distinct broadening of Bragg reflection bands in the visible wavelength range [dashed curves in Fig. 3 (a)]. Previously, we reported that the Bragg reflection peak disappears by photopolymerization using 4HBA as a liquid monomer [8]. A liquid monomer of BAOB has two acryloyl sites per molecule, whereas 4HBA used in our previous report has only one acryloyl site [8,21]. Therefore, the addition of BAOB would facilitate the photopolymerization at more rapid rates rather than 4HBA. Thus, we could observe the Bragg reflection band in the visible wavelength range even after photopolymerization by using BAOB as a liquid acrylate monomer.

In addition, when the irradiation with UV light, the resultant CLC cells showed the shift of reflection band to shorter wavelengths, whose ranges were dependent on the amount of HMPP added in HPC-PrE_BAOB [solid and dashed curves in Fig. 3 (a)]. Especially, we confirmed that the shift range of reflection wavelength before and after irradiation with UV light is wide for the HPC-PrE_BAOB mixture with 1 wt% of HMPP rather than those with 3 wt% and 5 wt% of HMPP. In other word, as the addition amount of HMPP increased in HPC-PrE_BAOB mixtures, the shift range of reflection wavelength through the photopolymerization became adequately narrow.
It is plausible that the photopolymerization of HPC-PrE_BAOB mixtures with a large amount of HMPP is rapidly finished due to the increase in the added amount of HMPP.

From the viewpoint of optical properties, we determined the most suitable amount of HMPP added to HPC-PrE_BAOB mixture for applications to color materials. As shown in Fig. 3 (a), we judged that the HPC-PrE_BAOB mixture with 1 wt% of HMPP is not suitable for color materials owing to the wide shifting range of reflection wavelength by irradiation with UV light. On the other hand, when HMPP was added to HPC-PrE_BAOB mixture at 5 wt%, the UV-induced shift range was narrow. However, we observed remarkable reduction of the base line in transmission spectrum of this CLC cell, as compared to others. This experimental result suggests that phase separation of HPC-PrE and polymerized BAOB occurs in the HPC-PrE_BAOB mixture with 5 wt% of HMPP, thereby leading to light scattering. In contrast, we judged that the HPC-PrE_BAOB mixture with 3 wt% of HMPP is the most suitable for applications to color materials in terms of both relatively narrow shift range of reflection band and highly optical transparency after UV-irradiation. Thus, we fabricated color films of the HPC-PrE_BAOB mixture with 3 wt% of HMPP by photopolymerization of BAOB, as will be discussed below.

Subsequently, we evaluated the thermal stability in the CLC cells of HPC-PrE_BAOB mixture before and after UV-irradiation. As mentioned in the preceding section, the pristine HPC-PrE_BAOB mixture exhibited the longer wavelength shift of reflection wavelength as a function of temperature in a thermotropic way [Fig. 2 (b)]. On the other hand, we observed that the reflection peak of CLC cell irradiated with UV light was adequately stable and unchanged from 30 °C to 120 °C [open circles in Fig. 3 (b)]. It implies that the periodic helicoidal structure of CLC is robustly preserved by photopolymerization between the acryloyl groups in BAOB. Thus, we succeeded in fabrication of reflection color films with thermal stability even after heating up to 120 °C.

Finally, we found that the reflection color can be controlled by tuning the light intensity of irradiation UV light. This motivated us to fabricate multicolored films by the photolithographic method.

When a lyotropic HPC-PrE_BAOB mixture which was prepared at 76 wt% of HPC-PrE in BAOB, followed by addition of HMPP at 3 wt% in the mixture, the CLC cell showed a reflection peak around 650 nm as red color [left-side area in Fig. 4 (a) and curve I in Fig. 4 (b)]. After that, we irradiated of the right-side area of the CLC cell with UV light with the intensity of 14 mW cm⁻² for 7.0 seconds through a photomask. It turned out that the reflection wavelength shifts to shorter wavelength to be ca. 540 nm as green reflection color [right-side area in Fig. 4 (a) and curve III in Fig. 4 (b)]. Moreover, the reflection band was broadened after UV-irradiation. Successively, the middle area was irradiated with UV light with the intensity of 80 mW cm⁻² for 1.2 seconds through a photomask. At this stage, the reflection wavelength appeared at ca. 580 nm, corresponding to yellow reflection color [middle area in Fig. 4 (a) and curve II in Fig. 4 (b)]. Thus, it was found that when the UV light intensity was set at higher, the reflection band was relatively sharp, and the UV-induced shift range was narrow. It is anticipated that irradiation of the CLC cell with UV light of higher intensity brings about the photopolymerization of BAOB at more rapid rates, thereby resulting in immobilization of the CLC helical molecular structure without phase separation of HPC-PrE and photopolymerized BAOB or

![Fig. 4. (a) Reflection image of the photopatterned CLC cell. (b) Changes in reflection spectrum of non-irradiated area (I) and irradiated areas with UV light of 80 mW cm⁻² (II) and 14 mW cm⁻² (III) in the photopatterned CLC cell.](image-url)
deterioration of CLC structure. In this way, we successfully fabricated multi-colored films by the photolithographic method.

In this report, we demonstrated the facile fabrication of multi-colored solid-state CLC film with green and yellow reflection colors. However, the multi-colored film with full colors of red, green, and blue would be realized by optimizing the acryloyl liquids, photopolymerization initiators, and cellulose derivatives.

4. Conclusion
We have successfully demonstrated the fabrication of multi-colored films of a cellulose derivative by photopolymerization of a diacrylate liquid in the lyotropic CLC mixture. The reflection peak of the lyotropic CLC mixture was easily shifted as a function of the temperature. On the other hand, when the CLC mixture was irradiated with UV light, we obtained the robust solid-state CLC film with Bragg reflection colors. Such reflection peak was stable even by heating at high temperatures up to 120 °C. Moreover, we found that the reflection wavelength is controllable by tuning the light intensity of irradiation UV light for the photopolymerization of diacrylate liquid. Therefore, we succeeded in the preparation of multi-colored films with different reflection colors by the photolithographic technique. The present report provides promising clues to create the recyclable photonic devices derived from biomass of cellulose [22–24].

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References
1. G. Wieslander, D. Norbäck, E. Björnsson, C. Janson, and G. Boman, Int. Arch. Occup. Environ. Health., 69 (1997) 115.
2. J. Geurts, J. Bouman, and A. Ovebeek, J. Coat. Technol. Res., 5 (2008) 57.
3. S. N. Bhadani and D. G. Gray, Mol. Cyst. Liq. Cryst., 102 (1984) 255.
4. M. Muller, R. Zentel, and H. Keller, Adv. Mater., 9 (1997) 159.
5. H. Kosho, H. Ise, Y. Tanaka, S. Kawauchi, and J. Watanabe, Shikizai, 72 (1999) 604 (in Japanese).
6. R. Chiba, Y. Nishio, Y. Sato, M. Ohtaki, and Y. Miyashita, Biomacromolecules, 7 (2006) 3076.
7. D. Wenzlik and R. Zentel, Macromol. Chem. Phys., 214 (2013) 2405.
8. M. Fukawa, K. Suzuki, and S. Furumi, J. Photopolym. Sci. Technol., 31 (2018) 563.
9. M. Fukawa and S. Furumi, EKISHO, 22 (2018) 219 (in Japanese).
10. M. Müller and R. Zentel, Macromol. Chem. Phys., 201 (2000) 2055.
11. J. Kim, S. Yun, and Z. Ounaises, Macromolecules, 39 (2006) 4202.
12. W. Yuan, J. Zhang, H. Zou, T. Shen, and J. Ren, Polymer, 53 (2012) 956.
13. K. Sugimura and Y. Nishio, EKISHO, 22 (2018) 228 (in Japanese).
14. S. L. Tseng, G. V. Laivins, and D. G. Gray, Macromolecules, 15 (1982) 1262.
15. J. C. Thies and J. M. G. Cowie, Polymer, 42 (2001) 1297.
16. L. Wang and Y. Huang, Macromolecules, 37 (2004) 303.
17. K. Miyagi and Y. Teramoto, J. Mater. Chem. C, 6 (2018) 1370.
18. S. Furumi, Chem. Rec., 10 (2010) 396.
19. F. F.-L. Ho, R. R. Kohler, and G. A. Ward, Anal. Chem., 44 (1972) 178.
20. T. Ishizaki, S. Uenuma, and S. Furumi, Kobunshi Ronbunshu, 72 (2015) 737 (in Japanese).
21. D. J. Broer, J. Lub, and G. N. Mol. Nature, 378 (1995) 467.
22. S. Furumi, S. Yokoyama, A. Otomo, and S. Mashiko, Appl. Phys. Lett., 84 (2004) 2491.
23. S. Furumi and N. Tamaoki, Adv. Mater., 22 (2010) 886.
24. S. Furumi, Polym. J., 45 (2013) 579.