Syntheses and Properties of Cellulosic Derivatives for Reflection Color Films

Masashi Fukawa, Akane Kawaguchi, Kenichiro Hayata, Ruri Aoki, Mami Furukawa, and Seiichi Furumi*

Department of Chemistry, Graduate School of Science, Tokyo University of Science, 1–3 Kagurazaka, Shinjuku, Tokyo 162–8601, Japan
* furumi@rs.tus.ac.jp

This report describes the syntheses and properties of cellulosic derivatives for reflection color films. As hydroxypropyl cellulose (HPC) was reacted with acryloyl chloride, we prepared a series of HPC derivatives tethering acryloyl side chains (HPC-Ac) at their different esterification degrees. When the cell of HPC-Ac was heated in a stepwise manner, we observed thermotropic cholesteric liquid crystal (CLC) feature with Bragg reflection in the full-visible wavelength range. Such temperature dependence of Bragg reflection could be controlled by tuning esterification degree of acryloyl side chains of HPC-Ac. We succeeded in the permanent preservation of periodic helical CLC structure by thermo- or photo-induced crosslinking reaction between the acryloyl side chains of HPC-Ac, resulting in fabrication of reflection color films with thermal stability up to 180 °C. This report provides promising clues to fabricate the robust multi-colored films, derived from biomass of cellulose, for novel photonic devices.

Keywords: Cellulose, Cholesteric liquid crystals, Thermotropic, Bragg reflection, Color

1. Introduction

Cholesteric liquid crystals (CLCs) exhibit periodic helicoidal structure consisting of nematic liquid crystalline layers that are self-assembled by the chiral molecules through their intrinsic twisting abilities. One of unique and important optical properties of CLCs is selective Bragg reflection. When the CLCs are exposed to non-polarized white light, circularly polarized reflection light can be selectively observed at a specific wavelength (λ) defined as follows,

\[ \lambda = np \]  

(1)

where, \( p \) means the helical pitch length of CLCs, and \( n \) is the average refractive index \([1–3]\). Interestingly, the reflection light has the same handedness of circularly polarized light as the CLC molecular helical sense. Due to anisotropic fluids of supramolecular assemblages, the helical pitch length of CLCs is tunable by external stimuli such as temperature, electric field, and so on, resulting in the on-demand control of the reflection colors. From technological viewpoints, such CLC materials have been the subject of long-standing attention for their versatile applications to reflection displays, full-color recording media, reflectors, painting substances, and so on \([4–10]\).

In this context, cellulosic derivatives tethering appropriate side chains are well known to form CLCs \([11–20]\). Recently, there are many reports on the fabrication of solid-state films with visible reflection color from cellulosic CLC materials by crosslinking reaction \([21–26]\). In this communication, we have succeeded in fabrication of multi-colored CLC films from cellulosic derivatives. We synthesized three kinds of hydroxypropyl cellulose (HPC) derivatives possessing acryloyl groups in their side chains (HPC-Ac) at their different esterification degrees. Thermo- or photo-induced crosslinking of HPC-Ac between acryloyl side chains brought about the permanent preservation of periodic...
helical CLC structure with thoroughly thermal stability even after heating up to 180 °C.

2. Experimental

2.1. Materials

Figure 1 shows the chemical structures of a pristine hydroxypropyl cellulose (HPC) and its derivative possessing acryloyl side chains (HPC-Ac). In order to synthesize HPC-Ac, we used commercially available HPC (Wako Pure Chemical Industries, Ltd.; Hydroxypropyl cellulose 2.00~2.90; Weight average molecular weight; \(M_w = 2.80 \times 10^4\)) as the starting material. When we measured \(^1\)H-NMR spectrum of this pristine HPC in CDCl\(_3\), the molar amount of chemically combined propylene oxide per anhydroglucose unit (molar substitution; \(MS\)) was found to be 4.04 according to a previous report [27]. The \(MS\) value denotes the sum of \(x, y\) and \(z\) depicted in Fig. 1. Therefore, the average molecular weight per anhydroglucose unit can be calculated to be 394 g/mol. Subsequently, we analyzed \(^1\)H-NMR spectra of HPC during titration with trichloroacetyl isocyanate. From the changes in \(^1\)H-NMR spectrum, the number of hydroxy groups substituted per anhydroglucose unit (degree of substitution; \(DS\)) was estimated to be 2.40 [27].

![Chemical structures of a pristine hydroxypropyl cellulose (HPC) and its derivative possessing acryloyl side chains (HPC-Ac).](image)

Fig. 1. Chemical structures of a pristine hydroxypropyl cellulose (HPC) and its derivative possessing acryloyl side chains (HPC-Ac).

In this study, we prepared a series of HPC-Ac tethering acryloyl side chains at their different esterification degrees. HPC-Ac was synthesized by esterification of HPC with acryloyl chloride [20]. Briefly, acryloyl chloride (6.00 mL, 74.0 mmol; Tokyo Chemical Industry Co., Ltd.) was added to powdered HPC (3.00 g, 7.60 mmol), which was dried under reduced pressure over 12 hours in advance. The reaction mixture was stirred under dark condition for 48, 60, and 72 hours to control the esterification degrees of acryloyl groups. When the reaction mixture was poured into water, white-sticky product was precipitated. The impurities were removed through repeated purification processes by dissolving in acetone and subsequently reprecipitating in water. Finally, the product was dried in atmospheric pressure at room temperature for 2 weeks.

2.2. Fabrication of CLC cells

First, we prepared a rubbed alignment layer of poly(vinyl alcohol) (PVA) on a glass substrate according to our previous reports [20,26]. HPC-Ac was dissolved with acetone, and the mixture was placed on the PVA layer. After drying in vacuo at room temperature, a CLC cell were assembled by sandwiching a pair of dried HPC-Ac films on the glass substrates. At this time, the CLC cell gap was controlled by using polytetrafluoroethylene films with a thickness of ca. 200 \(\mu\)m.

3. Results and discussion

3.1. Syntheses of HPC-Ac

In order to elucidate the esterification of HPC with acryloyl chloride for the reaction time of 48 hours, we compared the FT-IR spectra of HPC and HPC-Ac. In a range of wavenumber from 3000 cm\(^{-1}\) to 3600 cm\(^{-1}\), the pristine HPC showed an intense peak due to O-H stretching vibration of the terminal OH groups. On the other hand, in the FT-IR spectrum of HPC-Ac, the peak intensity of O-H stretching vibration of HPC-Ac became weaker than that of the pristine HPC. The results suggest that the OH groups of HPC are not completely modified by acryloyl chloride.

![1H-NMR spectrum of HPC-Ac.](image)

Fig. 2. A signal "e" corresponded to other protons such as glucose units. The integrated value of the signal "a" is defined as \(B\), and the sum of the integrated values of the signals "a", "b", "c", "d", and "e" is defined as \(W\). The esterification degree of acryloyl side chains per anhydroglucose (AcE) is numerically expressed as the following equation.

\[
AcE = (-7B - 6B \times MS)/(3B - W)
\] (2)
The theoretically maximum value of $AcE$ corresponds to 3.00 because anhydroglucose unit has three OH groups in their side chains. From this equation, we estimated the $AcE$ value of 2.65. This $AcE$ value suggests that 88% of the OH groups of HPC are esterified by acryloyl chloride [20]. Therefore, the OH groups of HPC were not completely esterified by acryloyl chloride, as supported by the FT-IR spectral result of HPC-Ac. As prolonged esterification times of HPC with acryloyl chloride for 60 and 72 hours, we prepared two kinds of HPC-Ac with different values of $AcE$ of 2.75 and 2.85, respectively.

### 3.2. Reflection properties of thermotropic HPC-Ac

The HPC-Ac ($AcE = 2.65$) was found to exhibit Bragg reflection in the visible wavelength even at room temperature and thermotropic CLC characteristic. Figure 3 (a) shows the changes in transmission spectrum of a CLC cell of HPC-Ac were measured upon heating process from 25 °C to 70 °C in a stepwise manner. At 25 °C, HPC-Ac showed Bragg reflection with blue light, whose peak appeared at 450 nm. When the temperature of CLC cell was elevated over 25 °C, the reflection wavelength was shifted to longer wavelengths in a continuous way due to increasing the helical pitch length of periodic helicoidal structure [17,20]. Eventually, as the cell was heated at 70 °C, the reflection peak reached 790 nm. Thus, we found that HPC-Ac showed Bragg reflection property in the full-visible wavelength range. After heating at 70 °C at once, followed by gentle cooling to room temperature, the reflection peak did not return to initial wavelength of 450 nm, implying that the periodic helicoidal structure of CLC was preserved by thermo-induced crosslinking between the acryloyl side chains of HPC-Ac heated at 70 °C. In other words, we succeeded in fabrication of the cellulosic CLC films with Bragg reflection properties, which were quite stable to thermal treatment.

Figure 3 (b) shows the temperature dependence of reflection peak wavelength of three kinds of HPC-Ac (closed circles: $AcE = 2.65$, open squares: $AcE = 2.75$, closed squares: $AcE = 2.85$). From the profiles, we found that the reflection peaks of HPC-Ac appear at longer wavelengths at same temperature as the $AcE$ value is lower. It is plausible that when HPC-Ac possesses unreacted OH groups at their termini, the helical twisting power of periodic helicoidal CLC structure is hindered by hydrogen bonds among their terminal OH groups. As the result, the helical pitch length increased as the $AcE$ value

![Fig. 2. $^1$H-NMR spectrum of HPC-Ac ($AcE = 2.65$) with CH=CH$_2$ side chains in CDCl$_3$ with tetramethylsilane as the internal standard.](image)

![Fig. 3. (a) Representative experimental results on the changes in transmission spectrum of a CLC cell of HPC-Ac ($AcE = 2.65$) upon stepwise heating process from 25 °C to 70 °C. (b) Temperature dependence of Bragg reflection wavelengths of CLC cells of HPC-Ac with different $AcE$ values (closed circles: $AcE = 2.65$, open squares: $AcE = 2.75$, closed squares: $AcE = 2.85$).](image)
decreases. Therefore, we could control the temperature dependence of reflection peak wavelength of HPC-Ac by tuning of value of AcE.

3.3. Photo-induced crosslinking of HPC-Ac

In the preceding section, we described the fabrication procedure of the cellulosic CLC films with reflection colors by thermo-induced crosslinking reaction. However, we could not fabricate the patterned color film by the thermo-induced crosslinking reaction. Thereby, we attempt to fabricate the colorful cellulosic CLC films by photo-induced crosslinking reaction between the acryloyl side chains of HPC-Ac.

For this purpose, we irradiated of a CLC cell of HPC-Ac (AcE = 2.65) with UV light at 365 nm of a 300 mJ/cm² at 60 °C. In this study, we did not use a photoinduced radical polymerization initiator. Figure 4 (a) shows the temperature dependence of reflection peak wavelength of HPC-Ac before and after photo-induced crosslinking reaction. Before irradiation with UV light, the HPC-Ac showed thermotropic CLC property. The results are shown as closed circles in Fig. 4 (a). On the other hand, after irradiation with UV light at 60 °C, the reflection peak was slightly shifted from 680 nm to 650 nm. This shift of reflection wavelength happens probably from the shrinking of helical pitch owing to many crosslinking points of HPC-Ac. Importantly, the reflection peak was adequately stable and unchanged by heating from 30 °C to 180 °C. The results are shown as open circles in Fig. 4 (a). Thus, it was found that the periodic helicoidal structure of CLC is also preserved by photo-induced crosslinking between acryloyl groups in their side chains, leading to possibility to fabricate colorful cellulosic CLC films.

As mentioned above, HPC-Ac showed thermotropic CLC property, and their periodic helicoidal structure could be preserved by thermo- or photo-induced crosslinking between acryloyl side chains. These results motivated us to demonstrate the fabrication multicolored cellulosic CLC films by the photolithographic method.

First, we irradiated of one-half area of CLC cell of HPC-Ac (AcE = 2.65) with UV light through a photomask at room temperature. Subsequently, as heated at 50 °C, the other area was irradiated of UV light. As can be observed in Fig. 4 (c), we could fabricate cellulosic CLC films with patterned reflection colors of blue and yellow. In this way, we successfully demonstrated the facile fabrication of multicolored cellulosic CLC films, which reflected light at different wavelengths depending on the specific areas.

4. Conclusion

In this report, we have found that HPC-Ac
shows thermotropic CLC property, and their temperature dependence of reflection peaks can be controlled by tuning the $AcE$ value. Therefore, we have succeeded in fabrication of cellulosic CLC films with Bragg reflection properties from HPC-Ac by thermo- or photo-induced crosslinking between terminal acryloyl groups in their side chains. The reflection wavelengths of the cellulosic CLC films have been adequately stable even at 180 °C. The photo-induced crosslinking procedure made it possible to tune and preserve the visible reflection by control of temperature and irradiation with UV light, respectively. Furthermore, we successfully fabricated a multicolored cellulosic CLC film by the photolithography method. This report opens a promising way to fabricate the environment and human friendly, low cost, and recyclable full-color films and versatile photonic devices by utilizing biomass of cellulose [28].

Acknowledgements
All of the authors express sincere thanks to Mr. T. Ishizaki and Ms. K. Suzuki for our experimental assistance. One of the authors (S. F.) is deeply indebted to the Grant-in-Aid for Scientific Research (B) (No. 25288103) from the Ministry of Education, Science, Sports and Culture (MEXT) of Japan, the Cosmetology Research Foundation, IMRA Japan, and Shorai Foundation for Science and Technology for financial supports on this research project.

References
1. D. M. Makow, Color Res. Appl., 4 (1979) 25.
2. N. Tamaoki, A. V. Parfenov, A. Masaki, and H. Matsuda, Adv. Mater., 9 (1997) 1102.
3. S. Furumi, Chem. Rec., 10 (2010) 394.
4. P. J. Shannon, Mol. Cryst. Liq. Cryst., 110 (1984) 135.
5. D. J. Broer, J. Lub, and G. N. Mol, Nature, 378 (1995) 467.
6. N. Tamaoki, A. V. Parfenov, A. Masaki, and H. Matsuda, Adv. Mater., 9 (1997) 1102.
7. M. R. A. Hikmet and H. Kemperman, Nature, 392 (1998) 476.
8. S. Furumi, S. Yokoyama, A. Otomo, and S. Mashiko, Appl. Phys. Lett., 82 (2003) 16.
9. S. Furumi, S. Yokoyama, A. Otomo, and S. Mashiko, Appl. Phys. Lett., 84 (2004) 2491.
10. S. Furumi and N. Tamaoki, Adv. Mater., 22 (2010) 886.
11. R. S. Werbowyj and D. G. Gray, Mol. Cryst. Liq. Cryst., 34 (1976) 97.
12. J. Bheda, J. F. Fellers, and J. L. White, Colloid Polym. Sci., 258 (1980) 1335.
13. R. S. Werbowyj and D. G. Gray, Macromolecules, 13 (1980) 69.
14. S. N. Bhadani and D. G. Gray, Mol. Cryst. Liq. Cryst., 99 (1983) 29.
15. J. X. Guo and D. G. Gray, Macromolecules, 22 (1989) 2082.
16. M. Müller, R. Zentel, and H. Keller, Adv. Mater., 9 (1997) 159.
17. H. Kosho, S. Hiramatsu, T. Nishi, Y. Tanaka, S. Kawauuchi, and J. Watanabe, High Perform. Polym., 11 (1999) 41.
18. M. Ito, Y. Teramoto, and Y. Nishio, Biomacromolecules, 13 (2012) 565.
19. P. Ohlendorf and A. Greiner, Polym. Chem., 6 (2015) 2734.
20. T. Ishizaki, S. Uenuma, and S. Furumi, Kobunshi Ronbunshu, 72 (2015) 737 (in Japanese).
21. H. Kosho, H. Ise, Y. Tanaka, S. Kawauchi, and J. Watanabe, Shikizai, 72 (1999) 604 (in Japanese).
22. R. Chiba, Y. Nishio, Y. Sato, M. Ohtaki, and Y. Miyashita, Biomacromolecules, 7 (2006) 3076.
23. D. Wenzlik and R. Zentel, Macromol. Chem. Phys., 214 (2013) 2405.
24. K. Miyagi and Y. Teramoto, J. Mater. Chem. C, 6 (2018) 1370.
25. Md. T. I. Mredha, Y. Z. Guo, T. Nonoyama, T. Nakajima, T. Kurokawa, and J. P. Gong, Adv. Mater., 30 (2018) 1704937.
26. M. Fukawa, K. Suzuki, and S. Furumi, J. Photopolym. Sci. Technol., 31 (2018) 563.
27. F. F.-L. Ho, R. R. Kohler, and G. A. Ward, Anal. Chem., 44 (1972) 178.
28. S. Furumi, Polym. J., 45 (2013) 579.