Thermotropic Cholesteric Liquid Crystals from Cellulose Derivatives with Ester and Carbamate Groups

Kenichiro Hayata, Tatsuya Suzuki, Masashi Fukawa, and Seiichi Furumi*

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

In this report, we synthesized hydroxypropyl cellulose (HPC) derivatives tethering both ester and carbamate groups by chemical modifications of HPC with both alkanoyl chlorides and alkyl isocyanates. They exhibited thermotropic cholesteric liquid crystal (CLC) phase. The differences in side chain lengths and bonding species of HPC derivatives affected the thermotropic CLC properties. We observed visible Bragg reflection from the HPC ester-carbamate derivatives at lower temperature than from those of the HPC esters. Moreover, the shifting wavelength ranges of Bragg reflection of the HPC ester-carbamate derivatives as heating temperature were narrow rather than those of the HPC esters probably due to their hydrogen bonding between carbamate bonds.

Keywords: Cellulose, Cholesteric liquid crystals, Thermotropic liquid crystals, Bragg reflection, Side chain effects

1. Introduction

Liquid crystals are anisotropic fluids of supramolecular assemblies that exist as intermediate phases of condensed matters between isotropic fluid and solid-state crystalline phases. Calamitic liquid crystals, i.e., liquid crystals of rod-like molecules, generally are classified into three types by the arrangement of molecules: nematic, smectic, and cholesteric. Nematic liquid crystal phase is solely assembled by the rod-like molecules in parallel with the long axis. On the other hand, cholesteric liquid crystal (CLC) phase is accumulated by parallel aligned layers of rod-like molecules with chirality in twisting ways, thereby resulting in the formation of periodic helicoidal molecular structures [1,2].

About five decades ago, Goossens proposed that the helical structure of CLCs is caused by the attractive dispersion force due to dipole-dipole and dipole-quadrupole interactions between chiral molecules. The following reports made a conclusion that the helical pitch length is independent of temperature [3–5]. However, the CLC helical pitch was experimentally found to be dependent on temperature. Therefore, the temperature dependence of twisting power forming the CLC helical structures can be explained by taking account of new intermolecular interactions in the theory [6–9].

Cellulose is the most abundant natural polymer on the Earth, and essential for our life. Hydroxypropyl cellulose (HPC) derivatives are known to exhibit thermotropic CLC phase with unique optical properties [8–17]. One of the outstanding optical properties is Bragg reflection. The maximum wavelength of Bragg reflection ($\lambda$) is numerically determined by two parameters such as the average refractive index ($n$) and helical pitch length ($p$) of CLCs, which can be expressed according to the following equation.

$$\lambda = np$$ (1)

In general, the reflection wavelength of low-molecular weight CLCs is tunable by external stimulus such as temperature, magnetic and electric field, and so on [18,19]. With
regard to HPC derivatives, previous reports have shown that the differences of molecular weight of HPC and side chain length in HPC ester derivatives affect the twisting power of CLCs, resulted in their helical pitch length [9,15].

In this report, we describe the syntheses of HPC ester-carbamate derivatives by modifications of HPC with both alkanoyl chlorides and alkyl isocyanates at their different side chain lengths. We found the effects on thermotropic CLC properties by the differences in side chain lengths and bonding species of HPC derivatives.

2. Experimental

2.1. Materials

Figure 1 shows the chemical structures of HPC derivatives and the side chains. We used hydroxypropyl cellulose (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. HPC was dried in vacuo overnight prior to use. The number of moles of combined propylene oxide per anhydroglucose unit (molecular substitution; MS) was evaluated by \(^1\)H-NMR spectrum of the pristine HPC in CDCl\(_3\) [20]. We estimated the MS value of 4.0, meaning the sum of \( x, y, \) and \( z \) values illustrated in Fig. 1. Additionally, we determined the number of hydroxy groups substituted per anhydroglucose unit (degree of substitution; DS) in HPC as 2.4 by titration with trichloroacetyl isocyanate [20].

We synthesized an HPC propionyl ester (HPC-C\(_2\)E) by esterification with propionyl chloride according to our previous report [21]. In contrast, HPC derivatives with different substituents in the side chains were synthesized by two-step pathway of chemical reactions. Briefly, HPC (1.0 eq) was completely dissolved in acetone at room temperature, and subsequently was added by pyridine (2.0 eq). After heating at 55 °C, the corresponding alkanoyl chlorides or alkyl isocyanates (0.3 eq) was added into the solution. After the reaction proceeded for 4 hours, propionyl chloride (1.3 eq) was added. Successively, the reaction was continued for another 20 hours. The reaction solution was dropwise poured into a large excess of ultra-pure water for purification. The resultant viscous polymer obtained from water was dissolved again in acetone, and dropped into water in the repeated manner. The purified HPC derivatives were dried in vacuo at room temperature [21]. In this way, we obtained HPC derivatives of HPC-C\(_2\)E/C\(_2\)C (HPC mixed ester derivatives) and HPC-C\(_2\)E/C\(_3\)C (HPC ester-carbamate derivatives).

2.2. Fabrication procedure of CLC cells

We fabricated CLC cells according to the following procedure. In order to form the alignment layer, a glass substrate was spin-coated with an aqueous 2.0 wt% solution of poly(vinyl alcohol) (PVA), and dried at 100 °C for 1 hour. The surface of PVA thin layer on substrate was uniaxially rubbed for fabrication of well-aligned CLC cells. HPC derivatives were sandwiched between the pair of the glass substrates. The CLC cell gap was controlled by polytetrafluoroethylene film spacers with the thickness of ca. 200 \( \mu \)m.

3. Results and discussion

3.1. Syntheses of HPC derivatives

We evaluated the degrees of modifications to ester and carbamate from the \(^1\)H-NMR spectra of HPC derivatives in CDCl\(_3\). In this study, the numbers of modifications by alkanoyl chlorides and alkyl isocyanates are defined as alkanoyl ester degree (C\(_k\)E) and alkyl carbamate degree (C\(_l\)C), respectively. As complete modifications of HPC, the total C\(_k\)E and C\(_l\)C value corresponds to 3.0. This is because the monomer unit of HPC has three hydroxy groups at the terminal positions. For instance, the esterification degree
by propionyl chloride was determined as $C_2E = 3.0$ from $^1H$-NMR spectrum of HPC-C$_2$E [10,21]. In the same way, the values of HPC-C$_2$E/C$_4$E, HPC-C$_2$E/C$_4$C, and HPC-C$_2$E/C$_4$ were estimated as $C_2E:C_4E = 2.7:0.3$, $C_2E:C_2C = 2.7:0.3$, and $C_2E:C_4C = 2.7:0.3$, respectively [21].

3.2. Reflection properties of thermotropic HPC derivatives

Figures 2 (a) and 2 (b) show the transmission spectral change of HPC-C$_2$E and HPC-C$_2$E/C$_4$E as a function of temperature, respectively. When the CLC cells of HPC-C$_2$E and HPC-C$_2$E/C$_4$E were heated, Bragg reflection peaks shifted to the longer wavelength [8,9]. We found the differences in the reflection shift behavior between HPC-C$_2$E and HPC-C$_2$E/C$_4$E. HPC-C$_2$E/C$_4$E with long side chains showed Bragg reflection peak in visible wavelength range at lower temperature by ca. 15 °C rather than that of HPC-C$_2$E. This result is attributed to the reduction of van der Waals interaction of side chains forming the twisting power as the side chain length is longer [9,15]. Moreover, as heating over ca. 130 °C, Bragg reflection peaks were broadened due to the deterioration of CLC helical structure by enhancement in thermally induced molecular motion of the side-chain [22]. We serendipitously found that HPC ester-carbamate derivatives exhibit thermotropic CLC phase with visible reflection. In a similar way to the behavior of HPC ester derivatives, the reflection peaks of both HPC-C$_2$E/C$_2$C and HPC-C$_2$E/C$_4$C shifted to longer wavelength upon heating process, as shown in Figs. 3 (a) and 3 (b). Moreover, although the visible Bragg reflection was observed for both HPC-C$_2$E/C$_2$C and HPC-C$_2$E/C$_4$C, the CLC phase appeared at slightly lower temperature rather than HPC-C$_2$E. This experimental result implies that the bond length of carbamate is longer than that of ester due to an amino group so that the interaction depending on the side chain length would be diminished.

Figure 4 compiles the temperature dependences of Bragg reflection wavelengths of HPC derivatives with different side chain lengths and/or bonding species. As the aliphatic chain lengths including alkyl chains and binding moiety

![Fig. 2. Transmission spectral changes of HPC propionyl ester (a: HPC-C$_2$E; C$_2E = 3.0$) and HPC propionyl-pentanoyl mixed ester (b: HPC-C$_2$E/C$_4$E; C$_2E:C_4E = 2.7:0.3$) as a function of temperature.](image1)

![Fig. 3. Transmission spectral changes of HPC propionyl ester-ethyl carbamate (a: HPC-C$_2$E:C$_2$C; C$_2E:C_2C = 2.7:0.3$) and HPC propionyl ester-butyl carbamate (b: HPC-C$_2$E:C$_4$C; C$_2E:C_4C = 2.7:0.3$) as a function of temperature.](image2)
was longer, the visible Bragg reflection peak was slightly longer at the same temperature. In addition, it turned out that the reflection wavelengths are elongated in proportion to elevating temperature. The slope coefficients of changing profiles from 400 nm to 600 nm as a function of temperature were calculated to be 6.96 nm/ºC for HPC-C2E, 6.94 nm/ºC for HPC-C2E/C4E, 5.70 nm/ºC for HPC-C2E/C2C, and 5.87 nm/ºC for HPC-C2E/C4C. As is evident from the slope coefficients, HPC ester-carbamate derivatives showed smaller slope coefficients rather than those of HPC ester derivatives. This fact suggests that the thermally induced expansion of CLC helical pitch is hampered by hydrogen bonding between carbamate moieties.

Both HPC-C2E and HPC-C2E/C4E maintained the reflection peaks as heating up to 135 ºC. On the other hand, the reflection peaks of HPC-C2E/C2C and HPC-C2E/C4C disappeared at lower temperatures of 120 ºC and 130 ºC, respectively. Interestingly, we revealed that the reflection peaks of both HPC ester-carbamate derivatives disappear around 640 nm. In order to rationalize these results, we considered the following points. Firstly, the expansion of the helical pitch length induced by heating is attribute not only to the reduction of twisting power, but also to the expansion of neighboring distance between nematic layers [23]. Secondly, it is known that hydrogen bonding is stronger than van der Walls force. Lastly, the average refractive indices of HPC-C2E/C2C and HPC-C2E/C4C would be almost same values because of their similar chemical structures [16]. In other words, it is anticipated the helical pitches of both HPC-C2E/C4C and HPC-C2E/C2C are almost same lengths according to the equation (1). Therefore, as the reflection peaks exceed 640 nm, cleavage of hydrogen bonding of carbamate moieties would occur, thereby resulting in the deterioration of CLC helical structure. From a technological viewpoint, such thermally induced disappearance of Bragg reflection at a specific wavelength would be greatly advantageous in the fabrication of thermal sensors.

4. Conclusion
We describe the syntheses and reflection properties of HPC derivatives possessing both ester and carbamate groups in the side chains. Such HPC ester-carbamate derivatives exhibited thermotropic CLC phase with visible reflection. In case of the HPC derivatives with two substituents, we found the effect of interaction between the side chains in HPC ester-carbamate derivatives on reflection properties. Furthermore, the temperatures showing visible Bragg reflection peaks were slightly lower rather than that of the HPC propionyl ester. The shift range of reflection wavelength as a function of temperature was narrowed probably by hampering the expansion of CLC helical pitch due to hydrogen bonds between carbamate bonds. Furthermore, the thermally induced disappearance of reflection peak was dependent on the side chains of HPC derivatives. Such specific reflection property can be used for thermal sensors.

Acknowledgements
All of the authors express sincere thanks to Messrs. T. Ishizaki, G. Ishida, Mses. R. Aoki, A. Kawaguchi, and M. Furukawa 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, Cosmetology Research Foundation, IMRA Japan, and Shorai Foundation for Science and Technology for financial supports on this research project.

References
1. F. C. Frank, *Discuss. Faraday Soc.*, 25 (1958) 19.
2. G. H. Heilmeier, L. A. Zanoni, and L. A. Barton, *Proc. IEEE*, 56 (1968) 1162.
3. W. J. A. Goossens, *Phys. Lett.*, 31A (1970) 413.
4. W. J. A. Goossens, *Mol. Cryst. Liq. Cryst.*, **12** (1971) 237.
5. B. W. van der Meer, G. Vertogen, A. J. Dekker, and J. G. J. Ypma, *J. Chem. Phys.*, **65** (1976) 3935.
6. H. Kimura, M. Hosino, and H. Nakano, *J. Phys. Colloq.*, **40** (1979) C3-174.
7. H. Kimura, M. Hosino, and H. Nakano, *J. Phys. Soc. Jpn.*, **51** (1982) 1584.
8. J. Watanabe and T. Nagase, *Macromolecules*, **21** (1988) 7.
9. H. Kosho, S. Hiramatsu, T. Nishi, Y. Tanaka, S. Kawaguchi, and J. Watanabe, *High Perform. Polym.*, **11** (1999) 41.
10. S.-L. Tseng, G. V Laivins, and D. G. Gray, *Macromolecules*, **15** (1982) 1262.
11. S. N. Bhadani, S.-L. Tseng, and D. G. Gray, *Makromol. Chem.*, **184** (1983) 1727.
12. S. N. Bhadani and D. G. Gray, *Mol. Cryst. Liq. Cryst.*, **99** (1983) 29.
13. H. Steinmeier and P. Zugenmaier, *Carbohydr. Res.*, **173** (1988) 75.
14. A. M. Ritcey and D. G. Gray, *Macromolecules*, **21** (1988) 1251.
15. I. Rusig, H. Godinho, L. Varichon, P. Sixou, J. Dedier, C. Filliatre, and A. F. Martins, *J. Polym. Sci. B: Polym. Phys.*, **32** (1994) 1907.
16. B. Huang, J. J. Ge, Y. Li, and H. Hou, *Polymer*, **48** (2007) 264.
17. H. Ishii, K. Sugimura, and Y. Nishio, *Cellulose*, **26** (2019) 399.
18. H. De Vries, *Acta. Crystallogr.*, **4** (1951) 219.
19. S. Furumi, *Chem. Rec.*, **10** (2010) 394.
20. F. F.-L. Ho, R. R. Kohler, and G. A. Ward, *Anal. Chem.*, **44** (1972) 178.
21. T. Ishizaki, S. Uenuma, and S. Furumi, *Kobunshi Ronbunshu*, **72** (2015) 737 (in Japanese).
22. M. Fukawa, K. Suzuki, and S. Furumi, *J. Photopolym. Sci. Technol.*, **51** (2018) 563.
23. K. Miyagi and Y. Teramoto, *J. Mater. Chem. C*, **6** (2018) 1370.