Cholesteric Liquid Crystals from Cellulose Derivatives with Alkyl Ether Groups

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In this study, we synthesized hydroxypropyl cellulose (HPC) derivatives possessing alkyl ether side chains through Williamson ether synthesis. Such HPC ether derivatives exhibited thermotropic cholesteric liquid crystals (CLCs) with Bragg reflection. The temperature dependence of reflection wavelength could be controlled by changing the side chain lengths and etherification degrees in the HPC derivatives. Moreover, the thermal stability of both HPC ester and ether was evaluated before and after heating at 60 °C for 20 days. The reflection peak of HPC ester shifted to the longer wavelength upon the heating treatment due to the hydrolysis of ester linkage. On the other hand, we found that the reflection peak of HPC ether can be robustly preserved even after the prolonged heating treatment, arising from the thermal stability of ether linkage. The rational approach addressed here provides promising clues to fabricate the stable photonic CLC devices with reflection features by exploiting anti-hydrolysis of the cellulose ether derivatives.

Keywords: Cellulose, Cholesteric liquid crystals, Williamson ether synthesis, Thermotropic liquid crystals, Bragg reflection

1. Introduction

Cellulose is the most abundant natural polymer on the planet earth and a major chemical component in plants. Hydroxypropyl cellulose (HPC) is prepared by etherifying hydroxy groups of cellulose with propylene oxide. Such HPC is frequently used as one of inexpensive and environment-friendly substances for food and pharmaceutical additives in our daily life. From the perspective of liquid crystals, HPC derivatives are known to exhibit cholesteric liquid crystal (CLC) phase with visible reflection characteristics in the thermotropic manner through the chemical modification of appropriate side chains [1–8]. In the CLC phase, chiral molecules self-assemble the periodic helicoidal molecular structures consisting of nematic liquid crystal layers by the intrinsic molecular chirality, thereby leading to the emergence of selective light reflection. Such unique reflection property corresponds to a kind of Bragg reflection [9–13]. The maximum wavelength of Bragg reflection peak ($\lambda$) is numerically expressed by the following equation:

$$\lambda = np$$  \hspace{1cm} (1)

where $p$ denotes the helical pitch length, and $n$ is the average refractive index of CLC. The helical molecular structure of thermotropic CLC formed by cellulose derivatives is considerably affected by parameters such as temperature, side chain structure, polymerization degree, and so on. Among them, the optimization of side chains in cellulose derivatives is of prime importance for precise tuning of reflection peak wavelength.

In this report, we focused on HPC derivatives exhibiting thermotropic CLC phase. Hitherto, there have been numerous reports on thermotropic CLCs derived from HPC derivatives. However, most of them are reported by using HPC ester derivatives chemically modified with acyl chlorides or carboxylic anhydrides [1–4,14–16]. Very recently, we have developed the CLCs with visible reflection prepared from a wide variety of HPC ester-carbamate derivatives, which were synthesized by modifications of HPC with both

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alkanoyl chlorides and alkyl isocyanates at their different side chain lengths [17,18]. Nevertheless, there are a few reports of HPC derivatives possessing alkyl ethers in the side chains. Ester linkage is easily cleaved due to its lower interatomic binding energy, resulting in the hydrolysis with formation of carboxy and hydroxy groups. Previous report has pointed out that optical properties of HPC derivatives with ester groups would deteriorate after heating or aging owing to the hydrolysis of ester linkages [19]. On the other hand, ethyl cellulose (EC) with ethyl ether and EC derivatives with acetyl ester are known to exhibit lyotropic CLC phase [20,21]. However, no report has made on the thermotropic CLCs of cellulose ethers. In this report, we synthesized a series of HPC derivatives with butyl and/or propyl ether groups in the side chains. Furthermore, the reflection properties were evaluated for the HPC ether derivatives.

2. Experimental

2.1. Syntheses of HPC ether derivatives

Figure 1 shows the chemical structures of HPC ether derivatives and the side chains. We used a commercially available substance of HPC (Wako Pure Chemical Industries, Ltd.; Viscosity of 2.0 wt% aqueous solution, 2.0~2.9 mPa·s; Weight average molecular weight, $M_w = 2.8 \times 10^4$; Number average molecular weight, $M_n = 1.1 \times 10^4$) as the starting material. HPC was dried in vacuo overnight prior to use. 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 [22]. 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 [22].

We synthesized a series of HPC ether derivatives according to Williamson ether synthesis as follows. HPC (1.0 eq) was completely dissolved in dry $N,N$-dimethyl formamide, and was subsequently added by 1-bromobutane (3.5 eq). After stirring for 30 minutes at 65 ºC, powdered NaOH (5 eq) was added quickly. After stirring for 2 hours under dried N$_2$ atmosphere, 1-bromobutane (3.5 eq) was added again and the reaction mixture was stirred at 65 ºC for 48 hours [23]. When the reaction mixture was poured into water, yellow-sticky product was precipitated. The impurities were removed through repeated purification processes by dissolving in tetrahydrofuran and subsequently reprecipitating in water. Finally, the product was dried in vacuo at room temperature over 2 days to obtain a purified HPC butyl ether derivative (HPC-Bue). In this way, we also prepared HPC propyl-butyl mixed ether derivatives (HPC-Pre/Bue) and HPC propyl ether derivative (HPC-Pre).

2.2. Fabrication procedure of CLC cells

In order to produce the alignment film, a glass substrate was spin-coated with a 2.0 wt% aqueous solution of poly(vinyl alcohol) (PVA), and dried on a hot stage at 100 ºC for 1 hour. The surface of PVA thin layer on substrate uniaxially rubbed for well-alignment of CLC. After that, the HPC derivatives were sandwiched between the pair of the glass substrates coated with PVA layers. The CLC cell gap was adjusted by polytetrafluoroethylene film spacers with the thickness of ca. 200 μm.

3. Results and discussion

3.1. Syntheses of HPC ether derivatives

We evaluated the number of substituents by butyl and/or propyl ethers from the $^1$H-NMR spectral results. In this study, the etherification degrees of butyl and propyl groups are defined as $Bue$ and $Pre$, respectively. According to our previous report [24], the $Bue$ value of HPC-Bue was estimated to be
2.8. In the same way, the Pre value of HPC-Pre was 2.7. In addition to HPC-Bue and HPC-Pre, we prepared three kinds of HPC propyl-butyl mixed ethers with Pre:Bue of 0.7:2.1, 1.6:1.4, and 2.5:0.2. Accordingly, ca. 90% hydroxy groups of HPC were etherified with butyl and/or propyl ethers in the side chains, and ca. 10% hydroxy groups remained intact after the syntheses of HPC ether derivatives.

3.2. Reflection properties of thermotropic HPC derivatives

Figure 2 (a) shows the changes in transmission spectrum of HPC-Bue (Bue = 2.8) upon heating process. At 90 °C, a reflection peak as blue color appeared at ca. 420 nm. When the CLC cell of HPC-Bue was stepwise heated from 90 °C, the reflection peak continuously shifted to longer wavelength, arising from the thermally induced expansion of the helical pitch length. As heated at 125 °C, the reflection peak eventually reached ca. 610 nm, corresponding to the red color. Additionally, when the CLC cell of HPC-Bue was heated over 130 °C, the reflection band thoroughly disappeared. In order to confirm the disappearance of reflection peak, we observed the optical birefringence of CLC cell of HPC-Bue by using a polarized optical microscope upon heating process. As a result, we revealed the transition from CLC to isotropic phase at ca. 140 °C. This result implies that the disappearance of reflection peak is attributed to the thermally induced phase transition to isotropic.

In order to elucidate the effect of the side chain lengths, we measured the transmission spectra of HPC-Pre/Bue (Pre:Bue = 1.6:1.4) upon heating process. The experimental result is shown in Fig. 2 (b). As a CLC cell of HPC-Pre/Bue was heated at 100 °C, we observed a reflection peak around 400 nm. Prolonged heating of the CLC cell from 100 °C to 130 °C led to the continuous shift of reflection peak from 400 nm to 570 nm. We found the differences in the reflection shift behavior between HPC-Bue and HPC-Pre/Bue. HPC-Pre/Bue with short propyl side chains showed Bragg reflection peak in visible wavelength range at higher temperature by ca. 10 °C, as compared that of HPC-Bue. Similar effect of side chain lengths was also confirmed for HPC ester derivatives [24].

We synthesized HPC ether derivatives with butyl and propyl mixed ether side chains at different etherification degrees. Figure 3 compiles the temperature dependences of Bragg reflection wavelengths of HPC derivatives. We found that the reflection peaks of HPC ether derivatives appear at longer wavelengths at same temperature as the Bue value is higher. Thus, we succeeded that the reflection wavelength can be controlled by tuning etherification degree of butyl and propyl ether side chains.

3.3. Stability of HPC ether and ester derivatives after heating

Finally, we evaluated the stability of HPC-Bue and HPC butyl ester (HPC-BuE) after storing them as bulk state settled on the petri dishes in an oven at 60 °C for 20 days. For this purpose, HPC-BuE was synthesized by esterification of HPC with butyryl...
chloride according to our previous report [24]. Figure 4 shows the changes of FT-IR spectra before and after heating at 60 °C for 20 days. The stability of HPC-BuE and HPC-Bue was evaluated from the changes of FT-IR spectra.

Before heating of HPC-BuE, there was no peak in the wavenumber range from 3000 cm\(^{-1}\) to 4000 cm\(^{-1}\) in the FT-IR spectrum, as shown in the upper figure of Fig. 4, because of full esterification of HPC by butyryl chloride. After heating treatment of HPC-BuE at 60 ºC for 20 days, the peak intensity of O-H stretching vibration around 3500 cm\(^{-1}\) increased owing to the hydrolysis of ester linkage.

On the other hand, HPC-Bue has not only butyl ether side chains, but also remaining hydroxy groups, as mentioned above. Therefore, we observed a peak of O-H stretching vibration at 3500 cm\(^{-1}\) even before heating. The peak intensity of HPC-Bue did not change even after heating for 20 days. Such unchanged behavior of O-H stretching vibration is attributed to the thermal stability of robust ether linkage.

In order to evaluate the changes of reflection properties after heating at 60 ºC for 20 days, we measured the transmission spectra of HPC-Bue and HPC-BuE before and after heating at 60 ºC for 20 days. As a result, no change in reflection peak wavelength was observed for HPC-Bue even after the heating treatment. On the other hand, the reflection peak of HPC-BuE shifted to longer wavelength at the same temperature after the heating treatment. This is because the helical pitch is longer as the amount of residual hydroxy groups in the side chains of HPC ester derivatives increases, as indicated by the precedent [14]. Such salient stability of HPC ether derivatives provides a promising research strategy to fabricate the stable photonic CLC devices with reflection properties by using cellulose derivatives.

4. Conclusion

We have successfully synthesized HPC derivatives with alkyl ether side chains through Williamson ether synthesis. Such HPC ether derivatives exhibited thermotropic CLC phase with visible reflection characteristics. The thermally induced shifting behavior of reflection peak was controllable by changing etherification degree of alkyl side chains. We found that HPC-BuE hydrolyzes after heating at 60 ºC for 20 days, resulting in the longer wavelength shift of reflection peak, as confirmed by both FT-IR and transmission spectral measurements. On the other hand, HPC-Bue exhibited adequate stability of reflection peak after heating at 60 ºC for 20 days, arising from the robust ether linkage of HPC-Bue. The present report includes promising guideline for the rational design and fabrication of novel photonic CLC devices based on the cellulose derivatives.

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