

Cellulose Derivatives for Color Imaging Applications

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ABSTRACT

Cellulose which is the most abundant naturally occurring polymer on the planet earth has attracted considerable interest as one of sustainable materials from the viewpoint of environment and natural resource issues. Cellulose derivatives are well-known to exhibit cholesteric liquid crystal (CLC) phase. When the CLC helical pitch corresponds to several hundred nanometers, the CLCs allow us to visualize Bragg reflection as the colors. This presentation reports on our recent accomplishments of the cellulose CLC materials for versatile applications of not only full-color imaging, but also mechanical stress sensing.

1 INTRODUCTION

Chlorophyll pigments in the leaf of green plants absorb light energy, usually from the sun, thereby leading to the photosynthesis converting from light energy to chemical energy. In this chemical process, carbon dioxide reacts with water to produce the cyclic monosaccharide molecule of glucose, i.e., sugar, concurrently releasing oxygen as a by-product. Subsequently, the glucose molecules are condensed to produce polysaccharides as starch or cellulose. The former is stored inside the plant cell as grains, and the latter is used to build the cell wall of plant cells.

Thus, cellulose is a primary chemical component in the cell walls of green plants, supporting the plants to grow stiffly and uprightly. Therefore, cellulose is the most plentiful among any organic compounds existed on the planet earth. In our daily life, we can find cellulose in natural products as paper, cotton, wood, linen, and wood building materials. In addition, cellulose derivatives such as cellophane, rayon, and cellulose acetate also are commercially available as synthetic products of resins, textiles, films, and plastic objects.

Cellulose is a linear polymer of β -glucose units through the glycosidic bonds, as shown in Figure 1. Inter- and intra-macromolecular hydrogen bonds of hydroxy groups in cellulose lead to the formation of tough microfibrils like as cellulose nanofibers [1]. Due to the multiple hydrogen bonding, it is extremely difficult to solubilize pristine cellulose in water and common organic solvents. However, when cellulose is etherified with propylene oxide, we can dissolve hydroxypropyl cellulose (HPC, Figure 1) in water. Moreover, the highly concentrated aqueous solutions of HPC are well-known to exhibit lyotropic cholesteric liquid crystal (CLC) phase with light reflection [2].

In the CLC phase, the chiral liquid crystal molecules are self-assembled into the hierarchical molecular helical 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 (λ_{Ref}) is numerically expressed as following equation.

$$\lambda_{Ref} = n_{Av} \times p$$

where p means the helical pitch length, and n_{Av} is the average refractive index of CLC materials. When the helical pitch of CLCs corresponds to several hundred nanometers, uniform CLC cells allow us to visualize Bragg reflection phenomenon as the reflection colors.

Following the first observation of lyotropic CLC phase from aqueous solutions of HPC [2], thermotropic CLC materials with visible reflection can be prepared by chemical modification of terminal hydroxy groups of β -glucose monomer units in HPC to ester or ether derivatives [3-8]. In most cases, the HPC derivatives show visible reflection by heating over 100 °C. In other words, such heating treatment at relatively high temperature is prerequisite for generation of the

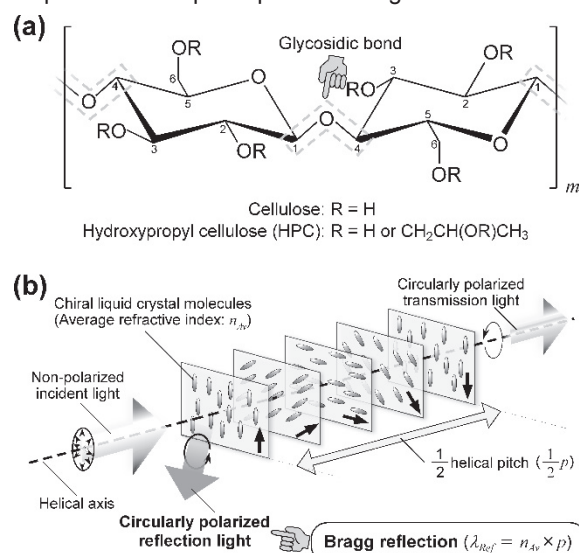


Figure 1 (a) Chemical structures of cellulose and hydroxypropyl cellulose (HPC). (b) Schematic illustration of self-assembled molecular helical structure of cholesteric liquid crystals (CLCs) leading to Bragg reflection phenomenon.

reflection colors by using the previously reported HPC derivatives. In this context, numerous efforts have been so far made on the syntheses and fabrications of color materials derived from cellulose. However, it seems that such thermotropic CLCs of cellulose derivatives would be impractical for color materials due to cumbersome heating treatment to induce the desired reflection colors.

This presentation provides our recent accomplishments of cellulose derivatives as CLC materials. Based on our molecular design, we can prepare the HPC derivatives exhibiting CLC phase with visible reflection below 100 °C. When the crosslinkable HPC derivatives tethering acryloyl groups in the side chains are irradiated with UV light, the acryloyl groups are crosslinked between the polymer networks, resulting in the simple fabrication of full-color imaging films. Such CLC films of HPC derivatives can be also applied to the mechanical stress sensing.

2 EXPERIMENTAL SECTION

In order to prepare thermotropic CLCs of cellulose derivatives with reflection colors heated at relatively low temperature, we designed and synthesized HPC esters possessing propionyl group (HPC-Pr), butyryl group (HPC-Bu), and propionyl/butyryl mixed groups (HPC-Pr/Bu). The chemical structures are shown in Figure 2. Briefly, the HPC-R' were prepared by esterification of pristine HPC with alkanoyl chlorides, and subsequently were purified through repeated reprecipitation in water. Finally, the products were dried at room temperature for several weeks. From the ¹H-NMR spectra, we estimated the esterification degrees of propionyl (PrE) and butyryl groups (BuE) of HPC-R' esters.

The HPC derivatives were sandwiched between a pair of glass substrates coated with uniaxially rubbed poly(vinyl alcohol) films to induce well-aligned CLC structure. The cell gap was adjusted by using poly(tetrafluoroethylene) films with the thickness of 100~500 μm.

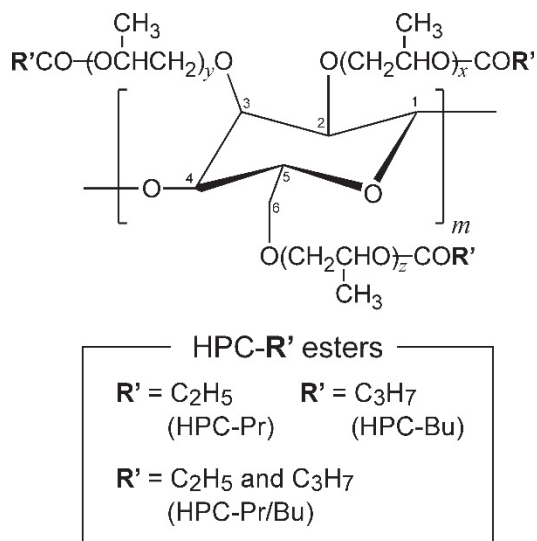


Figure 2 Chemical structures of HPC esters used in this study.

3 RESULTS AND DISCUSSION

3.1 Reflection Properties of HPC-R' Esters

Figure 3 (a) shows the changes in transmission spectrum of a CLC cell of HPC-Pr measured upon stepwise heating process from 90 °C to 130 °C. As heated at 90 °C, HPC-Pr exhibited Bragg reflection as blue color, whose peak appeared around 400 nm. When the temperature of CLC cell was elevated from 90 °C to 130 °C, the reflection peak wavelength shifted to longer wavelengths in continuous way due to increasing the pitch length of molecular helical structure at CLC phase. Eventually, when the cell was heated at 130 °C, the reflection peak reached 650 nm. At this stage, we observed Bragg reflection as red color. Thus, we investigated that HPC-Pr shows the thermally induced reflection changes throughout the full-visible wavelength range.

In order to evaluate the effect of side chains of HPC-R' on the reflection properties, we synthesized the HPC ester tethering butyryl groups that the number of carbon increases by one than propionyl group (HPC-Bu, Figure 2). As a result, we found that HPC-Bu shows visible reflection properties in lower temperature range between 70 °C and 120 °C than that of HPC-Pr. Moreover, the reflection wavelength shifting range by temperature broadened from 480 to 780 nm.

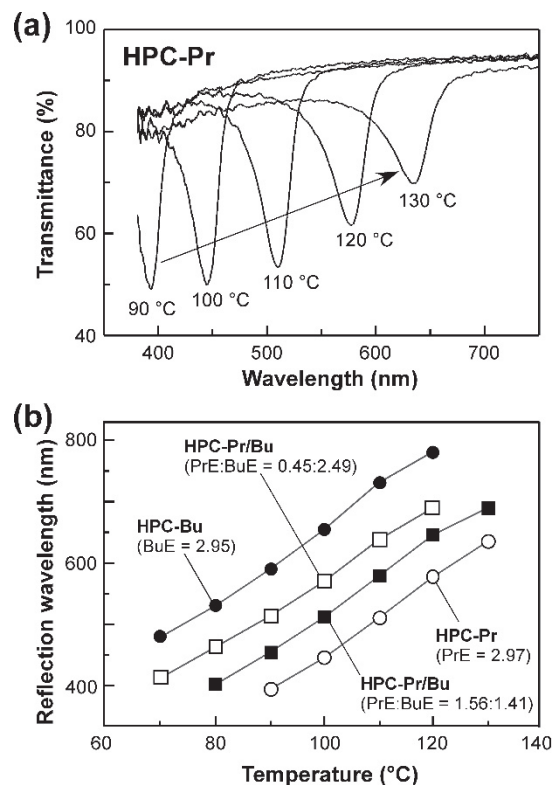


Figure 3 (a) Transmission spectral changes of HPC-Pr upon heating process. (b) Temperature dependences of reflection peak wavelengths observed from HPC-R' esters.

On account of the experimental results of HPC-Pr and HPC-Bu, we attempted to measure the transmission spectral changes for two kind of HPC propionyl/butyryl mixed esters (HPC-Pr/Bu) with different esterification degrees. In this study, we prepared the HPC mixed esters with PrE:BuE of 0.45:2.49 and 1.56:1.41. Figure 3 (b) compiles the changes in reflection peak wavelengths of HPC-Pr, HPC-Bu, and HPC-Pr/Bu as a function of temperature. As evident from the profiles, all of HPC-R' esters showed the continuous red-shift of reflection peaks upon heating process. However, the reflection peaks of HPC-R' esters measured at same temperature appeared at longer wavelengths as increasing the BuE values of HPC-R' esters. In this way, we revealed that the reflection properties are controllable by changing the chemical structures of side chains in HPC-R' esters.

3.2 Full-Color Imaging Films

On-demand control and physical stabilization of molecular alignment patterns on large area are of prime importance for the practical fabrication of next-generation optoelectronic devices with high performances.

For this purpose, we prepared crosslinkable HPC derivatives tethering acryloyl and butyryl side chains (HPC-Ac/Bu) by esterifying the terminal hydroxy groups of β -glucose monomer units in HPC with acryloyl chloride and butyryl chloride. We found that some kinds of HPC-Ac/Bu derivatives show the continuous changes of Bragg reflection peak throughout the full visible-wavelength range between 400 nm and 800 nm by changing the temperature below 100 °C. The reflection wavelength shift was reversible by both heating and cooling processes.

Subsequently, photoirradiation of a cell of HPC-Ac/Bu with UV light brought about the intermacromolecular photocrosslinking reaction between the acryloyl side chains of HPC-Ac/Bu, resulting in the formation of robust CLC solid-state films with visible reflection at a particular wavelength. Such reflection wavelengths preserved by the intermacromolecular photocrosslinking reaction were thermally stable even after heating up to 180 °C. Furthermore, as the photocrosslinking reaction of HPC-

Ac/Bu was carried out at the different CLC phase temperatures, we could prepare the colorful patterned CLC films by the photolithographic technique, as shown in Figure 4. Thus, we succeeded in the simple fabrication of flexible, environmentally friendly, low-risk CLC films of cellulose derivatives with full-color images.

3.3 Mechanical Stress Sensing Films

More interestingly, we developed the crosslinkable cellulose derivatives for CLC elastomer films with an intrinsic capability to shift the reflection wavelengths by mechanical stress. When the CLC elastomer film of HPC derivative was compressed by mechanical stress along the film-thickness direction, the reflection peak shifted to shorter wavelength due to geometric reduction in the molecular helical pitch of CLCs. Moreover, after releasing the CLC elastomer films from the compressed state, the reflection peak could be returned to the initial wavelength. Therefore, we confirmed that such reflection wavelength changes by mechanical stress are fully reversible.

In this way, we successfully demonstrated the quantitative visualization of physical pressure on the target objects through the reflection color changes. Taking advantage of these salient features, we can envisage that the CLC elastomer films of cellulose derivatives would be available as the social infrastructure sensors for deterioration or damage of objects such as metals and concretes, wearable sensors for human medical care, and so forth.

4 CONCLUSIONS

This presentation provides the technological developments of cellulose materials for the versatile applications of full-color imaging and mechanical stress sensing. Nowadays, we encounter serious problems on global environment, natural resources, and microplastics. In this kind of situation, we utilized the naturally occurring, earth abundant polymer of cellulose to fabricate the environment and human benign, low cost, recyclable photonic devices for the sustainable societies. Therefore, our strategy would contribute to a wide variety of research fields of not only material sciences and photonics, but also environmental sciences.

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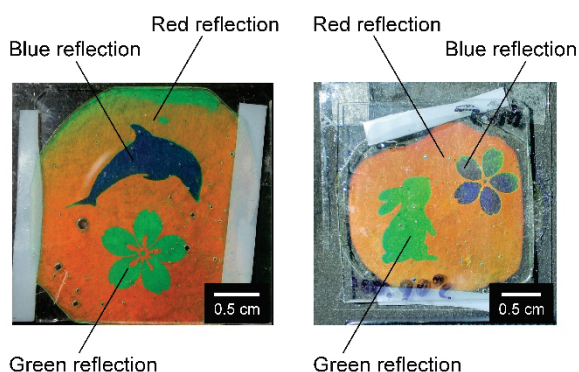


Figure 4 Full-color imaging films of crosslinkable cellulose derivatives fabricated by the photolithographic technique.

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