

A TEMPERATURE AND pH DOUBLE SENSITIVE CHOLESTERIC POLYMER FILM FROM A PHOTOPOLYMERIZABLE CHIRAL HYDROGEN-BONDED ASSEMBLY*

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Abstract In this study, a novel H-bonded cholesteric polymer film responding to temperature and pH by changing the reflection color was fabricated. The H-bonded cholesteric polymer film was achieved by UV-photopolymerizing a cholesteric liquid crystal (Ch-LC) monomers mixture containing a photopolymerizable chiral H-bonded assembly (PCHA). The cholesteric polymer film based on PCHA can be thermally switched to reflect red color from the initial green/yellow color as temperature is increased, which is due to a change in helical pitch induced by the weakening of H-bonded interaction in the polymer film. Additionally, the selective reflection band (SRB) of the cholesteric polymer film in solution with $\text{pH} > 7$ showed an obvious red shift with increasing pH values. While the SRB of the cholesteric polymer film in solutions with $\text{pH} = 7$ and $\text{pH} < 7$ hardly changed. This pH sensitivity in solutions with $\text{pH} > 7$ could be explained by the breakage of H-bonds in the cholesteric polymer film and the structure changes induced by $-\text{OH}^-$ and $-\text{K}^+$ ions in the alkaline solution. In contrast, it couldn't happen in the neutral and acidic solutions. The cholesteric polymer film in this study can be used as optical/photonic papers, optical sensors and LCs displays, etc.

Keywords: Cholesteric polymer film; Reflection band; Stimulus responsive; Chiral hydrogen-bonded assembly.

INTRODUCTION

Over the last few years, responsive materials and sensors, which are able to change their optical and electrical properties due to external stimuli, have aroused great interest in the scientific world^[1–11]. Cholesteric liquid crystals (Ch-LCs) possess characteristics of wavelength- and polarization-selective reflection when placed between glass plates coated with rubbed polyimide, due to the periodic helical structure of the molecules arrangement^[12]. The selective reflection band (SRB) is centered at the wavelength $\lambda = n \cdot P$ where P is the pitch of the chiral LC^[13], and $n = (n_e + n_o)/2$ where n_e and n_o are the extraordinary and ordinary indices of refraction respectively. The bandwidth ($\Delta\lambda$) is defined as $\Delta\lambda = \Delta n \cdot P$ where Δn is the birefringence of the liquid crystal. Ch-LC can reflect circularly polarized light with the same sense of the cholesteric helix within the reflection band while both circularly polarization lights outside the reflection band were transmitted^[14, 15]. Ch-LC has the ability to shift the selective reflection by changing external factors including electric, magnetic, acoustic fields, temperature and light irradiation^[16–20]. Therefore, Ch-LCs have been widely studied as colorimetric sensors and information-display devices due to the great importance of reflection characteristics with respect to fundamental properties and applications^[21–27]. Colorimetric Ch-LCs monitors for gaseous carbon dioxide and oxygen were prepared by Sijbesma's group, in which responsive chiral compounds were used as dopants^[21]. A polymer

* The work was financially supported by the National Natural Science Foundation of China (No. 50903004).

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Received June 5, 2012; Revised August 16, 2012; Accepted August 29, 2012
doi: 10.1007/s10118-013-1244-5

stabilized Ch-LCs array with various polymer concentrations was fabricated by Yang's group, which shows distinct colorimetric responses to primary amine vapors at wider temperature ranges^[22].

H-bonded thermotropic LCs and supramolecular structures are promising candidates for a variety of sensors because they are readily fabricated and have the potential to form a variety of structures with a broad range of new properties. With H-bonded cholesteric polymer films containing donor/acceptor side groups, one can expect much higher sensitivity of the helical supramolecular structure toward molecules disrupting H-bonds^[28–31]. A responsive cholesteric polymer film based on H-bond effect of carboxylic acid dimers H-bonded was fabricated by Shibaev^[32, 33], it exhibited optically pumped lasing at the various wavelengths, depending on the SRB position determined by the pH of the chemical environment, as well as color changing and SRB shifting responding to the presence of the basic amino acids in surrounding aqueous solutions.

In this study, we investigated temperature/pH dual tuning of the cholesteric polymer films based on H-bond effect between pyridyl groups and carboxylic acid in the films. The cholesteric polymer films prepared in this study were capable of responding to temperature/pH by shifting the SRB and changing reflection color due to the sensitivity of H-bonds in the films. The relationship between the temperature/pH-induced H-bonds change and the cholesteric helical structure was revealed. This provides a new insight into the design and development of novel functional materials based on the cholesteric polymer film.

EXPERIMENTAL

Materials

Chiral photopolymerizable LC monomer CPLCM (BASF Co., Ltd.) and photoinitiator, 2,2-dimethoxy-1,2-diphenyl-ethanone (Irgacure651, TCI Co., Ltd) were used. Photopolymerizable LC acid, 4-(6-acryloyloxyhexyloxy) benzoic acid (AHBA, proton donor), and components of nematic photopolymerizable LC mixture (NPLCM) were synthesized according to the method suggested by Broer *et al.*^[34]. Isosorbide isonicotinate (ISIN, proton acceptor) was synthesized by us in previous paper^[35]. Photopolymerizable chiral hydrogen-bonded assembly (PCHA, ISIN-AHBA) was prepared by mixing of ISIN with AHBA in THF, followed by removal of the solvent. Figure 1 shows the chemical structures of NPLCM, CPLCM, PCHA and Irgacure 651.

Experiment Cells

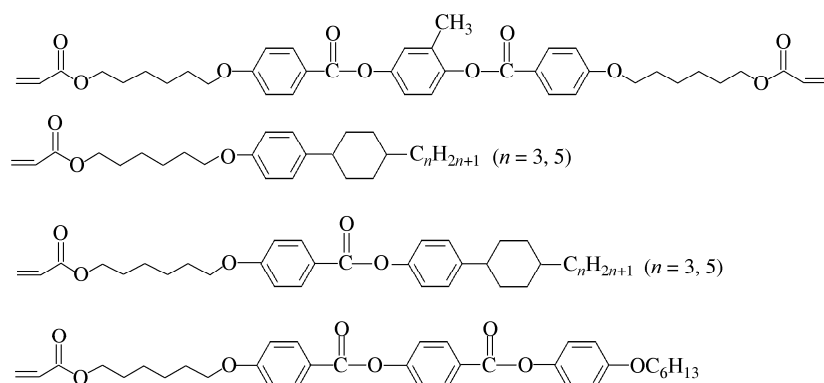
In order to induce a planar orientation of LC molecules, the inner surfaces of glass cells were coated with a 3.0 wt% polyvinyl alcohol (PVA) aqueous solution. The deposited film was dried at 80 °C for 30 min and subsequently rubbed with a textile cloth under a pressure of 2.0 g/cm² along one direction. PET (polyethylene terephthalate) films of (25 ± 5) μm thickness were used as the cell spacers. The samples were filled into the cells by capillary action at an appropriate temperature. To induce photo-polymerization, the cells containing an H-bonded Ch-LC composite were irradiated for 5 min with UV light (5.0 mW/cm², 365 nm). The compositions of the samples are listed in Table 1.

Table 1. The compositions of the samples used in this study

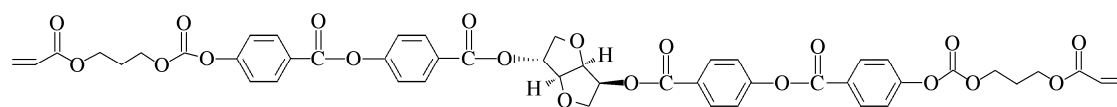
Sample	Weight ratio	$T_{\text{Ch-I}}$ (°C) ^a
I	4.5% CPLCM/10% PCHA/83.5% NPLCM/2% Irg651	92
II	4.0% CPLCM/13.5% PCHA/80.5% NPLCM/2% Irg651	86
III	3.5% CPLCM/16% PCHA/78.5% NPLCM/2% Irg651	77
IV	2.5% CPLCM/20% PCHA/75.5% NPLCM/2% Irg651	65

^a $T_{\text{Ch-I}}$ clearing temperature from cholesteric to isotropic phase, measured by POM

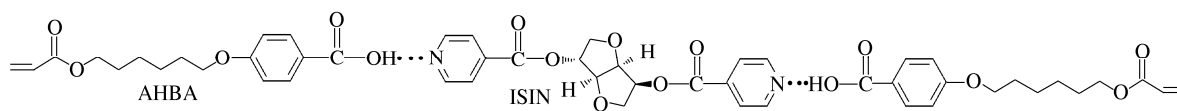
(a) Nematic photopolymerizable liquid crystal mixture: NPLCM



(b) Chiral photopolymerizable liquid crystal monomer: CPLCM



(c) Photopolymerizable chiral hydrogen-bonded assembly: PCHA



(d) Photoinitiator: Irgacure 651

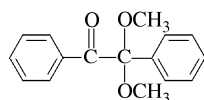


Fig. 1 Chemical structures of NPLCM, CPLCM, PCHA and Irgacure651

Fabrication of the H-bonded Cholesteric Polymer Films

The H-bonded cholesteric polymer films were fabricated by carrying out the following procedures as shown in Fig. 2. At first, the samples as listed in Table 1 were filled into the cells by capillary action at their cholesteric phase temperature. Then these cells were irradiated with UV light (365 nm, 5.0 mW/cm²) at this temperature for 5 min for polymerization purposes, and Fig. 2(b) represents the cell containing the H-bonded Ch-LC composite after polymerization. After that, the cholesteric polymer films were peeled off the glass substrates ready for the study of temperature and pH responsibility. On one hand, the above achieved polymer films were placed on a hot stage and heated from 60 °C to 200 °C at 10 K/min for the investigation of temperature responsibility. On the other hand, several cholesteric polymer films were immersed in five aqueous solutions with different pH values, pH = 14, 12, 10, 7, and 1, respectively. The aqueous solutions with different pH values were prepared by KOH and HCl aqueous solutions and followed by refreshed once a day in order to keep the pH value constant. The eventual response of the films depending on the helical pitch change from P1 to P2 and the swelling of the polymer network were simulated by the model in Figs. 2(b)–2(c). Furthermore, partial enlargement drawing of Fig. 2(c) reveals the mechanism of reduction or disruption of H-bonds induced by temperature and pH, which would be indicated later.

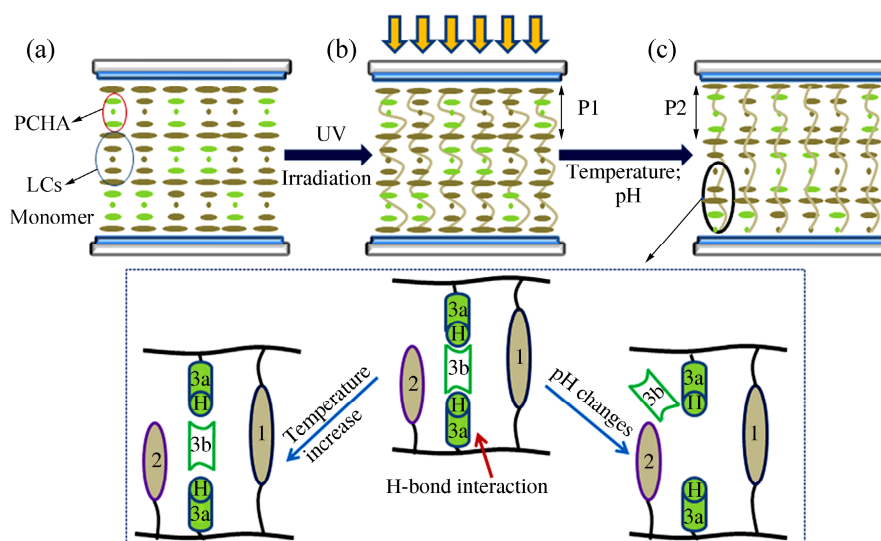


Fig. 2 Illustration of the fabrication procedure of the H-bonded cholesteric polymer film: (a) and (b) cells containing H-bonded Ch-LC composites before and after polymerization, (c) cholesteric polymer film after being treated by temperature and pH

The partial enlargement drawing is the mechanism of the weakening and disruption of H-bonds induced by temperature and pH in the polymer structure, 1 is nematic or chiral cross-linker, 2 is nematic group, 3 is PCHA with 3a/3b corresponding to the proton donor AHBA and the proton acceptor ISIN, and H is the —COOH group.

Measurements

RT-IR (real time) spectra were also taken on the Nicolet 5700 spectrometer at frequencies ranging from 400 cm^{-1} to 4000 cm^{-1} . Sample was prepared by heating the H-bonded Ch-LC composite to 60°C of its cholesteric phase temperature, followed by coating to a KBr pellet and covering with another KBr pellet. Then the sample at 60°C was placed in the IR spectrometer chamber and exposed to the UV light (365 nm) at an intensity of 5.0 mW/cm^2 through the quartz window with the aid of an optical fiber cable. Subsequently, the reduction in the IR absorbance of double bonds at specific wavenumber was monitored to determine the reaction rate. The conversion of the carbon double bond at a given time was calculated according to the equation, $\alpha_w(t) = \{(A_w)_{t0} - (A_w)_t\} / (A_w)_{t0}$, where w is the wavenumber; $\alpha_w(t)$ is the conversion of the bond at w wavenumber; $(A_w)_t$ is the area of that bond when the sample is irradiated for t time. In this study, we calculate the conversion by the wavenumber at 811 cm^{-1} .

The phase transition behavior of the H-bonded Ch-LC composite was observed by POM (Leica, DM2500P) with a hot stage calibrated to an accuracy of $\pm 0.1\text{ K}$ (Linkam, THMS-600). The reflection spectra were collected on an AvaSpec-USB2 version 7.3 fiber spectrophotometer in reflection mode. Herein, the size and thickness of the film sample are $1\text{ cm} \times 2\text{ cm}$ and about $25\text{ }\mu\text{m}$, respectively. The morphology of the polymer network was observed by scanning electron microscopy (SEM; Hitachi, S-4700). The samples for SEM studies were prepared according to the method described in the previous study^[36, 37].

RESULTS AND DISCUSSION

As mentioned above, Ch-LCs as stimuli responsive optical materials, capable of dynamic color tuning or switching, have been widely investigated recently. Herein, we fabricated a kind of H-bonded cholesteric polymer films by photopolymerizing a Ch-LCs monomers mixture containing a PCHA which can respond to temperature and aqueous solutions with different pH values. First, we used the RT-IR technique to monitor the polymerization process of Ch-LCs monomer mixtures. Figures 3(a) and 3(b) show the RT-IR spectra of cell A with sample I containing H-bonded Ch-LC composite irradiated with UV light intensity of 5.0 mW/cm^2 and the corresponding conversion of double bonds in the H-bonded Ch-LC composite during the photo-polymerization

process. The cross-linking reaction rate of double bonds was determined by monitoring the reduction of IR absorbance at about 811 cm^{-1} , corresponding to the C—H stretching vibration on the $-\text{C}=\text{CH}$ group. As shown in Fig. 3(a), with the exposure time increasing from 0 s to 120 s, the intensities of bands at 811 cm^{-1} decrease dramatically and this results from the loss of C=C bonds caused by photo-polymerization. The conversion of C=C double bonds increases sharply at the first 5 s, indicating a fast curing reaction of the polymerizable Ch-LC composite. After 120 s, the conversion reached a stable value of about 85% and could reach a higher conversion by prolonging time, but by no means increase up to 100% because the viscosity dramatically increases during the fast curing reaction^[38], as seen in Fig. 3(b). This indicates that the double bonds in the polymerizable H-bonded Ch-LC composite almost finished reaction in the first several seconds and there were un-reacted LC monomers left in the final cured film, which provided free volume for molecular movements. Figure 4 shows SEM images of the cross-section of cell A after polymerization. Herein, Figure 4(b) is a partial enlarged image of Fig. 4(a), from which the distribution of the pitch length of the cholesteric polymer film can be observed clearly.

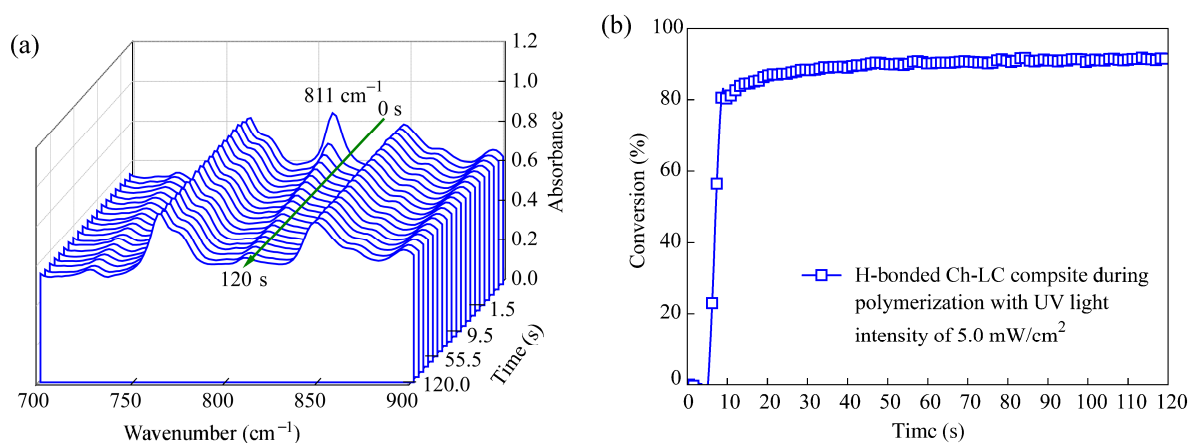


Fig. 3 (a) RT-FTIR spectra of cell A with sample I containing H-bonded Ch-LC composite irradiated with UV light at intensity of 5.0 mW/cm^2 ; (b) Corresponding conversion of double bonds during the photo-polymerization

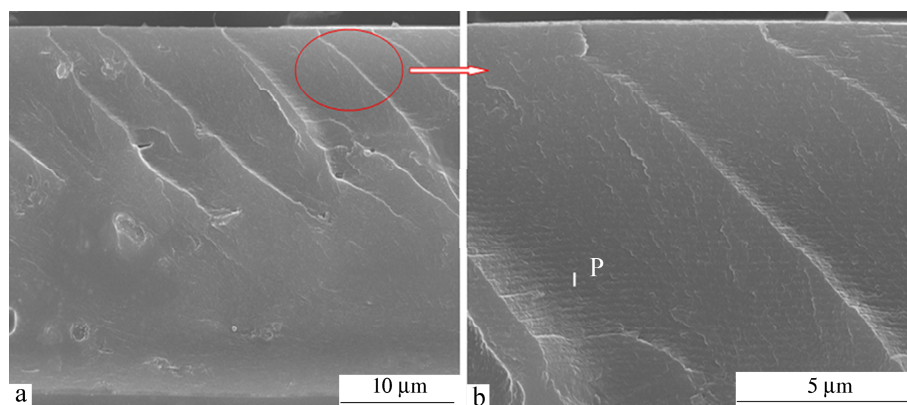


Fig. 4 SEM micrograph of the cross-section of the cell A after polymerization (a) and a partial enlarged image (b)

Figure 5 represents the temperature dependence of the reflection spectra of cell A with sample I before polymerization. Herein, CPLCM was added to adjust the reflection band of the composite to the visible region, and the helical pitch of CPLCM hardly changed with increasing temperature, which would impossibly

contributes to the final helical pitch change of the H-bonded Ch-LC composite as well as the cholesteric polymer film. The reflection wavelength of cell A before polymerization exhibited an obvious red shift from 570 nm to 680 nm with a constantly increasing temperature from 60 °C to 90 °C, and the reflection color of the cell A changed from green/yellow to red, which results from the helical twisting power (HTP) of PCHA in the H-bonded Ch-LC composite decreasing with the temperature increasing as described for HTP test in our previous study^[35]. The high viscosity of the polymerizable Ch-LC led to the difficulty of thermal conductivity and reorientation of Ch-LC molecules when applying to a thermal field, as a result of the inhomogeneous color distribution at 80 °C as shown in the insets of Fig. 5. It is noteworthy that the reflection intensity decreases when the cell A is heated up to 90 °C, which is ascribed to that the temperature is close to the clear point of the H-bonded Ch-LC composite.

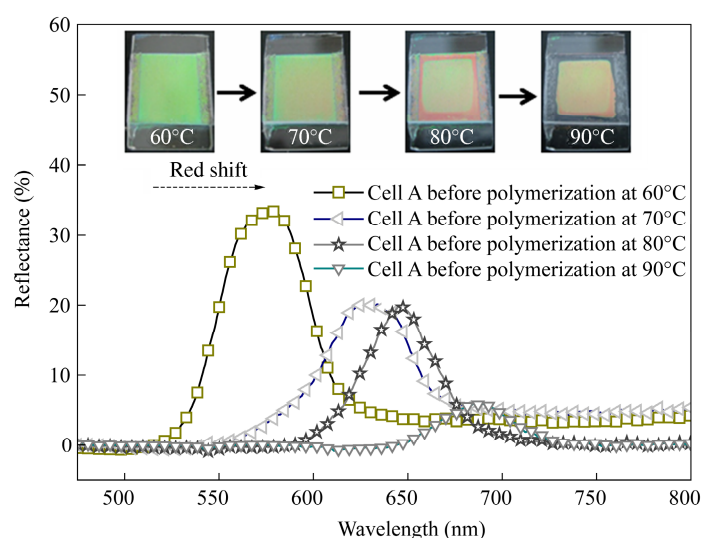


Fig. 5 Temperature dependence of the reflection spectra of the cell A before polymerization. The insets are the photos of the cell taken at different temperatures.

Figure 6 shows the temperature dependence of the reflection spectra of cell A with sample I after polymerization and the insets are the photos of the film taken at different temperatures. With temperature increasing from 60 °C to 200 °C, the reflection wavelength of the cell A after polymerization showed a red shift from 570 nm to 611 nm and the corresponding reflection color changed from green/yellow to yellow/red. These observations were consistent with two reasons. First, as we all know, H-bond is a kind of un-covalent chemical bond, which is highly sensitive to external stimuli, such as temperature, pH and so on. According to our previous study, PCHA possess good thermally responsibility depending on the temperature inducing weakening of the H-bond strength. That is, HTP of PCHA has an obvious change with increasing temperature^[35]. This indicates the H-bonds actually influenced the SRB shift and the color changes of the cholesteric polymer film heated from 60 °C to 200 °C. Additionally, the RT-IR measurement results suggest the existence of free volume due to the un-reacted LCs monomers in the final cured film, and thus the free volume in the cholesteric polymer film led to possibility of the reorientation of molecules in the solid film due to the thermal field. On the basis of the above two factors, the H-bond interaction distance in the polymer film can change freely as well as the reorientation of the Ch-LC molecules. Herein, the distance of H-bond interaction between the proton donor and acceptor is widened by heating, which has a diagrammatic presentation in the partial enlargement drawing of Fig. 2(c). And this contributes to the increase of the helical pitch from P1 to P2 as simulated in Figs. 2(b) and 2(c), which results in the red shift of the SRB and the reflection color changes from green/yellow to red. Therefore, H-bonds played a key role in the thermally switching of the cholesteric polymer film. It is noteworthy that the position of SRB of the cholesteric film during temperature decreasing from 200 °C to 60 °C overlapped with that of

temperature-rise period as well as the recoverable reflective color of the film, which indicates that the cholesteric film is able to be reversibly switched by heating and cooling due to the reversibility of H-bonds in the film. Finally, it is interesting that the film maintained the selective reflection properties during the temperature increasing from 60 °C to 200 °C as shown in Fig. 6, which indicates a wider cholesteric phase in the cholesteric polymer film was formed, compared to that of the H-bonded Ch-LC composite before polymerization as shown in Fig. 5. The possible reason is that the transition of monomer to polymer in the film enlarges the cholesteric phase temperature range and raises the isotropic temperature of the cholesteric polymer film.

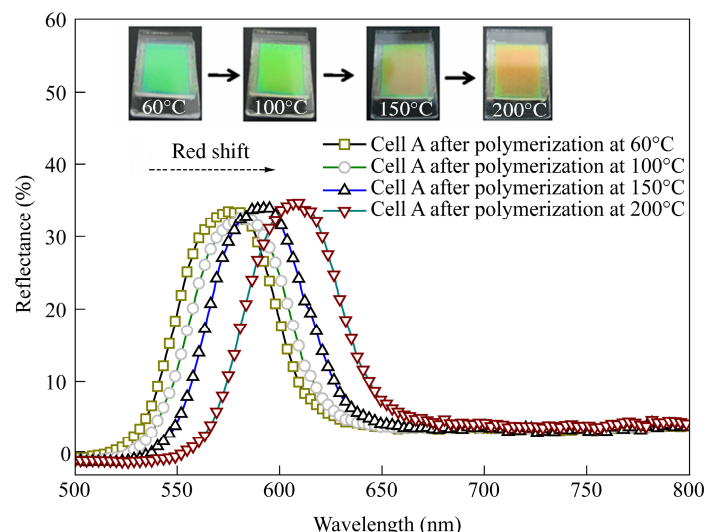


Fig. 6 Temperature dependence of the reflection spectra of the cell A after polymerization
The insets are the photos of the film taken at different temperatures.

The cell A after polymerization (called film A) were immersed in aqueous solutions with different pH values to investigate the pH responsibility. The films A related to different pH were kept in the corresponding aqueous solutions for the same time of 5 days at room temperature. The photos of color response of the film A were recorded as shown in the insets of Fig. 7. It can be seen that the initial films corresponding to the five aqueous solutions with different pH values reflect green/yellow color. After 5 days, the film A in aqueous solutions with pH = 14 and 12 showed an obvious red color, while no visible color change could be observed in aqueous solutions with pH = 7 and pH = 1. Meanwhile, the SRB shifts of the film A corresponding to the five pH solutions at wet state were measured as shown in Fig. 7, where ‘measured at wet state’ means the spectra was recorded when the films were taken from the solutions of 5 days later without any drying processing. It can be seen in Fig. 7 that the films immersed in aqueous solution with pH > 7 presented bigger SRB shift than those of pH < 7 and pH = 7. These results indicate the SRB of the film A was more sensitive to the alkaline solution than the acidic and neutral solutions, which could be explained by the chemical structures in Fig. 8. In aqueous solutions with pH > 7, the OH^- and K^+ ions were able to diffuse into the film A and interacted with the COOH groups as a result of the ionization of COOH group, resulting in the rupture of the H-bond. It kept COO^- group away from the pyridyl groups as shown in the partial enlargement drawing in Fig. 2(c), which caused the swelling of the film as a result of the longer helical pitch. It can be concluded the breakage of H-bonds in the cholesteric polymer film plays a major role in the shift of the SRB and the color change, which determine the pH responsibility of the cholesteric polymer film^[32, 33]. It can also be seen in Fig. 7 that the film A in aqueous solutions with higher pH values has a bigger red shift, due to that aqueous solutions with higher pH values contain higher OH^- and K^+ concentration as a result of quicker H-bonds breaking speed. So it can come to the conclusion that the films possess bigger sensitivity in aqueous solutions with higher pH values with the same treatment time.

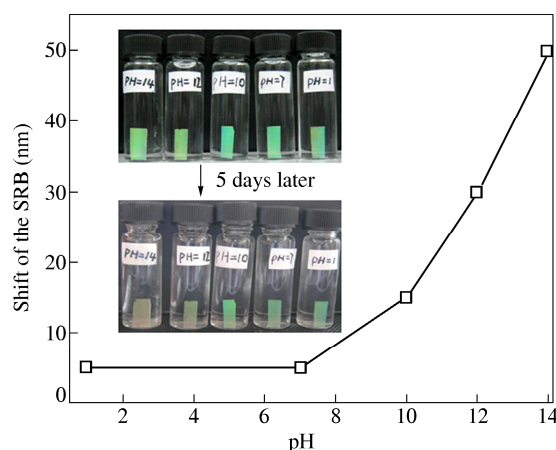


Fig. 7 Shift of the SRB of the film A after treatment in aqueous solutions with different pH values for 5 days. The insets are the corresponding photos of the initiative films and the films after 5 days treatment.

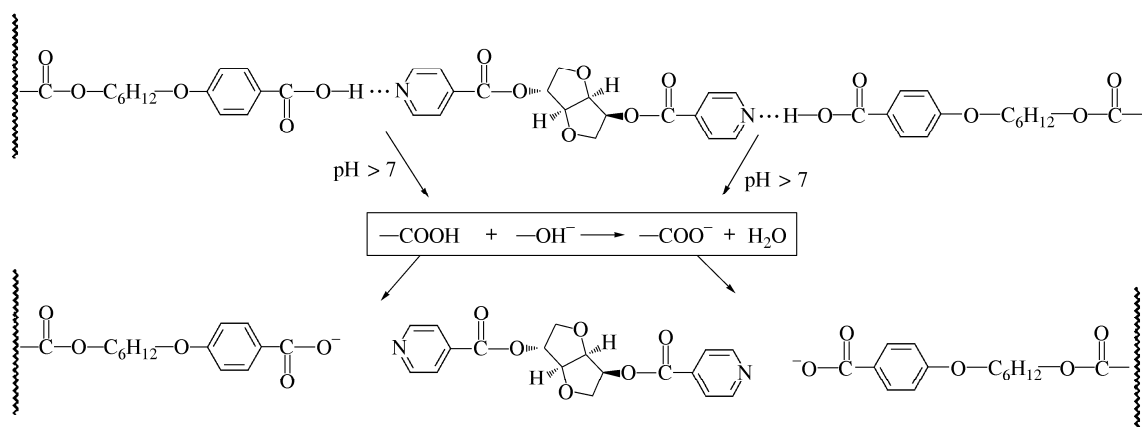


Fig. 8 Drawing of breaking H-bonds in the cholesteric polymer films

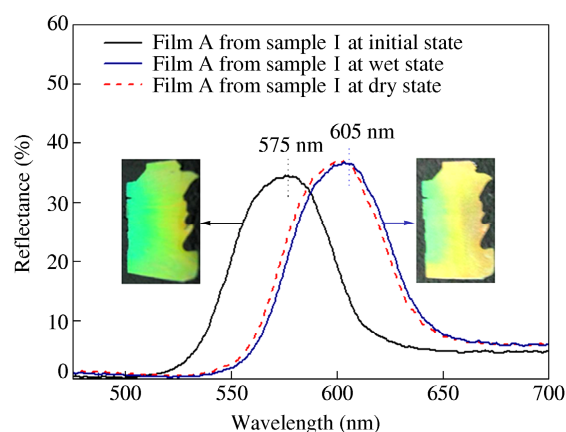


Fig. 9 Reflection spectra of the film A at the initial state, wet state after treatment and dry state after treatment. The insets are the photos of the film A at the initiative and wet state.

Figure 9 shows the reflection spectra of the film A at different states, including initial state before treatment, the wet and dry state after a five days' treatment in aqueous solution with pH = 12, where the film A at dry state was obtained by taking the film out of the solutions at the fifth day, followed by drying in *vacuo* for a week. Before treatment, the center of the SRB of the film A lay at 575 nm and the corresponding photo of the green color film was shown in the insets of Fig. 9. After treating for 5 days, the film A at wet state displayed a selective reflection band at the position of 605 nm and reflected an obvious yellow as shown in the insets of Fig. 9. And the magnitude of the SRB shift toward longer wavelength was about 30 nm. The SRB position of the film A at dry state almost overlapped with that of the wet film, if ignoring several nanometers' blue shift derived from the shrinkage of the polymer network.

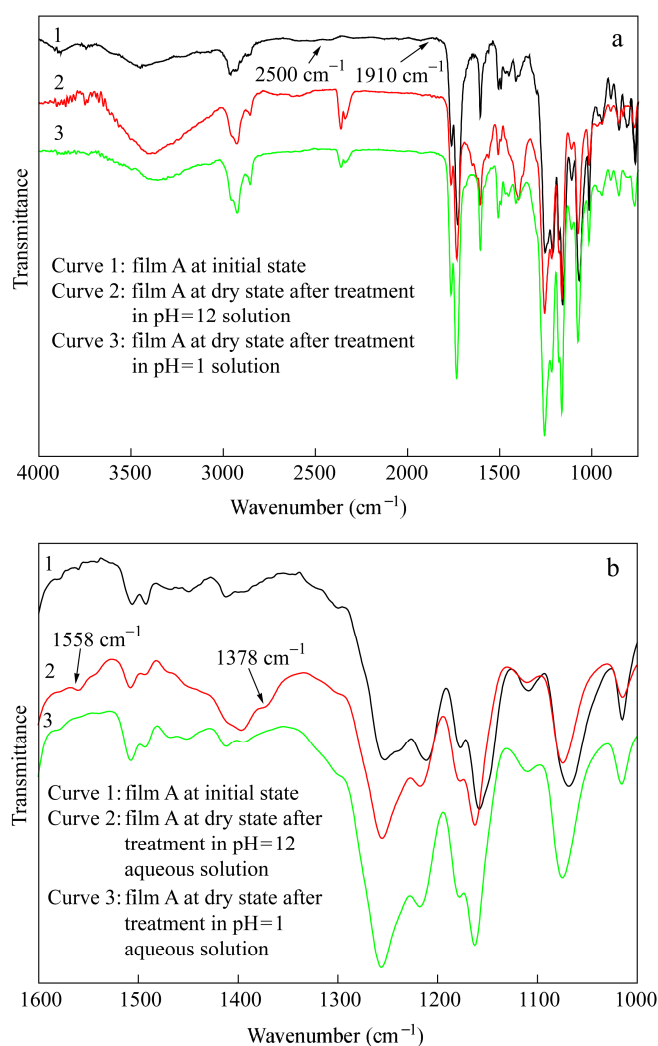


Fig. 10 (a) FT-IR spectra of film A at initial state, dry state after a five days' treatment in pH = 12 and pH = 1 aqueous solution, and (b) a partial image of FT-IR spectra

Figure 10 shows the FT-IR spectra of the film A at initial state (curve 1), dry state after a five days' treatment in aqueous solutions with pH = 12 and pH = 1 (curve 2 and curve 3), respectively. It is obvious that the small peaks at 2500 cm^{-1} and 1910 cm^{-1} disappear at dry state of the film A after a five days' treatment in aqueous solution with pH = 12 (curve 2), which indicates that the H bonds in the PCHA were broken (Fig. 10a). Additionally, the occurrence of two new peaks at $\nu_s = 1558\text{ cm}^{-1}$ and $\nu_{as} = 1378\text{ cm}^{-1}$ suggests the formation of a

potassium carboxylate salt (Fig. 10b). These data reveal the perpetual breakage of H-bonds in alkaline solutions as shown in Fig. 8. However, FT-IR spectrum (curve 3) of the film A after a five days' treatment in aqueous solution with pH = 1 shows little changes compared to that the film A at initial state (curve 1) from the Fig. 10(a) and Fig. 10(b). These observations confirm that pH sensitivity in pH > 7 solutions results from the breakage of hydrogen bonds and the structure changes in the cholesteric polymer film, which is in accordance with our previous explanation.

In order to study the effect of H-bond interaction on the reflection properties of the cholesteric polymer film, films B–D containing samples II–IV with different concentrations of PCHA were prepared as listed in Table 1. The SRB shift of films A–D as a function of treating time in aqueous solution with pH = 12 was monitored as shown in Fig. 11. During the first day, little SRB shift can be detected because enough time is necessary for the OH^- ions to diffuse into the polymer film. After that, the SRB shift increases quickly due to the increasing breakage of H-bonds, it suggests more and more COOH groups are reacted with OH^- ions. Additionally, it is obvious that shift of SRB increases from film A to film D in the same time. For example, after 5 days, the SRB shift of the film D is about 70 nm compared to a 30 nm shift of the film A as shown in Fig. 11, it suggests that increasing the concentration of PCHA (concentration of proton acceptors or donors in H-bonds) in Ch-LCs composites can improve the pH responsibility of the cholesteric polymer films. It should be noted that other factors such as the molecular architecture of chiral H-bonded assembly and film thickness should be optimized in future systematic investigation, in order to achieve a cholesteric LCs polymer which exhibits a faster and more effective response to temperature and pH stimuli.

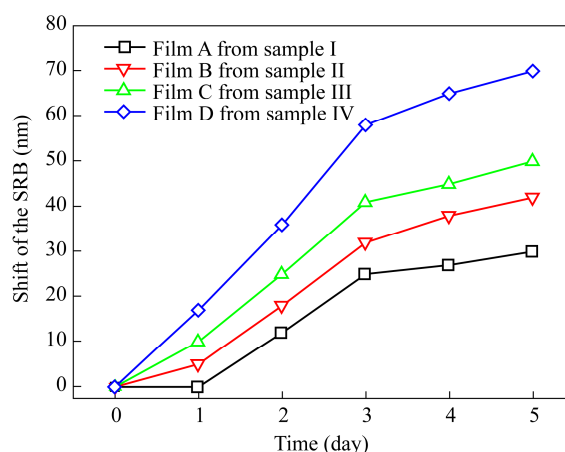


Fig. 11 SRB shift of films A–D as a function of treating time in aqueous solution with pH = 12

CONCLUSIONS

In summary, a cholesteric polymer film with photopolymerizable chiral H-bonded assembly as chiral dopant has been developed, which could respond to temperature and alkaline solution by shifting the SRB and changing the reflection color. The results demonstrated that cholesteric polymer films can be reversibly thermally switched to reflect red color from the initial green/yellow color resulting from increased helical pitch with the temperature increasing due to the weakening of hydrogen bonds. Additionally, the cholesteric polymer film shows different sensitivity to aqueous solutions with different pH values, which is sensitive to the aqueous solutions with pH > 7 and unresponsive to the aqueous solutions with pH = 7 or pH < 7. The H-bonds weakening induced by environment temperature and the H-bonds disruption induced by the pH of the chemical environment are found to be the key factors to the helical pitch change, which determine the dual temperature and pH tuning of the cholesteric polymer film. What's more, the responding rate to different pH values of the aqueous solutions depends on the concentration of the proton acceptors or donors in the cholesteric polymer film as well as the OH^- and K^+ ions in the aqueous solutions. The functional film described here may find applications as simple temperature and pH sensors, responding to the environment by changing their color.

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