Influence of Swelling Solutions on the Behavior of Cholesteric Networks

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ABSTRACT: The swelling behavior of an ethyl-cyanoethyl cellulose/crosslinked poly(acrylic acid) cholesteric network in different swelling solutions was studied. The swelling behavior of the cholesteric network was reversible in acid or neutral solutions and was irreversible in basic solutions. The cholesteric network retained the cholesteric structure during the swelling process in NaCl aqueous solutions, and the swelling behavior was incompletely reversible. J Appl Polym Sci 95: 724–729, 2005

Key words: composites; networks; swelling

INTRODUCTION

A cholesteric liquid crystal (LC) has a particular helical structure and can show many characteristic optical properties, including selective reflection, circular dichroism, and strong optical rotary dispersion, that are widely used in display and information materials or devices. The cholesteric structure and optical properties of cholesteric LC polymers are sensitive to the composition and temperature of the systems, the effects of external fields, and swelling.[1–6]

It is known that 70% of the weight of the human body is water, and most muscles and tissues are LCs. It has been shown that swelling occurs in many physiological systems, and this plays a crucial role in physiological processes such as nerve excitation, muscle contraction, and cell locomotion.[7,8] Suto and Kawano reported that temperature and swelling solutions can strongly affect the swelling behavior of the cholesteric mesophase of hydroxypropyl cellulose.[9] Suto and Inoue found that handedness of cholesteric LC changes during swelling in water for crosslinked hydroxypropyl cellulose films filled with cellulose powders.[10] Both measurements of the swelling and circular dichroism studies for cholesteric LC have revealed that swelling behavior is correlated to a change of cholesteric pitch (P).[11]

According to de Vries's theory, cholesteric LCs show selective reflection, and the relationship between the maximum wavelength of the selective reflection (λ_{max}) and P can be described by the following equation:[12]

$$\lambda_{max} = nP \sin \varphi \quad (1)$$

where n is the mean refractive index of the system and ϕ is the angle between the direction of incident light and the molecular layer surface. According to this equation, the shift in λ_{max} for the cholesteric network can reflect the variation of the cholesteric order in the systems.

Ethyl-cyanoethyl cellulose [(E-CE)C], which is a cellulose derivative with two different ester groups, can form cholesteric LCs in many organic solvents, such as dichloroacetic acid and acrylic acid (AA), when the concentration is higher than the critical one.[13] After the photopolymerization of AA, cholesteric order in (E-CE)C/AA solutions can be restored in (E-CE)C/poly(acrylic acid) (PAA) cholesteric networks.[14] (E-CE)C/crosslinked PAA cholesteric networks can be prepared by the addition of a crosslinking reagent into the solution before polymerization. When an (E-CE)C/crosslinked PAA cholesteric network was swelled in water, the selective reflection of the cholesteric phase shifted to the long wavelength direction, and X-ray diffraction of the film showed that the diffraction angle at about 10° shifted to the high-angle direction.[15]

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In this study, the swelling and drying processes of an (E-CE)C/crosslinked PAA cholesteric network were investigated, and the effects of the pH value of the swelling solutions and the addition of NaCl into the solution on the swelling behavior of the cholesteric network were examined.

EXPERIMENTAL

Materials

(E-CE)C was prepared by the reaction of ethyl cellulose and acrylonitrile.[16] The degrees of substitution for ethyl and cyanoethyl, determined by elemental analysis (CHN-O-RAPID, Heraeus, Germany), were about 2.1 and 0.37, respectively. The number-average molecular weight of (E-CE)C, measured by gel permeation chromatography (Waters-410-515-GPC; Waters, Milford, MA) and calibrated by standard polystyrene, was 1.09×10^5. Benzoinethyl ether was used as the initiator, and the crosslinking reagent was divinylbenzene. All of the reagents were chemically pure.

Preparation of (E-CE)C/crosslinked PAA cholesteric networks

We prepared the (E-CE)C/AA solution by mixing the (E-CE)C, AA, photopolymerizing initiator (benzoinethyl ether at 4 wt % with respect to AA), and crosslinking reagent (divinylbenzene at 10 wt % with respect to AA) together at room temperature. Then, the solution was stored in the dark at room temperature for about 2 weeks to achieve an equilibrium state. The solution was sandwiched between two glass slides and sealed with solid wax and stored in the dark for 4–5 h to achieve films of equilibrium texture. The thickness of the solution film, controlled by Teflon space, was 0.45 mm. The length and width of the film were about 10 mm each. Then, the solution film was placed in an ice-water bath and irradiated with a high-intensity mercury arc lamp for 5 min. The intensity of the mercury lamp was 250 W, and the distance between the sample and the lamp was about 5 cm. The [(E-CE)C]/crosslinked PAA cholesteric network was formed after polymerization was completed.

Swelling behavior

The (E-CE)C/crosslinked PAA cholesteric network was swelled in different swelling solutions: aqueous solutions with different pH values and NaCl solutions with different NaCl concentrations. During the swelling process, the swelling ratio (R_S) was calculated by the following equation:

$$R_S = [(M - M_0)/M_0] \times 100\% \quad (2)$$

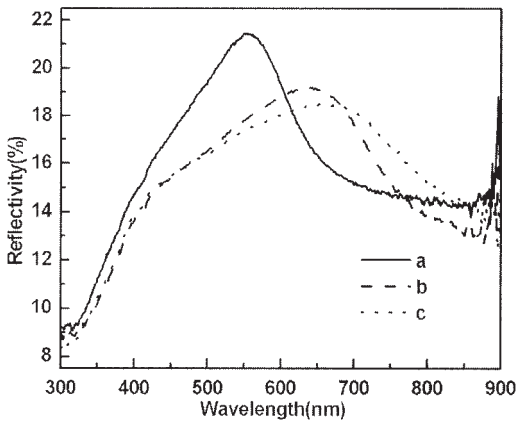

Figure 1 Reflection spectra of the 50 wt % (E-CE)C/crosslinked PAA cholesteric network during the swelling process in water. The swelling times were (a) 0, (b) 8.0, and (c) 30.0 h.

where M_0 is the original weight of the cholesteric network and M is the weight during swelling. The film at equilibrium swelling state was then dried in a desiccator over silica gels (relative humidity = 45%) in the drying process. R_S in the drying process was calculated as in the swelling process. M was the weight of the system after drying from the equilibrium swelling state, and M_0 was the original weight before swelling.

The variation of the selective reflection during the swelling and drying processes was measured by an ultraviolet–visible spectrometer (UV-2550, Shimadzu, Tokyo, Japan). The distance between neighboring molecular layers in the cholesteric phase (d) was measured with wide-angle X-ray scattering (WAXS),[17–21] and WAXS measurement was carried out with an X-ray diffractometer (D/max-1200, Rigaku, Tokyo, Japan). n was measured with an Abbe refractometer (2WA, Shanghai Optical Instrument Factory, Shanghai, China), and the pH values of the swelling solutions were measure with a pH meter (PHB-3, Shanghai WeiYe Instrument Plant, Shanghai, China) calibrated by phosphate compound (pH = 6.86 at room temperature). All of the experiments were performed at room temperature.

RESULTS AND DISCUSSION

Influence of the pH values of the solution

Figure 1 shows that the selective reflection of the cholesteric network shifted to the long wavelength direction (redshift) with swelling time when the system was swelled in water. Also, the reflection peak broadened during the swelling, which means that the selectivity of the reflection decreased. Figure 2 shows the time dependence of R_S and λ_{max} in the water swelling process. Both R_S and λ_{max} increased rapidly with swelling time in the first swelling stage, but the

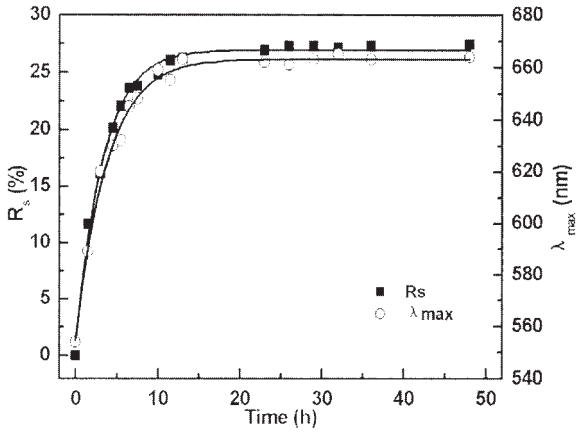

Figure 2 Time dependence of R_S and λ_{max} of the 50 wt % (E-CE)C/crosslinked PAA cholesteric network during the swelling process in water.

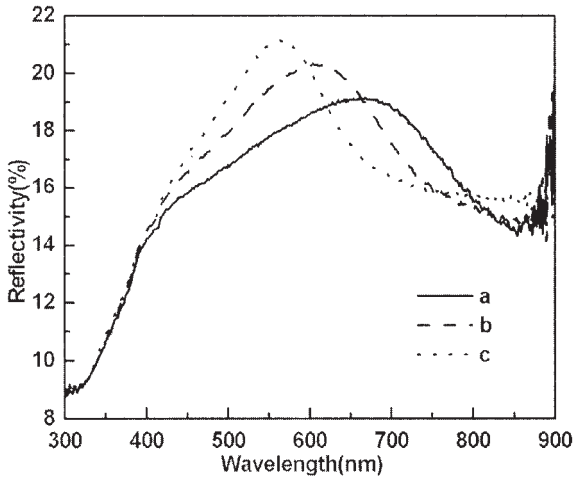

Figure 4 Reflection spectra of the 50 wt % (E-CE)C/crosslinked PAA cholesteric network during the drying process. The drying times were (a) 0, (b) 5.0, and (c) 30.0 h.

variation gradually slowed down and, finally, reached a plateau, where both of them did not change anymore after swelling for about 15 h. This indicated that the swelling process had reached the equilibrium state after the cholesteric network was swollen in water for 15 h, where the swelling ratio at the equilibrium state [$R_S(e)$] was 28 wt %. In the swelling process, n and ϕ were only slightly changed, and the variation of both was less than 1.2%.[22] According to eq. (1), the redshift of λ_{max} reflected the increase in P of the cholesteric network. In our previous study, we found by a WAXS technique that the (E-CE)C/crosslinked PAA cholesteric network had a characteristic peak, which was attributed to its cholesteric structure.[14] As shown in Figure 3, this characteristic peak at about $2\theta = 10.0°$ was reserved after the swelling process, which suggested that the cholesteric structure was retained in the network.

In the drying process, the selective reflection of the cholesteric phase shifted back to the short wavelength direction (Fig. 4), and both the intensity and the selectivity of the reflection increased with increasing drying time. The weight and λ_{max} of the cholesteric network were restored after the water was totally volatilized from the film (Fig. 5). These results indicate that the swelling behavior of the cholesteric network in water was reversible. Actually, the swelling behavior was mainly attributed to the crosslinked PAA chains in the network, which could absorb water molecules during swelling, whereas the (E-CE)C chains could not. The PAA chains in the network were dispersed within the ordered (E-CE)C chains layers and between them in the cholesteric phase. The water absorption of the PAA chains, therefore, may have resulted in the variation of the arrangement and ordering of the (E-

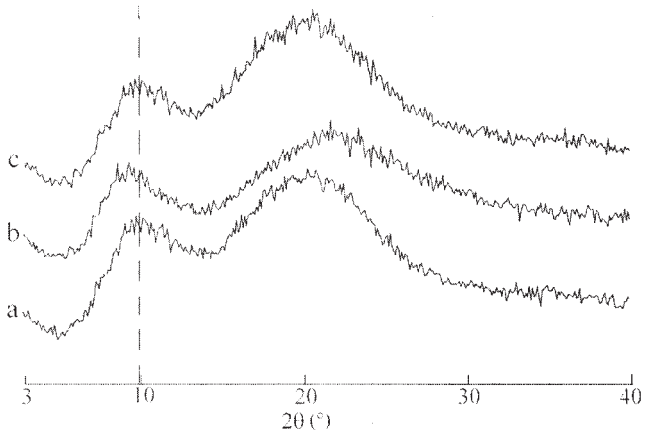

Figure 3 X-ray spectra of the 50 wt % (E-CE)C/crosslinked PAA cholesteric network (a) before swelling, (b) after swelling in water for 24 h, and (c) after drying for 48 h.

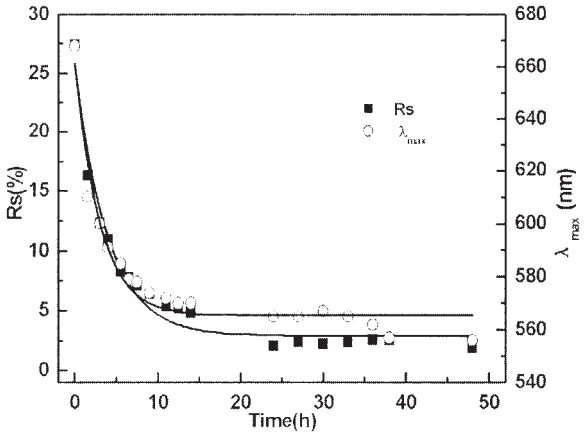

Figure 5 Time dependence of R_S and λ_{max} during the drying process for the 50 wt % (E-CE)C/crosslinked PAA cholesteric network.

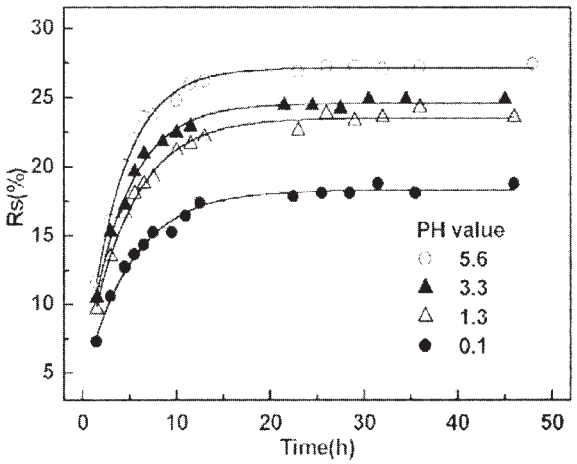

Figure 6 Time dependence of R_S during swelling in HCl solutions with different pH values for the 50 wt % (E-CE)C/crosslinked PAA cholesteric network.

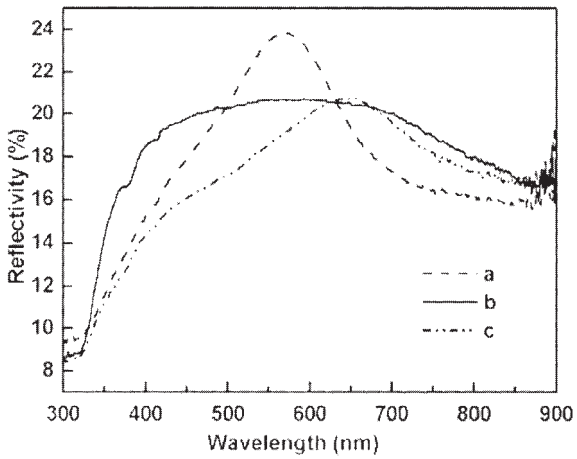

Figure 7 Reflection spectra of the 50 wt % (E-CE)C/crosslinked PAA cholesteric network (a) before swelling, (b) after swelling in an aqueous solution of NaOH (pH 12.7) for 4.5 h, and (c) after drying for 48 h.

CE)C chains in the cholesteric phase. We believed that the infiltration of water into the network of PAA resulted in the increase in P in the cholesteric network, and the value of λ_{max} also increased during the swelling process.

Figure 6 shows the time dependence of R_S during swelling in the HCl solution with different pH values. The swelling behavior of the cholesteric network in acid solutions was similar to that in water, but $R_S(e)$ decreased with decreasing pH value. It is well known that the ionization of carboxyl groups in the network of PAA chains will be restrained with increasing acidity of the swelling solution and that there is strong hydrogen bonding among the un-ionized carboxyl groups. Therefore, the ability of the deformation of the PAA network was weaker in the solution with a lower pH value, and the $R_S(e)$ of the cholesteric network was smaller than that in the acid solution with a higher pH value.

However, the swelling behavior of the cholesteric network in basic solutions was very different from that in acid solutions or water. The surface of the sample became coarse, and the vivid color faded away after the cholesteric network was swollen in the NaOH aqueous solution. Figure 7 shows the reflection spectra of the (E-CE)C/crosslinked PAA cholesteric network during swelling in the NaOH aqueous solutions. The selective reflection of the cholesteric network disappeared after the network was swollen for about 4.5 h, and the $R_S(e)$ was more than 100 wt % (Fig. 8), which was much larger than that in water or acid solutions. We observed from the WAXS spectra of the cholesteric network (Fig. 9) that the characteristic peak of the (E-CE)C/crosslinked PAA cholesteric network at about $2\theta = 10.0°$ disappeared after swelling, which indicated that the cholesteric structure of the network was destroyed. The PAA chains could react with NaOH molecules, because PAA is a kind of polyelectrolyte, and form sodium polyacrylate, which resulted in an increase the electrostatic repulsion between the COO^- groups and a decrease in the hydrogen bonding among the un-ionized carboxyl groups. Therefore, the cholesteric structure of the cholesteric network was destroyed, and $R_S(e)$ increased. After the network was dried from the equilibrium swelling state in the basic solution for some hours, the selective reflection of the cholesteric network appeared again, but λ_{max} shifted to the long wavelength direction, and the selectivity was much lower than that before swelling (Fig. 7). The characteristic peak at about $2\theta = 10.0°$ in the WAXS spectra also appeared, but the intensity of the peak was much lower than that before swelling (Fig. 9). We concluded that the swelling behavior of

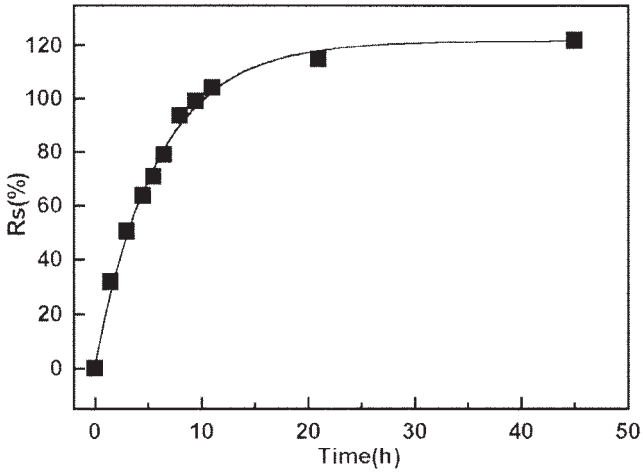

Figure 8 Time dependence of R_S during swelling in an aqueous solution of NaOH for the 50 wt % (E-CE)C/crosslinked PAA cholesteric network.

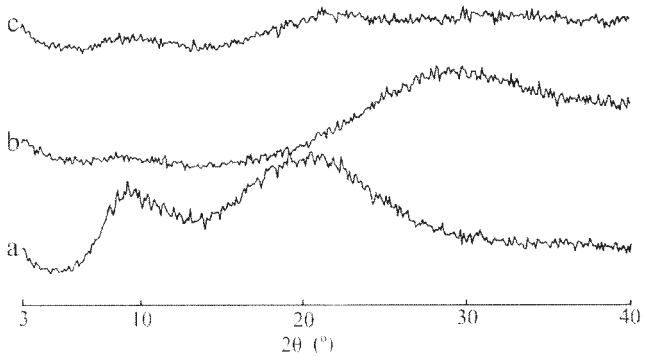

Figure 9 X-ray spectra of the 50 wt % (E-CE)C/crosslinked PAA cholesteric network (a) before swelling, (b) after swelling in an aqueous solution of NaOH (pH 12.7) for 24 h, and (c) after drying for 48 h.

the cholesteric network in the NaOH aqueous solution was irreversible.

Influence of NaCl

The swelling behavior of the cholesteric network in the NaCl aqueous solutions was similar to that in water. Figure 10 shows the time dependence of R_S and the shift in λ_{max} of the (E-CE)C/crosslinked PAA cholesteric network during swelling in the NaCl aqueous solutions. As shown in Figure 10, both R_S and λ_{max} increased during the swelling process at the first swelling stage and gradually approached the equilibrium swelling state. Finally, both of them were almost unchanged after they were swollen for about 15 h. The selective reflection spectra and the WAXS spectra indicated that the cholesteric structure of the cholesteric network was reserved during swelling in the NaCl solutions.

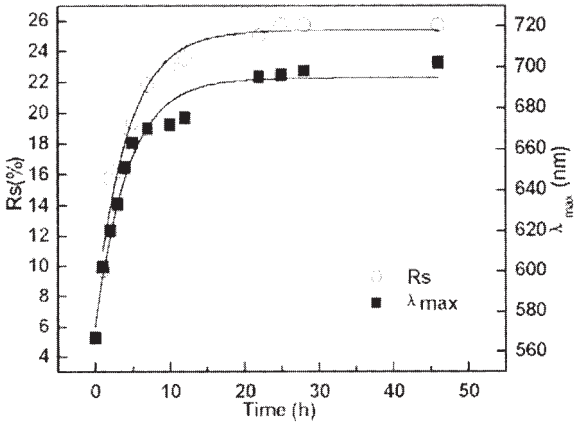

Figure 10 Time dependence of R_S and λ_{max} of NaCl for the 50 wt % (E-CE)C/crosslinked PAA cholesteric network during swelling in 0.9 wt % aqueous solution.

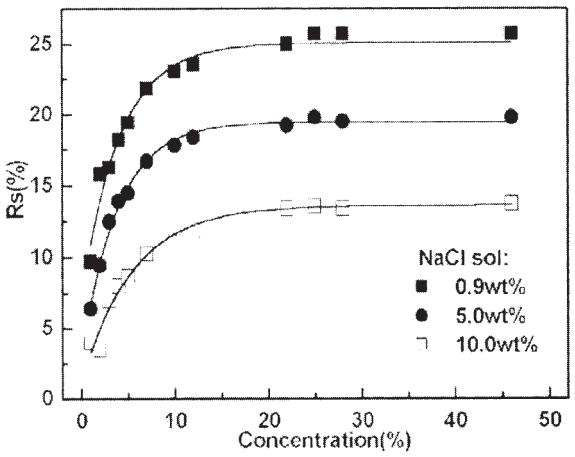

Figure 11 Time dependence of the R_S for the 50 wt % (E-CE)C/crosslinked PAA cholesteric network during swelling in NaCl solutions with different NaCl concentrations.

The weight of the cholesteric network after it was dried from the equilibrium swelling state was larger than that before swelling in the NaCl solution, and λ_{max} had a small redshift compared to that before swelling. The slight differences in weight and λ_{max} between the original network and that after the swelling and drying processes may have been due to the ionization of the carboxyl groups in the PAA network and the exchange of H^+ in the film with Na^+ in the solution. In the swelling process, hydrogen bonding among the un-ionized carboxyl groups was destroyed by the infiltration of Na^+ into the PAA network, and then the cholesteric structure was changed. In the drying process, the water in the film was volatilized, but Na^+ in the PAA network was retained in the cholesteric network. Therefore, the cholesteric order in the network could only be recovered incompletely. For the same reason, the weight of the cholesteric network after drying was larger than that before swelling. The results suggest that the swelling behavior of the cholesteric network in the NaCl solutions was incompletely reversible.

Figure 11 shows that the variation of R_S with swelling time was similar when the cholesteric network was swollen in the solutions with different NaCl concentrations, and the $R_S(e)$ decreased with increasing concentration of the NaCl solution. Two possible reasons may have been responsible for this phenomenon. The first one may have been related to the existence of the osmotic pressure in the salt solution. In this case, the equilibrium swelling state was attained when the chemical potentials of all of the mobile components in the coexisting phases were the same. It is not difficult to understand that water molecules infiltrated into the network easier than Na^+. So the concentration of NaCl within the network was lower than that out of the network, and there existed osmotic pressure to force

the network to shrink. Therefore, increasing the NaCl concentration in the swelling solution may have resulted in more shrinking of the cholesteric network, and the sample may have had a higher density, which meant that $R_S(e)$ of the network was lower. The second reason is that the presence of salt may have changed the behavior of water molecules. The activity of water molecules decreased with increasing concentration of NaCl because Na^+ was more active in the reaction with —COOH groups on the PAA chains than water molecules, which also resulted in the decrease in $R_S(e)$.

CONCLUSIONS

The swelling behavior of (E-CE)C/crosslinked PAA cholesteric network was reversible when the pH value of the swelling solution was less than or equal to 7.0, although in the equilibrium swelling state, the λ_{max} showed a redshift, and the distance between neighboring molecular layers in the cholesteric phase increased during the swelling process. $R_S(e)$ of the cholesteric network decreased with decreasing pH value of the swelling solutions. Moreover, the cholesteric order of the network could be restored after the sample was dried from the equilibrium swelling state. After the network was swollen in the NaOH aqueous solutions, the cholesteric structure of the network was destroyed, and the selective reflection of the cholesteric network disappeared. The cholesteric structure could not recover after the network was dried from the equilibrium swelling state. The cholesteric structure of the network was reserved during the swelling process in the NaCl solutions, and the swelling behavior of the network was incompletely reversible.

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