Preparation of Cholesteric (Hydroxypropyl)cellulose/Polymer Networks and Ion-Mediated Control of Their Optical Properties

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(Hydroxypropyl)cellulose (HPC)/vinyl polymer networks were synthesized in film form from liquid-crystalline solutions of HPC in a mixed solvent of methacrylate monomer/methanol/water (2:1:2 in weight) containing cross-linking agents, via photopolymerization of the methacrylate monomer. Di(ethylene glycol) monomethyl ether methacrylate (DEGMEM) or 2-hydroxypropyl methacrylate (HPMA) was used as the polymerizing monomer, and tetra(ethylene glycol) diacrylate and glutaraldehyde were the cross-linkers for the monomers and HPC, respectively. The polymer composite films, HPC/PDEGMEM and HPC/PHPMA, prepared at ca. 60−70 wt % concentrations of HPC in the starting solutions, were iridescently colored due to the selective light reflection, originating from the cholesteric helical arrangement carried over successively into the network system. When the cholesteric films were immersed and swollen in water containing an inorganic neutral salt, their coloration and optical turbidity varied according to a strength of ‘chaotropicity’ of the impregnant ions. This ionic effect may be interpreted as essentially identical with that found formerly in the coexistent salt-sort dependence of the cholesteric pitch and lower critical solution temperature for HPC aqueous solutions. It is also demonstrated that visual appearance of the swollen networks can be changed by application of an electric potential of practical magnitude between both edges of the samples of rectangular shape.

Introduction

(Hydroxypropyl)cellulose (HPC) is readily capable of forming a cholesteric type of liquid-crystalline phase both in a variety of common solvents[1−5] and in melt,[6] derived from some degree of rigidity and a chiral nature in the molecular structure. The cholesteric mesophase indicates a color due to selective light reflection, if the pitch in the supermolecular helicoidal structure is comparable to wavelengths of visible light. HPC solutions in water exhibit such a typical cholesteric character at polymer concentrations of ca. 50−70 wt %.[1,7] The aqueous solutions also show a phase separation behavior with the lower critical solution temperature (LCST) usually located at <45 °C.[1,8,9]

Our previous papers[10,11] reported that the cholesteric structure and LCST-type phase separation behavior, and ensuing optical properties of the lyotropic system of HPC in water, were much affected by addition of an adequate amount of neutral salts with a universal dependence on the sort of the constituent ions. From quantitative measurements by spectrophotometry, the wavelength (λ_M) of maximal light reflectance and the cloud point (T_c), and therefore the cholesteric pitch (P) and the phase separation temperature, were found to vary systematically with a change in strength of a so-called “chaotropic” effect of the added salt ions. The degree and directional sense of the effectiveness of a given salt in altering the optical parameters were determined by the algebraic sum of the respective effects of its constituent ions, and thus the coloration and turbidity of the aqueous HPC lyotropic system could be controlled desirably by selecting the combination of cation and anion species. Moreover, by utilizing electrophoretic motility of the ions present as P and/or T_c perturbants in the viscous cellulosic medium, the dynamic variation in cholesteric coloration and/or optical turbidity of the lyotropic system was realized under a relatively weak electric field.[11−13]

Meanwhile, there have been many efforts to perpetuate the cholesteric structural order of HPC and of other cellulosics into the solids or gels, for the purpose of elucidating the internal morphology or exploiting the possibilities as specific optical filters, informative data-recording media, and other functional materials. Preparations of such cholesteric films can be made by several methods: casting from liquid-crystalline solutions, accompanied by solvent evaporation;[14] cross-linking of cellulosic polymers in the liquid-crystalline melts[15] or solutions;[16] polymerization of monomers as lyotropic solvent for cellulose derivatives;[17−19] etc.

In the present study, conditions for preparing an interpenetrating network type of polymer composite retaining the cholesteric arrangement of HPC are described. An essential part of the preparation is photopolymerization and cross-linking of methacrylate monomers as a solvent component of concentrated HPC solutions in a mixed solvent containing a diacrylate cross-linker, with a concurrence of chemical cross-linking of the HPC component by using dialdehyde. The mesomorphic structure and optical properties of the HPC/polymer networks are investigated not only in the dried state but also in the swollen state where

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the samples are immersed in aqueous solutions of different inorganic salts. An applicable extension is the attempt to electrically control visual appearances of the swollen polymer networks.

Experimental Section

Materials. The powdered HPC used was a commercially available sample (Tokyo Kasei Kogyo Co., Ltd.): weight-average and number-average molar masses, $M_w = 15.3 \times 10^4$ and $M_n = 5.7 \times 10^4$, respectively (from GPC measurements); degree of side-group substitution, DS = 1.4 and MS = 3.9 (from ^{1}H and quantitative ^{13}C NMR measurements), where DS and MS denote an average number of substituted hydroxyls and that of introduced hydroxypropyl groups, respectively, per anhydroglucose residue. Di(ethylene glycol) monomethyl ether methacrylate (DEGMEM) and 2-hydroxypropyl methacrylate (HPMA), both purchased from Tokyo Kasei Kogyo Co., Ltd., were distilled under reduced pressure (~2 Torr) at 63 and 58 °C, respectively, before use. The side chains of these monomers have a structural similarity to that of HPC. As cross-linking agents, tetra(ethylene glycol) diacrylate (TEGDA; Tokyo Kasei Kogyo Co., Ltd.) and a 25% glutaraldehyde (GA) aqueous solution (Wako Pure Chemical Industries, Ltd.) were used without further purification.

Preparation of HPC/Polymer Composite Networks. A lyotropic solvent for HPC was made by mixing vinyl monomer (DEGMEM or HPMA), methanol, water, and TEGDA (weight content, 2.0/1.0/2.0/0.025). As a radical initiator of polymerization of the vinyl monomers, α,α′-azobis(isobutylonitrile) (AIBN) was added at a concentration of 0.5 wt % with respect to the mixed solvent. The mixing ratios of water and methanol to DEGMEM or HPMA were determined for the best through a preliminary test, where a lower level of dissolution of HPC into the monomers and an incomplete compatibility of the monomers with water were taken into consideration. HPC solutions of different polymer concentrations (46−72 wt %) were prepared by simply mixing weighed amounts of the solvent concoction and solute HPC in light-blocked glass vials over a period of 4 weeks. During this period, the vials were usually stored in a refrigerator (<4 °C); however, they were sometimes turned upside down in a centrifuge for the purpose of accelerating the dissolution of HPC. The lyotropic samples thus obtained are designated as HPC/DEGMEM or HPC/HPMA mixed solutions in case of the need of distinction.

An aliquot (~1 g) of each lyotropic HPC/monomer mixed solution was replaced to another vial and stirred by using a glass rod, with addition of a GA aqueous solution and a slight amount of hydrochloric acid that was a catalyst for cross-linking HPC side chains by the dialdehyde. The concentration of GA was adjusted to 1.5−3 wt % with respect to the total quantity of the resulting respective solutions, which were then centrifuged at 2000−3000 rpm for 1 h to remove air bubbles and stored in a refrigerator overnight. Each of the solutions was deposited on a glass plate and spread into a filmy shape (ca. 20 mm × 55 mm) with a glass rod which was slid slowly on a Teflon spacer of adjustable thickness (0.5−1.0 mm). To relax the shear-induced orientation of HPC, the plates with the solution sample attached were placed in a light-resistant container saturated with water vapor at 20 °C for 24−48 h. After the standing, the respective solutions were allowed to solidify at 20−25 °C over a period of 2−2.5 h (unless otherwise noted), via polymerization and cross-linking of DEGMEM (or HPMA) by irradiation of UV light with an intensity maximum at 352 nm. In this process, a large portion of methanol/water was gradually evaporated away from the samples, and thus the condensation would promote the cross-linking between HPC side chains by GA jointers.[16] When HPMA was employed as the polymerizing monomer, the hydroxyl groups of PHPMA (poly-HPMA) as well as those of HPC were possibly involved in the cross-linking reaction with the dialdehyde.

The polymer composites thus synthesized were washed with distilled water and then air-dried at room temperature (20−25 °C) and stored in a desiccator until used as HPC/PDEGMEM and HPC/PHPMA films.

Strips 15 × 15 mm cut from the composite films were used to prepare gelatinous samples by immersion in aqueous solutions of different inorganic salts (usually 0.5 M) at ~20 °C for 24 h. The volume of the respective salt solutions was much larger than the sample volume, so that the salt concentration was virtually unchanged. Following the immersion, the salt-containing gels were dried under normal room conditions or employed for an electrooptical experiment in the swollen state, after the liquid trickling on the film surface was blotted out with a filter paper.

Measurements. Selective light-reflection and optical turbidity of mesomorphic samples were examined by visual inspection, and the quantitative measurements of reflection bands were conducted with a UV−visible spectrometer (Hitachi U-2000) equipped with a thermo-regulated cell-holder. Fluid samples were encapsulated in a glass cell of 500 μm thickness and then allowed to equilibrate for at least 12 h prior to the measurement, while solid films were directly fixed to a glass plate. Apparent circular dichroism (CD) spectra were also recorded for selected samples at 20 °C with a Jasco J-720 spectropolarimeter, to determine the handedness of the cholesteric helical structure.

Selected samples of the cholesteric polymer networks impregnated with an aqueous salt solution were used for an electrooptical observation. The square gel film (see above) was placed between a pair of carbon electrodes, so that two edges (ca. 1 mm × 15 mm each) of the sample were kept in contact with the respective electrode surface. An electric generator, Multifunction Synthesizer 1946 (NF Electric Instruments Inc.) was used for the electrification conducted at ~20 °C. The electromotive force applied was usually 4.5 V; thereby the electric field strength was ~3 V cm^{-1}.

Results and Discussion

Optical Behavior of HPC/Monomer Mixed Solutions. HPC solutions in the mixed solvent of DEGMEM or HPMA/methanol/water/TEGDA were completely anisotropic at polymer concentrations of at least 46−72 wt %. In particular, at the concentrations of 60−72 wt %, the lyotropic samples showed definite colors, resulting from the selective light reflection in a range of visible wavelengths due to the cholesteric supramolecular arrangement, as in the case of HPC/water solutions of ca. 50−70 wt %.[1,7,10] The cholesteric coloration of the HPC/monomer mixed solutions varied from reddish to bluish at 5 °C when the polymer concentration changed from 60 to 70 wt %, for either type of methacrylate monomer used.

Figure 1 displays light-reflection spectra obtained for a series of cholesteric liquid-crystalline HPC/DEGMEM mixed solutions, compared between different HPC concentrations at 5 °C (Figure 1a) and between different temperatures at a polymer concentration of 68 wt % (Figure 1b). Generally, the reflection bands of the HPC/monomer mixed solutions were rather broad in comparison with those of the corresponding liquid crystals formed in water[1,7,10] or methanol[1,20] alone. It may be deduced, therefore, that the cholesteric order in the present system seems not to be as uniform as those in the HPC/water and HPC/alcohol systems. From the data shown in Figure 1a, it can be seen that the wavelength (λ_M) of maximum reflection intensity shifts to the blue side with increasing HPC concentration in the liquid-crystalline solutions at the constant temperature. Figure 1b reveals a progressive shift of the λ_M location to the red side in spectrum with an elevation of temperature for the 68 wt % HPC solution. The wavelength λ_M can be related to the cholesteric pitch (P) by the de Vries equation,[21] $\lambda_M = \tilde{n}\cdot P$; where $\tilde{n}$ is an average refractive index of the mesophase and the value was actually invariable against temperature (<30 °C) and polymer concentration (<72 wt %) to the first place of decimals for the present HPC solutions ($\tilde{n} > 1.42$). Therefore, the variation of

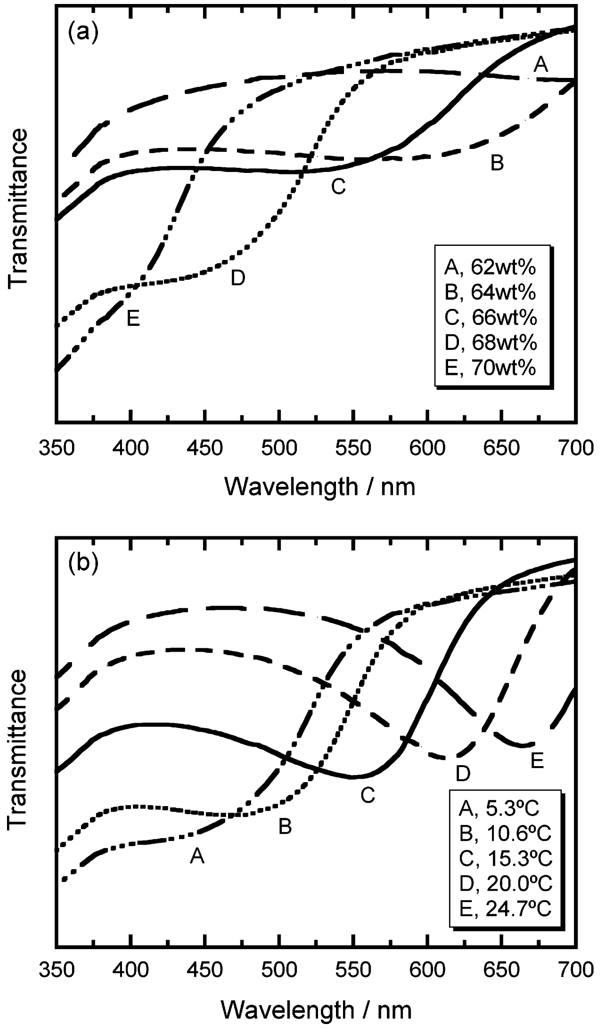

Figure 1. Selective light-reflection spectra for cholesteric liquid-crystalline HPC/DEGMEM mixed solutions. Comparisons (a) between different HPC concentrations at 5 °C, and (b) between different temperatures at an HPC concentration of 68 wt %.

λ_M is substantially parallel to that of P; viz., straightforwardly, the cholesteric pitch of the HPC/DEGMEM mixed system diminishes when the HPC concentration increases and/or the temperature decreases. This tendency, similar to that for the HPC/water system,[10] was also confirmed in the case using HPMA instead of DEGMEM.

Immobilization of Cholesteric Order in HPC/Polymer Networks. HPC/ PDEGMEM films could be obtained successfully from HPC/DEGMEM mixed solutions containing cross-linking reagents, TEGDA and GA, by photopolymerization of the methacrylate monomer and cross-linking of the two respective polymer components. The films, which would be furnished with an interpenetrating polymer network (IPN)-type of architecture, exhibited a reflection color when they were prepared from the solutions of HPC concentrations ranging from 56 to 70 wt % in feed. This ensures that a cholesteric helical structure developed in the original solutions was carried over considerably into the composite networks through the polymerization process.

In visual inspection, the cholesteric HPC/PDEGMEM films 300−500 μm thick produced at HPC concentrations of 56−60 wt % in the mixed solvent were mostly orangey or reddish, whereas a greenish or bluish hue was dominant as to the film products obtained at HPC concentrations of 62−68 wt % in feed. It should be noted here that the original solutions of HPC = 56 and 58 wt % were translucent without coloration at 20 °C, i.e., λ_M locating in an invisible range of >800 nm, but the polymerized samples showed a red-orange color in their dried state. In contrast, when a violet solution of HPC = 72 wt % was photopolymerized, the resulting film was colorless due to shifting of λ_M to the ultraviolet region.

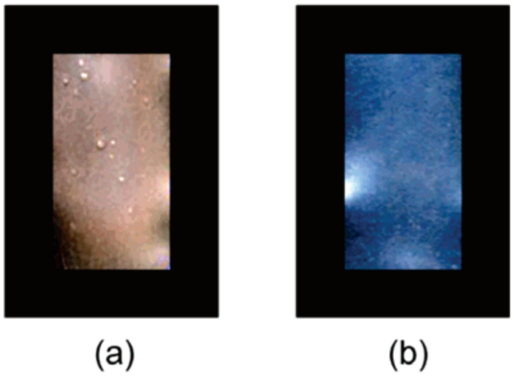

Figure 2. Visual appearance of cholesteric HPC/PDEGMEM films prepared from HPC/DEGMEM mixed solutions. HPC concentration: (a) 58 wt % and (b) 70 wt % in feed.

Several factors other than the in-fed HPC concentration would be involved in determination of the visual appearance of the solid films; for instance, the concentration of the cross-linking agents, the sample thickness, the orientation relaxation time after spreading viscous solutions on a glass plate, the temperature for polymerization, etc., should be the factors. In fact, the colorations of a series of films mentioned above were not of a single hue but rather heterogeneous, which might have been caused mainly by the nonuniformity in film thickness and remaining shear-orientation. Moreover, fine bubbles generated during the photopolymerization reaction remained more or less in the solid films. For comparison with the above series of films, thinner films 200−250 μm thick were prepared by UV irradiation at 32−35 °C. In the in-feed condition of 56−70 wt % HPC, the HPC/PDGMEM films obtained had a comparatively flat, smooth surface and smaller bubbles, and, consequently, they imparted a more uniform cholesteric color in comparison with the thicker films. Figure 2 demonstrates the uniform colors acquired for two HPC/PDEGMEM films, reddish and bluish ones from 58 wt % and 70 wt % HPC solutions, respectively, in the mixed solvent. Again, however, the reflection colors of the original solutions changed toward the violet end of the spectrum after polymerization, in a similar manner as that observed for the thicker samples. This shift of λ_M may be attributed to the solvent evaporation and volume shrinkage of the samples in the polymerization process, as well as to the change in methanol/water content of the mixed solvent during the relaxation process of the spread solutions.

Figure 3 displays CD spectra for two HPC/PDEGMEM films and for the corresponding solutions prepared at 58 and 66 wt % HPC concentrations prior to polymerizing, all measured at ca. 20 °C. Generally, such a CD measurement for cholesteric liquid crystals provides information of the handedness of the supramolecular helical arrangement, in addition to that of the wavelength range of selective light reflection. In Figure 3, the CD spectra for the solution and film of higher HPC concentration are both characterized by a negative ellipticity curve with a peak maximum centering 605 nm (for solution) or 415 nm (for film). The CD data for the other couple of lower HPC concentration also show a negative ellipticity peak, centered at 700 nm for the film and probably at a wavelength longer than 800 nm for the solution. Such a negative CD signal indicates

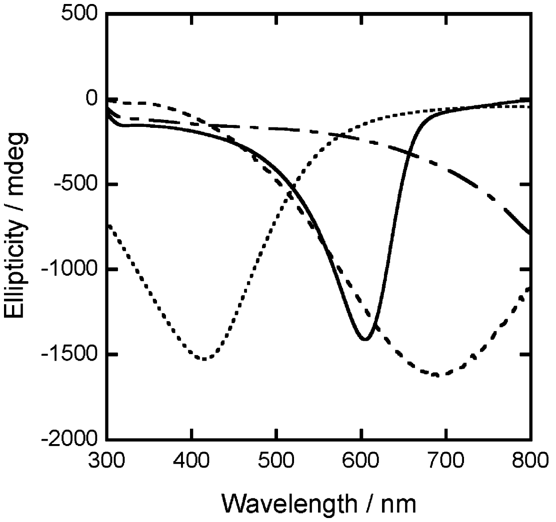

Figure 3. CD spectra of cholesteric HPC/DEGMEM mixed solutions and HPC/PDEGMEM films, measured at 20 °C. −, solution (66 wt %); ········, film (66 wt % in feed); − - −, solution (58 wt %); ---, film (58 wt % in feed). HPC concentrations are indicated in parentheses.

prevalence of a right-handed cholesteric structure, as in the case of HPC liquid crystals formed in water and in most organic solvents.

Optical results similar to the above were obtained in visual and spectroscopic observations for the sample pairs of HPC/PHPMA film and corresponding original HPC/HPMA mixed solution; however, the λ_M shift to the blue side following the solidification process was of lesser extent compared with the case using DEGMEM. As a possible explanation, this may be ascribable to somewhat rapid fixation of the mesomorphic organization and development of a tighter network, owing to the possible cross-linking between PHPMA and HPC in addition to that between the same species of polymer components.

Appearance of HPC/Polymer Networks in Aqueous Salt Solutions. Effects of salt-ion incorporation on the optical properties of the cholesteric HPC/PDEGMEM IPN composites were investigated. It was confirmed previously that both HPC and PDEGMEM components, which were cross-linked individually, were not eluted from the network in any of the aqueous solutions tested. When the HPC/ PDEGMEM composites were immersed in distilled water at 20 °C, they swelled slightly and became clouded. Taking into account the fact that a PDEGMEM hydrogel with no HPC began to become turbid around 22 °C on heating, due to a pseudo-LCST phenomenon of the polymer with a di(ethylene glycol) unit in the side chains, the observed cloudy appearance can be attributed mainly to segregation of the PDEGMEM chains in the hydrated composites. Thus the reflection colors of the cholesteric networks swollen in distilled water was often made indistinct at room temperature (20−25 °C), by the optical turbidity coupled with some extent of inhomogeneity in the supramolecular helical arrangement.

When an inorganic salt was present in the aqueous swelling medium, however, the coloring state of the cholesteric composites changed discernibly after immersion, in a certain range of spectrum with a dependence on the sort of the additive salt. The upper two series of photographic data in Figure 4 show the examples for HPC/PDEGMEM films prepared from (a) 65 wt % and (b) 70 wt % HPC solutions (GA content, 0.02 wt/wt HPC) by UV irradiation for 3 h. The film of lower HPC concentration gave a pale orange color in the initial dried state (Figure 4a-1). The swelling in an aqueous solution of 0.5 M LiSCN (Figure 4a-2) rendered the coloration feeble, accompanied by a decease in the optical clarity, but with new attendance of a faint reddish hue (not clear in the photography). After taking out of the solution followed by drying at ambient temperature, the film recovered a considerable transparency and imparted a deep red color (Figure 4a-3). When the salted sample was washed in distilled water and then dried, it regained the completely original appearance (Figure 4a-4). The other film of higher HPC concentration, colored blue with a greenish tinge in the initial state (Figure 4b-1), became pale violet and appreciably turbid when immersed in an aqueous KNO_3 solution (Figure 4b-2). Then, the salt-incorporated sample turned white with a still remaining violet hue in the course of drying (Figure 4b-3), and recovered the greenish blue and transparency after eluting the salt ions with distilled water followed by drying (Figure 4b-4).

Figure 4 includes additional series of photographic data obtained in a similar experiment for two HPC/PHPMA composites, which were synthesized from (c) 70 wt % and (d) 66 wt % HPC solutions (GA content, ~0.044 wt/wt HPC) through the polymerizing and cross-linking reaction at 32 °C. For the LiSCN-containing states (Figs. 4c-2 and 4c-3) of one of the samples, we clearly found reflective colors at longer wavelengths compared to the situations in the salt-free states (Figs. 4c-1 and 4c-4). The change in coloration in the swollen state of the HPC composite with PHPMA may be discerned rather easily than the case using PDEGMEM; because we observed no whitening due to phase separation of PHPMA at least below 35 °C for a plain hydrogel of this polymer in distilled water. As demonstrated by the lowest photographic series in Figure 4, however, a serious turbidity was again observed for the KNO_3-containing states (Figs. 4d-2 and 4d-3), together with perception of a dimly reflective color shifted to the blue side from the original color in the salt-free state (Figure 4d-1).

In the salting experiment using other combinations of cation/anion species, the following observations are worth noting: When $LiNO_3$ was employed as the impregnant for cholesteric HPC/methacylate polymer composites, the reflective coloration and the degree of clarity of the salted but dried films were almost identical with those in their respective initial states. The adoption of $NaNO_3$ resulted in lowering of the optical clarity of the test film in both swollen and dried states after the immersion in the salt solution; however, the extent of the lowering was smaller compared with the case using KNO_3. Regarding the effectiveness in enhancing such a turbidity of salted samples, CsCl was superior to KNO_3 and KCl.

In the preceding papers,[10,11] it was shown that the salt addition to aqueous HPC solutions gave rise to systematic alterations of the cholesteric pitch P and of the LCST or cloud point T_c, depending on the ion species constituting the added salt. The observation was interpretable in terms of the so-called chaotropic effect of the salt ions, generally associated with the potency to alter the strength of the hydrophobic interaction in which the side chains (precisely nonpolar portions therein) of water-soluble polymers participate. Figure 5 illustrates an established diagram[10−12] to rank the relative potency of representative univalent ions in increasing or decreasing P and T_c of the HPC/water system, the respective potential levels reflecting the strength of chaotropicity of the corresponding ions to this lyotropic system. A highly chaotropic anion SCN^- acts as the water-structure breaker and disrupts hydrophobic assemblage of nonpolar substances (alkyl side chains in HPC), to increase their solubility in water. In contrast, Cl^- and major alkali-metal cations are structure formers (i.e. antichaotropic) for the aqueous cellulosic solutions and behave as salting-out agents to enhance

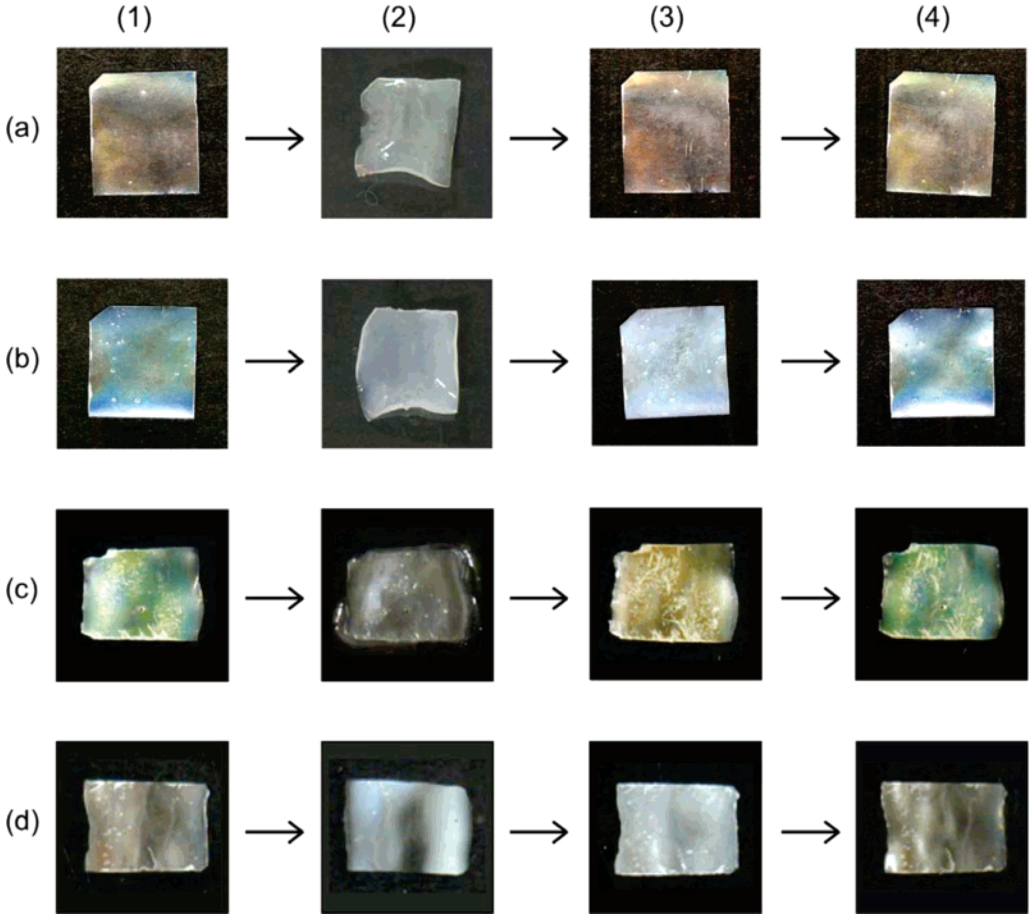

Figure 4. Variations in reflection color and optical turbidity of cholesteric HPC/polymer networks, demonstrating an effect of the immersion in different salt aqueous solutions (∼20 °C). HPC/polymer samples: (a) HPC/PDEGMEM (65 wt % HPC in feed, 0.02 wt GA/wt HPC); (b) HPC/PDEGMEM (70 wt % HPC in feed, 0.02 wt GA/wt HPC); (c) HPC/PHPMA (70 wt % HPC in feed, 0.043 wt GA/wt HPC); (d) HPC/PHPMA (66 wt % HPC in feed, 0.044 wt GA/wt HPC). Photographic data were taken at different stages: (1) original dried state; (2) state swollen in a 0.5 M LiSCN (for samples a and c) or KNO_3 (for samples b and d); (3) state dried after the salting-in; (4) state dried after another immersion in distilled water.

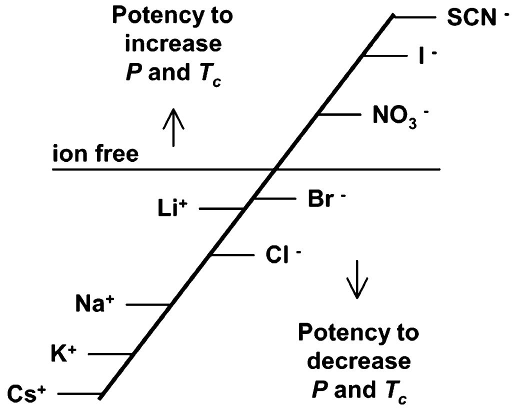

Figure 5. Schematic representation of a rank order of the relative effectiveness of different ions in altering the cholesteric pitch (P) and cloud point (T_c) of aqueous HPC solutions.

the hydrophobic interaction of the nonpolar substances. The actual effectiveness of a given salt in altering the optical parameters P and T_c may be determined by algebraic sum of the respective effects of its constituent ions. From a deuteron NMR study,[10] it was also suggested that the added salts would be able to subtly control the conformational state of liquid-crystalline HPC, which was assumed to prefer a possible twisting habit,[22,23] to induce a marked change of the cholesteric twisting power (P^{-1}) without disturbing the molecular orientation order in each of the closely stacked nematic layers.

The salting effect on the visual appearance of the HPC/polymer composites, found in the present work, may be explicable in substantially the same view as that applicable to the liquid-crystalline aqueous solution system. The changing manners in both coloration and turbidity of the cholesteric networks between the salted state and the salt-free state were in accordance with qualitative predictions from the chaotropic potential levels (Figure 5) of the salt ions employed. Especially concerning the turbidity phenomenon, however, the impregnant ions would affect the hydrophobic interaction associated with the side chains of the methacrylate polymer component as well as the interaction between the HPC side chains. Therefore, some observations of cloudy or turbid gelatinous composites should have been derived from a doubly enhanced effect due to the possible phase segregations of both polymers. In relation to this, caution should be exercised to the following result: For comparison, cholesteric HPC/methacrylate polymer samples were prepared into relatively hard films, under a condition where the GA content exceeded 4.5 wt % to HPC and the reaction time for polymerization and cross-linking was prolonged to 5 h. In a general trend, the original reflection colors of the resulting composites were lost or unchanged at their salted states, but their transparency alterations were detected more rapidly and noticeably. It seems that the network structures were developed with a considerably high density of cross-linking points, so that the respective cholesteric supramolecular arrangements could

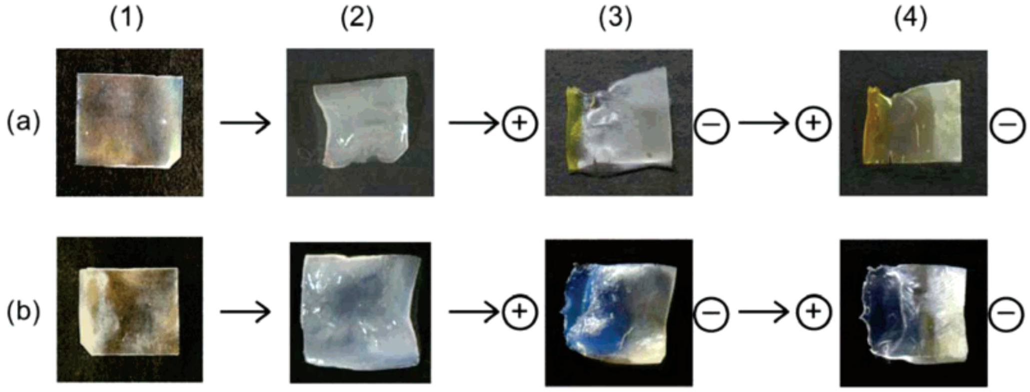

Figure 6. Variations in reflection color and optical turbidity of a cholesteric HPC/PDEGMEM network (65 wt % HPC in feed), realized at ∼20 °C by application of an electric field of 4.5 V/15 mm after swelling in a 0.5 M (a) LiSCN or (b) KNO_3 aqueous solution. Photographic data were taken at different stages: (1) original dried state; (2) state swollen in the respective salt solutions; (3) still swollen state after 30 min (for (a)) or 60 min (for (b)) electrification; (4) state dried after cessation of the electrification.

not be allowed to change the periodicity in good response to a given ionic atmosphere, in contrast to the easiness of the LCST-type microphase segregation.

Electrooptical Behavior of Cholesteric HPC/Polymer Networks. Results of electrooptical observations are illustrated in Figure 6 for cholesteric liquid-crystalline HPC/PDEGMEM networks impregnated with a 0.5 M (a) LiSCN or (b) KNO_3 aqueous solution. The two sample specimens were actually cut from the same composite film as that used to demonstrate the salting effect with LiSCN in Figure 4a, both being colored dark orange in the dried state before immersion in the aqueous salt solutions. It was confirmed that the turbid gel swollen in aqueous KNO_3 (Figure 6b-2) became more whitened with a reflective tincture of shorter wavelengths in the dried state without washing but recovered the original orange color and transparency via the drying preceded by sufficient washing in distilled water.

In the electrification experiment at ∼20 °C, a pair of carbon electrodes were brought into contact with both ends of the respective swollen samples (ca. 1.5 × 1.5 cm), and the potential difference applied between them was 4.5 V. In the initial stage free of the electric field, both of the salted HPC/PDEGMEM gels were clouded more or less and their cholesteric colorations were overall faded, as has been stated above. However, the voltage application to the samples gave rise to a definite variation in the reflection color and/or transparency with a regional dependence. For example, about 30 min after imposing the electric stimulation, the LiSCN-containing gel gained a degree of transparency on the positive side of the sample and left a large potion with slightly increased cloudiness on the negative side (Figure 6a-3). In this stage, the reflection color was not yet observed explicitly for the gelatinous film; however, a yellow color was detected in the vicinity of the positive film-end, where thiocyanate ions aggregated. The other hydrogel containing KNO_3 displayed a clear blue color in the positive half of the film plane and a still-cloudy appearance in the counter half, after application of the electric field over a time period of ∼60 min (Figure 6b-3). In the course of the respective electrification processes, the direct circuit was opened by separating the sample from the pair of electrodes; the photographs given in Figures 6a-3 and 6b-3 were actually taken right after discontinuing the supply of electricity. Afterward, the respective electrified gels were air-dried without any washing. The result is also shown in Figure 6. As can be seen from Figure 6a-4, the LiSCN-treated film became deep red in a wide range from the central part toward the positive end, with a yellowish or greenish turbid region on the negative side. On the other hand, the KNO_3-treated film was colored bluish violet in occupancy of the positive-side area, while a large part of the negative-side area became heavily whitened (Figure 6b-4). These findings of dynamic change in the coloration and optical turbidity indicate formation of a magnitude gradient referring both to the cholesteric pitch and to the critical temperature of phase separation in the liquid-crystalline HPC/PDEGMEM networks, possibly coming from an uneven distribution in salt concentration which would take place according to the mechanism shown below.

When an electric potential difference is applied to a salt-containing HPC/polymer hydrogel loaded between a pair of electrodes, the cation and anion impregnants will be localized with time on the negative and positive sides, respectively, due to their electrophoretic migrations; generally, however, the rate of migration would be mutually different between them. Thus it follows that some degree of gradient in concentration of the salt ions occurs in the network system. In response to this change in ionic environment, the cholesteric helical pitch of the HPC mesophase should also fluctuate correlatively, which results in the gradation in reflection color instead of the originally unified one. In a case where the added salt is composed of a pair of alkali cation/chaotropic anion, as in the above examples, a display of colors with longer wavelengths may be available at the positive electrode side and, conversely, a display of colors with shorter wavelengths at the negative electrode side, in comparison with the coloring situation in which no electric field is applied. In the electrification experiment conducted for salt-containing liquid-crystalline aqueous solutions of HPC,[12] it was often observed that an opaque colorless zone developed with time on the negative side of the sample. This can be ascribed to a lowering of T_c to less than the room temperature, which was regionally induced by concentration of the constituent cations as T_c-depressant on the negative side. Similar interpretation based on this cloud point variation responding to the ion fluctuation may hold in observations of the turbidity change for the electrified network system.

Conclusions

It was shown that cholesteric HPC/polymer networks were prepared successfully in film form by photopolymerization of a methacrylate monomer DEGMEM or HPMA from the lyotropic liquid-crystalline state of HPC in the methacrylate/methanol/water mixed solvent containing adequate amounts of cross-linking agents TEGDA and GA. The HPC/PDEGMEM or PHPMA composite films exhibited selective reflection colors when they were synthesized at HPC concentrations of 56−70 wt % in the starting lyotropics. When the mesomorphic polymer networks were immersed into different aqueous salt solutions, their coloration and optical turbidity and therefore the cholesteric periodicity and LCST-type phase segregation behavior of the respective samples varied depending on the sort of the impregnant salt used. The effectiveness of the salt ions in altering the optical properties was in good obedience to a rank order regarding their chaotropic strength, established formerly for the salt-containing HPC/water solution system.

Visual appearances of HPC/polymer networks swollen with different aqueous salt solvents were further changeable by application of a relatively weak electric field between both edges of the respective rectangular samples. The gradation in color and turbidity, definitely perceptible with a passage of several tens of minutes after the electrification, can be interpreted as due to formation of an uneven ionic distribution occurring in consequence of the possible electrophoretic migration of the salt-ion particles in the mesomorphic hydrogels. Somewhat surprisingly, the changing manner appeared rather rapid despite the lack of quite a beautiful array of color bands, in comparison with the situation experienced previously for the electrified cholesteric HPC/salt aqueous solutions. This result may reflect a higher heterogeneity in structure of polymer hydrogels composed of a mixture of dense and sparse domains.

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