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Controlling the Selective Light Reflection of a Cholesteric Liquid Crystal of (Hydroxypropyl)cellulose by Electrical Stimulation

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Rigid or semiflexible polymers possessing a chiral nature in their molecular structure, which may be represented by polypeptides and cellulosics, are capable of forming a cholesteric type of mesophase in a condensed fluid state. Some concentrated solutions and/or melts of such liquid-crystalline polymers are colored due to the selective reflection of visible light, originating from the cholesteric helical periodicity. As a typical example, (hydroxypropyl)cellulose (HPC) is known well to exhibit this optical property in aqueous solutions at polymer concentrations of ca. 50−70 wt %.[1,2]

Quite recently, we have investigated systematically the effects of addition of neutral salts on the phase behavior and optical characteristics of aqueous HPC solutions by spectrophotometry and NMR techniques.[3,4] In a process of execution of the study, we struck upon a new idea to control externally the slective light reflection from HPC liquid crystals. The present communication is concerned with the first observation of variations in cholesteric color and turbidity by application of electric potential to a cellulosic liquid-crystalline system.

The HPC sample used was of commercial origin (Scientific Polymer Products, Inc.); the manufacture's literature claims a molecular weight of $M_w = 60\,000$. The average number of substituted hydroxyls (DS) and that of introduced hydroxypropyl groups (MS) per anhydroglucose residue of this cellulosic sample were 1.8 and 3.3, respectively, which were determined by ^{13}C NMR specroscopy, following the peak assignments given in earlier literature.[5] Distilled water and reagent-grade salts were used directly to prepare concentrated HPC solutions. The solutions were made by mixing weighed HPC and water containing an appropriate amount of salt in glass vials over a period of 4 weeks, with the aid of repeated centrifugation to accelerate the dissolution of HPC. The vials were usually stored in a refrigerator (4 °C) before use. Throughout this work, the polymer concentration is denoted by the weight percent of HPC in each solution, and the salt concentration is designated in terms of a usual molarity (M) with respect to only the aqueous solvent.

Selective light-reflection of liquid crystals was examined by visual observations, and quantitative measurements of the reflection band were conducted with a UV−visible spectrometer (Hitachi U-2000). The samples were usually sandwiched between parallel glass plates separated by a Teflon spacer 200 μm thick and then allowed to equilibrate for at least 12 h prior to estimation. Selected liquid-crystalline samples were sealed into a cell made up of two slide glasses, two platinum plates as a pair of electrodes and spacers, each 500 μm thick, and a supplementary Teflon spacer.

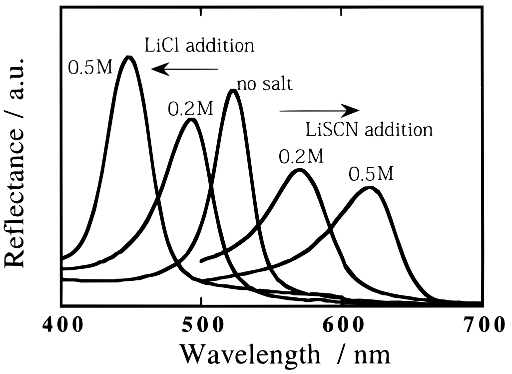

Figure 1. Selective light-reflection spectra of aqueous HPC liquid crystals at 20 °C (HPC concentrated, 62.5 wt %), showing an effect of addition of different salts on the peak location.

The effect of lithium salts on the selective light-reflection phenomenon of aqueous HPC liquid crystals is illustrated in Figure 1. All the spectral bands shown here emerge due to a periodic twisted structure constructing the cholesteric mesophases of HPC, not extinction bands due to intrinsic absorption of the polymer solute and/or salts. The wavelength (λ_M) of maximal reflectance can be related to the cholesteric pitch (P) by the de Vries equation,[6] $\lambda_M = \tilde{n}P$, where $\tilde{n}$ is the average refractive index of each anisotropic solution. The 62.5 wt % HPC/water sample containing no salt is greenish at 20 °C and gives a reflection band centered at ca. 520 nm. The maximum position shifts to the blue side when a small amount of lithium chloride is present in the solvent. In contrast to this, the addition of lithium thiocyanate results in a red shift in λ_M. In both cases, the higher the salt concentration, the greater the extent of the λ_M shift. Replacing the lithium cation by a sodium or potassium cation, we observed the corresponding reflection peaks centered at shorter wavelengths. The use of K^+ gave a smaller value of λ_M than the other case with Na^+.

The effectiveness of a given salt in altering the λ_M was, roughly, determined by the algebraic sum of the respective effects of its constituent ions, and thus various combinations of cation and anion sorts gave rise to different colorations of the aqueous HPC liquid crystals. Through the systematic examination by UV−visible specrophotometry,[3] it turned out that the value of λ_M and therefore that of P, too, increased with an increase in strength of the so-called chaotropic effect[7] of additive salts; this effect becomes pronounced, e.g., in the order of $Cl^- < Br^- < NO_3^- < I^- < SCN^-$, when compared in a series of salts with a common cation. SCN^- and I^- ions, usually acting as water-structure breakers, are highly chaotropic and disrupt hydrophobic assemblage of nopolar substances to increase their solubility in water, while Cl^- and Br^-, both rather water-structure makers, behave as salting-out agents

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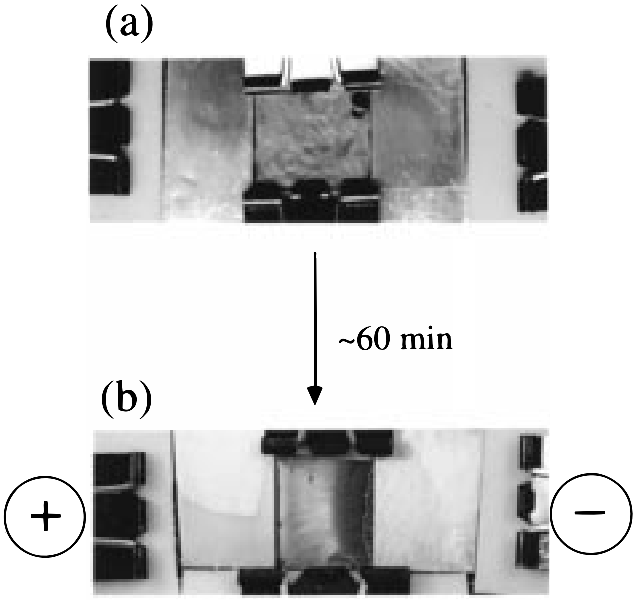

Figure 2. Photographs of a 62.5 wt % HPC/water liquid crystal containing 0.5 M lithium iodide at 20 °C, demonstrating the variation in the cholesteric color with time caused by the action of an electric field (3.0 V/cm): (a) initial quiescent state; (b) after ~60 min.

to enhance the hydrophobic interaction of the substances in water.

As is generally believed, it is not easy to control the mesomorphic ordering and ensuing optical behavior of a main-chain type of liquid-crystalline polymer by external electrical stimulation. Yet, what about using the aqueous HPC/salt system described above? As a simple case, let a liquid-crystalline HPC solution with an aqueous salt solvent be placed between inert metal plates serving as a pair of electrodes. If an appropriate, electric potential difference is applied between the metal plates, the salt-constituent cation and anion particles (possibly hydrated in the solution) will migrate toward the cathode and anode, respectively, in analogy with the electrophoresis for colloidal electrolytes. In the liquid-crystalline sample, as a consequence, there should occur some degree of gradient in concentration of the salt ions as perturbant of the cholesteric ordering, resulting in the gradation in reflection color from the originally unified one.

Acting on such a possibility, we made a simple device: Aqueous HPC liquid crystals containing a lithium salt were sealed in a layer of solution between parallel slide glasses spaced by a pair of platinum (Pt) plates of 500 μm thickness. The two plates were laid on both sides of the layered solution so that their sectional planes would be 1.5 cm apart. Then, a potential difference of 4.5 V was applied between the Pt electrodes at 20 °C; 1.5 V dry batteries connected in series were utilized for the electromotive force. The result of the experiment is visualized in Figure 2. The sample is an HPC (62.5 wt %)/LiI (0.5 M)/water solution, which was colored orange in the initial stage free of the electric field, as shown in Figure 2a. With an elapse of time, the reflective color changed dramatically. About 30 min after imposing the electric potential, the sandwiched solution imparted yellow to green colors in the vicinity of the cathode. On standing for another half hour in the electric field, the colors of the cholesteric sample ranged from red-orange on the positive side through yellow and green in the central part to striking blue in the neighborhood of the cathode, as demonstrated in Figure 2b. Further electrification over a period of 1 h resulted in the colors at the negative and positive sides moving sparingly toward the violet and red ends, respectively, of the spectrum; concomitantly, the central part of the sandwiched sample was enriched with a greenish hue. After more than 2 h elapsed in the total time of electrification, the coloration of the liquid crystal no longer changed appreciably with time. When the supply of electric power from the dry batteries was discontinued in the course of the above coloring process, a sequence of reflection colors at that time remained almost intact for at least 1 week. In the case where the situation in polarity of the pair of electrodes was exchanged in mid course, the sample virtually recovered the original uniform color (orange) with the passage of almost the same time as consumed until the exchange. Another attempt was made to raise the imposed electric potential to 6.0 V or above, yielding a field strength of ≥4.0 V/cm in the sample cell. Despite the indication of a more rapid change in coloration with time, however, air bubbles present in the concentrated solution prevented the regular formation of an array of reflective color bands.

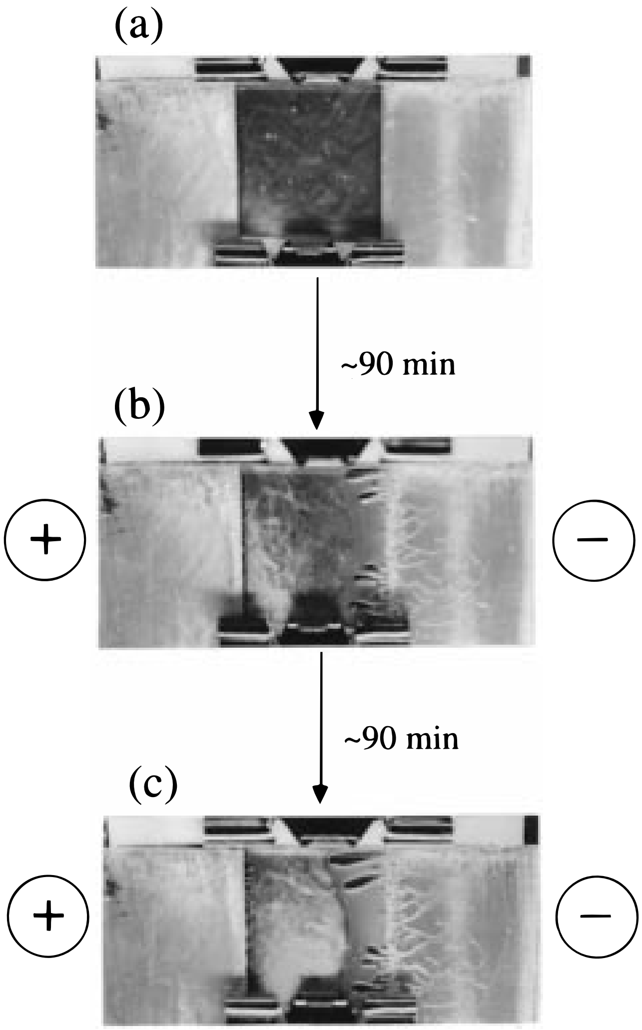

Figure 3. Variation in cholesteric reflection color of an HPC (62.5 wt %)/KI (0.5 M)/water system, followed with an elapse of time under the same condition as applied for the example shown in Figure 2: (a) initial quiescent state; (b) after ~90 min; (c) after ~180 min.

Figure 3 displays the result of a similar experiment carried out for a 62.5 wt % HPC liquid crystal containing 0.5 M potassium iodide. The field strength is 3.0 V/cm here, too. The sample assumed a deep green color in the initial state, as shown in Figure 3a. In less than 30 min after imposing the electric potential between the Pt electrodes, a yellowish color appeared on the positive side and a bluish one on the negative side. After 30 min more, these emerging colors encroached gradually upon the central greenish area from both sides, followed by the development of an opaque violet-colored or cloudier zone on the negative edge of the electrified sample (see Figure 3b). When 3 h passed away in the total time, a yellowish hue covered more than a half of the liquid crystal and one-third of the sample area became heavily turbid, as demonstrated in Figure 3c. In this photograph, we can see a brown to dull red color in the close vicinity of the anode; presumably, this coloring is not due to the selective light reflection by the cholesteric mesophase but is ascribed to the tincture characteristic of condensed iodine solution. The visual appearance was little changed after further time.

It is already known[2,8,9] that HPC solutions in water phase-separate and become turbid at an elevated temperature; i.e., the system shows an LCST-type phase diagram. A so-called cloud point is usually situated around 40 °C for isotropic solutions and lowered significantly for higher polymer concentrations, giving rise to the cholesteric mesophase.[9] As can readily be inferred, the addition of various salts into the HPC/water system would also affect the phase separation behavior, more or less depending on the sort and concentration of the employed additive. In fact, it has been ascertained for this system[3] that the effectiveness of a given salt in shifting the cloud point (T_c) either down or up was very similar to that of the salt in altering the pitch of the cholesteric helical structure, i.e., the T_c shifted according to the magnitude order of the total chaotropic effect of the constituent ions. In the above observation under the action of an electric field, the sharp increase in turbidity in part of the sample may be attributed to the lowering of T_c to ≤ 20 °C (room temperature) on the negative side, where K^+ ions as a highly potent depressor of T_c were, presumably, concentrated into a thicker band running perpendicular to the imposed direction of the electric field.

It was thus found for the aqueous cellulosic polymer/salt system that not only the coloration but also the optical turbidity was changeable by the action of a relatively weak elctric field (3.0 V/cm). Further work on the electrical control of the optical properties for this system and other ones with different cellulose derivatives is now in progress, in papallel with a more detailed study on the interaction of the cellulosic polymer solute with aqueous salt solvents.

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