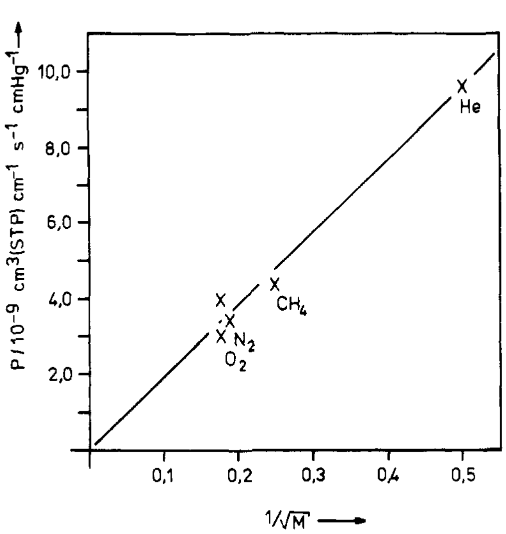

Figure 7. Permeability coefficients, P, of different gases through a polymeric cast film (compound 1, thickness 180 μm) as a function of the molecular weight, M, of the gases.

dispersions. Monomeric membranes were also polymerized by UV irradiation after having been dried. The cast films have an ordered multibilayer structure, as was demonstrated by wide-angle X-ray scattering. When cast films are prepared from polymerized vesicles, the degree of order is lower than it is in films polymerized after casting. The DODAA films cast from polymerized vesicles swell in electrolyte solution, whereas the films polymerized after casting remain stable in this environment. Thus these films may, for example, be suitable for application in reverse-osmosis membranes. With the help of gas permeation measurements it was demonstrated that the permeability depends only on the molecular weight of the gas and not on its chemical nature.

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Registry No. 1, 105336-86-5; O_2, 7782-44-7; N_2, 7727-37-9; CH_4, 74-82-8; He, 7440-59-7.

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Solid Cholesteric Films Cast from Aqueous (Hydroxypropyl)cellulose

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ABSTRACT: (Hydroxypropyl)cellulose films cast from water solutions assume a planar cholesteric arrangement, with pitches in the range 100–200 nm, depending on the casting conditions. The reflection wavelength moves into the visible range upon heating between 130 and 175 °C, the thermotropic order being characterized by a positive temperature dependence of the cholesteric pitch. This process is irreversible; the pitch values decrease only slightly on cooling. The cholesteric properties of (hydroxypropyl)cellulose films are therefore metastable and are induced either by shearing the polymer melt or by casting from the liquid crystalline solutions. The persistence of cholesteric order in the cast films at room temperature and the behavior of the optical properties on heating are consistent with dynamic mechanical measurements, which reveal an increase in the molecular mobility above 120 °C.

Introduction

In the past decade, numerous reports, reviewed in ref 1–3, have shown that most cellulose derivatives form cholesteric liquid crystalline phases in solution or in the bulk. (Hydroxypropyl)cellulose (HPC) has been widely studied because mesophases can be prepared in both water and common organic solvents. Optical anisotropy of HPC solutions has been shown to arise from a right-handed helicoidal arrangement of the polymer molecules in concentrated solution.[4,5] Strong indications have also been given that cholesteric order could be promoted on cooling HPC from the melt.[6,7]

Considerable effort has been devoted to the preparation of free-standing films exhibiting cholesteric order in view of their potential usefulness as chiroptical filters. Different routes have been studied, including (i) synthesis of thermotropic polymer liquid crystals with cross-linkable side chains,[8] (ii) incorporation of cholesteryl derivatives as side chains in acrylate[9] and siloxane polymers,[10] (iii) bulk polymerization of polymeric lyotropic mesophases in vinyl solvents,[11,12] (iv) quenching of copolyesters from their thermotropic range to room temperature,[13,14] and (v) casting from a lyotropic liquid crystalline solution.[15,16]

In this paper the optical properties of HPC films cast from water solutions are studied as a function of temperature between 25 and 200 °C, and a route to self-supporting HPC cholesteric films is presented.

Experimental Section

Film Preparation. (Hydroxypropyl)cellulose (Aldrich Chemical Co., nominal molecular weight M_w = 100000) was mixed with distilled water at room temperature. All samples were allowed to dissolve for at least 6 weeks. Both isotropic solutions and cholesteric mesophases were prepared. Three methods were used to cast HPC films from the solutions. Dilute, fluid solutions were poured on a flat Teflon surface, and water was allowed to evaporate in the normal laboratory environment (method A). The polymer was recovered from its more viscous anisotropic solutions by either of the following procedures. The mesophase was first mounted between two glass plates. After a planar texture had formed, the two slides were separated by sliding lengthwise. The samples were then kept under their own vapor pressure for several minutes in order to allow for complete relaxation before drying (method B). Alternatively, the mesophase was mounted between two flat plates made from a material permeable to water vapor (e.g., polyethylene) and allowed to dry in air (method C). Expectedly, the drying rate in method C was much lower than in method B. All films were finally dried thoroughly under vacuum for at least a week and then kept in a dry atmosphere. For comparative purposes, some HPC samples were also prepared from the melt at 260 °C, either by compression molding or at rest under nitrogen, followed by slow cooling to room temperature. For all methods, the initial quantity of water solution or pure polymer was adjusted so that the thickness of the resulting films was between 20 and 30 μm.

Optical Properties. Circular reflectivity (CR) spectra of the polymer films were recorded at temperatures between 25 and 200 °C with a Jasco J-500C spectropolarimeter and a Mettler FP52 hot stage. To minimize convective heat losses and maintain temperature accuracy, thin quartz slides were mounted with epoxy resin on the walls of the hot stage. (Hydroxypropyl)cellulose films prepared from the melt or by methods A and C were heated free-standing. Those obtained by method B were heated with one face in contact with quartz or glass. In order to study the effect of sample mounting, a method B film cast on glass was peeled from the supporting slide and heated as a free-standing film. The spectropolarimeter measured the differential transmitted intensity of left- and right-handed circularly polarized light, and results are expressed in terms of the ellipticity of the transmitted light as a function of wavelength. It should be noted that peaks in the recorded spectra correspond to the selective reflection of circularly polarized light and not to the selective absorption (dichroism) usually measured by spectropolarimetry. The method proved to be a better tool than UV-visible spectrophotometry to detect cholesteric order because the latter technique is highly sensitive to crystalline scattering and, at high temperature, to absorption resulting from polymer degradation.

Dynamic Mechanical Properties. Dynamic mechanical properties were measured with a Rheovibron DDV-IIC mechanical spectrometer (Toyo Baldwin Co., Japan) at frequencies of 3.5, 11, and 110 Hz. The experiments were performed from −160 °C to the "softening" point of the polymer at a heating rate of less than 1 °C/min^{-1}. The onset of "softening" occurs when a constant tension on the sample cannot be maintained for the dynamic measurements.

Differential Scanning Calorimetry. Differential scanning calorimetry (DSC) thermograms were obtained between −120 and +250 °C for a compression-molded film with a Perkin-Elmer DSC-2C and conventional subambient procedures. Measurements were carried out on heating at 20 °C/min^{-1}.

Results and Discussion

In an extensive study of the solid-state properties of HPC, Samuels[17] showed that polymer films cast from dilute water solutions were anisotropic and that the polymer molecules lay preferentially in the plane of the film. In light of the subsequent observations of liquid crystalline properties for HPC solutions, this result suggests that the water-cast polymer might assume a planar cholesteric arrangement in the bulk, rather than a random in-plane alignment. The existence of a cholesteric arrangement of solid HPC at room temperature has been reported,[18] but no details about the sample preparation were given. It is also consistent with observations made during the drying of a HPC water mesophase mounted between two glass slides without any sealing agent. Over days, the effect of solvent evaporation is clearly visible from the rainbow-like appearance of the edge of the sample, where the reflected color shifts to shorter wavelength. UV-visible spectrophotometric measurements performed radially across the rainbow edge of the drying mesophase showed that the degree of order, as seen from both reflection peak intensity and bandwidth, is essentially unperturbed upon water removal. A similar, though less intense and narrower ring of colors is observed as the solvent is allowed to evaporate from an initially dilute HPC solution (method A). To ascertain the presence of order in water-cast HPC, films were recovered from solutions of different concentrations using various procedures. Circular reflectivity (CR) spectra measured at room temperature for typical water-cast samples are given in Figure 1. Negative CR peaks, which indicate that the films reflect right-handed circularly polarized light, are observed irrespective of the casting method or the original solution concentration. In contrast, the polymer prepared from the melt gives no CR peak in the same wavelength range, showing that its degree of cholesteric order, if any, is below the detection limits of the spectropolarimeter. It is therefore concluded that water-cast HPC films do keep, to a certain extent, the planar right-handed cholesteric structure which either prevailed in the original mesophase or which developed as the solvent evaporated from an isotropic solution. However, both reflection wavelength and minimum ellipticity appear to depend drastically on the casting conditions. Films prepared from a mesophase are characterized by reflection wavelengths at 250 nm (method B) or less than 190 nm (method C), the higher wavelength being observed at the higher drying rate. Also, the ellipticity at the reflection wavelength, which can be roughly considered as a measure of the degree of order for films of similar thicknesses, is much higher for slowly dried samples. Understandably, the lowest CR peak intensity

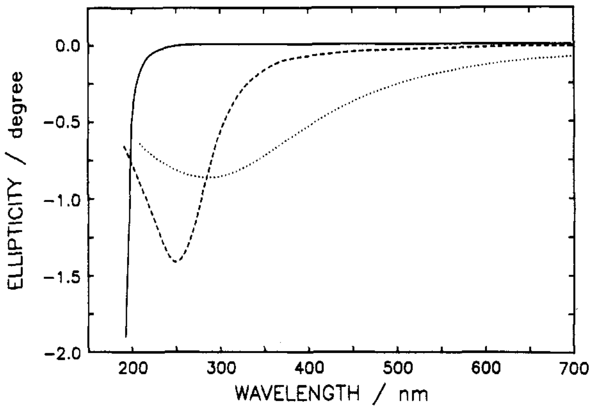

Figure 1. Circular reflectivity spectra at room temperature for HPC films cast from water solutions using method A (dotted), B (dashed), and C (full line). In contrast, samples prepared by slow cooling from the melt show no circular reflectivity between 190 and 900 nm.

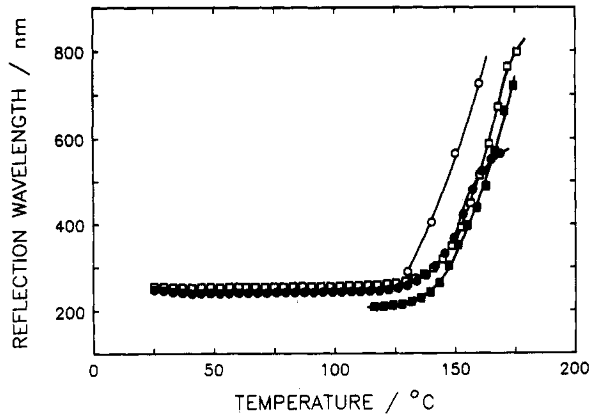

Figure 2. Reflection wavelength as a function of temperature for water-cast HPC films heated at 0.2 °C/min^{-1}: filled circles, sample cast on a quartz slide using method B; open squares, free-standing film initially cast on glass using method B and removed from the supporting plate after drying; filled squares, free-standing film prepared using method C. The reflection wavelengths measured under isothermal conditions (Figures 4 and 5) are also plotted (open circles).

is recorded for the films cast from isotropic solutions (method A) since, in the course of drying, the polymer solution did not remain in the anisotropic concentration range long enough to achieve a high degree of order. These samples generally exhibit the highest reflection wavelength, although the reproducibility is lower than for mesophase-cast films, which probably reflects a greater variability in the drying rate of dilute solutions. For this reason, samples prepared from dilute solutions were not investigated further. No systematic study of the effect of concentration on the reflection wavelength of HPC films cast from cholesteric mesophase has been performed, but preliminary measurements showed that the effect is likely to be low. The dependence of CR spectra on casting conditions demonstrates that the order in the films does not represent the ultimate equilibrium state of the polymer bulk, but rather that the cholesteric arrangement of the solution, whose pitch experienced a continuous decrease in the course of water evaporation, has been at some point "frozen-in" before complete drying. A previous study[5] of the optical properties of HPC water mesophases as a function of their concentration has shown that the reflection wavelength decreases monotonously as the concentration increases. A linear correlation is observed on a log–log plot, and extrapolation toward the pure polymer for HPC samples of molecular weight between 6×10^4 and 30×10^4 gives a reflection wavelength at about 80 nm, far below those observed in Figure 1. This corresponds to a cholesteric pitch of about 55 nm, according to the de Vries theory.[19] Such a low pitch is probably of no real physical significance because of the limits in twist angle and/or interlayer distance encountered in packing polymer chains of finite diameter.

Optical Properties at High Temperature. The water-cast HPC films displayed some unexpected optical properties when heated. Figure 2 gives the reflection wavelength as a function of temperature for films heated at 0.2 °C/min^{-1} from 25 to 200 °C. The results are essentially independent of the casting method or whether the films are heated free-standing or deposited on glass. The reflection wavelength is constant with temperature up to 130 °C and then increases very rapidly, with a rate of change on the order of 20 nm·deg^{-1}. This rapid variation is indicative of thermotropic liquid crystalline properties characterized by a positive temperature dependence of the pitch. Such a dependence is consistent with results obtained for other right-handed cholesteric mesophases prepared from thermotropic cellulosics.[20] Figure 3 give the typical variation of the ellipticity at the reflection wavelength as a function of temperature. Although the reflection wavelength is essentially constant below 130 °C, the ellipticity changes, a rapid increase in the magnitude being noticed up to 40 °C. Furthermore, the drastic variation of cholesteric pitch above 130 °C is accompanied by a decrease in the ellipticity at the reflection wavelength. At the same time, the CR peak broadens, revealing an overall decrease in liquid crystalline orientation. As seen in Figure 2, a slower variation of the reflection wavelength with temperature is sometimes noticeable just before the disappearance of the CR peak, which occurs consistently between 170 and 175 °C for all samples. However, large differences in the highest attainable reflection wavelength are observed. They could not be consistently related to the casting conditions and are thus likely to reflect less controllable factors such as the residual water content or the degree of crystallinity. As expected, the melt-processed sample, which did not show any CR peak at room temperature, did not develop any detectable cholesteric order upon heating between 25 and 200 °C.

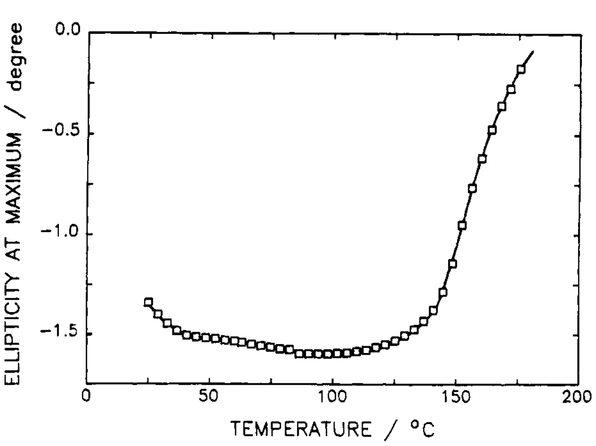

Figure 3. Ellipticity of water-cast HPC at the wavelength of maximum reflection as a function of temperature. The intensities were taken from the CR spectra used for Figure 2 and the free-standing film prepared by method B.

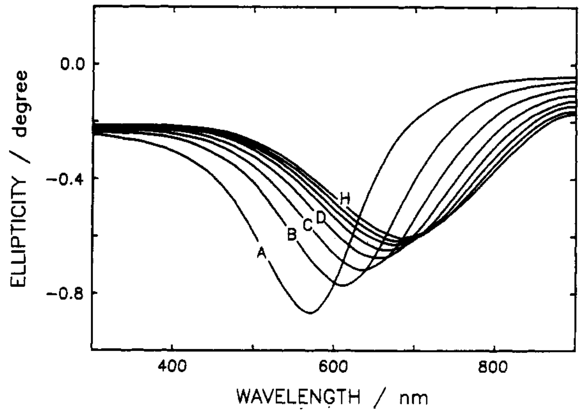

Figure 4. Circular reflectivity of a water-cast HPC film at 160 °C. The sample, prepared by method B, was placed in the preheated hot stage. Spectra were recorded 2 min after heating (A) and then at 15-min intervals (B–H).

Measurements were also performed under isothermal conditions in the 120–170 °C range. Polymer films were heated rapidly to a constant temperature by positioning the sample in the preheated Mettler hot stage. The circular reflectivity of the films was then recorded as a function of time. Typical spectra obtained at 160 °C are given in Figure 4. The first spectrum was recorded after

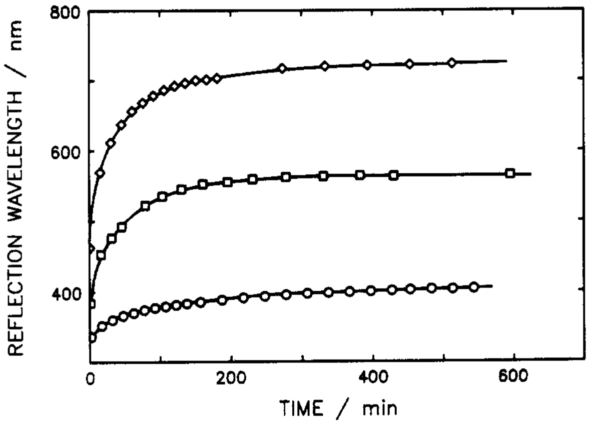

Figure 5. Reflection wavelength of water-cast HPC films as a function of time at 140 (circles), 150 (squares), and 160 °C (diamonds).

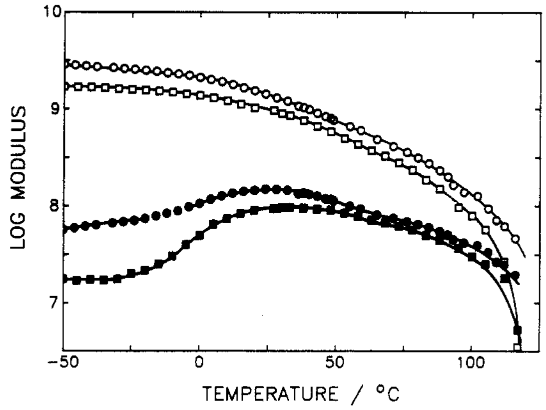

Figure 6. Dynamic mechanical properties of HPC films at 110 Hz. The storage modulus (open symbols) and loss modulus (filled symbols) are plotted as a function of temperature for a film cast from water mesophase using method C (circles) and a sample compression molded at 260 °C (squares).

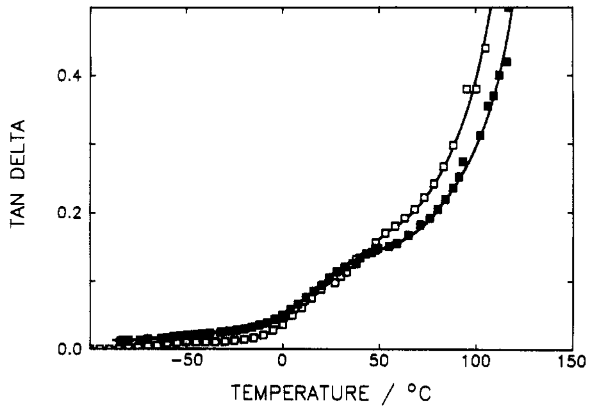

Figure 7. Dynamic mechanical properties of HPC films at 110 Hz. The loss tangent is plotted as a function of temperature for a film cast from water mesophase using method C (filled squares) and a sample compression molded at 260 °C (open squares).

heating the film for only 2 min. The very fast onset of the reflection peak confirms that cholesteric order was already present in the dried sample at room temperature. With time the peak shifts to higher wavelengths, broadens, and decreases in intensity but, after about 3 h, a time-independent CR spectrum, stable over hours, is recorded. The equilibrium reflection depends on temperature, as shown in Figure 5, where the isothermal variation of the reflection wavelength is plotted as a function of time. A reflection in the 400–700-nm visible range is observed between 140 and 160 °C. For comparison, the limiting isothermal values have been added in Figure 2. The temperature dependence of the reflection wavelength is about the same, whether the films were studied isothermally or at a constant heating rate. As shown in Figure 5, however, a few hours are necessary to reach an equilibrium pitch so that a large difference in absolute values of the reflection wavelength, on the order of 200 nm, is observed at a given temperature between the two heating procedures.

Dynamic Mechanical Properties. The discontinuous temperature variation of cholesteric order in water-cast HPC may be better understood by considering the dynamic mechanical properties of the polymer. The dynamic moduli and the loss tangent measured at 110 Hz for a compression-molded film and a sample cast by slow drying of a water mesophase (method C) are respectively plotted as a function of temperature in Figures 6 and 7. Both samples exhibit the same general features. In the 10–50 °C range, a maximum is observed in loss modulus and tan δ while the storage modulus decreases smoothly, possibly with a shoulder around 50 °C. The sharp decrease of both moduli above 100 °C is accompanied with a drastic increase of tan δ. At a lower frequency of deformation, the curves are essentially the same except for a small shift of the loss tangent maximum to higher temperature. Due to the softness of the polymer, no measurements were possible above 120 °C so that any difference between cast and melt-processed samples cannot be ascertained. The broad maximum of loss modulus at about 25 °C is indicative of the polymer glass transition, in agreement with previous measurements[21] of the temperature dependence of the gas chromatographic retention volumes of nonsolvent vapors on a HPC stationary phase. The glass transition is apparent in the optical properties of water-cast HPC from the increase in ellipticity at the reflection wavelength shown in Figure 3. The exact nature of the relaxation phenomenon observed at the higher temperature is difficult to determine. Differential scanning calorimetry proved to be of little help. The thermogram is composed of several very broad and small transitions whose order is impossible to ascertain due to base-line curvature. No distinct change in heat capacity or clear melting endotherm is observed but a broad endotherm could possibly be distinguished between 130 to 200 °C, in agreement with literature DSC data.[7,18] On the other hand, HPC is known to have a low crystalline content, of the order of 10–20%, which melts[6,17] around 200 °C. The drastic softening of HPC around 125 °C is therefore unlikely to be related to the melting of the polymer. As with other polymers containing hydroxyl groups, HPC is notoriously difficult to dry. Despite extensive drying under dynamic vacuum, cast films are observed to lose up to 2% of their weight upon heating at 180 °C for 2 h. The change in the mechanical properties of the polymer at high temperature may thus be related to the release of tightly bound water in the HPC film. However, this alone cannot explain satisfactorily the behavior of HPC cast films (e.g., the *increase* of mobility above 120 °C, the persistence of cholesteric order upon drying, or the lack of reversibility upon cooling discussed later). Rather, the high-temperature relaxation phenomenon is tentatively associated with the breaking of intermolecular hydrogen bonds. This is consistent with earlier findings[17] by infrared spectroscopy. A noticeable change in the IR spectrum of water-cast HPC films has been reported between 135 and 160 °C and was attributed to an increasing mobility of the molecular skeleton. Although most hydrogen bonds were found to be essentially intramolecular and to persist up to 260 °C, some changes in the IR spectrum have been convincingly related to the breaking of intermolecular bonds, resulting, for instance,

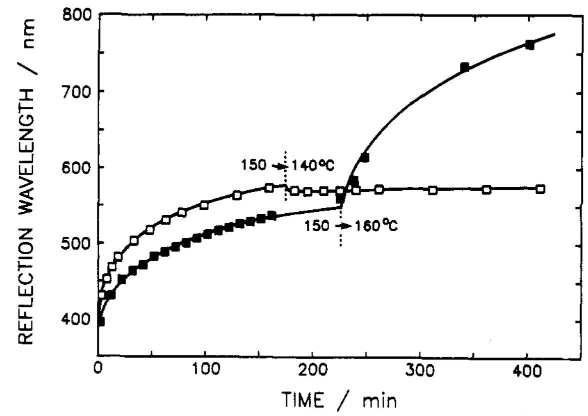

Figure 8. Reflection wavelength of water-cast HPC films as a function of time. The samples, prepared by method B, were heated directly at 150 °C. After 3–4 h, the temperature was rapidly changed to 140 (open squares) or 160 °C (filled squares). (The difference between the two curves prior to the temperature change is often observed. It is transitory and disappears with time. The reproducibility in the equilibrium reflection wavelength at a given temperature was on the order of 15–20 nm.)

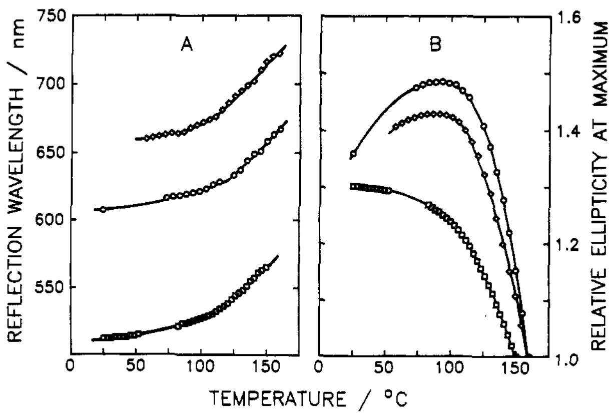

Figure 9. Circular reflectivity of water-cast HPC as a function of temperature upon cooling at 0.2 °C/min^{-1} from 150 (squares) or 160 °C (diamonds) after the film reached a constant CR under isothermal conditions (see Figure 3) or upon cooling at 1 °C/min^{-1} from 160 °C (circles) immediately after the film reached that temperature upon heating at 1 °C/min^{-1} from room temperature: (A) reflection wavelength; (B) ellipticity at the reflection wavelength, relative to the initial intensity at the highest temperature.

in the appearance of vibrations characteristic of unbonded hydroxyl groups.[17] The above description is quite consistent with the data reproduced in Figure 2. A variation of the cholesteric pitch is only observed above 130 °C, where the breaking of interchain hydrogen bonding allows changes in the angle between segments in adjacent chains.

Reversibility of Thermotropic Properties. The origin of cholesteric order in water-cast HPC film proposed above raises the following question. Does the thermotropic cholesteric behavior of the polymer between 130 and 175 °C represent a true thermodynamic equilibrium state? As already pointed out, HPC films prepared from the melt and slowly cooled to room temperature do not show any CR peak, so that thermotropic properties seem limited to samples that already possess cholesteric order prior to heating. However, samples prepared by compression molding immediately followed by quenching in liquid nitrogen generally exhibit a constant negative circular reflectivity of low intensity, suggesting that they assume some liquid crystalline order characterized by a very broad cholesteric pitch distribution. Also, rheooptical and birefringence studies[6,7] of a low molecular weight sample (Klucel E, nominal $M_w = 6 \times 10^4$) have given indirect evidence of the HPC thermotropic character. Suto et al.[7] reported an increase in the polymer birefringence upon heating between 160 and 210 °C but gave no details about the sample preparation. Other indications of cholesteric order were observed upon cooling from the melt but they all involved some shearing of the HPC melt. This suggests that the formation of a cholesteric liquid crystalline phase can be induced by a mechanical deformation of the HPC liquid, in agreement with our observation of some optical activity for quenched compression-molded films. The cholesteric ordering of the randomly arranged and highly entangled polymer prepared from the melt in quiescent conditions could be thermodynamically favored although it would then be a very slow process, unobservable before degradation occurs. This hypothesis is not supported by a study of the reversibility of the optical properties of water-cast samples. Figure 8 emphasizes the effect of cooling or heating a HPC film after it has been brought rapidly to 150 °C and then left to equilibrate for a few hours. Upon heating to 160 °C, the reflection wavelength changes rapidly and tends to a value close to that obtained when the film is heated directly from room temperature to 160 °C. In contrast, very little change in the CR spectrum is caused by cooling to 140 °C. The lack of reversibility is also apparent when HPC films are cooled at a constant rate. Plots of the reflection wavelength (Figure 9A) and the CR intensity at the reflection wavelength (Figure 9B) as a function of temperature present general features that are independent of the sample thermal history or the cooling rate (see caption for details). The reflection wavelength experiences very little change upon cooling, on the order of 50–60 nm, in contrast with the drastic increase observed on heating (Figure 2). This small pitch decrease is likely to originate from changes in the polymer volume upon cooling. A higher rate of change is observed above 110–120 °C, which confirms that a transition in the polymer mobility takes place in this temperature range. Upon cooling, the ellipticity at the reflection wavelength also shows a discontinuous variation, a maximum being even observed for some samples. The large increase in intensity, up to 50%, indicates that the degree of order increases substantially, even though the cholesteric pitch remains nearly constant. Thus, for HPC in the absence of diluent, the formation of the cholesteric structure is irreversible. In contrast with the large dependence of the thermotropic properties of HPC on its thermal, mechanical, and solvent histories, equilibrium cholesteric mesophases are obtained from water-cast films, as emphasized from the stability of isothermal optical properties with time (Figure 5). Therefore, the mesomorphic properties of HPC are of a metastable nature. Water-cast HPC films heated above 130 °C show a cholesteric orientation whose pitch depends drastically on temperature upon heating only, indicating that the lowest free energy minima, i.e., the largest stability, are attained for cholesteric structures of the highest pitch.

Conclusion

When dried, water-cast HPC films maintain the helicoidal supermolecular arrangement of the cholesteric state which developed in the solution. On heating between 130 and 175 °C, the helicoidal pitch increases to give reproducible constant reflection wavelengths in the visible region. This process is irreversible; the pitch values decrease only slightly on cooling to room temperature. Thus the cholesteric water-cast HPC film exists as a metastable phase.

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Registry No. HPC, 9004-64-2.

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Synthesis and Characterization of Pyrene-Labeled (Hydroxypropyl)cellulose and Its Fluorescence in Solution

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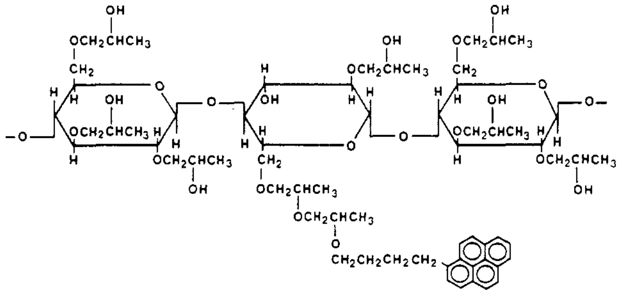
ABSTRACT: The fluorescence spectroscopy of pyrene-labeled (hydroxypropyl)cellulose was examined in solution in various alcohols and in water. The low relative excimer fluorescence intensity in alcohol solvents such as methanol is typical of a randomly coiled polymer containing a small fraction of pyrene groups. The very intense excimer intensity in water suggests that the polymer adopts a different conformation in aqueous solution, characterized by extensive ground-state dimerization and aggregation of the pyrene groups. There is also strong evidence for polymer–polymer association, even at very low polymer concentration, which also contributes to the extent of excimer emission. Other experiments involving fluorescence and UV absorption measurements on these samples also support this view.

(Hydroxypropyl)cellulose (HPC) is a polymer with many important industrial applications. Like (hydroxymethyl)cellulose and (hydroxyethyl)cellulose, HPC is a soluble derivative obtained by chemical functionalization of cellulose. Scientific interest in these polymers derives from the fact that they are semiflexible, nonionic, linear polymers[3] and that they form liquid crystalline states in the melt and in concentrated solutions.[4] A variety of their properties have been investigated, including dilute solution viscosity,[3,5] fluorescence depolarization in sheared solutions,[6a] and polymer interaction with surfactants in aqueous solutions.[6b]

Fluorescence labeling techniques have proved useful in studying a wide range of properties of various polymers and their mixtures. We anticipate that these techniques will also be useful in the study of HPC-containing systems. In this paper we describe the synthesis of pyrene-labeled HPC (HPC-Py), its characterization, and some of its fluorescence properties in dilute solution.

In order to carry out experiments in aqueous solution without concern for the possible loss of label through hydrolysis, we chose to attach the pyrene groups by means of an ether linkage. A convenient method involves treating a solution of HPC with a strong base to generate alkoxide sites, followed by reaction with 4-(1-pyrenyl)butyl tosylate. The pyrenes become attached, presumably, to oxypropyl pendant groups, leading to the kind of structure depicted below:



From our experiments, we show, for example, that the pyrene groups are attached to sites of considerable local flexibility. In alcohol solvents, the pyrene groups are predominantly unassociated, but form excimers by a dynamic mechanism after photoexcitation. In water, a different behavior is observed. The pyrenes stack or dimerize in a face-to-face configuration, so that the excimer and monomer emissions derive from different populations of

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