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Propanoate Ester of (2-Hydroxypropyl)cellulose: A Thermotropic Cholesteric Polymer That Reflects Visible Light at Ambient Temperatures

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ABSTRACT: The propanoate of (2-hydroxypropyl)cellulose was prepared by esterification of (hydroxypropyl)cellulose. Thin layers of the bulk polymer between glass surfaces were colored at room temperature, due to cholesteric reflection from a liquid crystalline structure. On heating, the color moved to longer wavelengths and disappeared; the liquid crystalline–isotropic transition was complete at 167 °C. The polymer also forms a lyotropic mesophase in acetone at concentrations above ~30 wt % polymer.

Introduction

In 1956, Flory predicted that polymers with stiff linear chains would form ordered phases in the melt[1] and in concentrated solutions.[2] The predicted solution behavior has now been observed for a wide range of polymers, and some examples of ordered melts are also known.[3] The lyotropic systems include (hydroxypropyl)cellulose in water; concentrated solutions of this cellulose ether reflect visible light, due to a cholesteric structure that results from the chiral nature of the cellulose chain.[4,5] Evidence for ordered solutions of many other cellulosic polymers has since been published.[6] Although far from rigid, the cellulose backbone appears to be sufficiently stiff to allow formation of ordered phases. Recently, the acetate ester of (hydroxypropyl)cellulose has been prepared; (acetoxypropyl)cellulose, without solvent, displays cholesteric colors on heating.[7] A similar phenomenon was subsequently observed with (hydroxypropyl)cellulose at higher temperatures,[8] and the trifluoroacetate ester of (hydroxypropyl)cellulose also forms a birefringent fluid.[9] Thus, some cellulose derivatives evidently also form *thermotropic* liquid crystalline phases. The wavelength of the cholesteric reflection in these systems increases with temperature, and in lyotropic systems the wavelength also increases with increasing dilution of the polymer. Thus, based on the observations on (hydroxypropyl)- and (acetoxypropyl)cellulose, it seemed possible that if the chiral interactions between the cellulose backbones were decreased slightly by increasing the side-chain length, then the resultant cholesteric cellulose derivative would reflect visible light at room temperature. Here, we report the preparation of such a derivative.

Experimental Section

The propanoate ester of (hydroxypropyl)cellulose ([(propionyloxy)propyl]cellulose, PPC) was prepared from propionyl chloride and (hydroxypropyl)cellulose. (Hydroxypropyl)cellulose (HPC) (Aldrich, nominal mol wt 100000) (25 g) was dissolved in 300 mL of acetone, and 60 mL of propionyl chloride (Aldrich, 97%) was added to the solution. After stirring for 1 h at room temperature, the mixture was refluxed for a further hour. The solution was poured into a large excess of distilled water, and the propanoate ester separated as a white, sticky mass. After washing with water to remove water-soluble residues in the polymer, the polymer was purified by repeated solution in acetone and reprecipitation in water. The final yield after drying under vacuum was 31.5 g of a tacky polymer with a distinct iridescent color that varied from pink to green, depending on the viewing angle. The observations reported below were made on this sample; other samples of PPC displaying iridescent colors were readily prepared from HPC and propionyl chloride or propionic anhydride using a variety of reaction conditions.

An idealized representation of the polymer repeat unit is shown in Figure 1. The degree of etherification of the starting material was estimated to be 3.4 by means of the terminal methyl group analysis of Purves and Lemieux.[10] Note that hydroxypropyl side chains at any of the three hydroxyl positions on the anhydroglucose residue may react further to give multiple-unit side chains. It is thus possible that some of the main-chain hydroxyls are unsubstituted. The number of ester groups that had reacted with the (hydroxypropyl)cellulose was measured by saponification. After drying overnight at 50 °C under vacuum, the PPC was dissolved in absolute ethanol, and a known amount of 1 M aqueous sodium hydroxide solution was added and allowed to react with the polymer for several hours. The excess base was then back-titrated with sulfuric acid, using phenolphthalein as indicator. The propionyl (CH_3CH_2CO) content of the polymer was estimated to be 20.9 ± 0.6% by weight by this method. This corresponds to a degree of esterification of 1.64 for a degree of etherification of 3.4. The maximum degree of esterification is 3. Infrared spectra of the polymer showed strong peaks at 1735 and 1190 cm^{-1}, as expected for ester substituents. A large peak at 3500 cm^{-1}, attributed to hydroxyl groups, indicated that esterification was incomplete, in accord with the ester group analysis.

The weight-average molar mass, $\bar{M}_w$, of the polymer was measured in acetone solution with a Chromatix KMX6 low-angle laser light scattering photometer. The solutions were filtered with a 0.2-μm Millipore Type FG filter and then passed through the light scattering cell at a flow rate of 0.05 mL/min. The value of the specific refractive index increment, $d\mu/dc$, for PPC in acetone was determined to be 0.104 with a Brice-Phoenix differential refractometer. The measurements gave a value for $\bar{M}_w$ of 2.2×10^5, with a value for the apparent second virial coefficient of -0.6×10^4 mL/g. This slightly negative value may indicate that the polymer tends to aggregate in acetone.

The visible–ultraviolet absorption spectrum and wavelength of cholesteric reflection were measured with a Pye-Unicam SP8-150 spectrophotometer. The wavelength of the reflection band of the polymer was measured by pressing polymer samples between a microscope slide and cover plate and allowing the samples to stand until a reasonably uniform planar texture was achieved. The sample was then placed perpendicular to the spectrophotometer beam. Reflection from the cholesteric structure resulted in an apparent absorption peak at the wavelength of the reflection band. Refractive index measurements were made with an Abbê refractometer (Carl Zeiss). Birefringence of the samples was observed with a Reichert polarizing microscope equipped with a Mettler FP-52 hot stage. The variation in birefringence with temperature was measured by replacing one microscope eyepiece with a Mettler 18100 photocell and recording the output on a Varian A25 strip chart recorder. The thermal properties of the polymer were investigated with a Perkin-Elmer DSC-2C differential scanning calorimeter.

A preliminary fractionation of PPC was performed from benzene solution with *n*-heptane as nonsolvent. Four fractions were isolated by freeze-drying from benzene.

Results and Discussion

The appearance and behavior of PPC resembled that of the (acetoxypropyl)cellulose samples previously reported,[7] except that the PPC displayed iridescent colors

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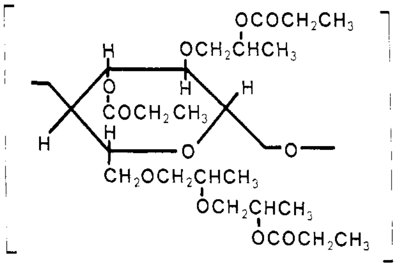

Figure 1. Schematic representation of a substituted anhydroglucose unit of [(propionyloxy)propyl]cellulose (PPC); molar etherification = 3, molar esterification = 3.

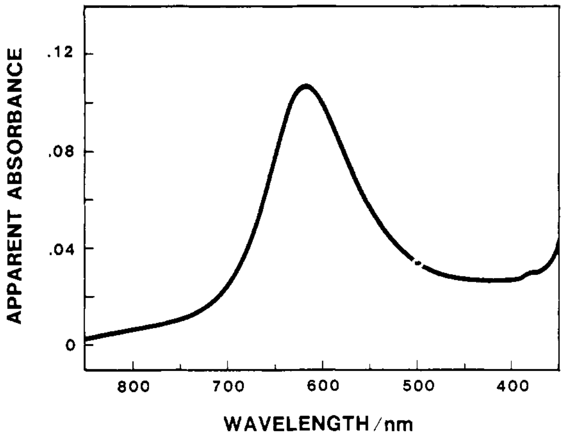

Figure 2. Cholesteric reflection peak for PPC at room temperature, measured by transmission through a 0.23-mm-thick sample between glass slides placed perpendicular to the spectrophotometer beam.

in the final stage of drying. The wavelength of the cholesteric reflection peak was measured spectrophotometrically (Figure 2). Dilute samples of the polymer were transparent in the visible region, but a thin layer of the pure polymer placed between two glass surfaces normal to the spectrophotometer beam showed an apparent absorbance maximum, λ_0, at about 620 nm, due to the reflection of the beam at this wavelength. The mean refractive index of the polymer, $\bar{\mu}$, was 1.469, so that the cholesteric pitch given by $P = \lambda_0/\bar{\mu}$[10] was about 420 nm. The intensity of the apparent absorption of light corresponded to a maximum reflectance of 20% from the sample at the peak wavelength. For an ideally oriented cholesteric of sufficient thickness, the maximum expected reflectance is 50%.[11] The low reflectance observed for the polymer film was probably due to imperfect orientation of the sample. On heating, the color moved to longer wavelengths and disappeared. On cooling, the color slowly reappeared.

At room temperature, the polymer was a sticky, birefringent solid. On warming, the material became more fluid and the birefringence decreased over a very broad temperature range but disappeared sharply at 167 °C to give an isotropic phase. At slow heating rates the temperature at which the isotropic phase appeared, the "clearing temperature", was quite reproducible. On cooling the isotropic phase, the anisotropic phase reappeared. For a sample heated to 170 °C at 1 °C/min and then immediately cooled at 1 °C/min, the reappearance of the anisotropic phase was first detected at about 163 °C. Heating the sample beyond 170 °C or leaving the sample for a prolonged time in the isotropic phase increased the degree of hysteresis observed in the re-formation of the anisotropic phase.

Hysteresis in the mesophase–isotropic phase transition was also evident in the differential scanning calorimetric

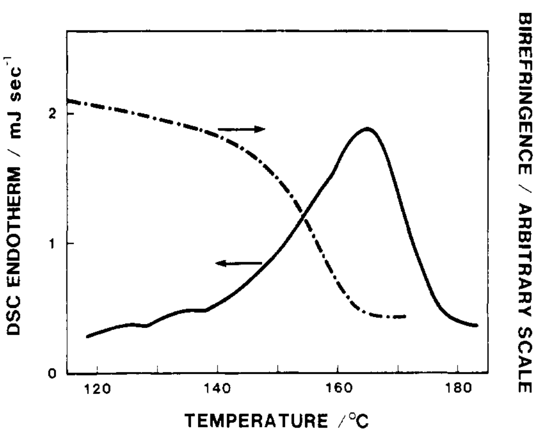

Figure 3. Thermal and optical evidence for mesophase–isotropic transition on heating PPC. Differential scanning calorimeter (DSC) curve for 35.9 mg of polymer heated at 20 °C/min. The disappearance of birefringence on heating at 1 °C/min was followed by means of a polarizing microscope equipped with a photoelectric detector and a sample heating stage.

experiments. On heating at 20 °C/min, an endothermic peak was observed with a maximum at 166 °C (Figure 3). On cooling at the same rate, the exotherm resulting from the formation of the anisotropic phase showed a peak at 143 °C. Thus the transition from the anisotropic to isotropic phase for this polymer covered a broad temperature range and showed a significant hysteresis. The transition thus differs from that for low molecular weight liquid crystals, but the difference is not surprising in view of the high molecular weight and high viscosity of the polymer. The heat associated with the transition to isotropic fluid was ~2.5 J/g at a heating rate of 20 °C/min.

In a preliminary fractionation, part of the PPC sample (0.5 g) was dissolved in benzene, and fractions were isolated by the addition of *n*-heptane. The fractions were redissolved in benzene and freeze-dried. The first fraction (~0.1 g) was isolated as a white porous powder, which when pressed between microscope slide and cover glass at ~100 °C gave a tacky birefringent film. On heating at 1 °C/min, the birefringence remained constant up to 164 °C, at which temperature it dropped sharply, becoming isotropic at 174 °C. On cooling from this temperature at the same rate, the birefringence was detected again at 166 °C and had regained its initial value within a 10 °C temperature span. This transition was very much sharper than that observed for the whole polymer (Figure 3). Sample polydispersity may be the main reason for the broad transition observed for the unfractionated polymer. Some observations on the development of cholesteric color were made on the second freeze-dried fraction (~0.15 g). One portion of this fraction, pressed into a film between a black plastic sheet and cover glass, slowly developed a faint cholesteric color over a period of weeks. A second portion of the freeze-dried fraction was dissolved in acetone and reprecipitated by pouring the acetone solution into water, where the polymer separated as a white soft mass. When the polymer was pressed into a thin film between cover glass and black plastic, the white color disappeared as the water evaporated, leaving in a few days a bright cholesteric layer. The color in both cases was similar to that of the original unfractionated polymer. The possibility that traces of water play a crucial role in the formation of the cholesteric structure cannot be ruled out on the basis of these observations. However, we suggest that the planar cholesteric arrangement (in which the long axes of the molecules are aligned parallel to the constraining planes in a helicoidal array) is the *equilibrium* structure for thin layers of these polymers. Rapid freeze-drying from dilute solution initially produces a randomly oriented material. The molecular migration necessary to form the long-range order of the cholesteric state must be a slow process, especially for high molar mass or unplasticized samples. Thus freeze-dried samples develop color very slowly. On the other hand, during slow evaporation of organic solvents or water, the polymer chains have greater freedom to migrate and form more rapidly the stable planar cholesteric arrangement. The stability of the cholesteric structure was observed with a number of unfractionated PPC samples of differing degrees of esterification that were prepared as thin layers between planar glass or plastic surfaces. The colors of these unsealed samples have remained unchanged for periods of up to 2 years.

PPC also forms lyotropic liquid crystalline phases in organic solvents. A series of solutions was prepared with concentrations ranging from 5% by weight to 95% by weight PPC in acetone. Dilute solutions were clear; concentrated solutions showed increasing turbidity, and at 90% PPC the solutions were iridescent. No distinct two-phase region was observed visually, even after prolonged standing. Visual observations with a polarizing microscope showed that the 30% solution was isotropic, and the 35% solution showed birefringence. The onset of birefringence was also detected by observations with an Abbê refractometer.

[(Propionyloxy)propyl]cellulose thus forms an ordered phase at concentrations between 30 and 35% by weight polymer in acetone. This is a somewhat lower concentration than required for (acetoxypropyl)cellulose in the same solvent[7] and for (hydroxypropyl)cellulose in a variety of solvents.[5,12] It is a much higher concentration than would be expected for a rodlike polymer of equivalent molecular weight[2] and, as suggested previously,[5] indicates that the cellulosic derivatives are not rigid in solution. The relationship between chain flexibility, critical concentration for mesophase formation, and side-chain structure is not yet quantitatively understood.

In summary, PPC forms lyotropic liquid crystalline phases in organic solvents, and the pure polymer forms a thermotropic liquid crystalline phase that shows cholesteric reflection at ambient temperatures. We suggest that the relatively stiff cellulose backbone forces a parallel orientation of the chains, the chirality of the cellulose chain imparts a twist to the parallel arrangement, and the flexible side chains allow the polymer molecules to migrate and form the equilibrium cholesteric arrangement. In the absence of solvent, the side chains control the average spacing between the almost-parallel cellulose backbones, and hence influence the pitch of the cholesteric helix.

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References and Notes

(1) Flory, P. J. *Proc. R. Soc. London, Ser. A* **1956**, *234*, 60.
(2) Flory, P. J. *Proc. R. Soc. London, Ser. A* **1956**, *234*, 73.
(3) Samulski, E. T.; DuPrê, D. B. In *Adv. Liq. Cryst.* **1979**, *4*, 121.
(4) Werbowyj, R. S.; Gray, D. G. *Mol. Cryst. Liq. Cryst.* **1976**, *34*, 97.
(5) Werbowyj, R. S.; Gray, D. G. *Macromolecules* **1980**, *13*, 69.
(6) See, for example: Panar, M.; Willcox, O. B. Belgian Patent Application 656 359, 1976. Maeno, J. U.S. Patent 4 132 464, 1979. Aharoni, S. M. *Mol. Cryst. Liq. Cryst.* **1980**, *56*, 237. Chanzy, H.; Peguy, A.; Chaunis, S.; Monzie, P. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1137. Tsutsui, T.; Tanaka, R. *Polym. J.* **1980**, *12*, 473.
(7) Tseng, S.-L.; Valente, A.; Gray, D. G. *Macromolecules* **1981**, *14*, 715.
(8) Shimamura, K.; White, J. L.; Fellers, J. F. *J. Appl. Polym. Sci.* **1981**, *26*, 2165.
(9) Aharoni, S. M. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 495.
(10) Lemieux, R. U.; Purves, C. B. *Can. J. Res., Sect. B* **1947**, *25*, 485.
(11) de Vries, H. *Acta Crystallogr.* **1951**, *4*, 219. Fergason, J. L. *Mol. Cryst.* **1966**, *1*, 293.
(12) Bheda, J.; Fellers, J. F.; White, J. L. *Colloid Polym. Sci.* **1980**, *258*, 1335.

Odd–Even Effect in Thermotropic Liquid Crystalline 4,4′-Dihydroxy-2,2′-dimethylazoxybenzene–Alkanedioic Acid Polymers

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ABSTRACT: The thermal properties of a homologous series of mesogenic, thermotropic polyesters based on 4,4′-dihydroxy-2,2′-dimethylazoxybenzene and alkanedioic acids from $n = 2$ to $n = 14$ were studied. Because of moderate transition temperatures and molecular weights sufficiently high to minimize the dependence of thermal properties on molecular weight, a meaningful comparison of thermal properties could be obtained. The data indicate a remarkably regular odd–even effect for the transition temperatures, enthalpies, and entropies for the nematic (N) $\rightleftharpoons$ isotropic (I) transition. ΔH_{IN} and ΔS_{IN} are much higher than the corresponding values for low molecular weight analogues and increase continuously with the length of the flexible methylene sequence. The increase proceeds with approximately the same increment for the odd and even series of $[\Delta(\Delta H_{\mathrm{IN}})]_{\mathrm{av}} = 0.46$ kJ and $[\Delta(\Delta S_{\mathrm{IN}})]_{\mathrm{av}} = 1.52$ J/K per methylene group. This indicates that the flexible spacer takes part in the ordering process and that N $\rightleftharpoons$ I transition has a pronounced first-order character.

Thermal properties of linear, thermotropic polyesters have been recently an object of extensive investigations. An odd–even effect of the nematic to isotropic transition temperature was reported.[1-4] However, poor knowledge of molecular weights and molecular weight distributions (often in the oligomer range), high temperatures of isotropization impinging on decomposition, complex thermograms reflecting multiple melting, and the absence of

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