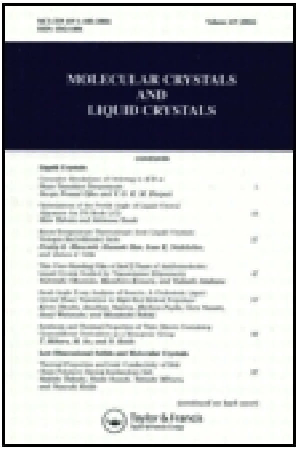

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Liquid Crystalline Structure In Aqueous Hydroxypropyl Cellulose Solutions

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LIQUID CRYSTALLINE STRUCTURE IN AQUEOUS HYDROXYPROPYL CELLULOSE SOLUTIONS

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Concentrated aqueous solutions of hydroxypropyl cellulose form lyotropic mesophases displaying a range of iridescent colors. Evidence from light microscopy and optical rotatory dispersion suggests that the mesophase has helicoidal structure, resembling in some respects that of cholesteric liquid crystals.

Recently, renewed interest has developed in the structure and properties of macromolecular mesophases, spurred in part by the commercialization of high strength fibres spun from anisotropic polymer solutions[1]. The macromolecular component in such solutions is generally stiff and rod-like; the separation of a concentrated solution of rod-like species into ordered and disordered phases has been interpreted in a lattice model[2]. Perhaps the best known example is the cholesteric mesophase formed by polypeptides in certain organic solvents[3,4]. In this letter, we report the finding of a second type of polymer which forms a lyotropic cholesteric mesophase, in this case with water as the solvent. This mesophase was first accidentally observed when a drop of fairly concentrated aqueous hydroxypropyl cellulose* solution was placed between glass plates, and the water allowed to evaporate from the outer edges of the drop. The solution dried to a clear film at the outside. Just inside this film, an iridescent rainbow-like ring developed, ranging in color from violet at the outside through blue and green to red at the inside. A cloudy grey area developed between the iridescent ring and the clear solution at the centre of the sample.

To try and explain this phenomenon, concentrated aqueous solutions of hydroxypropyl cellulose were prepared, and the resultant iridescent materials were examined by optical microscopy and optical rotatory dispersion. Samples ranging from 20% to 50% water were both fluid and birefringent. The microscopic textures observed between crossed polarizers varied somewhat with the MW and concentration of the hydroxypropyl cellulose, and with time. A birefringent pattern of smooth curves was initially visible, presumably reflecting the flow pattern induced in the anisotropic fluid when preparing the slide. On standing for several hours, preparations with higher water contents developed a striated grid-like pattern of birefringence enclosing dark apparently isotropic areas, which suggested that such samples consist of a mixture of the true mesophase and an isotropic solution of the polymer. (Some confirming evidence was obtained by centrifugation; a partial separation into a clear upper layer and a cloudy lower layer was achieved.) The isotropic areas were less in evidence at lower moisture contents, which displayed a more uniform grainy birefringence. On long standing in a moist atmosphere, the graininess sometimes became resolved into the moasic of dark distorted

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*A commercially available product, "Klucel L" (Hercules Inc.), reported to have a molecular weight of 100,000 and to contain about four hydroxypropyl substituents per glucose chain residue was used. (Substantially similar phenomena have been observed on "Klucel J" and "G" grades, and on fractionated material). For further details, see the product literature and E.D. Klug in Encyclopedia of Polymer Science and Technology, Vol. 15, N.M. Bikales, Ed. (Wiley-Interscience, New York, 1971) p. 307.

crosses shown in Figure 1. In thin samples, (∿10μm), it was also possible to observe extensive homeotropic regions.

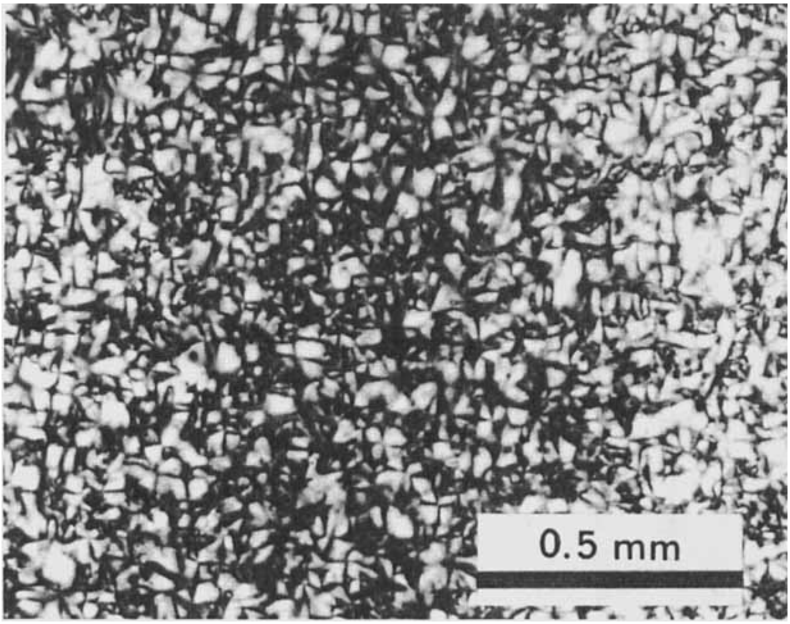

FIGURE 1. Microscopic texture exhibited between crossed polarizers by a fluid mesophase of hydroxyproryl cellulose containing 30% (by weight) water.

The iridescent colors reflected by layers of the mesophase in white light ranged from a red-orange at ∿45% water content through orange and green to a striking violet at <30% water. At any given composition the reflected color depended to some extent on viewing angle and temperature; the complementary color was transmitted by the material. The samples exhibited marked optical activity, with the sign and magnitude dependent on the wavelength of the incident light. The optical rotatory dispersion of samples with a range of water contents is shown in Fig. 2. The reflected color of each sample corresponds approximately to the wavelength at which the sign of the optical activity changes from positive to negative. Cholesteric liquid crystals have similar optical properties[5], which are explained by assuming a layer-like structure, where each "layer" is a plane section of the mesophase in which the constituent molecules are in a predominantly parallel orientation, but with each layer rotated slightly

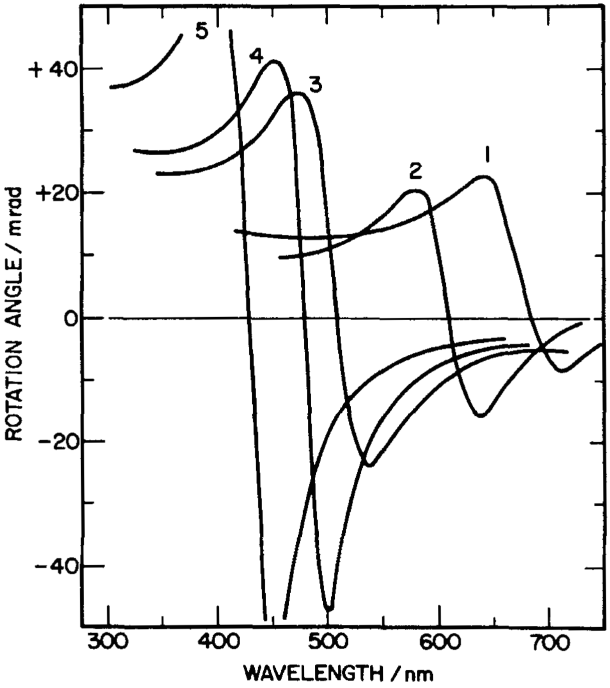

FIGURE 2. Optical rotation as a function of wavelength for hydroxypropyl cellulose mesophases. Curves 1-5 correspond to samples containing respectively 42%, 40%, 34%, 33% and 30% by weight water. Spectra were obtained on samples varying in thickness from 10μm to 50μm using a Jasco Model ORD/UV-5 spectrometer.

with respect to its neighbours about an axis perpendicular to the layers. The twist in the supermolecular structure is ascribed to the chirality of the constitutent molecules, and results in a periodicity in the distance between two layers having identical orientation. The dimensions of the period correspond to the wavelength of the scattered light, which gives cholesteric materials their characteristic iridescent colors.

Aqueous hydroxypropyl cellulose thus apparently forms a lyotropic mesophase with a cholesteric structure. Presumably, on reaching sufficiently high volume fractions, the bulky hydroxypropyl cellulose chains separate from the isotropic phase as an ordered phase with predominantly parallel orientation[2]. (It is not known whether the stiffness of the molecules is enhanced by a helical conformation of the individual molecules in solution, similar to that proposed for the crystalline solid[6].) The chirality of the molecules, which may be due either to a helical molecular conformation, or simply to the presence of optically active centres along the cellulose chain, results in the helicoidal supermolecular structure, with the axis of the helix normal to the direction of chain orientation. The dimensions of the structure may be estimated approximately using the model of the cholesteric state proposed by de Vries[5]. The wavelength λ_0 at which the rotation angle is zero (which corresponds to the wavelength of the reflected circularly polarized light) is simply related to the pitch p of the supermolecular helix by $\lambda_0 = np/2$ where n is an average refractive index of the mesophase. Consider for example sample 3, Figure 2, which contains about 11 water molecules for every anhydroglucose ether chain unit. With $\lambda_0 = 510$ nm and $n = 1.43$ the distance p/2 between planes having parallel orientation of the constituent molecules, or molecular aggregates, is 360 nm. The sample thickness is 51μm, so it may contain a maximum of 140 such planes, between microscope slide and cover glass, assuming perfect orientation in the plane of the sample. Furthermore, preliminary X-ray experiments show a diffuse ring corresponding to a spacing in the mesophase of 1.2 nm. If this is taken as the distance between adjacent "layers" then to achieve the required 180° rotation in 360 nm, the long axes of the species in adjacent layers must be displaced from parallel by an average of 0.6°. The maximum rotary power of this sample expressed conventionally as specific rotation [α], is of the order of ± 4 x 10^3 (degree ml. decimetre^{-1}, per g. hydroxypropyl cellulose). This is lower than that of many thermotropic cholesteric liquids, but is two orders of magnitude larger than the specific rotation of <u>isotropic</u> aqueous hydroxypropyl cellulose solutions, which was determined to be $[\alpha] \simeq -30$ in the wavelength range in question. As the water content of the mesophase is increased, the wavelength of the reflected light moves to the red end of the spectrum, with a corresponding change in the optical rotatory dispersion (Figure 2). The relationship between λ_0 and the water content is approximately linear for wavelengths in the visible region. This may reflect a decrease in the average angle between the long axes of the species in adjacent layers, or an increase in the distance between layers, as the water content is increased.

Although hydroxypropyl cellulose is thought to be a relatively stiff molecule[7], the phase separation appears to take place at a volume fraction of polymer higher than that predicted by the Flory theory[2,4]. This may be due to some chain flexibility, or to side group interactions[8]. It should however be noted that hydroxypropyl cellulose is somewhat amphiphilic in character and is a surfactant in aqueous solutions, suggesting an analogy with lyotropic soap mesophases, and also with certain block copolymer systems[9], where phase separation is apparently not related to the rod-like nature of one component. It is evident that further work on carefully fractionated material is required to elucidate the reason for the phase separation. Nevertheless, the spontaneous development of a helicoidal structure, in water, by a derivative of cellulose appears of interest in several fields.

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