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CROSSLINKED CHOLESTERIC NETWORK FROM THE ACRYLIC ACID ESTER OF (HYDROXYPROPYL)CELLULOSE

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The acrylic acid ester of (hydroxypropyl)cellulose was prepared from (hydroxypropyl)cellulose and acryloyl chloride. The resultant polymer, with 2.2 ester groups per anhydroglucose unit, formed a thermotropic cholesteric mesophase with visible reflection bands at temperatures between ambient and 60° C. By exposing a thin layer of the mesophase to UV light, the mesophase structure was stabilized to give a crosslinked cholesteric film.

Cellulose and its derivatives often form cholesteric liquid crystals under appropriate conditions[1,2]. The concentrated solution (lyotropic mesophase) or the melt (thermotropic mesophase) of these polymers displays cholesteric reflection colors when the cholesteric helical pitch approximates the wavelength of visible light. Most strongly-reflecting cellulosic cholesterics reported to date are either lyotropic mesophases, or are thermotropic mesophases with glass transition temperatures close to or below ambient temperatures. Thus not only are the materials fluid and tacky, but the reflection band wavelengths are sensitive to solvent composition[3,4] and changes in temperature[5-7]. A mechanically strong free-standing cholesteric film with good stable reflection properties based on cellulose is more desirable. In this preliminary report, we describe one of several possible routes to such a material.

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EXPERIMENTAL PART

The acrylic acid ester of (hydroxypropyl)cellulose was readily prepared by reacting acryloyl chloride with (hydroxypropyl)cellulose (HPC). Acryloyl chloride (Aldrich, 20 mL) was added to 10 g of dried HPC (nominal mol.-wt. 100 00 from Aldrich Chemical Co.) in a 100 mL round bottom flask flushed with dry nitrogen at room temperature. An exothermic reaction ensued immediately with frothing. The flask was swirled to ensure the homogeneity of the reaction mixture. The final reaction mass appeared as a faint yellow viscous solution and was allowed to stand at room temperature overnight in the dark. Then it was poured into a large excess of cold distilled water. The polymer separated as a white sticky mass which was washed several times with water to remove reactants. The crude product was purified by dissolution in acetone and reprecipitation in water. The purified polymer was dissolved in spectroscopic grade acetone and the solution was slowly evaporated at room temperature and finally dried under vacuum for 48 h. The dried polymer was a deformable tacky material which displayed a bluish-green reflection color. The heat- and light-sensitive polymer was stored in a freezer.

The infrared spectra of the polymer was measured on a Perkin-Elmer model 298 Infrared Spectrometer. The characteristically intense ester carbonyl band was observed at 1720 cm^{-1}. Also evident were bands at 1620 and 1640 cm^{-1}, due to the C=C double bond in the acrylate ester group, and vinyl C-H deformation at 1400 cm^{-1} with a C-H out-of-plane deformation at 810 cm^{-1}. These bands were absent in spectra of the HPC starting material. However the ester showed a significant broad hydroxyl peak in the 3500 - 3400 cm^{-1} region. Although much smaller than the corresponding peak in the HPC spectra, this indicated that complete esterification of all the hydroxyl groups had not occurred.

When the polymer film was subjected to irradiation under a UV lamp (UVL 22, Fisher Scientific), the intensity of all these bands began to decrease with irradiation time and finally disappeared. The irradiated film was infusible and insoluble.

The NMR spectrum of the original polymer in carbon tetrachloride, recorded by a Varian T-60 spectrometer showed bands characteristic of vinylene protons (δ 5.6 to δ 6.4 ppm). The ester content was found to be 26 wt.-% by the saponification of the polymer in acetone at room temperature[6]. This value corresponds to 2.2 ester groups per anhydroglucose unit, assuming that there are 3.4 hydroxypropyl groups per anhydroglucose unit in the HPC starting material[6]. The limiting viscosity [η] of the polymer was determined to be 0.67 dL g^{-1} in acetone at 25° C.

Optical observations were made with a Reichert polarizing microscope equipped with a Mettler FP52 hot stage. The variation in birefringence with temperature was measured by replacing one microscope eyepiece with a Mettler 1800 photocell and recording the output on a Varian A25 strip chart recorder. The wavelengths of cholesteric reflection colors at varying temperatures were recorded by means of a Pye-Unicam SP8-150 UV/VIS spectrophotometer and a modified Mettler FP52 hot stage. A thin film of the sample, placed between a microscope slide and cover glass was kept at the desired temperature in the hot stage which was placed in a vertical position in the spectrophotometer beam.

RESULTS AND DISCUSSION

The dried polymer was a tacky mass with a blue-green iridescent color at room temperature. The iridescent color is characteristic of cholesteric mesophases where the pitch of the helical structure corresponds to the wavelength of the visible light and is due to the selective reflection of a circularly polarized component of the light. Slow evaporation of a solution of the polymer in acetone gave rise to a green iridescent film which on heating at 50° C turned to red. The initial green reflection color with some red tint gradually reappeared on cooling the film to room temperature. The material thus resembles other esters of (hydroxypropyl)cellulose[5-7]. However, when the film was subjected to UV irradiation for 5 h, the reflection color did not change with subsequent changes in temperature. The irradiated film was insoluble and infusible and was strongly birefringent under the polarizing microscope. This shows the formation of the crosslinked polymer network with "locked in" cholesteric organization.

The anisotropic-isotropic phase transition temperature of the polymer was determined by means of the polarizing microscope. A thin film, sandwiched between a microscope slide and cover glass, was heated on a hot stage. The intensity of the birefringence began to decrease and finally disappeared completely at 145° C (Fig. 1, broken line), as indicated by the complete extinction of transmitted light between crossed polars. On the other hand, the crosslinked polymer film retained its birefringence undiminished up to 208° C (Fig. 1, solid line). At higher temperatures, the birefringence intensity began to decrease and eventually disappeared at about 250° C due to decomposition of the polymer. Thus, the cholesteric structure fixed in the crosslinked polymer persisted over a relatively wide temperature range.

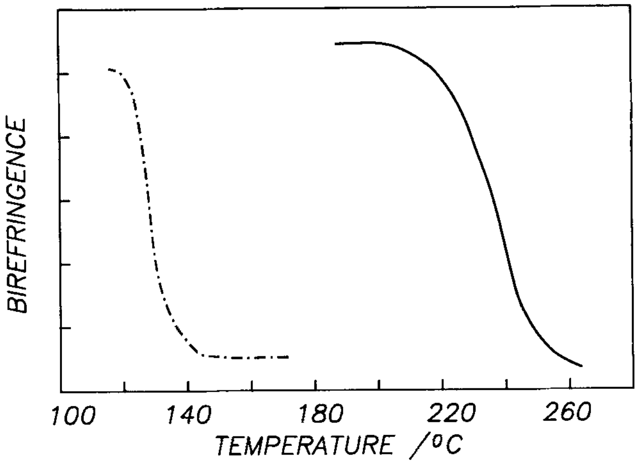

FIGURE 1 Effect of temperature on the light transmitted through a thin film of bulk acrylic acid ester of (hydroxypropyl)cellulose before (broken line) and after (solid line) crosslinking. Transmittance measured between crossed polars decreases with decreasing sample birefringence; heating rate, 1° C/min.

The wavelengths of maximum reflectivity, λ_0, of the uncrosslinked polymer film at different temperatures were recorded spectrophotometrically. The results are presented in Fig. 2 (open circles), which shows that λ_0 increases with temperature, as observed for most cellulosic cholesterics. A thin film of the polymer was subjected to UV irradiation at 50° C for 5 hr and then its λ_o was recorded at different temperatures. It is seen from Fig. 2 (closed circles), that λ_o did not change significantly from 50° C to 140° C. Thus, as the cholesteric structure is interlocked in the solid state by the crosslinks, the helical pitch becomes insensitive to the change in temperature.

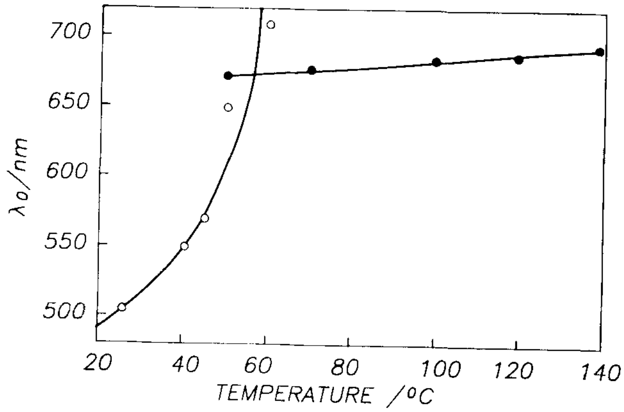

FIGURE 2 Temperature dependence of the reflection band maximum wavelength, λ_o, for a thin layer of the acrylic acid ester of (hydroxypropyl)cellulose before (open circles) and after (filled circles) crosslinking.

No attempt has been made here to optimize the optical or mechanical properties of the crosslinked film. The reflection band absorbances were of the order of 0.1 for films about 1 mm thick, with peak widths at half height of 90 nm. Free-standing films were rather brittle. Obviously more work is required to achieve a better initial planar texture, and to photosensitize and control the crosslink density more effectively. There are other routes to polymeric cholesteric films (8). These include polymerization of stiff chain polymeric lyotropic mesophases in vinyl solvents (9), incorporation of cholesteryl derivatives as side chains in acrylate (10) and siloxane polymers (11), and incorporation of optically active main chain diacids in aromatic polyesters (12). Potential advantages of this cellulose derivative include the relatively low cost of cellulosics and the apparently small degree of disruption of the thermotropic mesophase structure resulting from the photoinitiated crosslinking.

REFERENCES

(1) D.G. Gray, J. Appl. Polym. Sci., Appl. Polym. Symposium, 37, 179 (1983)
(2) R.D. Gilbert and P.A. Patton, Prog. Polym. Sci., 9, 115 (1983)
(3) F. Fried, J.M. Gilli and P. Sixou, Mol. Cryst. Liq. Cryst., 98, 209 (1983)
(4) R.S. Werbowyj and D.G. Gray, Macromolecules, in press
(5) S.-L. Tseng, A. Valente and D.G. Gray, Macromolecules, 14, 715 (1981)
(6) S.-L. Tseng, G.V. Laivins and D.G. Gray, Macromolecules, 15, 1262 (1982)
(7) S.N. Bhadani and D.G. Gray, Mol. Cryst. Liq. Cryst., 99, 29 (1983)
(8) J. Watanabe, S. Sasaki and I. Uematsu, Polymer J., 9, 337 (1977)
(9) T. Tsutsui and R. Tanaka, Polymer Commun., 21, 1351 (1980)
(10) P. Shannon, Macromolecules, in press
(11) H. Finkelmann and G. Rehage, Makromol. Chem., Rapid Commun., 1, 733 (1980)
(12) W.R. Krigbaum, A. Cifferi, J. Asrar, H. Toriumi and J. Preston, Mol. Cryst. Liq. Cryst., 76, 79 (1981)