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Preparation and Liquid Crystalline Properties of (Hydroxypropyl)cellulose Perfluorooctanoate

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Introduction

Numerous polymers containing cholesteryl derivatives have been synthesized.[1] Cellulose and its ether and ester derivatives appears to be good substrates for preparing new cholesteric materials in melts and solutions. This is due to the large number of chiral centers in the anhydroglucose units and the sufficiently stiff molecular structure of the cellulose backbone according to Flory.[2,3] Moreover, (2-hydroxypropyl)cellulose (HPC) seems to be an ideal reactant because it is more soluble in many different solvents and possesses more accessible hydroxyl groups than cellulose. The average degree of substitution (DS) for each hydroxyl group attached to C-2, C-3, and C-6 in the glucopyranose ring could be estimated by ^{1}H- and ^{13}C-NMR methods,[4] and the distribution of the total DS of some cellulose derivatives was evaluated by thin-layer chromatography.[5] Nevertheless, even with such a chain rigidity described by the Kuhn segment, there is some basis for assuming that a transition to the liquid crystalline state is possible for this polymer.[6]

To date, many researchers have described the preparation and physical properties of cellulose[7] and its derivatives[8-17] in systematic studies of the cholesteric liquid crystalline mesophases in lyotropic and/or thermotropic systems. HPC also forms a lyotropic mesophase in a mixture with an inorganic polymer.[18] Most HPC derivatives are substituted by a hydrocarbon chain.[19] So far, [(trifluoroacetoxy)propyl]cellulose is the only derivative containing a fluorocarbon component and has been reported to form a birefringent fluid.[15] In this paper a new cellulose derivative containing a perfluorocarbon chain, the perfluorooctanoate of HPC (FOPC), is prepared and the cholesteric properties are determined and compared with those of the hydrocarbon derivative.

Experimental Section

Synthesis. The perfluorooctanoate of HPC was prepared from HPC (Hercules Klucel, MW = 60000) and perfluorooctanoyl chloride using the following procedure. Fresh perfluorooctanoyl chloride (17.6 g) obtained by distilling a mixture of perfluorooctanoic acid salt (20.9 g) and 30 mL of phthaloyl chloride was added dropwise to a three-necked flask containing 2.9 g of HPC at room temperature under a nitrogen atmosphere. The mixture was stirred for 3 h at room temperature and then was diluted with acetone. The acetone solution was poured into a large volume of hot water. The product separated as a sticky white mass. The polymer was washed and was purified by repeated dissolution in acetone and precipitation in hot water until the wash was neutral. The purified polymer was dried with absolute ethanol and then put in vacuo (0.05 mmHg) for 72 h at 65-70 °C. The final yield was 92%. An idealized representation of the repeating unit is shown in Figure 1.

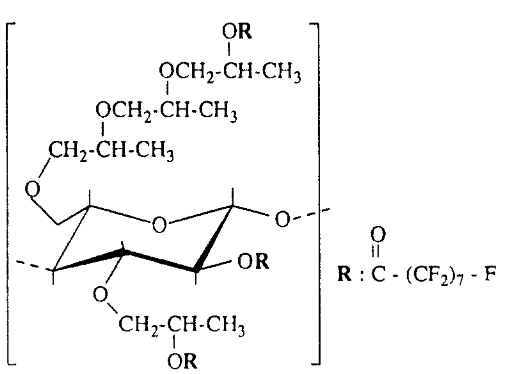

Figure 1. Schematic representation of a substituted anhydroglucose unit of (hydroxypropyl)cellulose perfluorooctanoate (molar etherification = 4, mole esterification = 3).

Measurements. The liquid crystalline textures were observed with an Olympus BH-2 polarizing microscope equipped with a Mettler FP-52 hot stage. The cholesteric to isotropic phase transition temperature (clearing temperature) was determined with a Setaram Model 111 DSC from 25 to 190 °C with a scanning rate of 2 °C/min and also by the polarizing microscope described above. The cholesteric reflection spectra were measured with automatic control of the monochromator and light intensity. CD spectra were measured with a JASCO J-500A CD spectrometer. IR spectra were recorded with a Bruker IFS-45 spectrometer at room temperature. ^{1}H-NMR ($(CH_3)_4Si$ as an internal reference) and ^{19}F-NMR ($CFCl_3$ as an internal reference) spectra were recorded with a Bruker AC 200 MHz spectrometer, using $CDCl_3$ and CD_3COCD_3 solutions (5-10 wt %).

Results and Discussion

Polymer Characterization. FOPC displayed iridescent colors in the final stage of drying. At room temperature, the polymer was a sticky mass with birefringence. The characterization of FOPC was performed by both NMR and IR measurements. The ^{19}F-NMR spectrum of FOPC clearly exhibits the chemical shift with the exact integration of the perfluoroheptyl chain as shown in Figure 2a. The multiplet centered at -80.81 ppm was assigned to the terminal trifluoromethyl group, and the resonances at -118.77, -121.39, and -125.93 ppm were assigned respectively to CF_2 in the α, β, and ω positions. The resonances of the three CF_2 groups in the γ position appear between -122.4 and -122.7 ppm. In the ^{1}H-NMR spectrum (Figure 2b), the main difference between HPC and FOPC is the appearance of the multiplet centered at 5.98 ppm due to the CH_2 protons of propyl in the α position of the ester perfluoroalkyl group. The signals for the terminal methyl group of the propylene oxide unit occur at 1.16 and 1.42 ppm. The appearance of these two signals indicates that the chemical environment of this group is not identical throughout the molecule. This nonequivalence may be caused by incomplete esterification and/or may reflect the differing degree of the branches in the propylene oxide chain in HPC. All other protons should appear in the broad multiplet from 3.10 to 4.20 ppm.

According to the literature[20] for the IR band assignments for HPC, the most apparent differences between the spectra of HPC and FOPC are the reduction in the size of the broad hydroxyl stretching peak in the 3700-3200 cm^{-1} region and the appearance of a strong carbonyl peak at 1740 cm^{-1}. We observed a strong and large peak centered at 1220 cm^{-1} corresponding to the perfluoroalkyl chain stretching peak and the asymmetric ether stretching peak. The esterification reaction in this work may be incomplete, because a reduced but still significant hydroxyl stretching band is observed. The absence of a peak corresponding to perfluorooctanoic acid implies that the acid was removed

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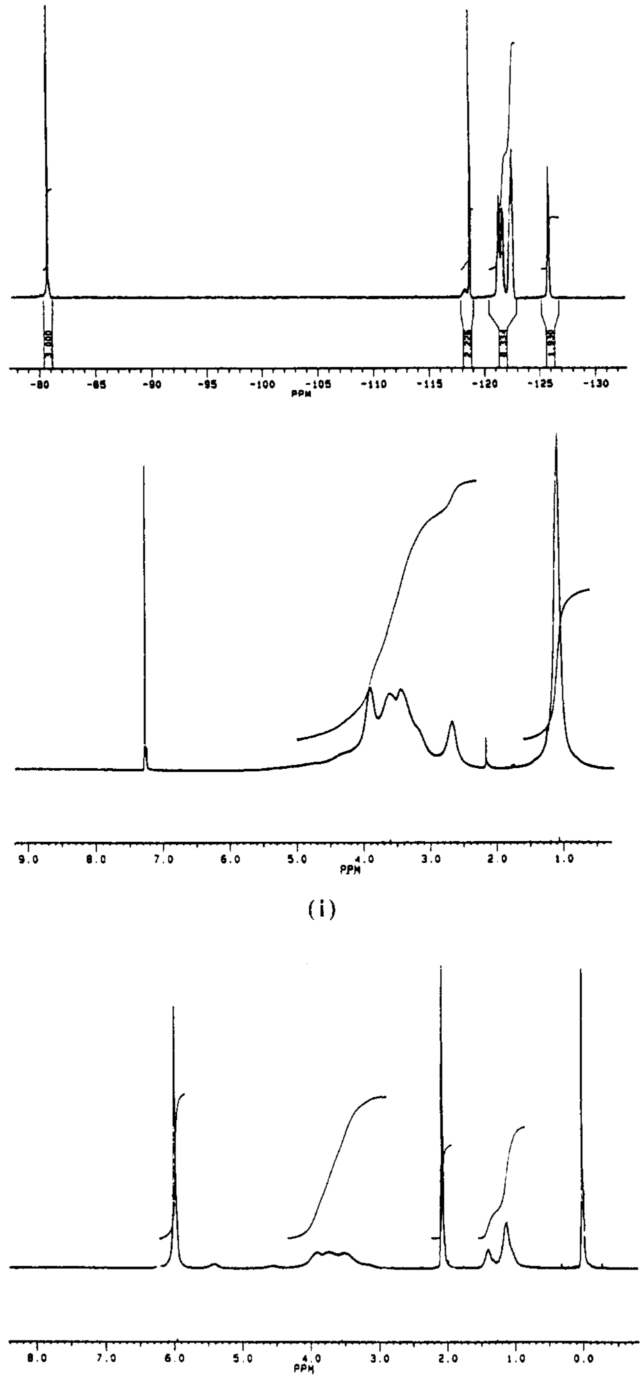

Figure 2. (a) ^{19}F-NMR spectrum of (2-hydroxypropyl)cellulose perfluorooctanoate. (b) ^{1}H-NMR spectrum of HPC (i) and (2-hydroxypropyl)cellulose perfluorooctanoate (ii).

by washing. The DSC experiments (Figure 3) show two main peaks on heating: one endothermic peak at 153 °C and the other at 164 °C corresponding to the clearing temperature and the degradation temperature, respectively.

Thermotropic Behavior. A thin layer placed between a microscope slide and a cover glass showed birefringence under a cross-polarizing microscope. When the sample was heated on a hot stage, the birefringence disappeared at 145 °C, and the polymer became a viscous isotropic melt. On cooling, the birefringence reappeared slowly below 140 °C. However, if the sample was heated above 160–165 °C, the birefringent texture and the cholesteric color did not reappear, even when the sample was cooled to room temperature. The wavelength of the cholesteric reflection peak was measured spectrophotometrically. The

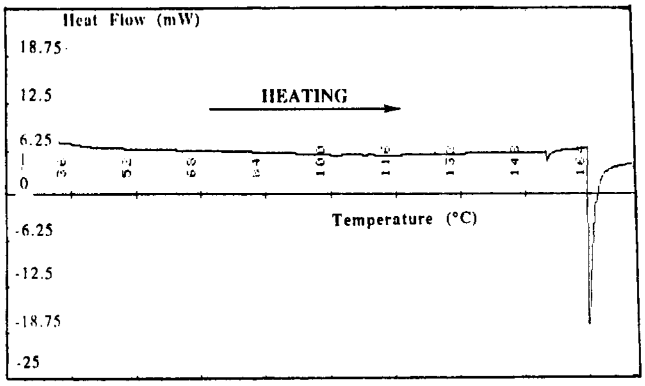

Figure 3. Differential scanning calorimetry (DSC) curve for HOPC on heating with a scaning rate of 2 °C/min from room temperature to 190 °C.

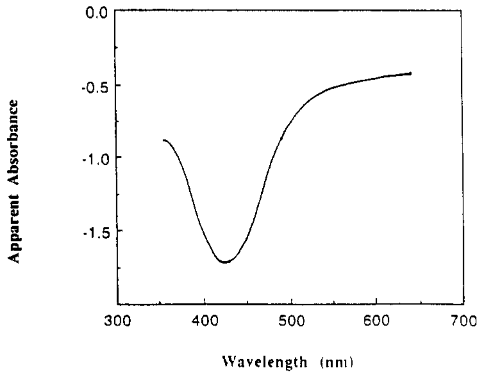

Figure 4. CD peak of FOPC resulting from reflection of light by the mesophase at room temperature.

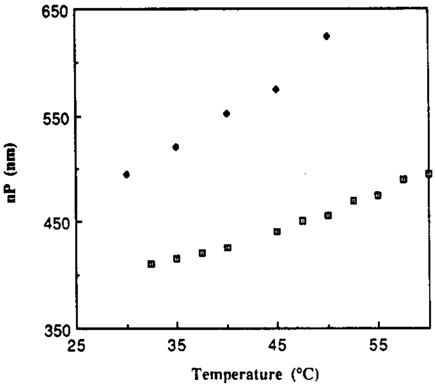

Figure 5. Comparison of the pitch between FOPC (◆) and the butanoate ester of (2-hydroxypropyl)cellulose (□).

wavelength of the maximum reflection band, λ_m, obtained normally from a planar cholesteric layer is given by $\lambda_m = nP$, where n is the average refractive index of the liquid crystalline phase and P is the pitch of the helicoidal arrangement.[21] A typical CD spectrum of the sample obtained at room temperature from reflection of light by the mesophase is shown in Figure 4. The curve is negative, indicating that the thermotropic cholesteric mesophase is a right-handed helicoidal structure. This helical sense is the same as that of other HPC derivatives. The optical pitch, nP, of the sample changed to a longer wavelength with increasing temperature as shown in Figure 5. In addition, a fingerprint pattern was observed above 85 °C. The figure also shows the temperature dependence of the optical pitch, nP, of the butanoate of HPC (BPC).[22] On comparison of the behavior of the optical pitch, two observations were made: (1) in spite of the difference in the length of the side chain, the value of the optical pitch at room temperature is almost equal in the two derivations and (2) the optical pitch of FOPC increases more rapidly than that of BPC [$(\mathrm{d}nP/\mathrm{d}T)_{\mathrm{FOPC}} > (\mathrm{d}nP/\mathrm{d}T)_{\mathrm{BPC}}$].

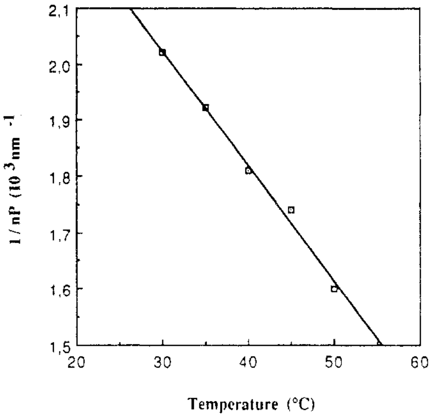

Figure 6. Plot of reciprocal pitch against temperature for thermotropic HOPC.

It seems that the introduction of the perfluorooctyl chain into the cellulose backbone implicates different thermal and cholesteric behavior. In the case of FOPC, the lateral perfluorocarbon chains introduced are packed more closely together than in the corresponding hydrocarbon chains.[23] In fact, the carbon–fluorine bond is shorter and has a stronger bond energy to reduce the carbon–carbon bond energy. The optical pitch of the cholesteric mesophases formed by HPC derivatives increases with increasing length of the side chain.[22] Flexibility of the chain becomes greater as the chain becomes longer. The flexibility of the perfluorooctyl chain in FOPC seems to be equal to that of the butyl chain in BPC. It is well known that the perfluorocarbon chain has a low surface energy and is more hydrophobic than the hydrocarbon chain. The HPC backbone is rather hydrophilic, so a microphase separation between the HPC backbone and the side chain containing the fluorocarbon component may occur in the FOPC molecule. It has been reported that the optical pitch of (tri-*O*-butoxyethyl)cellulose increased faster than that of [(tri-*O*-methoxyethoxy)ethyl]cellulose, even though the length and flexibility of the side chain were almost equal.[17] In this case, the butoxyethyl group is more hydrophobic than the (methoxyethoxy)ether group. A microphase separation between the cellulose backbone and the side chain may occur more easily in the (tri-*O*-butoxyethyl)cellulose molecule. The microphase separation must contribute to the chiral interaction between cellulose backbones.

The temperature dependence of the pitch has been expressed for lyotropic and thermotropic systems of polypeptides and cellulose derivatives by the following empirical equation:[24]

$$1/P = b(1 - T/T_n)$$

where P is the cholesteric pitch, T is the temperature in kelvin, and b is a constant factor which depends on the concentration of the solution or the kind of thermotropic component. T_n is the compensation temperature at which the cholesteric pitch is infinite. This equation has been found to be satisfied for the thermotropic cholesteric mesophases formed by the hydrocarbon ester derivatives of HPC. A plot of the reverse optical pitch of FOPC against temperature is shown in Figure 6. The curve is linear and the equation also holds for FOPC. The extrapolation of this curve to $1/nP = 0$ gives a value of 400 K as T_n. An infinite pitch and a sense inversion were not observed clearly in this work because T_n is close to the decomposition temperature.

Lyotropic Behavior. FOPC also forms a lyotropic liquid crystalline mesophase in many organic solutions. In practice, FOPC is dissolved in diethyl ether, which is a nonsolvent for HPC and hydrocarbon ester derivatives, and forms an iridescent mesophase at room temperature. This indicates that the HPC molecule is surrounded by perfluorocarbon chains in the FOPC molecule. The lower critical concentration for formation of a lyotropic liquid crystalline mesophase in acetone for FOPC (about 25 wt %) is almost equal to that for the trifluoroacetate of HPC[15] and is lower than that for the hydrocarbon derivatives.

Conclusions

(Hydroxypropyl)cellulose perfluorooctanoate (FOPC) formed both thermotropic and lyotropic cholesteric mesophases. The optical pitch of the thermotropic mesophase increased more rapidly with temperature than that of the hydrocarbon ester derivative. The variation of pitch of FOPC with temperature was wider in the range from the ultraviolet region to microns than that of the hydrocarbon derivative. FOPC dissolved in diethyl ether and formed an iridescent cholesteric mesophase. Since the perfluoroalkyl chain has a low surface energy and a high hydrophobicity, a new liquid crystalline property is expected for HPC derivatives containing fluorocarbon components and further studies are necessary to determine the general behavior.

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