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Comparison of thermal and cholesteric mesophase properties among the three kind of hydroxypropylcellulose (HPC) derivatives

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Summary

Three kind series of (2-hydroxypropyl)cellulose (HPC) derivatives, the esters (ES), the ethers (ET) and the esters containing fluorocarbon components (FES) were prepared, and the thermal and cholesteric mesophase properties were compared among them. The optical pitch of ES increased with decreasing the degree of substitution (DS). Contrary to ES, the optical pitch of ET decreased with decreasing DS. The cholesteric-isotropic transition temperature of FES exhibited the even-odd oscillation according to the number of carbons in substituent. The reverse optical pitches of ET and FES were larger than that of ES, respectively, at the same temperature and at the same number of carbons in substituent.

Introduction

It is well known that cellulose[1] and its derivatives[2] form cholesteric liquid crystalline mesophases in lyotropic and thermotropic systems. In celluloses, (2-hydroxypropyl)cellulose (HPC) was first reported to form a cholesteric mesophase in concentrated aqueous solutions[3]. And HPC itself[4], and its derivatives[5-9] were found to readily melt and form thermotropic cholesteric mesophases on heating.

Recently, fully substituted cellulose derivatives have been prepared and the effect of substituents on the thermal and cholesteric properties have been discussed[10,11]. And it was concluded[10] that the type of liquid crystalline phase and cholesteric properties were strongly affected by the kind of chemical linkage between main chain and side chain (ester- or ether linkage) and the chemical structure of side chain. Thermotropic HPC derivatives are mainly classified into two groups, that is, one is ester derivative and the other ether one. It is expected that the thermal and cholesteric properties of mesophases formed by the ester derivatives are different from that of the ether one. In this paper, the thermotropic properties of mesophases formed by HPC ester and ether derivatives are determined and the cholesteric properties of ester and ether derivative are compared. In addition, since HPC chain is rather hydrophilic, the hydrophilicity or hydrophobicity of substituent in HPC derivative might play an important part

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to form cholesteric mesophases. In order to discuss this aspect, HPC derivatives having fluorocarbon side chain are prepared, and the cholesteric properties are determined and compared with that of the hydrocarbon derivatives. Moreover, due to the low surface energy of CF_2 and CF_3, a new property of liquid crystalline mesophase will be expected for the HPC derivative containing fluorocarbon components.

Experimental section

A series of ester derivatives of HPC (Acetic to Heptanoic acid esters) were prepared from the corresponding acid chloride and HPC (Hercules Klucel E, Mw=120000 g / mol) without solvent at room temperature according to the procedure described previously[12]. The ether derivatives (butyl and pentyl ethers) were prepared from the alkyl iodides and HPC (Hercules Klucel, Mw=60000 g / mol) in dimethylsulfoxide (DMSO) with powdered sodium hydroxide[13]. The HPC esters containing fluorocarbon components (perfluorobutanoic to perfluorooctanoic acid esters) were prepared from the corresponding perfluoroalkyl acid chloride and HPC (Hercules Klucel, Mw=60000 g / mol) according to the following procedure.

A fresh perfluoroalkyl acid chloride (0.0407 mol) obtained by distilling a mixture of the corresponding perfluoroalkyl acid salt (0.0480 mol) and 30 mL of phthaloyl chloride was added dropwise to a three necked flask contaning 2.9 g of HPC at room temperature under a nitrogen atmosphere. The mixture was stirred for 2 - 5 h at room temperature and then diluted with acetone. The acetone solution was poured into a large amount of hot water. The product separated as a sticky mass. The polymer was washed and purified by repeated solution in acetone and precipitation in hot water until the wash water was neutral. The purified polymer was dried with absolute ethanol and then in vacuo (0.05 mmHg) for 72 h at 65 - 70 °C. The final yield was 84 - 92 %, depending on perfluoroalkyl acid chlorides.

Each HPC ester, ether and ester containing fluorocarbon components are symbolized ES-x, ET-y and FES-z, respectively, where x, y and z are the number of carbons in the substituent. For ES-4 or ET-4, to obtain samples with different degree of esterification or etherification, we used different amounts of butyryl chloride for ES-4 or butyl iodide for ET-4 in feed stock, as listed in Table I.

The degree of esterification of ES series was determined by ^1H-NMR measurement (Brucker AC 250 MHz spectrometer) in $CDCl_3$ at 40 °C and by the acidimetric method[12]. The degree of etherification of ET series and the degree of esterification of FES series were estimated by the absorption areas due to hydroxyl groups in the infrared (IR) spectra.

IR spectra were measureed with a Perkin-Elmer 580 IR-spectrophotometer at room temperature. A thin film for IR measurement was prepared to cast from dilute chloroform solution onto a sodium chloride plate. The selective reflection wavelength (visible light region) in normal incidence was measured with an automatic control of the monochromator and of the light intensity. The wavelength of maximum reflection, lm, is related to the cholesteric pitch P

by de Vries[14] relationship, λm = nP, where n is an average refractive index of the polymer. The samples with cholesteric pitch values well beyond the wavelength of visible light display a fingerprint pattern of light and dark lines, between which the distance is equal to $P/2$. On determining the temperature dependence of optical pitch, a thin layer of the mesophase was prepared by slightly pressing polymer sample between a microscopic slide and cover plate separated by a 50 μm thick Teflon spacer. Liquid crystalline textures were observed with an Olympus BH-2 polarizing microscope equipped with a Mettler FP-52 hot stage. Cholesteric-isotropic phase transition temperature (clearing temperature) was determined with a Perkin Elmer DSC-2C differential scanning calorimeter and by a polarizing microscope.

Results and Discussion

The HPC derivatives of the ester and ether type can form thermotropic cholesteric mesophases[5-7,9]. The mesophases of HPC ester derivatives[5-7] have been reported to form right-handed helical structure and that of ether derivative[9] was also reported to form right-handed one. No difference in the type of liquid crystalline phase and the helical sense of mesophases formed by the ester and ether derivatives have been observed.

The effect of the degree of substitution (DS) on the temperature dependence of optical pitch (nP) for ES-4 and ET-4 was represented in Figures 1 and 2. Both the optical pitch of ES and ET derivatives increased with temperature. In ES-4, the optical pitch increased with decreasing DS at the same temperature (Figure 1). Contrary to ES, in ET-4 the optical pitch decreased with decreasing DS (Figure 2). The effect of DS on the thermal and structural properties for other cellulose derivatives have been investigated[15-17].

Table I
Amounts of butyryl chloride and butyl iodide to prepare samples with different degree of esterification and etherification.

DS[a)]	$CH_3CH_2CH_2COCl$ (g / 10g HPC)	$CH_3CH_2CH_2CH_2$-I (g / g HPC)
1.0		9.5
2.2	7.6	
2.4	8.1	
2.5	8.6	
2.7		11.6
2.8	14.9	
2.9	15.4	
3.0		20.4

a) Degree of substitution of butyryl chloride or butyl iodide per repeat unit of HPC.

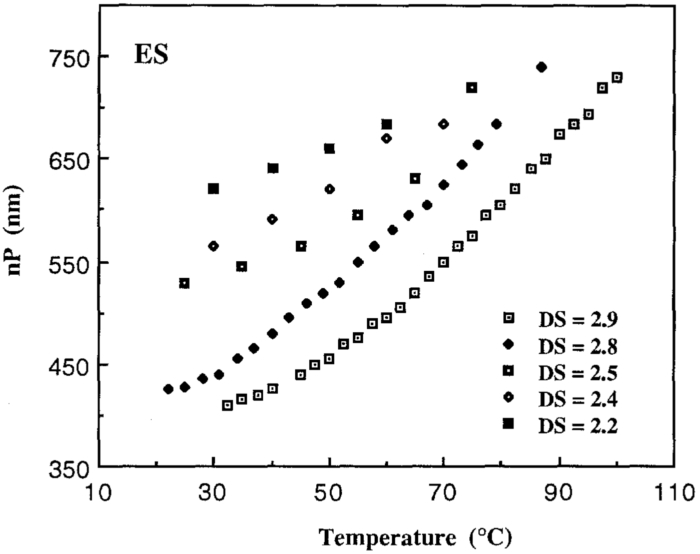

Figure 1. Temperature dependence of the optical pitch of ES-4 with different degree of subsutitution (DS).

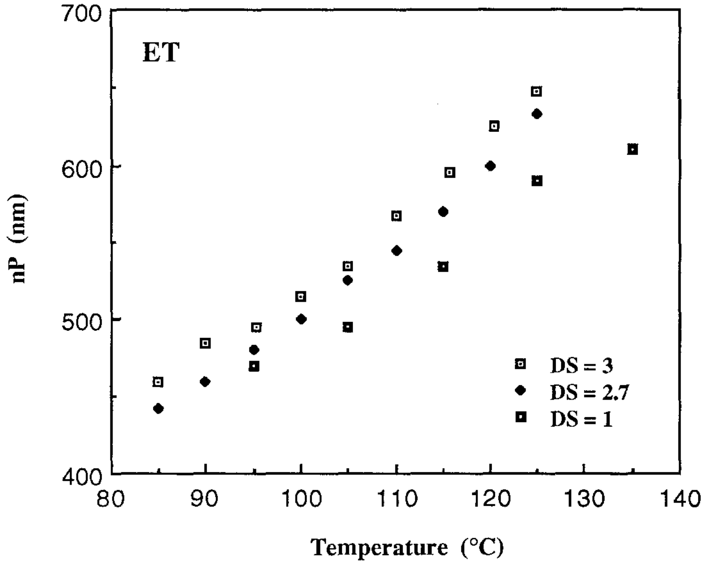

Figure 2. Temperature dependence of the optical pitch of ET-4 with different degree of subsutitution (DS).

It has been suggested[15,17] that the increase in chain regularity with increasing DS leads to the increase in crystallinity and the conformation of cellulose backbone changes with DS. It is no doubt that the helical structure in cholesteric mesophases results from the asymmetric carbons on the cellulose main chain.

The conformation of cellulose main chain might be affected by the chemical structure of side chain. And the helical structure might be formed by the combination of the main chain and the side chain. In HPC derivatives, the contribution of side chain containing the ester linkage to helical structure may be different from that of chain containing the ether linkage. This seems to arise from the hydrogen bond. The effect of hydrogen bond in mesophases formed by the sample with lower DS on the helical structure must differ between ES and ET derivatives. Since ES has carboxyl groups, the hydrogen bond between hydroxyl and carboxyl groups may be more easily formd in ES derivatives, rather than that in ET one.

The cholesteric-isotropic phase transition temperature (clearing temperature, T_c) was determined for ES, ET and FES derivatives with DS=2.8-3.0. The effect of the length of substituents on T_c for the ES and FES series was shown in Figure 3. The values of T_c of ES derivatives smoothly decreased with increasing the length of substituent. The T_c of ET series was almost equal to that of ES. The value of T_c of FES-2 was referred to the literature.[8] Each T_c of FES derivative was lower than that of ES one at the same number of carbons in substituent. This difference seems to be related to the degree of molecular ordering of mesophases. The perfluoroalkyl chain is more hydrophobic than the hydrocarbon chain, and HPC chain is rather hydrophilic. So that, a micro-phase separation may occur in FES samples. The fact[18] that HPC and poly(vinylidene fluoride), which is the polymer containing fluorocarbon components, is incompatible strongly supports this speculation. The degree of molecular ordering in FES derivatives must be reduced by this micro-phase separation, and so lower than that in ES one.

It is worth noting that T_c of FES series exhibits the usual even-odd oscillation according to the number of carbons in substituent. The mesophases formed by even-numbered FES derivatives may be more highly ordered. It is suggested that the molecular arrangement and packing of cellulose backbone and side chain containing fluorocarbon components is different between the FES derivative with even- and odd-numbered fluorocarbon substituent.

The inverse optical pitch, $1/nP$, at 85 °C of ES, ET and FES series were summarized as a function of the number of carbons in substituent in Figure 4. The plot of ET-2 was referred to the literature[9]. The values of ES-2 and FES-8 were obtained by extrapolating to 85 °C in the plots of $1/nP$ against temperature. The optical pitch is strongly affected by sample conditions, that is, the temperature, the DS and the molecular weight. All plots were obtained for the samples with DS=2.8-3.0. The molecular weight of ES series is larger than that of ET and FES

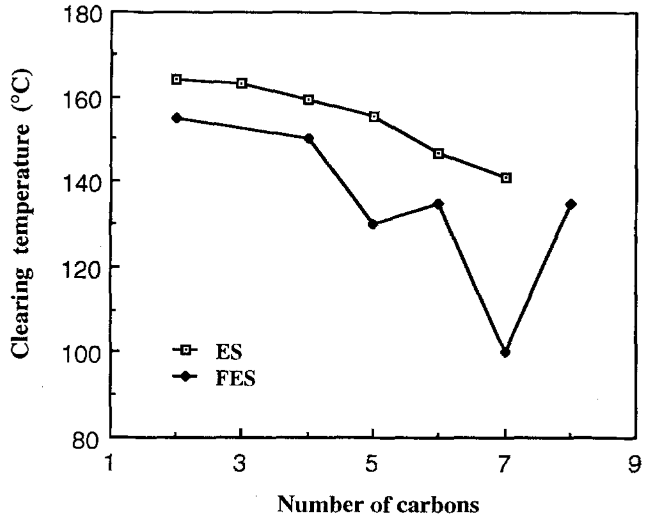

Figure 3. Variation of the clearing temperature of ES and FES with the number of carbons in substituent.

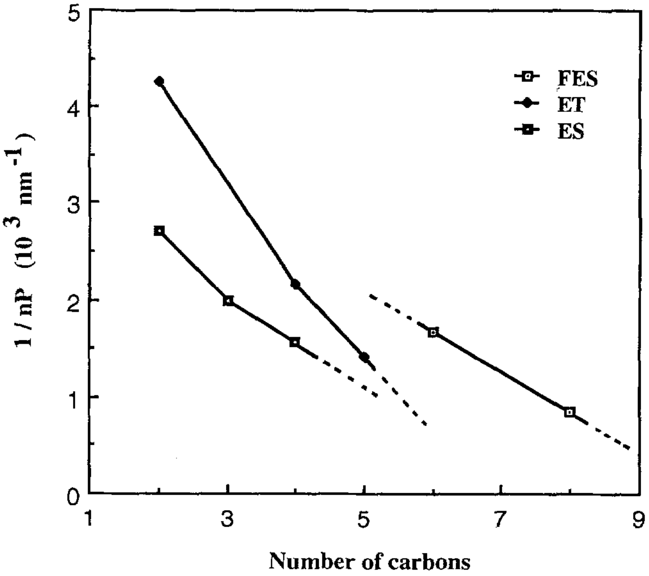

Figure 4. Variation of the inverse optical pitch (1/nP) of ES, ET and FES at 85 °C with the number of carbons in substituent.

one. It has been found that the optical pitch of ES derivatives increased with decreasing molecular weight[16,19]. On the assumption that the molecular weight of ES series becomes equal to that of ET and FES series, the optical pitch, n*P*, of ES becomes larger, so the 1/n*P* becomes smaller than that shown in Figure 4. Therefore, it is obvious that 1/n*P* of ET is larger than that of ES. 1/n*P* is proportional to the twisted angle and twisted power. And the twisted power is related to the chiral interaction. So, in other words the chiral interaction of ET derivative is stronger than that of ES one.

On comparing between ES and FES series, 1/n*P* of FES series seems to be larger than that of ES one, and so the chiral interaction of FES is stronger. This is considered to result from two factors : one is that the length of perfluoroalkyl chain is shorter than that of hydrocarbon chain at the same number of carbons and the degree of package of perfluoroalkyl chain is higher[20]. And the other is the occurrence of micro-phase separation and aggregation of HPC main chain due to the incompatibility between hydrophilic HPC and hydrophobic perfluoroalkyl chain. The physical and optical properties of FES derivatives is significantly different from that of ES. For example, FES-6 and FES-8 are dissolved in diethyl ether, which is non-solvent for other HPC derivatives, and formed a lyotropic cholesteric mesophase with iridescent color at ambient temperature. It is observed[21] that the cholesteric pitch of FES increases more rapidly with temperature than that of ES and FES-6 and FES-8 show a fingerprint pattern like texture under a polarizing microscope at higher temperature. FES-6 and FES-8 can exhibit the wide variation of cholesteric pitch from visible light wavelength to a few micrometers. However, ES-6 and ES-7 only show a fingerprint pattern near the T_c. Consequently, the latter factor may be more reasonable rather than the former one according to these experimental facts[11]. The structural and cholesteric properties of mesophases formed by FES series will be described in more detail in a succeeding paper[21].

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