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Thermotropic cellulose derivatives with flexible substituents

II. Effect of substituents on thermal properties

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Summary

Three kinds of fully substituted cellulose derivatives, cellulose triheptanoate (CTH), tri-O-heptyl cellulose (THC) and tri-O-2-butoxyethyl cellulose (TBC) were prepared. These polymers, having a side chain of similar length but of differing chemical structure, were found to show significantly different thermotropic behavior: TBC forms a cholesteric liquid crystalline phase at temperatures between 50 ℃ and 165 ℃, the cholesteric pitch covering the region of visible lights. THC also displays a cholestric structure at temperatures between 80 ℃ and 130 ℃ with pitches on the order of several micrometers. CTH appears to show liquid crystallinity only in a very limited temperature range around 100 °C.

Introduction

Cellulose can be transformed to thermotropic liquid crystalline polymers by introducing flexible substituents of appropriate length. Typical examples are hydroxypropyl cellulose (HPC) and its ester or ether derivatives (1-3). We previously reported that a fully substituted cellulose derivative, tri-O-2-(2-methoxyethoxy)ethyl cellulose (TMEC) forms a cholesteric liquid crystalline phase in the wide temperature range extending from room temperature to the isotropization temperature of 180 °C (4). The substituents in these derivatives are considered to act like a solvent, giving certain mobility to the otherwise immobile system. In this context, the flexibility or mobility of the side chains as well as their lengths may be important factors determining the thermotropic behavior of cellulose derivatives. Moreover, since cellulose is rather hydrophilic, the hydrophilicity or -phobicity of the side chain components might play some role. Thus the thermotropic properties of cellulose derivatives are to be expected to depend not only on the chemical structure and length of the side chains but also on the kind of chemical linkage between the main and side chains.

In this report, we prepared three kinds of fully substituted cellulose derivatives, cellulose triheptanoate (CTH), tri-O-heptyl cellulose (THC) and tri-O-2-butoxyethyl cellulose (TBC). In these polymers, the weight fraction of substituent is approximately the same, but its chemical structure and/or the main chain-side chain linkage are different from one another. We then examined their thermal properties and compared them with those of TMEC.

Sample Preparation

CTH was prepared by trifluoroacetic anhydride (TFAA)-fatty acid esterification according to Morooka et al.(5). TFAA and heptanoic acid were

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mixed together and stirred mildly at 50 ℃ for 20 min for aging. The solution was added to regenerated cellulose, and the reaction was carried out at 50 ℃ for 5 h under stirring. Then the mixture was poured into a large amount of methanol, and the precipitate was filtered and repeatedly washed with fresh methanol.

THC was synthesized via a two-step procedure. Firstly, a heptyl cellulose with a relatively high DS value was prepared by using a SO_2-diethylamine(DEA)-dimethylsulfoxide(DMSO) solvent system. To the cellulose solution with this system prepared as described in the literature (6) was added powdered NaOH to have a suspension system, to which heptyl bromide was added. The system was slowly heated to 60 ℃ and kept at that temperature for 12 h. This gave a heptyl cellulose with a DS value of about 2. The fully substituted heptyl cellulose, i.e., THC was prepared by further treating this product in tetrahydrofuran solution with sodium naphthalene and then with heptyl iodide at room temperature for 24 h. Complete etherification was confirmed by the absence of the IR absorption band around 3400 cm^{-1} due to hydroxyl groups.

TBC was also prepared by the two-step procedure: By the use of SO_2 - DEA-DMSO/powdered NaOH system and 2-butoxyethyl iodide, a butoxyethyl cellulose having a DS of about 2 was obtained. Complete etherification was performed by further treating the product with 2-butoxyethyl iodide and methylsulfinyl anion in a DMSO-NaH system (4).

Measurements

The thermal properties of the prepared samples were studied by means of differential scanning calorimetry (DSC) and polarization light microscopy. DSC measurements were made on a Rigaku Denki Model DSC-8230, Japan, at a constant heating/cooling rate of 10 ℃/min. Microscopic observation was made on a Nikon Model Optiphoto-Pol, Japan, along with the use of a Mettler hot stage Model FP-82 equipped with a temperature controler Model FP-80. The heating/cooling rate employed was the same as for the DSC study, except for temperatures near the anisotropic-isotropic transition point, where an extremely low rate, e.g., 1 ℃/h, was often emplyed to obtain well-defined transition temperatures.

Results and Discussion

Figure 1a shows the DSC thermogram for TBC. When heated for the first time this polymer exhibited two endothermic peaks, one at 34 °C, and the other at 165°C. On cooling, it gave a single exothermic peak at 154 ℃, which may be considered to correspond to the 165°C endothermic peak. In the second cycle and thereafter, the 34°C peak was undetectable, whereas the higher temperature peaks were found to be quite reproducible. This indicates that the polymer undergoes a well-defined thermal transition at a temperature roughly around 165°C, the enthalpy and entropy of transition being about 0.4 kcal/mol and 0.8 cal/mol K, respectively. Examination under the microscope indicates that this polymer, apparently in a solid state at room temperature, becomes a birefringent liquid at a temperature somewhat below 50 ℃ and ceases to be birefringent above about 165 ℃. The birefringent thin liquid placed between crossed polars shows a grainy appearance characteristic of cholesteric polydomain structure. Most notably, observation by naked eyes confirms that this polymer has iridescent colors in a limited temperature range, say, between 50 and 70°C. All these show that TBC forms a cholesteric liquid crystalline phase at temperatures roughly between 50 °C and 165°C, having the cholesteric pitch in the region of visible lights, at relatively low temperatures. The low temperature limit for liquid crystallinity is rather poorly defined. It can be considerably

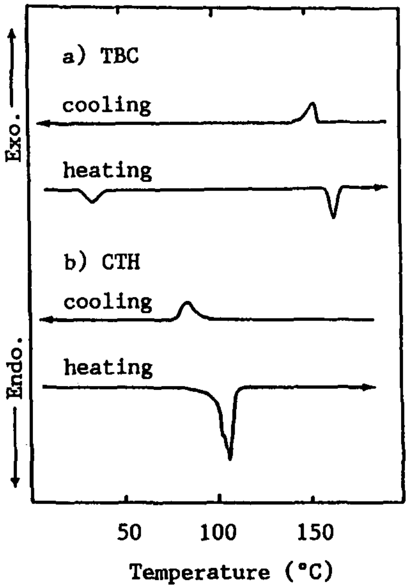

Figure 1. DSC thermograms for (a) tri-O-2-butoxyethyl cellulose (TBC) and (b) cellulose triheptanoate (CTH).

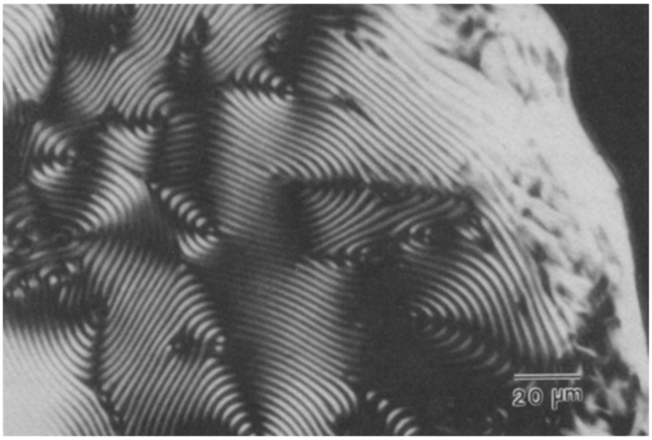

Figure 2. Optical micrograph between crossed polars for tri-O-heptyl cellulose (THC) at 85°C.

lower than 50 ℃, if the DSC peak at about 34 ℃ observed in the first heating run is associated with "melting" of the polymer. Even though no such peak was detected in the second and later runs as already noted, it did appear again, once the sample was cooled down to about -100 °C. In any case, this matter remains unsettled, and the figure 50 °C given in Table 1 should be understood as a "safety limit". This is also the case with THC to be described below, for which no solid-liquid transition was thermally observed even for the virgin polymer.

THC shows, on heating, a small but distinct and reproducible endothermic peak at about 143 ℃ (data not shown). Microscopic observation confirms that it is associated with an anisotropic-to-isotropic transition. The associated enthalpy and entropy are very small, about 0.02 kcal/mol and about 0.04 cal/mol K, respectively. Figure 2 shows the "fingerprint" pattern displayed by this polymer after having been stood at 85 °C for several days. The spacing of the alternating light and dark lines indicates a cholesteric pitch of about 10 µm. Insofar as the microscopic observation is concerned, this polymer shows liquid crystallinity between 80 and 130 °C, approximately.

The temperature range of liquid crystallinity for CTH, if it ever exists, seems very narrow. Figure 1b shows the thermogram for this polymer. There is a large endothermic peak near 100 ℃, which seems to consist of two smaller peaks close to each other. Under the microscope, this polymer is observed to liquefy at about 100 ℃ and show some birefringence at this and nearby temperatures, but with increasing temperature, it quickly turns into an isotropic liquid. This seems to suggest that the lower temperature branch of the DSC peak is associated with some kind of melting, e.g., of the crystalline side chains, which brings about mobility to the cellulose main chains, whereas the higher temperature branch is associated with the isotropization of the thermotropic phase. We have as yet observed for this polymer no structure characteristic of cholesterics, however.

Table 1. Comparison of phase transition temperatures for various fully-substituted cellulose derivatives.[a)]

Derivative	Structure	T_{sa}[b)] (°C)	T_{ai}[c)] (°C)	Cholesteric pitch
CTH	Cell-O-CO-$CH_2CH_2CH_2CH_2CH_2CH_3$	$\sim$100	100	-----
THC	Cell-O-$CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	$\sim$ 80	130	5 - 10 µm[d)]
TBC	Cell-O-CH_2CH_2-O-$CH_2CH_2CH_2CH_3$	< 50	165	visible region
TMEC	Cell-O-CH_2CH_2-O-CH_2CH_2-O-CH_3	< 30	180	visible region

a) Abbreviations : CTH = cellulose triheptanoate, THC = tri-O-heptyl cellulose, TBC = tri-O-2-butoxyethyl cellulose, TMEC = tri-O-2-(2-methoxyethoxy)ethyl cellulose.

b) Solid - anisotropic liquid transition temperature.

c) Anisotropic liquid - isotropic liquid transition temperature.

d) By polarization microscopy (fingerprint pattern).

Table 1 summarizes the thermotropic properties of the new derivatives along with those of TMEC reported previously (4). The substituents in these four derivatives are all approximately the same in molecular weight. Nevertheless, the thermotropic properties have been observed to be sensitive to the chemical structure of the substituents. Moreover, the properties are significantly different even among the derivatives that are different only in the chemical linkage between the main and side chains (cf. CTH and THC). Very recently, Ritcey and Gray reported that 2-ethoxypropyl cellulose (EPC) forms a thermotropic cholesteric phase from room temperature up to about 160 ℃(3). EPC is structurally similar, although to a limited extent, to TBC and TMEC, and in fact, these polymers show analogous phase transition behavior. However, with respect to the cholesteric pitch and its temperature dependence, there exist quite large differences among these derivatives, as will be described in detail elsewhere (7).

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