Chain-Length Dependence of the Mesomorphic Properties of Fully Decanoated Cellulose and Cellooligosaccharides

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A large number of cellulose derivatives have been found to form a lyotropic and/or thermotropic liquid crystal, mostly classified into cholesteric (or nematic) phases.[1-8] We recently reported that unlike other cellulose derivatives, fully alkanoated celluloses exhibit a columnar phase in the bulk.[9] In this phase, the cellulosic main chains lie *parallel* to the column axis to give a hexagonal order in the plane normal to the column axis, a unit hexagonal lattice including two chains (Figure 1a). On the other hand, fully alkanoated cellobiose and cellotriose were found to give a discotic hexagonal columnar phase.[10] In this phase the columns are formed by stacking of cellobiose or -triose moieties with the molecular axes *perpendicular* to the column axis, as schematically shown in Figure 1b.

The above-mentioned observation for the polymeric (cellulose) alkanoates was relevant to the samples whose degree of polymerization (DP) was about 200, while the alkanoated cellobiose and -triose can be regarded as dimer and trimer homologues of the polymer derivatives. Then an interesting question arises as to the structure and stability of the phases which will be formed by the alkanoates with an intermediate or a still higher DP: Is there any critical value of DP at which the structure changes from Figure 1a type to 1b type or vice versa? This is the topic to be dealt with in this report. We will study the mesophase properties of fully decanoated celluloses of fairly narrow distribution in DP, covering a wide range of DP from oligomeric to high-polymer regions throughout.

Experimental Section

Materials. Cellobiose, -tetraose, -pentaose, and -hexaose were supplied by Yaizu Suisan Kagaku, Ltd., Japan. A cellulose with a nominal DP of 360 was supplied by Daicel Chemical Industries, Ltd., Japan. Other chemicals were commercially obtained. A cellulose with a number-average DP of about 15 was prepared by hydrolyzing a cellulose triacetate with a nominal DP of 210 (Daicel Chemical Industries) and regenerating the hydrolysate, according to the method described previously.[11]

Preparation of Fully Decanoated Derivatives. The low-DP cellulose and cellooligosaccharides were esterified by the acid chloride method.[12] The high-DP cellulose was esterified by the trifluoroacetic anhydride method.[13] The details of the procedures were described elsewhere.[9,10] Both proton nuclear magnetic resonance and infrared analyses of the purified products have confirmed that they are fully decanoated compounds.

Fractionation. The low- and high-DP derivatives, coded L and H, respectively, were fractionated into several parts by use of a Toso semipreparative gel permeation chromatograph (GPC) Model HLC-827, Japan, installed with Toso gel columns GMHG6 and G2000HG8/G3000H8. Chloroform was used as eluent and a flow rate of 6.0 mL/min was maintained. The obtained fractions will be coded L-1, L-2, H-1, H-2, and so forth.

Measurements. The weight-average molecular weights M_w of L-1 through L-5 were determined by the sedimentation equilibrium method on a Hitachi ultracentrifuge Model UCA-1A, Japan. The M_w values of other fractions and the values of polydispersity index M_w/M_n of all fractions were estimated by GPC on the basis of the calibration curve established for narrow fractions of tri-*O*-heptyl cellulose (THC),[14] a cellulose derivative hydrodynamically nearly equivalent to cellulose decanoate. A minor correction to the THC calibration curve was made by use of the knowledge of the M_w values for fractions L-1 through L-5.

Differential scanning calorimetry (DSC) was conducted on a Rigaku Denki Model DSC-8230, Japan, at a constant heating/cooling rate of 10 °C/min.

Wide-angle X-ray diffractograms were obtained with a flat-plate camera by use of a Rigaku Denki X-ray generator with Ni-filtered Cu Kα radiation. A Mettler hot stage Model FP-80 was used to regulate the sample temperature.

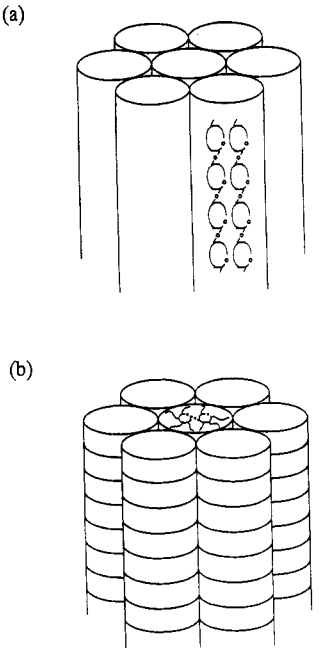

Figure 1. Schematic representations of (a) the columnar phase of cellulose tridecanoate and (b) the hexagonal discotic columnar phase of cellobiose octadecanoate.

Results and Discussion

The molecular characteristics of the samples are presented in Table 1, which shows that all of the obtained fractions are fairly to reasonably narrow in distribution. The oligomeric derivatives, coded dimer through hexamer, are essentially pure products with $M_w/M_n = 1.0$. For reference, we have also cited in the table values of M_w estimated by the polystyrene-calibrated GPC, showing that those values are very different from the more reliable values obtained by the above-mentioned methods. We also note that the oligomeric derivatives were found to be a mixture of the α and β anomers (with respect to the configuration of the reductive end of the cellooligosaccharides) with an α to β anomeric ratio of roughly 1:2 in all cases. One of the reasons for the scattering of data points in the oligomeric region (see below) may be ascribed to a rather minor difference in the anomeric ratio among samples. Our recent result suggests that the transition temperatures of cellooligosaccharide derivatives depend significantly on this ratio.[14] This problem, however, is not essential in this study.

Figure 2 shows the DSC thermograms of several samples recorded in the heating mode. Dimer, trimer, and tetramer gave two endothermic peaks, of which the lower-temperature (T) peak was assigned to the melting temperature T_m and the higher-T peak was assigned to the isotropization temperature T_i. Pentamer, hexamer, and polymeric fractions with a weight-average degree of polymerization DP_w smaller than about 20 gave a single

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Table 1. Molecular Characteristics, Transition Temperatures, and Transition Enthalpies of Fully Decanoated Celluloses

sample code	DP_w	$DP_{w,app}$[c]	M_w/M_n[b]	T_m[d] (°C)	T_i[d] (°C)	ΔH_m[d] (cal/g)	ΔH_i[d] (cal/g)
dimer	2		1.0	57.6	92.8	4.5	1.6
trimer	3		1.0	44.5	93.0	2.4	1.6
tetramer	4		1.0	59.0	78.0	1.2	1.1
pentamer	5		1.0	67.8		1.8	
hexamer	6		1.0	66.0		1.8	
L5	14.4[a]	17.6	1.29	65.0		2.1	
L3	20.6[a]	25.6	1.14	66.7		1.7	
L2	27.0[a]	43.2	1.17	66.1	80.4	1.2	0.8
L1	42.3[a]	70.4	1.16	64.5	84.3	0.5	1.0
H5	128[b]	192	1.23	59.1	105.7	0.6	1.5
H4	250[b]	480	1.30	56.8	107.5	0.7	1.2
H3	371[b]	800	1.14	64.4	109.3	0.5	1.2
H2	531[b]	1310	1.19	55	108.7		1.2
H1	1980[b]	4960	1.23	55	108.6		1.1

[a] Determined by sedimentation equilibrium. [b] Estimated by GPC (see text). [c] Apparent value estimated by polystyrene-calibrated GPC. [d] Determined by DSC in the heating mode.

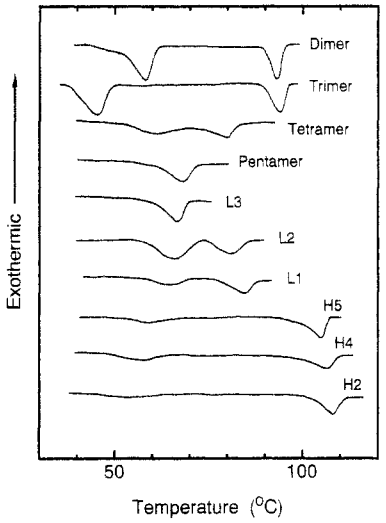

Figure 2. DSC thermograms recorded at a heating rate of 10 °C/min.

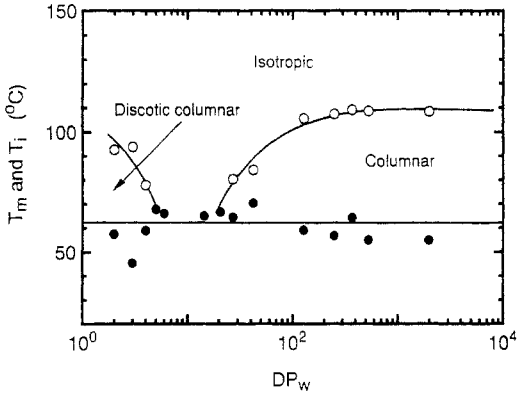

Figure 3. Transition temperatures as a function of DP_w; isotropization temperature T_i (○) and melting temperature T_m (●).

peak, assignable to T_m. Higher-DP fractions showed two peaks, again, which were assigned to T_m and T_i, respectively. The calorimetric data are summarized in Table 1.

Figure 3 shows the T_m and T_i as a function of DP. This phase diagram consists of four regions, i.e., a crystalline solid region, an isotropic liquid region, and two mesomorphic regions. The existence of the two mesomorphic regions which are clearly separated from each other suggests that they are different phases. In fact, the oligomeric phase, which is relevant to samples with DP < 5, exhibits, under a polarization microscope, textures characteristic of discotic columnar phases.[10] On the other hand, the polymeric phase, relevant to samples with DP_w > 20, is characterized by a high viscosity and low birefringence.[9]

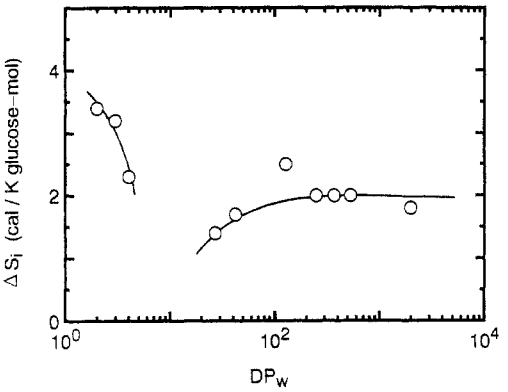

Figure 4. Isotropization entropy ΔS_i per mole of anhydroglucose unit as a function of DP_w: $\Delta S_i = \Delta H_i/T_i$.

The isotropization entropy ΔS_i per mole of anhydroglucose unit is plotted in Figure 4 as a function of DP. In the oligomeric region, ΔS_i decreases with increasing DP, while in the polymeric region, it increases at first and with a further increase in DP, it attains a nearly constant value of about 2 cal K^{-1} mol.$^{-1}$ This limiting value is considerably lower than the value of about 3 cal K^{-1} mol^{-1} observed for dimer and trimer, which also indicates that the structuring principles are different for the oligomeric and polymeric phases.

The previous X-ray analysis showed that dimer and trimer form a discotic hexagonal columnar phase,[10] while a polymer homologue (broad in molecular weight distribution with an average DP of about 200) gives a hexagonal columnar phase[9] (see Figure 1). Here we have extended the analysis to many of the present samples. Unlike dimer and trimer, which gave three equatorial reflections and one meridional reflection, aligned tetramer gave only one, rather weak, equatorial reflection. Even though it is not possible to deduce the mesophase structure from this X-ray analysis alone, we believe that the tetramer phase belongs to a discotic, if not hexagonal ordered, columnar phase, as its texture is analogous to those of dimer and trimer. Presumably, the order in the tetramer phase is not high enough, as judged from the low value of ΔS_i for this phase (Figure 4). The diffractograms of all the polymeric fractions studied were consistent with the structure given in Figure 1a. Figure 5 shows the d_{100} spacing, which measures the size of hexagonal lattices, as a function of DP. Clearly, d_{100} increases with increasing DP in the oligomeric phase, while it stays constant in the polymeric phase, as it should be if the structures shown in Figure 1a

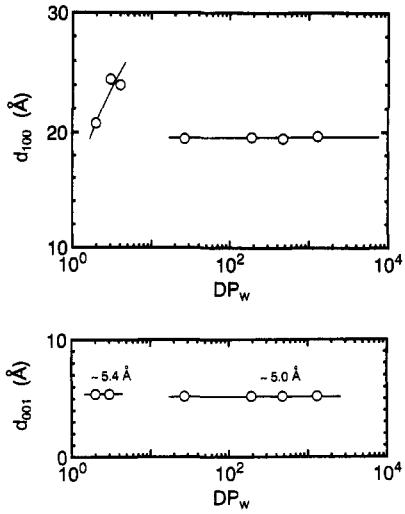

Figure 5. d_{100} and d_{001} spacings as a function of DP_w.

and Figure 1b are correct for the polymeric and oligomeric phases, respectively. The d_{001} spacings, the periodicity along the column axis, can also characterize the phases. As given in Figure 5, the spacings are 5.4 and 5.0 Å for the oligomeric and polymeric phases, respectively. These values are consistent with the assumed structure.[9,10]

To conclude, oligomeric derivatives with DP < 5 form a discotic columnar phase, while polymeric derivatives with DP larger than about 20 form a hexagonal columnar phase. In the oligomeric phase, the molecular axis is perpendicular to the column axis, while in the polymeric phase it is parallel to the column axis. The transition from the perpendicular to the parallel orientation of the molecular axis is expected to occur at a DP around 10, as Figure 3 suggests, but it cannot be actually observed, as the transition temperature will be well below T_m.

It should be noted that both oligomeric and polymeric phases have a common structural principle in which the glucose moieties associate to form the core of the column and the alkyl side groups surround the core. In other words, both phases are characterized by a microsegregation of the two components, the glucose and alkyl moieties. This is not the characteristic of ether-type cellulose derivatives, which commonly form a cholesteric phase. The driving force to facilitate the segregation of the two components is not yet well understood, but we believe that the carbonyl groups in the alkanoates enhance the amphiphilic contrast between the glucose and alkyl moieties as compared with the case of ether derivatives.[9]

Since in the present system the number of alkyl side chains stacking out of a glucose unit is little dependent on DP (this number is 4 for the dimer and 3 for the polymer), the columnar phases should have a similar segregation morphology in its shape and size. In fact, the dimer and polymer phases have a common structural feature such that the column has a diameter of about 24 Å and includes two glucose units in a repeat distance of about 5 Å along its axis. This implies that the number density of alkyl chains on the surface of the glucose "core" is about the same in the two phases, if the core density is assumed to be the same in the dimer and polymer phases.

The above discussion suggests that the stability of the columnar phases depends on a delicate balance between the number of alkyl chains and the size of the glucose core, and there is an optimum ratio between these. Then the observed decrease of T_i and ΔS_i or the destability of the oligomeric phase with increasing DP may be understandable, since the discotic arrangement of the glucose moieties would change the density of alkyl chains on the core surface, breaking the optimum balance. The observation also appears to be in line with the general view that discotic columnar phases will favor flat and symmetrical molecules over asymmetrical ones. It is also reasonable that the further increase of DP induces the transformation of molecular arrangement from the discotic type to the polymeric columnar type, a phase structurally akin to the most stable dimer phase. The observed increase and saturation of T_i and ΔS_i with increasing DP in the polymeric phase might be caused by the decrease of the number of chain ends that could bring about a significant crystallographic defect. Alternatively, it could be interpreted from the viewpoint of the flexibility and its temperature dependence of cellulosic chains, which has been shown to be responsible for the chain-length dependence of the T_i and ΔS_i of the cholesteric phase of alkyl cellulose.[8,14]

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