

REVIEW

Characteristics of Cellulosic Thermotropics*

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Main characteristics of thermotropic liquid crystals of cellulose derivatives were described. Essentially three types of cellulosic or oligocellulosic mesophases have been hitherto observed, which are cholesteric, columnar and smectic (possibly, chiral smectic C*). Evidence suggests that cellulosic cholesterics are essentially rigidity-driven mesophases, while the other phases appear to be stabilized mainly by "soft" interactions. The structure of cellulosic cholesterics is a delicate function of the side-chain chemistry and the lengths of the main and side chains. Some remarks are also given about the effects of chemical orders and molecular motions on the thermal properties of cellulotics.

KEY WORDS: Thermotropic liquid crystals/Cellulose derivatives/Cholesteric vs. columnar/Rigidity-driven mesophase/Helicoidal pitch and sense

INTRODUCTION

Derivatives of cellulose and its oligomers are potential sources of a number of new thermotropic mesogens.¹⁻³⁾ However, previous studies were mostly concerned with hydroxypropyl-related derivatives. Those are chemically disordered polymers, with which it is often difficult to establish molecular structure-property relationships. For some time we have been engaged in a systematic study of cellulosic liquid crystals mainly using fully substituted derivatives, which are chemically ordered polymers. This paper describes some of the fundamental features of cellulosic thermotropics that have been noted in that study. Some unpublished preliminary results will also be included.

CHOLESTERIC VS. COLUMNAR PHASES

All cellulosic LC's, lyotropic or thermotropic, that had been previously known were cholesteric (or nematic). Recently, we noted a different type of LC, which is the

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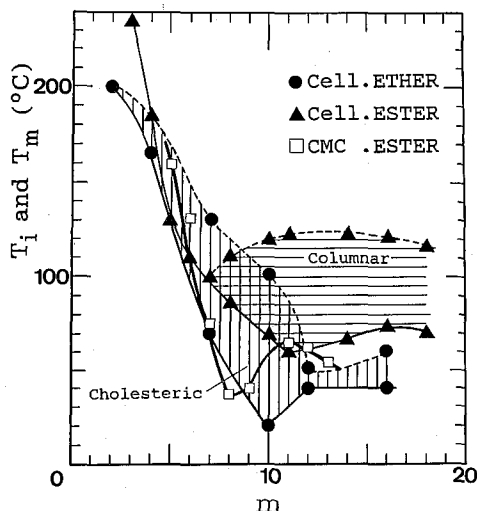


Fig. 1 The melting temperature T_m and isotropization temperature T_i of n-alkyl ester and ether derivatives of cellulose. The ester derivatives of CMC (tri-O-carboxymethyl cellulose) hardly form a mesophase for any m .

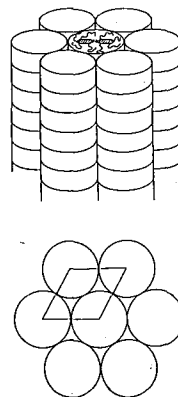


Fig. 2 Schematic representation of two-dimensional hexagonal packing of columns. Each column is built up by the regular stacking of cellobiose or cellotriose moiety.

one formed by cellulose trialkanoates (CTAI's) having relatively long alkyl length.⁴⁾ This phase, characterized by a low birefringence and a high viscosity compared to the cholesteric phases, was confirmed to be classed as a columnar LC in which molecules are packed in a two-dimensional hexagonal order in the plane normal to the chain axis with two chains being included in a unit lattice.

In Figure 1, the phase transition temperatures of CTAI's^{4,5)} and also of trialkyl celluloses (TAIC's)⁵⁾ and trialkyl esters of tricarboxymethyl cellulose (CMCAI's)⁶⁾ are shown as a function of side chain length m , where m is the number of the C and O atoms forming the side chain skeleton: for example, $m=7$ for heptyl cellulose (Cell-O-C₇H₁₅) and cellulose heptanoate (Cell-O-CO-C₆H₁₃), and also for butyl ester of carboxymethyl cellulose (Cell-O-CH₂-COOC₄H₉). In all cases, the melting temperature T_m decreases in a similar fashion with increasing m . The alkyl ethers form a cholesteric phase in the vertically hatched region, while the alkyl esters give a columnar phase in the horizontally hatched region. The CMC derivatives hardly exhibit liquid crystallinity for any m .

Interestingly, fully acylated oligomers of cellulose such as cellobiose and cellotriose were found to form a columnar phase of discotic type (cf. Figure 2)⁷⁾, while fully alkylated ether equivalents showed no liquid crystallinity whatever. This suggests different origins for the cholesteric and columnar phases of cellulose derivatives. As will be described below, the cholesteric phases are believed to originate essentially in "hard interactions", i.e., orientation-dependent excluded-volume effects. In the columnar phase, however, energetic interactions or "soft interactions" as well as hard interactions are presumed to be important. In this regard, the CMC derivatives may be understood as being short of both hard and soft interactions to stabilize a mesophase.

It should also be noted that another type of mesophase was recently observed for alkyl-1-O- β -D-cellobiose.^{8,9} Even though exact classification of the phase has not been performed yet, it is very likely to belong to chiral smectic C* in type. Hydrogen-bonding among glucopyranose rings that are stacked face by face is believed to be a main factor to stabilize the LC phase.

CHEMICAL ORDER VS. DISORDER

The chemical order or homogeneity has a large effect on the transition behavior of cellulosic LC's. Figure 3 compares the DSC thermograms of two cholesterics, HEC-C5 and TBC¹⁰. HEC-C5 is a hydroxyethyl cellulose (HEC) fully acylated with pentanoic acid. Because the chemical structure of the HEC is disordered (DS=1.5 and MS=3.0), that of the tripentanoate also is disordered. TBC is tributoxyethyl cellulose (Cell-O-C₂H₄-O-C₄H₉), a chemically ordered polymer. The thermogram of TBC shows a sharp isotropization transition at about 160°C, while that of HEC-C5 shows a very broad transition extending from about 40°C to about 130°C.

The difference in the thermal properties between the two polymers can be seen even more clearly in their rheological properties¹⁰. Figure 4 shows the dynamic viscosity η' of the two polymers as a function of temperature at a constant angular frequency of 1 rad s⁻¹. The figure shows that the isotropization of TBC is accompanied

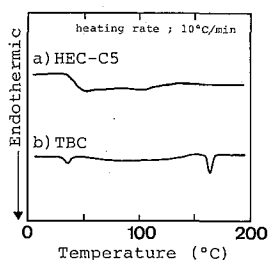


Fig. 3 DSC thermograms of HEC-C5 and TBC.

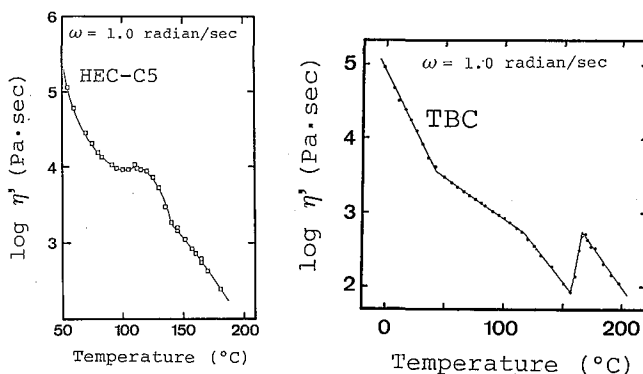


Fig. 4 Dynamical viscosity η' as a function of temperature at a constant frequency of 1.0 rad sec⁻¹.

by a sharp increase (nearly by a factor of 10) of η' in a narrow temperature span ($< 10^\circ\text{C}$) around 160°C . The same polymer shows another bend of the η' curve at about 40°C , apparently corresponding to the small peak in the DSC curve (see Figure 3). Aside from the origin of this transition-like point (see below), the η' curve of HEC-C5 gives no such information except for an indication of a long transition "region". The main reason for the broadness of transition is believed to be the chemical disorder of this polymer. Another factor that can be equally important, especially for short chains, is the chain-length distribution. In fact a very broad biphasic region was observed for an oligomeric TALC with a broad mass distribution¹¹⁾ (for chain-length dependence of isotropization temperature, see below).

MOLECULAR MOTIONS

Fully cyanoethylated O-(2,3-dihydroxypropyl) cellulose (CN-DHPC) is another chemically disordered LC polymer characterized by a low T_g , a wide temperature range of mesophase, a long biphasic region, and an extraordinarily high dielectric constant. This polymer exhibits three dielectric relaxations α , α' and β , of which the β relaxation, active essentially below T_g , is assignable to local motions in the side chain.¹²⁾ The α and α' relaxations are active above T_g , the former appearing at lower temperatures than, and having an activation energy about twice as large as, the latter. Both of them are assigned to main chain motions of different modes that set in at T_g (Figure 5). It was suggested that the slower α' mode is associated with a rotational motion of the whole side chain about the cellulosic backbone axis, while the faster α mode is associated with the center-of-mass motions of the main and side chains. The semirigidity of cellulosic chains is presumed to be responsible for the appearance of these two clearly separated relaxations above T_g ¹²⁾.

The dielectric relaxations were found to have no direct relevance to the LC order

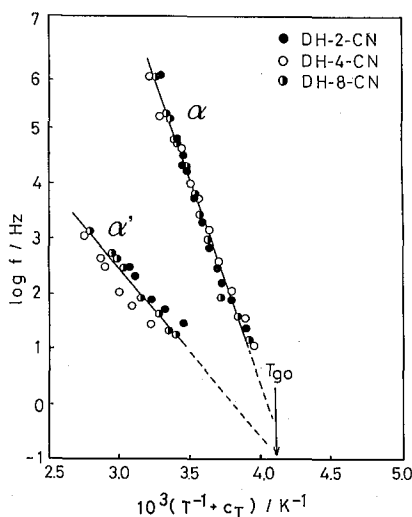


Fig. 5 Plots of $\log f_{\max}$ against $T^{-1} + c_T$ for three CN-DHPC samples: $c_T = T_{g0}^{-1} - T_g^{-1}$, where T_{g0} refers to the glass transition temperature of a reference sample.

of the CN-DHPC molecules. Calorimetrically, however, a transition-like point similar to the one noted for TBC (see above) was observed about 50°C above T_g , which was interpreted as a temperature at which main-chain motions become fast enough so that the semirigid molecules can order by themselves to form a LC phase in the time scale of observation.¹²⁾ If this is the case with cellulosic LC's in general, the TBC data in question may be understandable in the same context.

AN ORIGIN OF THERMOTROPICITY

As already noted, most cellulosic LC's are cholesteric (or nematic). Triheptyl cellulose (THC) is a typical cholesteric polymer whose thermal and molecular characteristics have been studied in some detail. By combined use of solution- and GPC-fractionations, we have obtained reasonably narrow fractions of THC ($M_w/M_n \approx 1.2$) with degrees of polymerization ranging from about 10^1 to about 10^3 . Preliminary results of intrinsic viscosity and light scattering studies yielded the following expression for the persistence length P (in Å) as a function of T (°C):¹³⁾

$$P = 95e^{-\alpha(T-30)}; \alpha = 0.005_0 \quad (1)$$

This relation shows that THC is a typical semiflexible polymer with a large temperature coefficient α .

The anisotropic-isotropic transition temperature T_i of THC was observed to increase with DP for small values of DP and level off for sufficiently large DP. Figure 6 shows the plot of $\alpha(T_0 - T_i)$ vs. $\log N$, where $N = L/P$ with L being the chain contour length and T_0 is the value of T_i for sufficiently long chains. The curves are theoretical predictions for the freely-jointed (FJ) and the wormlike (W) chain models¹⁴⁾. The theory takes account of hard interactions only. Qualitative agreement between theory and experiment is evident. The closer agreement of the experimental data to the W-chain model indicates that cellulosic chains may be better represented by wormlike chains.

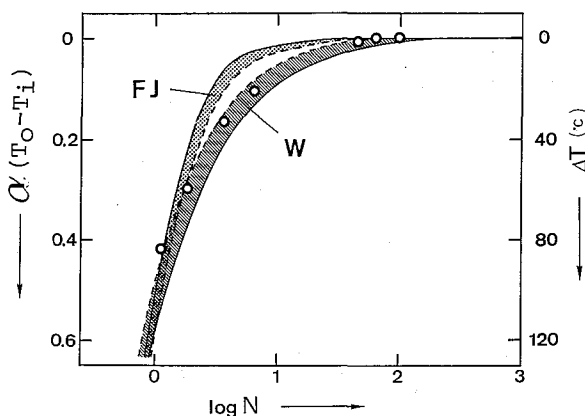


Fig. 6 Plot of $\alpha(T_0 - T_i)$ vs. $\log N$. The solid and broken curves are for the lattice model and the Onsager-Kimura type model, respectively.

In any case, these results would mean that the mesophase of this polymer originates essentially in the semirigidity of the cellulose backbone. The side-chain length dependence of T_i observed for TA1C's (Figure 1) could also be quantitatively interpreted by a similar hard-interaction argument¹⁵⁾.

CHOLESTERIC STRUCTURE

The helicoidal pitch P_t of cholesterics can be determined either by CD spectroscopy or polarization optical microscopy. The CD method is applicable for samples with P_t roughly between 200 and 500nm, and the microscopic method, for those with P_t larger than about 1 μm . The CD (and ORD) method also provides information of helicoidal sense. The P_t and sense of cellulosic cholesterics depend on many factors such as temperature, side-chain chemistry and its length, and main-chain length.^{4,11,16-18)}

Particularly noteworthy is the temperature-induced sense inversion observed for some derivatives. Figure 7a shows the P_t vs. T plot for an oligomeric tri(methoxyethoxy)ethyl cellulose (TMEC; $\text{Cell}-(\text{O}-\text{C}_2\text{H}_4-\text{O})_3-\text{O}-\text{CH}_3$).¹⁸⁾ At low temperatures, P_t increases with increasing T , diverges at around 110°C, and then decreases with a further increase in T . An ORD analysis showed that the handedness of the helicoidal sense changes from right to left as one passes through the diverging point. In Figure 7b, P_t^{-1} is plotted against T . Because P_t^{-1} is roughly proportional to the twist angle δ between adjacent pseudonematic layers in the cholesteric, the above-noted phenomenon may be understood as a monotonous change of δ with temperature. The diverging or pseudonematic point T_N is less ambiguously defined in the P_t^{-1} vs. T plot than in the P_t vs. T plot. T_N is 108°C in this example. A similar inversion of sense was observed also for oligomeric THC samples. The T_N of this polymer was found to increase with chain length.¹¹⁾

Figure 8 is a representation (schematic to some extent) of the P_t^{-1} vs. T data for the cellulosic cholesterics studied so far. TDC stands for tridecyl cellulose, and TMEEC, for tri(methoxyethoxyethoxy)ethyl cellulose [$\text{Cell}-(\text{O}-\text{C}_2\text{H}_4-\text{O})_3-\text{O}-\text{CH}_3$]. A positive P_t indicates a right-handed helix, and a negative P_t , a left-handed one. Regarding those derivatives for which two curves are shown in the figure, the one on

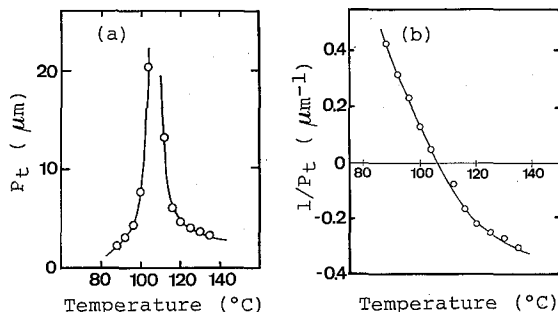
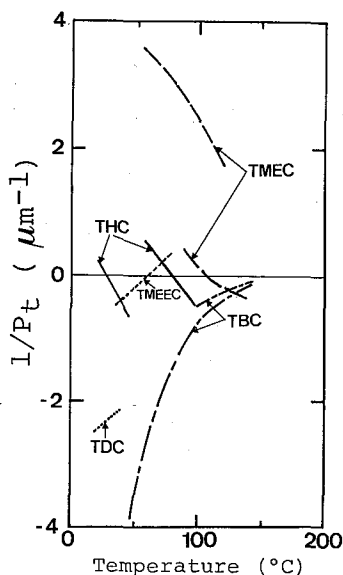


Fig. 7 P_t vs. T plot (left) and P_t^{-1} vs. T plot (right) for TMEC.


 Fig. 8 Plot of P_t^{-1} vs. T for cellulosic cholesterics.

the lower-temperature side corresponds to an oligomeric sample, and the one on the higher-temperature side, to a polymer homologue. The positions that each derivative occupy on the P_t vs. T plane clearly depend, in an apparently complicated fashion, on the chemistry and lengths of the side and main chains. Clearly, whether a sense-inversion is observable or not depends simply on the relative positions of the three characteristic temperatures T_m , T_N , and T_i , on the temperature axis. Very interestingly, there seems to exist essentially two types of cholesterics. In one type, P_t^{-1} decreases with increasing T , while in the other type, the T dependence reverses. This might have something to do with the conformation of cellulosic chains.

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