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Thermotropic cellulose derivatives with flexible substituents IV. Columnar liquid crystals from ester-type derivatives of cellulose

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Thermotropic cellulose derivatives with flexible substituents

IV. Columnar liquid crystals from ester-type derivatives of cellulose

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Cellulose tri-*n*-alkanoates, fully substituted ester-type derivatives of cellulose, having acyl groups with n carbon atoms ($3 \leqslant n \leqslant 18$), are prepared and their thermal behaviour studied. It is found that samples of cellulose tri-*n*-alkanoates with $n \geqslant 8$ form a novel thermotropic mesophase, characterized by a low birefringence and an extremely high viscosity compared with those of cholesteric mesophases of ether-type derivatives. Photomicroscopic, differential scanning calorimetry, and X-ray diffraction studies indicate that the mesophase formed by the cellulose tri-*n*-alkanoates is of a hexagonal columnar type in which two polymer chains are included in one hexagonal lattice. Two possible packing structures, resembling direct and inverse hexagonal phases of amphiphilic molecular systems, are proposed and discussed in relation to the chemical structure of the polymer.

1. Introduction

Since 1976, cellulose and cellulose derivatives have been found to form lyotropic liquid crystals [1–3]. Thermotropic liquid crystals have also been observed for derivatives of hydroxypropyl cellulose [4]. Recently, we have prepared many fully substituted ether-type derivatives of cellulose that form thermotropic liquid crystals. These include tri-*o*-2-(2-methoxyethoxy)ethyl cellulose, tri-*o*-butoxyethyl cellulose and the tri-*o*-*n*-alkyl celluloses with various alkyl groups [5–8]. The lyotropic or thermotropic liquid crystals formed by these derivatives were found to be cholesteric in all cases.

In this study, we have prepared a homologous series of cellulose tri-*n*-alkanoates (CTAl's). These ester-type derivatives were observed to form thermotropic columnar phases that are remarkably different from the cholesteric phases so far observed for other cellulose derivatives. The thermal behaviour of these materials and their columnar mesophase structure will be discussed later.

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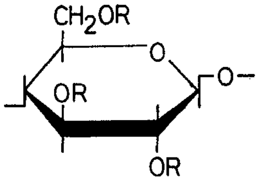
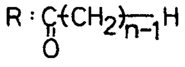
2. Experimental

2.1. *Materials*

Regenerated cellulose with a number average degree of polymerization of 210 was used as a starting material to prepare a series of CTAIs with the following formula





$R: \underset{O}{\overset{\|}{C}}(CH_2)_{n-1}H$

where the length of the ester side chain ranges from 3 to 18 carbon atoms (n = carbon atom number). The esterification was carried out by reacting cellulose with the corresponding fatty acid activated by trifluoroacetic anhydride. Complete esterification was confirmed by elemental analysis, IR spectroscopy and back titration.

2.2. *Measurements*

Differential scanning calorimetry (DSC) measurements were made with a Rigaku-Denki model DSC-8230 calorimeter, at a constant scan rate of 10°C min^{-1}. Polarizing microscopic observations were made with a Nikon model Optiphoto-Pol microscope equipped with a Mettler hot stage model FP 82 and a temperature controller model FP 80. Wide angle X-ray patterns were recorded with a flat-plate camera using a Rigaku-Denki X-ray generator with Ni filtered Cu–Kα radiation.

3. Results and discussion

3.1. *Phase behaviour of CTAls*

Figure 1 shows the DSC thermograms of CTAls obtained on heating. The polymers with $n \leqslant 7$ exhibit only one peak, while the polymers with $n \geqslant 8$ show two or three transitions. These transition temperatures are plotted as a function of acyl length n in figure 2. The results indicate that there exist four different phases I, M, C and C′.

Photomicroscopic observations confirmed that C is a solid semi-crystalline phase and I is an isotropic liquid phase. Polymers with $n \leqslant 7$ undergo only one transition from C to I. On the other hand, those with $n \geqslant 8$ exhibit a third intermediate phase M. As n is increased from 8 to 12, the temperature region of the M phase becomes wider as the result of a decrease in the melting temperature of the C phase and an increase in the isotropization temperature; at values of $n > 12$ it remains somewhat constant from 80 to 120°C. The transitions shown by the triangles in figure 2, as exhibited by the polymers with $n \geqslant 14$, correspond to the melting of side chain crystallites included in phase C′. The intermediate phase M that appears in the polymers with $n \geqslant 8$, shows some birefringence and fluidity, indicating that it is a liquid crystal mesophase. The mesophase, however, is highly viscous and shows no clear texture except for a banded texture that appears upon shearing the sample. These features clearly distinguish this mesophase from the cholesteric phases which have been observed in the ether-type derivatives of cellulose [5–8]. In figure 3, the change of the isotropization entropy of the mesophase can be found to be independent of n. The average value of 9·6 J mol^{-1} K^{-1}(2·3 cal mol^{-1} K in figure 3) is about twice as large as those for the cholesteric derivatives [7] suggesting that the present mesophase has a higher structural order than the cholesteric phases.

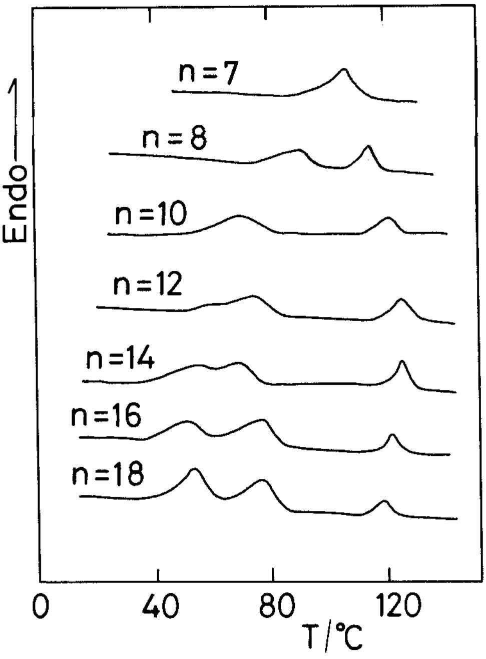


Figure 1. DSC heating thermograms of CTAl polymers.

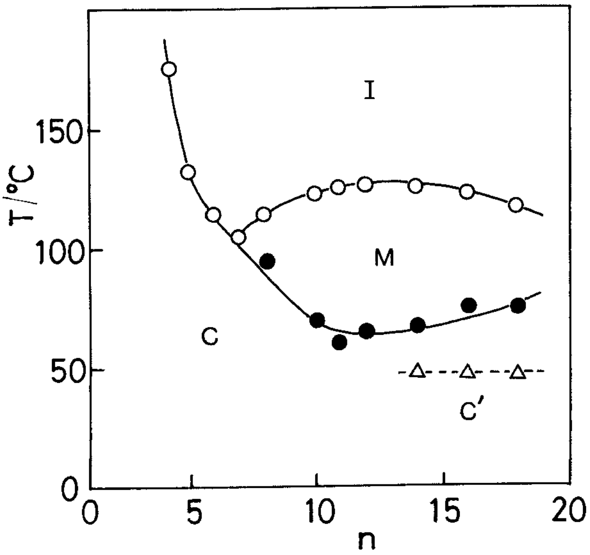


Figure 2. Dependence of transition temperatures upon *n*. The data are based on the DSC heating curves.

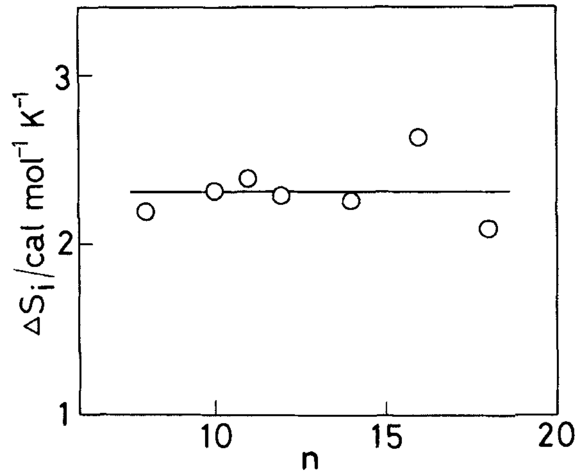


Figure 3. Dependence of the change in the isotropization entropy of the mesophase, ΔS_i, upon n.

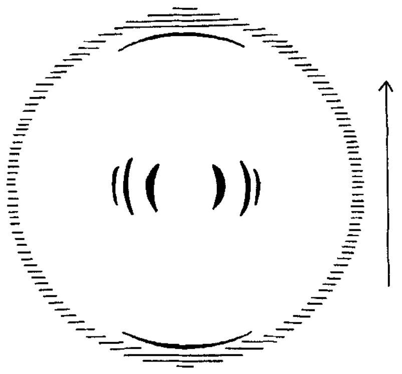


Figure 4. Illustration of the oriented X-ray pattern observed for the mesophase of CTAl with $n = 16$. Here, the oriented sample was prepared as a fibre which was drawn from the isotropic liquid. The arrow indicates the fibre axis.

3.2. *Columnar mesophase properties of phase M*

Figure 4 illustrates the X-ray diffraction pattern observed at 100°C (in the M region) for the polymer with $n = 16$ which had been drawn into a fibre from the isotropic liquid. The arrow in the figure indicates the fibre axis. The diffraction pattern includes a meridional reflection at 5·0 Å and three equatorial reflections at 23·4 Å, 13·3 Å and 11·5 Å, respectively. The spacing of the meridional reflection, d_{001}, coincides with the length of the repeat unit of the cellulose skeleton [9] and indicates that the molecules are fully extended along the stretching direction. The equatorial reflections indicate regular displacements of the molecules in the plane normal to the director. These reflections can be assigned to a two dimensional hexagonal lattice with $a = b = 26·6$ Å.

Such a hexagonal packing was observed for all samples in the M region. Figure 5 shows the spacing of the first equatorial reflection, d_{100}, together with d_{001}, as a function of n. As can be seen in this figure d_{001} remains constant at 5·0 Å while d_{100} increases linearly as n increases.

The number of polymers included in a two dimensional hexagonal lattice can be deduced by density considerations. If this number is assumed to be one, the density, calculated from the known parameters of the hexagonal lattice and the molar mass, turns out to be about 0·5 g ml^{-1} in all cases, which is half the actual bulk density. It is thus obvious that a unit lattice includes two polymer chains. This strongly suggests that each polymer molecule is not equivalent crystallographically and so some specific interaction exists between molecules even in the liquid-crystalline state.

Liquid crystals that are characterized by a hexagonal packing structure include the classical smectic and columnar hexagonal phases. Among them, the smectic phase can be ruled out in this case because the lattice containing two molecules is not a general characteristic of a smectic phase and also the wide distribution of the molecular length seems to be unsuitable for a layered structure. Our system may therefore be assigned to a columnar hexagonal phase.

Two classes of molecules are known to form a columnar phase; these are amphiphilic molecules [10] and disc-shaped molecules with long side chains [11]. In both cases, a columnar phase may be viewed as a kind of micellar structure derived from differences in polarity and/or geometric shape between the two groups in a molecule. The present materials have these structural peculiarities since they are composed of a hydrophilic cellulose main chain core with hydrophobic side chains

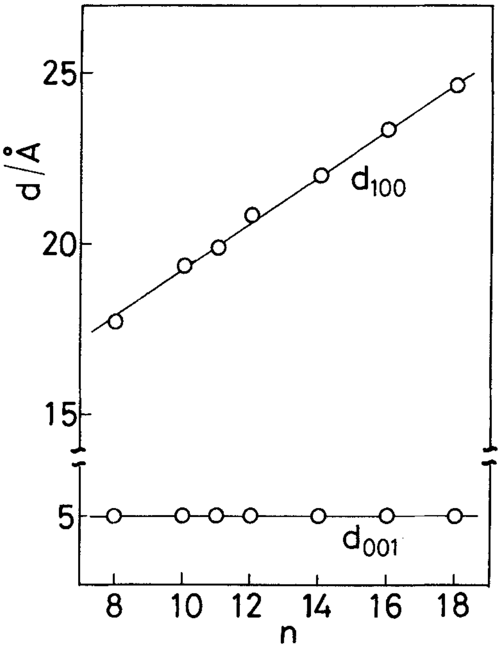


Figure 5. Variation of X-ray spacings observed for the mesophases versus the number of carbon atoms, n. Here d_{100} and d_{001} indicate the spacings of first equatorial and meridional reflections, respectively.

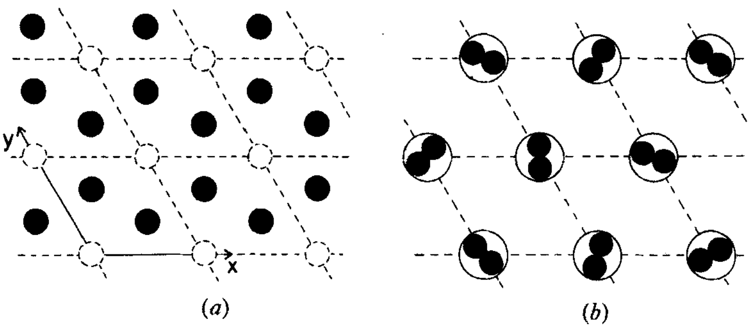


Figure 6. Two possible packing structures in the hexagonal columnar phase. In model (*a*), the hydrophobic side chains gather together to fill the open space (dashed circle) surrounded by the six cellulose main chains (closed circles). In model (*b*), the cellulose main chains of two polymers associate closely and are surrounded by the hydrophobic side chains. In both models, the unit cell given by dashed lines includes two polymer chains.

extending from the core. In fact, the amphiphilic nature of these polymers is evident from the observation that fine Langmuir–Blodgett films can be formed from these materials [12].

For amphiphilic molecules, two hexagonal columnar phases in which rod-like micelles are packed into a two dimensional lattice have been observed [10]. One form is a direct hexagonal phase where a rod-like micelle is formed, with the hydrophobic groups surrounded by the hydrophilic ones. The other form is an inverse hexagonal phase composed of micelles with the opposite structure to the above mentioned phase. In this case, we can illustrate two structural models for hexagonal phases so as to satisfy the X-ray observation that two molecules are contained in a hexagonal unit cell; these are illustrated in figures 6 (*a*) and (*b*). In a model of figure 6 (*a*), two polymer chains are located at $(x, y) = (2/3, 1/3)$ and $(1/3, 2/3)$ in fractional coordinates and one open space is located at $(x, y) = (1, 0)$. In other words, each open space in a unit cell is surrounded by the six polymer chains. Crystallographically, such a packing structure is rather unusual but not in this case since one open space can be filled by the hydrophobic side chains sticking out of the six surrounding cellulose chains. Such a structure resembles that of a direct hexagonal phase in the amphiphilic molecular systems. In a model of figure 6 (*b*), which we can more easily envisage, the cellulose main chains of two polymers associate closely with each other and locate at each unit cell [13]. In this case, the two hydrophilic main chains are surrounded by the hydrophobic side chains resembling an inverse hexagonal phase. Although there is no decisive data to indicate which of these two structures is correct, it is likely that the columnar mesophase arises from the amphiphilic nature of molecules.

Finally, it is worth noting that different types of mesophases are formed by ether-type and ester-type derivatives. We have observed that all of the ether-type derivatives prepared so far form the cholesteric mesophases [5–8]. These include the tri-*o*-*n*-alkyl celluloses, which have a similar amphiphilic structure to the present materials. Obviously, this indicates that not only the amphiphilic nature but also the ester linkage are necessary for these molecules to form the columnar phases. On this point, it is very interesting to note that a similar phenomenon has been found in cellobiose and cellotriose derivatives with the corresponding alkyl groups (regarded as dimeric and trimeric models of cellulose derivatives) [14]. These ester-type derivatives form discotic columnar phases while the ether-type ones give only isotropic liquids [15]. These phenomena can be understood if the ester groups interact between molecules and facilitate the specific association of cellulose main chains required to form a rod-like micelle.

4. Conclusion

Ester-type derivatives form thermotropic mesophases if long acyl groups more than $n = 8$ are attached. The mesophase formed by these polymers was identified as a hexagonal columnar phase, quite different from the cholesteric phase formed by the ether-type derivatives. Considering the structural characteristic that two polymer chains are located in a hexagonal lattice, a columnar phase with two possible structures has been described. These are similar to the direct and inverse hexagonal phases generally observed in the amphiphilic molecular systems, indicating that the amphiphilic nature of the molecules may be responsible for the formation of columnar mesophase.

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