# Thermal and Structural Properties of Tri-*O*-Substituted Cellulose Ethers

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## Synopsis

Tri-*O*-substituted cellulose ethers prepared by the use of $SO_2$–diethylamine (DEA)–dimethylsulfoxide (DMSO) and powdered sodium hydroxide were characterized by measurement of melting points and degradation points and by differential scanning calorimetric (DSC) and X-ray analyses. Their thermal and structural characteristics were ascertained to be dependent on the kinds of substituents. Among the ethers examined, four kinds of arylmethylcelluloses showed the characteristics of thermotropic liquid crystals (smectic). Tri-*O*-α-naphthylmethylcellulose showed the three transformations due to a solid–smectic phase, a smectic–nematic phase, and a nematic–isotropic phase transformation. This thermotropic liquid crystal was enantiotropic below 200°C.

## INTRODUCTION

As described in the previous paper[1] tri-*O*-arylmethylcelluloses, and tri-*O*-allyl- and its related cellulose ethers were prepared almost quantitatively by the use of a nonaqueous cellulose solvent, $SO_2$–DEA–DMSO. These new derivatives may be used as intermediates for the preparation of cellulose derivatives having some special functionalities, because of containing chemically reactive groups such as aromatic rings or double bonds. It was found that they are soluble in many organic solvents, and that all tri-*O*-arylmethylcelluloses and tri-*O*-2-butenylcellulose prepared from Avicel have melting points.

This paper deals with physical studies on thermal and structural characteristics of tri-*O*-substituted celluloses. During the studies, most of tri-*O*-arylmethylcelluloses together with tri-*O*-benzylcellulose[2] were found to have the characteristics of thermotropic liquid crystal. This characteristics were studied in detail.

## EXPERIMENTAL

**Preparation of Tri-*O*-Substituted Cellulose Ethers.** Tri-*O*-substituted cellulose ethers were prepared as described in the previous paper.[1] Outlines of this preparation is as follows. Cellulose was dissolved in an $SO_2$–DEA–DMSO mixture, and powdered NaOH was added to the solution. An etherifying reagent was added to the cellulose-powdered NaOH suspension with heating. The reaction products were isolated by chloroform extractions and purified repeatedly by using good and poor solvents. Tri-*O*-substituted cel-

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lulose ethers thus prepared, except tri-*O-p*-isopropylbenzylcellulose, were obtained as fine white powders.

**General Analyses.** Melting points were determined using a Yanaco micromelting point apparatus with a polarizing microscope (×60). Thermogravimetric (TG) and DSC curves were measured using a Rigaku-denki standard model TG and DSC. Ten mg of a sample was set in an alminium pan, and TG and DSC curves were measured from room temperature at the rate of 5°C or 10°C/min in helium atmosphere. x-ray diffraction patterns were obtained by the use of a disk of a sample (30 mg), which were prepared by compressing a sample at the pressure of 100 kg/cm$^2$. The equational diffraction patterns were measured from 5° to 35° values of $2\theta$ using Cu-K$\alpha$ radiation at 35 kV and 35 mA. Scanning rate and slit width were set up at 1°C/min and 2 mm, respectively.

## RESULTS AND DISCUSSION

Thermal and crystallographic characteristics of cellulose derivatives are important both from practical and academic points of view. Glass transition points ($T_g$), melting points ($T_m$), crystallinities, and other characteristics were reported for cellulose esters such as acetates, propionates, and butylates. Dependence of softening points on molecular weights were observed for cellulose ethers such as ethyl- (DS = 2.5), *n*-propyl- (DS = 2.1), and benzyl- (DS = 2.0) celluloses.[3] Cellulose ethers so far examined have high $T_m$ and/or degradation points ($T_d$) owing to low DS.

The authors could succeed in the quantitative preparation of tri-*O*-arylmethylcelluloses, and tri-*O*-allylcellulose and its related cellulose ethers by the use of $SO_2$–DEA–DMSO and powdered NaOH as a cellulose solvent and a base, respectively.[1]

### Thermal Characteristics

$T_m$ and $T_d$ of these new cellulose derivatives were measured (Table I). Since all the derivatives in Table I were prepared under the same condition, they are expected to have similar degree of polymerization (DP). The dif-

TABLE I
Melting and Degradation Points of Tri-*O*-Substituted Cellulose Ethers

| Ethers | $T_m$ [a](°C) | $T_d$ [b](°C) |
|---|---|---|
| Tri-*O*-benzylcellulose | ca. 200 | 210 |
| Tri-*O-p*-methylbenzylcellulose | ca. 170 | 215 |
| Tri-*O-o,p*-dimethylbenzylcellulose | ca. 165 | 225 |
| Tri-*O-p*-isopropylbenzylcellulose | ca. 130 | 235 |
| Tri-*O-p*-methoxybenzylcellulose | ca. 140 | 200 |
| Tri-*O-p*-chlorobenzylcellulose | ca. 180 | 235 |
| Tri-*O-p*-bromobenzylcellulose | ca. 160 | 240 |
| Tri-*O*-α-naphthylmethylcellulose | ca. 140 | 235 |
| Tri-*O*-allylcellulose | — | 260 |
| Tri-*O*-methallcellulose | — | 390 |
| Tri-*O*-2-butenylcellulose | ca. 160 | 290 |

[a] Melting points were measured on a hot stage.

[b] Degradation points were determined from TG curves.

ference in $T_m$ values, therefore, depends on the kinds of substituents. $T_d$ values of tri-$O$-arylmethylcelluloses measured from the TG curves were also found to depend on the kinds of substituents. For instance, the introduction of halogens to aromatic rings increases $T_d$ value. Among three derivatives having allyl-type substituents, only tri-$O$-2-butenylcellulose showed a $T_m$ value. All the derivatives having allyl-type substituents showed higher $T_d$ values than tri-$O$-arylmethylcelluloses in helium atmosphere. However, allylcellulose (DS = 2.0) is known to deteriorate easily by heating in air into polyacrolein-like products, formaldehyde, water, and allylalcohol.[4] The three tri-$O$-allyl-type cellulose ethers were also found to be very unstable to light and oxygen. They became insoluble in organic solvents after being kept at room temperature in air for 3 days, whereas they were kept unchanged in nitrogen below 0°C in the dark for a few months. Tri-$O$-benzyl-, tri-$O$-$p$-methylbenzyl-, tri-$O$-$p$-methoxybenzyl-, tri-$O$-$p$-bromobenzylcellulose, and tri-$O$-$\alpha$-naphthylmethylcellulose in Table I were found to show the characteristic patterns of thermotropic liquid crystal in a hot stage of a microscope with crossed polarizers. These characteristics are discussed in a later section.

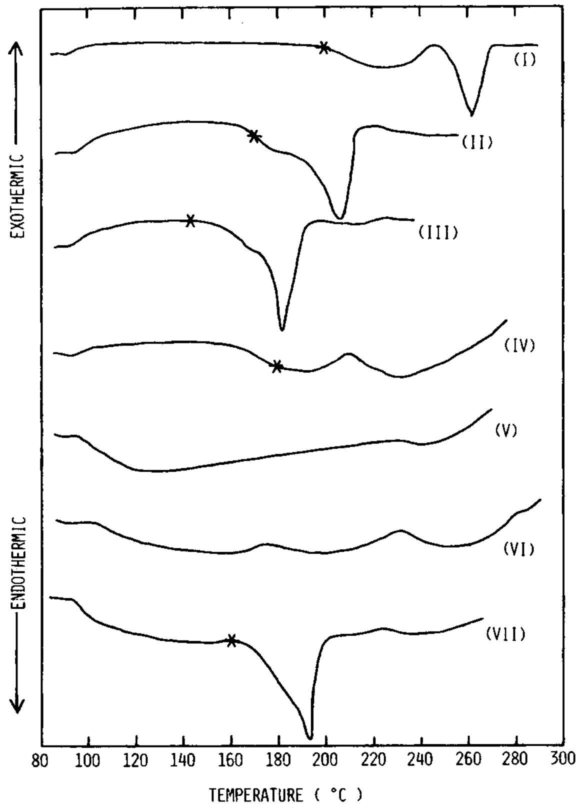

Fig. 1. DSC curves of tri-$O$-substituted cellulose ethers: (I) tri-$O$-benzylcellulose; (II) tri-$O$-$p$-methylbenzylcellulose; (III) tri-$O$-$p$-methoxybenzylcellulose; (IV) tri-$O$-$p$-chlorobenzylcellulose; (V) tri-$O$-allylcellulose; (VI) tri-$O$-methallylcellulose; (VII) tri-$O$-2-butenylcellulose; (*) $T_m$ values measured on a hot stage.

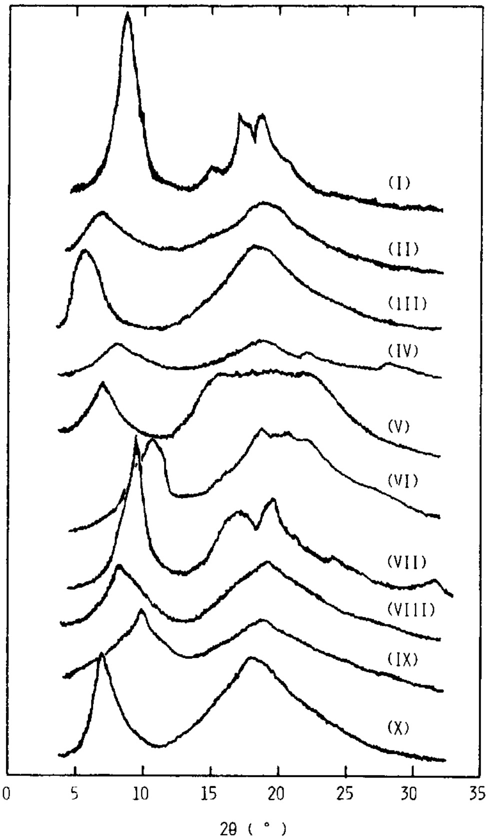

Fig. 2. X-ray diffraction patterns of tri-*O*-substituted cellulose ethers: (I) tri-*O*-benzylcellulose; (II) tri-*O*-*p*-methoxybenzylcellulose; (III) tri-*O*-*p*-isopropylbenzylcellulose; (IV) tri-*O*-*p*-chlorobenzylcellulose; (V) tri-*O*-α-naphthylmethylcellulose; (VI) tri-*O*-allylcellulose; (VII) tri-*O*-methallylcellulose; (VIII) tri-*O*-2-butenylcellulose; (IX) benzylmethylcellulose (Bn, DS = 1.4; Me, DS = 1.6), (X) tri-*O*-benzylamylose.

Figure 1 shows DSC curves of tri-*O*-substituted cellulose ethers. All these ethers are found to show a deviation from the base lines around 95°C. However, these points do not seem to be glass transition points ($T_g$), because these ethers having different substituents and crystallinities (Fig. 2) should give different $T_g$ values. Furthermore, any peaks due to $T_g$ could not be detected around 95°C in the logarithmic decrement curve of tri-*O*-benzylcellulose measured by tortional braid analysis.[2] Therefore, these tri-*O*-substituted cellulose ethers can be concluded not to show any $T_g$ points in their DSC curves. The points around 95°C are thought to be due to a solid–solid transformation, which is sometimes observed in DSC analyses of polymers.

$T_m$ values determined as the starting points of melting on a hot stage were found to be equal to the starting points of melting endothermic peaks. $T_m$ values and the shapes of melting endothermic peaks were different each other due to the difference in substituents. However, the introduction of different substituents into aromatic rings in cellulose ethers could not be expected to cause the difference in rigidities of cellulose main chains. Different $T_m$ values, therefore, are ascribed to the difference in intermolecular van der Waals forces.

## Crystallographic Characteristics

Figure 2 shows the x-ray diffraction patterns of tri-*O*-substituted cellulose ethers. They differ considerably each other. As seen from the peaks around $2\theta$ of 18°, only tri-*O*-benzyl- and tri-*O*-methallylcellulose have high crystallinities. The peaks around 18° of tri-*O*-*p*-methoxybenzyl- and tri-*O*-*p*-isopropylbenzylcellulose are almost equal to wide-angle halos due to low degrees of crystallinities. Nevertheless, every ether has its special simple peak between 5° and 11° due to certain long range positional orders.

Table II compares the longest wide angle x-ray spacing with sizes of substituents which were determined by the use of molecular models. As expected, the periodic intervals increase with increase in length or width of substituents for tri-*O*-arylmethylcelluloses I–V. The periodic intervals are about twice as much as the length (I–IV) or width (V) of substituents. With benzylmethylcellulose (IX), its periodic interval is the middle value between the length of benzyl group ×2 and methyl group ×2, indicating that the value depends on the average length of substituents. Tri-*O*-benzylamylose (X) has a larger value (12.6 Å) than tri-*O*-benzylcellulose, and this large value should be due to the characteristic helix of the amylose main chain. Also with the ethers having allyl-type substituents VI–VIII, there is a parallel relation between the periodic intervals and the sizes of substituents. These results indicate that cellulose main chains in tri-*O*-substituted cellulose ethers are rigid, and the periodicities are caused by the side groups. Furthermore, it was found that the periodic intervals corelate inversely with $T_m$ values in the case of tri-*O*-arylmethylcelluloses I–V (see Tables I and II).

## Characteristics of Thermotropic Liquid Crystals

A liquid crystalline structure in polymer systems was first observed in concentrated solutions of polypeptides in the mid-1950s[5] and have been

TABLE II

Longest Wide Angle Spacing from X-Ray Diffraction Compared to Sizes of Substituents

| | Ethers | Interval (Å) | Size of substituent | |
|---|---|---|---|---|
| | | | $L$[a](Å) | $W$[b](Å) |
| I | Tri-*O*-benzylcellulose | 10.2 | 5.4 | 4.3 |
| II | Tri-*O*-*p*-methoxybenzylcellulose | 12.6 | 6.9 | 4.3 |
| III | Tri-*O*-*p*-isopropylbenzylcellulose | 16.0 | 8.1 | 4.3 |
| IV | Tri-*O*-*p*-chlorobenzylcellulose | 10.7 | 6.1 | 4.3 |
| V | Tri-*O*-α-naphthylmethylcellulose | 12.8 | 5.4 | 6.7 |
| VI | Tri-*O*-allylcellulose | 9.3 | 2.6 | 3.2 |
| VII | Tri-*O*-methallylcellulose | 8.5 | 2.6 | 3.7 |
| VIII | Tri-*O*-2-butenylcellulose | 11.2 | 3.9 | 3.7 |
| IX | Benzylmethylcellulose | 8.8 | Bn 5.4 | 4.3 |
| | (Bn, DS = 1.4; Me, DS = 1.6) | | Me 0.9 | 0.6 |
| X | Tri-*O*-benzylamylose | 12.6 | 5.4 | 4.3 |

[a] $L$ = length of substituents (for example, the distance from the benzyl carbon to the aromatic $C_4$ proton of the benzyl group for I).

[b] $W$ = width of substituents (for example, the distance from the aromatic $C_2$ proton to the aromatic $C_6$ proton of the benzyl group for I). Both $L$ and $W$ values were obtained by the use of molecular models.

extensively studied from the standpoint of improvement of physical properties of spun fibers. As to cellulose, this structure was observed in hydroxypropylcellulose–water solutions by Werbowyj and Gray[6,7] for the first time. In succession to this finding, cellulose,[8,9] cellulose butylate,[10] and cellulose acetate[11] were found to show the lyotropic liquid crystals in their concentrated solutions. Furthermore, hydroxypropylcellulose[12] and its trifluoroacetate,[13] acetate,[14] propionate,[15] and benzoate[16] were reported to have the thermotropic liquid crystals, and these properties were characterized by polarizing microscopic, x-ray, DSC, and other analyses. These lyotropic and thermotropic liquid crystalline structures of all these cellulose derivatives were found to be cholesteric.

In the present work tri-*O*-benzyl-, tri-*O*-*p*-methylbenzyl-, tri-*O*-*p*-methoxybenzyl-, tri-*O*-*p*-bromobenzylcellulose and tri-*O*-α-naphthylmethylcellulose were found to show birefringence in a molten state on a hot stage of a microscope with crossed polarizers as described in the previous section. The substituents in the cellulose derivatives don't show liquid crystalline properties by themselves. Therefore, the combination of the rigidity of cellulose main chains and the introduction of substituents must be responsible for the appearance of thermotropic liquid crystalline properties. In the case of tri-*O*-benzyl-, tri-*O*-*p*-methylbenzyl-, and tri-*O*-*p*-methoxybenzylcellulose, the birefringence could be observed around or above each $T_m$ value in Table I during the course of cooling after melting. The microscopic and x-ray analyses of these three derivatives indicated that smectic structures might be assigned to these cellulose derivatives.[17]

Tri-*O*-*p*-bromobenzylcellulose was found to have a solid–smectic and a smectic–isotropic transformation point around 160 and 240°C, respectively. This thermotropic liquid crystalline property could be observed repeatedly during the course of both heating and cooling (enantiotropic), and the smec-

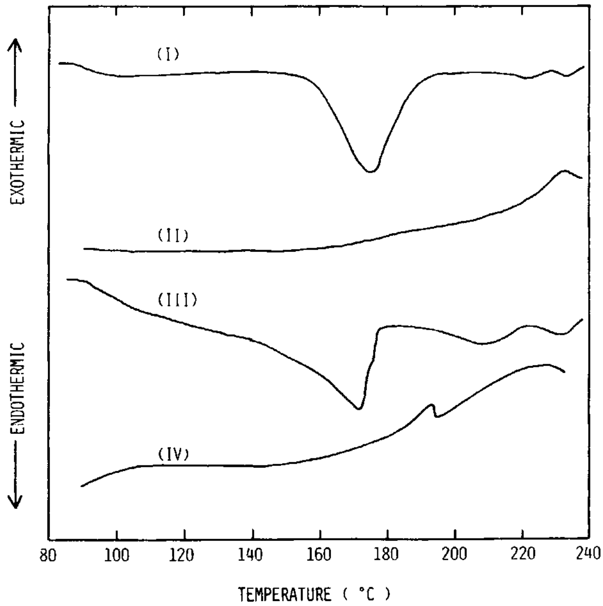

Fig. 3. DSC traces of tri-*O*-*p*-bromobenzylcellulose; (I) first heating run; (II) first cooling run; (III) second heating run; (IV) second cooling run.

tic birefringent state could be observed even in the solid state after cooling to room temperature. These smectic glassy state were often observed in thermotropic liquid crystalline polymers.[18] The results of DSC traces support the microscopic observations (Fig. 3). Namely, the endothermic peaks around 170 and 235°C in the first heating run correspond well to the solid–smectic and the smectic–isotropic transformations, respectively. In the first cooling run, the isotropic–smectic transformation was observed around 235°C as a exothermic peak, but the smectic–solid transformational peak could not be detected clearly. Irrespective of this result, an endothermic peak corresponding to the solid–smectic transformation appeared in the second heating run. This suggests that the smectic–solid transformation occurred during the cooling run, but since its speed was slow, the peak corresponding to this transformation could not be observed. The endothermic peak around 170°C in the second heating run was broad, when compared with that in the first heating. Possibly this difference is ascribed to that between the glassy smectic solid–smectic transformation and partially crystalline solid–smectic one.

Tri-*O*-α-naphthylmethylcellulose, however, showed slightly different thermal properties from other four derivatives. It showed a characteristic solid–smectic transformation around 140°C, a smectic–nematic transfor-

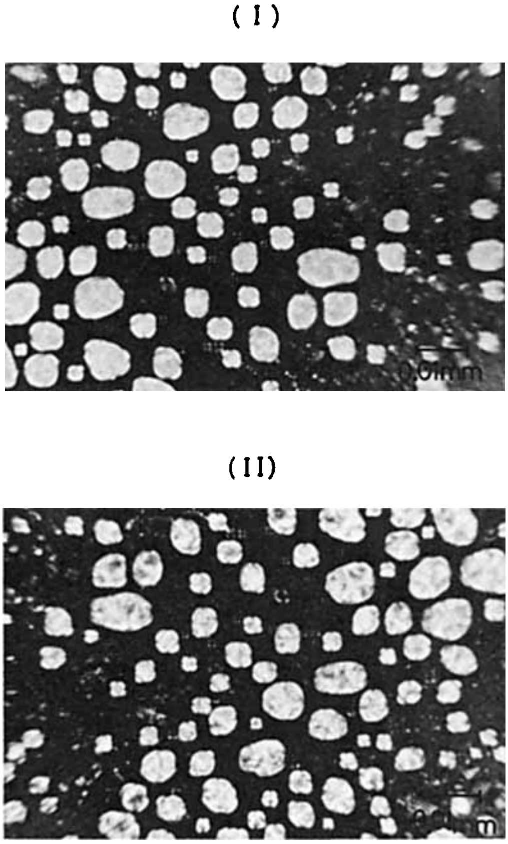

Fig. 4. Photomicrograph of tri-*O*-α-naphthylmethylcellulose taken with crossed polarizers: (I) smectic states at 140–160°C; (II) nematic states at 160–200°C.

mation around 160°C, and a nematic–isotropic transformation around 200°C on a hot stage of a microscope with crossed polarizers (Fig. 4). This enantiotropic characteristics could be observed only for the sample which was not subjected to heating over 200°C. Once it is heated over 200°C to the isotropic state, the birefringence cannot be observed even during the course of cooling. This result indicates that the complete destruction of the orientational order gives only isotropic or amorphous glassy states, and reorientation of molecular chains is disturbed by bulky α-naphthylmethyl groups. In the case of tri-*O*-α-naphthylmethylcellulose, the birefringence could not be observed below 120°C during the course of cooling; therefore, a smectic glassy state could not be formed in contrast to the other four tri-*O*-arylmethylcelluloses. Figure 5 shows the DSC curves of tri-*O*-α-naphthylmethylcellulose in heating and cooling runs. In the heating runs (I, II, and III in Fig. 5), endothermic peaks coincide well with the solid–smectic and smectic–nematic transformation points, respectively, which were determined by heating on a hot stage of the microscope with crossed polarizers. The endothermic peak around 200°C (II) should be assigned to the nematic–isotropic transformation. In the second heating run (V), however, the clear endothermic peaks due to the transformation points could not be detected in contrast to the first heating runs. In the course of cooling (IV–VI), clear exothermic peaks could be detected around 130–120°C due to the smectic–solid transformation, but other peaks were not detected clearly. This supercooling hysteresis was observed for also the benzoate of hydroxypropylcellulose.[16] X-ray diffraction patterns of tri-*O*-arylmethylcelluloses (Fig. 2) indicate that these derivatives have long range orders as shown by the sharp peaks at relatively small angles. The polymers having such diffraction patterns are known to have a tendency to show the smectic structure.[19]

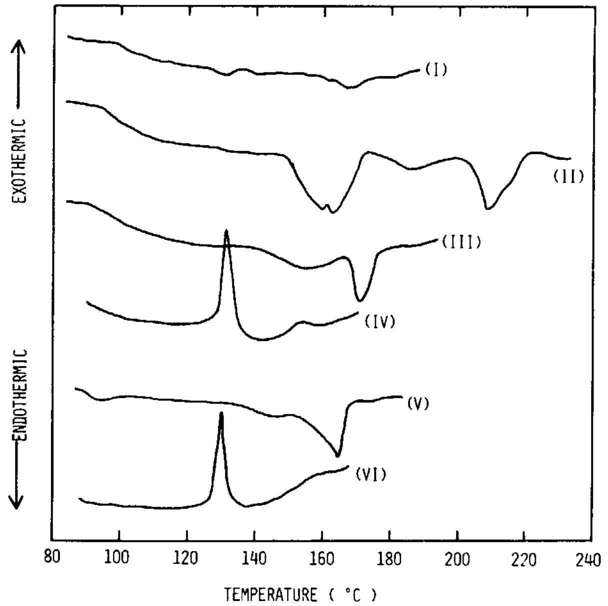

Fig. 5. DSC traces of tri-*O*-α-naphthylmethylcellulose: (I) first heating run at 5°C/min; (II) first heating run at 10°C/min; (III) first heating run at 20°C/min; (IV) first cooling run; (V) second heating run at 10°C/min; (VI) second cooling run.

## CONCLUSION

1. Melting points were observed for all tri-*O*-substituted cellulose ethers prepared from cellulose powder with the exception of tri-*O*-ally- and tri-*O*-methallylcelluloses.

2. X-ray analyses indicate that tri-*O*-substituted cellulose ethers have the periodicities which correlate with the size of the side groups. For tri-*O*-arylmethylcelluloses, the periodic intervals are about twice as much as the length or width of substituents.

3. Tri-*O*-benzyl-, tri-*O*-*p*-methylbenzyl-, tri-*O*-*p*-methoxybenzyl- and tri-*O*-*p*-bromobenzylcellulose showed the characteristics of thermotropic liquid crystal (smectic). Tri-*O*-$\alpha$-naphthylmethylcellulose showed the characteristic solid–smectic, smectic–nematic, and nematic–isotropic transformations. These results of microscopic observations coincide well with those of DSC analyses.

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## References

1. A. Isogai, A. Ishizu, and J. Nakano, *J. Appl. Polym. Sci.,* **29**, 2097 (1984).
2. A. Isogai, A. Ishizu, and J. Nakano, *J. Appl. Polym. Sci.,* **29**, 3873 (1984).
3. N. Migita et al. *Mokuzai-Kagaku I,* Kyoritsu, 1968, p. 228.
4. M. Yoshimura, *Sen-i Gakkai-shi,* **21**, 410 (1965).
5. C. Robinson, *Tetrahedron,* **13**, 219 (1961).
6. R. S. Werbowyj and D. G. Gray, *Mol. Liq. Cryst.,* **34**, 97 (1976).
7. R. S. Werbowyj and D. G. Gray, *Macromolecules,* **13**, 69 (1980).
8. H. Chanzy, M. Dube, and R. H. Marchessault, *J. Polym. Sci., Polym. Lett. Ed.,* **17**, 219 (1979).
9. H. Chanzy, A. Peguy, S. Chaunis, and P. Monzie, *J. Polym. Sci., Polym. Lett. Ed.,* **18**, 1137 (1980).
10. J. Bheda, J. F. Fellers, and J. L. White, *Coll. Polym. Sci.,* **258**, 1335 (1980).
11. S. Dayan, P. Maissa, M. J. Vellutini, and P. Sixou, *J. Polym. Sci., Polym. Lett. Ed.,* **20**, 33 (1982).
12. K. Shimamura, J. White, and J. F. Fellers, *J. Appl. Polym. Sci.,* **26**, 2165 (1981).
13. S. M. Aharoni, *J. Polym. Sci., Polym. Lett. Ed.,* **19**, 495 (1981).
14. S.-L. Tseng, A. Valents, and D. G. Gray, *Macromolecules,* **14**, 715 (1981).
15. S.-L. Tseng, G. V. Laivins, and D. G. Gray, *Macromolecules,* **15**, 1262 (1982).
16. S. N. Bhadani and D. G. Gray, *Macromol. Chem., Rapid Commun.,* **3**, 449 (1982).
17. K. Kageyama, K. Iiyama, A. Isogai, and J. Nakano, *Mokuzai-Gakkaishi,* to appear.
18. A. Blumstein, *Liquid Crystalline Order in Polymers,* Academic, New York, 1978, p. 31.
19. A. Blumstein, *Liquid Crystalline Order in Polymers,* Academic, New York, 1978, p. 30.

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