Preparation of Tri-*O*-Alkylcelluloses by the Use of a Nonaqueous Cellulose Solvent and Their Physical Characteristics

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Synopsis

Tri-*O*-methyl-, -ethyl-, -*n*-propyl-, -*n*-butyl-, -*n*-pentyl-, -iso-amyl-, -*n*-hexyl-, -*n*-heptyl-, -*n*-octyl-, -*n*-decyl-, and -3-phenoxypropyl-celluloses have been prepared with powdered sodium hydroxide and the corresponding alkyl iodides or bromides in one of nonaqueous cellulose solvents, SO_2–diethylamine–dimethylsulfoxide. These new tri-*O*-alkylcelluloses were characterized by infrared spectra, ^{13}C-NMR spectra, and optical rotations. The first six tri-*O*-alkylcelluloses described above were obtained as white powders and most of them (tri-*O*-methyl-, -ethyl-, -*n*-propyl-, and -*n*-pentyl-celluloses) showed thermotropic liquid crystals due to smectic or short pitch cholesteric phases. On the other hand, the latter five derivatives were obtained as gummy solids even at room temperature, and easily showed lyotropic liquid crystals in their concentrated chloroform solutions due to choresteric phases. Some of these tri-*O*-alkylcelluloses (tri-*O*-methyl-, -ethyl-, -*n*-propyl-, and -*n*-butyl-celluloses) were characterized by differential scanning calorimetric and X-ray diffractometric analyses.

INTRODUCTION

Cellulose ethers have been utilized in various fields using their chemical and physical characteristics. They are usually prepared by reactions of aqueous alkalicellulose with alkyl halides or epoxides. However, the heterogeneity of this reaction system as well as the presence of water in reaction media made it difficult to prepare cellulose ethers with high degrees of substitutions (DS), which may have some new characteristics.

Recently, the authors[1] succeeded in the quantitative preparation of tri-*O*-benzylcellulose by the use of powdered sodium hydroxide and benzyl chloride in one of nonaqueous cellulose solvents, an SO_2–diethylamine (DEA)–dimethylsulfoxide (DMSO) system. By this method, furthermore, many tri-*O*- substituted cellulose ethers containing chemically reactive aromatic rings and double bonds could be quantitatively prepared in one step,[2] and some of these cellulose derivatives were found to have some special thermal characteristics such as thermotropic liquid crystals.[3]

Alkylations of cellulose are thought to bestow some special characteristics on cellulose. These cellulose derivatives have possibilities to be utilized as column fillers for separation of, for example, racemi mixtures.[4] In one of eariler papers,[2] it was found that *n*-butylation of cellulose with *n*-butyl chloride and powdered NaOH in the cellulose solution yielded a poorly substituted ether (DS < 0.5), and methylation with methyl iodide brought about gelations of reaction mixtures, possibly by severe preparation con-

ditions. In another paper,[5] the authors succeeded in the quantitative preparation of tri-O-methylcellulose with powdered NaOH and methyl iodide in the cellulose solution under a milder condition than that for benzylation of cellulose. This new permethylation method is superior to the Hakomori's method[6] for structural analyses of various polysaccharides.

In this paper, therefore, this methylation method of cellulose were applied for preparation of n-alkylcelluloses by the use of powdered NaOH and alkyl iodides or bromides in the SO_2–DEA–DMSO system, and thermal and structural properties of new derivatives thus prepared were analysed by differential scanning calorimetries (DSC), X-ray diffractions and so on.

EXPERIMENTAL

Materials. Avicel (Asahi Chemical Ind. Co. Ltd., $\overline{DP}_v = 250$) was adopted as a cellulose sample, and used after drying at 105°C for 3 h. The pure grade DMSO was dried over molecular sieve 3A. Other solvents and reagents of pure grade were used without further purification.

Preparation of Cellulose Solutions. An SO_2/DMSO solution (ca. 0.3 g SO_2/mL) was prepared as described in the previous paper,[5] and the solution has been stored for 2 months in the dark without any degradations. One gram of cellulose was dispersed in 57 mL of DMSO, and this suspension was heated at 60°C for 0.5 h and then cooled to room temperature. The SO_2 solution containing 1.19 g of SO_2 and 1.91 mL of DEA were added successively to the suspension. A clear solution of cellulose (1.5%, wt/wt) was obtained under stirring within 10 min.

Preparation of Cellulose Ethers. Powdered NaOH was prepared quickly from flakes of NaOH (assay > 96%) in a mortar in air, and have been stored in a sample tube with a screw cap for at least 2 months. To the solution containing 1 g of cellulose, 9.7 g of powdered NaOH were added in N_2 atmosphere at room temperature, and the mixture was stirred for 1 h in N_2. Then, equimolecular amounts of alkyl iodide or bromide to NaOH were added dropwise at room temperature. When an alkyl iodide was used, the mixture was stirred at room temperature for 1 h and then heated at 40°C for 0.5 h, at 50°C for 0.5 h, and finally at 60°C for 1 h. If the mixture was solidified during stirring, minimum amounts of DMSO was added to return it to the slurry. On the other hand, when an alkyl bromide was used, the reaction mixture was heated to 90°C soon after the addition of reagent and stirred at that temperature for 6 h. After cooling to room temperature, highly substituted cellulose ethers were generally extracted with chloroform. Highly substituted ethyl-, n-propyl-, n-butyl-, n-pentyl-, and iso-amyl-celluloses were obtained as white powders by addition of methanol to concentrated chloroform extracts. Methylcelluloses with various DS were obtained as white powders by dialysis and subsequent lyophilization. On the other hand, highly substituted n-hexyl-, n-octyl-, and n-decyl-celluloses were obtained as gummy solids by the addition of methanol or acetoe to concentrated chloroform-extracts (see Tables I and III). When cellulose ethers could not be extracted with chloroform because of low DS, they were isolated by dialysis and subsequent lyophilization.

General Analyses. Infrared spectra were measured with a Shimazu model IR-400 Spectrometer by deposited film techniques from chloroform

TABLE I
Cellulose Ethers Prepared with Powdered NaOH and Alkyl Iodides in Cellulose Solution[a]

No.	Reagent	DS[b]	Form	$[\alpha]_{20}^{D}$ [c]
1	CH_3I	3	White powder	+11°
2	CH_3CH_2I	3	White powder	+15°
3	$CH_3CH_2CH_2I$	2.9	White powder	+5°
4	$(CH_3)_2CHI$	ca. 0.5	White powder	
5	$CH_3(CH_2)_2CH_2I$	3	White powder	+6°
6	$(CH_3)_2CHCH_2I$	ca. 0.5	White powder	
7	$CH_3CH_2CH(CH_3)I$	ca. 0.5	White powder	
8	$CH_3(CH_2)_3CH_2I$	3	White powder	−4°
9	$CH_3(CH_2)_4CH_2I$	3	Gummy solid	
10	$CH_3(CH_2)_5CH_2I$	3	Gummy solid	
11	$CH_3(CH_2)_6CH_2I$	3	Gummy solid	
12	ICH_2COONa	0.6[d]	White powder	

[a] The SO_2–DEA–DMSO system was used as a cellulose solvent.

[b] DS were roughly estimated by the absorption areas due to hydroxyl groups in infrared spectra of ethers.

[c] C 1.0, $CHCl_3$.

[d] Determined by ^{1}H-NMR method.

solutions or KBr disk techniques. Contents of sulfur were determined by the micro combustion method.[7] ^{1}H- and ^{13}C-NMR spectra were measured using JEOL MH-100 and JEOL FX 100 type spectrometers, respectively. Optical rotations were measured using Jasco SIP-4 Digital Polarimeter. Melting points and thermotropic liquid crystalline phases were observed using a Yanaco-micro melting point apparatus with crossed polarizers. Thermogravimetric (TG) and DSC curves were measured using a Rigaku-denki Standard Model TG and DSC as described in the previous paper.[3] X-ray diffraction patterns were measured as described in the previous paper.[3]

RESULTS AND DISCUSSION

Preparation of Alkylcellulose

Figure 1 shows the relation between the DS of methylcellulose prepared with methyl iodide or dimethylsulfate and the amounts of powdered NaOH as a base. The DS were calculated from methoxyl contents. Tri-*O*-methylcellulose could be prepared by the addition of more powdered NaOH than 12.5 mol/mol of a hydroxyl group in cellulose and methyl iodide by the use of the SO_2–DEA–DMSO system. It is interesting that this value is equal to those for the preparation of tri-*O*-benzyl- and tri-*O*-allylcellulose reported in the previous papers.[1,2] On the other hand, tri-*O*-methylcellulose could not be prepared with powdered NaOH and dimethylsulfate even by the use of the SO_2–DEA–DMSO system. Namely, the combinations of powdered NaOH and alkyl iodides are necessary for the preparation of tri-*O*-alkylcelluloses.

Table I shows the DS of alkylcelluloses prepared with powdered NaOH and various kinds of alkyl iodides in the cellulose solutions. As shown in
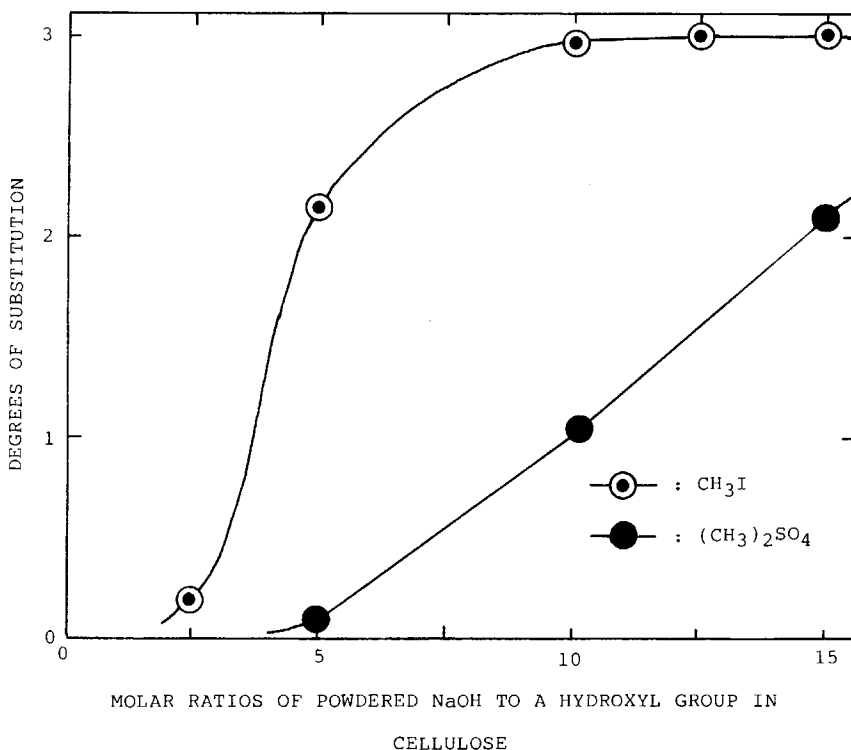
Fig. 1. Relation between degrees of substitution of methylcellulose and amounts of powdered NaOH and methylating reagents. The amounts of methyl iodide or dimethylsulfate added were equal to the moles of NaOH added.

the table, n-alkyl iodides gave the corresponding tri-O-alkylcelluloses in one step. Secondary alkyl iodides (nos. 4 and 7 in Table I), the primary alkyl iodide branched at β-carbon (no. 6) and sodium iodoacetate (no. 11), however, could not give cellulose ethers with high DS. The low DS of cellulose ethers prepared with secondary alkyl iodides can be explained to be ascribed to elimination reactions which occur to the reagents themselves to yield alkenes under basic conditions and thus compete with substitution reactions. Alkyl iodides such as isobutyl iodide (no. 6) also react with NaOH to produce the corresponding alkenes by rearrangements of carbocations. The low DS of carboxymethylcellulose (no. 12) is suggested to be due to ionic factors and/or low solubility of sodium iodoacetate in DMSO. On the other hand, n-alkyl iodides can react with Cell-O$^-$ and OH$^-$ to produce cellulose ethers and alcohols as byproducts, respectively, by S$_N$2.

As shown in Table I, tri-O-methyl-, tri-O-ethyl-, tri-O-n-propyl-, tri-O-n-butyl, and tri-O-n-pentyl-celluloses were obtained quantitatively as white powders by addition of methanol or acetone to concentrated chloroform-extracts. On the other hand, tri-O-n-hexyl-, tri-O-n-heptyl-, and tri-O-n-octyl-celluloses were obtained quantitatively as gummy solids by the same method. This may be ascribed to the prevention of chain arrangement, which is caused by the introductions of large amounts of flexible long aliphatic chains onto cellulose. Okamura et al.[8] reported that highly substi-

tuted cellulose esters having long aliphatic chains were obtained as white powders. However, those cellulose esters prepared by acylations of cellulose powder with trifluoroacetic anhydride and various kinds of aliphatic acids seems to contain some trifluoro ester groups together with aliphatic ester groups.[9]

Figure 2 shows the infrared spectra of tri-*O*-aklylcelluloses prepared with *n*-alkyl iodides. The absorptions around 2800–3000 cm^{-1} due to C—H stretching vibrations and at 1450 and 1360 cm^{-1} due to C—H bending vibrations increased with the increase in chain length of substituents. No other reactions than *n*-alkylations, such as oxidation, were shown to occur in Figure 2.

Table II shows the results obtained by ^{13}C-NMR spectroscopies of tri-*O*-methyl-, tri-*O*-ethyl-, tri-*O*-*n*-propyl-, and tri-*O*-*n*-butyl-celluloses. The chemical shifts of the corresponding carbons in glucose residues were roughly equal each other among four tri-*O*-alkylcelluloses.

As described above, new cellulose ethers completely substituted with long aliphatic chains could be prepared by the use of alkyl iodides. Alkyl iodides, however, are somewhat expensive and the kinds of them are limited. Thus, tri-*O*-alkylations of cellulose were attempted by the use of alkyl bromides under more severe conditions than those used for alkylation with alkyl iodides.
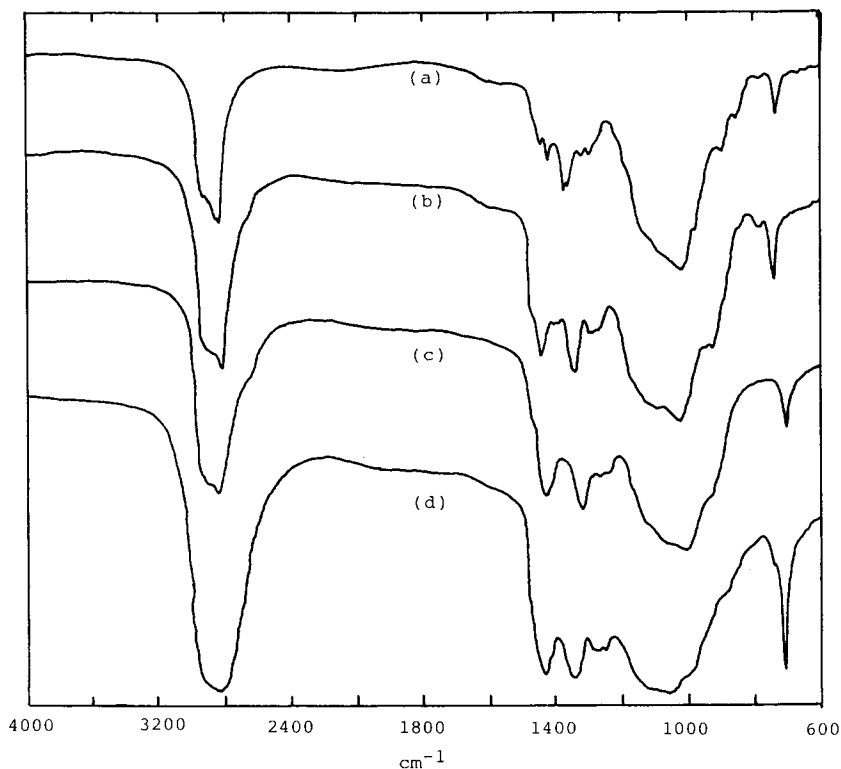

Fig. 2. Infrared spectra of tri-*O*-*n*-alkylcelluloses: (a) ethyl-; (b) *n*-butyl-; (c) *n*-hexyl-; (d) *n*-octyl-.

TABLE II

Chemical Shifts (ppm) of Tri-O-Alkylcelluloses Measured by ^{13}C-NMR Spectroscopies

Tri-O-Alkylcellulose	Glucose residue						Substituent[a]			
	C1	C2	C3	C4	C5	C6	C_α	C_β	C_γ	C_δ
Methyl	103.1	83.7	85.1	77.5	74.9	70.4	⎧59.1[b] ⎨60.4 ⎩60.6			
Ethyl	103.0	82.1	82.6	77.4	75.3	68.8	⎧66.6 ⎨68.4 ⎩68.8	⎧15.2 ⎨15.6 ⎩15.7		
n-Propyl	102.6	82.2	83.8	77.2	76.7	68.7	⎧72.9 ⎨74.9 ⎩75.6	⎧23.4 ⎨23.5 ⎩23.6	⎰10.5 ⎱10.6	
n-Butyl	102.8	82.3	84.0	77.0	75.6	68.7	⎧71.1 ⎨73.1 ⎩73.4	⎰32.6 ⎱32.3	⎰19.5 ⎱19.9	⎰14.2 ⎱14.3

[a] Greek letters mean the position of carbons in substituents. C_α is the nearest carbon to glucose residues.
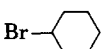
[b] Three values in each set means chemical shifts of carbons linked to C2, C3, and C6.

Table III shows the DS of cellulose ethers prepared with alkyl bromides by the method described in the Experimental section. Tri-*O*-alkylcelluloses have been prepared quantitatively with *n*-alkyl bromides (nos. 13, 14, 15, 17, 18, 19, and 20), with an alkyl bromide branched at the γ-position (no. 16) and with an alkyl bromide substituted at γ-position (no. 21). On the other hand, secondary alkyl bromide (no. 29), alkyl bromides whose β-carbons easily produce carbocations by rearrangements (nos. 26 and 27) and alkyl bromides containing an ionic group (nos. 22, 23, 24, and 25) could not give highly substituted cellulose ethers as observed in alkylations with iodine compounds (Table I). Tri-*O*-iso-amylcellulose (no. 16) was prepared quantitatively as white powders, whereas tri-*O*-*n*-alkylcelluloses containing longer chains than *n*-pentyl group were prepared as gummy solid as shown in cellulose ethers prepared with alkyl iodides, although yields were quantitative.

Thermal and Structural Characteristics of Tri-*O*-Alkylcelluloses

In the previous paper,[3] thermal and structural characteristics of tri-*O*-substituted cellulose ethers containing aromatic rings and double bonds prepared by the use of the SO_2–DEA–DMSO system were investigated, and it was found that they had special X-ray diffraction patterns, DSC curves, melting and degradation points and some of those derivatives

TABLE III
Cellulose Ethers Prepared with Powdered NaOH and Alkyl Bromides in the Cellulose Solution[a]

No.	Reagent	DS	Form
13	$CH_3CH_2CH_2Br$	3	White powder
14	$CH_3(CH_2)_2CH_2Br$	3	White powder
15	$CH_3(CH_2)_3CH_2Br$	3	White powder
16	$(CH_3)_2CHCH_2CH_2Br$	3	White powder
17	$CH_3(CH_2)_4CH_2Br$	3	Gummy solid
18	$CH_3(CH_2)_5CH_2Br$	3	Gummy solid
19	$CH_3(CH_2)_6CH_2Br$	3	Gummy solid
20	$CH_3(CH_2)_8CH_2Br$	3	Gummy solid
21	$C_6H_5OCH_2CH_2CH_2Br$	3	Gummy solid
22	$BrCH_2COOH$	0.8[b]	White powder
23	$BrCH_2CH_2COOH$	0.4[b]	White powder
24	$BrCH_2CH_2SO_3Na$	1.8[c]	White powder
25	$BrCH_2CH_2NH_2 \cdot HBr$	0.1[d]	White powder
26	Br—⟨ ⟩	ca. 0.5	White powder
27	$BrCH_2CH(OEt)_2$	ca. 0.5	White powder
28	$BrCH_2CH_2C_6H_5$	ca. 0.5	White powder
29	$BrCH(C_6H_5)_2$	ca. 0.1	White powder

[a] See Table I.
[b] Determined by ^{1}H-NMR method.
[c] Determined by sulfur contents.
[d] Determined by nitrogen contents.

showed thermotropic liquid crystals. Therefore, tri-O-n-alkylcelluloses were also expected to have some specific physical properties.

Table IV shows thermal properties of tri-O-alkylcelluloses. The first five derivatives had melting points at higher than 160°C, whereas the last four derivatives were gummy solid even at room temperature. Tri-O-methylcellulose showed the thermotropic liquid crystal from 190 to 220°C on heating run, and this characteristic could be observed during the course of cooling from 210°C to room temperature on a hot stage with crossed polarizers. Judging from microscopic observations, this liquid crystal seemed to be due to smectic or short pitch cholesteric phases,[10] and this polarization could be observed at room temperature after melting. Smectic and cholesteric states are known to be maintained quite often in glassy states, too. Tri-O-n-propyl- and -n-pentyl-celluloses also showed the enantiotropic thermotropic liquid crystal. Tri-O-ethylcellulose showed monotropic thermotropic liquid crystal, but tri-O-n-butylcellulose did not show such liquid crystals.

On the other hand, the last four tri-O-n-alkylcelluloses in Table IV showed easily lyotropic liquid crystals in their concentrated chloroform solutions. Recently, lyotropic liquid crystalline properties of cellulose[11] and cellulose derivatives[12-16] have been found in succession, and the properties have been widely investigated. However, several delicate conditions are generally required for the formations of lyotropic liquid crystalline states. In the case of tri-O-n-alkylcelluloses, rainbow colored states could be easily observed during evaporation of their chloroform solutions, and these states were stable for more than 1 month at room temperature. These lyotropic liquid crystals are due to cholesteric phases as reported in other cellulose[11] and cellulose derivatives.[12-16]

Figure 3 shows DSC traces of the first four tri-O-alkylcelluloses in Table IV. Tri-O-methyl- and tri-O-n-propyl-celluloses have relatively broad and small endothermic peak in the heating run due to solid–liquid crystalline states transformation points around 200°C. The starting point of each peak coincided with each melting point or liquid crystal-isotropic transformation point observed by microscope (Table IV). In second heating runs of tri-O-methyl-, tri-O-ethyl-, and tri-O-n-butyl-celluloses, two split sharp peaks appeared, corresponding to the broad peak in first heating runs. The appearance of these two peaks may be due to the formations of two crystals different in forms or sizes by melting.[17] A single sharp exothermic peaks were observed in every cooling run.

Figure 4 shows X-ray diffraction patterns of four tri-O-alkyl celluloses. In the previous paper,[3] the authors reported that tri-O-substituted cellulose ethers containing aromatic rings and double bonds have peaks at small angles (2θ) due to the substitutents and that there is a positive relation between the lengths of substituents and the values of 2θ. As shown in Figure 4, tri-O-ethyl-, tri-O-n-propyl-, and tri-O-n-butyl-celluloses had relatively large peaks consisting of two peaks, and, in these three cellulose ethers, the longer the chains of substituents were, the smaller the peak angles of the corresponding cellulose ethers. A similar tendency was found in the DSC curves in Figure 3, too. Namely, cellulose ethers containing longer range orders in their structures have melting peaks or liquid crystal–isotropic transformation peaks at lower temperature.

TABLE IV
Thermal Properties of Tri-*O*-Alkylcelluloses

Cellulose ether	td[a]	mp[b]		Remarks
Tri-*O*-methylcellulose	320°C	220°C	Heating run: Cooling run:	190°C→220°C, liquid crystal[c] 210°C→room temp, liquid crystal[c]
Tri-*O*-ethylcellulose	330°C	200°C	Cooling run:	260°C→room temp, liquid crystal[c]
Tri-*O-n*-propylcellulose	310°C	230°C	Heating run: Cooling run:	180°C→230°C, liquid crystal[c] 220°C→room temp, liquid crystal[c]
Tri-*O-n*-butylcellulose	330°C	195°C		
Tri-*O-n*-pentylcellulose	—	165°C	Heating run: Cooling run:	130°C→165°C, liquid crystal[c] 155°C→room temp, liquid crystal[c]
Tri-*O-n*-hexylcellulose				
Tri-*O-n*-heptylcellulose	Gummy solids at room temp			Lyotropic liquid crystals in concentrated CHCl₃ solutions
Tri-*O-n*-octylcellulose				
Tri-*O-n*-decylcellulose				

[a] Degradation points were measured by thermogravimetric curves.
[b] Melting points.
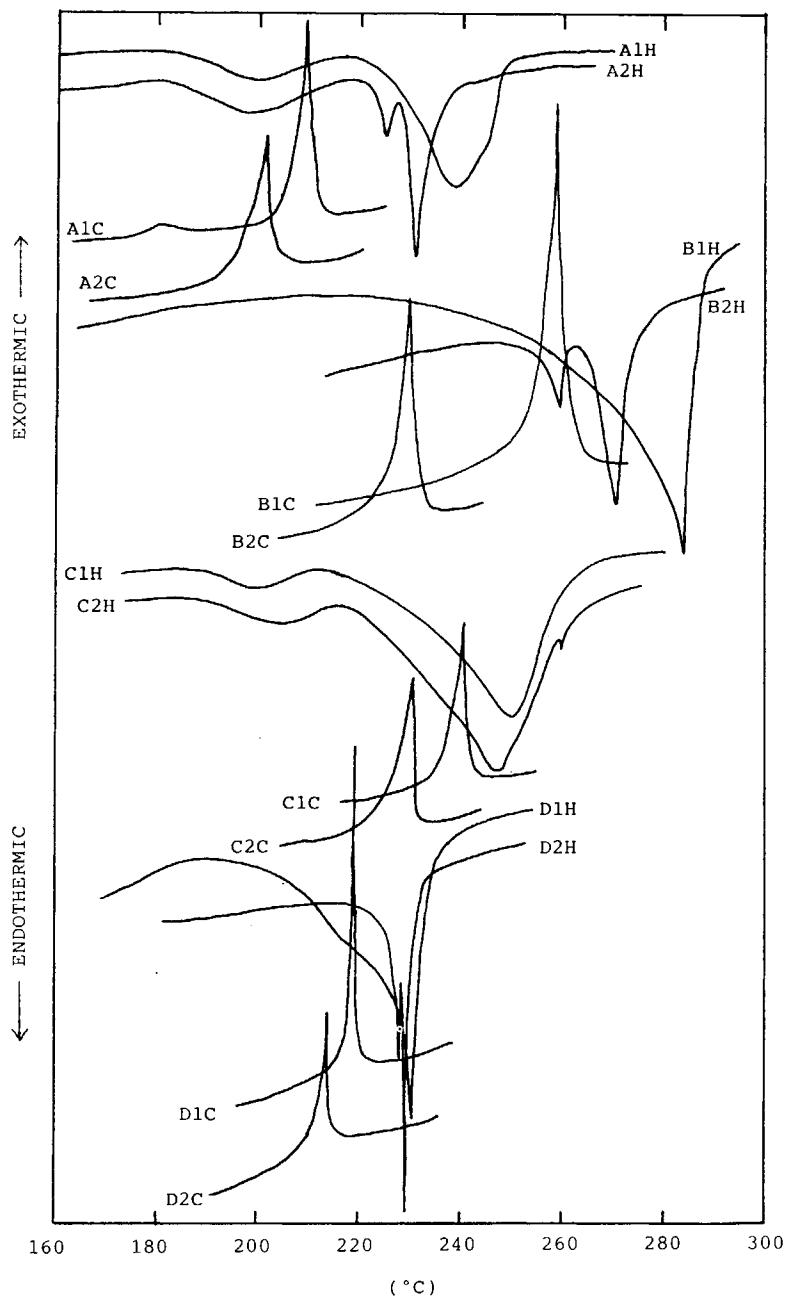[c] Thermotropic liquid crystals were measured on a hot stage with crossed polarizers.

Fig. 3. DSC traces of tri-O-alkylcelluloses: (A) tri-O-methyl cellulose; (B) tri-O-ethylcellu-lose; (C) tri-O-n-propylcellulose; (D) tri-O-n-butylcellulose. 1H = first heating run, 1C = first cooling run, 2H = second heating run, 2C = second cooling run.

On the other hand, tri-O-methylcellulose had a unique X-ray diffraction pattern. Although the methyl group is smaller than the other substituents of four derivatives, it had a relatively broad single peak due to a relatively long range order (11 Å). This unique property may be caused by the prep-
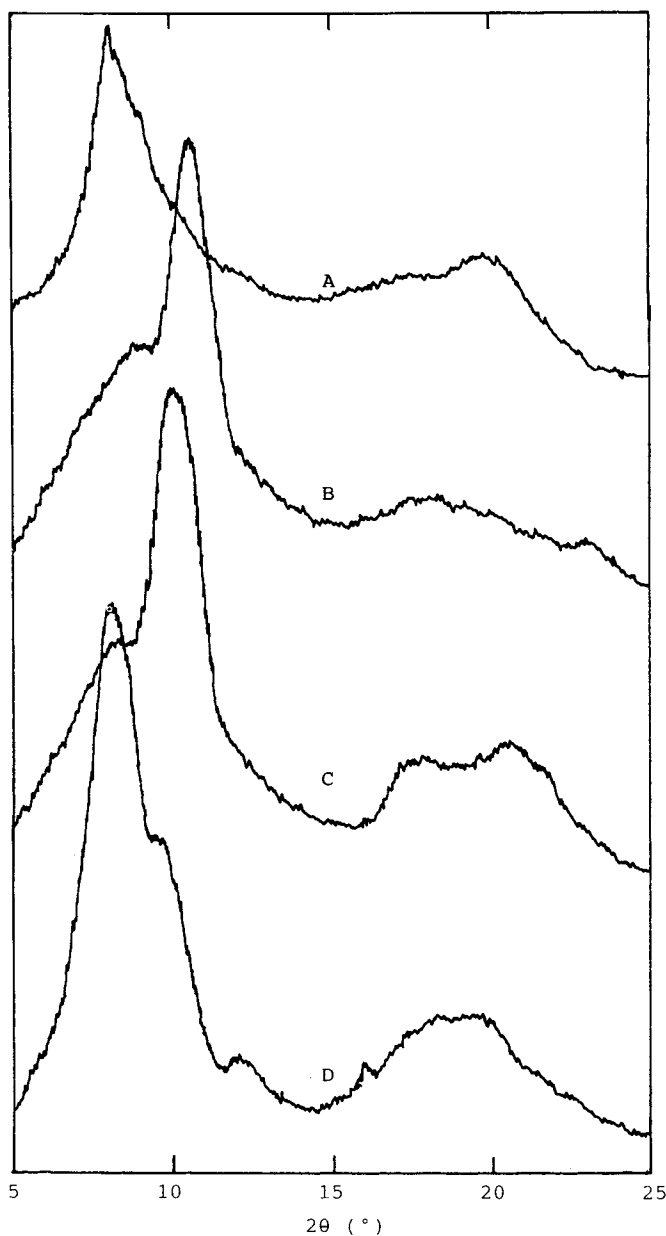
Fig. 4.   X-ray diffraction pattern: (A) tri-O-methylcellulose; (B) tri-O-ethylcellulose; (C) tri-O-n-propylcellulose; (D) tri-O-n-butylcellulose.

aration method of tri-O-methylcellulose. As described in the Experimental section, it was obtained by dialysis and subsequent lyophilization, differing from the other three products (tri-O-ethyl-, tri-O-n-propyl-, and tri-O-n-butyl-celluloses), which were obtained as white powders by addition of methanol to concentrated chloroform solutions. Tri-O-methylcellulose, therefore, may have a special crystal structure.

SUMMARY

1. Tri-*O*-alkylcelluloses could be prepared with powdered NaOH and corresponding iodides or bromides in cellulose/SO_2–DEA–DMSO solutions.

2. Linear primary alkyl bromides and iodides, and those branched or substituted at γ-positions could give the corresponding tri-*O*-alkylcelluloses.

3. Tri-*O*-methyl-, tri-*O*-ethyl-, tri-*O*-*n*-propyl-, tri*O*-*n*-butyl-, tri-*O*-*n*-pentyl-, and tri-*O*-iso-amyl-celluloses were obtained as white powders, and some of them showed thermotropic liquid crystalline states (smectic or short pitch cholesteric).

4. Tri-*O*-*n*-hexyl-, tri-*O*-*n*-heptyl-, tri-*O*-*n*-octyl-, tri-*O*-*n*-decyl-, and tri-*O*-3-phenoxypropyl-celluloses were obtained as gummy solids, and all of them showed liquid crystalline states (choresteric) easily.

5. Tri-*O*-alkylcelluloses showed characteristic DSC curves and X-ray diffraction patterns depending on substituents.

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