# Cationic Graft Copolymerization of Tetrahydrofuran onto Bromodeoxycellulose

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SYNOPSIS

Cationic graft copolymerization of tetrahydrofuran onto halodeoxycelluloses, which were prepared under homogeneous conditions, was studied with silver tetrafluoroborate as an initiator. 6-Bromo-6-deoxycelluloses gave graft copolymers, insoluble but swollen in tetrahydrofuran, whereas chlorodeoxycelluloses gave no graft copolymer. The graft copolymers were hydrolyzed in 2*N* HCl to give hydrolyzate solutions and insoluble solids. The hydrolyzate was found to be composed of 6-*O*-(4-hydroxybutyl)glucose and 6-*O*-(9-hydroxy-5-oxanonyl)glucose as well as oligomers of tetrahydrofuran by gas chromatography and gas chromatography–mass spectrometry after trifluoroacetylation. The insoluble solid was cross-linked polyoxytetramethylene, which could be hydrolyzed only very slowly in 2*N* HCl to yield oligomers of tetrahydrofuran. Thermal behavior of the graft copolymer was compared with that of cellulose and of homopolymer of tetrahydrofuran. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Chlorination of cellulose has been extensively studied[1] and chlorodeoxycellulose (Cell-Cl) has often been used as a starting material for the preparation of cellulose derivatives such as 6-azide-6-deoxycellulose[2] and 6-amino-6-deoxycellulose[3] by nucleophilic substitution reactions. Bromodeoxycellulose (Cell-Br) could be more appropriate than Cell-Cl as a substrate for nucleophilic substitution reactions since bromine is a better leaving group than is chlorine.[4] However, reaction of Cell-Br has not been explored much, mostly because no convenient method had been reported until recently for the synthesis of Cell-Br.

In a previous article[5] we reported a facile synthesis of Cell-Br under homogeneous conditions with *N*-bromosuccinimide and triphenylphosphine (TPP) in a new cellulose solvent, a mixture of LiBr and *N*,*N*-dimethylacetamide (DMA). Bromination took place selectively at C-6 positions and the degree of substitution (*DS*) by bromine of Cell-Br samples reached up to 0.9. Chlorination of cellulose was studied also with *N*-chlorosuccinimide and TPP in a mixture of LiCl and DMA.[6] The maximum *DS* attained in the chlorination was 1.9.

Certain silver salts such as $AgBF_4$ and $AgSbF_6$ initiate cationic ring-opening polymerization of tetrahydrofuran (THF) with suitable organic halides.[7] This initiation system was applied for graft and block copolymerizations of THF with halogen-containing polymers such as poly(vinyl chloride)[8] and $\alpha$-brominated polystyrene.[9] Feger and Cantow[10-12] reported the synthesis of cellulose-*b*-polyoxytetramethylene from HCl-treated trimethylcellulose and THF with $AgSbF_6$.

In this article, the reaction of THF with halodeoxycellulose (Cell-X) samples in the presence of $AgBF_4$ is described as an attempt to synthesize cellulose-*g*-polyoxytetramethylene (Cell-*g*-POTM), which is composed of soft and hydrophobic branches of polyoxytetramethylene (POTM) and a hard, hydrophilic trunk polymer of cellulose. Cell-Br samples reacted with THF to yield insoluble graft copolymers with apparent graft % of 102–326, whereas Cell-Cl samples did not react.

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## EXPERIMENTAL

### Materials

Cell-X samples used in this study were synthesized from microcrystalline cellulose (Art 2331 Cellulose mikrokristallin, Merck) by homogeneous halogenation with *N*-halosuccinimide/TPP.[5,6] Halogen contents of the samples were determined by an oxygen-flask combustion method.[13] The *DS* by halogen was calculated from the halogen content.

Commercial THF was dehydrated with sodium wire and distilled. Ethyl acetate was washed with water, dehydrated with magnesium sulfate, and distilled. Organic halides were distilled just before use. $AgBF_4$ (Wako Pure Chemical Ind.) was stored in pentane at 6°C, and the pentane was removed under reduced pressure just before use. $AgSbF_6$ (PCR Inc.) was used without further purification.

### Polymerization of THF with Silver Salt and Organic Halide

$AgBF_4$ or $AgSbF_6$ was put into a Schlenk tube. The tube was evacuated and filled with nitrogen. This cycle was repeated several times to replace air completely with nitrogen. THF was added to the Schlenk tube by a trap-to-trap method. The Schlenk tube was weighed after the addition of each reagent. Alkyl halide was added at −78°C using a microsyringe. The weight of the alkyl halide used was determined from the difference between the weights of the microsyringe before and after injection of alkyl halide. The content was stirred by a magnetic stirrer while the temperature was raised gradually from −78°C to room temperature. The content was stirred further at room temperature for 3 days or until the solution became too viscous for stirring. The reaction mixture was poured into 2*N* ammonia to obtain POTM. POTM was dissolved in ethyl acetate and the solution was washed with 2*N* ammonia several times until the washings became free from silver ions. The solution was evaporated to obtain POTM as a white solid, which was dried under reduced pressure.

### Graft Copolymerization of THF onto Cell-X

Graft copolymerization of THF onto Cell-X was carried out using almost the same procedure as described above. A Cell-X sample (0.2 g) was added to a Schlenk tube before the addition of THF. In this case, the reaction system was a suspension throughout the reaction. After 1 week at room temperature, the suspension was poured into 2*N* ammonia and the precipitates obtained were washed with 2*N* ammonia until the washings became free from silver ions. The graft copolymers were extracted with ethyl acetate to remove the POTM and dried under reduced pressure.

### Measurements

The molecular mass of POTM was calculated from the intrinsic viscosity in ethyl acetate at 30°C.[14] The apparent graft % was calculated according to the following equation:

$$G\% = \frac{(\text{Weight of Cell-}g\text{-POTM}) - (\text{Weight of Cell-X used})}{\text{Weight of Cell-X used}} \times 100 \quad (1)$$

Infrared spectra were recorded on a Fourier-transform infrared spectrophotometer FT/IR-3 (Nihon Bunko Co.). POTM samples were measured as a film and other samples were in KBr disks. Differential thermal analysis and thermogravimetry were carried out with a Shimadzu DT-40 thermal analyzer at a heating rate of 10°C/min in $N_2$ (flow rate, 50 mL/min).

Cell-*g*-POTM samples were hydrolyzed for gas chromatography and gas chromatography–mass spectrometry in 2*N* HCl under reflux for 4 h. The filtered solutions were evaporated and the hydrolyzates were converted into *O*-trifluoroacetyl derivatives by the reaction with trifluoroacetic anhydride in dichloromethane at 100°C for 20 min.[15] The stationary phase used was Silicone GE SE-30 coated on Gas Chrom Q (100–120 mesh) and the details of operation conditions for gas chromatography and gas chromatography–mass spectrometry were the same as those previously reported.[6]

## RESULTS AND DISCUSSION

### Polymerization of THF with Various Alkyl Halides

Dreyfuss and Kennedy[7] studied the cationic polymerization of THF with various organic chlorides in the presence of inorganic salts and concluded that the reactivity of organic chlorides was in the order acyl > allyl ≥ benzyl > tertiary > secondary > primary ≈ 0. Reactivity of organic bromides was not studied in their work and they did not much describe $AgBF_4$ and $AgSbF_6$, which we intended to use in this work.

As a model for graft copolymerization of THF onto Cell-X, polymerization of THF with simple

**Table I Polymerization of THF with Silver Salts and Organic Halides**

| | Organic Halide | | Ag | THF | Reaction | Yield | |
|---|---|---|---|---|---|---|---|
| | RX | (mmol) | (mmol) | (g) | Time | (%) | *DP* |
| $AgBF_4$ | *n*-BuCl | 0.553 | 0.520 | 7.261 | 3 days | No reaction | — |
| | *sec*-BuCl | 0.312 | 0.313 | 7.298 | 3 days | No reaction | — |
| | BzCl | 3.91 | 3.63 | 7.853 | 2.5 h | 76.5 | 93 |
| | *n*-BuBr | 0.371 | 0.231 | 9.187 | 3 days | 51.3 | 1276 |
| | *i*-PrBr | 0.240 | 0.225 | 7.873 | 3 days | 36.8 | 922 |
| $AgSbF_6$ | *n*-BuCl | 0.370 | 0.416 | 7.471 | 3 days | No reaction | — |
| | *sec*-BuCl | 0.553 | 0.530 | 9.440 | 3 days | No reaction | — |
| | BzCl | 0.509 | 0.499 | 6.152 | 2.5 h | 24.0 | 622 |
| | *n*-BuBr | 0.350 | 0.421 | 7.219 | 3 days | 8.5 | 182 |
| | *i*-PrBr | 0.381 | 0.380 | 8.449 | 3 days | 75.9 | 844 |

halides, i.e., *n*-butyl and *sec*-butyl chlorides and *n*-butyl and isopropyl bromides, was studied in combination with $AgBF_4$ or $AgSbF_6$ (Table I). The molar amounts of the silver salts used were approximately equal to those of the halides. None of the chlorides gave POTM either with $AgBF_4$ or $AgSbF_6$. On the other hand, both bromides induced polymerization of THF with each of the silver salts. Polymerization of THF with benzyl chloride was also studied for comparison. In this case, polymerization took place more rapidly than with the bromides.

The effect of the presence of polar compounds, water, methanol, and glucose pentaacetate on the polymerization of THF was studied with benzyl chloride and $AgSbF_6$ (Table II). Water and methanol retarded the polymerization more significantly than did acetate, but it was still possible to obtain POTM in the presence of these polar compounds. This finding implies that both unmodified Cell-Br with free hydroxyl groups and acetylated Cell-Br could yield graft copolymers.

## Graft Copolymerization of THF onto Bromodeoxycellulose

The Cell-Cl and Cell-Br samples used in this study were prepared from microcrystalline cellulose under homogeneous conditions with *N*-chlorosuccinimide/TPP in LiCl/DMA[6] and with *N*-bromosuccinimide/TPP in LiBr/DMA,[5] respectively. Cell-Cl samples with *DS* values up to 0.8 contained 6-chloro-6-deoxyglucose (6-Cl-Glc) and unmodified glucose (Glc) units, and those with higher *DS* values contained 3,6-dichloro-3,6-dideoxyallose (3,6-$Cl_2$-All) and 6-Cl-Glc units. Cell-Br samples prepared in LiBr/DMA contained 6-bromo-6-deoxyglucose (6-Br-Glc) and Glc units. Bromination at C-3 positions did not take place under the conditions studied.

Cell-Cl samples, even those with high *DS* values containing 3,6-$Cl_2$-All units, did not give graft copolymers when treated with THF in the presence of $AgBF_4$ or $AgSbF_6$. Cell-Cl samples with a low *DS* that did not contain 3,6-$Cl_2$-All units were acetylated under homogeneous conditions in LiCl/DMA in a way similar to that of Yabune and Utida.[16] Acetylated Cell-Cl samples also did not give graft copolymers with THF in the presence of $AgBF_4$ or $AgSbF_6$. These results are consistent with those of the model experiments with primary and secondary alkyl chlorides.

Graft copolymerization of THF onto Cell-Br samples with *DS* values around 0.9 was studied next with $AgBF_4$ as an initiator. This initiator was chosen because it gave POTM in a conversion higher than

**Table II Effects of Hydroxyl and Acetyl Groups on Polymerization of THF**

| Hydroxy or Acetyl Compound | Molar Ratio[a] | Time (h) | $AgSbF_6$ (mmol) | BzCl (mmol) | THF (g) | Yield (%) | *DP* |
|---|---|---|---|---|---|---|---|
| Water | 0.5 | 72 | 0.496 | 0.508 | 15.16 | 41.5 | 401 |
| Methanol | 0.4 | 93 | 0.313 | 0.307 | 8.908 | 20.6 | 256 |
| Glucose pentaacetate | 1.0 | 17 | 0.465 | 0.456 | 8.163 | 38.9 | 855 |

[a] Molar ratio of each functional group to $AgSbF_6$.

**Table III Graft Copolymerization of THF onto Cell-Br[a]**

| Run | Cell-Br | | Ag/Br (mol/mol) | THF/Cell-Br (g/g) | Cell-*g*-POTM | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Br% | *DS* | | | G% | Br% | $DS_{Br}$[b] | $DS_G$[b] | $DP_G$[b] |
| 1 | 33.0 | 0.91 | 9.96 | 210.0 | 102 | 2.88 | 0.16 | 0.75 | 5.0 |
| 2 | 33.0 | 0.91 | 2.59 | 50.1 | 127 | 6.66 | 0.42 | 0.50 | 8.7 |
| 3 | 32.6 | 0.89 | 0.36 | 92.9 | 326 | 3.59 | 0.42 | 0.47 | 21.8 |
| 4 | 36.0 | 1.02 | 0.31 | 88.5 | 253 | 3.83 | 0.38 | 0.64 | 13.3 |

[a] Polymerization was carried out for 7 days at room temperature in the presence of $AgBF_4$.
[b] Calculated from *G*% and Br% of Cell-*g*-POTM and *DS* by bromine of Cell-Br using Eqs. (6)–(8).

that with $AgSbF_6$ when *n*-butyl bromide was used for the polymerization of THF. During the reaction, formation of silver bromide was observed. The reaction mixture (suspension) did not become so viscous as in the model experiment. The mixture was poured into aqueous ammonia and precipitates were collected. Silver bromide and POTM were removed by extraction with aqueous ammonia and ethyl acetate, respectively.

Table III shows the effect of molar ratio (from 0.3 to 10) of the silver salt to 6-Br-Glc unit. Graft copolymers were obtained in all cases. The apparent graft % values (*G*%) ranged from 100 to 300 and tended to increase with decreasing molar ratio.

Cameron and Sarmouk[17] reported the graft copolymerization of THF onto brominated butyl rubber with $AgClO_4$. In their case, homopolymerization of THF took place in a high yield when a large excess of the silver salt was used at temperatures above 0°C. In the present study, $AgBF_4$ was added to the reaction system at −78°C, and the temperature of the reaction mixture was slowly raised to room temperature and kept long at this temperature for the polymerization. The initiation was considered to occur rapidly at −78°C with accessible 6-Br-Glc units in the solid Cell-Br. The amount of homopolymer (POTM) extracted was only 5.9% of the recovered material when a large excess of $AgBF_4$ was used (Run 1 in Table III). This amount of homopolymer is much smaller than that observed in the case of brominated butyl rubber.[17]

It was attempted to calculate *DS* by bromine ($DS_{Br}$), *DS* by POTM branch chain ($DS_G$), and number-average degree of polymerization (*DP*) of POTM branch chain ($DP_G$) from the bromine content and *G*%. Average molecular masses of the repeating unit of Cell-*g*-POTM ($M_1$) and Cell-Br used ($M_2$) are defined as

$$M_1 = (1 - DS_0) \times M_{Glc} + DS_{Br} \times M_{Br} + DS_{POTM} \times (72 \times DP_G + M_{Glc}) \quad (2)$$

$$M_2 = (1 - DS_0) \times M_{Glc} + DS_0 \times M_{Br} \quad (3)$$

where $M_{Glc}$ and $M_{Br}$ are molecular mass of the glucose repeating unit (162.1) and the 6-Br-Glc unit (225.0), respectively. $DS_0$ is *DS* by bromine of the Cell-Br used. Using $M_1$ and $M_2$, *G*% and Br% are represented as

$$G\% = (M_1 - M_2) \times 100/M_2 \quad (4)$$

$$\mathrm{Br}\% = 79.9 \times DS_{Br} \times 100/M_1 \quad (5)$$

From Eqs. (2)–(5), we obtained the following equations:

$$DS_{Br} = A \times (B + C \times DS_0) \times \mathrm{Br}\%/D \quad (6)$$

$$DS_G = DS_0 - DS_{Br} \quad (7)$$

$$DP_G = \frac{A \times (B + C \times DS_0) \times (D - C \times \mathrm{Br}\%) - B \times D}{72.11 \times \{D \times DS_0 - 72.11 \times (1 - A) \times (B + C \times DS_0)\}} \quad (8)$$

where *A*, *B*, *C*, and *D* are 1 + *G*%/100, 162.1, 62.9 ($M_{Br} - M_{Glc}$), and 79.9 × 100, respectively.

$DS_{Br}$, $DS_G$, and $DP_G$ values calculated with Eqs. (6)–(8) for Cell-*g*-POTM are also shown in Table III. Except for Run 1 where a very excessive amount of $AgBF_4$ was used, about one-half (only 52.8–62.7%) of bromine atoms in Cell-Br were used to initiate graft copolymerization of THF. These values appear relatively high if we consider that the reaction proceeds under heterogeneous conditions: Cell-Br is not soluble or swollen in THF.

$DP_G$ values (5–22) of Cell-*g*-POTM samples are much lower than the *DP* values of POTM obtained in the model experiments, suggesting that chain transfer and/or termination takes place in case of graft copolymerization. Franta et al.[18] studied the kinetics of polymerization of THF with benzyl chloride and $AgSbF_6$ and concluded that the initiation reaction proceeded rapidly and no termination

**Table IV Attempted Graft Copolymerization of THF onto Acetylated Cell-Br[a]**

| Initiator | | BDCA[b] | Br | THF | Time | $G$% |
|---|---|---|---|---|---|---|
| AgX | mmol | (mg) | (mmol) | (g) | (Day) | (%) |
| $AgSbF_6$ | 0.626 | 50.2 | 0.158 | 11.048 | 18 | 18.9 |
| $AgBF_4$ | 0.699 | 49.8 | 0.157 | 13.853 | 16 | 47.9 |

[a] Br% = 25.2%, $DS_{Br}$ = 0.9, $DS_{Ac}$ = 1.7.
[b] Acetylated cell-Br.

took place. In our case, Cell-Br bears unprotected hydroxyl groups and such polar groups may cause chain transfer and/or termination. Feger and Cantow[10-12] used trimethylcellulose with a glycosyl chloride terminal for the block copolymerization of THF so that chain transfer or termination could not occur. Methylation of hydroxyl groups of Cell-Br, however, is not suitable for the protection of the hydroxyl groups in the present case because C—Br bonds would be broken during methylation under strongly alkaline conditions. Possible methods for the protection of the hydroxyl groups include esterification.

A Cell-Br sample was acetylated under homogeneous conditions in a way similar to the acetylation of Cell-Cl but in LiBr/DMA. The acetylated Cell-Br with $DS$ by bromine of 0.9 and $DS$ by acetyl of 1.7 was subjected to graft copolymerization of THF with $AgBF_4$ or $AgSbF_6$ at room temperature for more than 2 weeks (Table IV). The $G$% of the products were only 47.9 and 18.9 for $AgBF_4$ and $AgSbF_6$, respectively. Judging from the results of the model experiments (Table II), these low $G$% values as compared to those for unmodified Cell-Br are unexpected.

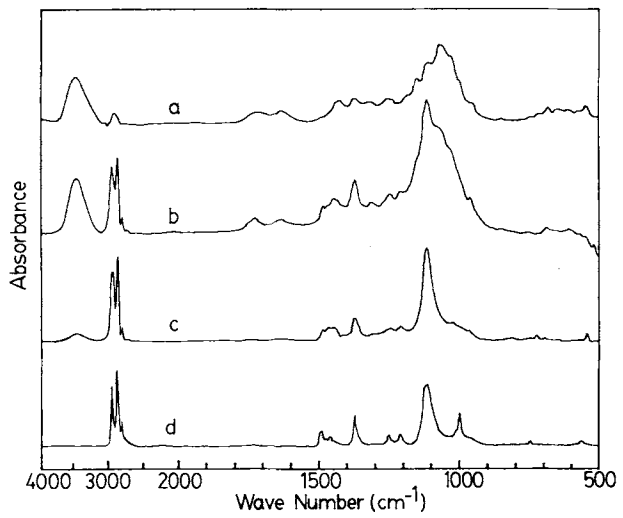


**Figure 1** IR spectra of (a) Cell-Br (Br%, 33.0; $DS$, 0.91), (b) Cell-$g$-POTM ($G$%, 127%), (c) POTM extracted from Cell-$g$-POTM, and (d) POTM ($DP$, 1276).

Figure 1 compares an infrared (IR) spectrum of Cell-$g$-POTM with those of Cell-Br and POTM. Both Cell-Br and POTM show strong absorptions in the $\nu_{C-O-C}$ region. However, the strongest absorption of POTM in this region appears at a wavenumber (1114 $cm^{-1}$) higher than that of Cell-Br. The $\nu_{C-H}$ absorptions of POTM are strong while those of Cell-Br are weak. Cell-$g$-POTM shows strong $\nu_{O-H}$ absorptions due to cellulose hydroxyl groups and strong $\nu_{C-H}$ absorptions due to POTM. The absorptions in the $\nu_{C-O-C}$ region of Cell-$g$-POTM are primarily a superposition of the absorptions of POTM and cellulose. POTM extracted from the reaction product of graft copolymerization gives an IR spectrum almost identical to that of POTM [see Fig. 1(c)].

Table V summarizes the solubilities of Cell-$g$-POTM and related materials. POTM is soluble in all solvents examined and cellulose is soluble only in LiCl/DMA. Cell-$g$-POTM is insoluble and only swells in a common solvent for cellulose and POTM: LiCl/DMA. This insolubility is probably due to its cross-linked structure formed by chain transfer and/or termination during polymerization.

## Gas Chromatographic and Gas Chromatographic–Mass Spectrometric Analyses

Cell-$g$-POTM was hydrolyzed in 2$N$ HCl under reflux for 4 h. The graft copolymer was partially

**Table V Solubility[a] of Cell-$g$-POTM[b]**

| | THF | $CH_2Cl_2$ | AcOEt | LiCl/DMA |
|---|---|---|---|---|
| Cell-$g$-POTM | △ | △ | △ | △ |
| Cellulose | × | × | × | ○ |
| Cell-Br | × | × | × | ○ |
| POTM | ○ | ○ | ○ | ○ |

[a] (○) Soluble; (△) swollen; (×) insoluble.
[b] Run 1 in Table III.

dissolved and a swollen part remained. The dissolved fraction was converted to *O*-trifluoroacetyl (TFA) derivatives and studied by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS).

Figure 2 compares a GC chromatogram of the hydrolyzate of Cell-*g*-POTM with that of the hydrolyzate of a 1 : 2.3 mixture (wt/wt, corresponding to the composition of the Cell-*g*-POTM with *G*% of 230%) of microcrystalline cellulose and POTM. The peak material of the largest peak for the mixture was determined to be the TFA derivative of THF dimer, 5-oxanonane-1,9-diol. Peaks of THF trimer, tetramer, and pentamer also appear with intensities decreasing with increasing molecular mass. MS fragmentation patterns of the THF oligomers are given in Table VI. Glucose-related peaks are all weak as compared to the peaks of THF oligomers. This is due to the low susceptibility of the microcrystalline cellulose toward acid hydrolysis in 2*N* HCl.

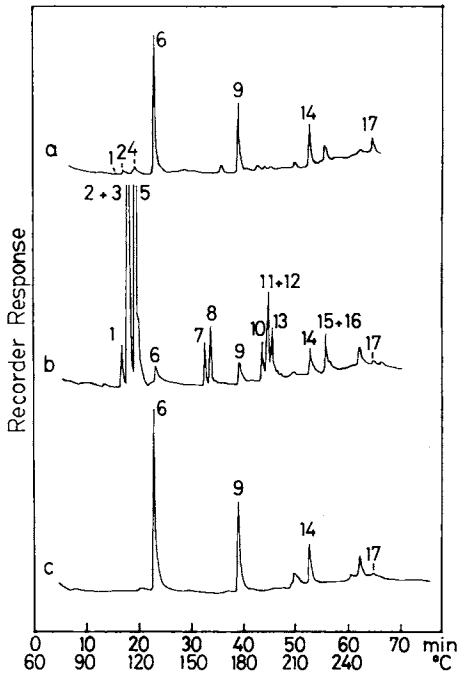


**Figure 2** Gas chromatograms of TFA derivatives of hydrolyzates obtained after refluxing in 2*N* HCl for 2 h: (a) mixture of cellulose and POTM (weight ratio, 1 : 2.3); (b) Cell-*g*-POTM (*G*%, 127%); (c) residue of (b) after additional refluxing for 8 h in 2*N* HCl. Peaks 1 and 2, Glc (pyranose); 3 and 5, 6-Cl-Glc; 4, Glc (furanose); 7 and 8, 6-HB-Glc; 10 and 11, 4-O-(6-chloro-6-deoxy-β-D-glucopyranosyl)-6-chloro-6-deoxy-β-D-glucopyranose; 12 and 13, 6-$HB_2$-Glc; 15, 6-HB-CB; 16, 6′-HB-CB. Peaks 6, 9, 14, and 17: linear oligomers of THF (*DP* = 2, 3, 4, and 5, respectively).

Peaks for THF oligomers also appear on the chromatogram of the hydrolyzed fraction of the Cell-*g*-POTM. In this case, however, glucose-related peaks are relatively stronger as compared to the oligomer peaks. Strong anomer peaks for 6-Cl-Glc appear but none for 6-Br-Glc. The formation of 6-Cl-Glc is due to the facile exchange of bromine of the remaining 6-Br-Glc units in the Cell-*g*-POTM with chlorine under the hydrolysis conditions in 2*N* HCl. It is difficult to estimate the ratio of Glc and 6-Cl-Glc from GC peak areas because peaks 2 (Glc) and 3 (6-Cl-Glc) overlap each other. From the relative abundance of $A_3$ fragment ions[6] (*m*/*z*: 319 for Glc, and 319, 241, and 243 for 6-Cl-Glc) on the mass spectrum of the overlapping peak, the ratio of 6-Cl-Glc and Glc were estimated to be 4.6, which is close to the value expected from the bromine content and *G*% of the Cell-*g*-POTM (6-Cl-Glc/Glc = 5.5).

Peaks of TFA derivatives of Glc, cellobiose, 6-*O*-(4-hydroxybutyl)glucose (6-HB-Glc), 6-*O*-(9-hydroxy-5-oxanoyl)glucose (6-$HB_2$-Glc), and 4-*O*-(6-hydroxybutylglucopyranosyl)glucose (6′-HB-CB) also appear on the chromatogram. The peak of 6′-HB-CB overlaps with another disaccharide peak on the GC chromatogram [Fig. 2(b)], but is separated from each other on a total-ion-current chromatogram in the GC–MS analysis. The structure of disaccharide (peak 16) was assigned to 6′-HB-CB based on the presence of an ion at *m*/*z* 479, assignable to a unique fragment ion, $abJ_3$[6], in its mass spectrum. The other disaccharide (peak 15) did not give an ion at *m*/*z* 479 and its structure was tentatively assigned to an isomeric 4-*O*-glucopyranosyl-6-*O*-(4-hydroxybutyl)glucose (6-HB-CB). MS fragmentation patterns of these four compounds are given in Table VII and Figure 3.

The insoluble part of the Cell-*g*-POTM was further hydrolyzed under the same conditions for additional 8 h and the dissolved fraction was studied in a similar way. Only THF oligomers were found on a GC chromatogram of hydrolyzate of the insoluble part.

Most of the assignments of the peak materials based on their MS fragmentation patterns are supported by their GC retention values. Unfortunately, the fragmentation patterns were not sufficient for identification in some cases because only few fragment ions, important for the determination of molecular mass, were found in high *m*/*z* regions. Comparison of retentions (as Kováts' retention indices[19]) of these peak materials with those of known compounds offers information on their molecular masses. Kováts' retention index corresponds to 100 times the number of carbon atoms in a hy-

**Table VI Mass Fragmentation of TFA Derivatives of THF Oligomers**

| | | | Peak No.[a] | | | |
|---|---|---|---|---|---|---|
| | | | 6 | 9 | 14 | 17 |
| | | | $CF_3CO(OC_4H_8)_nOCOCF_3$ | | | |
| Ion | | m/z | $n = 2$ r.a.[b] | $n = 3$ r.a. | $n = 4$ r.a. | $n = 5$ r.a. |
| $CF_3CO(OC_4H_8)_5OCOCF_3$ | $[M^+]$ | 570 | | | | 0.05 |
| $CF_3CO(OC_4H_8)_4OCOCF_3$ | $[M^+]$ | 498 | | | 0.09 | |
| $CF_3CO(OC_4H_8)_3OCOCF_3$ | $[M^+]$ | 426 | | 0.04 | | |
| $CF_3CO(OC_4H_8)_4O$ | | 401 | | | | 0.3 |
| $CF_3CO(OC_4H_8)_4$ | [1] | 385 | | | 0.03 | |
| $CF_3CO(OC_4H_8)_2OCOCF_3$ | $[M^+]$ | 354 | 0.5 | | | |
| $CF_3CO(OC_4H_8)_3O$ | | 329 | | 0.0 | 0.8 | 1.2 |
| $CF_3CO(OC_4H_8)_3$ | [2] | 313 | | 0.0 | 0.0 | 0.3 |
| [2]-$C_2H_5$ | | 284 | | 0.0 | 0.1 | 0.3 |
| [1]-$CF_3COOH$ | | 271 | | 0.1 | 0.1 | 0.1 |
| $CF_3CO(OC_4H_8)_2O$ | | 257 | 0.04 | 5.9 | 7.2 | 3.1 |
| $CF_3CO(OC_4H_8)_2$ | [3] | 241 | 1.1 | 13.5 | 39.2 | 57.4 |
| [3]-$C_2H_5$ | | 212 | 18.6 | 17.5 | 12.7 | 7.6 |
| [2]-$CF_3COOH$ | | 199 | 7.6 | 0.6 | 0.06 | 0.3 |
| $CF_3COOC_4H_8O$ | | 185 | 3.9 | 1.4 | 1.3 | 0.6 |
| $CF_3COOC_4H_8$ | [4] | 169 | 100 | 47.3 | 47.4 | 38.4 |
| [4]-$C_2H_5$ | | 140 | 6.3 | 1.0 | 0.6 | 0.0 |
| [3]-$CF_3COOH$ | | 127 | 2.1 | 1.3 | 2.1 | 1.7 |
| $CF_3CO$ | | 97 | 6.0 | 1.5 | 1.4 | 1.2 |
| $C_4H_9O$ | | 73 | 9.2 | 14.1 | 24.8 | 22.6 |
| $C_3H_7O$ | | 71 | 55.8 | 62.2 | 85.5 | 58.8 |
| $CF_3$ | | 69 | 58.5 | 11.4 | 7.6 | 4.1 |
| $C_4H_7$ | | 55 | 99.8 | 100 | 100 | 100 |

[a] Peak numbers are the same as used in Figure 2.
[b] r.a., relative abundance (%).

pothetical *n*-paraffin that is supposed to have the same retention time as the given peak material under the same GC operation conditions. The retention index of a given peak material is determined by interpolation with the retention times of an *n*-paraffin and the next *n*-paraffin in the carbon number, both coinjected, in temperature-programmed GC operation. The retention indices vary only very slightly with accidental slight alteration in the operation conditions. In the present study, only $C_{11}$, $C_{15}$, and $C_{20}$ *n*-hydrocarbons were used for the interpolation at a constant heating rate for simplicity in the determination.

Retention indices of some THF oligomers, glucose derivatives, and cellobiose derivatives are plotted against their molecular masses of the TFA derivatives in Figure 4 along with the indices of 1,4-butanediol, glucose, and cellobiose. The compounds under discussion are classified into three groups: THF oligomers, Glc derivatives, and cellobiose derivatives. The linearity of the plot for each group and the parallel shift of the three lines in the figure are consistent with the given assignment.

## Thermal Behavior

Differential thermal analysis (DTA) of Cell-*g*-POTM and POTM was made (Fig. 5). A weak endothermic peak at 39.9°C, near melting point of POTM (43.9°C on the DTA curve of POTM), appears on the DTA curve of Cell-*g*-POTM. Cai and Yue[9] found a peak near 40°C on a DSC curve of α-brominated polystyrene grafted with THF. They reported that the peak was found only for samples with *G*% values higher than 150%. In the present study, the *G*% value of Cell-*g*-POTM used for the DTA measurement was 326%. Samples with a lower *G*% values such as 102% did not give any peak near

**Table VII Mass Fragmentation Patterns of Hydroxybutyl Derivatives of Mono- and Disaccharides as TFA Derivative[a]**

| Ion | 6-HB-Glc *m/z* (r.a.[b]) | 6-$(HB)_2$-Glc *m/z* (r.a.) | 6-HB-CB *m/z* (r.a.) | 6'-HB-CB *m/z* (r.a.) |
|---|---|---|---|---|
| $M^+$ | 732 (—) | 804 (—) | 1182 (—) | 1182 (—) |
| $M-CF_3COO$ | 619 (0.6) | 691 (0.0) | 1069 (—) | 1069 (—) |
| $M-CF_3COO-CF_3COOH$ | 505 (1.2) | 577 (0.0) | 955 (—) | 955 (—) |
| $M-CF_3COO-2CF_3COOH$ | 391 (1.2) | 463 (0.2) | 841 (—) | 841 (—) |
| $M-CF_3COO-3CF_3COOH$ | 277 (0.4) | 349 (0.5) | 727 (—) | 727 (—) |
| $M-(CH_2)_3OTFA$ | 577 (—) | 649 (—) | 1027 (—) | 1027 (—) |
| $M-(CH_2)_3OTFA-CF_3COOH$ | 463 (0.3) | 535 (—) | 913 (—) | 913 (—) |
| $M-(CH_2)_3OTFA-2CF_3COOH$ | 349 (0.6) | 421 (—) | 799 (—) | 799 (—) |
| $M-(CH_2)_3OTFA-3CF_3COOH$ | 0.6 (0.3) | 307 (—) | 685 (—) | 685 (—) |
| 619[a] | (0.6) | (12.2) | (18.8) | (11.2) |
| $619-CF_3COOH$ | 505 (—) | 505 (—) | 505 (0.3) | 505 (0.0) |
| 547[a] | (1.0) | (1.1) | (0.4) | (2.2) |
| $547-2CF_3COOH$ | 319 (17.5) | 319 (27.5) | 319 (18.2) | 319 (8.6) |
| $abJ_3$ | (—) | (—) | 551 (—) | 479 (0.0) |
| $TFAO(CH_2)_4$ | 169 (24.2) | 169 (23.1) | 169 (29.5) | 169 (21.6) |
| $C_4H_9O$ | 73 (1.0) | 73 (9.4) | 73 (21.4) | 73 (23.1) |
| $C_4H_7O$ | 71 (3.7) | 71 (51.0) | 71 (89.9) | 71 (84.9) |
| $CF_3$ | 69 (24.7) | 69 (13.4) | 69 (15.4) | 69 (18.6) |
| $C_4H_7$ | 55 (100) | 55 (100) | 55 (100) | 55 (100) |

[a] Structures, see Figure 3.
[b] r.a., relative abundance (%).

40°C. These findings show that the peak near 40°C for the Cell-*g*-POTM is due to the POTM branch chain.

An exothermic peak appears at 189°C on the DTA curve of Cell-*g*-POTM. An exothermic peak, which is not assigned, appears at 167°C on the curve of a Cell-Br, whereas no peak is found in the same temperature range in the case of POTM and microcrystalline cellulose. The peak temperature is dependent on the bromine content of Cell-Br.[20] The

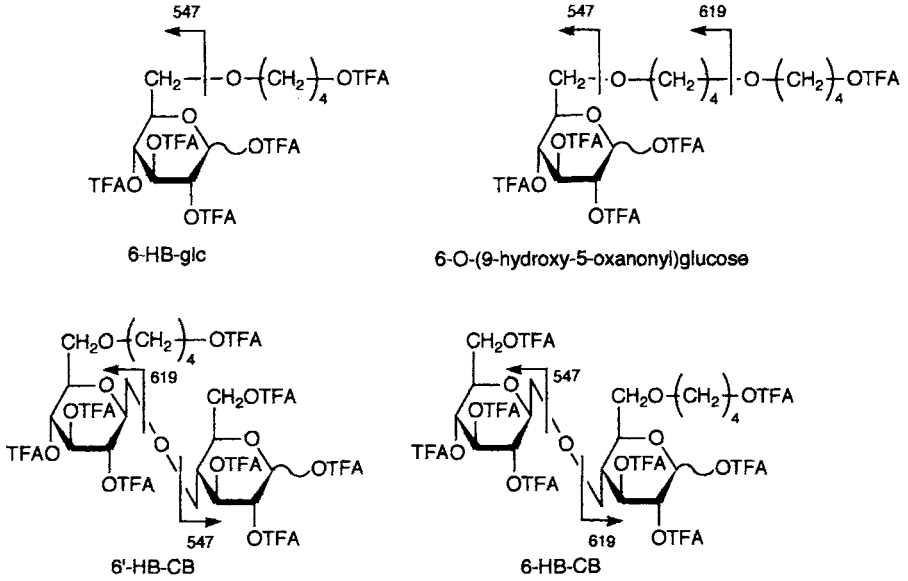


**Figure 3** Structures of TFA derivatives of mono- and disaccharides found in the hydrolyzates of Cell-*g*-POTM.

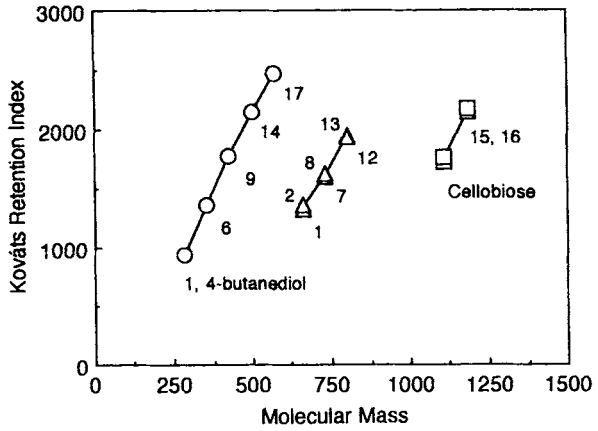


**Figure 4** Relation between Kováts' retention index and molecular mass ($M$) for TFA derivatives: (○) 1,4-butanediol and THF oligomers ($DP$ = 2–4); (△), glucose and 6-HB-Glc homolog; (□), cellobiose, 6-HB-CB and 6′-HB-CB. Nos. for symbols correspond to the peak numbers shown in Figure 2.

exothermic peak of Cell-$g$-POTM is probably due to remaining 6-Br-Glc units in the Cell-$g$-POTM.

Thermogravimetric (TG) curves of POTM, microcrystalline cellulose, and Cell-Br are shown in Figure 6. TG and differentiated TG (DTG) curves of Cell-$g$-POTM are shown in Figure 7. The thermal

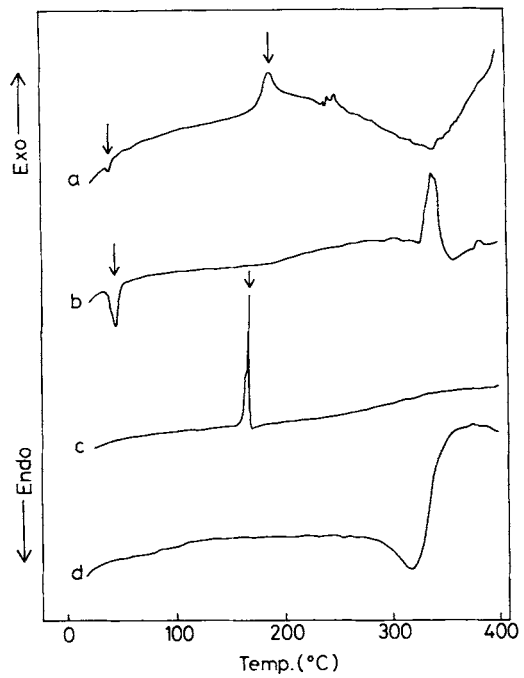


**Figure 5** DTA curves of Cell-$g$-POTM and related compounds: (a) Cell-$g$-POTM ($G$%, 326%); (b) POTM ($DP$, 855); (c) Cell-Br (Br%, 24.8%; $DS$, 0.62); (d) microcrystalline cellulose.

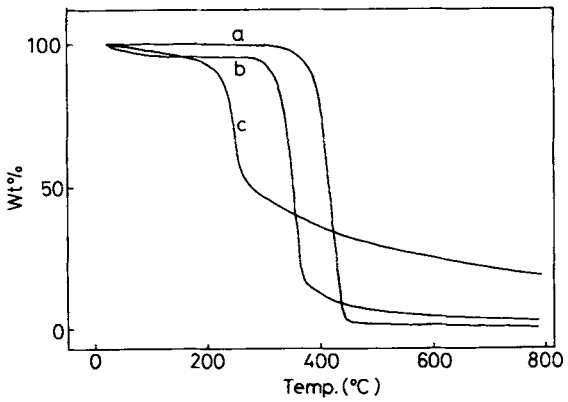


**Figure 6** TG curves of (a) POTM ($DP$, 855), (b) microcrystalline cellulose, and (c) Cell-Br (Br%, 4.3%).

decomposition of Cell-$g$-POTM proceeds in three steps. The first peak around 255°C and the second one around 360°C on DTG curve of Cell-$g$-POTM agree with those of Cell-Br with low $DS$ and cellulose, respectively. The third peak around 430°C on the DTG curve agrees with that of POTM. The most likely explanation for the agreement is that the degradation of the trunk polymer of Cell-$g$-POTM occurs first in two steps and the degradation of POTM branch chain follows at a higher temperature. To confirm this, thermal degradation residues of Cell-$g$-POTM obtained at different temperatures were analyzed by IR spectroscopy (Fig. 8). The IR spectra of the thermal degradation residues obtained at 300°C [Fig. 8(b)] and 350°C [Fig. 8(c)] are similar to that of POTM [Fig. 8(a)] and the adsorption around 1050 $cm^{-1}$ assigned to cellulose is very weak. The IR spectrum of the residue obtained at 400°C, however, is different from that of POTM, and several new adsorptions appear. These findings are consistent with the assumption given above. It is note-

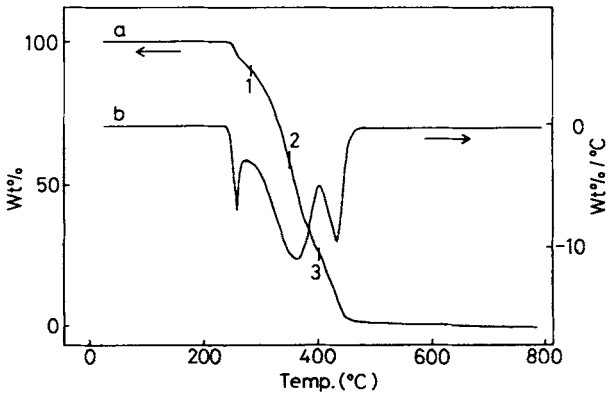


**Figure 7** (a) TG and (b) DTG curves of Cell-$g$-POTM ($G$%, 326%).

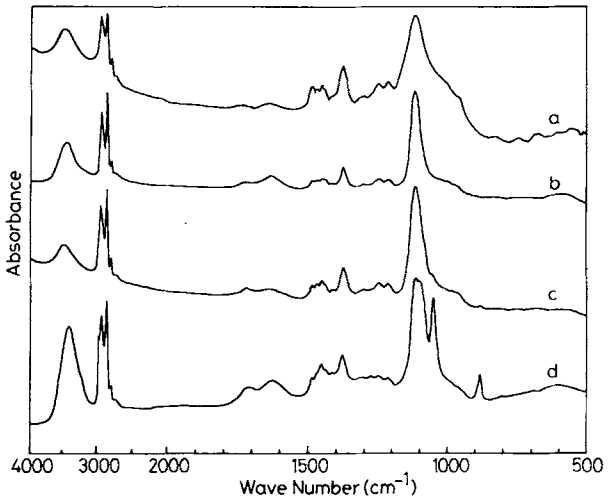


**Figure 8** IR spectra of (a) Cell-*g*-POTM (*G*%, 326%) and its thermal degradation residues obtained at (b) 280°C, (c) 350°C, and (d) 400°C. Samples (b), (c), and (d) were obtained at points 1, 2, and 3 in Figure 7, respectively.

worthy that Cell-Br with low *DS* by bromine show only one peak on the DTG curve but Cell-Br components in Cell-*g*-POTM show two peaks. This difference may be due to the grafting structure.

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