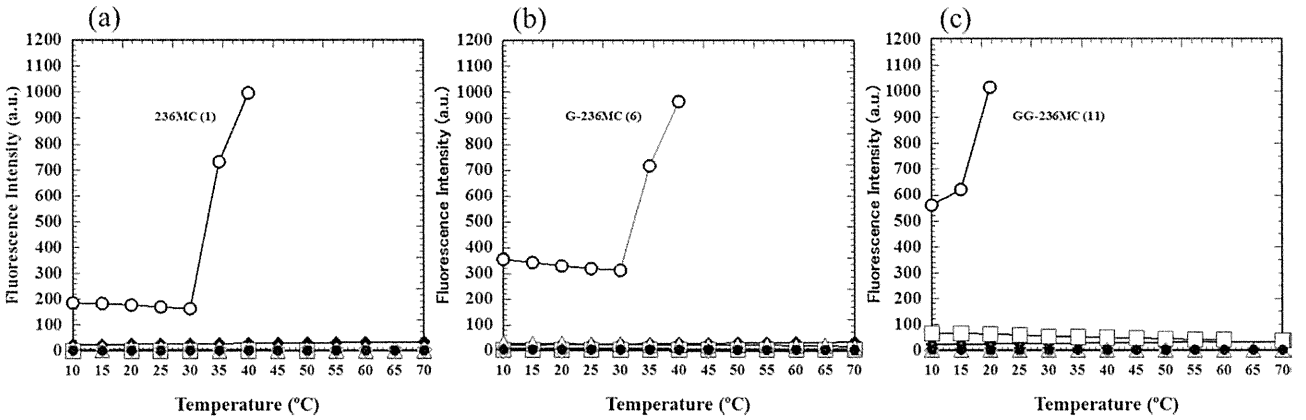

FIGURE 6 Fluorescent intensities of compounds **1–15** as a function of temperature. (a) regioselectively methylated celluloses, ○: 236MC (**1**); △: 23MC (**2**); □: 26MC (**3**); ◇: 3MC (**4**); ●: 6MC (**5**). (b) diblock copolymers consisting of glucose as hydrophilic block, ○: G-236MC (**6**); △: G-23MC (**7**); □: G-26MC (**8**); ◇: G-3MC (**9**); ●: G-6MC (**10**). (c) diblock copolymers consisting of cellobiose as hydrophilic block, ○: GG-236MC (**11**); △: GG-23MC (**12**); □: GG-26MC (**13**); ◇: GG-3MC (**14**); ●: GG-6MC (**15**).

Fluorescence Measurements

Fluorescent probe method using ANS-Mg was carried out to detect hydrophobic micro or nano environment as aforementioned. The ANS-Mg is an anionic probe, which is essentially nonfluorescent in water, and is highly fluorescent in nonpolar environments, such as in micelles. It is well known that the fluorescence intensities increase and that the fluorescence wavelength is blue-shifted in the hydrophobic environments.[16,17] Fluorescence intensities of 2.0 wt % aqueous solution of compounds **1–15** with 10 μM of ANS-Mg as a function of temperature were measured and plotted in Figure 6. The fluorescence intensities of only 236MC (**1**, DP_n = 3.7), G-236MC (**6**, DP_n = 10.7), and GG-236MC (**11**, DP_n = 13.8) having a sequence of 2,3,6-tri-*O*-methyl-glucopyranosyl units sharply increased at a certain temperature, while the fluorescence intensities of other compounds 23MC (**2**), 26MC (**3**), 3MC (**4**), 6MC (**5**), G-23MC (**7**), G-26MC (**8**), G-3MC (**9**), G-6MC (**10**), GG-23MC (**12**), GG-26MC (**13**), GG-3MC (**14**), and GG-6MC (**15**) remained almost constant in the whole range of tested temperature. No blue shift of fluorescence wavelength was observed except for compounds **1**, **6**, and **11** having a sequence of 2,3,6-tri-*O*-glucopyranosyl units.

The fluorescence wavelengths were shifted from 518 nm at 20 °C in water to 481, 470, 469 nm at 20 °C in 2.0 wt % aqueous solutions of 236MC (**1**), G-236MC (**6**), and GG-236MC (**11**), respectively. The onset temperatures of 236MC (**1**), G-236MC (**6**), and GG-236MC (**11**) where fluorescent intensities increased were 30, 30, and 15 °C, respectively. The fluorescent intensities at 10 °C were in the order: GG-236MC (**11**) > G-236MC (**6**) > 236MC (**1**).

Fluorescence measurements revealed that only 236MC (**1**), G-236MC (**6**), and GG-236MC (**11**) having a sequence of 2,3,6-tri-*O*-methyl-glucopyranosyl units formed the hydrophobic micro or nano environment in water. In conclusion, endothermic peaks in DSC curves were attributed to the dehydration around the 2,3,6-tri-*O*-methyl glucopyranosyl units.

DLS Measurements

Aggregation behavior of water-soluble cellulose ethers such as MC is closely related to their gelation property. We therefore investigated the relationship between aggregation and gelation behavior of aqueous solutions of compounds **1–15**.

To investigate thermo-induced aggregation behaviors of 2.0 wt % aqueous solutions of compounds **1–15**, DLS measurements were performed in the temperature range from 10 to 90 °C. Figure 7 illustrates hydrodynamic diameters of compounds **1–15** as a function of temperature. The hydrodynamic diameters of 236MC (**1**), 23MC (**2**), 26MC (**3**), 6MC (**5**), G-236MC (**6**), G-23MC (**7**), G-26MC (**8**), GG-236MC (**11**), GG-23MC (**12**), and GG-26MC (**13**) increased with increasing temperature, while the hydrodynamic diameters of 3MC (**4**), G-3MC (**9**), G-6MC (**10**), GG-3MC (**14**), and GG-6MC (**15**) did not increase in the temperature range from 10 to 90 °C. The onset temperatures of the increasing hydrodynamic diameter of diblock copolymers G-236MC (**6**), G-23MC (**7**), G-26MC (**8**), GG-236MC (**11**), GG-23MC (**12**), and GG-26MC (**13**) were in this order: G-23MC (**7**) (55 °C) > GG-23MC (**12**) (50 °C) > G-26MC (**8**) (45 °C) > GG-26MC (**13**) (35 °C) > G-236MC (**6**) (25 °C) > GG-236MC (**11**) (20 °C). Aggregation behaviors of the aforementioned compounds differed, whereas they had almost the same *DS*, at least within each class of glucosylated or cellobiosylated copolymers (see Table 1).

Moreover, DLS measurements demonstrated that aggregation occurred in 2.0 wt % aqueous solutions of 23MC (**2**), 26MC (**3**), 6MC (**5**), G-23MC (**7**), G-26MC (**8**), GG-23MC (**12**), and GG-26MC (**13**) under heating conditions, although the dehydrations around their compounds and the formation of hydrophobic micro or nano environment did not occur as discussed in the former section. In conclusion, there was no relationship between the dehydrations detected by DSC measurements and the aggregation behaviors on heating measured by DLS experiments.

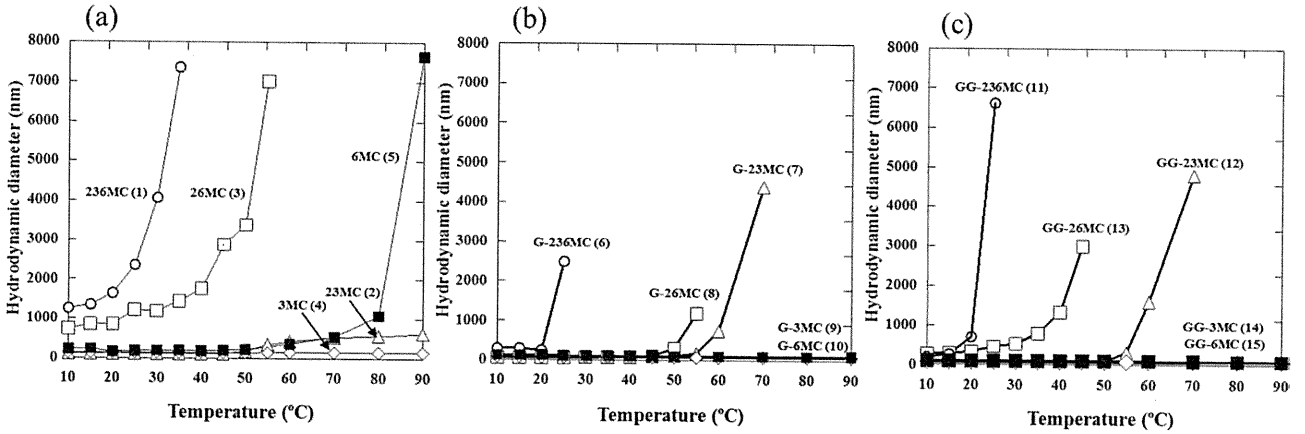

FIGURE 7 Hydrodynamic diameter of compounds **1–15** as a function of temperature. (a) regioselectively methylated celluloses, ○: 236MC (**1**); △: 23MC (**2**); □: 26MC (**3**); ◇: 3MC (**4**); ●: 6MC (**5**). (b) diblock copolymers consisting of glucose as hydrophilic block, ○: G-236MC (**6**); △: G-23MC (**7**); □: G-26MC (**8**); ◇: G-3MC (**9**); ●: G-6MC (**10**). (c) diblock copolymers consisting of cellobiose as hydrophilic block, ○: GG-236MC (**11**); △: GG-23MC (**12**); □: GG-26MC (**13**); ◇: GG-3MC (**14**); ●: GG-6MC (**15**).

LCST-Type Phase Separation of Aqueous Solutions of 236MC (1), G-236MC (6) and GG-236MC (11) Having 2,3,6-tri-*O*-methyl-glucopyranosyl Units: The Formation of Hydrogel

Figure 8 shows photographs of 2.0 wt % aqueous solutions of 236MC (**1**), G-236MC (**6**), and GG-236MC (**11**) at 5, 50, and 70 °C. Aqueous solutions of these polymers aggregated and became turbid with increasing temperature. Interestingly, only diblock copolymer, GG-236MC (**11**) consisting of hydrophilic cellobiosyl block and a hydrophobic sequence of 2,3,6-tri-*O*-methyl-glucopyranosyl units exhibited thermoreversible gelation behavior at ~70 °C. The gelation temperature decreased with increasing DP_n and DS. Aqueous solution of compound **11** having DP_n = 28.2 and DS = 2.76 formed a gel at ambient temperature (ca. 25 °C), as shown in Figure 9.

Kato et al. concluded that the "crosslinking loci" of MC hydrogels are "crystalline" and consist of 2,3,6-tri-*O*-methyl-glucopyranosyl units, and between 4 and 8 units long.[5] A sequence of 2,3,6-tri-*O*-methyl-glucopyranosyl units of compound **11** were between about 10 and 30 units long. Our results revealed that a sequence of approx. ten 2,3,6-tri-*O*-methyl-glucopyranosyl units was, at least, of crucial significance for thermoreversible gelation of aqueous MC solution. Furthermore, the gelation temperature of aqueous MC solution could be controlled by the length of a sequence of 2,3,6-tri-*O*-methyl-glucopyranosyl units, the molecular weight of such a

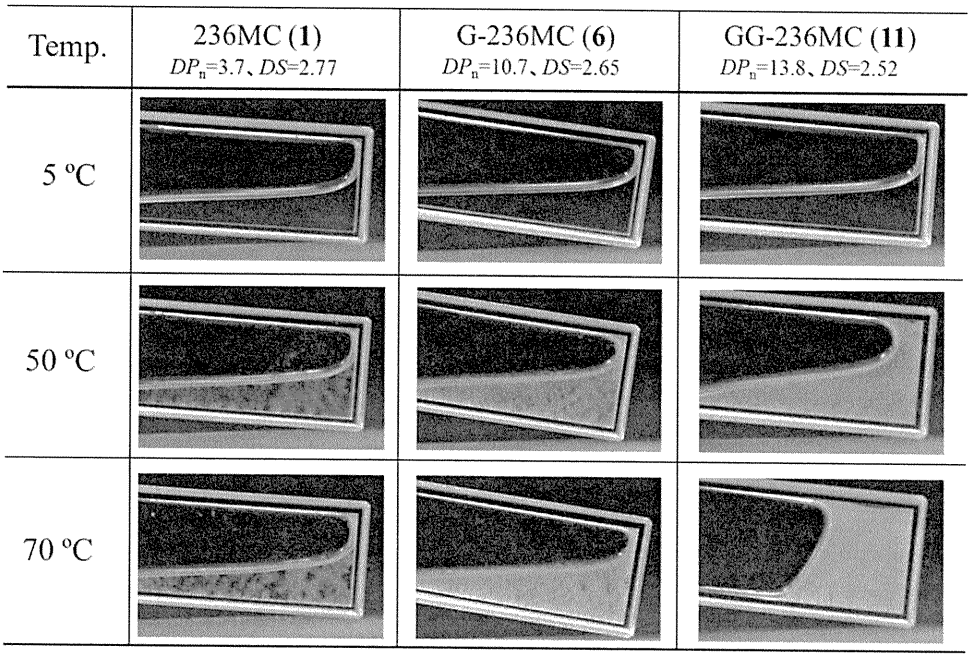

FIGURE 8 Photographs of 2.0 wt % aqueous solutions of 236MC (**1**), G-236MC (**6**), and GG-236MC (**11**).

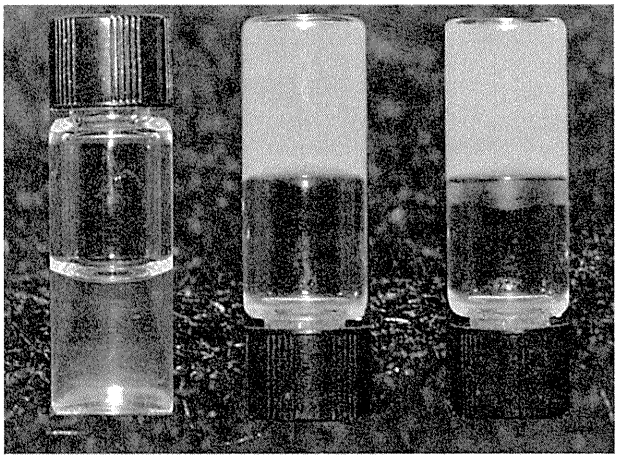

FIGURE 9 Photographs of 2.0 wt % aqueous solutions of GG-236MC (**11**) having $DP_n = 28.2$.

diblock copolymer, in wide range of temperature from ambient temperature to about 70 °C.

CONCLUSIONS

We found, for the first time, the direct evidence that a sequence of 2,3,6-tri-*O*-methyl-glucopyranosyl units causes thermoreversible gelation of aqueous MC solution, and that idealized diblock structure consisting of 2,3,6-tri-*O*-methyl-glucopyranosyl and unmodified cello-oligosaccharides caused gelation. Surface activity and temperature-dependent aggregation behavior of aqueous solutions of regioselectively methylated cellulose derivatives (236MC (**1**), 23MC (**2**), 26MC (**3**), 3MC (**4**), and 6MC (**5**)) and diblock copolymers of regioselectively methylated cellulose and unmodified cello-oligosaccharides (G-236MC (**6**), G-23MC (**7**), G-26MC (**8**), G-3MC (**9**), G-6MC (**10**), GG-236MC (**11**), GG-23MC (**12**), GG-26MC (**13**), GG-3MC (**14**), and GG-6MC (**15**)) were investigated by means of surface tension, DSC, fluorescent and DLS measurements. The surface activities of diblock copolymers consisting of a sequence of 2,3,6-tri-*O*-methyl-glucopyranosyl units as hydrophobic block were similar to that of industrially produced MC. The onset of aggregation temperature of diblock copolymers measured by DLS measurement appeared in the following: 236MC > 26MC > 23MC. Compounds **1** (236MC), **6** (G-236MC), and **11** (GG-236MC) formed the hydrophobic environments by clustering of the sequences of 2,3,6-tri-*O*-methyl-glucopyranosyl units diagnosed by fluorescent probe method. Only diblock copolymer **11** (GG-236MC) consisting of hydrophilic cellobiosyl block and a hydrophobic sequence of 2,3,6-tri-*O*-methyl-glucopyranosyl units caused thermoreversible gelation under heating process, at least within the diblock copolymers tested. DSC measurement revealed that a sequence of more than five 2,3,6-tri-*O*-methyl-glucopyranosyl units was, at least, indispensable for the appearance of endothermic peaks in DSC curves attributed to the dehydration caused by hydrophobic cluster formation. Furthermore, our results revealed that a sequence of ~10 2,3,6-tri-*O*-methyl-glucopyranosyl units, at least, played important role in thermoreversible gelation of aqueous MC solution. Formation of supermolecular structure consisting of diblock copolymer **11** (GG-236MC) is considered as essential reason for the gelation. Detailed discussion on hydrogel formation will appear elsewhere.

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Synthesis of Diblock Methylcellulose Derivatives with Regioselective Functionalization Patterns

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ABSTRACT: This article describes a new synthesis strategy to prepare diblock copolymers as model compounds for industrially produced cellulose ethers exemplified with methylcellulose (MC). To elucidate a key structure for thermoreversible gelation of MC, five regioselectively methylated celluloses **1–5** (236, 23, 26, 3, and 6 MC), five corresponding methyl-β-D-glucopyranosyl-(1→4)-cellulosides **6–10**, and five equiv methyl-β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl-(1→4)-cellulosides **11–15** were synthesized for the first time via combination of the glycosyl trichloroacetimidate method and the acid-catalyzed methanolysis method. The structure of compounds **1–15** was confirmed by means of NMR spectroscopy and MALDI-TOF MS. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 4964–4976, 2011

KEYWORDS: diblock copolymers; gelation; glycosylation; methylcellulose; oligomers; polysaccharides; regioselective functionalization

INTRODUCTION Methylcellulose (MC) is one of the most important commercial cellulose ethers.[1] Industrially produced MC has heterogeneous functionalization patterns along the polymer chain. It is well known that MCs with degrees of substitution (DS) equal from 1.7 to 2.3 are water soluble.[2] These aqueous solutions of MCs exhibit surface activity. Furthermore, MCs with DS of 1.4–2.0 undergo the sol–gel transition upon heating (typically above 60 °C) and the gel–sol transition upon cooling.[3] The thermoreversible gelation of aqueous MC solution was first investigated by Heymann,[4] and it was concluded that the gelation is due to the dehydration of hydrated MC molecules. Utilizing its surface activity and hydrogel-forming ability, MCs are widely used as thickeners, water binders, film-forming agents, and in the fields of pharmaceuticals and foods.[5] Furthermore, physicochemical properties of MC in water depend on the degree of polymerization (DP), DS, and the functionalization pattern.[6] The functionalization pattern includes the distribution of the functional groups within the anhydroglucopyranose unit, along the polymer chain, and between the chains. The determination of the functionalization pattern within the anhydroglucopyranose unit of industrially produced MC with a DS of ~1.9 was achieved by high-performance liquid chromatography analysis of the products of complete hydrolysis.[7] These hydrolyzed products included glucose (5.58%), 2,3,6-tri-*O*-methyl- (25.85%), 2,3-di-*O*-methyl- (9.98%), 2,6-di-*O*-methyl- (26.47%), 3,6-di-*O*-methyl- (5.36%), 2-*O*-methyl- (14.33%), 3-*O*-methyl- (2.01%), and 6-*O*-methyl-glucoses (10.42%). The structure–property relationship of MC with heterogeneous functionalization pattern is complicated because these anhydroglucopyranose units are sequenced at random. Although many studies have been performed on the properties of MC solutions, it is still unknown how the chemical structure of MC plays a role on the solution behavior. As a consequence, the weak knowledge of structure–property relationships of MC prevents the improvement of industrial products.[8]

Synthesis followed by characterization of a model compound is a powerful tool to elucidate structure–property relationships of a compound with complex structure. Regioselectively methylated cellulose derivatives as model compounds for MC have been prepared so far for the elucidation of the structure–property relationships of industrially produced MC with heterogeneous functionalization pattern. 2,3,6-Tri-*O*-methyl-,[9] 2,3-di-*O*-methyl-,[6,10,11] 2,6-di-*O*-methyl-,[12] 3-*O*-methyl-,[13] and 6-*O*-methyl-celluloses[14] from natural cellulose and 2,3,6-tri-*O*-methyl-, 2,3-di-*O*-methyl-, 2,6-di-*O*-methyl-, 3,6-di-*O*-methyl-, 2-*O*-methyl-, 3-*O*-methyl-, and 6-*O*-methyl-celluloses via ring-opening polymerization of glucopyranose orthopivalate derivatives[15,16] were water insoluble.

Additional Supporting Information may be found in the online version of this article.

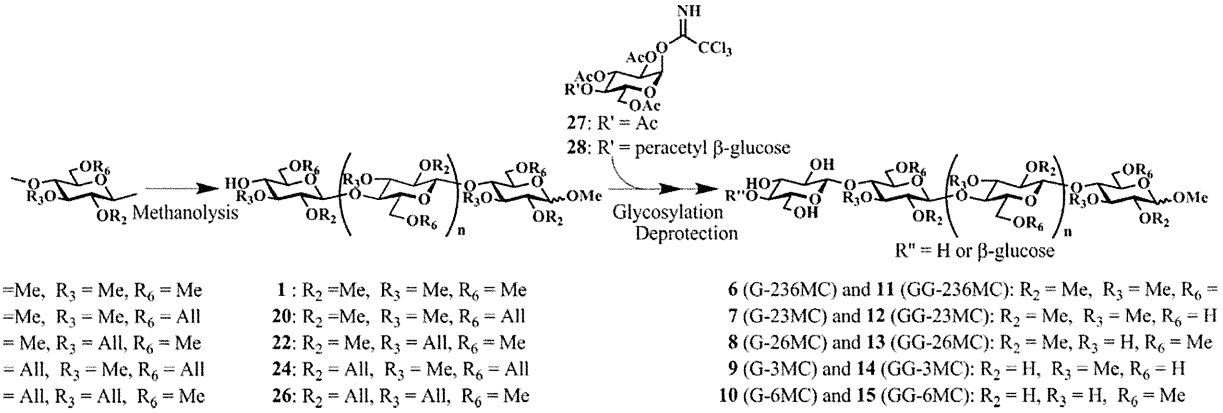


FIGURE 1 Syntheses of diblock copolymers of regioselectively methylated cellulose and unmodified cello-oligosaccharides.

On the other hand, Kamitakahara et al. have reported the preparation of co-oligomers of tri-*O*-methylated and unmodified cello-oligosaccharides as model compounds to study the chemical structure around crosslinking points of MC gel on heating. Namely, AB diblock and ABA, or BAB-triblock co-oligomers having hydrophobic completely methylated and hydrophilic unmodified blocks have been synthesized and their properties in aqueous solutions have been investigated.[17–21] Aqueous solutions of these compounds did not exhibit thermoreversible gelation, though they had surface activities and formed self-assembled aggregates. Thus, we investigated a new synthesis strategy for models of MC.

Hydrophobic blocks were prepared by sulfuric acid–catalyzed methanolysis of regioselectively methylated cellulose derivatives, 2,3,6-tri-*O*-methyl-, 6-*O*-allyl-2,3-di-*O*-methyl-, 3-*O*-allyl-2,6-di-*O*-methyl-, 2,6-di-*O*-allyl-3-*O*-methyl-, and 2,3-di-*O*-allyl-6-*O*-methyl-celluloses from natural cellulose to synthesize diblock MC having different hydrophilic–lipophilic balance. After the removal of allyl groups, regioselectively methylated celluloses, methyl 2,3,6-tri-*O*- (**1**, 236MC), methyl 2,3-di-*O*- (**2**, 23MC), methyl 2,6-di-*O*- (**3**, 26MC), methyl 3-*O*- (**4**, 3MC), and methyl 6-*O*-methyl-cellulosides (**5**, 6MC) were obtained from the corresponding regioselectively methylated cellulose derivatives.

To create a library of MC sequences by making all possible combinations from two hydrophilic and five hydrophobic regioselectively methylated blocks, these building blocks were glycosylated to give 10 diblock copolymers of regioselectively methylated celluloses and unmodified cello-oligosaccharides, methyl β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-methyl- (**6**, G-236MC, G: hydrophilic glucosyl residue), methyl β-D-glucopyranosyl-(1→4)-2,3-di-*O*-methyl- (**7**, G-23MC), methyl β-D-glucopyranosyl-(1→4)-2,6-di-*O*-methyl- (**8**, G-26MC), methyl β-D-glucopyranosyl-(1→4)-3-*O*-methyl- (**9**, G-3MC), methyl β-D-glucopyranosyl-(1→4)-6-*O*-methyl- (**10**, G-6MC), methyl β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-methyl- (**11**, GG-236MC, GG: hydrophilic cellobiosyl residue), methyl β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl-(1→4)-2,3-di-*O*-methyl- (**12**, GG-23MC), methyl β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl-(1→4)-2,6-di-*O*-methyl- (**13**, GG-26MC), methyl β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl-(1→4)-3-*O*-methyl- (**14**, GG-3MC), and methyl β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl-(1→4)-6-*O*-methyl-cellulosides (**15**, GG-6MC).

In this article, we describe the synthetic method of regioselectively methylated celluloses and diblock copolymers of regioselectively methylated celluloses and unmodified cello-oligosaccharides as model compounds of industrially produced MC.

RESULTS AND DISCUSSION

Basic Design for Diblock Methylcellulose of Regioselectively Methylated Cellulose and Unmodified Cello-Oligosaccharide

Figure 1 illustrates the synthetic method for diblock copolymers of regioselectively methylated cellulose and unmodified cello-oligosaccharides **6**–**15** consisting of the glycosyl trichloroacetimidate method and the acid-catalyzed methanolysis method. Regioselectively methylated cellulose derivatives **1**, **20**, **22**, **24**, and **26** as glycosyl acceptors having a free hydroxyl group at C-4 of nonreducing end were glycosylated with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl 2,2,2-trichloroacetoimidate (**27**) or 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl 2,2,2-trichloroacetoimidate (**28**) as glycosyl donors. Glycosylation products were deprotected to give diblock copolymers of regioselectively methylated cellulose and unmodified cello-oligosaccharides **6**–**15**.

Syntheses of Regioselectively Methylated Cellulose Derivatives

Regioselectively methylated and allylated cellulose derivatives were synthesized from industrially produced MC and 2,3-di-*O*-methyl-, 3-*O*-allyl-, 3-*O*-methyl-, and 2,3-di-*O*-allyl-celluloses.

Industrially produced MC (**16**) was completely methylated using CH_3I in the presence of NaH in DMSO to give 2,3,6-tri-*O*-methyl-cellulose (**17**) in 78.4% yield according to our previous article,[21] as shown in Figure 2(a).

The synthesis of 2,3-di-*O*-methyl-cellulose via 6-*O*-trityl cellulose has been reported by many researchers. Kondo and

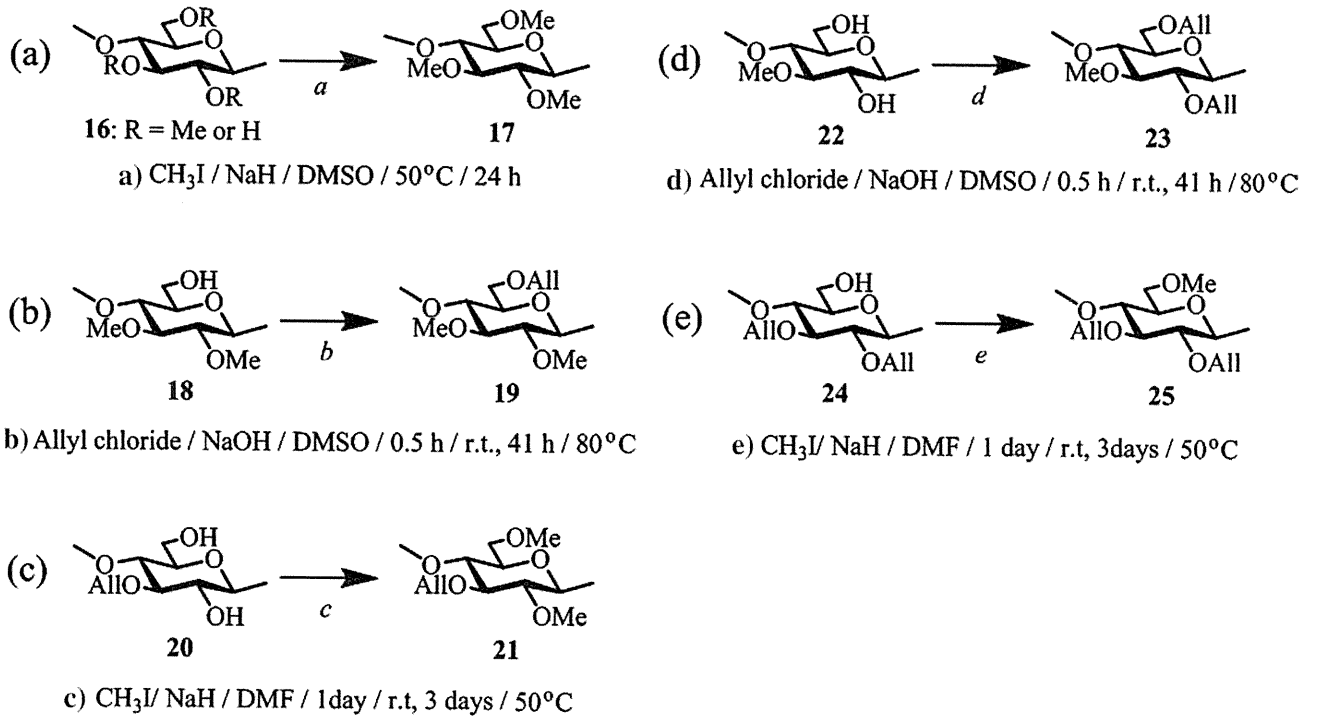


FIGURE 2 Syntheses of regioselectively methylated cellulose derivatives, 2,3,6-tri-*O*- (**17**), 6-*O*-allyl-2,3-di-*O*-(**19**), 3-*O*-allyl-2,6-di-*O*-(**21**), 2,6-di-*O*-allyl-3-*O*- (**23**), and 2,3-di-*O*-allyl-6-*O*-methyl-celluloses (**25**).

Gray have reported that 2,3-di-*O*-methyl-cellulose via 6-*O*-trityl cellulose was soluble in DMSO and DMAc and partially soluble in MeOH and $CHCl_3$, but not soluble in water.[10,11] In addition, Kern et al. have reported that 2,3-di-*O*-methyl-cellulose via 6-*O*-trityl cellulose was soluble in water.[6] 2,3-Di-*O*-methyl-cellulose (**18**) can be prepared via 6-*O*-thexyldimethylsilyl-cellulose[22,23] and dissolves in *N*-methylpyrrolidone and in MeOH/$CHCl_3$, not in water. Koschella et al. have therefore concluded that the structure of 2,3-di-*O*-methyl-cellulose prepared via 6-*O*-thexyldimethylsilyl-cellulose is more uniform compared with 2,3-di-*O*-methyl-cellulose prepared via 6-*O*-trityl-cellulose.[24] Thus, we selected 6-*O*-thexyldimethylsilyl-cellulose to synthesize 2,3-di-*O*-methyl- (**18**) and 2,3-di-*O*-allyl-celluloses (**24**) for 6-*O*-allyl-2,3-di-*O*-methyl- (**19**) and 2,3-di-*O*-allyl-6-*O*-methyl-celluloses (**25**), respectively. 2,3-Di-*O*-methyl-cellulose (**18**) prepared from 6-*O*-thexyldimethylsilyl-cellulose (DS_{Si} = 0.97) was allylated using allyl chloride in the presence of NaOH as a base in DMSO to give 6-*O*-allyl-2,3-di-*O*-methyl-cellulose (**19**) in 40.6% yield, as shown in Figure 2(b).

3-*O*-Allyl-cellulose (**20**) was prepared according to the method of Koschella et al. via 2,6-di-*O*-thexyldimethylsilyl-cellulose (DS_{Si} = 1.92). The compound **20** was treated with CH_3I and NaH in DMF for 4 days to give 3-*O*-allyl-2,6-di-*O*-methyl-cellulose (**21**), as shown in Figure 2(c).

3-*O*-Methyl-cellulose (**22**) was treated with allyl chloride and NaOH in DMSO for 2 days to give 2,6-di-*O*-allyl-3-*O*-methyl-cellulose (**23**), as shown in Figure 2(d).

2,3-Di-*O*-allyl-cellulose (**24**) was prepared via 6-*O*-thexyldimethylsilyl-cellulose (DS_{Si} = 0.97). Methylation of compound **24** using CH_3I and NaH in DMF afforded 2,3-di-*O*-allyl-6-*O*-methyl-cellulose (**25**) in 87.3% yield, as shown in Figure 2(e).

TABLE 1 Molecular Weights and DPs of Compounds **17**, **19**, **21**, **23**, and **25**

		Position							
Compound	Abbr.	2	3	6	M_w(×10⁴)	M_n(×10⁴)	M_w/M_n	DP_w	DP_n
17	236MC	Me	Me	Me	11.1	4.10	2.71	544	201
19	6All23MC	Me	Me	All	3.86	0.67	5.78	168	29.1
21	3All26MC	Me	All	Me	6.55	3.47	1.88	285	151
23	26All3MC	All	Me	All	5.04	0.93	5.39	197	36.5
25	23All6MC	All	All	Me	4.27	2.46	1.75	167	96.1

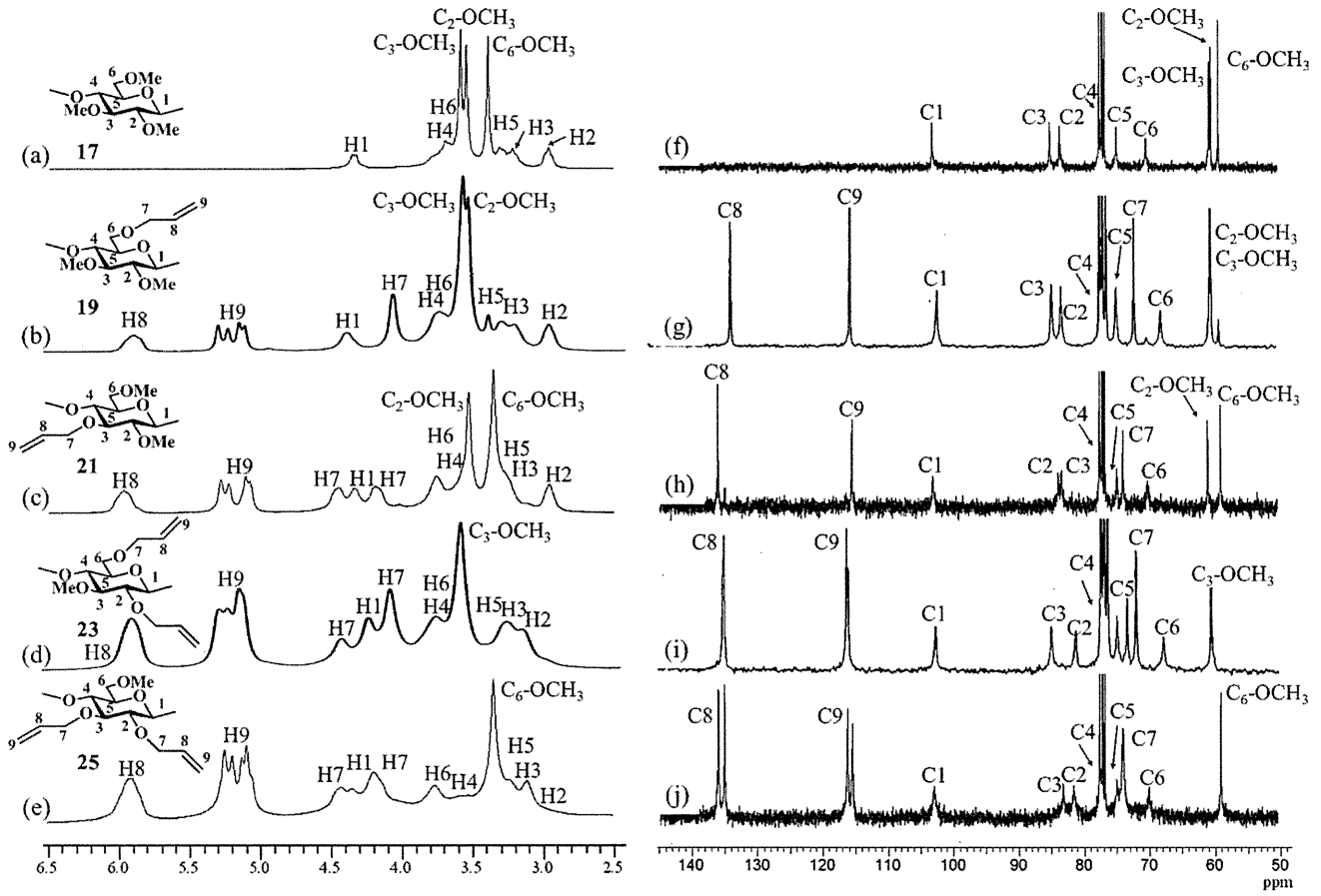


FIGURE 3 ^{1}H and ^{13}C NMR spectra of compounds **17** (a, f), **19** (b, g), **21** (c, h), **23** (d, i), and **25** (e, j) taken in $CDCl_3$.

The molecular weights, DPs, and the polydispersity index (M_w/M_n) estimated by GPC measurement of 236MC (**17**), 6All23MC (**19**), 3All26MC (**21**), 26All3MC (**23**), and 23All6MC (**25**) (All: allyl group) are summarized in Table 1. The DP_ns of 6All23MC (**19**) and 26All3MC (**23**) were found to be lower compared with those of 236MC (**17**), 3All26MC (**21**), and 23All6MC (**25**). Furthermore, the M_w/M_n values of 6All23MC (**19**) and 26All3MC (**23**) were higher than those of 236MC (**17**), 3All26MC (**21**), and 23All6MC (**25**). These GPC results suggest that, in the case of 6All23MC (**19**) and 26All3MC (**23**), degradation occurred because of higher reaction temperature.

The ^{1}H and ^{13}C NMR spectra of 236MC (**17**), 6All23MC (**19**), 3All26MC (**21**), 26All3MC (**23**), and 23All6MC (**25**) measured in $CDCl_3$ are shown in Figure 3. Chemical shifts of 236MC (**17**), 6All23MC (**19**), 3All26MC (**21**), 26All3MC (**23**), and 23All6MC (**25**) are summarized in Table 2.

The substituent groups, such as methoxylated or allyloxylated groups, influenced the chemical shifts of protons and carbons.

The resonances of methoxylated protons at C-2 of 236MC (**17**), 6All23MC (**19**), and 3All26MC (**21**) appeared at around 2.94 ppm in higher magnetic field than those of allyloxylated protons at C-2 of 26All3MC (**23**) and 23All6MC (**25**) at around 3.10 ppm, as shown in Figure 3(a–j) and Table 2. The differences of chemical shifts of H-2 between 2-*O*-methylated and 2-*O*-allylated compounds were ~0.2 ppm. In contrast to the H-2, the substituent groups did not affect the resonances of H-3 and H-6.

The influences of the substituent groups on the chemical shifts of protons and carbons were quite reverse. That is, methoxylated carbons appeared at a lower magnetic field than allyloxylated carbons.

The differences at C-2, C-3, and C-6 were ~2.0 ppm, as shown in Figure 3(f–j) and Table 2.

Acid-Catalyzed Methanolysis of 2,3,6-Tri-*O*-methyl-(17), 6-*O*-Allyl-2,3-di-*O*-methyl- (19), 3-*O*-Allyl-2,6-di-*O*-methyl- (21), 2,6-Di-*O*-allyl-3-*O*-methyl- (23), and 2,3-Di-*O*-allyl-6-*O*-methyl-celluloses (25): Syntheses of Regioselectively Methylated Cellulose Derivatives 236MC (1), 23MC (2), 26MC (3), 3MC (4), and 6MC (5)

We have recently reported the synthesis method for methyl 2,3,6-tri-*O*-methyl-D-glucopyranoside as hydrophobic blocks of surfactants by sulfuric acid–catalyzed methanolysis of 2,3,6-tri-*O*-methyl-cellulose.[21] According to the strategy of acid-catalyzed methanolysis, cellulose derivatives having appropriate DP_ns from 10 to 30 were prepared by adjusting depolymerization time to investigate the influence of the longer hydrophobic blocks on their physicochemical

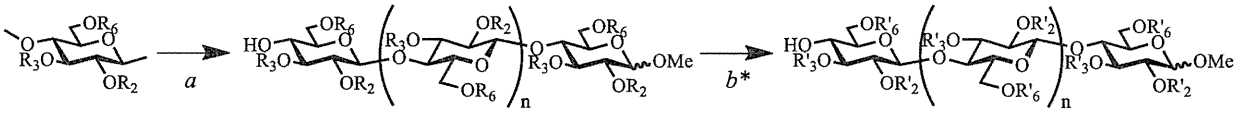
TABLE 2 Chemical Shifts of Compounds **17**, **19**, **21**, **23**, and **25**

Compound	Position			δ (ppm)											
	2	3	6	C-1	H-1	C-1	H-2	C-3	H-3	C-4	H-4	C-5	H-5	C-6	H-6	C-7	H-7	C-8	H-8	C-9	H-9	$C2\text{-}OCH_3$	$C3\text{-}OCH_3$	$C6\text{-}OCH_3$
17	Me	Me	Me		4.33		2.95		3.21		3.69		3.30		3.62-3.68		–		–		–	3.54	3.59	3.39
19	Me	Me	All		4.36		2.94		3.28		3.52–3.90		3.37		3.52–3.90		4.04		5.87		5.19	3.52	3.55	–
21	Me	All	Me		4.34		2.95		3.26		3.74		3.24		3.65, 3.76		4.19, 4.44		5.97		5.17	3.53	–	3.35
23	All	Me	All		4.41		3.10		3.23		3.74		3.26		3.80, 3.71		4.05, 4.40		5.88		5.21	–	3.55	–
25	All	All	Me		4.35		3.11		3.32		3.75		3.23		3.75, 3.57		4.20, 4.43		5.92		5.16	–	–	3.35
	2	3	6	C-1	H-1	C-1	H-2	C-3	H-3	C-4	H-4	C-5	H-5	C-6	H-6	C-7	H-7	C-8	H-8	C-9	H-9	$C2\text{-}OCH_3$	$C3\text{-}OCH_3$	$C6\text{-}OCH_3$
17	Me	Me	Me	103.1		83.4		84.9		77.1		74.8		70.2		–		–		–		60.3	60.5	59.1
19	Me	Me	All	102.8		83.5		85.0		77.2		74.9		68.0		72.2		135.0		116.4		60.3	60.4	–
21	Me	All	Me	102.9		83.7		83.2		77.2		74.7		69.9		73.7		136.0		115.4		60.7	–	58.8
23	All	Me	All	102.7		81.3		85.0		77.1		75.0		67.9		73.5, 72.1		135.0, 135.2		116.1, 116.4		–	60.6	–
25	All	All	Me	103.2		81.3		83.0		77.2		74.7		69.8		73.7, 73.9		135.0, 136.1		115.4, 116.1		–	–	58.8

properties such as gelation upon heating. Moderate depolymerization of 2,3,6-tri-*O*-methyl-cellulose (**17**) was carried out in MeOH and $CHCl_3$ (4/5, v/v) using concentrated sulfuric acid, as shown in Figure 4. The DP_ns of obtained cellulose derivatives were estimated by GPC measurement using polystyrene standards. Figure 5 shows ^1H NMR spectra of 2,3,6-tri-*O*-methyl-cellulose (**17**) and compounds obtained after different depolymerization time (1, 2, 3, and 9 h). The resonance of H-1 of the repeating units of compound **17** appeared at 4.34 ppm. On the other hand, the resonances of H-1α of methyl 2,3,6-tri-*O*-methyl-α-D-glucopyranoside and H-1β of methyl 2,3,6-tri-*O*-methyl-β-D-glucopyranoside appeared at 4.87 and 4.21 ppm, respectively. The resonance of H-1 of the repeating units at 4.34 ppm decreased, and those of methyl 2,3,6-tri-*O*-methyl-D-glucopyranosides increased with increasing reaction time of depolymerization. Namely, DP_n of compound **17** decreased with increasing reaction time, and eventually compound **17** was completely depolymerized to give methyl 2,3,6-tri-*O*-methyl-D-glucopyranoside after 9 h. As a hydrophobic block for a following glycosylation reaction, compound **1** with DP_n = 11.7 was finally obtained after depolymerization time of 1 h, because methyl glucosides were obviously produced after 2 h. The MALDI-TOF MS spectrum of compound **17** will be shown in later section.

We allylated regioselectively methylated cellulose derivatives before sulfuric acid–catalyzed methanolysis and glycosylation reaction, because allylated cellulose derivatives were more stable under acidic conditions. Because of the low solubility of 3-*O*-allyl-2,6-di-*O*-methyl-cellulose (**21**) in the reaction medium consisting of MeOH and $CHCl_3$ (4/5, v/v), the depolymerization did not proceed in such a mixed solvent, although in the case of compound **17**, the depolymerization in MeOH and $CHCl_3$ (4/5, v/v) proceeded to give compound **1** with DP_n = 11.7. Depolymerization of compound **21** with DP_n = 151 with concentrated sulfuric acid in MeOH and $CHCl_3$ (4/5, v/v) for 1, 2, and 3 h gave products with DP_n = 95.0, 64.2, and 67.5, respectively. Thus, we changed a reaction medium to more hydrophobic one consisting of MeOH and $CHCl_3$ (2/7, v/v) for 1, 2, and 3 h to give depolymerization products with DP_n = 13.0, 6.1, and 5.0, respectively.

As a result, depolymerization of compound **21** for 1 h gave methyl 3-*O*-allyl-2,6-di-*O*-methyl-celluloside (**22**) with DP_n = 13.0 successfully. The same solvent ratio for compound **22** was applied to the methanolysis of 6-*O*-allyl-2,3-di-*O*-methyl- (**19**), 2,6-di-*O*-allyl-3-*O*-methyl- (**23**), and 2,3-di-*O*-allyl-6-*O*-methyl-celluloses (**25**) to give depolymerization products **20**, **23**, and **26** having DP_n from 10 to 30, as summarized in Table 3. Figure 6 shows ^1H NMR spectra of compounds **1**, **20**, **22**, **24**, and **26** measured in $CDCl_3$. Resonances for H1α protons of glucosyl residue at the reducing end could be observed at about 4.8 ppm, indicating the successful chain degradation.



17: R_2 =Me, R_3 = Me, R_6 = Me
19: R_2 =Me, R_3 = Me, R_6 = All
21: R_2 = Me, R_3 = All, R_6 = Me
23: R_2 = All, R_3 = Me, R_6 = All
25: R_2 = All, R_3 = All, R_6 = Me

1 (236MC): R_2 =Me, R_3 = Me, R_6 = Me
20: R_2 =Me, R_3 = Me, R_6 = All
22: R_2 = Me, R_3 = All, R_6 = Me
24: R_2 = All, R_3 = Me, R_6 = All
26: R_2 = All, R_3 = All, R_6 = Me

2 (23MC): R'_2 =Me, R'_3 = Me, R'_6 = H
3 (26MC): R'_2 = Me, R'_3 = H, R'_6 = Me
4 (3MC) : R'_2 = H, R'_3 = Me, R'_6 = H
5 (6MC) : R'_2 = H, R'_3 = H, R'_6 = Me

a) H_2SO_4 / MeOH / $CHCl_3$ / 60°C / 1 h; b) $PdCl_2$ / MeOH / $CHCl_3$ / r.t. / 24 h
* Removal of allyl groups of compounds **20, 22, 24, and 26**

FIGURE 4 Synthetic route for glycosyl acceptors **20, 22, 24**, and **26** and compounds **1–5**.

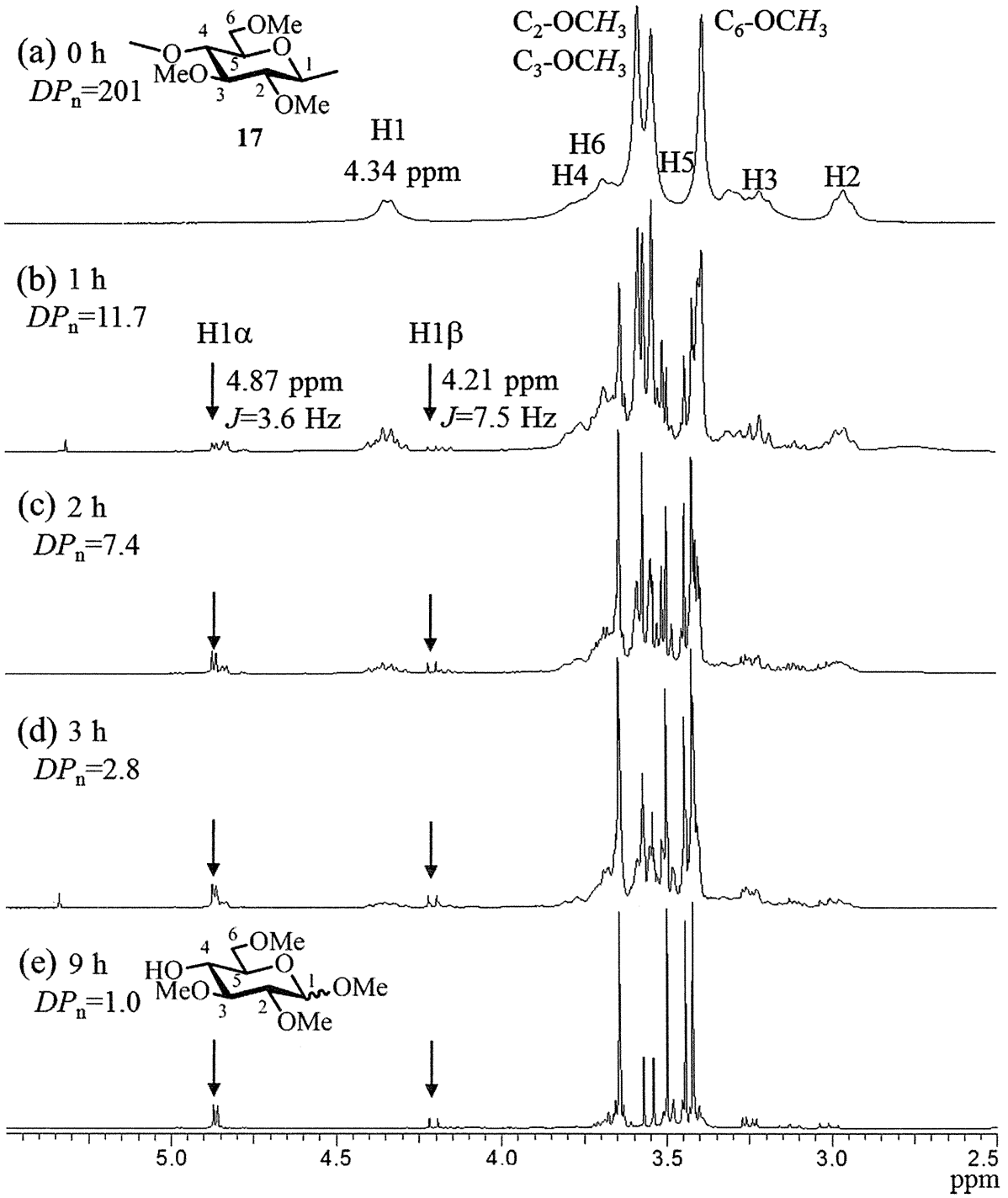


FIGURE 5 ^1H NMR spectra measured in $CDCl_3$ of compound **17** and products after different depolymerization time.

TABLE 3 Molecular Weights and DPs of Compounds **1**, **20**, **22**, **24**, and **26**

		Position							
Compound	Abbr.	2	3	6	M_w ($\times 10^3$)	M_n ($\times 10^3$)	M_w/M_n	DP_w	DP_n
1	236MC	Me	Me	Me	4.70	2.38	1.96	23.0	11.7
20	6All23MC	Me	Me	All	3.49	2.30	1.52	15.2	10.0
22	3All26MC	Me	All	Me	5.79	3.0	1.93	25.2	13.0
24	26All3MC	All	Me	All	3.30	2.89	1.13	12.9	11.3
26	23All6MC	All	All	Me	16.0	8.39	1.90	62.5	32.8

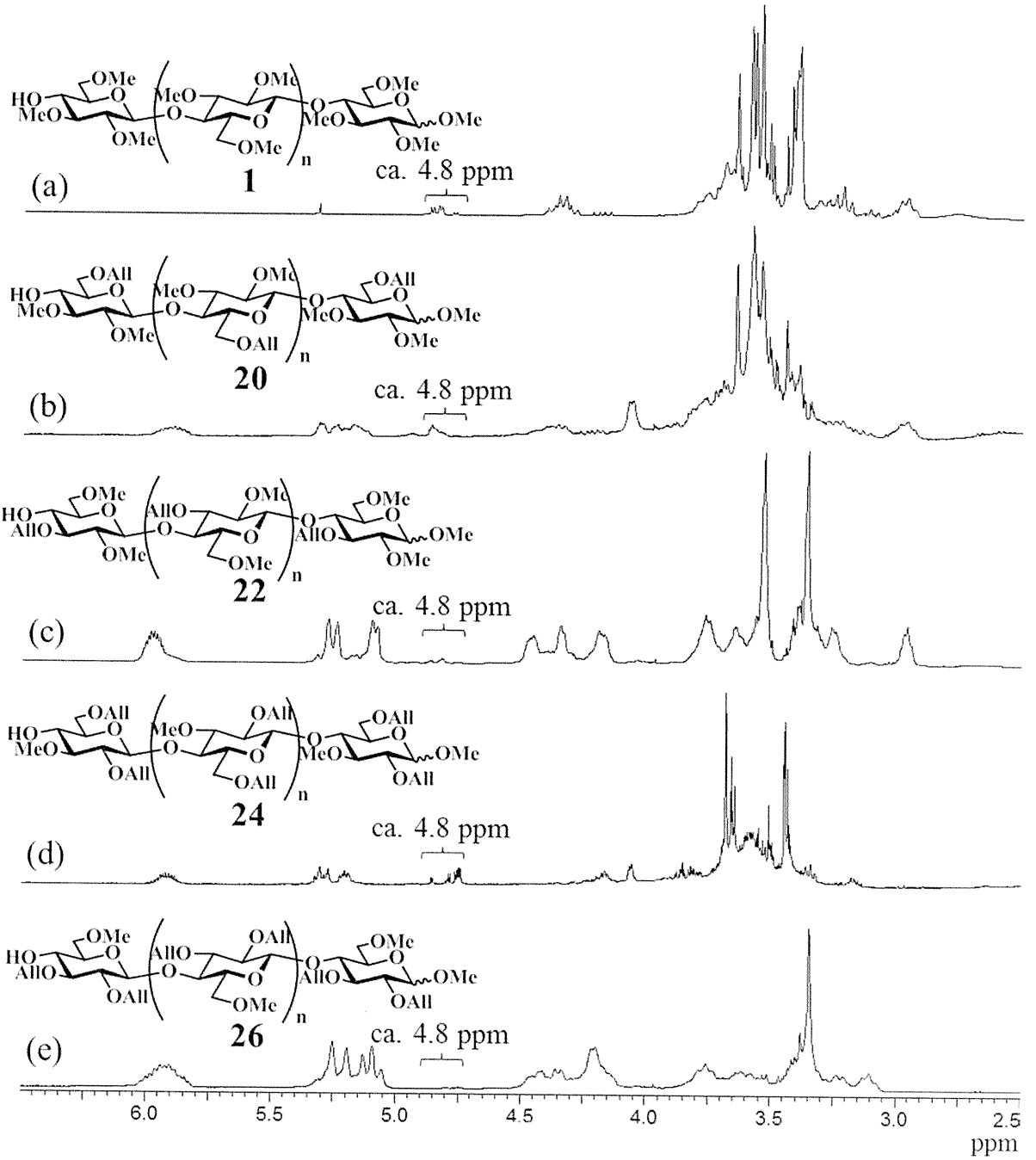
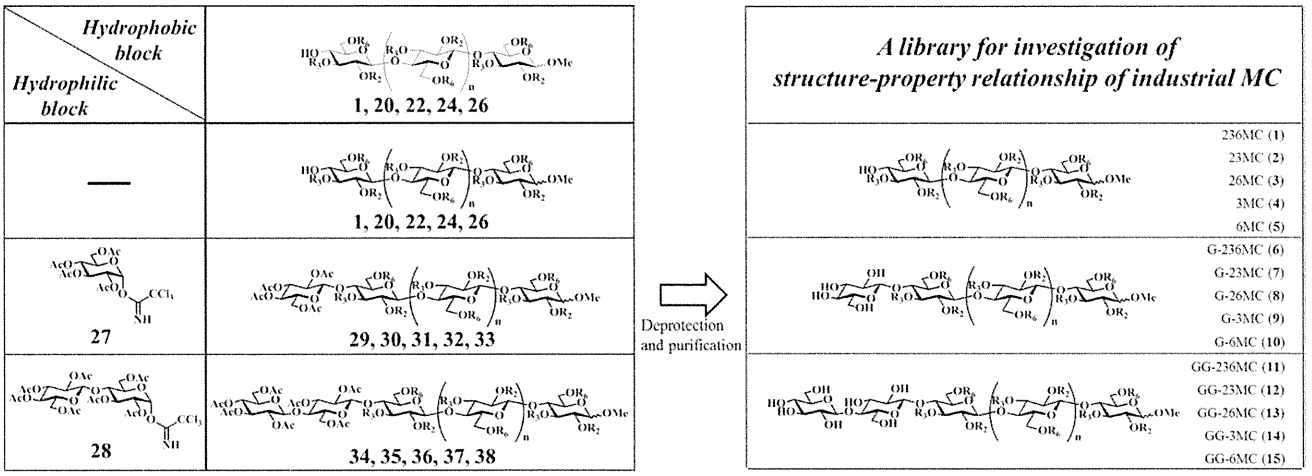


FIGURE 6 ^1H NMR spectra measured in $CDCl_3$ of compounds **1**, **20**, **22**, **24**, and **26**.



1, **29**, **34**: R_2=Me, R_3=Me, R_6=Me; **20**, **30**, **35**: R_2=Me, R_3=Me, R_6=All; **22**, **31**, **36**: R_2=Me, R_3=All, R_6=Me; **24**, **32**, **37**: R_2=All, R_3=Me, R_6=All; **26**, **33**, **38**: R_2=All, R_3=All, R_6=Me

1, **6**, **11**: R_2=Me, R_3=Me, R_6=Me; **2**, **7**, **12**: R_2=Me, R_3=Me, R_6=H; **3**, **8**, **13**: R_2=Me, R_3=H, R_6=Me; **4**, **9**, **14**: R_2=H, R_3=Me, R_6=H; **5**, **10**, **15**: R_2=H, R_3=H, R_6=Me

Reaction condition of glycosylation: trimethylsilyl trifluoromethane sulfonate (TMSOTf) / CH_2Cl_2 / MS 4Å / 0 °C / 24 h / under a high vacuum system
Reaction condition of deacetylation: 28% $NaOCH_3$ in MeOH / MeOH / THF / r.t. / 24 h
Reaction condition of deallylation: $PdCl_2$ / MeOH / $CHCl_3$ / r.t. / 24 h

FIGURE 7 Syntheses of regioselectively methylated cellulose derivatives **1–5** and diblock copolymers of regioselectively methylated cellulose and unmodified cello-oligosaccharides **6–15.**

Glycosylation for Diblock Copolymers of Regioselectively Methylated Celluloses and Unmodified Cello-Oligosaccharides 6–15

In general, glycosyl donors having an ester group at C-2 capable of neighboring group participation give the corresponding 1,2-*trans* glycoside with quite high stereoselectivity in glycosylation reaction. However, the sugar orthoesters are frequently produced as intermediates or undesired products.[25] On the other hand, it is well known that in the presence of protic or Lewis acids, such as trimethylsilyl trifluoromethanesulfonate (TMSOTf), the sugar orthoesters formed during glycosylation subsequently rearrange to the corresponding 1,2-*trans* glycosidic products.[26–28] This TMSOTf-promoted rearrangement has recently been put into good

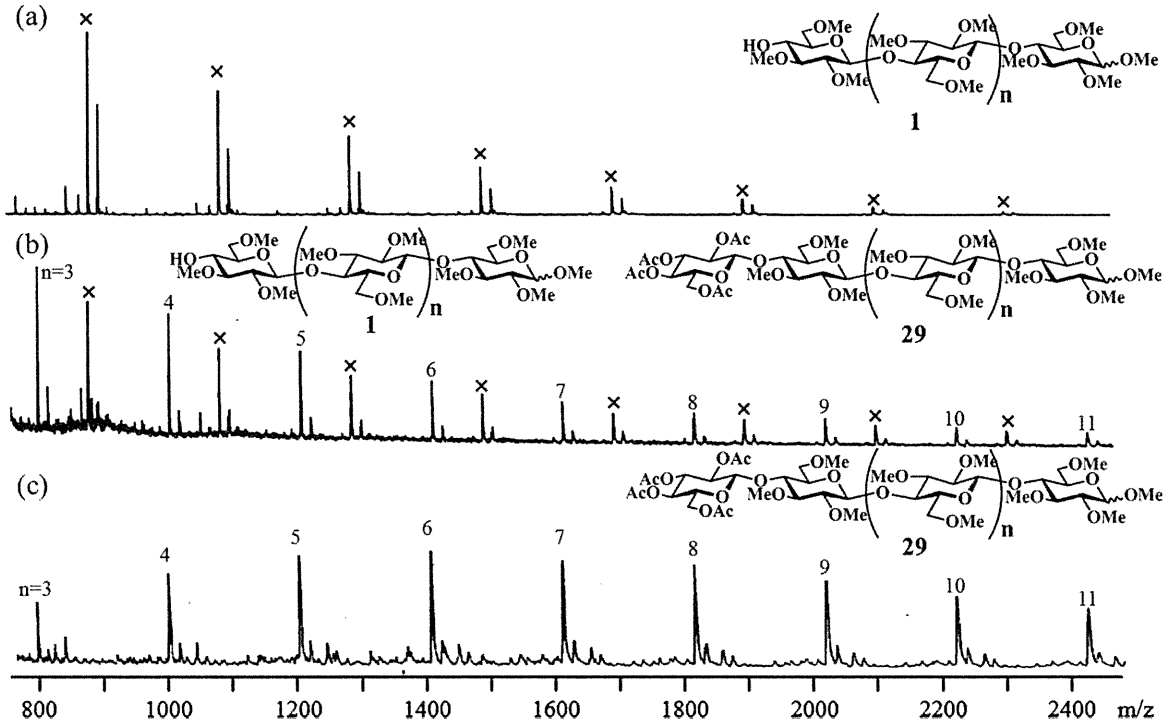


FIGURE 8 MALDI-TOF MS spectra of (a) glycosyl acceptor **1** (×), (b) product containing compound **1**, and (c) compound **29**.

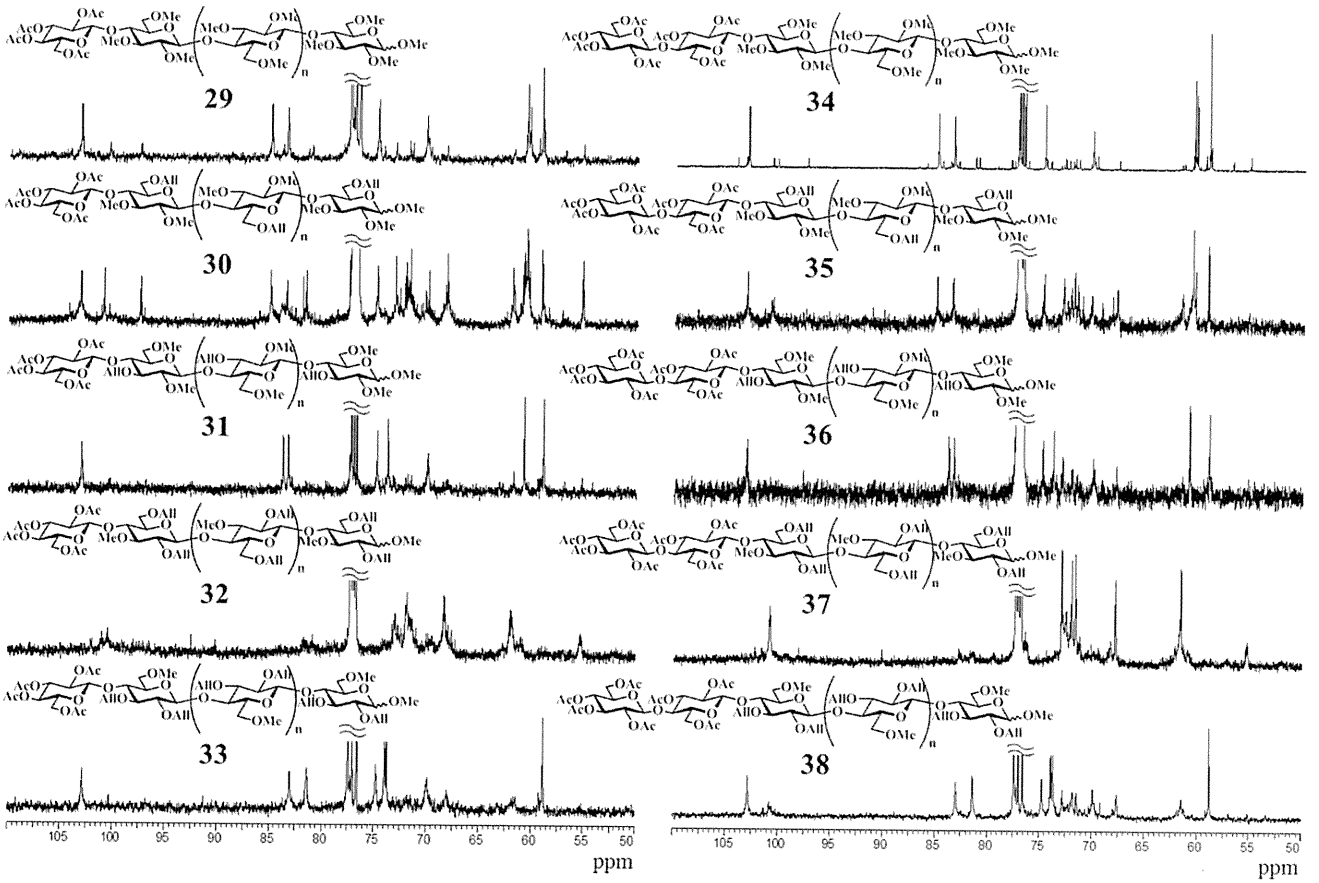


FIGURE 9 ^{13}C NMR spectra of compounds **29–38** taken in $CDCl_3$.

TABLE 4 Molccular Weights and DPs of Water-Soluble Parts of Compounds **1–15**

			Hydrophobic Block								
			Position of Substituents								
Compound No.	Abbr.	Hydrophilic Part	2	3	6	$M_w(\times10^3)$	$M_n(\times10^3)$	M_w/M_n	DP_w	DP_n	DS
1	236MC	–	Me	Me	Me	1.61	0.76	2.11	7.89	3.7	2.77
2	23MC	–	Me	Me	OH	4.21	1.29	3.26	18.1	5.5	1.94
3	26MC	–	Me	OH	Me	2.01	1.66	1.21	8.66	7.1	1.95
4	3MC	–	OH	Me	OH	7.52	4.20	1.79	28.9	16.1	1.00
5	6MC	–	OH	OH	Me	16.0	8.20	1.95	61.5	32.0	0.98
6	G-236MC	G	Me	Me	Me	3.43	2.30	1.49	16.2	10.7	2.65
7	G-23MC	G	Me	Me	OH	1.86	1.13	1.64	7.59	4.5	1.54
8	G-26MC	G	Me	OH	Me	3.65	1.74	2.09	15.3	7.1	1.69
9	G-3MC	G	OH	Me	OH	1.78	1.29	1.37	6.57	4.7	0.87
10	G-6MC	G	OH	OH	Me	12.0	6.90	1.74	45.8	26.2	0.94
11	GG-236MC	GG	Me	Me	Me	5.06	3.02	1.67	23.7	13.8	2.52
12	GG-23MC	GG	Me	Me	OH	4.86	2.28	2.12	20.2	9.2	1.56
13	GG-26MC	GG	Me	OH	Me	3.17	2.04	1.55	13.0	8.1	1.51
14	GG-3MC	GG	OH	Me	OH	1.84	1.39	1.32	6.70	5.0	0.71
15	GG-6MC	GG	OH	OH	Me	14.0	7.50	1.86	53.4	28.4	0.91

Molecular weight and DPs values were determined by means of GPC after acetylation. G:hydrophilic glucosy block, GG:hydrophilic cellobiosyl block.

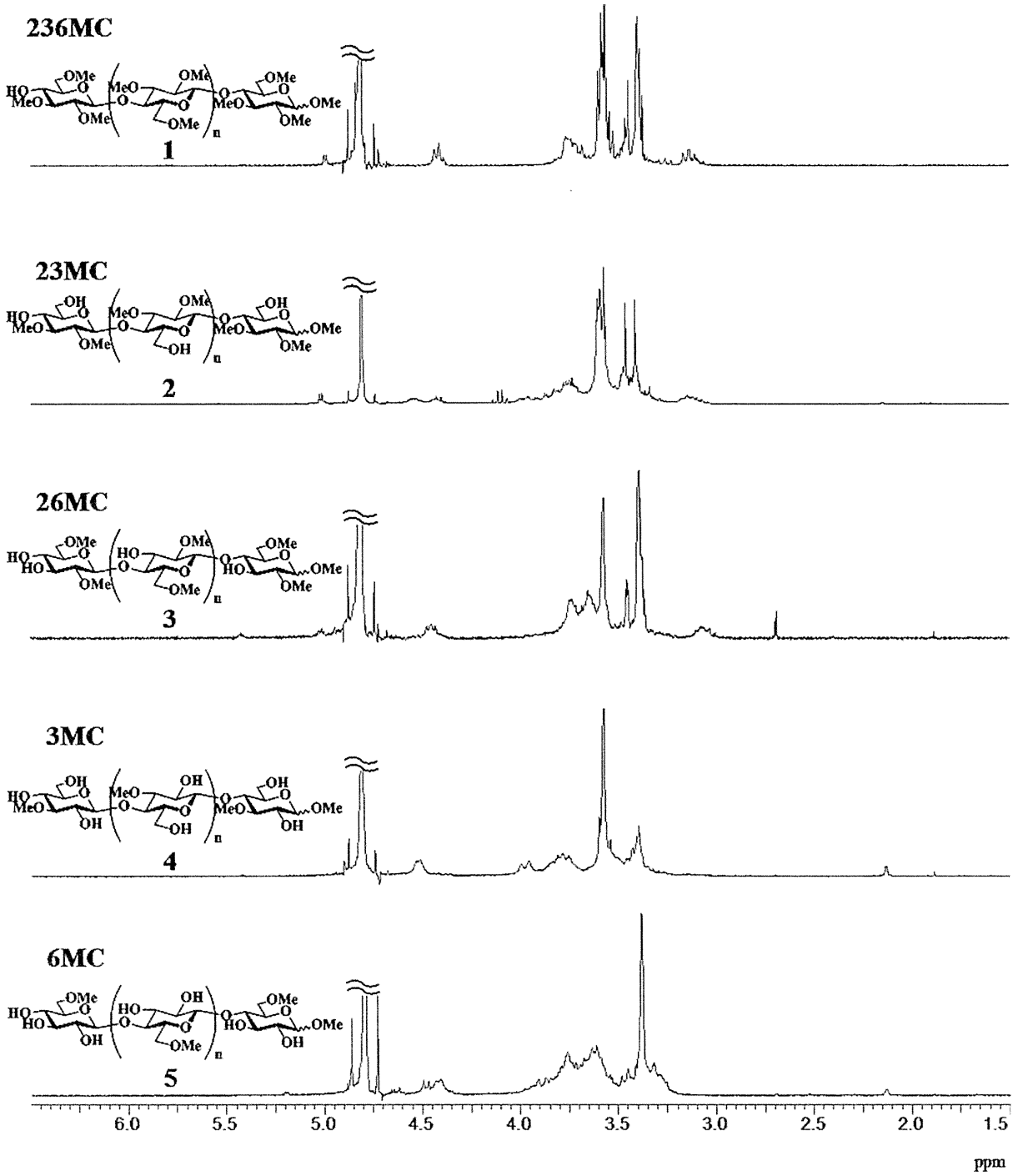


FIGURE 10 ^{1}H NMR spectra of compounds **1–5** taken in D_2O.

use. Thus, we selected TMSOTf as a catalyst for glycosylation reaction to prevent the production of undesired orthoesters.

A glycosyl donor, 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl 2,2,2-trichloroacetoimidate (**27**), was glycosylated with 2,3,6-tri-*O*-methyl-acceptor **1** using TMSOTf under high vacuum condition at 0 °C, illustrated in Figure 7. The amount of donor **27** and TMSOTf was calculated using the number-average molecular weight of the acceptor **1** calculated by GPC measurement, because the acceptor **1** was a polydisperse mixture of compounds having different molecular weights. First, 2 equiv of donor **27** was glycosylated with 1 equiv of acceptor **1**. MALDI-TOF MS spectrum shown in Figure 8(b) revealed that the acceptor **1** did not react completely after the reaction. The diblock copolymer **29** could not be separated from the acceptor **1** by gel filtration chromatography. Thus, excess amount of donor **27** (12 equiv) was reacted with the acceptor **1**. Crude glycosylation product was purified by silica gel chromatography (eluent: EtOAc) to give

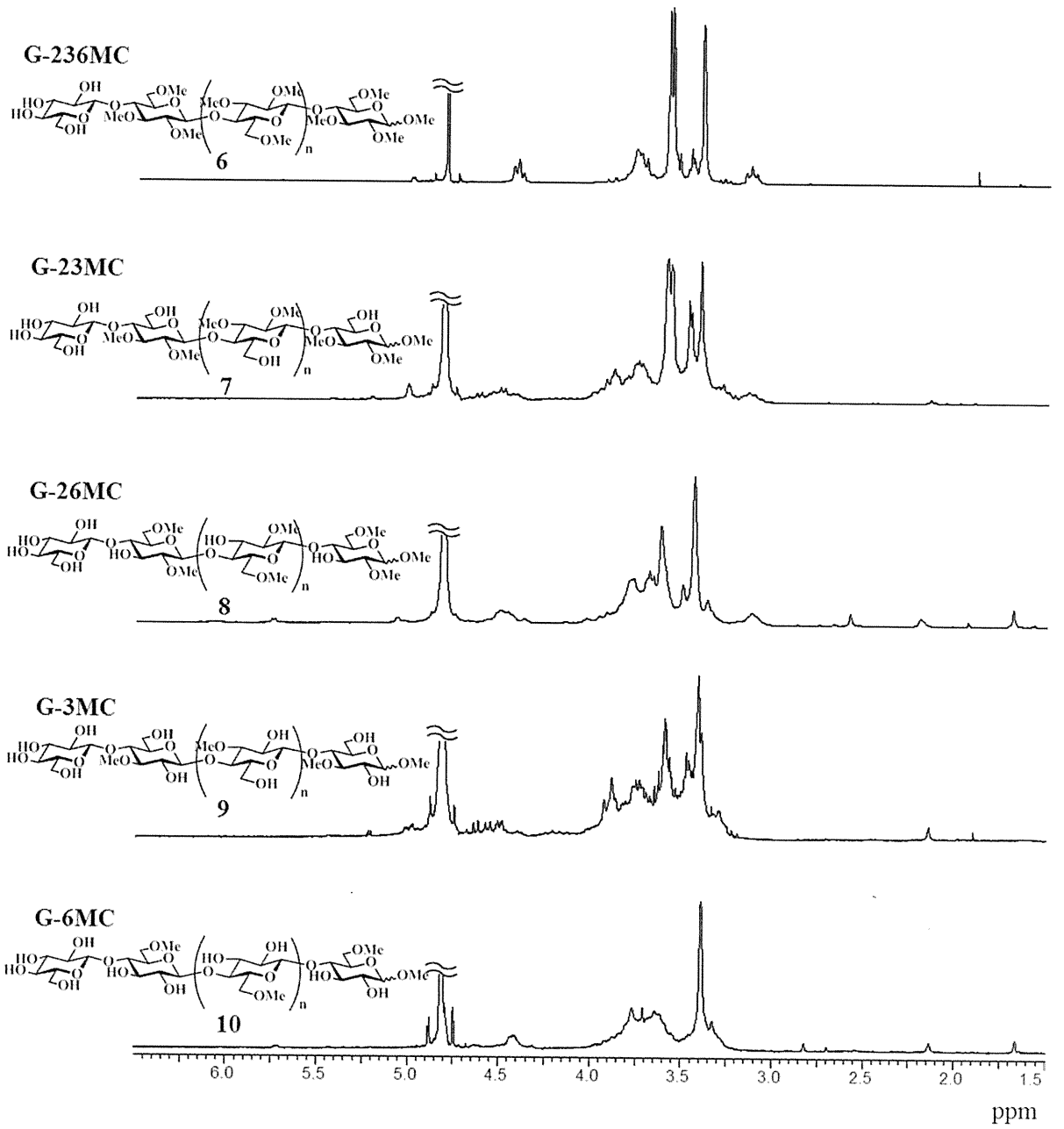


FIGURE 11 ^{1}H NMR spectra of compounds **6–10** taken in D_2O.

diblock copolymers, methyl 2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-methyl-celluloside (**29**). As shown in Figure 8(c), no peak of the acceptor **1** in MALDI-TOF MS spectrum indicates that no acceptor remained and the desired compound **29** was successfully obtained. According to the same reaction condition as compound **1**, glycosylation of glucosyl trichloroacetimidate derivative **27** with acceptors **20**, **22**, **24**, and **26**, and cellobiosyl trichloroacetimidate derivative **28** with acceptors **1**, **20**, **22**, **24**, and **26** gave diblock copolymers, methyl 2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl-(1→4)-6-*O*-allyl-2,3-di-*O*-methyl-celluloside (**30**) (G_{Ac}-6All23MC, G: glucopyranosyl residue, Ac: acetyl group, All: allyl group), G_{Ac}-3All26MC (**31**), G_{Ac}-26All3MC (**32**), G_{Ac}-23All6MC (**33**), methyl 2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-*β*-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-methyl-celluloside (**34**) (GG_{Ac}-236MC, GG: cellobiosyl residue), GG_{Ac}-6All23MC (**35**), GG_{Ac}-3All26MC (**36**), GG_{Ac}-26All3MC (**37**), and GG_{Ac}-23All6MC (**38**). As shown in Figure 9, the C-1 carbon resonances of acetylated glucosyl residue of compounds **29–38** appeared at about 100 ppm, indicating *β*-linkages between acetylated glucosyl or cellobiosyl block and methylated ones.

Allyl groups of compounds **20**, **22**, **24**, and **26** were removed using $PdCl_2$ in MeOH and $CHCl_3$ at room temperature to give

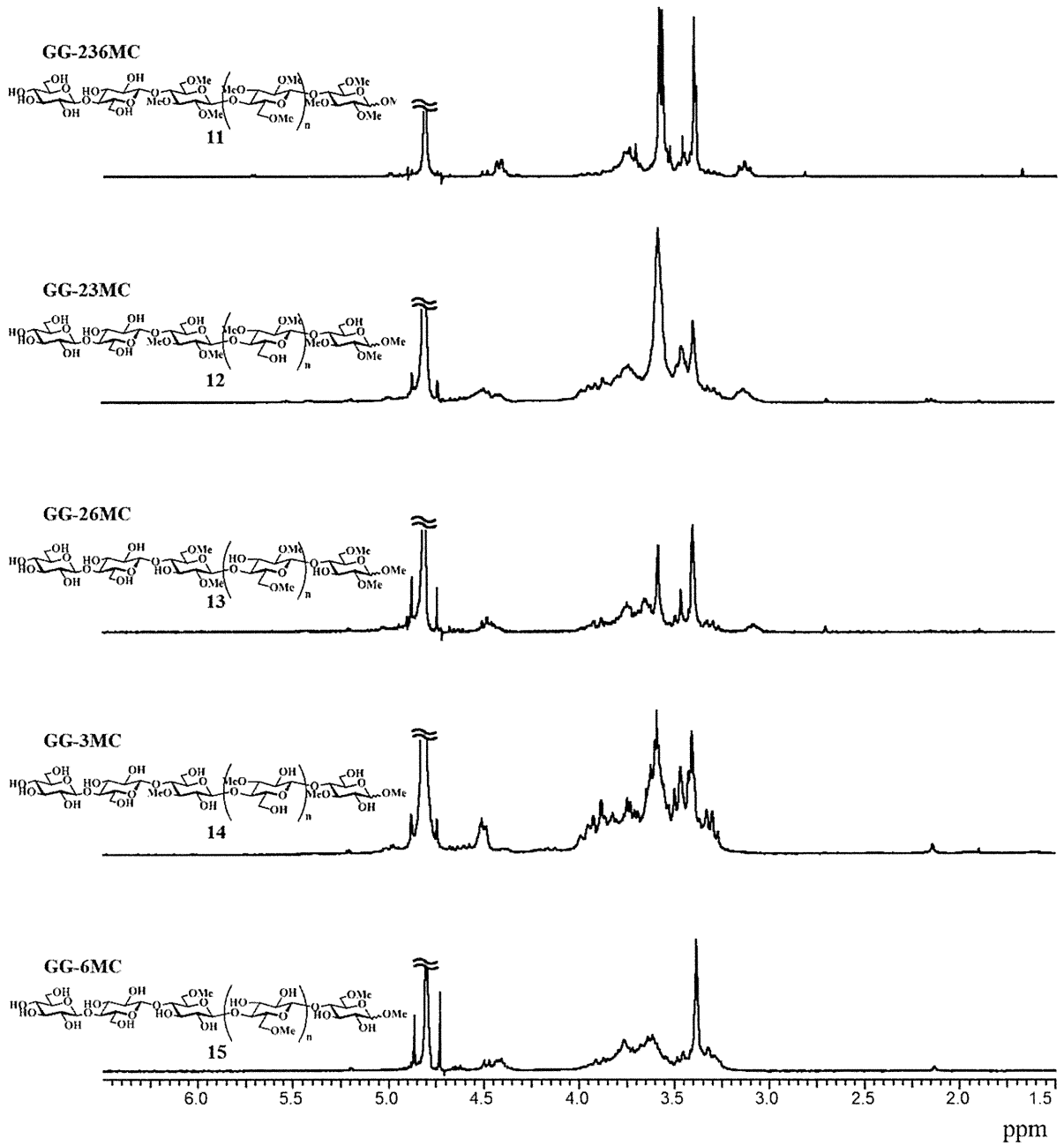


FIGURE 12 ^{1}H NMR spectra of compounds **11–15** taken in D_2O.

regioselectively methylated cellulose derivatives, **2** (23MC), **3** (26MC), **4** (3MC), and **5** (6MC) in 96.9, 86.3, 89.5, and about 100% yield, respectively. Acetyl groups of compounds **29–38** were removed using 28% $NaOCH_3$ in MeOH to give diblock copolymers **6** (G-236MC), **11** (GG-236MC), **39** (G-6All23MC), **40** (G-3All26MC), **41** (G-26All3MC), **42** (G-23All6MC), **43** (GG-6All23MC), **44** (GG-3All26MC), **45** (GG-26All3MC), and **46** (GG-23All6MC) in 96.4, 81.0, 95.7, 100, 69.8, 83.5, 84.1, 90.0, 55.2, and 82.7% yield, respectively. Compounds **39–46** had poor solubility in $CHCl_3$ and water, whereas they were soluble in 20% $MeOH/CH_2Cl_2$. Removal of allyl groups of compounds **39–46** was therefore carried out in MeOH and $CHCl_3$ (5/8, v/v) in the presence of $PdCl_2$ to produce diblock copolymers consisting of regioselectively methylated celluloses and unmodified cello-oligosaccharides, **7** (G-23MC), **8** (G-26MC), **9** (G-3MC), **10** (G-6MC), **12** (GG-23MC), **13** (GG-26MC), **14** (GG-3MC), and **15** (GG-6MC).

Preparation of Water-Soluble Compounds 1–15

Regioselectively methylated cellulose derivatives, 2,3,6-tri-*O*-,[9] 2,3-di-*O*-,[6,10,11], 2,6-di-*O*-,[12] 3-*O*-,[13] and 6-*O*-methyl-cellulose,[14] from natural cellulose were not soluble in water. It was therefore of importance to investigate the water solubility of compounds **1–15**, depending on their molecular weight. Actually, compounds **1–5** with low molecular weight were soluble in water. Diblock copolymers could be divided

in water-soluble and -insoluble parts, depending on their molecular weight. The water-soluble regioselectively methylated cellulose derivatives **1–5** and diblock copolymers of regioselectively methylated cellulose and unmodified cello-oligosaccharides **6–15** were collected by centrifugation method (IWAKI microcentrifuge CFM-100, room temperature, 5 min, three times) for the removal of water-insoluble parts. The molecular weights, DPs, and the polydispersity index (M_w/M_n) estimated by GPC measurement after acetylation of water-soluble compounds **1–15** are summarized in Table 4. The DP_n of water-soluble regioselectively methylated cellulose derivatives **1–5** increased with decreasing DS, whereas no detailed trends were observed regarding the relationships between the DP_n and DS of diblock copolymers **6–15**.

Compounds **1** (236MC), **6** (G-236MC), and **11** (GG236MC) were amphiphilic and soluble in $CHCl_3$, whereas compounds **2** (23MC), **3** (26MC), **4** (3MC), **5** (6MC), **7** (G-23MC), **8** (G-26MC), **9** (G-3MC), **10** (G-6MC), **12** (GG-23MC), **13** (GG-26M1C), **14** (GG-3MC), and **15** (GG-6MC) were not soluble in $CHCl_3$. ^1H NMR spectra of compounds **1–15** taken in D_2O are shown in Figures 10–12. The sharpness of the ^1H NMR resonances of compounds **1–15** in D_2O indicated that compounds **1–15** were soluble in water.

CONCLUSIONS

Diblock copolymers of regioselectively methylated celluloses and unmodified cello-oligosaccharides, methyl β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-methyl-celluloside **6** (G-236MC, G: hydrophilic glucosyl residue), **7** (G-23MC), **8** (G-26MC), **9** (G-3MC), **10** (G-6MC), methyl β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-methyl-celluloside **11** (GG-236MC, GG: hydrophilic cellobiosyl residue), **12** (GG-23MC), **13** (GG-26MC), **14** (GG-3MC), and **15** (GG-6MC) were synthesized for the first time via combination of the glycosyl trichloroacetimidate method and the acid-catalyzed methanolysis method. Sulfuric acid–catalyzed methanolysis of regioselectively allylated and methylated cellulose derivatives was a suitable method to prepare hydrophobic building blocks having a free hydroxyl group at C-4 at the nonreducing end as glycosyl acceptors for amphiphilic cellulosic diblock copolymers. A glycosylation method was shown to be capable of reacting such polymeric glycosyl acceptors with acylated glucose or cellobiose donors to give diblock copolymers of regioselectively methylated celluloses and unmodified cello-oligosaccharides **6–15** after the removal of temporary protective groups. Surface activity, thermal aggregation behavior, and hydrogel-forming ability of aqueous solutions of compounds **1–15** will be discussed in a separate article.[29]

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Note

Preparation of 6-azafulleroid-6-deoxy-2,3-di-*O*-myristoylcellulose

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ABSTRACT

6-Azafulleroid-6-deoxy-2,3-di-*O*-myristoylcellulose (**3**) was synthesized from 6-azido-6-deoxycellulose (**1**) by two reaction steps. The myristoylation of compound **1** with myristoyl chloride/pyridine proceeded smoothly to give 6-azido-6-deoxy-2,3-di-*O*-myristoylcellulose (**2**) in 97.0% yield. The reaction of compound **2** with fullerene (C_{60}) was carried out by microwave heating to afford compound **3** in high yield. It was found from FT-IR, ^{13}C NMR, UV–vis, differential pulse voltammetry (DPV), SEC analyses that compound **3** was the expected C_{60}-containing polymer. Consequently, maximum degree of substitution of C_{60} (DS_{C60}) of compound **3** was 0.33.

Cellulose is the most abundant biomacromolecule in nature, and is important as biodegradable and renewable organic material. Recently, new applications of cellulose derivatives as advanced materials such as shape memory-recovery material[1] and photoactive materials[2] have been reported. One of the proposals of cellulose derivatives for the advanced materials is the photocurrent generation system using porphyrin-containing cellulose derivatives as electron donor materials.[3–5] Sakakibara and Nakatsubo reported the Langmuir–Blodgett film of porphyrin–fullerene (C_{60}) system using the porphyrin-containing cellulose derivative and C_{60} with high photocurrent generation performance.[4] Then, C_{60}-containing cellulose derivative is also attractive for the photocurrent generation system as an electron acceptor material, because it is expected to be useful for forming an electron transporting pathway in the system. However, there is no report for the preparation of C_{60}-containing cellulose derivative. Addition reaction of organic azides with C_{60} has been widely applied to the preparation of C_{60}-bearing polymers.[6–12] Then, this paper describes the preparation of 6-azafulleroid-6-deoxy-2,3-di-*O*-myristoylcellulose (**3**) from 6-azido-6-deoxycellulose (**1**). In the target compound **3**, myristoyl group was selected as O-2 and O-3 substituent groups to enhance solubility for common organic solvents and formability of Langmuir–Blodgett film, because it was found to be preferable to the purposes in a preliminary experiment.

The synthetic route for 6-azafulleroid-6-deoxy-2,3-di-*O*-myristoylcellulose (**3**) from 6-azido-6-deoxycellulose (**1**)[13] by two reaction steps is shown in Scheme 1. Myristoylation of 6-azido-6-deoxycellulose (**1**) with myristoyl chloride in the presence of pyridine in LiCl/DMAc afforded 6-azido-6-deoxy-2,3-di-*O*-myristoylcellulose (**2**) in 97.0% yield.

Addition reaction of C_{60} to compound **2** was carried out according to the modified method of Okamura et al. to give 6-azafulleroid-6-deoxy-2,3-di-*O*-myristroyl cellulose (**3**).[9] That is, compound **2** and C_{60} were reacted at 140 °C for 3 h in *o*-dichlorobenzene (ODCB) to give product **3-i**. Microwave (MW) heating was used for the reaction because it was reported that MW heating has an advantage of shortening reaction times compared with conventional heating (an oil bath method) in the preparation of cellulose derivatives[14] and in the addition reaction of C_{60} to azido-compounds.[12,15,16]

Product **3-i**, which was easily soluble in organic solvents, such as $CHCl_3$, CH_2Cl_2, THF, toluene, chlorobenzene, and ODCB, was subjected to FT-IR, ^{13}C NMR, UV–vis, differential pulse voltammetry (DPV), and SEC measurement for its characterization. In FT-IR spectrum of product **3-i**, the band at 2104 cm^{-1} from azido groups was completely disappeared, suggesting that heating time for 3 h by MW heating was enough for the addition reaction. The small characteristic band at 527 cm^{-1} derived from C_{60}[8,10] was newly appeared. In ^{13}C NMR spectrum of product **3-i**, the broad peak in the range of 130–150 ppm assigned to C_{60} moiety[9,11] and the sharp peaks in the range of from 17 to 35 ppm derived from myristoyl groups were observed. Figure 1 shows UV–vis spectrum of product **3-i** and C_{60}. The characteristic peaks at 330 nm from C_{60}[7,10] were found in the spectrum of product **3-i**, although compound **2** has no absorption at the region. Electrochemical analysis such as cyclic

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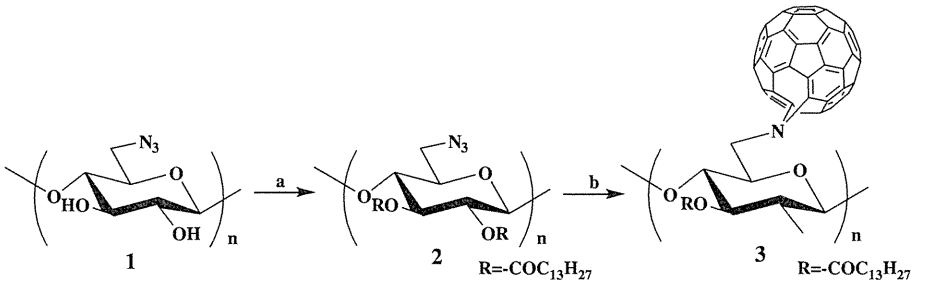

a: $C_{13}H_{27}COCl$ /pyridine /LiCl-DMAc /70°C/ 24h
b: C_{60} /ODCB / 100-140'C (by microwave) / 2-3h

Scheme 1. Synthetic route for 6-azafulleroid-6-deoxy-2,3-di-*O*-myristoylcellulose (**3**).

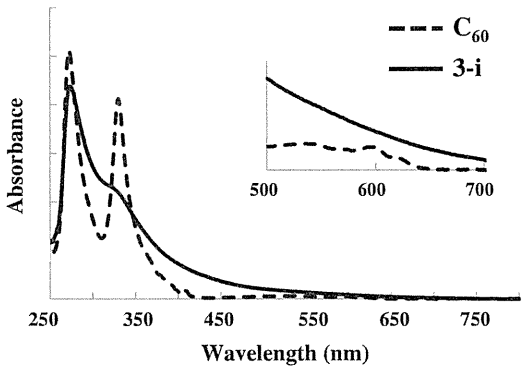

Figure 1. UV–vis spectra of product **3-i** and C_{60}.

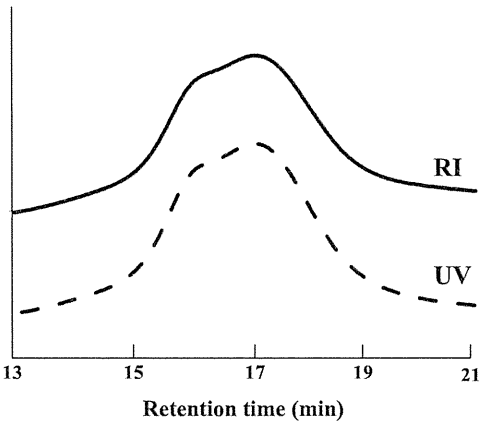

Figure 3. SEC elution curves of product **3-i**.

voltammetry (CV) and differential pulse voltammetry (DPV) is one of the methods for characterization of substituted C_{60}. It is reported that the reduction potential peaks, which are observed in CV or DPV of unsubstituted C_{60}, are negatively shifted in CV or DPV of substituted C_{60} such as azafulleroid.[10,17,18] Figure 2 shows the DPV curves of product **3-i** and C_{60} in 0.1 M tetrabutylammonium perchlorate (TBAP)/ODCB. The negative shifts of three characteristic reduction peaks of C_{60} were observed in DPV of product **3-i**. SEC is also important method for characterization of C_{60}-containing polymer. For example, Okamura et al. reported that C_{60}-pullulan derivatives were characterized by SEC with RI and UV (detective wavelength: 700 nm) detections.[9] Figure 3 shows SEC elution curves of product **3-i** by RI and UV detectors. UV detection was performed by UV-600 nm, because of the detection ability of our UV-detector. The RI and UV elution curves showed nearly identical elution profiles. All data suggested that product **3-i** was the desired C_{60}-containing cellulose derivative.

Figure 4 shows thermal gravimetric analysis (TGA) curve of product **3-i**. The thermolysis of product **3-i** started at 205 °C, suggesting that product **3-i** had an aza-bridged structure, but not triazol-bridged structure, because Ungurenasu and Pinteala reported that the thermolyses of aza-bridged type C_{60}-curdlan derivatives started at 205 °C.[11] There are two possibilities concerning aza-bridged types between nitrogen at C-6 position of the cellulose derivative and C_{60}, that is, [6,6]-close type and [5,6]-open type,[15,16,18–22] although it is reported that alkyl azides predominantly added at the [5,6]-open junction.[19,22] The absence of the peak at 425 nm, which is a characteristic peak of [6,6]-close aza substructure,[15,16,20] indirectly suggested that product **3-i** had a

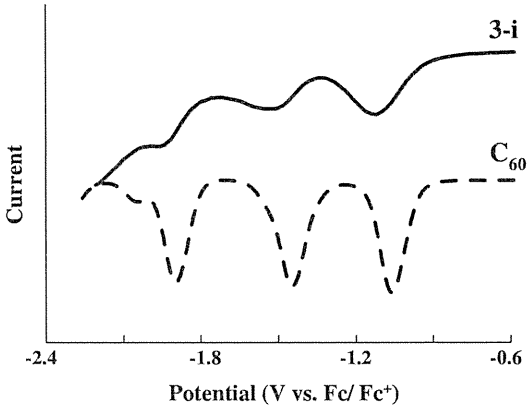

Figure 2. DPVs of product **3-i** and C_{60}.

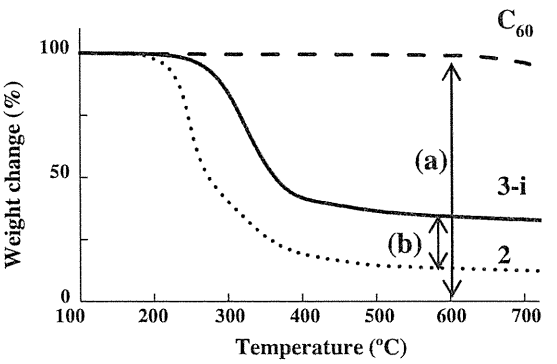

Figure 4. TGA curves of product **3-i**, C_{60} and compound **2**.

Table 1
Results of addition reaction of C_{60} to compound **2** under various reaction conditions

Entry	Concentration of **2** (mM)	Amount of C_{60}[a] (equiv)	Time (h)	Temperature (°C)	Heating method[b]	Product	DS_{C60}[c]	DPn	M_w/M_n
1	10	1	3	140	MW	**3-i**	0.25	14.5	3.64
2	5	1	3	140	MW	**3-ii**	0.21	13.0	2.66
3	20	1	3	140	MW	**3-iii**	0.28	13.2	3.04
4	25	1	3	140	MW	**3-iv**	0.30	15.9	4.15
5	10	0.1	3	140	MW	**3-v**	0.11	18.3	4.52
6	10	0.2	3	140	MW	**3-vi**	0.16	15.8	3.84
7	10	2	3	140	MW	**3-vii**	0.30	13.5	4.28
8	10	4	3	140	MW	**3-viii**	0.28	15.3	6.57
9	10	6	3	140	MW	**3-ix**	0.31	14.4	4.49
10	10	1	1	140	MW	**3-x**	0.23	19.7	6.26
11	10	1	2	140	MW	**3-xi**	0.27	18.1	4.72
12	10	1	3	100	MW	**3-xii**	0.14	n.m.[d]	n.m.[d]
13	10	1	3	130	MW	**3-xiii**	0.28	21.6	17.2
14	10	1	48	140	Oil bath	**3-xiv**	0.32	13.2	3.21
15	25	2	2	140	MW	**3-xv**	0.33	17.9	3.46
C1	10	0	3	100	MW	**2-i**	–	70.9	2.58
C2	10	0	3	120	MW	**2-ii**	–	49.6	2.64
C3	10	0	3	140	MW	**2-iii**	–	16.5	2.57
C4	10	0	3	180	MW	**2-iv**	–	n.m.[d]	n.m.[d]

[a] Per N_3-group.
[b] MW = microwave.
[c] DS_{C60} were calculated by TGA method.
[d] n.m. = Not measured (because the product was insoluble).

[5,6]-open type structure. This is also supported by ^{13}C NMR data. It is reported that the absence of the peak around 84 ppm accounted for a [5,6]-open type structure in ^{13}C NMR spectrum of C_{60}-curdlan derivative.[11] Indeed, no peaks were observed in the range of 80–90 ppm in ^{13}C NMR spectrum of product **3-i**.

The TGA method is widely used for determination of the weight percent of C_{60} in C_{60}-bearing polymer.[6,7,10] The degree of substitution of C_{60} (DS_{C60}) of product **3-i** was calculated from TGA method, that is, it was determined using the weight change values of compounds **2** and **3-i** at 600 °C, and was found to be 0.25. The low DS_{C60} suggested that multi-addition of azido groups of compound **2** with C_{60} might proceed, although further investigation is required. The degree of polymerization (DPn) of product **3-i** was determined from SEC, and was found to be 14.5. The DPn of product **3-i** was significantly lower than that of compound **2** (DPn = 78.3), suggesting that depolymerization occurred under the reaction conditions for product **3-i**.

Then, addition reaction of C_{60} with compound **2** was carried out under various conditions with different concentration, amount of C_{60}, reaction time, temperature and so on to investigate the influence of the reaction conditions to DS_{C60} and DPn of the products and to get compound **3** with higher DS_{C60}. The results are shown in Table 1. The reaction conditions for product **3-i** (entry 1) are regarded as criteria for the various reaction conditions.

The DS_{C60} of the products increased with increasing of the concentration of compound **2** (entries 1–4) and with increasing of the amount of C_{60} (entries 1 and 5–9), but leveled off when the concentration was 25 mM and when the amount of C_{60} was 2 equiv, respectively. The DPn of the products was not affected by the concentration of compound **2**, but it slightly decreased with increasing of the amount of C_{60}. The DS_{C60} of the products did not increase but the DPn decreased with an increase of reaction time (entries 1 and 10–11). It was found that the band at 2104 cm^{-1} from azido groups was completely disappeared after 1.5 h by the monitoring experiment of the reaction (entry 1) (data not shown). The DS_{C60} of the products increased and leveled off, but the DPn decreased with an increase of reaction temperature (entries 1 and 12–13). Control experiments without addition of C_{60}, that is, MW heating treatment of compound **2** with different temperature, were performed (entries C1–C4). DPn of the products clearly decreased with an increase of reaction temperature, especially at 180 °C, which corresponded to the boiling point of the solvent (ODCB), serious degradation of compound **2** was confirmed by FT-IR analysis. It was found that high reaction temperature was responsible for decreasing of DPn of the products, although it was favorable to high DS_{C60}. Product **3-xii**, prepared at 100 °C for 3 h, was insoluble in the solvents for product **3-i**, such as $CHCl_3$, CH_2Cl_2, THF, toluene, ODCB, product **3-xiii**, prepared at 130 °C for 3 h, became to be partially insoluble in the solvents two weeks later, while product **3-i**, prepared at 140 °C for 3 h, was easily soluble in the solvents two months later. These results suggest that higher DPn of the products **3** were undesirable to the solubility of the products **3**. The DS_{C60} of the product **3-xiv**, which was prepared at 140 °C for 48 h by oil-bath heating, was higher than that of product **3-i**, but the DPn of product **3-xiv** was almost same as that of product **3-i** (entries 1 and 14). MW heating had an advantage of only a shortening of reaction time as expected. Considering the results described above, the addition reaction was carried out under the optimal reaction conditions for higher DS_{C60} to afford product **3-xv** with maximum DS_{C60} of 0.33 and with DPn of 17.9 in 68.5% yield (entry 15). It was thought that C_{60} was too bulky to be introduced to the cellulose derivative with DS_{C60} of more than 0.33 by its steric hindrance.

1. Experimental

1.1. General

6-Azido-6-deoxycellulose (**1**) with DS_{N3} 0.88 was prepared according to the method of Matsui et al.[13] Fullerene-C_{60} (98%) was purchased from Sigma-Aldrich (Tokyo, Japan) and all other chemicals were purchased from commercial sources and used without further purification.

FT-IR spectra were recorded in KBr pellets with a Shimadzu FTIR-8600 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded with a Varian INOVA300 FT-NMR (300 MHz) spectrometer with TMS as an internal standard in $CDCl_3$. Chemical shifts (δ) are given in δ values (parts per million). The UV–vis spectra were recorded on a Jasco V-560 UV–vis spectrophotometer in CH_2Cl_2. Differential pulse voltammetry (DPV) measurements were performed in a MCA micro cell (BSA, Japan) at room temperature at

scan rate of 100 mV s^{-1} using a platinum electrode (1.6 mm diameter) as working electrode, Ag/AgCl (saturated KCl) as reference electrode, platinum wire as counter electrode by an ALS electrochemical analyzer (ALS650B). Ferrocene (Fc) was added as an internal standard. All potentials are given relative values to the ferrocenium/ferrocene couple (Fc^+/Fc). The electrolyte (0.1 M TBAP in ODCB) was degassed with nitrogen before use. SEC analyses were performed using a Shimadzu LC-10 system equipped with a Shimadzu UV–vis detector (SPD-10AVp) and a Shimadzu RI detector (RID-10A) (Conditions: column: KF-802.5 + KF-805, column temperature: 40 °C, eluent: THF, flow rate: 1.0 mL/min; standards; polystyrene standards (Shodex)). TGA was conducted in nitrogen with a Shimadzu TGA-50 thermal analyzer by heating from 100 to 700 °C at the programming rate of 10 °C min^{-1}.

1.2. 6-Azido-6-deoxy-2,3-di-*O*-myristoylcellulose (2)

LiCl (1.2 g, 28.3 mmol) was added to a suspension of 6-azido-6-deoxycellulose (**1**) (150 mg, 0.78 mmol) in *N*,*N*-dimethylacetamide (15 mL) at 60 °C. The reaction mixture became a clear solution within several minutes. Pyridine (1.3 mL, 16.2 mmol) and myristoyl chloride (2.18 mL, 8.04 mmol) were added to the solution. After stirring at 70 °C for 24 h, the solution was diluted with CH_2Cl_2. The organic layer was washed with 1 M HCl, water, and brine, dried over Na_2SO_4, and concentrated in vacuo to give an oil. The solution of the oil in a small amount of CH_2Cl_2 was dropped into EtOH (500 mL). The resulting precipitate was collected by centrifugation (15,000 rpm, 15 min), and was purified by the re-precipitation method again to give 6-azido-6-deoxy-2,3-di-*O*-myristoylcellulose (**2**) as a brown solid (470 mg, 97.0% yield).

Compound **2**; $DS_{myristroyl}$: 2.02 (determined by elementary analysis); DPn: 78.3 (M_w/M_n: 3.36); ^1H NMR ($CDCl_3$): δ 5.13 (H-3), 4.76 (H-2), 4.50 (H-1), 3.75 (H-4), 3.61 (H-5,6a), 3.41 (H-6b), 2.23 ($OC(=O)CH_2CH_2C_{10}H_{20}CH_3$), 1.53 ($OC(=O)CH_2CH_2C_{10}H_{20}CH_3$), 1.26, ($OC(=O)CH_2CH_2C_{10}H_{20}CH_3$), 0.88 ($OC(=O)CH_2CH_2C_{10}H_{20}CH_3$) ppm; ^{13}C NMR ($CDCl_3$): δ 172.5, 171.8 (C=O), 99.7 (C-1), 75.0–71.8 (C-2,3,4,5), 50.0 (C-6), 33.9, 31.9, 29.6, 24.7, 22.7 ($OC(=O)C_{12}H_{24}CH_3$), 14.1 ($OC(=O)C_{12}H_{24}CH_3$) ppm; FT-IR (KBr): ν 2104 ((N_3), 1757 (C=O) cm^{-1}.

1.3. 6-Azafulleroid-6-deoxy-2,3-di-*O*-myristoylcellulose (3)

Typical method: 6-Azido-6-deoxy-2,3-di-*O*-myristoylcellulose (**2**) (30 mg, 0.050 mmol) was reacted with fullerene (32 mg, 0.044 mmol) in ODCB (5 ml) at 140 °C for 3 h in a 10 ml-test tube by MW heating with a CEM Discover Synthesis Unit (CEM Corp., Matthews, NC), which consists of a continuous focused microwave power delivery system with power output from 0 to 300 W at 2.45 GHz. The reaction mixture was purified by a silica gel column eluted firstly with toluene to remove unreacted C_{60} and secondly with THF to be recovered, and concentrated in vacuo to give a crude product. The solution of the product in a small amount of CH_2Cl_2 was dropped into MeOH (200 mL). The resulting precipitate was collected by centrifugation (15000 rpm, 15 min), and was purified by the re-precipitation method again to give 6-azafulleroid-6-deoxy-2,3-di-*O*-myristoylcellulose (**3-i**) (31.9 mg, 85.1% yield).

Compound **3-i**; DS_{C60}: 0.25 (determined by TGA method); DPn: 14.5 (M_w/M_n: 3.64); ^{13}C NMR ($CDCl_3$): δ 172.4 (C=O), 150–130 (C_{60}), 68–76 (C-2,3,4,5), 34.2, 32.2, 30.0, 25.0, 23.0, ($OC(=O)C_{12}H_{24}CH_3$), 14.4 ($OC(=O)C_{12}H_{24}CH_3$) ppm; FT-IR (KBr): ν 1755 (C=O), 527 (C_{60}) cm^{-1}.

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