Polystyrene Microgel Amphiphiles with Maltohexaose. Synthesis, Characterization, and Potential Applications

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4-Vinylbenzyl maltohexaoside peracetate (**1**) was copolymerized with divinylbenzene (DVB) using 1-phenyl-1-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane (**2**) in *m*-xylene. The copolymerizations were performed at 138 °C for 20 h using the mole fraction of **1** in the total feed of **1** and DVB (F_1: [**1**]/[**1**]+[DVB]) varying from 0.11 to 0.38, affording polymeric products in yields ranging from 32 to 40%. The characterizations by linear PS-calibrated size exclusion chromatography (SEC), dynamic laser light scattering (DLS) measurements, and ^{1}H NMR spectroscopy indicated that the product was assignable to the cross-linked poly(4-vinylbenzyl maltohexaoside peracetate) particle which is able to produce stable solutions, i.e., the PSt microgel with acetyl maltohexaose, **3**. The specific rotations ($[\alpha]_D^{23}$, $c = 1.0$ $CHCl_3$) of **3** ranged from +43.3° to +85.6°. The average molar masses determined by the static laser light scattering (SLS) measurement of **3**, $M_{w,SLS}$'s, were from 64 700 to 118 000, which were calculated using the respective refractive index increments, d*n*/d*c*'s, ranging from 0.03387 to 0.08340. The apparent numbers of the **1**, **2**, and DVB units in **3**, N_1, N_2, and N_{DVB}, which were estimated from the respective $[\alpha]_D^{23}$ values, $M_{w,SLS}$'s, and real yields, ranged from 22 to 35, from 7 to 26, and from 146 to 506, respectively. The deacetylation of **3** was achieved by treatment with sodium methoxide in dry 1,4-dioxane to produce the PSt microgel with maltohexaose as the hydrophilic segment, **4**, as a white solid. The solubility of **4** in various solvents was examined, indicating that a hydrophilic property was effectively introduced. Notably, **4** gave clear solutions in the mixed solvent of 1,4-dioxane and H_2O. The ability to solubilize fullerite (mixture of fullerenes, C_{60}/C_{70} = ca. 9/1) in aqueous solutions was examined according to the literature method. Approximately, 100 mg of **4** (1.7 μmol) solubilizes 1.3 mg of fullerite (1.7 μmol).

Introduction

Saccharides have attracted much attention in polymer chemistry due to their potential of becoming renewable resources as organic raw materials and also their functions in biological recognition processes, so that various types of vinyl saccharides were synthesized and polymerized to produce glycoconjugated polymers.[1] In the field of poly(vinyl saccharide) synthesis, there has been noteworthy progress during the past decade, where various kinds of living polymerization methods have been applied to the polymerization of vinyl saccharide,[2] and saccharides have then been recognized as useful segments to provide high water-solubility for macromolecular amphiphiles. A typical example is the glycoconjugated AB diblock copolymers, which were synthesized by the two-step living polymerization of conventional vinyl monomers and vinyl saccharides.[3−14]

Moreover, the development of the living radical polymerization techniques[15−17] has opened up the construction of a new class of glycoconjugated polymers, such as a branched polymeric architecture with saccharides. For example, we reported that star-shaped polystyrenes with the core bearing a vinyl saccharide unit were prepared via the nitroxide-mediated living radical polymerization.[18] Müller and co-workers reported that hyperbranched glycopolymers were synthesized via the self-condensing atom transfer radical copolymerization of a sugar-carrying acrylate.[19] Stenzel and co-workers reported that glycopolymer stars were synthesized using reversible addition-fragmentation chain transfer polymerization.[20] However, such recent reports using new polymerization methods have been mostly limited to the application of vinyl monomers bearing monosaccharide derivatives. Thus, it is of increasing interest to prepare architecturally controlled polymers conjugated with a variety of saccharides including oligosaccharides and to elucidate their properties to explore new applications.

In this paper, we describe the synthesis of a polystyrene (PSt) microgel with maltohexaose as a new glycoconjugated macromolecular amphiphile. "Maltohexaose" is an α-1,4-linked oligosaccharide composed of six glucopyranose units being categorized as a malto-oligosaccharide. Some of the malto-oligosaccharides have been modified into vinyl monomer and polymerized from the viewpoint of biological interest.[21−23] It is known that an α-1,4-linked glucan such as amylose, the main component of starch, does not dissolve in H_2O due to the formation of a highly ordered structure, whereas malto-oligosaccharides are free from such a structure and possess numerous hydroxyl groups showing very high water-solubility. In addition, malto-oligosaccharide is one of the renewable oligosaccharides, because it is derived from starch. Hence, we

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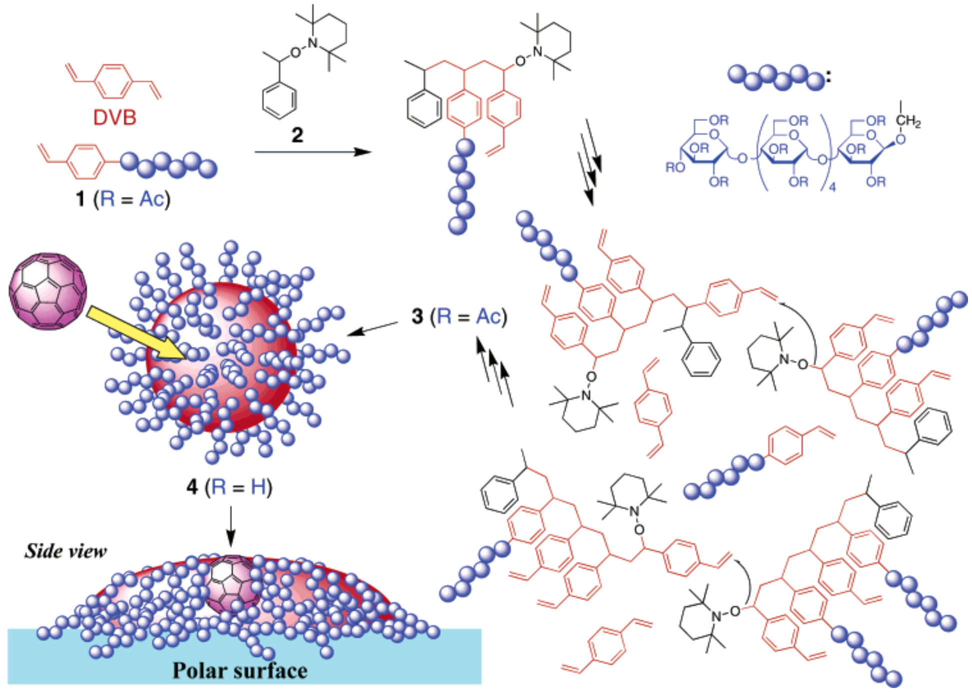
Scheme 1. Synthetic Procedure for the PSt Microgel Amphiphiles with Maltohexaose and the Schematic Illustration of a Fullerene-Coating on a Polar Surface with the Glycoconjugated PSt Microgel



have focused on the use of maltohexaose as the direct source for the site-specific hydrophilic modification of the hydrophobic polymers.[14,18,24] "Microgel" is one of the traditional branched polymers first described by Staudinger and Husemann,[25] which is defined today as consisting of cross-linked polymer particles being able to exist as a stable solution in appropriate solvents.[26] The traditional synthetic method for a microgel is the free-radical copolymerization of monovinyl monomers and divinyl monomers in suitable solvents under dilute conditions,[27] whereas Solomon et al. showed that the living radical polymerizations of *tert*-butylstyrene using divinylbenzene (DVB) as a linking agent was an efficient method for the synthesis of cross-linked microgels.[28] Thus, we report here that 4-vinylbenzyl maltohexaoside peracetate (**1**) was copolymerized with DVB using 1-phenyl-1-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane (**2**) as the initiator in *m*-xylene to afford the PSt microgel with acetyl maltohexaose (**3**), as shown in Scheme 1. The deacetylation of **3** was achieved to produce the PSt microgel amphiphiles with maltohexaose as the hydrophilic segment (**4**). The solubility of **4** was examined using appropriate solvents to clarify the ability of the malto-oligosaccharide as the hydrophilic segment of the PSt microgel. Micogels are used as substrates for biomedical and diagnostic purposes, monolithic stationary phases in liquid chromatography, and a support for catalysts as well as now becoming very important as coatings in industry. We mention here the ability of **4** to solubilize fullerene in the aqueous solution. Fullerenes have been extensively studied and shown to possess many new and unusual physical and chemical properties and also biological function.[29−31] However, there are still drawbacks in their use for several applications because of their poor polarity resulting in difficult processibility and incompatibility with various solid matrixes. The aqueous solution of **4** that could solubilize fullerene can be cast on a variety of materials including hydrophilic ones derived from, for example, carbohydrate, protein, and DNA. Therefore, the product has the potential of use as a tool for fullerene coatings on a polar surface.

Experimental Section

Materials. Divinylbenzene (DVB) (Aldrich, tech., mixture of isomers, 80%) and *m*-xylene (Kanto Chemical Co., >99.0%) were distilled just before use. 4-Vinylbenzyl maltohexaoside peracetate[18] (**1**) and 1-phenyl-1-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane[32] (**2**) were prepared according to literature procedures. Fullerite (Aldrich, mixtures of fullerenes, C_{60}/C_{70} = ca. 9/1), dry 1,4-dioxane (Kanto Chemical Co., Japan, >99.5%), sodium methoxide (Wako Pure Chemical Industries, Japan, 28% in methanol), and spectroscopy grade chloroform (Merck) were used without further purification. A seamless cellulose tube (UC24-32-100) was obtained from Viskase Sales Co.

Measurements. The ^{1}H and ^{13}C NMR spectra were recorded using JEOL JNM-GX270 instruments. Optical rotations were measured using a Jasco DIP-1000 digital polarimeter. The size exclusion chromatography (SEC) was performed at 40 °C in chloroform (1.0 mL·min^{-1}) using a Jasco GPC-900 system equipped with a Shodex KF-804L column (linear, 8 mm × 300 mm) and a Shodex KF-805L column (linear, 8 mm × 300 mm). The weight-average molecular weight ($M_{w,SEC}$) and polydispersity (M_w/M_n) of the polymers were calculated on the basis of polystyrene calibration. The static laser light scattering (SLS) measurement was performed in toluene at 25 °C on an Otsuka Electronics DLS-7000 light scattering spectrophotometer ($\lambda = 632.8$ nm; four-point measurements; $c = 2 \sim 10$ mg/mL). The refractive index increment (dn/dc) was measured in toluene at 25 °C on an Otsuka Electronics DRM-1021 double beam-differential refractometer ($\lambda = 632.8$ nm). Ultraviolet−visible (UV−vis) spectra were measured at 23 °C in H_2O/1,4-dioxane (7/3, v/v) with 5-mm path lengths using a Jasco V-550 spectrophotometer.

Copolymerization and Calculation Procedures. A mixture of **1** (3.34 g, 1.75 mmol), **2** (26.1 mg, 0.100 mmol), and DVB (457 mg, 2.8 mmol) in *m*-xylene (4.5 mL) was degassed by three freeze/thaw cycles, sealed under argon, and heated at 138 °C for 20 h. After cooling in liquid nitrogen, the mixture was diluted with chloroform (15 mL) and then precipitated in methanol (ca. 1 L). The precipitate was purified by reprecipitation with chloroform−methanol and dried in vacuo to give **3-V** as a white solid. Yield: 1.26 g (33.0% based on the total feed of **1**, **2**, and DVB). $M_{w,SEC} = 2.25 \times 10^4$, $M_w/M_n = 1.32$. $M_{w,SLS} = 8.79 \times 10^4$, d$n$/d$c$ = 0.03387 mL·g^{-1}. $[\alpha]_D^{23} = +85.6°$ (c = 1.0, $CHCl_3$).

The weight-fractions of the **1**, **2**, and DVB units (W_1, W_2, and W_{DVB}, respectively) in **3** were calculated as follows. The $[\alpha]_D^{23}$ (*c* 1.0, $CHCl_3$) of **3-V** (+85.6°) was divided by that of poly-**1** (+112.9°), giving a W_1 of 0.76. The result that **2** (26.1 mg) was quantitatively consumed gave a W_2 of 0.02. The relationship ($W_1 + W_2 + W_{DVB} = 1$) gave a W_{DVB} of 0.22. The W_1, W_2, and W_{DVB} values were multiplied by $M_{w,SLS}$ of 8.79×10^4 and then divided by the molecular weights of the corresponding units, i.e., $W_1M_w1903^{-1}$, $W_2M_w261^{-1}$, and $W_{DVB}M_w130^{-1}$. These values equal the numbers of the **1**, **2**, and DVB units (N_1, N_2, and N_{DVB}) in **3-V** of 35, 7, and 149, respectively.

Deacetylation. Typically, a solution of **3-V** (0.700 g) in dry 1,4-dioxane (10 mL) was added to a dry 1,4-dioxane solution containing 2 wt-% sodium methoxide (2 mL). The reaction mixture was stirred for 24 h at room temperature and then poured into water (ca. 80 mL). The mixture was transferred to a cellulose tube and dialyzed for 2 days against distilled water, followed by freeze-drying to yield **4-V** as a white solid, as shown in Figure 2a. Yield: 0.470 g (98.7%).

Solubilization of Fullerite. To a solution of **4-V** (100 mg, 1.67 μmol) in DMF (4 mL) was added a toluene solution (3 mL) containing fullerite (3 mg). The mixture was shaken at 30 °C for 18 h and evaporated to dryness. To the mixture was added an aqueous solution containing 30% 1,4-dioxane (10 mL), and the mixture was allowed to stand overnight. Any undissolved fullerite was removed using a glass filter and a 0.5-μm PTFE membrane filter to give an amber-colored stable solution, followed by freeze-drying to yield fullerene/**4** as a pale brown solid, as shown in Figure 2b. Yield: 100 mg (100%). The fullerene/**4** was redissolved in aqueous solution containing 30% 1,4-dioxane (1.89 $mg \cdot mL^{-1}$) and characterized by a UV−vis spectrum. UV−vis (H_2O/1,4-dioxane = 7/3, v/v, 5 mm cell): Abs. = 0.92 (340 nm). Solubilized fullerite: 1.3 mg (1.7 μmol). The amount is based on the ϵ value of fullerene C_{60} solubilized in poly(vinylpyrrolidone) in H_2O (4.9×10^4 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$ at $\lambda = 340$ nm).

Results and Discussion

Synthesis and Characterization of the PSt Microgel with Acetyl Maltohexaose. 4-Vinylbenzyl maltohexaoside peracetate (**1**) was copolymerized with divinylbenzene (DVB) using a general initiator for the 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated radical polymerization such as 1-phenyl-1-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane[16,32] (**2**), as shown in Scheme 1. The copolymerization was performed in *m*-xylene at 138 °C under constant conditions for the concentration of DVB ([DVB] = 0.62 $mol \cdot L^{-1}$) and the molar ratio of the DVB and **2** ([DVB]/[**2**] = 28), whereas the mole fraction of **1** in the total feed of **1** and DVB (F_1:[**1**]/[**1**]+[DVB]) was varied from 0.11 to 0.38. After 20 h, the homogeneous reaction mixtures were purified by reprecipitation to afford the products as white solids. Table 1 lists the results of the copolymerization. The yield of the products ranged from 32 to 40%, which were based on the total feed of the starting materials. Poly(DVB) was prepared by the polymerization of DVB with **2** as a control (59%).

It is well-known that the cross-linked polymers are insoluble in solvents. However, a microgel has the characteristic of being able to exist as a stable solution in appropriate solvents. Thus, standard characterizations available for soluble macromolecules have been applied to those for the microgels in the appropriate solvents. Such solvents for the products were toluene, chloroform, THF, 1,4-dioxane, pyridine, and DMF, similar to those for the poly(DVB). It should be noted that the respective copolymerizations did not produce any highly cross-linked species (macrogel), because there was no weight loss during the procedure in which the products were redissolved in chloroform, clarified using a 0.5-μm PTFE membrane filter, poured into methanol, and the precipitates were then recovered. Earlier, the product was characterized by a linear PSt-calibrated size exclusion chromatography (SEC) in chloroform, because the weight-average molecular weights ($M_{w,SEC}$) and polydispersity (M_w/M_n) should provide information about the apparent hydrodynamic volumes and their distributions, respectively. Figures 1a−e show the SEC traces of the products with $M_{w,SEC}$'s and M_w/M_n's that ranged from 22 000 to 30 500 and from 1.32 to 2.63, respectively. These were low values compared to the $M_{w,SEC}$ of 118 000 and the M_w/M_n of 12.4 of the poly(DVB) obtained from the multimodal SEC trace in Figure 1h. The products in toluene solution showed a very strong scattering intensity for dynamic laser light scattering (DLS) measurements. This strongly suggested that the product was assignable to the microgel particles formed by cross-linking. The average diameters (*d*'s) of the microgel ranged from 11 to 15 nm (Table 1). Notably, the DLS analysis also indicated that the product possessed a size comparable to the statistical dimensions of non-cross-linked macromolecules (10−100 nm), thus being able to exist as stable solutions.

Figure 1i shows the ^1H NMR spectrum of poly(DVB) in $CDCl_3$, which exhibited signals assignable to the aromatic protons (5.9∼8.0 ppm) along with the methine and methylene protons (0.5∼3.5 ppm). The signals were extremely broadened, because the intramolecular mobility of the protons on the polymer backbone is suppressed by cross-linking. Similar broad signals due to the aromatic protons appeared in the ^1H NMR spectrum of the product in $CDCl_3$ (Figure 1f), whereas those due to the methine and methylene protons were difficult to detect because of overlapping. The spectrum of the product also showed signals due to the **1** units, the methine and methylene protons of the saccharides (3.5∼5.8 ppm), and the acetyl protons (1.8∼2.5 ppm). The signals assignable to the methyl proton in the **2** units also appeared (0.8∼1.4 ppm). The specific rotations ($[\alpha]_D^{23}$, $c = 1.0$ $CHCl_3$) of the products ranged from +43.3° to +85.6°, which corresponded to that of +105.2° for the vinyl saccharide **1** and also to that of +112.9° for the poly(4-vinylbenzyl maltohexaoside peracetate), the homopolymer of **1**. These results indicated that the product was assignable to the cross-linked poly(4-vinylbenzyl maltohexaoside peracetate) particle which is able to produce stable solutions, i.e., the PSt microgel with acetyl maltohexaose, **3**.

Table 1 summarizes the synthesis of **3-I**, **II**, **III**, **IV**, and **V** which correspond to the products obtained by the copolymerizations using the F_1 values of 0.11, 0.20, 0.27, 0.33, and 0.38, respectively. The $[\alpha]_D^{23}$ values suggested that the contents of the chiral saccharide units in **3** increased with the increasing F_1's. To elucidate the structure of **3** in more detail, a static laser light scattering (SLS) measurement was carried out. Table 1 lists the average molar masses, $M_{w,SLS}$'s, of **3** ranging from 64 700 to 118 000, which were determined using the respective refractive index increments, d*n*/d*c*'s, ranging from 0.03387 to 0.08340. As expected from the SEC analysis, the $M_{w,SLS}$ of **3** was a smaller value than that of the poly(DVB). The copolymerizations were performed under constant conditions for the concentrations of DVB and **2**, whereas the feed of **1** was changed as above; hence, the results for the $M_{w,SLS}$ values can be explained by steric hindrance. Initially, **1** is copolymerized with DVB by **2** to afford short copolymers. The pendant vinyl groups in the copolymer then add to the carbon centered radical in the chain end, which are produced by the dissociation of alkoxyamine, of another copolymer chain. These copolymerization and cross-linking reaction proceed to form **3**. The cross-linking should be hindered when the very bulky **1** unit exists in the neighborhood of the pendant vinyl groups, resulting in a decreased N_{DVB} with the increasing F_1.

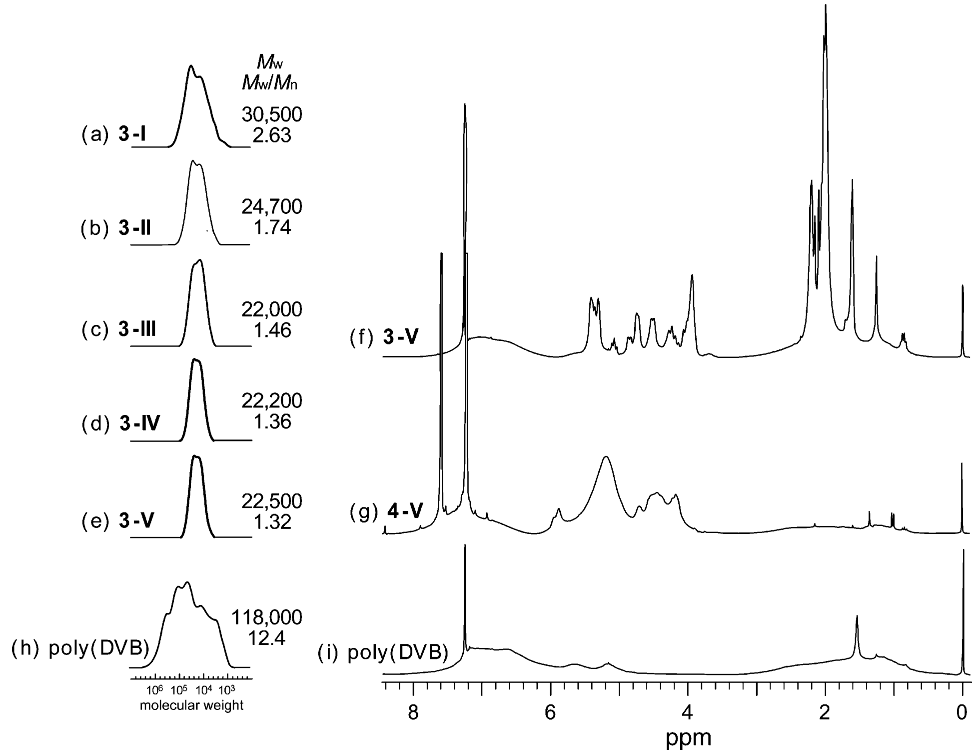


Figure 1. SEC traces of the products obtained through copolymerization of **1** and DVB using ppm the F_1's of (a) 0.11, (b) 0.20, (c) 0.27, (d) 0.33, and (e) 0.38. ^{1}H NMR spectra of (f) the product obtained through copolymerization of **1** and DVB using the F_1 of 0.38 in CDCl$_3$ and (g) that after deacetylation in pyridine-d_5. (h) SEC trace of poly(DVB). (i) ^{1}H NMR spectrum of poly(DVB). Sample codes **3-I**, **3-II**, **3-III**, **3-IV**, **3-V**, and **4-V** correspond to those in Tables 1 and 2.

Table 1. Synthesis and Characterization of **3** Obtained by the Copolymerization of **1** with DVB Using Initiator **2**

							number of units		
F_1[a]	product	yield, %	d,[b] nm	[α]$_D$,[c] deg	$M_{w,SLS}$[d]	dn/dc, mL·g^{-1}	N_1	N_2	N_{DVB}
0.11	**3-I**	40	15 ± 5	+43.3	118 000	0.08340	24	26	506
0.20	**3-II**	36	14 ± 4	+64.0	76 000	0.06224	23	12	229
0.27	**3-III**	33	11 ± 4	+73.7	64 700	0.05000	22	8	157
0.33	**3-IV**	32	13 ± 3	+80.6	72 600	0.04498	27	7	146
0.38	**3-V**	33	14 ± 2	+85.6	87 900	0.03387	35	7	149
e	poly(DVB)	59	54 ± 14		1,010,000	0.12906		354	7050

[a] Mole fraction of **1** in the total feed of **1** and DVB ([**1**]/[**1**]+[DVB]). [b] Particle diameter determined by DLS measurement in toluene at 22 °C. [c] Measured in CHCl$_3$ at 23 °C (c = 1.0). [d] Determined by SLS measurement in toluene at 25 °C. [e] Control.

We calculated the N_1, N_2, and N_{DVB} values, which are the apparent numbers of the **1**, **2**, and DVB units in **3** estimated from the respective $M_{w,SLS}$'s, the real yields, and specific rotations (see the Experimental Section). The N_1, N_2, and N_{DVB} of **3** ranged from 22 to 35, from 7 to 26, and from 146 to 506, respectively (Table 1). These characterizations and calculations revealed more important information; that is, **3** was shown to possess a large number of acetyl groups (potentially equal to hydroxyl groups) available in limited space. For example, **3-V** possesses 35 molecules of maltohexaose, which is equal to 665 acetyl groups, with small d values of 14 nm.

Solubility and Potential Application of the PSt Microgel Amphiphiles with Maltohexaose as the Hydrophilic Segment. The deacetylation of **3** was achieved by treatment with sodium methoxide in dry 1,4-dioxane to produce the PSt microgel with maltohexaose as the hydrophilic segment, **4** (Scheme 1). As shown in Figure 2a, **4** was a white solid. Figure 1g shows the ^{1}H NMR spectrum of **4** in pyridine-d_5. The signals due to maltohexaose appeared (3.8∼6.0 ppm), while the one assignable to the acetyl signals (observed at 1.8∼2.5 ppm for the spectrum of **3** in CDCl$_3$) did not appear. The signals assignable to the aromatic protons (6.0∼8.0 ppm) and the methine and methylene protons (0.5∼3.5 ppm) were not obviously observed, suggesting that the intramolecular mobility of the protons in the PSt microgel backbones was restricted, broadening the corresponding signals. We examined the properties of this new type of macromolecular amphiphiles. Table 2 shows the solubility of **4-I**, **II**, **III**, **IV**, and **V**, which were obtained by the deacetylation of **3-I**, **II**, **III**, **IV**, and **V**, respectively. As expected, **4** produced stable solutions in the good solvents for both PSt microgel and maltohexaose, such as pyridine and DMF. On the other hand, almost all of the samples produced a precipitate in the good solvents for the PSt microgel but poor ones for the maltohexaose, such as toluene, CHCl$_3$, THF, and 1,4-dioxane. In the poor solvents for the PSt microgel, but good ones for the maltohexaose, such as DMSO, the solubility improved with the increasing maltohexaose content. Thus, the hydrophilic property was effectively introduced into **4**. Interestingly, **4** gave clear solutions in the mixed solvent of H$_2$O and 1,4-dioxane. For example, **4-V** gave a clear solution in H$_2$O containing 30∼70% 1,4-dioxane. Consequently, the hydrophilic property[33] was successfully introduced into the highly hydrophobic PSt mi-

Table 2. Solubility of **4** in Various Solvents[a]

sample	toluene	$CHCl_3$	THF	1,4-dioxane	pyridine	DMF	DMSO	H_2O
4-I	±	±	±	±	+	+	±	−
4-II	−	−	−	−	+	+	±	−
4-III	−	−	−	−	+	+	±	−
4-IV	−	−	−	−	+	+	+	−
4-V	−	−	−	−	+	+	+	−
poly(DVB)[b]	+	+	+	+	+	+	−	−
maltohexaose[b]	−	−	−	−	+	+	+	+

[a] +, Clear solution; ±, suspension; −, precipitate. [b] Control.

crogel by utilizing maltohexaose, thus **4** should become a candidate for special coatings, a support for catalysts in aqueous media, and a substrate for biomaterials.

We describe here that the aqueous solutions of **4** solubilized fullerenes. According to the literature method,[34] to a clear solution of **4-V** in DMF was added a toluene solution containing fullerite (mixture of fullerenes, C_{60}/C_{70} = ca. 9/1), and the mixture was then shaken at 30 °C for 18 h. The mixture was evaporated to dryness and redissolved in H_2O containing 30% 1,4-dioxane, and any undissolved fullerite was removed using membrane filters to produce an amber-colored stable solution. The filtrates were freeze-dried to produce a pale brown solid, as shown in Figure 2b. Thus, fullerenes were solubilized in aqueous solution with **4**. Figure 2, panels c and d, shows the UV−vis spectra in aqueous solution containing 30% 1,4-dioxane of **4-V** and solubilized fullerite using **4-V**, respectively. The characteristic absorption due to fullerenes appeared in the visible area from 330 to 800 nm (Figure 2d). Approximately 100 mg of **4** (1.7 μmol) solubilized 1.3 mg of fullerite (1.7 μmol) in H_2O containing 30% 1,4-dioxane, which was calculated on the basis of the molar absorption coefficient of fullerene C_{60} solubilized in H_2O using poly(vinylpyrrolidone) ($\epsilon = 49\,000$ $dm^3 \cdot mol^{-1} \cdot cm^{-1}$ at $\lambda = 340$ nm).[34] It should be noted that the amber-colored solution was cast on a glass plate to produce a brown-colored homogeneous film after dryness. Therefore, the good film-forming property of the PSt microgel was combined with an excellent hydrophilic property derived from maltohexaose. Thus, **4** has a potential application as a special coating using functional but incompatible compounds such as fullerene on the surface of various materials including hydrophilic ones made from, for example, carbohydrate, protein, and DNA as illustrated in Scheme 1.

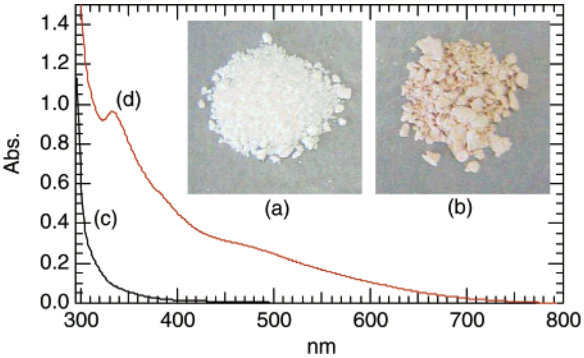


Figure 2. Pictures of (a) white solids of **4-V** and (b) pale brown solids obtained by the experiment for solubilization of fullerite using **4-V.** UV−vis spectra in aqueous solution containing 30% 1,4-dioxane (sample concentration:1.89 mg·mL^{-1}; path length: 5 mm) of (c) **4-V** and (d) solubilized fullerite using **4-V**.

Conclusions

A PSt microgel with maltohexaose, a branched polymer conjugated with a highly water-soluble oligosaccharide, was synthesized as a new family of glycoconjugated macromolecular architectures. The characterizations revealed that the glycoconjugated PSt microgel possessed a large number of hydroxyl groups (more than 400) in the limited space of diameters within 20 nm. The PSt microgel with maltohexaose showed a hydrophilic property, thus becoming a new class of polymeric amphiphiles. For example, the PSt microgel amphiphiles with maltohexaose solubilized fullerene, indicating a high potential for use as a tool for fullerene-coatings on a polar surface.

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