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Polystyrene Microgel Amphiphilies with Saccharide to Achieve a Fullerene-Coating on a Hydrophilic Surface

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Summary: Synthesis of a polystyrene (PSt) microgel with glucose and maltohexaose, in which a good coating property was combined with an excellent hydrophilic property, is described. The glycoconjugated PSt microgel showed the ability to solubilize fullerene in aqueous solution, thus having a potential application to achieve the coating of a functional but incompatible compound, such as fullerene due to the lack of polarity, on the surface of various hydrophilic materials.

Keywords: amphiphiles; coating; fullerene; living radical polymerization; polystyrene microgel

Introduction

There has been noteworthy progress in the field of glycoconjugated polymer synthesis, because living radical polymerization techniques have allowed both architectural control over the polymer backbone and the use of compounds containing glycosyl linkages. However, three-dimensional polymeric architectures with saccharides, such as glycoconjugated star polymers[1–3] and hyperbranched poly(vinyl saccharide)s[4] have been less studied, and thus their preparation is one of the current topics. Moreover, such precise synthesis of branched polymers has many potential applications, when they are conjugated with not only monosaccharides but also oligosaccharides to show biological function or high water-solubility.

In this paper, we report the synthesis of a polystyrene (PSt) microgel with saccharide as a new three-dimensional polymeric amphiphile, in which glucose and maltohexaose were used as the saccharide segments (Scheme 1). A microgel consists of cross-linked polymer particles able to exist as a stable solution in appropriate solvents and has now become very important for use in as coatings in industry.[5] Glucose is the most widely used monosaccharide, while maltohexaose is an α-1,4-linked oligosaccharide composed of six glucopyranose units. It is known that a carbohydrate consisting of α-1,4-linked glucopyranose, such as amylose, is insoluble in water due to the formation of the helical structure in spite of possessing numerous hydroxyl groups. However, maltohexaose is free from such a highly-ordered structure, thus becoming an efficient hydrophilic segment for PSt architectures.[1,6–8] We report here that the good coating property of the PSt microgel was combined with an excellent hydrophilic property derived from saccharides, which has the potential to be applicable to special coatings.

Experimental Part

Materials

Divinylbenzene (DVB) (Aldrich, tech., mixture of isomers, 80%) and *m*-xylene (Kanto Chemical Co., >99.0%) were distilled just before use. Fullerite (Aldrich, mixtures of fullerenes, C60/C70 = ca. 9/1), dry 1,4-dioxane (Kanto Chemical Co.,

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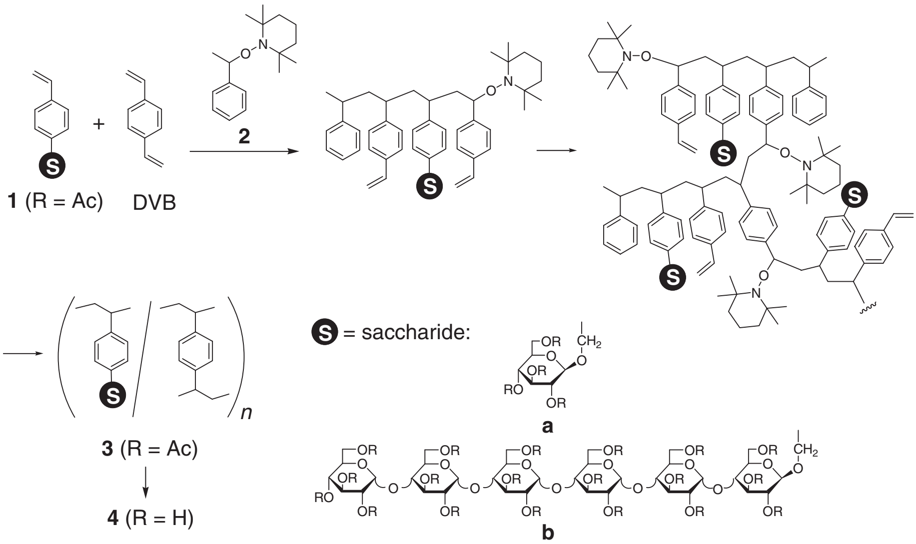

Scheme 1.
Copolymerization of vinyl saccharide (**1**) with divinylbenzene (DVB) using an initiator (**2**) to afford a PSt microgel with acetyl saccharide (**3**), followed by deacetylation generating PSt microgel amphiphiles with saccharides as the hydrophilic segments (**4**), where glucose (**a**) and maltohexaose (**b**) were used as the saccharides.

Japan, >99.5%), and other chemicals were used as received.

Measurements

The laser light scattering measurements were performed according to the literature procedure.[1,8] 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

Typically, a mixture of **1a**[9] (815 mg, 1.75 mmol), **2**[10] (26.1 mg, 0.100 mmol), and DVB (457 mg, ca. 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 using chloroform-methanol and dried in vacuo to give **3a** as a white solid. Yield: 586 mg (46.0%). $M_{w,SLS} = 96.9\ \text{kg} \cdot \text{mol}^{-1}$, $dn/dc = 0.07815\ \text{mL} \cdot \text{g}^{-1}$. $[\alpha]_D^{23} = -26.8°$ (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. The $[\alpha]_D^{23}$ of $-26.8°$ for **3a** was divided by that of $-50.4°$ for poly-**1a**, which equals a W_1 of 0.531. The initiator **2** (26.1 mg) was quantitatively consumed, giving a W_2 of 0.045. The W_{DVB} of 0.424 was calculated from the relationship of $W_1 + W_2 + W_{DVB} = 1$. The W_1, W_2, and W_{DVB} values were multiplied by the $M_{w,SLS}$ of 9.69 and then divided by the molecular weights of the corresponding units. These values are equal to the numbers of the **1**, **2**, and DVB units (N_1, N_2, and N_{DVB}) in **3a** of 111, 17, and 350, respectively.

Deacetylation

Typically, a solution of **3a** (300 mg) in dry 1,4-dioxane (5 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 **4a** as a white solid. Yield: 250 mg (97.6%).

Solubilization of Fullerite

To a solution of **4b** (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 produce an amber-colored stable solution, followed by freeze-drying to yield fullerene/**4b** as a pale brown solid. Yield: 100 mg (100%). The fullerene/**4b** 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 C60 solubilized in polyvinylpyrrolidone in H_2O (4.9×10^4 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$ at $\lambda = 340$ nm).[11]

Results and Discussion

PSt Microgel with Acetyl Saccharide – Synthesis and Characterization

4–Vinylbenzyl glucoside peracetate[9] (**1a**) was copolymerized with divinylbenzene (DVB) using a general initiator for the 2, 2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated radical polymerization[12,13] such as 1-phenyl-1-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane[10] (**2**) in *m*-xylene at 138 °C (Scheme 1). The copolymerization afforded a methanol-insoluble product in 46% yield (see experimental). For dynamic laser light scattering (DLS) measurements, the product in toluene solution showed a very strong scattering intensity. This strongly suggested that the product was assignable to the microgel particles formed by cross-linking. The average diameter (*d*) of the microgel was 12 nm, a size comparable to that of the statistical dimensions of noncross-linked macromolecules (10 ~ 100 nm), thus being able to produce stable solutions in appropriate solvents.

A crosslinked polymer is generally insoluble in a solvent, whereas microgels are characterized by standard techniques available for soluble macromolecules. Figure 1a shows the ^{1}H-NMR spectrum of the product, which exhibited signals due to the polystyrene (PSt) microgel backbone

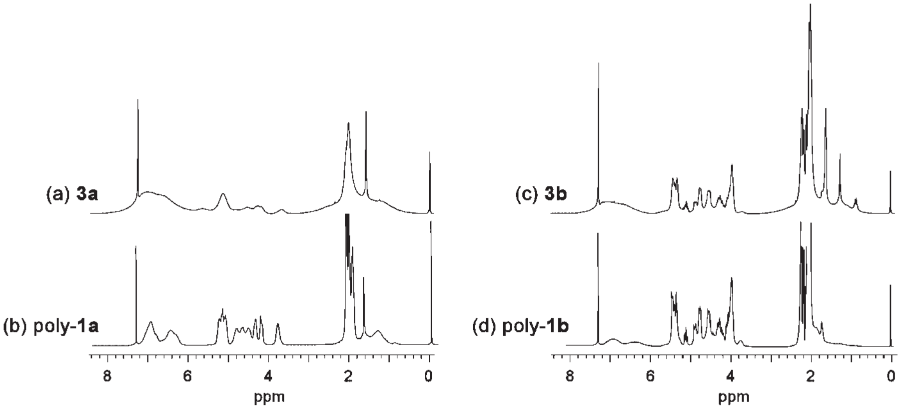

Figure 1.
^{1}H NMR spectra in $CDCl_3$ of (a) **3a** (b) poly-**1a**, (c) **3b**, and (d) poly-**1b**.

(0.5 ~ 3.5 and 5.9 ~ 8.0 ppm). These signals are extremely broadened compared to those for poly(4-vinylbenzyl glucoside peracetate), poly-**1a**, shown in Figure 1b, suggesting that the intramolecular mobility of the protons on the PSt backbone is suppressed due to the crosslinking by DVB. Figure 1a also shows the signals due to the **1a** unit (1.8 ~ 2.5 and 3.5 ~ 5.8 ppm). Notably, these signals were also broadened, so that the **1** unit may exist in the neighborhood of the PSt microgel backbone. The product showed the specific rotation ($[\alpha]_D^{23}$, c 1.0 $CHCl_3$) of −26.8°, whose sign was consistent with that of poly-**1a** (−50.4°). These results indicated that the product was assigned to the PSt microgel with acetyl glucose, **3a**.

Similarly, 4-vinylbenzyl maltohexaoside peracetate[9] (**1b**) was copolymerized with DVB using **2** to afford a product in 33% yield. The product was assignable to the microgel particles with a d of 14 nm by the DLS analysis. Figure 1c shows the ^{1}H-NMR spectrum of the product, which exhibited signals due to the PSt microgel (5.9 ~ 8.0 and 0.5 ~ 3.5 ppm) and the **1b** units (3.5 ~ 5.8 and 1.8 ~ 2.5 ppm), which were similar to those of poly(4-vinylbenzyl maltohexaoside peracetate), poly-**1b**, shown in Figure 1d. In addition, the product showed the $[\alpha]_D^{23}$ of +85.6°, whose sign was consistent with that of poly-**1b** (+112.9°). Thus, the product was assignable to the PSt microgel with acetyl maltohexaose, **3b**. As above, the signals of **3a** were broadened compared to those of poly-**1a**; however, there are no significant differences between the signals of **3b** and those of poly-**1b**. This may be attributable to the fact that most of the saccharide units are not directly connected to the PSt microgel backbone for **3b**.

In order to elucidate the structures in more detail, the molar mass of **3** was determined by a static laser light scattering (SLS) measurement. The weight-average molar masses, $M_{w,SLS}$'s, were 96.9 $kg \cdot mol^{-1}$ and 87.9 $kg \cdot mol^{-1}$ for **3a** and **3b**, which were based on the refractive index increments, dn/dc's, of 0.07815 and 0.03387, respectively. The N_1, N_2, and N_{DVB}, which means the apparent numbers of the **1**, **2**, and DVB units per **3** (see experimental), were estimated to be 111, 17, and 350 for **3a** and 35, 7, 149 for **3b**, respectively. Thus, **3a** and **3b** possess numerous glucose residues, which correspond to 444 and 665 acetyl groups (potentially equal to hydroxyl groups), available in limited space with the d values of 12 and 14 nm, respectively.

PSt Microgel Amphiphilies with Saccharide – Solubility and Fullerene-Coating on Hydrophilic Surface

The deacetylation of the microgels **3a** and **3b** was achieved by treatment with sodium methoxide in dry 1,4-dioxane to produce the PSt microgel with glucose and maltohexaose as the hydrophilic segment, **4a** and **4b**, respectively (Scheme 1). As expected, **4** produced stable solutions in DMF, which is a good solvent for both the PSt microgel and saccharide. In the good solvents for the PSt microgel, but poor ones for the saccharides, such as toluene and 1,4-dioxane, **4** produced a precipitate. In water, a poor solvent for the PSt microgel but a good one for the saccharide, **4** also gave precipitates. Interestingly, **4a** gave a clear solution in 1,4-dioxane containing 10 ~ 30% water. The hydrophilic property was found to be more effectively introduced into a PSt microgel by maltohexaose, because **4b** produced a clear solution in 1,4-dioxane containing 30 ~ 70% water.

We examined the ability of **4b** to solubilize fullerene according to the literature procedures.[11] In water containing 30% 1,4-dioxane, **4b** was found to solubilize fullerene to produce stable amber-colored solution, in which the molar ratio of **4b** and fullerene ([**4b**]/[fullerene]) is approximately 1/1 (see experimental). It should be noted that the amber-colored solution was cast on a glass plate to produce a brown-colored homogeneous film after drying. Therefore, the good film-forming property of the PSt microgel was combined with an excellent hydrophilic property derived from the saccharide. 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 derived from, for example, carbohydrates.

Conclusions

A PSt microgel with a saccharide was synthesized as a new family of glycoconjugated branched polymers. The PSt microgel with saccharides, especially maltohexaose, showed an excellent hydrophilic property and solubilized fullerene in aqueous solutions, indicating a high potential for use as a tool for fullerene-coatings on a polar surface.

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