

# Polystyrene Microgel with Maltohexaose. Synthesis and Potential Application for Fullerene-Coating on Hydrophilic Surface

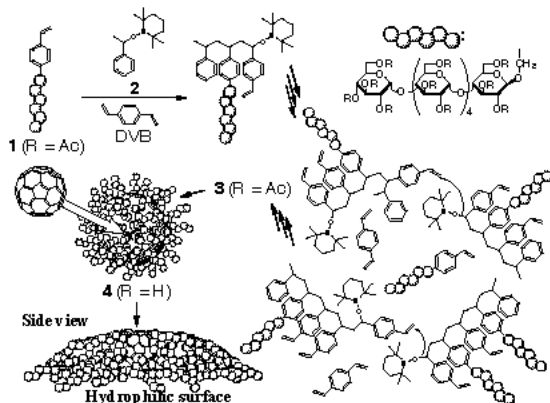
Atsushi Narumi

Graduate School of Engineering, Hokkaido University,  
Sapporo, 060-8628, Japan  
narumi@poly-bm.eng.hokudai.ac.jp

## Introduction

There has been noteworthy progress in the field of glycoconjugated polymer synthesis, because living radical polymerization techniques have allowed both of the macromolecular architectural control and the use of compounds containing glycosyl linkages. However, three-dimensional polymeric architectures with saccharides, such as glycoconjugated star polymers<sup>1-3</sup> and hyperbranched poly(vinyl saccharide)s<sup>4</sup> have been less studied, and thus their preparation is one of the current interesting topics.

We report here the synthesis of a polystyrene (PSt) microgel with maltohexaose as a new three-dimensional polymeric amphiphiles. "Maltohexaose" is an  $\alpha$ -1,4-linked oligosaccharide composed of six glucopyranose units. It is known that carbohydrate consisting of  $\alpha$ -1,4-linked glucopyranose, such as amylose, is insoluble in water due to the formation of helical structure in spite of possessing numerous hydroxyl groups. However, maltohexaose is free from such a highly-ordered structure, thus showing very high water-solubility. "Microgel" is cross-linked polymer particles being able to exist as a stable solution in appropriate solvents, and now becoming very important as coatings in industry. We report here that the good coating property of the PSt microgel was combined with an excellent



hydrophilic property derived from maltohexaose.

**Scheme 1.** Synthetic procedure for the synthesis of **4** and the schematic illustration of a fullerene-coating on a polar surface with **4**.

## Experimental

**Copolymerization.** A mixture of 4-vinylbenzyl maltohexaosiide peracetate (**1**) (3.34 g, 1.75 mmol), 1-phenyl-1-(2',2',6',6'-tetramethyl-1'-piperidinyl)oxyethane (**2**) (26.1 mg, 0.100 mmol), and divinylbenzene (DVB) (457 mg, 2.8 mmol) in *m*-xylene (4.5 mL) was degassed and 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** as a white solid. Yield: 1.26 g (33.0 %).

**Deacetylation.** A solution of **3** (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 dialyzed for 2 days against distilled water, followed by freeze-drying to yield **4** as a white solid. Yield: 0.470 g (98.7 %).

**Solubilization of Fullerite.** To a solution of **4** (100 mg, 1.67  $\mu$ mol) 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- $\mu$ m PTFE membrane filter to give an amber-colored stable solution, followed by freeze-drying to yield fullerene/**4** as a pale brown solid. Yield: 100 mg (100 %).

## Results and discussion

**Synthesis and Characterization of the PSt microgel with acetyl maltohexaose 3.** Vinyl saccharide **1** was copolymerized with DVB using initiator **2** to afford a methanol-insoluble product (see experimental). The characterizations by linear PS-calibrated size exclusion chromatography, <sup>1</sup>H-NMR spectroscopy, and dynamic laser light scattering (DLS) measurements indicated that the product was assignable to the cross-linked poly(4-vinylbenzyl maltohexaosiide peracetate) particle, i.e., the PSt microgel with acetyl maltohexaose, **3**, with the average diameters (*d*) of 14 nm. The specific rotation ( $[\alpha]_D^{23}$ , c 1.0 CHCl<sub>3</sub>) of **3** was +85.6°, which corresponded to that of +112.9° for the poly(4-vinylbenzyl maltohexaosiide peracetate), the homopolymer of **1**. The static laser light scattering measurement was performed for **3** to provide the average molar masses ( $M_{w,SLs}$ ) of 87900. The apparent numbers of the **1**, **2**, and DVB units in **3**,  $M_1$ ,  $M_2$ , and  $M_{DVB}$ , which were estimated from the  $[\alpha]_D^{23}$  value,  $M_{w,SLs}$ , and real yield, were 35, 7, and 149, respectively. Hence, **3** was shown to possess a large number of acetyl groups (potentially equal to hydroxyl groups) available in limited space (665 acetyl groups in the *d* value of 14 nm).

**Characteristic Property of the PSt microgel with Maltohexaose 4.** The deacetylation of **3** was achieved by treatment with sodium methoxide in dry 1,4-dioxane to produce the PSt microgel with maltohexaose, **4**, as a white solid. Interestingly, **4** gave a clear solution in H<sub>2</sub>O containing 30–70 % 1,4-dioxane. Thus, the hydrophilic property was successfully introduced into the highly hydrophobic PSt microgel by utilizing maltohexaose. According to the literature method,<sup>5</sup> we examined the ability of **4** to solubilize fullerene in aqueous solution. The experiment was performed using fullerite (mixture of fullerenes, C<sub>60</sub>/C<sub>70</sub> = ca. 9/1) to afford amber-colored aqueous solution. The characteristic absorption due to fullerenes appeared in the visible area from 330 to 800 nm for ultraviolet-visible (UV-vis) spectrum of the solution. Approximately 100 mg of **4** (1.7  $\mu$ mol) solubilized 1.3 mg of fullerite (1.7  $\mu$ mol), which was calculated on the basis of the molar absorption coefficient of fullerene C<sub>60</sub> solubilized in H<sub>2</sub>O using polyvinylpyrrolidone ( $\epsilon = 49000 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$  at  $\lambda = 340 \text{ nm}$ ).<sup>5</sup> Notably, the amber-colored solution was cast on a glass plate to produce a brown-colored homogeneous film after dryness. 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.

## Conclusions

A PSt microgel with maltohexaose was synthesized as a new family of glycoconjugated macromolecular architectures. This branched polymer conjugated with a highly water-soluble oligosaccharide solubilized fullerene, indicating a high potential for use as a tool for fullerene-coatings on a polar surface.

**Acknowledgments.** The author, A.N., thanks Dr. Harumi Kaga (National Institute of Advanced Industrial Science and Technology (AIST), Japan), Assistant Professor Toshifumi Satoh (Hokkaido University, Japan), and Professor Toyoji Kakuchi (Hokkaido University, Japan).

## References

- [1] Narumi, A.; Satoh, T.; Kaga, H.; Kakuchi, T. *Macromolecules* **2002**, *35*, 699.
- [2] Narumi, A.; Yamane, S.; Miura, Y.; Kaga, H.; Satoh, T.; Kakuchi, T. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 4373.
- [3] Muthukrishnan, S.; Jutz, G.; André, X.; Mori, H.; Müller, A. H. E. *Macromolecules* **2005**, *38*, 9.
- [4] Bernard, J.; Hao, X.; Davis, T. P.; Barner-Kowollik C.; Stenzel, M. H. *Bacromolecules* **2006**, *7*, 232.
- [5] Yamakoshi, Y. N.; Yagami, T.; Fukuyama, K.; Sueyoshi, S.; Miyata, N. *J. Chem. Soc., Chem., Commun.* **1994**, 517.