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Preparation of glycopolymer hollow particles by sacrificial dissolution of colloidal templates

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ABSTRACT

In this paper, a simple method for fabrication of glycopolymer hollow particles was demonstrated. The P(St-CPEM)-*g*-PVBSAELA core–shell particles were prepared by emulsifier-free emulsion polymerization of styrene (St) with 2-chloropropionyloxyethyl methacrylate (CPEM) using potassium persulfate as an initiator, followed by surface-initiated activator generated electron transfer–atom transfer radical polymerization (AGET–ATRP) of a styrene derivative bearing a lactose residue, i.e., *N*-2-4-(vinylbenzenesulfonamido)ethyl lactobionamide (VBSAELA). Dynamic light scattering measurement showed that the P(St-CPEM)-*g*-PVBSAELA core–shell particles possess graft layers of ca. 160 nm in thickness on the P(St-CPEM) core of 455 nm in diameter. By taking advantages of large difference in solubility between the PSt-based core and the PVBSAELA shell, the submicron-sized PVBSAELA hollow particles were obtained through a selective extraction of the core part from the P(St-CPEM)-*g*-PVBSAELA particles in tetrahydrofuran. The hydrodynamic diameter of the resulting hollow particles decreased by 15% compared to that of the corresponding core–shell particles. Finally, the micron-sized, raspberry-shaped, PVBSAELA hollow particles were successfully fabricated by a sacrificial dissolution of the PSt-based components from the PVBSAELA-grafted, core/shell heterocoagulates.

1. Introduction

Recently, much interest has been directed toward carbohydrates because they play a significant role in molecular recognition for biological substances. Since Lee first explained the importance of the sugar density for specific binding between oligosaccharides and receptor proteins [1], the multivalent effect on cell surfaces has lately become a major subject for better understanding of interactions in biology [2–9]. As carbohydrate interactions can be enhanced by linking several units to a single macromolecular carrier, a number of efforts have been devoted to the synthesis of polymers bearing pendant carbohydrate residues, the so-called glycopolymers [10,11]. Various types of well-defined glycopolymers have been prepared by controlled radical polymerization (CRP) for the purpose of dense accumulation of carbohydrates in a polymer chain. In particular, due to the merits such as easy handling and applicability to various monomers, ATRP is widely used to synthesize polymers with controlled molecular weights and narrow polydispersities [12–29]. Several attempts have been also made to apply ATRP to graft polymerization from solid substrates. As graft polymerization is expected as an effective and versatile technique for surface functionalization, surface-initiated ATRP on colloidal particles has been vigorously investigated for constructing polymer shell layers [30–40]. We succeeded in preparation of core–shell particles by surface-initiated activator generated electron transfer-atom transfer radical polymerization (AGET–ATRP) of unprotected, lactose-bearing styrene derivative, *N*-2-4-(vinylbenzenesulfonamido)ethyl lactobionamide (VBSAELA) from the P(St-CPEM) particles synthesized by miniemulsion polymerization of styrene (St) and 2-chloropropionyloxyethyl methacrylate (CPEM) [41]. Unfortunately, the molecular weight and the molecular weight distribution of the core–shell particles could not be measured because of a large difference in solubility between the core and shell. However, we conceived of the idea that insolubility of the PVBSAELA shell might be applied to the preparation of glycopolymer hollow particles through a selective dissolution of PSt-based components. The hollow particles are conventionally prepared by coating the surfaces of colloidal templates with thin layers of the desired material, followed by selective removal of the templates. This simple and straightforward approach works for a variety of materials that include polymers, ceramics, composites and metals [42–53]. Here, we first demonstrate a simple way to prepare submicron-sized glycopolymer hollow particles by a selective dissolution of a core part

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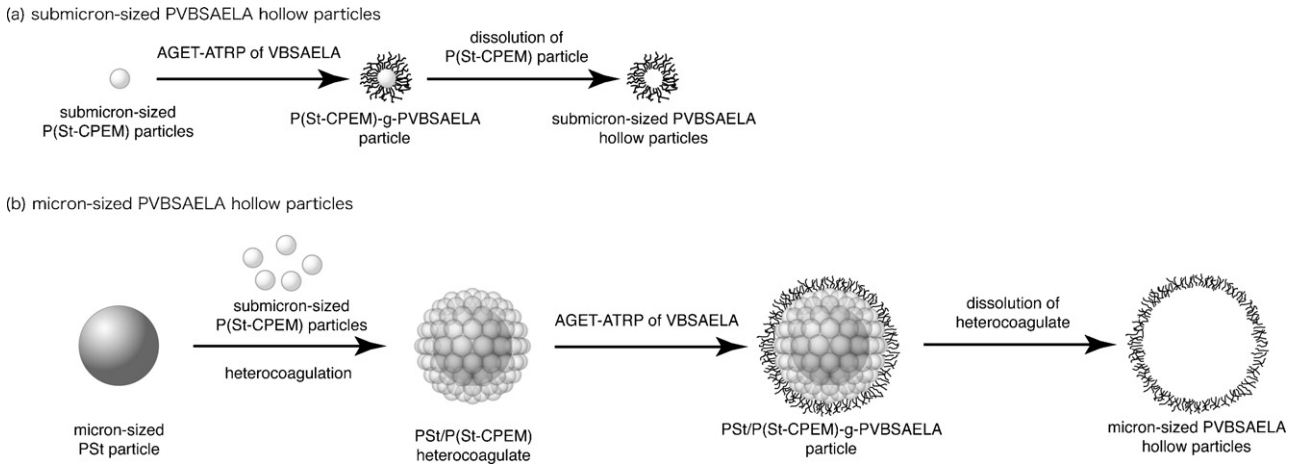

Fig. 1. Preparation of (a) submicron-sized and (b) micron-sized PVBSAELA hollow particles by sacrificial dissolution of colloidal template.

from the P(St-CPEM)-*g*-PVBSAELA core–shell particles (Fig. 1(a)). Finally, micron-sized hollow particles were also obtained by utilizing the PVBSAELA-grafted PSt/P(St-CPEM) heterocoagulates as a sacrificial colloidal template (Fig. 1(b)).

2. Experimental

2.1. Materials

Formaldehyde solution, formic acid, sodium hydroxide, chloroform, copper(II) dichloride dihydrate, L-(+)-ascorbic acid (AscA), methanol, thionylchloride, ethylenediamine, 2-methoxyethanol, toluene, pyridine, ethyl acetate, hexane, potassium persulfate (KPS), 2,2′-azobisisobutylonitrile (AIBN), and poly(vinyl pyrrolidone) (PVP (K = 30)) were obtained from Kanto Chemical. Tris(2-aminoethyl)amine (TREN) and 2-chloropropionyl chloride were purchased from TCI. Sodium *p*-styrenesulfonate and lactobionic acid were supplied by Wako Pure Chemical. Emulgen 109P was kindly supplied by Kao. The above chemicals were used as received. Tetrahydrofuran (THF) obtained from Kanto Chemical was purified by distillation. Deionized water with a resistance of 18.2 MΩ cm was obtained using a Millipore Simplicity UV. Styrene (St) provided by Nippon Steel Chemical and 2-hydroxyethyl methacrylate (HEMA) purchased from Kanto Chemical were distilled under reduced pressure. *N*-[2-(4-vinylbenzenesulfoneamido)ethyl] lactobioneamide (VBSAELA), 2-(2-chloropropionyloxy)ethyl methacrylate (CPEM), and tris(*N*,*N*-dimethylaminoethyl)amine (Me_6TREN) were synthesized according to the methods reported in the literature [54].

2.2. Preparation of P(St-CPEM) particles

The P(St-CPEM) particles were prepared by a batch, followed by shot-growth, emulsifier-free emulsion copolymerization [55]: St (100 mmol), KPS (1.52 mmol), and deionized water (300 mL) were placed in a four-necked separable flask equipped with a paddle stirrer, a thermometer, an argon inlet, and a reflux condenser. The mixture was deoxygenated by purging with argon for 15 min. The polymerization was initiated by heating to 70 °C with stirring at 200 rpm in argon atmosphere. CPEM was added 2 h after starting the polymerization. The particles obtained were purified with a hollow fiber dialyzer using a Spectrum Labolatories Pecyrum membrane (615 cm^2, 0.05 μm in hole diameter) and a Cole-Parmer Instrument Master Flex L/S tubing pump system to remove unreacted monomers and the initiator. The SEM image of P(St-CPEM) particles is shown in Fig. S1. The glass transition temperature (T_g) was measured by differential scanning calorimeter (DSC).

2.3. Preparation of heterocoagulates

The PSt/P(St-CPEM) core/shell heterocoagulates were prepared by hydrophobic heterocoagulation between the micron-sized PSt and the above P(St-CPEM) particles, according to our previous technique [61]. The PSt core particles were prepared by dispersion polymerization: St (130 mmol), AIBN (1.3 mmol), PVP (0.75 g), and emulgen 109P (0.80 mmol) were dissolved in a 2-propanol/water mixture (40 mL, 90/10 (v/v)) and placed in a four-necked separable flask. The system was purged with argon for 15 min to remove oxygen. The system was kept at 70 °C under stirring at 120 rpm. After 24 h, the polymerization was stopped by cooling in an ice bath. The PSt particles obtained were separated by centrifugation (3000 rpm, 10 min, 20 °C) and washed repeatedly with hot methanol to remove excess PVP from the particle surface. The SEM image of the PSt core particles is shown in Fig. S2. The heterocoagulation was carried out by stirring the PSt core (0.05 g) and the P(St-CPEM) shell particles (0.02 g) in a NaCl solution (150 mM, 10 mL) for 24 h at 70 °C. The PSt/P(St-CPEM) heterocoagulates obtained were separated and purified repeatedly by centrifugation (2000–4500 rpm, 10 min, 20 °C) and redispersion in deionized water to remove free shell particles.

2.4. AGET–ATRP of VBSAELA

Surface modification of the P(St-CPEM) core particles was carried out by AGET–ATRP of VBSAELA using Cu(II) complexed with Me_6TREN. The P(St-CPEM) particles (1.0 wt%, 10 mL), VBSAELA (1.0 mmol), $CuCl_2{\cdot}2H_2O$ (100 μmol), and Me_6TREN (100 μmol) were put in a round-bottom flask. The mixture was deoxygenated by purging with argon. To this was added an argon-purged solution of AscA. After 3 h, the polymerization was stopped by purging oxygen. The P(St-CPEM)-*g*-PVBSAELA core–shell particles obtained were purified by repetitive centrifugation (12,000 rpm, 15 min) and replacement of the aqueous medium with deionized water. The conversions of VBSAELA were determined by freeze-drying and weighing the supernatant. In the case of surface modification of heterocoagulates, AGET–ATRP was carried out by using the PSt/P(St-CPEM) heterocoagulates in the same manner as the P(St-CPEM)-*g*-PVBSAELA particles. The PSt/P(St-CPEM)-*g*-PVBSAELA obtained was separated by centrifugation (3000 rpm, 15 min) and washed repeatedly with water to remove unreacted VBSAELA.