



Diblock copolymer micelles as surface-functionalized particles and direct decoration of nanoparticles on their surface



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ABSTRACT

Surface modification is essential to attach optically or catalytically active nanoparticles on the surface of colloidal particles. In this article, we demonstrated that diblock copolymer micelles can be used as surface-functionalized particles and they can be coated with Ag or TiO₂ nanoparticles without surface modification. We first obtained dopamine-functionalized diblock copolymers which were synthesized by the reversible addition fragmentation chain transfer polymerization and followed by the post-polymerization modification. By dissolving this amphiphilic diblock copolymer in water, spherical micelles with the dopamine-functionalized coronas were induced, which are essentially equivalent to polymeric particles with dopamine-functionalized surface. Thus, without additional surface functionalization, we were able to directly decorate these particles with Ag and TiO₂ nanoparticles due to the dopamine functionality on their surface.

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1. Introduction

Dielectric particles coated by metallic shells or nanoparticles have been widely investigated for catalytic [1] and optical applications [2], including surface enhanced Raman scattering [3] and photonic crystals [4]. Silica particles synthesized by the sol–gel process are one of the most popular templates for decoration of shells and nanoparticles because their sizes are well-controllable in addition to their chemical and mechanical stability [5]. To attach metallic or inorganic nanoparticles on silica particles, however, modification of their surface by silane compounds or charged polymers is compulsory [3,6].

Polymeric particles, particularly with polystyrene (PS), are also commonly employed for spherical templates to be decorated by nanoparticles of metals, semiconductors, or oxides [7], which can be employed for applications in electronics, photonics, plasmonics, magnetics, and catalysis [8,9]. Compared to silica particles, one of the main advantages of PS particles is favorable dispersion in aqueous media due to relatively low densities of PS particles [7]. Polystyrene (PS) particles synthesized by the classical emulsion polymerization are largely used for such purpose [10]. However, surface modification is essential to attach nanoparticles to PS

particles. For example, the surface of PS particles can be directly sulfonated and then nanoparticles can be adsorbed on the sulfonated PS particles [11]. Surface functionalization can be also achieved by adding co-monomers of acrylic acid during the synthesis of PS particles, which provides functional groups of carboxylates on the surface of PS particles [12]. For effective attachment of nanoparticles, however, further modification of carboxylate-functionalized PS particles was performed by the reaction with thiol-functional molecules [13] or by layer-by-layer adsorptions of polyelectrolytes [14].

Since the surface area per volume increases with the decrease of the particle size, larger amounts of nanoparticles can be utilized if smaller particles are adopted as templates for decoration of nanoparticles. Since typical synthetic methods of silica and PS particles provide particles with the diameters larger than 100 nm [10], it requires great efforts to synthesize particles with the diameters smaller than 100 nm. For example, miniemulsion processes led to PS nanospheres with diameters less than 100 nm, which were further functionalized with Ag nanoparticles [15]. In contrast, spherical micelles of diblock copolymers generally have the diameters in the range of 10–100 nm [16]. Thus, they can be a potential candidate of smaller template particles for decoration of nanoparticles, compared to usual silica or PS particles.

In an aqueous solution, amphiphilic diblock copolymers form spherical micelles consisting of soluble hydrophilic coronas and insoluble hydrophobic cores [16]. A conventional usage of

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copolymer micelles is to solubilize otherwise insoluble substances such as drugs [17], dyes [18], and quantum dots [19] by encapsulating them in the cores. However, we will apply micelles of diblock copolymers to effective template particles with the diameter smaller than 100 nm to produce particles decorated with nanoparticles.

In this study, we first synthesized diblock copolymers of the PS block and the block containing activated esters by the reversible addition fragmentation chain transfer (RAFT) polymerization. Since activated esters can efficiently react with amine groups [20], we considered the copolymer containing activated esters as a template polymer, which can be modified to a copolymer containing a variety of functionality. We then replaced the activated ester with dopamine functionality, resulting in diblock copolymers consisting of the PS block and the dopamine-functionalized block. We selected the dopamine functionality [21] because it can strongly bind to the surface of metal oxides and can reduce metal ions without reducing agents [22]. There have been various reports on dopamine-functionalized diblock copolymers [23–27], including the synthesis based on activated esters [28–30]. For example, formation of metal nanoparticles on the dopamine units of diblock copolymers was exploited [27]. In addition, RAFT-polymerized block copolymers having a dopamine-containing anchor block as a solubilizing block for functionalization of TiO₂ nanorods was reported [31]. We here demonstrate the direct formation of PS particles having the dopamine-functionalized surface from diblock copolymers containing dopamine units, which can differentiate this work from the previous reports [23–30]. By dissolving this amphiphilic diblock copolymer consisting of the PS block and the dopamine-functionalized block in water, spherical micelles of ~40 nm in diameter were induced. Since these micelles have the PS cores with the dopamine-functionalized coronas, they can be considered as PS particles with dopamine-functionalized surface. Thus, without additional surface functionalization, we successfully decorated the PS particles, originated from the copolymer micelles, with Ag and TiO₂ nanoparticles due to the dopamine functionality on the surface of PS particles.

2. Experimental section

2.1. Materials

2,2'-azobisisobutyronitrile (AIBN, 98%), diethylether (>99.7%), N,N-dimethylformamide (DMF, 99.8%), dopamine hydrochloride (98.5%), trimethylamine (TEA, >99.5%), acryloyl chloride (>97%), cumyldithiobenzoate (99%), styrene (>99%), and calcium hydride (99.99%) were purchased from Sigma Aldrich and used as received unless otherwise stated. Each solvent was purified by a standard distillation procedure as described in the literature [32]. AIBN was recrystallized from diethylether. Styrene was dried over calcium hydride and distilled under reduced pressure. Pentafluorophenol (>99%) was acquired from Alfa-Aesar. Poly(acrylic acid)-*b*-polystyrene (PAA-*b*-PS) was purchased from Polymer Source Inc. The number-average molecular weights of PS and PAA were 61,000 and 4000 g/mol, respectively. The polydispersity index was 1.05.

2.2. Pentafluorophenyl acrylate (PFPA)

PFPA monomers were synthesized as described in the literature [20]. In a round bottom flask equipped with a dropping funnel and a magnetic stir bar, pentafluorophenol (17.1 mL, 0.16 mol) was dissolved in anhydrous dichloromethane (200 mL) under nitrogen atmosphere. Triethylamine (27.3 mL, 0.19 mol) was added via syringe through a septum. The dropping funnel was filled with acryloyl chloride (16.5 mL, 0.19 mol) under nitrogen atmosphere

and this component was then dropped slowly to the reaction mixture while stirring vigorously and cooling with an ice bath. After complete addition, the reaction mixture was cooled for 30 min and then slowly warmed to room temperature for overnight. It was extracted with water (200 mL) three times. The organic phase was dried over MgSO₄, concentrated by rotary evaporation and subsequently vacuum distilled. Pentafluorophenyl acrylate was isolated at 49 °C (9.8 × 10⁻² mbar) as a colorless liquid (19.43 g, 0.077 mol, 71%).

¹H NMR (CDCl₃, 300 MHz): δ [ppm] = 6.45 (m, 1H, C=CH₂-cis); 5.92 (m, 1H, C=CH₂-trans); 2.08 (s, 3H, -CH₃).

2.3. Poly(pentafluorophenyl acrylate) (PPFPA)

PPFPA was synthesized by the RAFT polymerization as shown in the literature [20]. For a typical procedure, a Schlenk tube equipped with a stir bar was loaded with pentafluorophenyl acrylate (PFPA) (15 g, 62.9 mmol), cumyl dithiobenzoate (272 mg, 0.99 mmol), and AIBN (23 mg, 0.14 mmol). All compounds were dissolved in anhydrous dioxane (2 mL). Following three freeze–pump–thaw cycles, the tube was immersed in an oil bath at 65 °C for about 24 h with vigorous stirring. The resulting polymer was isolated by precipitation in methanol. By re-dissolving the polymer in a few milliliters of THF, this process was repeated three times. The precipitated polymer was dried for 12 h at 23 °C under 10 mbar vacuum, providing P(PPFPA) (9 g, 60%) as slightly pink powder. The number average molecular weight is 5000 g/mol and polydispersity index is 1.1 by GPC with PS standards (Supporting information Fig. S1).

2.4. Poly(pentafluorophenyl acrylate)-*b*-polystyrene (PPFPA-*b*-PS)

To synthesize PPFPA-*b*-PS diblock copolymer, 1.12 g (0.22 mmol, 1 eq.) of the PPFPA macro chain transfer agent and 3.6 mg (0.022 mmol, 0.1 eq.) AIBN, and styrene monomers (10 g) were added together with 3 mL THF in a Schlenk tube. Oxygen was exchanged by nitrogen after three freeze–pump–thaw cycles and then polymerization was carried out at 65 °C for 24 h. The block copolymer was purified by precipitation in methanol three times, resulting in 5.8 g (58%) of the reactive block copolymer. To remove PS homopolymer, Soxhlet extraction was performed with cyclohexane for 24 h. The number average molecular weight is 66,800 g/mol and polydispersity index is 1.08 by GPC with PS standards (Supporting information Fig. S1). The block ratio between PPFPA and PS was 1:14 from the ratio of the peak integral of 0.07 at 3.08 ppm to that of 3.00 around 7.06 ppm in the ¹H NMR spectrum (Supporting information Fig. S2a).

¹H NMR (500 MHz, CDCl₃) (Supporting information Fig. S2a): δ [ppm]: 7.06 (m, 3H, Ph-H), 6.57 (m, 2H, Ph-H), 3.04 (m, 1H, CH₂-CH-), 2.38 (m, 1H, CH-CH₂), 1.87 (m, 1H, CH-CH₂), 1.84 (m, 1H), 1.39 (m, 2H).

¹⁹F NMR (CDCl₃, 400 MHz) (Supporting information Fig. S3a): δ [ppm] = -152.74 (d, J = 19 Hz, 2F, o-ArF); -158.17 (t, J = 19 Hz, 1F, p-ArF); -162.45 (t, J = 19 Hz, 2F, m-ArF).

2.5. Poly(dopamine acrylamide)-*b*-polystyrene (PDA-*b*-PS)

To modify the activated ester, post-polymerization modification was carried out. PPFPA-*b*-PS (300 mg, 0.004 mmol, 1 eq.), dopamine hydrochloride (217 mg, 1.1 mmol, 15 eq.), and triethylamine (116 mg, 1.1 mmol, 15 eq.) were dissolved in a mixture of 2 mL of THF and 2 mL of DMF and stirred under nitrogen at room temperature for 12 h. Then, the solution was filtered and precipitated in methanol three times, yielding 240 mg (80%) of the product. Conversion of PPFPA to PDA was monitored by appearance of the

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