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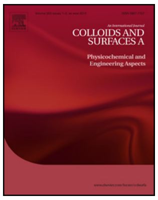

# In-situ assembly of diblock copolymers onto submicron-sized particles for preparation of core-shell and ellipsoidal particles

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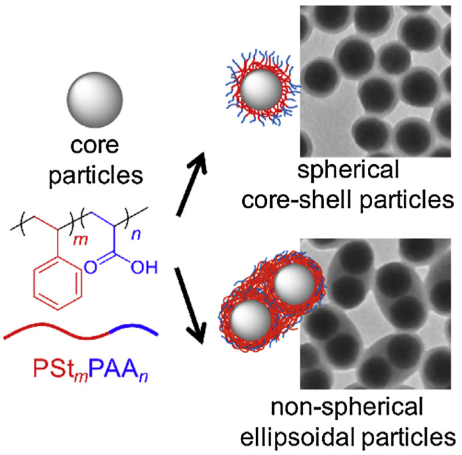
## HIGHLIGHTS

- In situ assembly of amphiphilic diblock copolymers in the presence of silica particles was investigated.
- Core-shell particles with tailored shell thickness were observed.
- Ellipsoidal particles containing two core particles were prepared.

## GRAPHICAL ABSTRACT



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## ABSTRACT

We describe a facile and simple method to prepare colloidal architectures by the in situ assembly of amphiphilic diblock copolymers onto submicron-sized core particles. Polystyrene-*b*-poly(acrylic acid) diblock copolymers (PSt$_m$PAA$_n$) were directly assembled onto hydrophobic silica (SiO$_2$) core particles, forming spherical core-shell particles. By varying the surface hydrophobicity of the core particles and the compositions of the diblock copolymers, core-shell particles with tailored shell thickness were observed. Furthermore, we demonstrated the preparation of ellipsoidal particles, which containing two core particles, based on this strategy.

## 1. Introduction

Amphiphilic diblock copolymers self-assemble into nanostructures, e.g., micelles, cylinders, and vesicles, which have attracted considerable attention due to the possibility of numerous applications, including drug delivery systems, nano reactors, and diagnostic imaging [1–4]. Moreover, hybrid materials composed of diblock copolymers and particles are of interest in several fields, including biotechnology, pharmaceuticals, and synthetic chemistry [5–9]. A wide variety of nanoparticles has been incorporated into various polymer assemblies. For example, Taton et al. reported the preparation of gold nanoparticle-loaded diblock copolymer

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micelles, which were shown to have polymer shell layers of approximately 15 nm in thickness on the hydrophobic gold nanoparticle cores of approximately 12 nm and 31 nm in diameter [5,6]. Park et al. demonstrated the control of the self-assembly structures of amphiphilic diblock copolymers in the presence of magnetic nanoparticles [7] or gold nanoparticles [8], which showed that the arrangement of nanoparticles and the polymer morphology could be controlled by changing the initial solvent composition, polymer chain lengths, and amount of nanoparticles. Eisenberg et al. also reported the preparation of gold nanoparticle aggregates with morphological control [9]. Nano-sized particles are incorporated into diblock copolymer assemblies such as micelles, cylinders, and vesicles. In these cases, it is required that the surface of nano-sized particles was usually pre-modified by diblock copolymers [5–9]. While most of the aforementioned research has focused on the use of nano-sized particles that were pre-coated by amphiphilic diblock copolymers, there are a few report that demonstrate block copolymer assembly using submicron-sized particle as a template [10,11]. The difference of submicron-sized particles and nano-sized particles for diblock copolymer assembly is the formation mechanism of assembled samples. For submicron-sized particles, diblock copolymer are assembled and aggregated onto the particles surface. Thus, assembled samples using submicron-sized particles and block polymer are easily obtained. Additionally, since block copolymers are simply assembled onto surface, variety of block copolymers, including functional polymers, will be applied to this method. It remains a challenge to develop an effective strategy for the direct preparation of colloidal architectures using submicron-sized particles.

Non-spherical particles, e.g., ellipsoidal, Janus, raspberry-like and dumbbell-like particles, have become attractive materials for basic research and industrial applications [12–18]. Although the seeded polymerization technique is effective for the preparation of non-spherical particles [19–22], it requires strict control of numerous parameters, such as the monomer composition, central seed particle size, polymerization time, reaction temperature, and density of the polymerizable groups on the seed surface, making it more difficult to optimize the reaction [23]. Therefore, it would be of great interest to develop a facile method for preparing non-spherical particles as well as spherical particles.

Here, we report a facile and simple procedure for the preparation of colloidal architectures by the in situ assembly of amphiphilic diblock copolymers onto submicron-sized core particles (Fig. 1). By tuning the surface hydrophobicity of silica ($SiO_2$) core particles and the compositions of polystyrene-*b*-poly(acrylic acid) diblock copolymers ($PSt_mPAA_n$), both spherical core-shell particles and non-spherical ellipsoidal particles were observed. A mechanism for the formation of the colloidal architectures is also proposed.

## 2. Experimental

### 2.1. Materials

Styrene (St), tetrahydrofuran (THF), and methanol were obtained from Kanto Chemical. 2,2′-Azobisisobutylonitrile (AIBN), trifluoroacetic acid (TFA), and octadecyltrimethoxysilane (OTMS) were purchased from Tokyo Chemical Industry. 1,1′-Azobis(cyclohexane-1-carbonitrile) (ACHN), *tert*-butyl acrylate (*t*BA), dichloromethane (DCM), *N*, *N*-dimethylformamide (DMF), propylene glycol monomethyl ether acetate (PGMEA), and hydrofluoric acid (HF) were obtained from Wako Pure Chemical. Ethyl-2-butyltellanyl-2-methyl-propionate (BTEE) was graciously supplied by Otsuka Chemical and was used as received. $SiO_2$ particles (MP-1040) were supplied by Nissan Chemical and were purified by stirring in concentrated nitric acid with subsequent washes with THF. St was dried over calcium hydride and distilled under reduced pressure. All other chemicals and solvents were of reagent grade and were used as received.

### 2.2. Measurements

Scanning electron microscopy (SEM) micrographs were obtained using a JSM-6510A scanning electron microscope (JEOL). Transmission electron microscopy (TEM) micrographs were obtained using an H-7650 transmission electron microscope (Hitachi). FT-IR spectra were measured with an FTIR-420 spectrophotometer (JASCO). Thermogravimetric analysis (TGA) was performed in air at 10 °C $min^{-1}$ with a TG8120 thermogravimetry/differential thermal analyzer (Rigaku). The hydrodynamic diameter (Dh) of the particles in water was measured by dynamic light scattering using an ELSZ-1000ZS (Otsuka Electronics). UV–vis spectra were obtained using a U-3010 spectrophotometer (Hitachi). Static contact angle measurements were performed using a P200A (Meiwafosis).

### 2.3. Preparation of hydrophobic $SiO_2$ core particles

$SiO_2$ particles (2.0 g) were dispersed in THF (50 mL) and stirred for 30 min under reflux. OTMS (3.6, 4.1, or 7.1 g, 9.6, 11, or 19 mmol) was then slowly added to the dispersion. After stirring for 24 h under reflux, the particles were separated and purified repeatedly by centrifugation (10,000 rpm, 10 min) before redispersion in DMF.

### 2.4. Synthesis of amphiphilic diblock copolymers ($PSt_mPAA_n$)

Amphiphilic diblock copolymers of different compositions were prepared by sequential telluride-mediated polymerization (TERP) processes as described in a previous publication [24]. For example, for the synthesis of $PSt_{41}PAA_{14}$, St (4.0 g, 38 mmol), ACHN (94 mg, 0.38 mmol), and BTEE (176 μL, 0.76 mmol) in PGMEA (4.1 mL) were added to a screw tube. The polymerization was conducted at 90 °C for 14 h under nitrogen atmosphere, allowing monomer conversion to reach approximately 100%. Subsequently, *t*BA (second monomer; 2.0 g, 16 mmol) and AIBN (63 mg, 0.39 mmol) in PGMEA (7.2 mL) were added to the screw tube and were left to react for 20 h at 70 °C. The polymers were purified by reprecipitation from THF into a large excess of methanol to form $PSt_{41}PtBA_{14}$. Excess TFA (5 eq. to *t*BA units) was added to the block copolymer obtained (2 g) in DCM (50 mL) and was stirred at room temperature under a nitrogen atmosphere. After 12 h, the solvents and regents were removed by evaporation, and the polymers were purified by reprecipitation from THF into a large excess of methanol, giving rise to $PSt_{41}PAA_{14}$ diblock copolymers.

### 2.5. In situ assembly of diblock copolymers onto core particles

To $PSt_mPAA_n$ (2.8 mg, 0.1 wt%) and $SiO_2$ core particles (5.7 mg, 0.2 wt%) in DMF (3 mL) was added deionized water (0.6 mL) in a dropwise manner (0.1 mL/min) using syringe pump (size of droplets: ca. 5 mm) at room temperature. The ratio of diblock copolymers to core particles was fixed to 1/2. The mixture was then stirred continuously for 1 h at 90 °C to anneal polymers onto particles surface. (Stirring speed: 500-2 000 rpm. In these range, the difference was not observed because of high affinity of water and DMF.) Subsequently, the obtained particles were separated and purified repeatedly by centrifugation (13,500 rpm, 10 min) and were redispersed in water.

Hollow particles were prepared as follows: $SiO_2(1.5)@PSt_{41}PAA_{14}$ core-shell particles (10 mg) were stirred in excess hydrogen fluoride (HF) to remove the $SiO_2$ core components. The sample was separated and purified repeatedly by