

Preparation of Organic-Inorganic Doublet Particles Using Seeded Polymerization

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Introduction

Recently, there has been great interest in organic-inorganic hybrid particles due to their extraordinary properties of combining organic and inorganic components. Various synthesis processes for organic-inorganic hybrid particles have been reported including Layer-by-Layer (LBL) assembly and emulsion polymerization. Using these methods, core-shell particles are commonly produced.¹⁻³ In our previous work, we produced organic-inorganic hybrid microsphere incorporated an inorganic network into the core polymer by simple dispersion polymerization.⁴ These techniques are useful for synthesis of organic-inorganic composite particles, but these are only suitable to prepare the spherical shaped particles. Besides, it is difficult to control the distribution of chemical composition of the particles.

In this study, we produced a unique doublet hybrid particle with a distinct organic and inorganic region through seeded polymerization. The doublet structure was controlled by the elastic-retractile force and phase separation due to a crosslink of the semi-interpenetrating polymer network (semi-IPN) seed particle. The obtained doublet particles had hydrophilic/hydrophobic properties on the distinct surface. Because of their controllable and superior properties of "chemical selectivity" and "amphiphilicity", it is expected that these particles can be applied to biosensors, colloidal stabilizers and self-assembling particles.

Experimental

Materials. Styrene (St, Kanto Chemical Co.) and divinylbenzene (DVB, mixture of isomer; 55%, Aldrich Chemical Co.) were purified through a removing column before use. 2,2'-Azobisisobutyronitrile (AIBN, Junsei Chemical Co.) and benzoyl peroxide (BPO, Lancaster) were recrystallized to remove an inhibitor from methanol before use. The other materials were used as received; polyvinylpyrrolidone

(PVP, $M_w = 4.0 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$, Sigma Aldrich Chemical Co.), ethanol (Carlo Erba), aerosol-OT (AOT, Wako), polyvinylalcohol (PVA, $M_w = 8.8 \times 10^4$ - $9.2 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$, 87-89% hydrolyzed, Sigma Aldrich Chemical Co.), sodium lauryl sulfate (SLS, Sigma Chemical Co.), 1-ethanolamine (Yokuri pure Chemical Co.) and 3-(trimethoxysilyl) propyl methacrylate (TMSPM, Aldrich Chemical Co.). All aqueous solutions were prepared using distilled water.

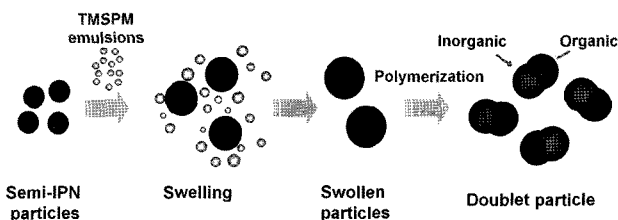
Synthesis of Semi-IPN Seed Particles. Highly monodisperse crosslinked seed particles were prepared through seeded polymerization. All reactions were carried out in a 250 mL four-neck glass reactor equipped with a mechanical stirrer, a refluxing condenser and a nitrogen inlet system. At first, linear PS seed particles were dispersed in 0.25 wt% SLS solution by applying ultrasonification for 30 min. The first monomer mixture of styrene, DVB, AIBN was emulsified by ultrasonic homogenizing in the 0.25 wt% SLS solution for 10 min and poured into the reactor. After complete disappearance of monomer emulsion, the swollen particles were stabilized with 5 wt% PVA aqueous solution. Then, the reactor was submerged into a preheated thermostatic oil bath and the polymerization was carried out with a stirring speed of 100 rpm at 70 °C for 12 h. The resulting latex was centrifuged at 4,000 rpm for 10 min. The supernatant was then decanted and the remaining precipitate was repeatedly washed with several centrifugation/re-dispersion cycles in a methanol/water mixture, followed by drying under a vacuum at ambient temperature.

Preparation of Organic-inorganic Doublet Particle. To prepare organic-inorganic doublet particles, the seeded polymerization was carried out again using the semi-IPN PS particles. Re-dispersed semi-IPN PS seed particles in 0.25 wt% SLS solution were swollen with second emulsified monomer solution; TMSPM and BPO (1 wt% based on the weight of the monomer). Swelling and polymerization followed as-above mentioned synthesis procedure of the semi-IPN seed particles. Finally chemical treatment was conducted with various silane coupling agents to incorporate functional groups to the hydrophilic domain of the particles.

Results and Discussion

The synthetic procedure for the production of organic-inorganic anisotropic particles is shown in Scheme 1. First, semi-interpenetrating polymer network (semi-IPN) polystyrene (PS) seed particles were prepared by seeded polymerization. Figure 1 shows swelling process of semi-IPN seed particles with emulsified TMSPM monomer solution, which was diffused into the seed particle by Ostwald ripening. In our experiments, the swelling process was clearly completed in a few minutes by ostwald ripening there was

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Scheme I. Schematic representation of the formation of the organic-inorganic doublet particles by seeded polymerization.

no trace of the residual TMSPM emulsion in the aqueous medium. After completion of swelling with emulsified monomer solution, seed particles were polymerized by raising the reaction temperature. During polymerization, the morphology of the swollen particle changed due to the elastic-retractile force. These morphological changes were consequent on the network structure of the semi-IPN seed particles, reaction temperature, swelling ratio of the monomer to seed and seed size. Furthermore, the phase separation of polymer and monomer enhanced the morphological changes.⁵⁻⁸ Therefore, a new silica domain was formed by expelling Poly-TMSPM from the semi-IPN PS seed particle because of the elastic-retractile force and phase separation.

Figure 2 shows the obvious difference of morphologies between the semi-IPN seed particles and doublet particles. Furthermore, as-synthesized particles had narrow size dis-

tribution (Figure 2(a)) and doublet morphology with identical domain size (Figure 2(b)). Table I shows a summary of the results for semi-IPN PS seed particles and organic-inorganic hybrid particles corresponding to Figure 2. About 100 individual particle diameters were measured from scanning electron microscope (SEM, JSM-6330F JEOL) photographs, and the average size was taken. From these facts, we conclude that the seed domain kept the character of the seed particles, and the other domain was newly formed with the Poly-TMSPM. In the case of crosslinked PS particles (not semi-IPN structures), full-crosslinked network structure disturbed the expelling of TMSPM monomer and newly formed chains. Hence acorn-like structure was obtained at the same experimental condition: same crosslink density, swelling ratio and reaction temperature (The results have not been shown in this paper). When linear PS particles were used as a seed, consequently spherical shape was observed since the elastic-retractile force is too weak to expel out the formed TMSPM chain and monomer.^{5,6,9,10}

In order to verify the composition, a FT-IR (Magna-IR 760 Nicolet) analysis of the organic-inorganic hybrid doublet particles was carried out for a comparison with semi-IPN PS seed particles. The seed particles consisted of hydrocarbons; hence, C-H and C=C stretching bands occurred in the range from 2900 to 3100 cm^{-1} and from 1600 to 1450 cm^{-1} , respectively (Figure 3(a)). In the case of

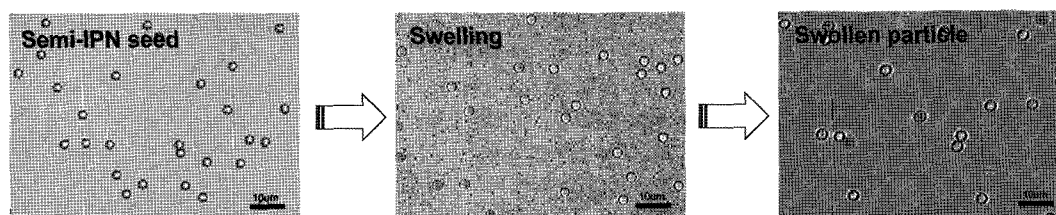


Figure 1. Optical microscope images for swelling procedure of TMSPM monomer mixture.

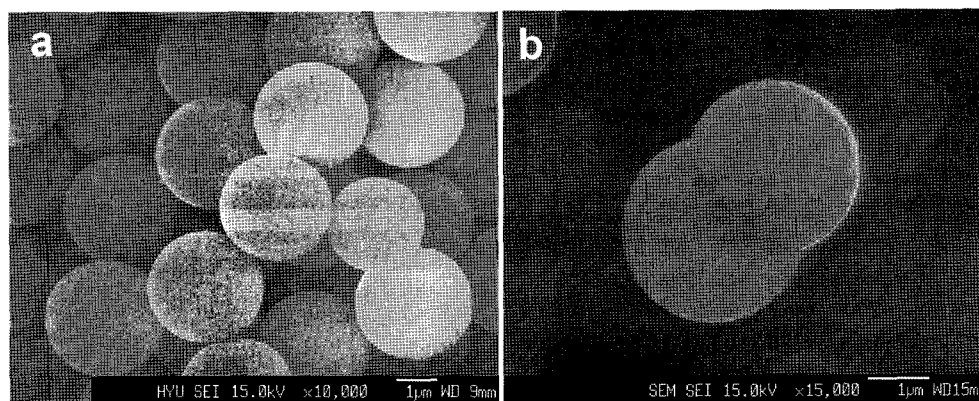


Figure 2. Scanning electron microscope (SEM) photographs of semi-IPN PS seed particles (a) and organic-inorganic anisotropic particles (b).

Table I. Characteristics of Semi-IPN Seed Particles and Organic-Inorganic Hybrid Doublet Particles

	D_n (μm)	PSD ^a	D_{no} (μm) ^b	D_{ni} (μm) ^c	Aspect Ratio
Seed Particle	2.77	1.008	-	-	-
Organic-inorganic Doublet Particle	-	-	2.8	2.97	1.516

^aParticle size distribution, D_w/D_n , where $D_n = \sum(D_i/N)$, $D_w = \sum D_i^4/D_i^3$. ^bAverage particle diameter of the organic polystyrene domain. ^cAverage particle diameter of the inorganic silica domain.

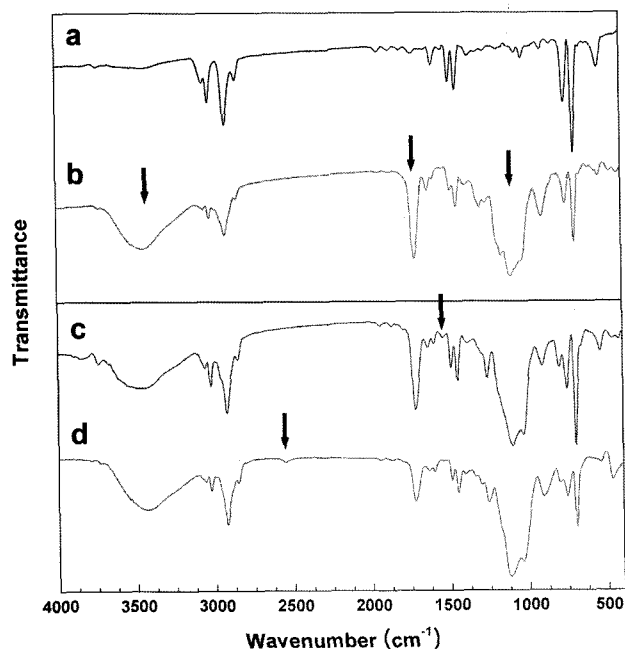


Figure 3. FT-IR spectra of the semi-IPN PS seed particle (a), organic-inorganic hybrid doublet particle (b), after incorporating the amine group with AMPTS (c), and the thiol group with MPTMS (d).

the organic-inorganic hybrid particles, however, a broad band at 3400 cm^{-1} stands for the presence of a hydroxyl group on the surface of the inorganic bulb (Figure 3(b)). The appearance of two strong bands at 1750 cm^{-1} (C=O) and near 1100 cm^{-1} (Si-O) corresponds well with the established characteristic band for TMSPM. Based on the FT-IR spectrum, TMSPM were successfully polymerized through seeded polymerization. Generally, silica particles can be easily modified for various functional groups by using a sol-gel reaction. Herein, the surface of the inorganic bulb was treated with 3-aminopropyl-trimethoxysilane (AMPTS) and 3-mercaptopropyl-trimethoxysilane (MPTMS). In Figure 3(c) and (d), the absorption bands of NH_2 and SH were observed near 1550 and 2550 cm^{-1} , respectively, after sol-gel reaction. These results indicate that organic-inorganic hybrid doublet particles can be widely applied by surface modification with various silane coupling agents.¹¹⁻¹⁴

To demonstrate the chemical anisotropy of the as-synthesized hybrid doublet particles, a fluorescence microscope (FM, Olympus BX51) was utilized. The doublet particles

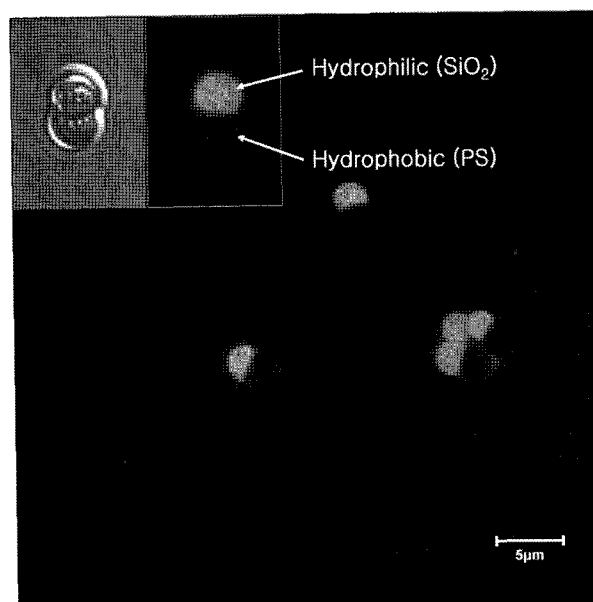


Figure 4. Fluorescent microscopic image of doublet particles having amphiphilic chemical composition of hydrophilic silica and hydrophobic PS. Fluorescence microscope equipped filter (excitation 510-550, emission 590, dichromatic mirror 570 nm) was utilized.

were labeled with rhodamine B isothiocyanate as following literatures.^{15,16} To avoid dye-adsorption on the hydrophobic PS domain, the particles were washed and the free RBITC was removed with 1-ethanolamine under ultrasonification for several times. When semi-IPN seed particles were used, as has been mentioned, the doublet morphology was obtained from the phase separation and the elastic-retractile force. Figure 4 provides support for TMSPM being perfectly separated from the original seed particle and forming a new domain. Red fluorescent (532 nm) was only observed in the hydrophilic TMSPM domain of the doublet particle. This image confirms that chemical composition and distribution of the hydrophilic TMSPM domain are distinctly different from those of the hydrophobic PS domain.

In this study, organic-inorganic hybrid doublet particles were successfully synthesized through simple seeded polymerization of semi-IPN PS seed particles swollen with TMSPM. The amphiphilic properties of the as-synthesized particles, hydrophilic silica and hydrophobic PS, were confirmed with a fluorescence microscope. These doublet parti-

cles could be applied to bio-screening materials, smart optical sensors, or photonic crystals by a simple modification of the hydrophilic silica domain.¹⁷⁻¹⁹

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