

Preparation of Functional Core-shell Particles by Heterocoagulation

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Cationic polymer shell particles with sulfonium groups were immobilized at hydrophobic surfaces of cross-linked polystyrene particles as core particles by heterocoagulation. Composite polymer particles with a core-shell structure were produced by heat treatment at a temperature above the T_g of shell particles.

Composite polymer particles with a core-shell structure have received much attention in recent years. The interesting morphology and designed functional surface properties of the core-shell particles have numerous application possibilities such as spacers, adhesives and catalysts. The composite polymer particles with heterogeneous structures are generally prepared by seeded polymerization and heterocoagulation techniques.¹⁻⁴ Seeded polymerization was the most general method developed to prepare latex particles having core-shell structure. As a first step, the core latex particles were prepared either separately or in situ and the next step of polymerization was usually a seeded swelling batch or semi-batch process. Several groups have also reported the formation of core-shell particles prepared by stepwise heterocoagulation of smaller cationic polymer particles onto larger anionic polymer particles, followed by heat treatment at a temperature above the T_g of the shell particles.⁵⁻⁷ For such heterocoagulation, the electrostatic interaction has mainly been utilized as driving force between the shell and the core particles.

Recently, we have found that cationic polymer particles produced by emulsifier-free emulsion copolymerization of styrene (ST) with methacryloyloxyphenyldimethylsulfonium methylsulfate (MAPDS) were spontaneously immobilized onto hydrophobic surfaces of solid substrates by hydrophobic interactions.⁸ In this paper, we describe the preparation of composite polymer particles produced by novel heterocoagulation of the cationic polymer particles with cross-linked polystyrene particles.

P(ST-*co*-MAPDS) shell particles with ca. 220 nm in diameter were prepared according to the procedure described elsewhere.^{9,10} Monodispersed P(ST-*co*-BA-*co*-MAPDS) shell particles having a lower glass transition temperature with ca. 270 nm in diameter were also prepared by emulsifier-free emulsion copolymerization of ST (320 mmol) and butyl acrylate (BA) (160 mmol) with MAPDS (3.2 mmol) at 60 °C using 2,2'-azobis(2-amidinopropane) dihydrochloride (V-50) (3.2 mmol) as an initiator (Figure 1). The compositions of ST and BA of P(ST-*co*-BA-*co*-MAPDS) were ca. 2 : 1 as estimated by ¹H NMR. Cross-linked polystyrene particles (core particles) with ca. 8.5 μ m in diameter from Sekisui Chemical Industries were stirred in latex dispersions (0.25 wt%) at 40 rpm. The coagulates were taken out by centrifugation, and washed by ultrasonic cleaning for 5 min with deionized water (Scheme 1). The morphology of the shell particles immobilized on the core particles was observed by a scanning electron microscope (SEM) (JEOL, JSM-5310) and the coverage with the shell particles was calculated.¹¹ The

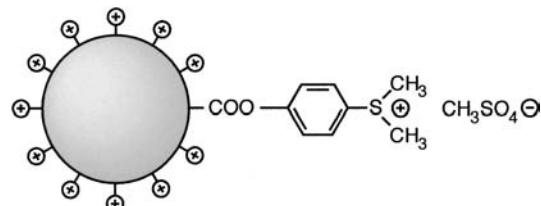
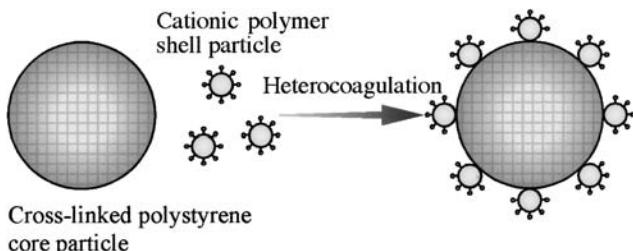


Figure 1. Structure of cationic shell polymer particles containing sulfonium groups and active ester groups.



Scheme 1. Schematic representation of immobilization of cationic polymer shell particles onto the hydrophobic surface of cross-linked polystyrene core particles.

coverage was determined by the following equations:

$$\text{Coverage (\%)} = (N/N_{\max}) \times 100 \quad (1)$$

$$N_{\max} = (2\pi/\sqrt{3}) \times [(R_{\text{core particle}} + R_{\text{shell particle}})/R_{\text{shell particle}}]^2 \quad (2)$$

$R_{\text{core particle}}$: radius of core particle

$R_{\text{shell particle}}$: radius of shell particle

where N and N_{\max} are number of shell particles on core particle and number of close-packed shell particles on core particle, respectively. The resulting heterocoagulates were heated at 80 °C above T_g of P(ST-*co*-BA-*co*-MAPDS) particles.

SEM photographs in Figure 2 show the heterocoagulates

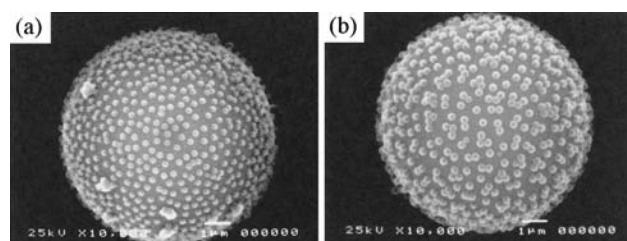


Figure 2. SEM photographs of heterocoagulates produced by heterocoagulation of cationic polymer shell particles with cross-linked polystyrene core particles. [Latex], 0.25 wt%; (a) P(ST-*co*-MAPDS) shell particle, (b) P(ST-*co*-BA-*co*-MAPDS) shell particle.

produced by heterocoagulation of P(ST-*co*-MAPDS) and P(ST-*co*-BA-*co*-MAPDS) shell particles with cross-linked polystyrene particles. The shell particles are immobilized onto the surface of the core particles. The surface charge number of core particles used in this study, determined by colloid titration, was nearly zero, though they exhibited a negative ζ -potential. The immobilization of shell particles also takes place in the presence of NaCl as an electrolyte where ζ -potential of core particles is approximately ± 0 mV. Therefore, the shell particles would be immobilized at the hydrophobic surfaces of the core particles by hydrophobic interaction. Furthermore, the shell particles are immobilized onto the core particles at relatively regular intervals, though some small aggregates are also observed. Such formation of regular array is due to the strong electrostatic repulsion between the shell particles.

The influence of electrolytes on the heterocoagulation was investigated in order to control the morphology of heterocoagulates. Core particles were stirred to latex dispersions (0.25 wt%) containing NaCl as an electrolyte. The relationship between NaCl concentration and the coverage is shown in Figure 3. For both P(ST-*co*-MAPDS) and P(ST-*co*-BA-*co*-MAPDS) shell particles, the coverage drastically increases with increasing the NaCl concentration. This can be ascribed to the decrease in the electrostatic repulsions between the shell particles.

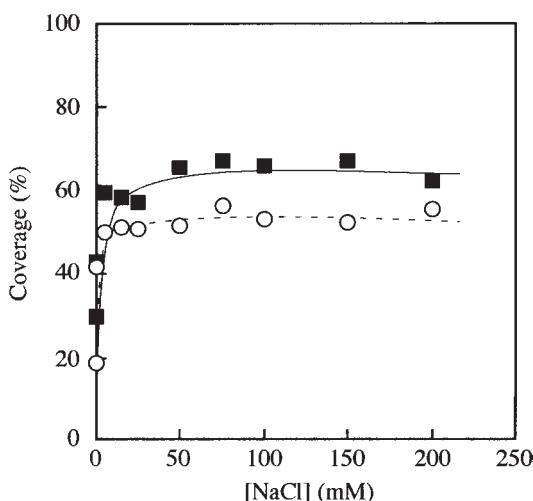


Figure 3. Coverage of cationic polymer shell particles immobilized onto cross-linked polystyrene core particles against NaCl concentration. [Latex], 0.25 wt%; ■, P(ST-*co*-MAPDS) shell particle; ○, P(ST-*co*-BA-*co*-MAPDS) shell particle.

Figure 4 shows SEM photographs of heterocoagulates produced by heat treatment at 80 °C above the T_g of P(ST-*co*-BA-*co*-MAPDS) shell particles for 3 h. For the heterocoagulation in the presence of 150 mM NaCl, the shell particles are immobilized onto the core particles as aggregates. The resulting

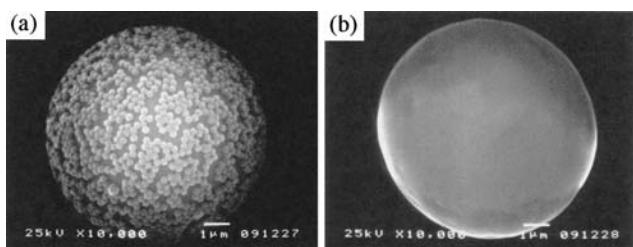


Figure 4. SEM photographs of composite polymer particles (a) before and (b) after heating at 80 °C for 3 h. Heterocoagulation, [P(ST-*co*-BA-*co*-MAPDS) latex], 0.25 wt%; [NaCl], 150 mM.

heterocoagulates were heated at 80 °C to produce composite polymer particles with a smooth surface. The particle size of the composite polymer particle was larger than that of the core particle.

In summary, cationic polymer particles containing sulfonium groups and active ester groups were newly found to be immobilized at the hydrophobic surface of cross-linked polystyrene particles. The hydrophobic interaction between the shell and the core particles would be a key role for the heterocoagulation. Composite polymer particles with a core-shell structure were obtained by heating above the T_g of P(ST-*co*-BA-*co*-MAPDS) shell particles. Shell particles used in this study have active ester groups at their surfaces exhibiting a high reactivity towards primary amino compounds. Therefore, composite polymer would be useful for further functionalizations by taking advantage of remaining active ester groups.

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