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ORIGINAL CONTRIBUTION

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Preparation of core–shell composite polymer particles by a novel heterocoagulation based on hydrophobic interaction

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Abstract Submicron-sized cationic polystyrene shell particles with active ester groups were effectively self-assembled on hydrophobic surfaces of cross-linked polystyrene (PST) particles, uncharged core particles with ca. 8.5-μm diameter in aqueous systems. The hydrophobic interactions between the shell particles and core particles play a key role in heterocoagulation. The resulting heterocoagulates were highly physically stable in water, and the morphology was controlled by several factors including the solid content of latex, self-assembling time, and electrolyte concentration. Composite polymer particles with a core–shell structure were successfully obtained from the heterocoagulates by heat treatment for 3 h at a temperature above the glass transition temperature (T_g) of the cationic polymer shell particles.

Keywords Cationic polymer particle · Self-assembling · Heterocoagulation · Hydrophobic interaction · Core–shell structure

Introduction

Core–shell particles are structured composite particles consisting of at least two different polymers: one in principle forms the core and the other the shell of the particles. The unique morphology and designed surface properties of the composite particles have many current and potential applications in the chemical, biological, and pharmaceutical industries. Approaches to the composite particles utilizing various techniques have been reported over the past few decades. In general, core–shell polymer particles are synthesized by two-stage emulsion polymerization [1, 2, 3, 4, 5]. In the first stage, the core particles are prepared by emulsion polymerization. For the second stage polymerization, the monomer feed modes are normally continuous addition or batch processes. Furthermore, the composite particles can be also prepared by seeded dispersion polymerization [6, 7, 8] and emulsion polymerization using reactive or polymeric surfactants [9, 10, 11, 12].

Composite particles with a core–shell structure have also been made by self-assembly of oppositely charged silica particles and polymers. For instance, layer-by-layer deposition techniques by sequential adsorption of polyelectrolytes onto silica particles through electrostatic interactions have been reported [13, 14]. Another example of particle assembly involves the heterocoagulation of oppositely charged core and shell particles [15, 16, 17, 18, 19]. The heterocoagulation of anionic polystyrene (PST) particles with cationic poly(butyl methacrylate) (PBMA) particles, followed by heating of the heterocoagulates at a temperature above the glass transition temperature (T_g) of PBMA, results in core–shell particles with a PST core and a PBMA shell [20, 21]. This technique is based on electrostatic interactions between the core and the shell particles. Furthermore, the heterocoagulation technique using specific chemical and biochemical interactions as a way to control the structure of the particle assembly has also been demonstrated [22].

We have demonstrated self-assembling of cationic polymer particles having sulfonium groups on hydrophobic solid surfaces such as polymer films and hydrophobically modified glass plates by silane coupling agents [23]. It was found that the hydrophobic interactions between the polymer particles and the solid surfaces are a main factor for the formation of particle monolayers. We have previously reported a novel heterocoagulation of cross-linked PST core particles and cationic shell particles [24]. This present paper reports the results on the preparation of the heterocoagulates from the core particles and the shell particles in further detail, and composite polymer particles composed of the core–shell structure by heating at a temperature above the T_g of shell particles.

Experimental

Materials

Freshly distilled, deionized water was used for the experiments in this study. Styrene (ST) and butyl acrylate (BA) were obtained from Wako Pure Chemical Industries, Ltd. and purified by distillation under reduced pressure in a nitrogen atmosphere. Water-soluble active ester monomer, methacryloyloxyphenyldimethylsulfonium methylsulfate (MAPDS), was prepared according to the method described before [25]. 2,2′-Azobis(2-amidinopropane) dihydrochloride (V-50) was purchased from Wako Pure Chemical Industries, Ltd. Monodispersed core particles, cross-linked PST particles with ca. 8.5-μm diameter, were received from Sekisui Chemical Co., Ltd.

Synthesis of cationic polymer shell particles

Poly(ST-*co*-MAPDS) shell particles were prepared by emulsifier-free emulsion copolymerization of ST with MAPDS, as described elsewhere [26, 27]. Poly(ST-*co*-BA-*co*-MAPDS) shell particles having a lower T_g were synthesized by emulsifier-free emulsion copolymerization of ST (64 mmol) and BA (32 mmol) with MAPDS (0.64 mmol) at 60 °C using V-50 (0.64 mmol) as an initiator. Those polymer shell particles were purified by centrifugation and washing with deionized water several times. The number-average diameter, d_n, volume-average diameter, d_v, standard deviation, σ, and the coefficient of variation, C_v, were determined using a scanning electron microscope (SEM) (JEOL, JSM-5310). The surface charges of the polymer particles were measured by colloid titration using potassium poly(vinyl sulfate) as titrant.

Preparation of heterocoagulates

Cross-linked PST core particles (0.1 g) were stirred in aqueous dispersions (10 mL) of cationic polymer shell particles at a given concentration at 40 rpm, and the heterocoagulates were separated out by centrifugation, and washed in water by ultrasonic cleaning (Branson, 5510J-MT) at 180 W and 42 kHz oscillation frequency for 10 min. The morphology of the shell particles self-assembled on the core particles was observed by a SEM and the coverage with the shell particles was calculated using Eq. 1:

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

where

$$N_{\max} = \left(2\pi/\sqrt{3}\right) \times \left[\left(D_{\text{coreparticle}} + D_{\text{shellparticle}}\right)/D_{\text{shellparticle}}\right]^2 \qquad (2)$$

$D_{\text{core particle}}$ is the diameter of the core particle, $D_{\text{shell particle}}$ is the diameter of the shell particle, and N and $N_{\max}$ are the number of shell particles on core particles and that of closely packed shell particles on core particles, respectively.

From heterocoagulates to core–shell particles

The aqueous dispersion of the purified heterocoagulates was dropped onto a freshly prepared glass plate and dried in vacuum. The heterocoagulates on the glass plate were heated at 80 °C, and the morphology was observed by a SEM. Figure 1 shows a schematic representation for the preparation of core–shell composite polymer particles using the heterocoagulation.

Results and discussion

Syntheses of P(ST-*co*-MAPDS) and P(ST-*co*-BA-*co*-MAPDS) shell particles

Monodispersed P(ST-*co*-MAPDS) and P(ST-*co*-BA-*co*-MAPDS) shell particles with diameters ∽220 and 240 nm, respectively, were used in this study and other characteristics are shown in Table 1. The surface charges of P(ST-*co*-MAPDS) and P(ST-*co*-BA-*co*-MAPDS)

Fig. 1 Schematic representation for the preparation of core–shell composite polymer particles by heterocoagulation

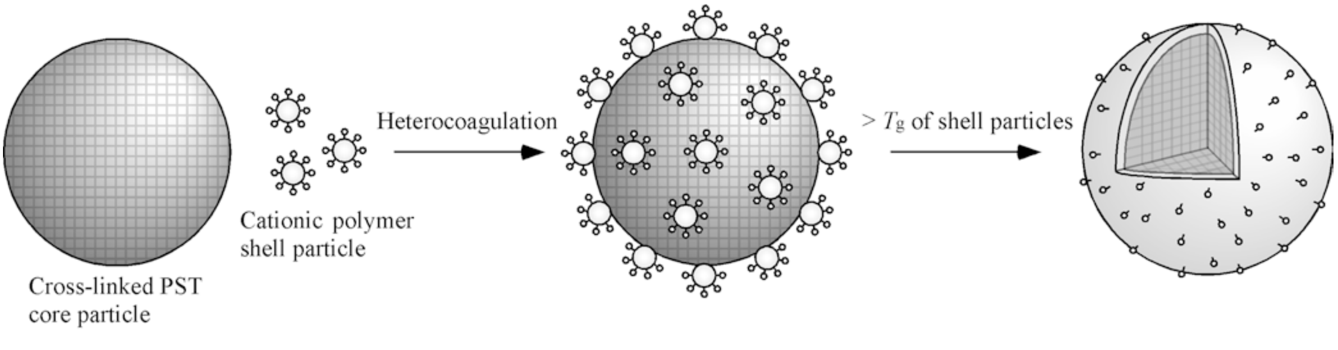


Table 1 Preparation of cationic polymer shell particles by emulsifier-free emulsion copolymerization and their characteristics

Shell particles	Yield (%)		Surface charge (μeq/g-latex)	Ap^a (Å^2)	Particle size^b			
	Latex	Coagulum			d_n (nm)	d_v (nm)	σ	C_v (%)
P(ST-*co*-MAPDS)	96.5	2.3	10	79.4	216	216	7.1	3.3
P(ST-*co*-BA-*co*-MAPDS)	93.8	5.7	7.3	127	242	242	14	5.6

[a] Area per positive charge

[b] Determined by a SEM; d_n, number-average diameter; d_v, volume-average diameter; σ, standard deviation; C_v, coefficient of variation of particle size distribution

shell particles were determined to be 10 and 7.3 μeq/g-latex by colloid titration, respectively. P(ST-*co*-MAPDS) shell particles have a higher positive surface charge density than P(ST-*co*-BA-*co*-MAPDS) shell particles. The proportions of ST and BA in P(ST-*co*-BA-*co*-MAPDS) shell particles determined by ^{1}H NMR spectroscopy were 2:1, in agreement with those in the feed.

Self-assembly of cationic polymer shell particles on cross-linked PST core particles

The surface charge of cross-linked PST core particles with ca. 8.5-μm diameter used in this study, determined by colloid titration, was nearly zero. The ζ potential of the core particles is approximately 0 mV in the presence of 10 mM NaCl, though they exhibited only a low negative ζ potential in the absence of added salts. These results mean that the core particles have almost no surface charge and hydrophobic surfaces. The core particles (0.1 g) were stirred into cationic polymer latex dispersions (10 mL) of 0.25 wt% at 40 rpm. Figure 2 shows SEM photographs of heterocoagulates produced by heterocoagulation of cationic polymer shell particles onto cross-linked PST core particles. The cationic shell particles are well self-assembled on the hydrophobic surfaces of the core particles. For the P(ST-*co*-MAPDS) particles as shell particles, the heterocoagulates are formed with a relatively regular array of the shell particles. On the other hand, the P(ST-*co*-BA-*co*-MAPDS) heterocoagulates are obtained with some shell particles in the form of small particles, and the number of the shell particles is lower than that of P(ST-*co*-MAPDS) shell particles.

The core particles were stirred in P(ST-*co*-MAPDS) latex dispersions of 0.25 wt%, and the stability of the resulting P(ST-*co*-MAPDS) heterocoagulates in water on ultrasonic cleaning was investigated. The relationship between ultrasonic cleaning time and the coverage of the core particles with the shell particles is shown in Fig. 3. Although the coverage slightly decreases in an initial period of ultrasonic cleaning, it becomes nearly constant after 5 min, indicating strong interactions between core and shell particles.

The formation process of P(ST-*co*-MAPDS) heterocoagulates was also investigated. The self-assembling time dependence of the coverage of the core particles with P(ST-*co*-MAPDS) shell particles is shown in Fig. 4. The coverage is nearly constant within the period examined, suggesting that the shell particles are rapidly self-assembled on the core particles.

Figure 5 shows the coverage of the core particles with P(ST-*co*-MAPDS) shell particles at various latex concentrations. The coverage increases with an increase in the latex concentration, and then the coverage is nearly

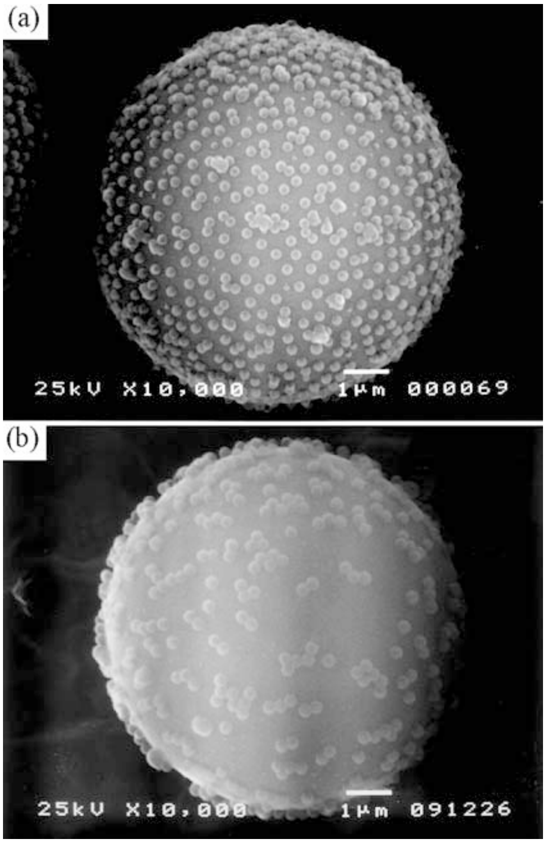


Fig. 2a, b SEM photographs of cationic polymer shell particles self-assembled on cross-linked PST core particles: [Latex] 0.25 wt%; **a** P(ST-*co*-MAPDS), **b** P(ST-*co*-BA-*co*-MAPDS) shell particles

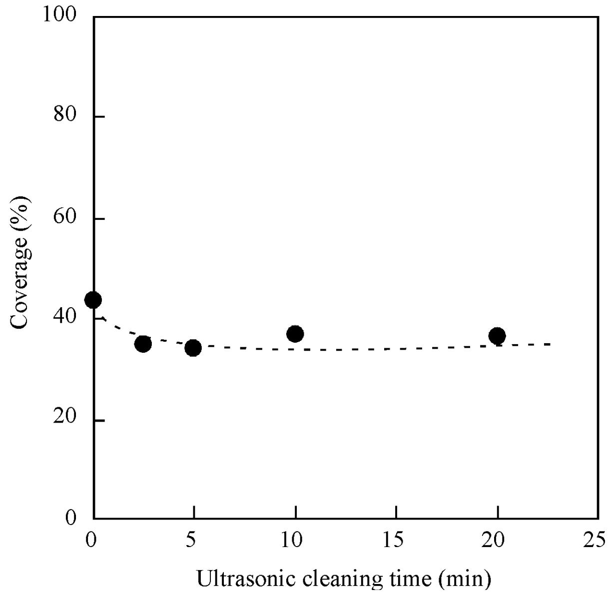


Fig. 3 Coverage of cross-linked PST core particles with P(ST-*co*-MAPDS) shell particles against ultrasonic cleaning time: [Latex] 0.25 wt%

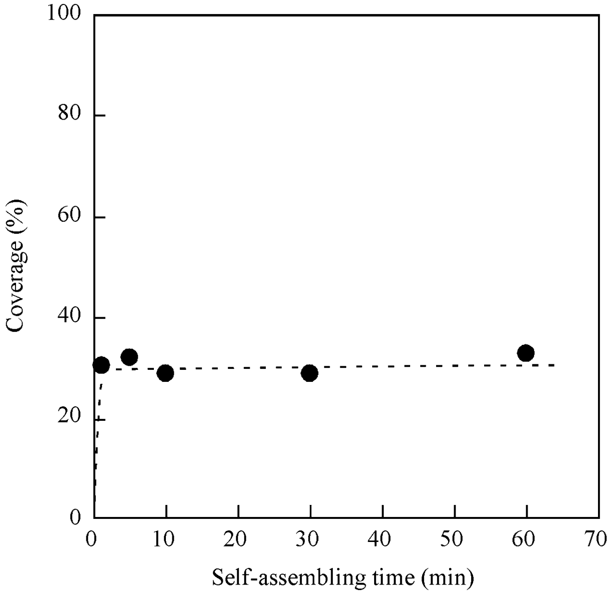


Fig. 4 Coverage of cross-linked PST core particles with P(ST-*co*-MAPDS) shell particles against self-assembling time: [Latex] 0.25 wt%

constant beyond the latex concentration of 0.05 wt%. When all the P(ST-*co*-MAPDS) shell particles are self-assembled with close packing, the theoretical maximum coverage of the core particles with the shell particles should be reached at a latex concentration of ca. 0.1 wt%. However, the coverage is only ca. 30% at this latex concentration. The results indicate the strong electrostatic repulsion between the shell particles self-assembled on the core particles and the shell particles in the latex dispersion.

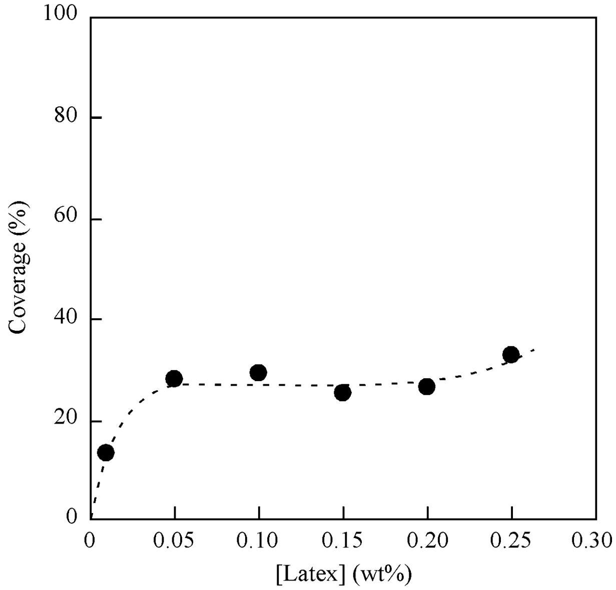


Fig. 5 Coverage of cross-linked PST core particles with P(ST-*co*-MAPDS) shell particles against latex concentration

The effect of NaCl as an electrolyte on heterocoagulation was studied in order to control the morphology of heterocoagulates. The core particles were stirred in cationic polymer latex dispersions of 0.25 wt% containing NaCl at various concentrations. The relationship between NaCl concentration and the coverage of core particles with P(ST-*co*-MAPDS) or P(ST-*co*-BA-*co*-MAPDS) shell particles is shown in Fig. 6. For both P(ST-*co*-MAPDS) and P(ST-*co*-BA-*co*-MAPDS) shell particles, the coverages greatly increase with an increase in the NaCl concentration, and reach ca. 66 and 53%, respectively, at 100 mM. Such marked increases in the coverage can be ascribed to the decrease in the electrostatic repulsion between the shell particles on the core particles. We have previously reported the adsorption of *n*-cetyltrimethylammonium bromide (CTAB) as a cationic surfactant on positively charged P(ST-*co*-MAPDS) shell particles [23]. One shell particle adsorbed ca. 1×10^4 CTAB molecules, demonstrating that the surface of the shell particles is of high hydrophobic character. Therefore, self-assembling of the shell particles at the hydrophobic surfaces would proceed through hydrophobic interactions. Furthermore, the coverage with P(ST-*co*-MAPDS) shell particles is higher than that with P(ST-*co*-BA-*co*-MAPDS) shell particles at all NaCl concentrations. The hydrophobicity of P(ST-*co*-BA-*co*-MAPDS) shell particles would be lower than that of P(ST-*co*-MAPDS) shell particles because they contain slightly hydrophilic BA units on their surfaces. The

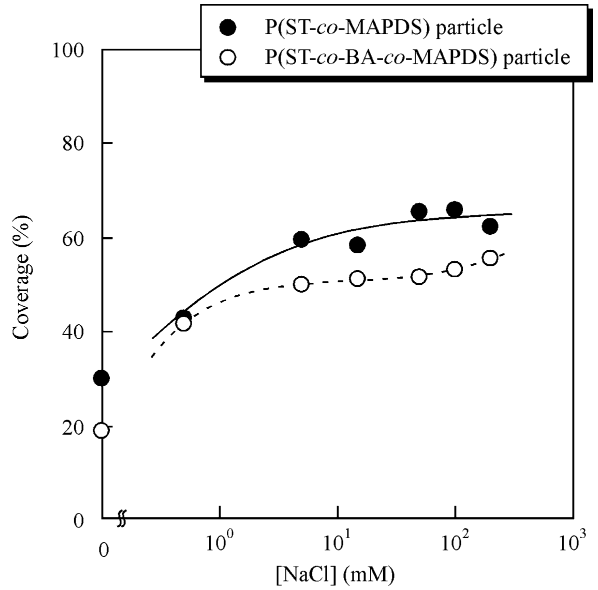


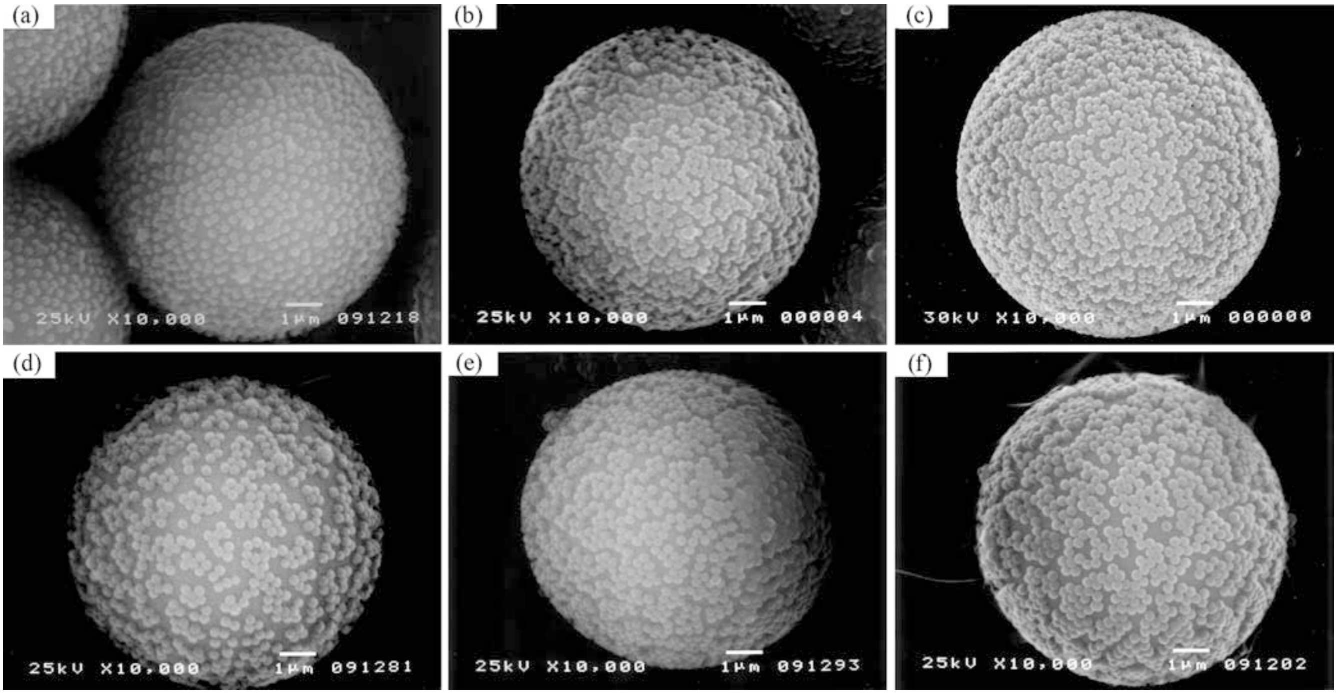
Fig. 6 Coverage of cross-linked PST core particles with cationic polymer shell particles against NaCl concentration: [Latex] 0.25 wt%

results mentioned above may be related to the difference in the hydrophilic/hydrophobic balance of the surfaces of shell particles. Figure 7 shows SEM photographs of cationic shell particles self-assembled on core particles at different NaCl concentrations. In the case of P(ST-*co*-MAPDS) shell particles, they are self-assembled on core particles at relatively regular intervals up to 0.5 mM NaCl concentration. At NaCl concentrations above 50 mM, larger aggregates are exclusively self-assembled. For P(ST-*co*-BA-*co*-MAPDS) shell particles, the number of small aggregates increases with increasing NaCl concentration.

Preparation of core–shell composite particles by heat treatment

The heterocoagulates were heated at 80 °C, and the morphology was observed by a SEM. The T_g of P(ST-*co*-BA-*co*-MAPDS) shell particles was calculated to be approximately 21 °C using the Fox equation [28], with a ratio of ST to BA of 2:1 in the particles. Figure 8 shows SEM photographs of heterocoagulates produced by heat treatment at 80 °C above the T_g of the shell particles. For heterocoagulation in the presence of 150 mM NaCl, the heterocoagulates self-assembled in the form of aggregates of P(ST-*co*-BA-*co*-MAPDS) particles on the core particles can be obtained at high coverage. After the resulting heterocoagulates were heated for 2 h, composite polymer particles with uneven surfaces were formed. Heat treatment for 3 h gave core–shell composite polymer particles with smooth surfaces. The size of the composite polymer particle became larger than that of the core particle.

Fig. 7a–f SEM photographs of cationic polymer shell particles self-assembled on cross-linked PST core particles against NaCl concentration: [Latex] 0.25 wt%; P(ST-*co*-MAPDS) shell particles, [NaCl] **a** 0.5 mM, **b** 50 mM, **c** 200 mM; P(ST-*co*-BA-*co*-MAPDS) shell particles, [NaCl] **d** 0.5 mM, **e** 50 mM, **f** 200 mM



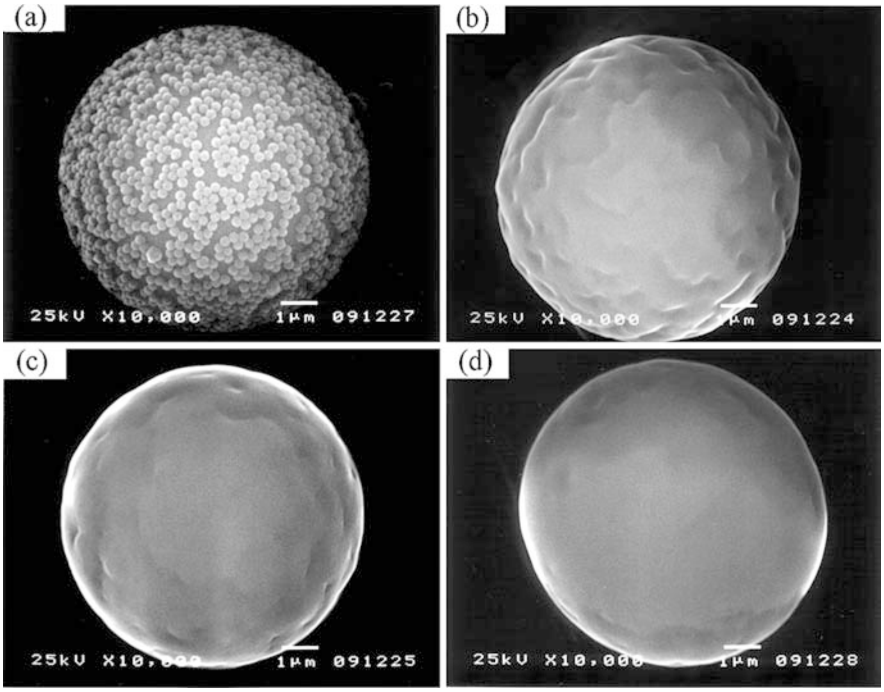


Fig. 8a–d SEM photographs of composite polymer particles produced by heating of heterocoagulates of P(ST-*co*-BA-*co*-MAPDS) shell particles with cross-linked PST core particles at 80 °C. Heterocoagulation, [Latex] 0.25 wt%; [NaCl] 150 mM; heating time **a** 0 h, **b** 1.0 h, **c** 2.0 h, **d** 3.0 h

Conclusions

It was found that P(ST-*co*-MAPDS) and P(ST-*co*-BA-*co*-MAPDS) shell particles with active ester groups were well self-assembled on hydrophobic surfaces of cross-linked PST core particles by a novel heterocoagulation through hydrophobic interactions. The number of P(ST-*co*-MAPDS) shell particles self-assembled on the core particles was higher than that of P(ST-*co*-BA-*co*-MAPDS) shell particles. The morphology of the heterocoagulates was dependent on the solid content of the latex dispersion, self-assembling time, and electrolyte concentration. The preparation of core–shell composite polymer particles with smooth surfaces was achieved by heating for 3 h at a temperature above the T_g of P(ST-*co*-BA-*co*-MAPDS) shell particles. The functional heterocoagulates produced by heterocoagulation of the core particles and shell particles having active ester groups should have numerous potential applications as biochemical, microelectronic, and optical materials.

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