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Variation of surface unevenness of anomalous composite polymer particles produced by the stepwise heterocoagulation of small particles onto large particle by heat treatment*)

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Abstract: Variation of surface unevenness of anomalous composite polymer particles produced by the "stepwise" heterocoagulation, which we had suggested in previous articles, of small cationic polymer particles onto large anionic polymer particle (*LP*) by heat treatment was examined with transmission and scanning electron microscopes. When the anomalous polymer emulsion was kept at higher temperature than the glass transition temperature of *LP*, the particle surfaces were continuously changed from uneven to smooth state with the treatment time.

Key words: Anomalous particles – emulsion polymerization – heterocoagulation – composite polymer particles – morphology

Introduction

We have reported that various anomalous composite polymer particles consisting of two kinds of polymers can be produced by seeded emulsion polymerization techniques [1–6]. Other anomalous composite polymer particles have been produced by Skjeltorp et al. [7] and Sheu et al. [8]. These anomalous polymer particles have some attractive characteristics, such as large surface area and high light-scattering ability. Recently, we suggested a new technique to produce anomalous polymer particles having uneven surfaces by depositing stepwise small cationic particles onto large anionic particle [9, 10], which was named the "stepwise" heterocoagulation method.

In this article, the variation of surface unevenness of such anomalous particles by heating treatment will be clarified.

Experimental

Materials

Methyl methacrylate (MMA), ethyl acrylate (EA), methacrylic acid (MAA), butyl acrylate (BA) and styrene (S) were purified by distillation under reduced pressure in a nitrogen atmosphere and stored in a refrigerator. Methacryloyoxyethyl trimethyl ammonium chloride (QDM, Nitto Chem. Ind. Co.) was used without further purification. Analytical grade potassium persulfate (KPS) and 2,2′-azobis (2-amidinopropane) hydrochloride (AIBA), as initiators were recrystallized. Commercial grade nonionic polyoxyethylene sorbitan monoleate (Tween 80, Kao Atlas Corp.) and polyoxyethylene nonylphenyl ether (Emulgen 950, Kao Atlas Corp.) were used as received. Analytical grade hydrochloric acid (HCl) and potassium hydroxide (KOH) were used directly. Deionized water was distilled before use.

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Preparation of polymer particles

Anionic large-size MMA-EA-MAA (66.5/30.5/3.0, molar ratio) terpolymer particles (*LP*), 450 nm in diameter, were produced by emulsifier-free emulsion polymerization. Two kinds of cationic small-size particles, S-QDM (97.0/3.0, molar ratio) copolymer particles (*SP*-1), 80 nm in diameter and S-BA-QDM (81.3/15.7/3.0, molar ratio) terpolymer particles (*SP*-2), 40 nm in diameter were produced by emulsion polymerizations. Their polymerization conditions were listed in Table 1. The glass transition temperature (T_g) of each base polymer was measured using a differential scanning calorimeter (Daini Seikosha SSC-560S) at a heating rate of 10 °C.

Stepwise heterocoagulation

Heterocoagulation of *LP* and *SP* was caused stepwise as follows. 1) *LP* and *SP* emulsions were separately diluted with water to 10 wt% solid and the pH values were adjusted at 3 with 0.5 N HCl. Tween 80 (cloud point = 70 °C) was added to the *LP* emulsion. 2) The *LP* and *SP* emulsions were blended and kept at room temperature for 10 min. The pH of the blend emulsion was adjusted from 3 to 9 with 0.1 N KOH and then the temperature was raised and kept at 70 °C for 10 min.

Heat treatment

When the temperature of heat treatment was over 70 °C, the Emulgen 950 (cloud point > 100 °C) was pre-added to the blend emulsion. These processes were carried out in gentle stirring. After unheterocoagulated *SP* were removed by centrifugation, the heterocoagulated particles were treated at various temperatures for a certain time.

ζ-potentials

The ζ-potentials of the particles were measured in 10 mM KCl with a laser electrophoriesis zeta-potential analyzer (Otsuka Electronics Inc., Model LEZA-600).

Particle sizes

The particle size in each step of the stepwise heterocoagulation was determined by dynamic

Table 1. Recipes for the preparation of MMA-EA-MAA, S-QDM and S-BA-QDM copolymer particles by emulsion polymerizations

No.		1	2	3
Ingredient		MMA-EA-MAA LP	S-QM SP-1	S-BA-QDM SP-2
Molar ratio		66.5/30.5/3.0	97.0/3.0	81.3/15.7/3.0
S	(g)		94.2	84.8
QDM	(g)		5.81	6.23
BA	(g)			20.2
MMA	(g)	106		
EA	(g)	49		
MAA	(g)	4.1		
KPS	(g)	0.32		
AIBA	(g)		0.48	0.56
Tween 80	(g)		4.8	5.6
Water	(g)	640	410	470
Temp.	(°C)	70	70	70
Time	(h)	24	48	72
Diameter	(nm)	450	80	40
Charge		anionic	cationic	cationic
T_g	(°C)	70	100	70

Abbreviations: S, styrene; BA, butyl acrylate; MMA, methacrylic acid; QDM, methacryloyoxyethyl trimethyl ammonium chloride; KPS, potassium persulfate; AIBA, 2,2′-azobis(2-amidinopropane) hydrochloride; Tween 80, polyoxyethylene sorbitan monoleate

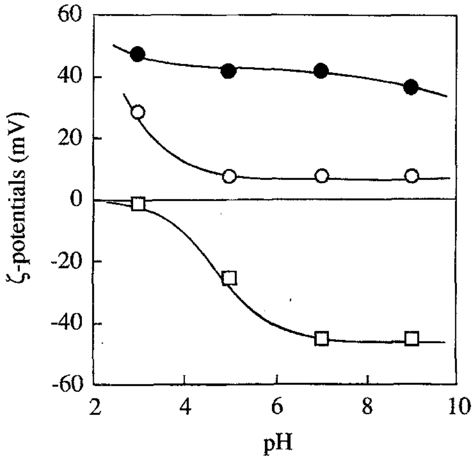

Fig. 1. ζ-potentials of *LP* (□), *SP*-1 (○), and *SP*-2 (●) produced under the conditions listed in Table 1 in 10 mM KCl: *LP*, MMA-EA-MAA (66.5/30.5/3.0, molar ratio) terpolymer emulsion; *SP*-1, S-QDM (97/3, molar ratio) copolymer emulsion; *SP*-2, S-BA-QDM (81.3/15.7/3.0, molar ratio) terpolymer emulsion

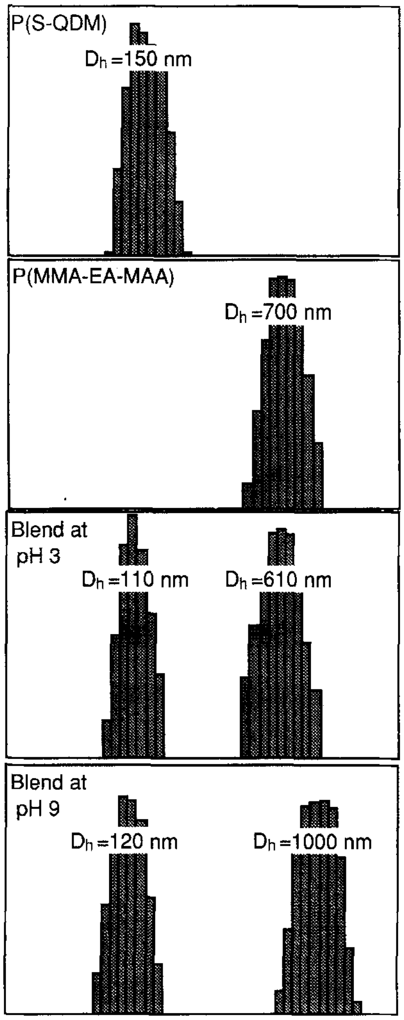

Fig. 2. Particle-size distributions of cationic small *SP*-1 emulsion, anionic large *LP* emulsion and their blend emulsions in the pH 3 and 9. D_h, hydrodynamic diameter. *LP*, MMA-EA-MAA; *SP*-1, S-QDM

light scattering spectroscopy with a particle analyzer (Otsuka Electronics Inc., Model DLS-700).

Morphology of particle surfaces

The heterocoagulated particle was observed with a scanning electron microscope (SEM, Hitachi Seisakusho S-2500) and a transmission electron microscope (TEM, Nippon Electron Inc. JEM 200).

Results and discussion

Figure 1 shows the ζ-potential values of *LP*, *SP*-1 and *SP*-2. The anionic ζ-potential value of *LP* was very low at pH 3 and clearly increased with an increase in pH because of neutralization of the carboxyl group with KOH. The cationic ζ-potentials of two kinds of *SP* were almost independent of the pH above 5 because the main cationic charges were due to the quarternary ammonium of QDM unit, though amidino end groups such as AIBA initiator fragment ionize at pH 3, resulting in the increase of cationic charges.

Figure 2 shows particle-size distributions of original *LP* and *SP*-1 at pH 3 and of the blend emulsions at pH 3 and 9, at room temperature. The two peaks of the blend emulsion at pH 3 were, respectively, nearly equal to those of the *LP* and *SP*-1 emulsions. This indicates that the heterocoagulation did not occur in the blend emulsion at pH 3. When the pH of the blend emulsion was adjusted at 9, the position of the peak due to *SP*-1 was almost not shifted, but the

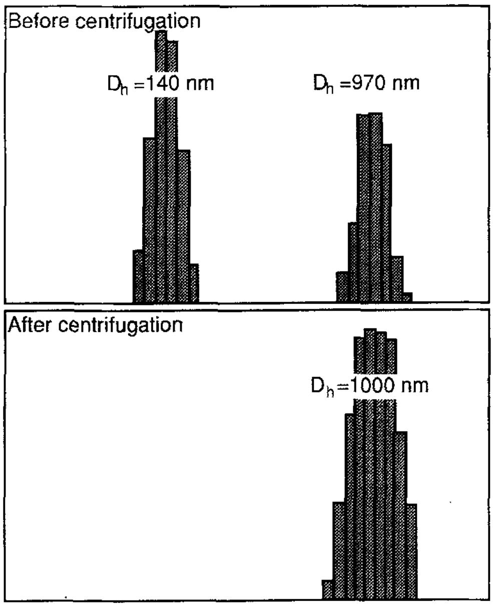

Fig. 3. Particle-size distribution of blend emulsion *LP*/*SP*-1 (1.0/0.7, w/w) treated at 70 °C for 10 min before and after the centrifugal separation to remove unheterocoagulated *SP*-1, D_h, hydrodynamic diameter. *LP*, MMA-EA-MAA; *SP*-1, S-QDM

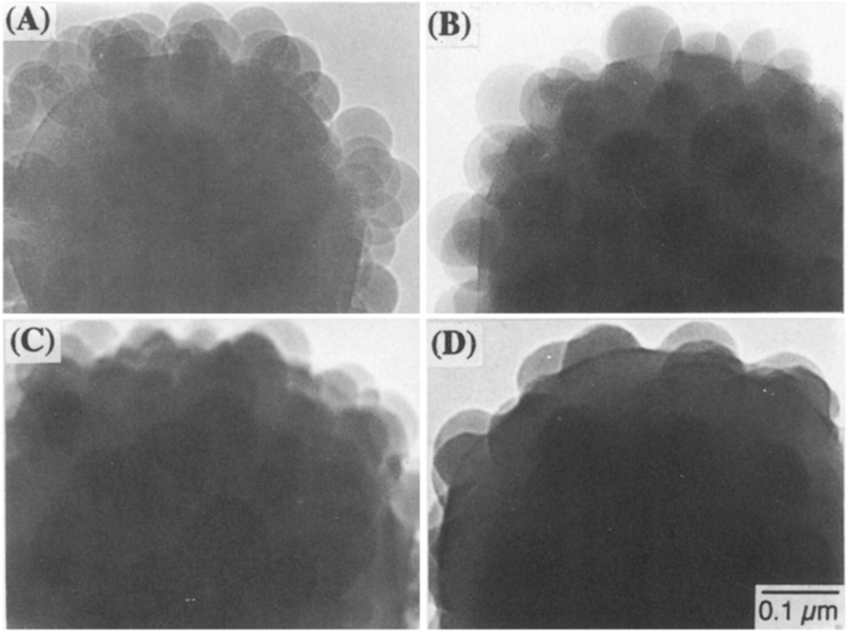

Fig. 4. TEM photographs of anomalous particles produced by heterocoagulation of *LP* and *SP*-1 after the heat treatment at various temperatures for 48 h; a) untreated; b) 70 °C c) 90 °C; d) 100 °C. *LP*, MMA-EA-MAA; *SP*-1, S-QDM

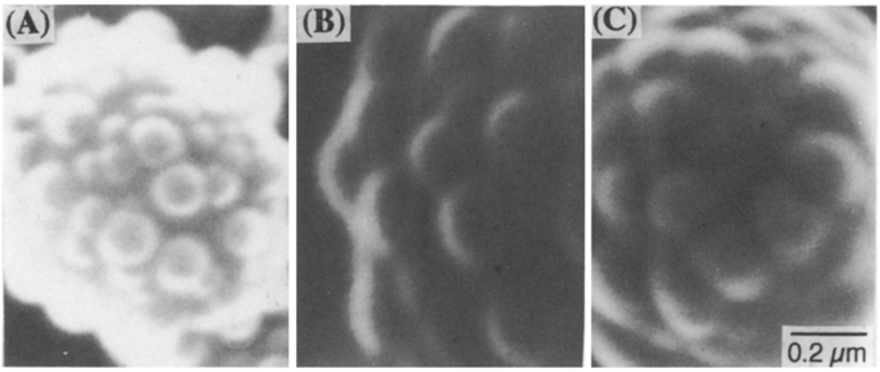

Fig. 5. SEM photographs of anomalous particles produced by heterocoagulation of *LP* and *SP*-1 after the heat treatment at various temperature: a) 70 °C, 10 min; b) 70 °C, 48 h; c) 90 °C, 48 h. *LP*, MMA-EA-MAA; *SP*-1, S-QDM

height decreased slightly, whereas the peak due to *LP* with about 700 nm in diameter disappeared and a new peak appeared around 1000 nm in diameter. This indicates that in the blend emulsion at pH 9 there existed many unheterocoagulated *SP*-1 and heterocoagulated particles which were formed by heterocoagulation of *SP*-1 onto *LP* with a monoparticle layer. However, when the pH of the blend emulsion was readjusted from 9 to 3 with 0.5 N HCl, the particle-size distributions came back again to those of the initial blend emulsion at pH 3 (The data was omitted.). Such a phenomenon was discussed in detail in the previous article [10]. The result indicates that *SP*-1 did not directly contact with *LP* in the heterocoagulated particles produced at pH 9, because of the existence of the hydrated protective layer at the surface of *LP* derived from the nonionic emulsifier. That is, the heterocoagulation was reversible.

Subsequently, the blend emulsion at pH 9 was kept at 70 °C for 10 min to reduce the colloid stability given by the nonionic emulsifier because the cloud point of Tween 80 is 70 °C, and then

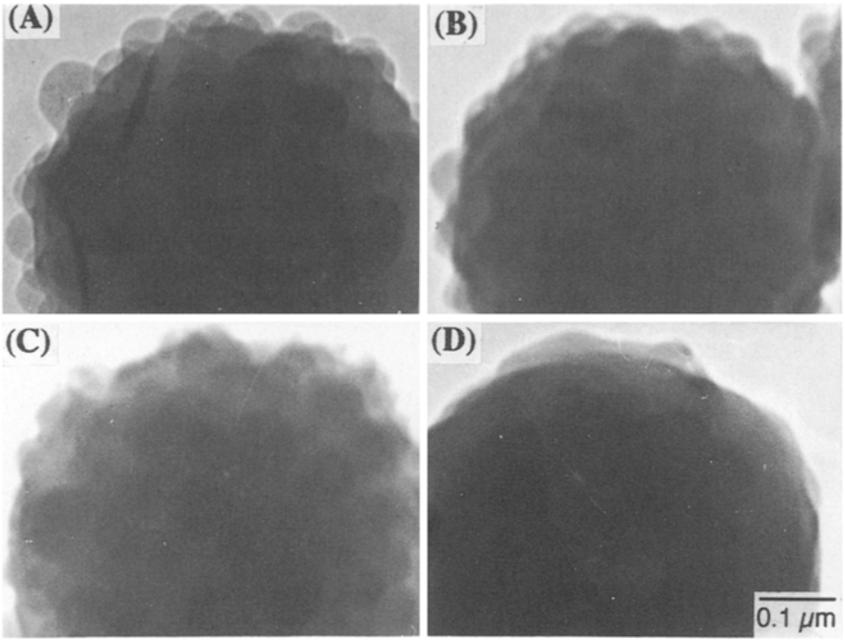

Fig. 6. TEM photographs of anomalous particles produced by heterocoagulation of *LP* and *SP*-2 after the heat treatment at various temperatures for 48 h: a) untreated; b) 70 °C; c) 90 °C; d) 100 °C. *LP*, MMA-EA-MAA; *SP*-2, S-BA-QDM

centrifugally washed three times under 450 g (2000 rpm) for 15 min to remove the unheterocoagulated *SP*.

Figure 3 shows the particle-size distributions before and after the separation treatment. The peak around 140 nm due to the unheterocoagulated *SP*-1 disappeared after the treatment. The peak due to the heterocoagulated particles was almost not shifted before and after the treatment. This indicates that the heterocoagulation was irreversible after the heat treatment at 70 °C. A similar result was obtained in the blend of *LP* and *SP*-2 under the same conditions. These results show that the production of the irreversible heterocoagulates (*IHP*) was based on the stepwise heterocoagulation process.

Figures 4 and 5 show, respectively, TEM and SEM photographs of *IHP* produced by the stepwise heterocoagulation of *SP*-1 ($T_g = 100\,°C$) onto *LP* treated at the various temperatures for 48 h. The surface unevenness was not changed by the treatment at 50 °C for 1 week. As the treatment temperature was raised above the T_g ($= 70\,°C$) of *LP*, the surface unevenness of anomalous particles somewhat decreased, but did not disappear completely.

Figures 6 and 7 show, respectively, TEM and SEM photographs of *IHP* produced by the stepwise heterocoagulation of *SP*-2 ($T_g = 70\,°C$) onto *LP* treated at various temperatures for 48 h. In

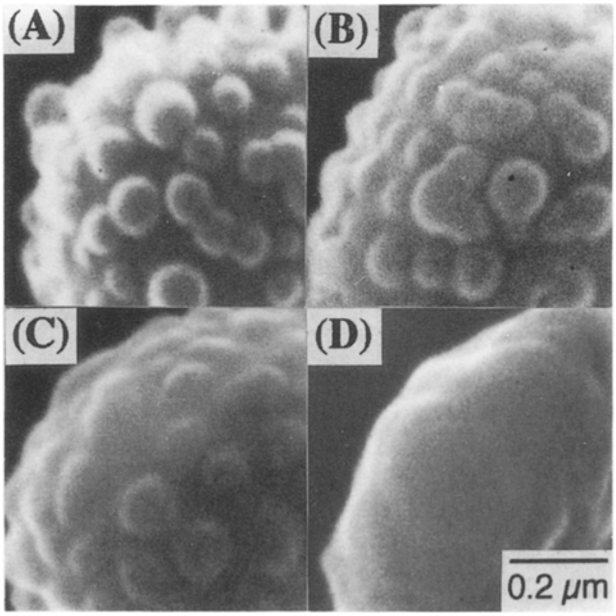

Fig. 7. SEM photographs of anomalous particles produced by heterocoagulation of *LP* and *SP*-2 after the heat treatment at various temperatures for 48 h: a) untreated; b) 70 °C; c) 90 °C; d) 100 °C. *LP*, MMA-EA-MAA; *SP*-2, S-BA-QDM

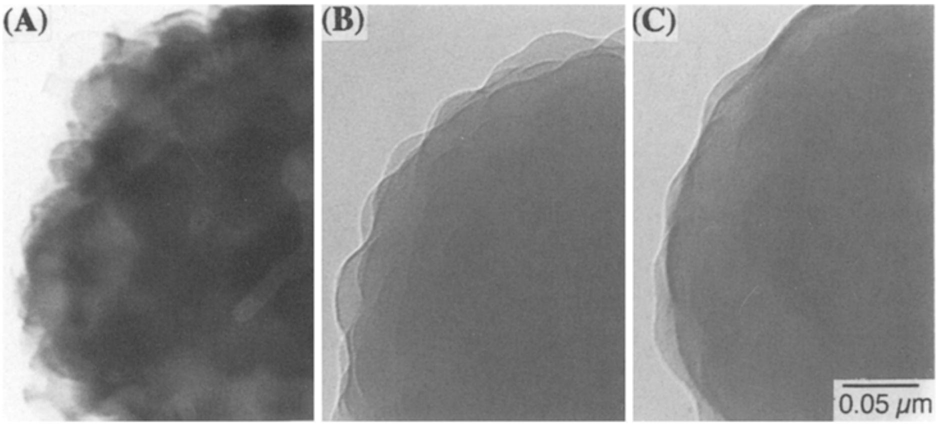

Fig. 8. TEM photographs of anomalous particles produced by heterocoagulation of *LP* and *SP*-2 after the heat treatment at 100 °C for various treatment times: a) untreated; b) 1 h; c) 3 h. *LP*, MMA-EA-MAA; *SP*-2, S-BA-QDM

comparison with the above case, the variation of the surface from uneven to smooth state was more clear. When the treatment temperature was raised to 100 °C, the surface of the *IHP* was almost smooth.

Figure 8 shows of TEM photographs of the surface morphology *IHP* produced by the stepwise heterocoagulation of *SP*-2 and *LP* with the treatment time at 100 °C. The particle surfaces were continuously varied from uneven to smooth state with the increase of the treatment time.

From these results, it is clear that the surface unevenness of *IHP* produced by the stepwise heterocoagulation can be changed continuously by the heat treatment.

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References

1. Matsumoto T, Okubo M, Schwab S (1976) Kobunshi Ronbunshu 33:575
2. Okubo M, Katsuta Y, Yamada A, Matsumoto T (1979) Kobunshi Ronbunshu 36:459
3. Okubo M, Katsuta, Matsumoto T (1981) J Polym Sci Polym Chem Ed 18:481
4. Okubo M, Ando M, Yamada A, Katsuta Y, Matsumoto T (1981) J Polym Sci Polym Lett Ed 19:143
5. Okubo M, Katsuta Y, Matsumoto T (1982) J Polym Sci Polym Lett Ed 20:45
6. Okubo M, Kanaida K, Matsumoto T (1987) Colloid Polym Sci 265:876
7. Skjeltorp AT, Ugelstad J, Ellingsen T (1986) J Colloid and Interface Sci 113:577
8. Sheu HR, Tseng CM, El-Aassen MS, Micale FJ, Vanderhoff JW (1985) Grad Res Progr Reps 24:6; (1986) ibid 25:7
9. Okubo M, Ichikawa K, Tsujihiro M, He Y (1990) Colloid Polym Sci 268:791
10. Okubo M, He Y, Ichikawa K (1991) Colloid Polym Sci 269:125

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