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SHORT COMMUNICATION

M. Okubo
Y. Lu

Estimation of surface morphology of composite polymer particles prepared by the stepwise heterocoagulation method with ζ-potential measurement*

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Prof. Dr. M. Okubo (✉) · Y. Lu
Department of Chemical Science
and Engineering
Faculty of Engineering
Kobe University
Rokko, Nada, Kobe 657
Japan
E-mail: okubo@cx.kobe-u.ac.jp

Abstract Core-shell composite polymer particle was prepared by the stepwise heterocoagulation of cationic small polymer particles (SPs) onto an anionic large polymer particle (LP), following heat treatment at temperatures which were higher than glass transition temperature ($T_g = 18\,^\circ\mathrm{C}$) of SP. At pH 9 ζ-potential of the heterocoagulated particle (HP) was negative, but it changed to positive by the heat treatment and increased with the treatment time and finally attained to that of SP. The treatment time to attain the ζ-potential of SP became short by elevating the treatment temperature. This indicates that during the heat treatment, SP continued to melt on the surface of LP and finally formed a continuous shell.

Key words Morphology – ζ-potential – stepwise heterocoagulation – composite polymer particle – emulsion polymerization

Introduction

In general, submicron-sized composite polymer particles are produced by seeded emulsion polymerization and their morphologies obey not only thermodynamics, but also kinetics because of high viscosity in polymerizing particles [1]. By utilizing this technique, some anomalous composite polymer particles, such as “raspberry-like” [2], “confetti-like” [3], “snowman-like” [4], “octopus ocellatus-like” [5], “void-containing” [6], “golfball-like” [7] and “sandwich-like” and “halfmoon-like” [8], were obtained. Their morphologies are thermodynamically unstable.

On the other hand, in previous articles [9–11] we suggested a novel technique to produce anomalous composite polymer particles having uneven surfaces by depositing stepwise many cationic small particles (SP) onto an anionic large particle (LP), which was named “stepwise heterocoagulation method”. Recently, we developed it to produce spherical core-shell composite polymer particle in which core and shell should be, respectively, derived from LP and SPs, regardless of the difference in hydrophilicities of the two kinds of base polymers [12, 13]. The transmission electron microscopic (TEM) observation of the heterocoagulated particle (HP) has shown that SPs melt on the surface of LP at the temperature above glass transition temperature (T_g) of SP and finally form a continuous shell.

In a series of above-mentioned investigations on the stepwise heterocoagulation method, anionic charges of LP were introduced as carboxyl and sulfate groups which were, respectively, derived from methacrylic acid (MAA) monomer and potassium persulfate (KPS) initiator. Since the amount of the former was larger than that of the latter, the negative ζ-potential should be increased with an increase in pH value in alkaline range. On the other hand, cationic charges of SP were introduced as quarternary ammonium and amidinium groups which were, respectively, derived from methacryloxyethyl trimethyl ammonium chloride (QDM) monomer and 2,2′-azobis(2-amidinopropane)hydrochloride (V-50) initiator. Since the amount of the former was larger than that of the latter, the positive ζ-potential should be almost independent of the pH value.

In this article, in order to estimate the variation of surface morphology of HP prepared by the stepwise heterocoagulation method with heat treatment at temperatures above T_g of SP, the change of ζ-potential of HP will be measured as a function of the treatment time.

Experimental

Materials

All reagents were the same as those in the previous paper [12].

Preparation of polymer particles

Anionic LP with 618 nm in hydrodynamic-average diameter (D_h) was produced by emulsifier-free emulsion terpolymerization of methyl methacrylate (MMA), ethyl acrylate (EA), and MAA under the conditions listed in Table 1. Cationic SP with 104 nm in D_h was produced by emulsion terpolymerization of styrene (S), butyl acrylate (BA), and QDM under the conditions listed in Table 2. The T_g values of the LP and SP were, respectively, 70 °C and 18 °C measured by using a differential scanning calorimeter (Seiko Instruments Inc., SSC-5200) at a heating rate of 10 °C/min.

Table 1 Recipe of emulsifier-free emulsion polymerization[a)] for preparing anionic large P(MMA-EA-MAA) (59.0/32.0/9.0, molar ratio) particles

MMA [g]	44.8
EA [g]	24.3
MAA [g]	6.0
KPS [g]	0.35
H_2O [g]	500
D_h [nm][b)]	618
D_w/D_n[b)]	1.01
T_g [°C][c)]	70

[a)] N_2; 70 °C; 24 h.

[b)] Hydrodynamic, number and weight average diameters, separately, measured by dynamic light scattering spectroscopy.

[c)] Glass transition temperature measured by differential scanning calorimeter.

Abbreviations: MMA, methyl methacrylate; EA, ethyl acrylate; MMA, methacrylic acid; KPS, potassium persulfate.

Table 2 Recipe of emulsion polymerization[a)] for preparing cationic small P(S-BA-QDM) (55.0/42.0/3.0, molar ratio) particles

S [g]	24.4
EA [g]	29.9
QDM [g]	2.66
Tween 80 [g]	2.5
V-50 [g]	0.250
H_2O [g]	200
D_h [nm][b)]	104
D_w/D_n[b)]	1.02
T_g [°C][c)]	18

[a)] N_2; 70 °C; 24 h.

[b)] Hydrodynamic, number and weight average diameters, separately, measured by dynamic light scattering spectroscopy.

[c)] Glass transition temperature measured by differential scanning calorimeter.

Abbreviations: S, styrene; BA, butyl acrylate; QDM, methacryloxyethyl trimethyl ammonium chloride; V-50, 2,2′-azobis(2-amidinopropane)hydrochloride; Tween 80, polyoxyethylene sorbitan monooleate.

Stepwise heterocoagulation and heat treatment

Heterocoagulation of LP and SP was carried out as follows. (1) The pH values of LP and SP emulsions were separately adjusted at 3 with 0.5 N HCl. Tween 80 (cloud point = 70 °C) of which amount was 8% per polymer solid was added to the LP emulsion before the blend. (2) The LP and SP emulsions were blended at 0 °C at the blend ratio of $\frac{1}{2}$ by weight and kept for 1 h. The polymer solid in the blend emulsion was about 10%. The pH of the blend emulsion was adjusted from 3 to 9 with 0.1 N KOH in gentle stirring at 0 °C. Then the temperature was raised and kept at 70 °C for 30 min. After unheterocoagulated SPs were removed by centrifugation at 6000 rpm for 6 min at 0 °C, twice. HP emulsion without free SP was treated at various heat treatment conditions.

Particle size

The particle sizes and their distributions of LP, SP and HP were determined by dynamic light scattering spectroscopy with a particle analyzer (Otsuka Electronics Inc., Model DLS-700), separately.

ζ-potential

The ζ-potential of each particle was measured in 10 mM KCl with a Laser Electrophoresis Zeta-potential analyzer (Otsuka Electronics Inc., Model LEZA-600) after each diluted emulsion was filtrated with a cellulose nitrate membrane having pore size of 3 μm. The pH of KCl was adjusted with 0.1 HCl or KOH. The ζ-potential was obtained as average value of three time measurements.

Results and discussion

Figure 1 shows D_h distributions of the blend emulsion at pH 3 (a) and of HP emulsion prepared by the stepwise heterocoagulation method with the heat treatment at 70 °C for 30 min, following centrifugal removal of free SP (b). The blend emulsion at pH 3 had two peaks of D_h at 99 and 566 nm which were, respectively, nearly equal to those (104 and 618 nm) of the original SP and LP emulsions. This indicates that the heterocoagulation did not occur, and LPs and SPs were independently dispersed stably in the blend emulsion. On the other hand, after the stepwise heterocoagulation with mild heat treatment at 70 °C for 30 min, many SPs were adsorbed onto LP to form HP. As shown in Fig. 1(b), after centrifugation, the peak of SP disappeared and a new peak appeared at 873 nm which accorded well with the diameter of HP calculated assuming that SPs are adsorbed onto one LP as single-particle layer. These results indicate that desired HP was prepared and free SP were removed completely by the centrifugation.

Figure 2 shows ζ-potentials of LP and SP measured, separately in 10 mM KCl solution at different pH values. The negative ζ-potential of LP clearly increased with an increase in pH because of ionization of the carboxyl groups. Whereas, positive ζ-potential of SP was independent with pH value because the cationic charges were mainly due to the quarternary ammonium group.

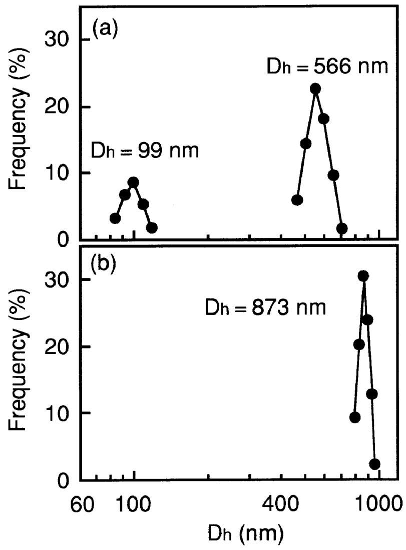

Fig. 1 Hydrodynamic particle-size distributions of blend emulsion of P(MMA-EA-MAA) (LP) and P(S-BA-QDM) (SP) at pH 3 and of heterocoagulated composite polymer emulsion after centrifugal removal of unheterocoagulated free-SPs (b)

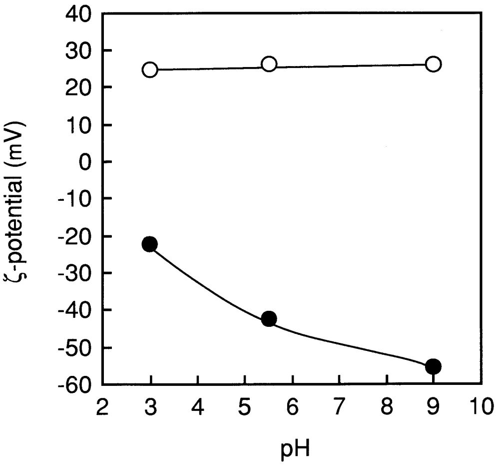

Fig. 2 ζ-potentials of LP (○) and SP (●) measured, separately, in 10 mM KCl solution at different pH values

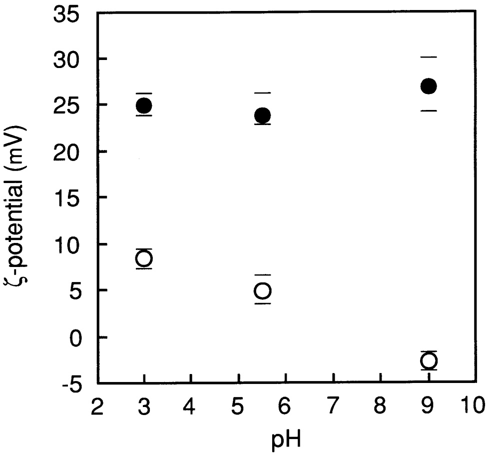

Fig. 3 ζ-potentials of heterocoagulated particles after heat treatment at 70 °C for 30 min (○) and 48 h (●), measured in 10 mM KCl solution at different pH values

Figure 3 shows ζ-potentials of HP treated at 70 °C for 48 h, 30 min measured in 10 mM KCl solution at different pH values. The ζ-potential of HP treated for 30 min was positive at pH 3 at which almost all carboxyl groups do not ionize, but it was negative at pH 9 at which all carboxyl groups ionize. These indicate that the HP still exposes fair amount of the carboxyl group at the surface, that is, "bare" surface of LP still exists. On the other hand, after the heat treatment for 48 h, the ζ-potentials were always positive regardless of the pH values. This suggests that the carboxyl groups disappear at the "surface", that is, the continuous shell consisting of SPs completely covers the surface of LP. This is well in accord with the results of TEM observation of ultrathin cross sections of HP in the previous article [12].

Figure 4 shows changes of ζ-potentials of HP with the treatment time at pH 9 at different temperatures above T_g of SP, which were measured at pH 5.5 at room temperature. The positive ζ-potential increased with the time and finally attained to that of SP. The treatment time to attain it is shortened by elevating the temperature. They were, respectively, less than 6, 24 and 48 h for 100 °C, 70 °C and 40 °C. These results also suggest that during the heat treatment, SPs continue to melt on the surface of LP and finally formed a continuous shell.

In this way, it is clarified that ζ-potential measurement is applicable for the estimation of surface morphology of HP.

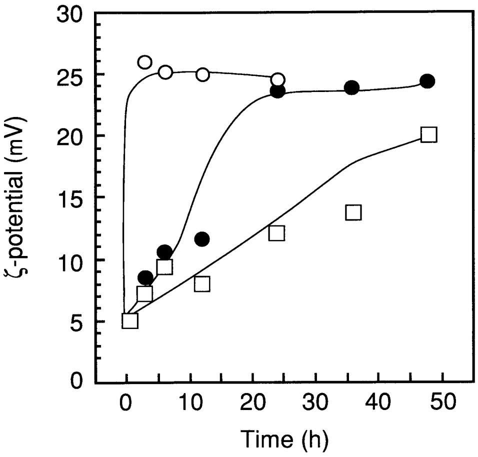

Fig. 4 Changes of ζ-potentials of heterocoagulated particles with treatment time at pH 9 at different temperatures (°C): (□), 40; (●), 70; (○), 100. The measurement was carried out in 10 mM KCl solution at pH 5.5 at room temperature

References

1. Okubo M (1990) Makromol Chem Macromol Symp 35/36:307
2. Okubo M, Katsuta Y, Matsumoto T (1981) J Polym Sci Polym Chem Ed 18:481
3. Matsumoto T, Okubo M, Shibao M (1976) Koubunshi Roununshu 33:575
4. O. kubo M, Katsuta Y, Matsumoto T (1982) J Polym Sci Polym Lett Ed 20:45
5. Okubo M, Kanaida K, Matsumoto T (1987) Colloid Polym Sci 265:876
6. Okubo M, Ando M, Yamada A, Katsuta Y, Matsumoto T (1981) J Polym Sci Polym Lett Ed 19:143
7. Okubo M, Murakami Y, Tsukuda Y (1993) Chem Express 4:253
8. Cho I, Lee KW (1985) J Appl Polym Sci 30:1903
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
11. Okubo M, Miyachi N, Lu Y (1994) Colloid Polym Sci 272:270
12. Okubo M, Lu Y (1996) Colloids Surf. A Physicochem Eng Aspects 109:49
13. Okubo M, Lu Y (1996) Colloid Polym Sci 274:1020