Effects of Hydrophobic Interactions on Swelling of Carboxylated Core–Shell Structured Latex Particles

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ABSTRACT: Carboxylated core–shell particles which contain carboxyl groups in the shell polymer swell in aqueous dispersion by electrostatic repulsion between carboxylate ions. Effects of hydrophobic interactions on the swelling of carboxylated core–shell particles were examined by measuring their diameters as a function of various hydrophobicities of the neutralizing amine, the shell polymer, and the dispersion medium. When the dispersion is neutralized by hydrophobic amine which does not contain a hydroxyl group, the swelling is promoted for low pH and suppressed for high pH with increasing the hydrophobicity of the amine. This result suggests that the amine is concentrated near the particle surface by hydrophobic attractions. This concentrated amine promotes dissociation of carboxyl groups of the shell polymer, but combines with dissociated carboxylate ion electrostatically just like a crosslinker. As the hydrophobicity of the amine increases, the amine becomes highly concentrated, and the dissociation of the carboxyl groups and crosslinking are promoted. The swelling is suppressed when the hydrophobicity of shell polymer increases, and that is promoted when the hydrophobicity of dispersion medium increases. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65**: 1933–1938, 1997

Key words: core–shell particle; carboxyl group; swelling; hydrophobic interaction; electorostatic interaction

INTRODUCTION

Core–shell structured latex particles (core–shell particles) consist of a mantle core polymer and a shell polymer. Core–shell particles which contain functional groups in the shell polymer have been used widely in various industries.[1–8] Carboxylated core–shell particles, which contain carboxyl groups in the shell polymer, have been used as a rheological modifier for water-borne coatings,[1,2] because aqueous dispersions of carboxylated core–shell particles neutralized by a base display a pseudoplastic flow.[1,2,9–12] Since carboxylated core–shell particles swell with the addition of a base in aqueous dispersions,[1,2,3,13] the mechanism of swelling of the particles is very important for the control of the rheology. It has been reported that swelling of the particles is caused by electrostatic repulsion between carboxylate ions.[3,13,14] But the effects of hydrophobic interaction which is generated by hydrophobic groups in an aqueous dispersion[15,16] on swelling of the particles have not been discussed.

In this article, the effects of hydrophobic interaction on the swelling of carboxylated core–shell particles are examined by measuring the particle diameter in cases of various hydrophobicities of a base, shell polymer, and solvent, and the mechanism of swelling of the particles is discussed.

EXPERIMENTAL

Carboxylated Core–Shell Particles

Carboxylated core–shell particles (CS1, CS2, and CS3) which were different in shell polymer com-

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position were synthesized by two-stage feed emulsion polymerization.[3,5,17] In all particles, the core polymer was crosslinked and the shell polymer was the liner and grafted to the core polymer, and the weight ratio of the core/shell monomers was 100/29.5. The core polymer was prepared with methacrylic acid, n-butyl acrylate, and allyl acrylate, and the composition of the core polymer was fixed. The shell polymer was prepared with methacrylic acid (MAA), 2-hydroxyethyl acrylate (HEA), n-butyl acrylate (n-BA), and methyl methacrylate (MMA), and the amounts of MAA and HEA were fixed, but the amounts of n-BA and MMA were varied. The weight ratios of n-BA/MMA of CS1, CS2, and CS3 were 69/31, 75/25, and 90/10, respectively. The hydrophobicity of the shell polymer was CS1 < CS2 < CS3.

Diameter and pH Measurements

Aqueous dispersions of the carboxylated core–shell particle CS1 were varied in pH by the added amounts of various bases, and the diameter of the particles and pH of dispersions were measured. NaOH, 2-methylamino ethanol (MAE), 2-dimethylamino ethanol (DMAE), 3-diethylamino-1-propanol (DEAP), triethylamine (TEA), tri-n-propylamine (TPA), tri-n-butylamine (TBA), and divalent bases which were $Ca(OH)_2$ and $Ba(OH)_2$ were used. MAE, DMAE, and DEAP contain hydroxyl groups and dissolve infinitely in water (hydrophilic amine). The hydrophobicity order of these amines is MAE < DMAE < DEAP. TEA, TPA, and TBA do not contain hydroxyl groups and hardly dissolve in water (hydrophobic amine). The hydrophobicity order of these amines is TEA < TPA < TBA. All dispersions were prepared in 0.1 wt %. The diameter of the particles was measured with dynamic light-scattering equipment (Otsuka Electronics ELS-800). The hydrogen ion concentration (pH) of the dispersions was measured with a pH meter (HORIBA D-13).

Aqueous dispersions of CS1, CS2, and CS3 were varied in pH by NaOH. The diameter of the particles and hydrogen ion concentration (pH) of the dispersions were measured, and the degree of dissociation of carboxyl groups of the particles was derived from the following method[18,19]: The dissociation equilibrium in a neutralizing carboxyl group (R—COOH) by a base (M—OH) is shown by the following equation:

$$R-COOH + M-OH \rightleftharpoons R-COO^- + M^+ + H_2O$$
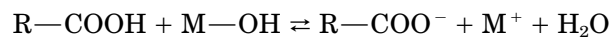
The dissociation constant and degree of dissociation are shown in eqs. (1) and (2), respectively:

$$K_a = [RCOO^-][H^+]/[RCOOH] \qquad (1)$$

$$\alpha = [RCOO^-]/([RCOO^-] + [RCOOH]) \quad (2)$$

where K_a is the dissociation constant ($pK_a = -\log K_a$); α, the degree of dissociation; $[H^+]$, the concentration of hydrogen ions ($pH = -\log[H^+]$); $[RCOO^-]$, the concentration of carboxylate ions; $[RCOOH]$, the concentration of carboxyl groups; and

$$\alpha = K_a/(K_a - 10^{-pH}) \qquad (3)$$

The degree of dissociation was estimated from pH measurements and the dissociation constant according to eq. (3). The dissociation constants of carboxyl groups were obtained by the pH of the dispersions which was 50% neutralized by NaOH in potentiometric titration, because $pK_a = pH$ when 50% of carboxyl groups are neutralized by a strong base. Potentiometric titration was carried out using potential titration equipment (Kyoto Denshi AT-310J). All measurements were carried out at $25.0 \pm 0.1°C$.

Dispersions of CS1 which were 100% neutralized by NaOH were varied with respect to the hydrophobicity of medium, and the diameter of the particles and the pH of dispersion were measured. The dispersion medium was a water/1-butanol mixture, and the hydrophobicity of the medium increases with the amount of 1-butanol. The amounts of 1-butanol were changed from 1 to 5 wt % of the dispersion medium; in every dispersion, 1-butanol dissolves completely in water.

RESULTS AND DISCUSSION

Effects of Hydrophobicity of Base on Swelling

Figure 1 shows the relationship between pH and the diameter of the CS1 particle neutralized by NaOH and hydrophilic amines (MAE, DMAE, and DEAP). The diameter of the particle increases with pH, in every dispersion, and the curves of the particle diameter vs. pH are superimposed. Since the concentration of the carboxylate ion increases with pH, the above result indicates that the particles swell by electrostatic repulsion between the carboxylate ions of the shell polymer. Although the hydrophobicities of these amines are
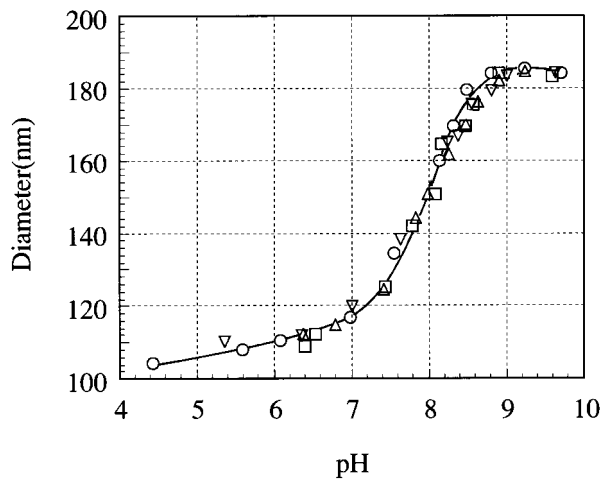
Figure 1 Diameter of core–shell particle CS1 plotted against pH of dispersion neutralized by various hydrophilic amines: (○) NaOH; (△) MAE; (□) DMAE; (▽) DEAP.

Figure 3 Diameter of core–shell particle CS1 plotted against pH of dispersion neutralized by divalent bases: (○) Ca(OH)$_2$; (□) Ba(OH)$_2$; (dotted line) NaOH.

different, no effect on swelling was found. This result demonstrates that the hydrophobicity of the hydrophilic amine which contains a hydroxyl group does not influence the swelling of core–shell carboxylated particles.

Figure 2 shows the relationship between pH and the diameter of the CS1 particle neutralized by hydrophobic amines (TEA, TPA, and TBA). When the pH is below about 7.5, the particle diameter follows the order TEA < TPA < TBA. When the pH is above about 7.5, the particle diameter follows the order TEA > TPA > TBA. Since hydrophobicity of these amines is TEA
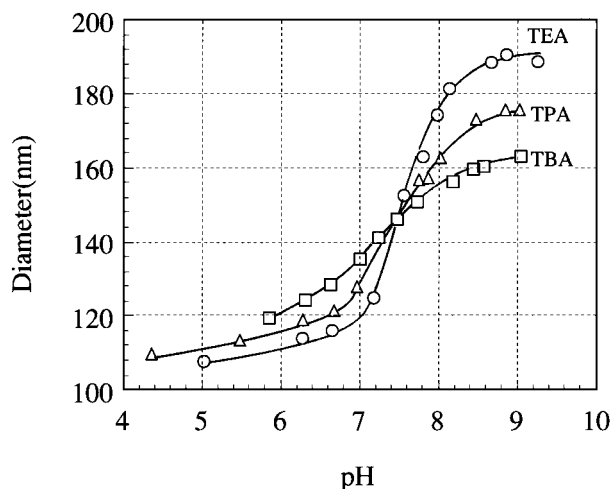
< TPA < TBA, the reason for above results is explained as the following: In the dispersion, hydrophobic amine is easy to localize and concentrate near the particles by hydrophobic attraction. This concentrated amine promotes dissociation of carboxyl group of the shell polymer, but combines with the dissociated carboxylate ion electrostatically, which is called counterion binding, i.e., the amine crosslinks the shell polymer and the shell polymer or the core polymer by two attractions: one is hydrophobic attraction between the hydrophobic group of the amine and that of shell polymer or core polymer, and the other is the electrostatic attraction between the amino ion of the amine and the carboxylate ion of the shell polymer. As the hydrophobicity of the amine increases, the amine becomes highly concentrated, and the dissociation of carboxyl groups and crosslinking are promoted. Consequently, the particle diameter becomes independent of the pH.

Counterion binding is proved from the fact that the diameter of the CS1 particle neutralized by divalent bases hardly increases even if the pH increases (Fig. 3). The reason is that a divalent ion crosslinks between the two carboxylate ions by counterion binding.

Figure 2 Diameter of core–shell particle CS1 plotted against pH of dispersion neutralized by various hydrophobic amines: (○) TEA; (△) TPA; (□) TBA.
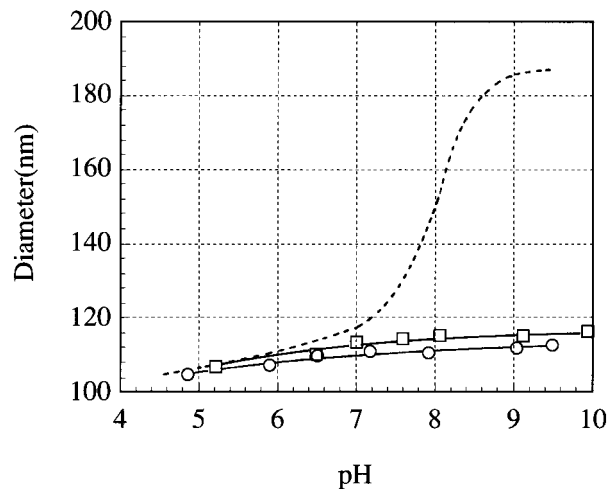
Effects of Hydrophobicity of Shell Polymer on Swelling

Figure 4 shows the relationship between the pH of dispersions and the diameter of the particles for dispersions of CS1, CS2, and CS3 neutralized
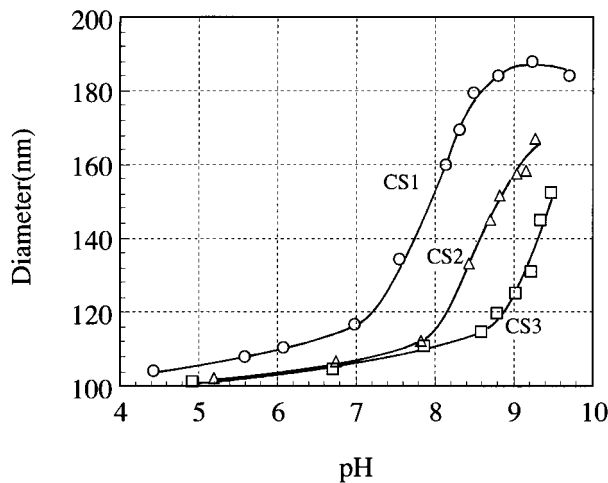
Figure 4 Diameter of core–shell particle plotted against pH of dispersion: (○) CS1; (△) CS2; (□) CS3.

Figure 6 Diameter of core–shell particle plotted against degree of dissociation of carboxyl groups: (○) CS1; (△) CS2; (□) CS3.

by NaOH. The particle diameter increases with pH, in every dispersion. To estimate the effects of hydrophobic interaction on the swelling of the particles, the effect of electrostatic interaction must be fixed; in other words, the concentration of carboxylate ions must be equal. But the concentrations of carboxylate ions in these dispersions are not equal at the same pH, because the pK_a of these dispersions, i.e., the pH of the 50% neutralized dispersion, is different, as shown in Figure 5. Since the concentration of the carboxyl groups is the same for these particles, the concentration of carboxylate ions is proportional to the degree of dissociation of the carboxyl groups. In Figure
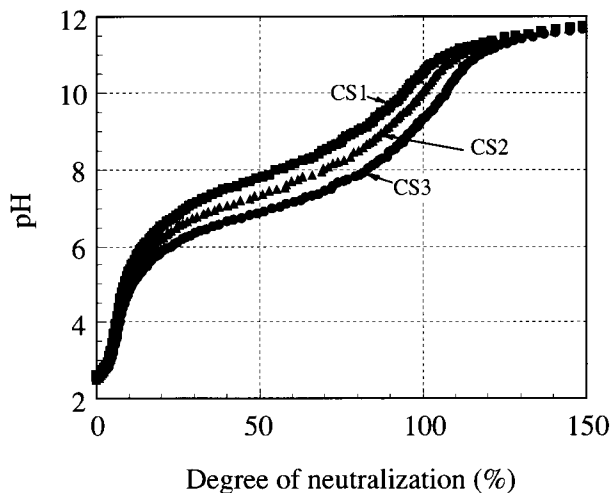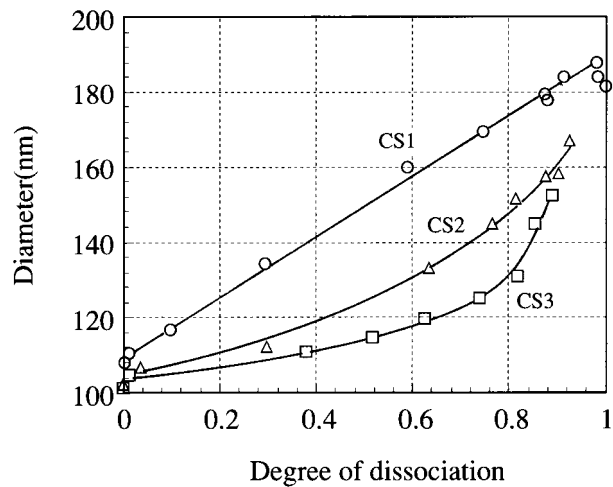
6, the particle diameter is plotted against the degree of dissociation for the above-mentioned dispersions. The particle diameter decreases with increasing of the hydrophobicity of the shell polymer. This result demonstrates that hydrophobic attraction between hydrophobic segments of the shell polymer and that of the shell polymer or the core polymer suppresses swelling of the particle. This hydrophobic attraction is generated between the hydrophobic polymer segments in water, because the hydrophobic segments are removed from the ordered structure of water molecules formed by its strong dipole moment.[15,16]

Effects of Hydrophobicity of the Dispersion Medium on Swelling

Table I shows the diameter of the CS1 particle which was 100% neutralized as a function of different hydrophobicities of the dispersion medium. The particle diameter increases with the hydro-

Figure 5 Titration curve of dispersion of core–shell particle by NaOH.

Table I Diameter of Core–Shell Particles in Solvent-Varied Amount of 1-Butanol 100% Neutralized by NaOH

Amount of 1-Butanol (wt %)	Diameter (nm)
1	178
2	179
3	178
4	186
5	192

phobicity of the medium. This will be caused by increasing the electrostatic repulsion or decreasing the above-mentioned hydrophobic attraction. Electrostatic repulsion between carboxylate ions decreases with increasing of amount of 1-butanol because the dielectric constant decreases. Consequently, the increase in diameter is caused by the decrease of hydrophobic attraction between the hydrophobic segments of the shell polymer and that of the shell polymer or the core polymer. Since the ordered structure of the water molecule is destroyed by the organic solvent molecule, the hydrophobic attraction will be weakened with increasing of the hydrophobicity of the solvent. This result supports the contention that the hydrophobic attraction between hydrophobic segments of the shell polymer and that of the shell polymer or the core polymer suppresses the swelling.

Mechanism of Swelling of the Core–shell Particles

The carboxylated core–shell particles swell in aqueous dispersion with the addition of a base by electrostatic repulsion between the carboxylate ions [Fig. 7(a)]. This swelling is suppressed by the hydrophobic attraction between hydrophobic segments of the shell polymer and that of the shell polymer or the core polymer [Fig. 7(b)].

When the dispersion is neutralized by hydrophobic amine which does not contain hydroxyl groups, the swelling of the particles is influenced by the hydrophobicity of hydrophobic amine. Since hydrophobic amine concentrates near the particle surface by hydrophobic attraction, the dissociation of the carboxyl groups are promoted, but the dissociated carboxylate ions combine with the amino ions, i.e., the amine crosslinks the shell polymer with the shell polymer or the core polymer by two attractions: One is the hydrophobic attraction between hydrophobic groups of the amine and hydrophobic segments of the shell polymer or the core polymer [Fig. 7(c)], and the other is the electrostatic attraction between amino ions of the amine and carboxylate ions of the shell polymer [Fig. 7(d)]. As the hydrophobicity of the amine increases, the amine becomes highly concentrated, and as a result, dissociation of the carboxyl groups and crosslinking are promoted. Consequently, the particle diameter increases for low pH, but decreases for high pH.

CONCLUSION

The effects of hydrophobic interactions on the swelling of carboxylated core–shell particles were
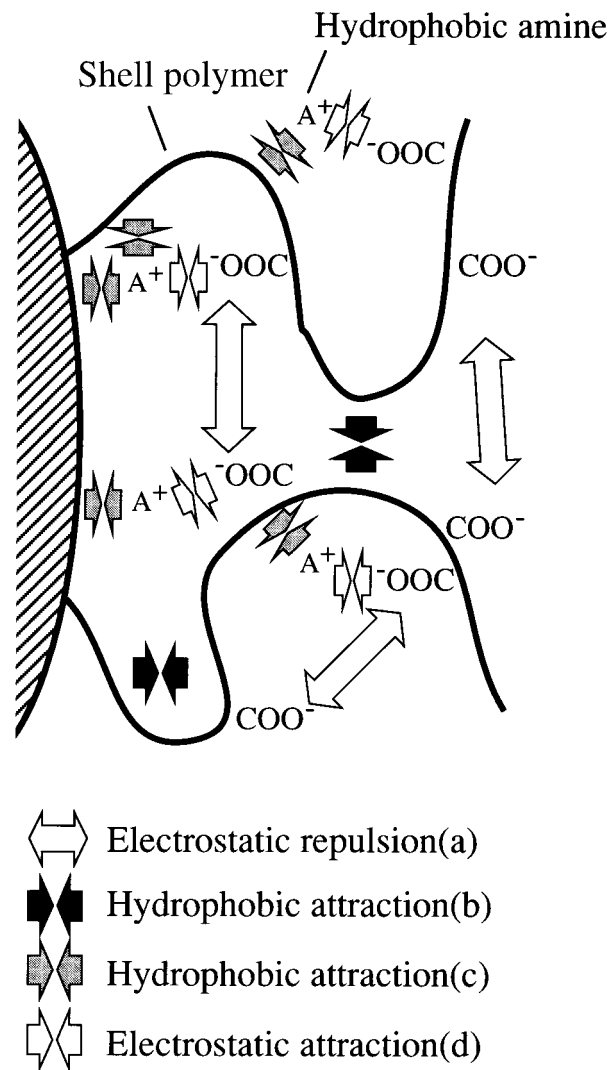
Figure 7 Schematic illustration of interaction for swelling of core–shell particle.

examined. The swelling of the particles is suppressed by the hydrophobic attraction between hydrophobic groups of amine or hydrophobic segments of the shell polymer and that of the shell polymer or the core polymer, although the particle swells in aqueous dispersion by electrostatic repulsion between carboxylate ions of the shell polymer. When the dispersion is neutralized by hydrophobic amine which does not contain hydroxyl groups, hydrophobic amine concentrates near the particle surface by hydrophobic attraction and promotes dissociation of carboxylate ions but combines with dissociated carboxylate ions just like a crosslinker. Consequently, the swelling is promoted for low pH and suppressed for high pH with increasing the hydrophobicity of the hydrophobic

amine. The swelling is suppressed when the hydrophobicity of shell polymer increases, which is promoted when the hydrophobicity of the dispersion medium increases.

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