# Surface Characterization of Styrene/Acrylamide Copolymer Latex Particles

H. TAMAI, T. MURAKAMI, and T. SUZAWA, *Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashihiroshima-shi, Japan*

## Synopsis

Surface characteristics of styrene/acrylamide copolymer latex particles prepared without emulsifier were investigated as a function of acrylamide fraction in charged monomers. The presence of swelling or water-soluble polymer layer at the particle surface was suggested, and its thickness increased with increasing acrylamide fraction. The surface charge densities by conductometric and potentiometric titrations were about half that of polystyrene latex particles at low pH and they increased slightly with increasing pH. Regarding the heterocoagulation between styrene/acrylamide copolymer latex particles and polystyrene latex particles, the critical coagulation concentration of KCl decreased with increasing acrylamide fraction. The consideration in terms of the interaction due to electrostatic and van der Waals forces also suggested that the swelling or water-soluble polymer layer at the particle surface plays an important role.

## INTRODUCTION

Monodispersed and highly spherical polymer latex particles have been used as carriers of antigens and antibodies for medical diagnostic tests.[1,2] In general, hydrophobic polystyrene (PS) latex particles are widely applied. However, PS latex particles are liable to be colloidally unstable in high electrolyte concentration such as vital systems and they are not necessarily suitable. Therefore, polymer latex particles stable in high electrolyte concentration are expected to be more useful, though the presence of antibodies and antigens at the particle surface must be considered.

It is well known that dispersed particles covered thickly with polymer are highly colloidally stable on account of the steric repulsive interaction. Recently, monodispersed styrene/acrylamide (St/AAm) copolymer latex was prepared without emulsifier,[3] and the authors found that St/AAm copolymer latex particles have thick swelling or water-soluble polymer layers (diffuse layer) on their surface.[4]

From these points of view, in this work, the surface characteristics of St/AAm copolymer latex particles have been studied in further detail as a function of acrylamide (AAm) fraction in charged monomers.

The thickness of swelling or water-soluble polymer layer at the particle surface was determined from the viscosity measurement. As surface electrical properties, the surface charge densities and the $\zeta$-potential were obtained by conductometric and potentiometric titrations and microelectrophoresis, respectively. The influence of the above-mentioned properties on the heterocoagulation between St/AAm copolymer latex particles and PS latex particles was considered.

## EXPERIMENTAL

### Materials

Styrene (Wako Pure Chemical Co., Ltd.) was distilled three times under reduced pressure. AAm (Wako Pure Chemical Co., Ltd.) and potassium persulfate (Wako Pure Chemical Co., Ltd.) were recrystallized from benzene and water, respectively. Potassium chloride (KC1), hydrochloric acid (HC1), sodium hydroxide (NaOH), and urea (Wako Pure Chemical Co., Ltd.) were all analytical grade materials and were used without further purification. Distilled and deionized water was used throughout the experiments.

### Latex Preparation

PS latex and St/AAm copolymer latexes were prepared in the absence of emulsifier by the methods of Kotera et al.[5] and Otsuka et al.[3], respectively. A series of polymerizations was performed in order to investigate the influence of AAm fraction in charged monomers on the surface characteristics of the particles. All polymerizations were carried out in a 500-mL flask fitted with a stirrer. The polymerization recipes are shown in Table I. The pH was adjusted with hydrochloric acid.

The latexes obtained were dialyzed using well-boiled Visking dialysis tubing for over 1 week. Furthermore, St/AAm copolymer latexes were centrifuged in urea solution (ca. 4 g L$^{-1}$) to remove free homopolymers dissolved in the latexes and were redispersed in water by ultrasonics. This procedure was repeated three times, and then the latexes were dialyzed again for over 2 weeks. In the supernatants of these latexes redispersed finally, no nitrogen was detected by Kjeldahl analysis. These St/AAm copolymer and PS latexes were finally purified with mixed a bed of cationic and anionic ion-exchange resins (Diaion PK 212-sulfonic acid type and PA 312-trimethylammonium type from Mitsubishi Kasei Co., Ltd.).

As shown in Table I, the particle diameters of the latexes determined by electron microscopy decreased from 604 nm (sample $L_0$) to 326 nm (sample $L_{20}$) with increasing AAm fraction in charged monomers. These latexes were all monodispersed.

TABLE I
Preparation of Styrene/Acrylamide Copolymer Latexes[a]

| Latex | $L_0$ | $L_3$ | $L_5$ | $L_8$ | $L_{12}$ | $L_{15}$ | $L_{20}$ |
|---|---|---|---|---|---|---|---|
| Total monomer (g) | 37.5 | 37.5 | 37.5 | 37.5 | 37.5 | 37.5 | 37.5 |
| Acrylamide fraction in monomers (wt %) | 0 | 3 | 5 | 8 | 12 | 15 | 20 |
| Potassium persulfate (mmol) | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 |
| Water (mL) | 300 | 300 | 300 | 300 | 300 | 300 | 300 |
| Particle diameter (nm) | 604 | 463 | 468 | 407 | 394 | 368 | 326 |

[a] Polymerization temperature 70°C; polymerization time 10 h.

## Methods

### *Elemental Analysis*

The copolymerized percentage of AAm monomer was determined from the contents of C, H, and N of the latex particles. The elemental analysis of the polymer particles was carried out with a Yanagimoto CHN Corder MT-2.

### *Viscosity*

Viscosities of latex dispersions were measured with an Ostwald viscosimeter at various volume fractions of latex particles between 0 and 0.067. The measurements were carried out at $10^{-3}$ mol $L^{-1}$ of KCl concentration and 25°C.

### *Conductometric and Potentiometric Titrations*

Conductometric titrations were performed on 60 mL samples of the cleaned latexes at 25°C. The solid contents in the latexes were 2 g. The titrations were done with $5 \times 10^{-4}$ mol $L^{-1}$ NaOH solution in a stirred vessel under $N_2$ atmosphere. The conductivity was measured using a conductivity dip cell and a TOA Model CM-30ET Conductivity meter.

Potentiometric titrations of the cleaned latexes were carried out at 25°C, using a Hitachi-Horiba Model F-7SS pH meter. The content of the titration vessel was stirred with a magnetic stirrer that was turned off during the pH measurement. The titrations were performed on 50 mL of the latexes (solid content 2 g) containing $10^{-3}$ mol $L^{-1}$ HCl and $10^{-2}$ mol $L^{-1}$ KCl; $5 \times 10^{-3}$ mol $L^{-1}$ NaOH solution was delivered. An equal volume of blank electrolyte was titrated in the same condition as the latexes in order to determine the extent of hydrogen and hydroxyl ion adsorption as a function of pH. This was given by the difference in concentrations of potential determining ions between the latex suspension and the blank titration.[6]

### *ζ-Potential*

ζ-Potentials of latex particles were obtained by the method of microelectrophoresis. The electrophoretic mobilities were measured with a Mitamura Riken microelectrophoresis apparatus. The measurements were carried out at 25°C as a function of KCl concentration. The ζ-potentials were calculated according to the Henry equation.[7]

### *Coagulation*

The heterocoagulations between St/AAm copolymer latexes and PS latex (sample $L_0$) were investigated as a function of KCl concentration. KCl solutions of various concentrations were added to the mixed dispersions of St/AAm copolymer latex and PS latex in test tubes. These dispersions were rotated 20 times with end-over-end and were kept for 24 h at 25°C. The

total number concentration of latex particles was kept constant at $3 \times 10^{13}$ particles $L^{-1}$ in all experiments. PS latex to St/AAm copolymer latex particle number ratio was 1. The transmission coefficients for the supernatants of dispersions were measured at 540 nm wavelength using a Hitachi 100-10 type spectrophotometer.

## RESULTS AND DISCUSSION

### Copolymer Compositon

The copolymerized percentage of AAm monomer in latex particles is shown in Table II. The amounts of AAm copolymerized increased with increasing amounts of AAm charged. However, the former was vanishingly lower than the latter. As a whole, the amounts copolymerized were about one-sixth of the amounts charged. This indicates that most of the AAm charged is dissolved independently as homopolymers in the latexes. These homopolymers would be removed by the purification of the latexes.

### Viscosity of Latex

The relations between the reduced viscosities of latex dispersions—$\eta_{sp}/\phi$— and the volume fraction of latex particles—$\phi$— were shown in Figure 1. The intercepts of the ordinate by $\eta_{sp}/\phi$ plots increased with increasing AAm fraction in the charged monomers. $\phi$ was calculated using the diameters of latex particles determined by electronmicroscopy. Thus, these increases in the intercepts indicate that the dispersed size of St/AAm copolymer latex particles is larger than that determined by electronmicroscopy, and this increase in particle size enlarges with increasing AAm fraction in charged monomers.

Because the observation in terms of electron microscopy showed that St/AAm copolymer latex particles were kept highly spherical for drying, the increase in particle size seems to be attributed to the surface properties of the particles, e.g., the presence of enormous swelling or a water-soluble polymer layer at the particle surface. This polymer layer would likely be polyacrylamide.

The thickness of swelling or water-soluble polymer layers was estimated

TABLE II
Characteristics of Styrene/Acrylamide Copolymer Latexes

| Latex | $L_0$ | $L_3$ | $L_5$ | $L_8$ | $L_{12}$ | $L_{15}$ | $L_{20}$ |
|---|---|---|---|---|---|---|---|
| Acrylamide fraction in monomers (wt %) | 0 | 3 | 5 | 8 | 12 | 15 | 20 |
| Copolymerized fraction of acrylamide (wt %) | — | 1.1 | 1.0 | 1.5 | 2.2 | 2.6 | 3.1 |
| Thickness of water-soluble polymer layer $\Delta$ (nm) | 0 | 7.5 | 9.0 | 16 | 18 | 23 | 25 |
| Surface charge density $\delta$ ($\mu C$ $cm^{-2}$) | 4.2 | 2.3 | 2.3 | 1.9 | 1.7 | 2.1 | 1.8 |
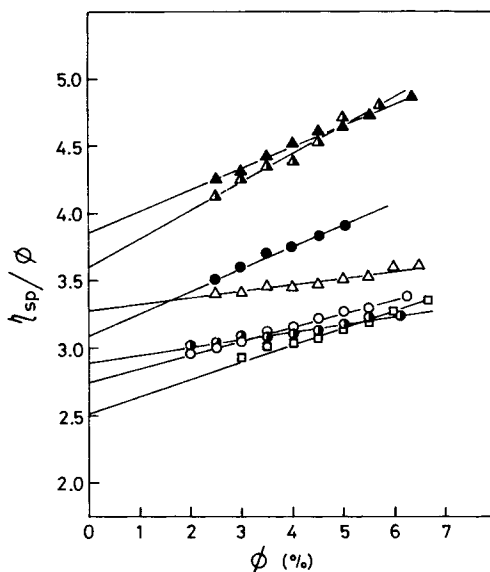
Fig. 1.   Relation between $\eta_{sp}/\phi$ and $\phi$ at $10^{-2}M$ KCl and 25°C: (□) L$_0$; (○) L$_3$; (◑) L$_5$; (●) L$_8$; (△) L$_{12}$; (▲) L$_{15}$; (▲) L$_{20}$.

according to the procedure by Fleer et. al.[8] The dependence of $\eta_{sp}/\phi$ on $\phi$ can be written as

$$\eta_{sp}/\phi = Kf + K'(Kf)^2\phi \tag{1}$$

where $K$ is the Einstein coefficient, $K'$ the Huggins constant, and $f$ a factor relating to swelling or water-soluble polymer layer. $K$ is 2.5 for spherical particles, and $f$ can be obtained from the intercepts $(Kf)$ of the ordinate by $\eta_{sp}/\phi$ plots in Figure 1. PS latex (sample L$_0$) was used as particles without swelling or water-soluble polymer layer. On the other hand, the relation between $f$ and the thickness of swelling or water-soluble polymer layer— $\Delta$— is as follows:

$$\Delta = a(f^{1/3}-1) \tag{2}$$

where $a$ is the particle radius obtained by electron microscopy. According to the eq. (2), $\Delta$ can be calculated.

The relation between AAm fraction in charged monomers and $\Delta$ is shown in Table II. $\Delta$ gradually increased with increasing AAm fraction, and $\Delta$ of St/AAm copolymer latexes L$_{15}$ and L$_{20}$ went up to over 20 nm. These values of $\Delta$ seem to be surprisingly large. It is imagined that the hydrophilic polymer layer at the particle surface enormously swell or form a very thick soluble layer (diffuse layer).

### Surface Charge Density

The conductometric titration curves of St/AAm copolymer latexes are shown in Figure 2. These titrations were carried out for the latexes after
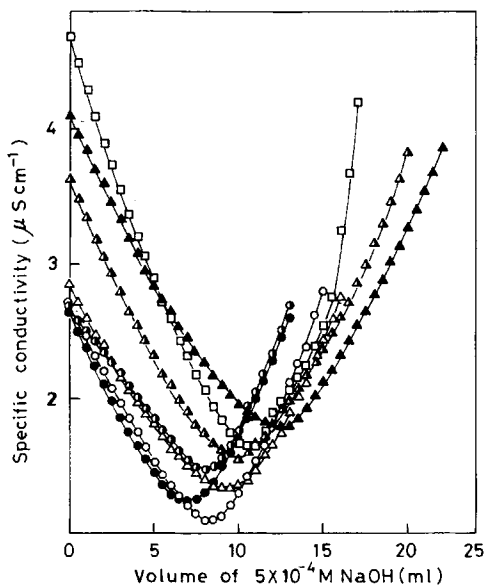
Fig. 2.   Conductometric titration curves: ($\square$) $L_0$; ($\bigcirc$) $L_3$; ($\ocircle$) $L_5$; ($\bullet$) $L_8$; ($\triangle$) $L_{12}$; ($\blacktriangle$) $L_{15}$; ($\blacktriangle$) $L_{20}$.

ion exchange in the absence of supporting electrolyte. For all latexes tested, the weak acid groups such as carboxyl groups were scarcely detected. This indicates that the hydrolysis of acrylamide units does not take place throughout the preparation of the latexes.

From the titration end points in Figure 2, the conductometric surface charge density $\delta$ was calculated from the equation

$$\delta = m \cdot N_A \cdot e/S \tag{3}$$

where $m$ is the molar quantity of added sodium hydroxide per 1 g of latex polymer at the end point, $N_A$ Avogadro's number, $e$ the electronic charge, and $S$ the surface area per 1 g of latex polymer. $S$ was calculated from the particle diameter (the diameter obtained from the viscosity measurement, $a + \Delta$) and the density of polystyrene. $\delta$ is shown in Table II. As a whole, $\delta$ of St/AAm copolymer latex is about half that of PS latex (sample $L_0$), and they are inclined to decrease with increasing AAm fraction. $\delta$ would result from —$OSO_3^-$ groups arising from the initiator. Therefore, —$OSO_3^-$ groups at the surface of St/AAm copolymer latex particles seem to be less than that of PS latex particles.

The potentiometric titration curves of the latexes are shown in Figure 3. The results of blank titrations are given also. The potentiometric titrations of St/AAm copolymer latexes indicate that acid groups are present at the particle surface, and they are less below pH 7 and more over pH 7 than that of PS latex $L_0$. Figure 4 shows the surface charges of the latexes as a function of pH. At pH 7, the surface charge densities were about 4 $\mu C$ cm$^{-2}$ and 2 $\mu C$ cm$^{-2}$ for PS latex (sample $L_0$) and St/AAm copolymer latexes, respectively. These surface charges are in fair agreement with those ob-
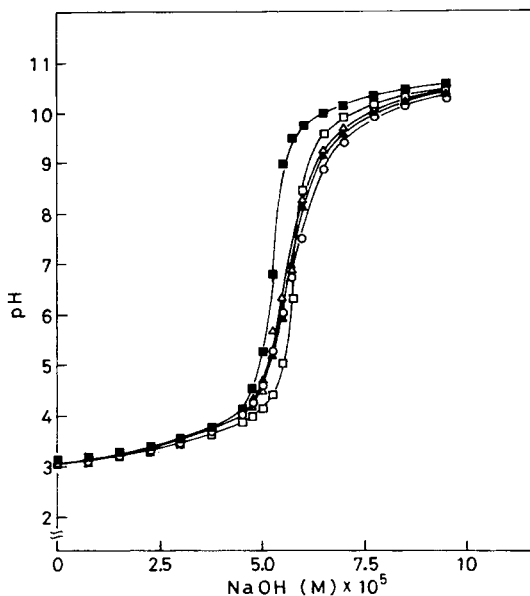
Fig. 3.   Potentiometric titration curves: ($\square$) $L_0$; ($\bigcirc$) $L_3$; ($\triangle$) $L_{12}$; ($\blacktriangle$) $L_{20}$; ($\blacksquare$) blank.

tained from the conductometric titrations. For pH > 7 the surface charge of St/AAm copolymer latexes increased with increasing pH. This may be due to the existence of weak acid groups at the particle surface. However, the presence of weak acid groups was not observed from the conductometric titrations. The expansion of the swelling or water-soluble polymer layer would take place by the increase in pH and the strong acid groups existing inside the swelling or water-soluble polymer layer may be detected.

## $\zeta$-Potential

In order to investigate the influence of AAm fraction in charged monomers on the electrokinetic properties of st/AAm copolymer latex particles,
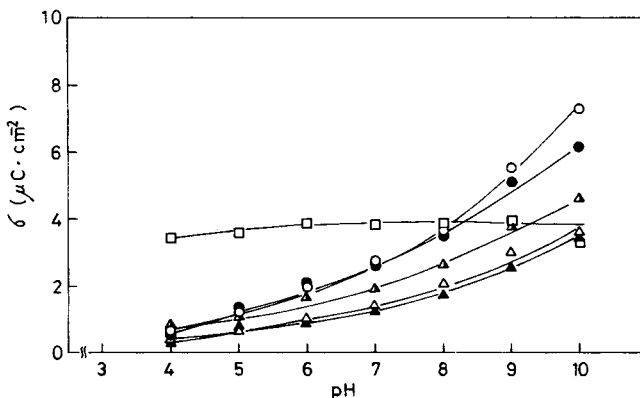


Fig. 4.   Surface charge densities as a function of pH: ($\square$) $L_0$; ($\bigcirc$) $L_3$; ($\bullet$) $L_8$; ($\triangle$) $L_{12}$; ($\blacktriangle$) $L_{15}$; ($\blacktriangle$) $L_{20}$.
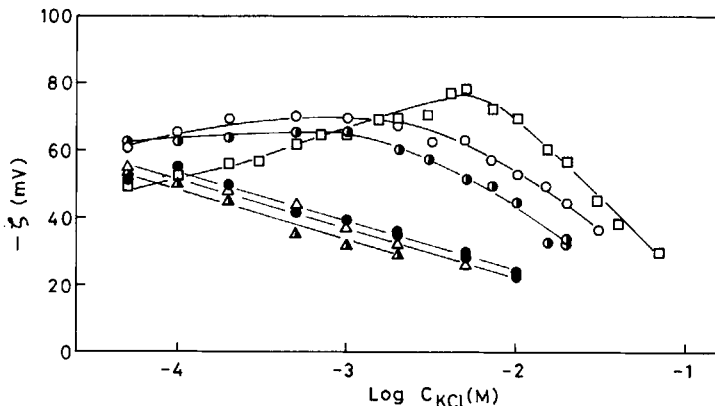
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Fig. 5. $\zeta$-Potential of styrene/acrylamide copolymer latexes as a function of KCl concentration at 25°C: ($\square$) $L_0$; ($\bigcirc$) $L_3$; ($\oplus$) $L_5$; ($\bullet$) $L_8$; ($\triangle$) $L_{12}$; ($\blacktriangle$) $L_{15}$.

$\zeta$-potentials were measured as a function of KCl concentration. The results are shown in Figure 5. As a whole, the $\zeta$-potentials of St/AAm copolymer latex particles decreased with increasing AAm fraction in charged monomers. This is in agreement with that of surface charge densities obtained from the conductometric and potentiometric titrations. The negative $\zeta$-potentials of high AAm fraction latexes (samples $L_8$, $L_{12}$, and $L_{15}$) decreased continuously with increasing KCl concentration. On the other hand, those of PS and low AAm fraction latexes (samples $L_0$, $L_3$, and $L_5$) showed maxima. Regarding the PS latex, the increase in negative $\zeta$-potential with increase in electrolyte concentration has been explained by the adsorption of negative ion.[9] The maxima in $\zeta$-potential seem to be shifted towards low KCl concentration with increasing AAm fraction.

## Coagulation

Figure 6 shows the influence of KCl concentration on the transmission coefficients of the mixed dispersions of St/AAm copolymer latexes and PS
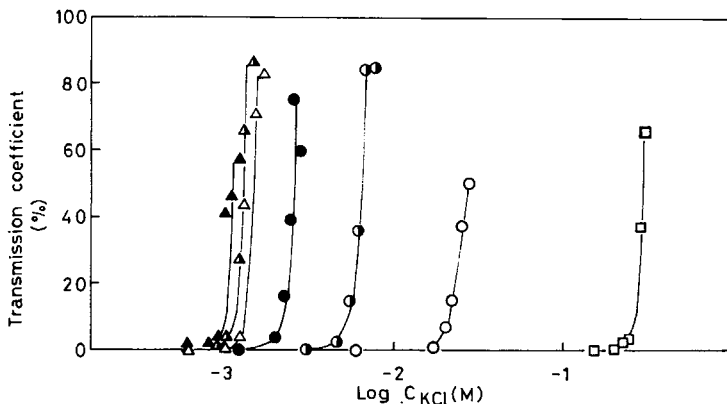


Fig. 6. Transmission coefficient of mixtures of polystyrene latex ($L_0$) and styrene/acrylamide copolymer latexes as a function of KCl concentration at 25°C: ($\square$) $L_0$; ($\bigcirc$) $L_3$; ($\oplus$) $L_5$; ($\bullet$) $L_8$; ($\triangle$) $L_{12}$; ($\blacktriangle$) $L_{15}$; ($\blacktriangle$) $L_{20}$.

latex (sample $L_0$). The KCl concentration at which the transmission coefficients begin to rise abruptly corresponds to the critical coagulation concentration (CCC) for the heterocoagulation between St/AAm copolymer latexes and PS latex ($L_0$). As shown in Figure 6, the CCC decrease with increasing AAm fraction of St/AAm copolymer latexes, and in the case of high AAm fraction latexes (samples $L_{12}$, $L_{15}$ and $L_{20}$), they are almost the same.

Regarding these coagulations at CCC, the interaction energies between St/AAm copolymer latex particles and PS latex particles were calculated according to the coagulation theories (DLVO theory [10,11] and heterocoagulation theory[12]). As Hamaker constant, $5 \times 10^{-21}$ J for polystyrene was used.[13] The interaction energies are shown in Figure 7 as a function of separation distance. On the coagulation between PS latex particles ($L_0 \sim L_0$ homocoagulation), there is no maximum in the interaction energy curve. This corresponds to the rapid coagulation, that is, the coagulation at CCC. On the other hand, large repulsive maxima exist in the interaction energy curves between St/AAm copolymer latex particles and PS latex particles. This indicates that the heterocoagulation between St/AAm copolymer latex and PS latex is not necessarily dependent on only the interaction due to electrostatic and van der Waals forces, which are considered in the coagulation theories.

The coagulation of St/AAm copolymer latex (homocoagulation) was not observed at $10^{-4} \sim 1$ mol $L^{-1}$ of KCl concentration tested. Therefore, the participation of swelling or water-soluble polymer layer of St/AAm copolymer latex particles in the coagulation is suggested. For the heterocoagulation, an attractive action seems to operate. Bridging due to polymer chains protruding from the surface of St/AAm copolymer latex particles may take place. This may be similar to the flocculation of silver iodide sols by poly(vinyl alcohol) with the two-portion method reported by Fleer and Lyklema.[14] On the other hand, for the homocoagulation of St/AAm copolymer latex particles, a repulsive force due to the steric effect would operate, and it would make St/AAm copolymer latex colloidally stable. These con-
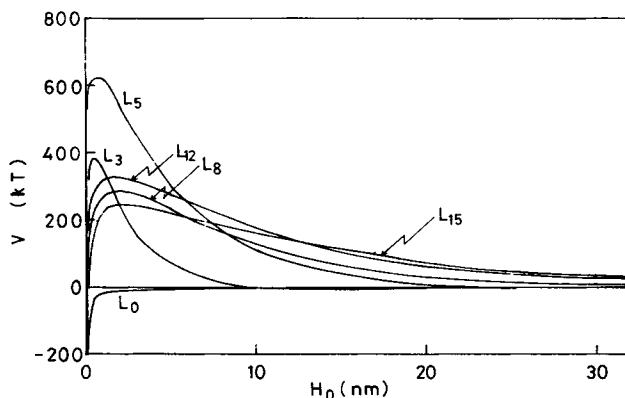


Fig. 7.   Interaction energy curves due to electrostatic and van der Waals forces between polystyrene latex ($L_0$) and styrene/acrylamide copolymer latexes at critical coagulation concentrations of KCl.

siderations suggest that the swelling or water-soluble polymer layer at the particle surface plays an important role for the coagulation of St/AAm copolymer latex particles.

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