

# Surface Characterization of Hydrophilic Functional Polymer Latex Particles

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

## Synopsis

Surface characteristics of styrene/acrylamide/acrylic acid copolymer and styrene/2-hydroxyethyl methacrylate/acrylic acid copolymer latexes prepared without emulsifier using potassium persulfate as initiator and their colloidal stabilities were investigated. The negative  $\zeta$ -potentials decreased with increasing the amount of acrylamide and 2-hydroxyethyl methacrylate copolymerized. In spite of the increase in surface charge density, the negative  $\zeta$ -potentials decreased through the maximum with increasing pH. The colloidal stabilities for NaCl concentration were remarkably enhanced with increasing both pH and the amount of acrylamide and 2-hydroxyethylmethacrylate. These results suggest that the contraction and expansion of water-soluble polymer layer surrounding the particles play an important role in the surface properties.

## INTRODUCTION

Polymer latex particles have been widely used as the carriers for medical diagnostic tests of syphilis and rheumatism,<sup>1</sup> since Singer<sup>2</sup> found that rheumatoid arthritis factor was simply detected by utilizing agglutination behavior of antibodies fixed latex particles. As the latex, polystyrene (PS) latex has been mostly used.

On the other hand, more extensive applications of PS latex as the carriers are mainly interfered by the following: (1) Nonspecific coagulation independent of antibody-antigen reaction disturbs the detection of coagulation based on specific antibody-antigen reaction. This is commonly attributed to the low dispersion stability of PS latex in high electrolyte solutions such as biofluids. (2) Antigens or antibodies detach from the latex particles since their fixation on PS latex particles is based on adsorption. The former (1) is expected to be resolved by enhancing the colloidal stability of latex particles themselves, e.g., providing latex particles with steric stabilization. It might be one of the effective approaches to giving steric repulsive interaction between latex particles to copolymerize hydrophilic monomers such as acrylamide, since they often form water-soluble polymer layer surrounding the particles.<sup>3,4</sup> For the latter problem (2), the fixation of antibodies by chemical bonding such as covalent bond has been expected, utilizing the latex particles having functional groups such as carboxyl groups at the particle surface.<sup>5-8</sup> From these points of view, it is important to clarify the surface characteristics of hydrophobic monomer/hydrophilic monomer/functional monomer copolymer latex particles and their colloidal stability.

In this work, the surface characteristics of styrene/acrylamide/acrylic acid copolymer [P(St/AAm/AA)] latex and styrene/2-hydroxyethyl methacry-

late/acrylic acid copolymer [P(St/HEMA/AA)] latex prepared in the absence of emulsifier and their dispersion stabilities have been investigated as a function of the amount of acrylamide (AAm) and 2-hydroxyethyl methacrylate (HEMA) copolymerized. Surface charge density, electrokinetic potential, and coagulation rate were measured.

## EXPERIMENTAL

### Materials

Styrene, HEMA and acrylic acid (AA) from Wako Pure Chemical Industries were distilled under reduced pressure in N<sub>2</sub> atmosphere. Potassium persulfate and AAm (Wako Pure Chemical Industries) were recrystallized from water and benzene, respectively. Sodium chloride (NaCl), sodium hydroxide (NaOH), and hydrochloric acid (HCl) used for adjustment of pH and ionic strength were all analytical grade from Wako Pure Chemical Industries and were used without further purification. Distilled and deionized water was used throughout the experiments.

### Latex

As hydrophobic monomer/hydrophilic monomer/functional monomer copolymer latex, P(St/AAm/AA) and P(St/HEMA/AA) latexes were prepared in the absence of emulsifier using potassium persulfate as initiator. The amounts of AAm and HEMA copolymerized were varied. The polymerization recipes of P(St/AAm/AA) latex and P(St/HEMA/AA) latex are shown in Tables I and II, respectively. The average particle diameters of the latexes were determined by electronmicroscopy. Approximately 30 particles were counted for each latex. The latexes obtained have almost the same particle size (400–500 nm) and were all monodispersed.

The latexes were dialyzed using well-boiled Visking dialysis tubing for over 2 weeks. Furthermore, the latexes were centrifuged and the sedimented particles were redispersed in water by ultrasonics. The above procedure was repeated three times, and finally the latexes were purified by ion exchange.

TABLE I  
Preparation of P(St/AAm/AA) Latex

| Latex                             | P(St/AAm <sub>0</sub> /AA <sub>2</sub> ) | P(St/AAm <sub>1</sub> /AA <sub>2</sub> ) | P(St/AAm <sub>2</sub> /AA <sub>2</sub> ) |
|-----------------------------------|--|--|--|
| Styrene ( <i>M</i> )              | 1  | 1  | 1  |
| Acrylamide ( <i>M</i> )           | —  | 0.01                                     | 0.02                                     |
| Acrylic acid ( <i>M</i> )         | 0.02                                     | 0.02                                     | 0.02                                     |
| Potassium persulfate ( <i>M</i> ) | $3 \times 10^{-3}$                       | $3 \times 10^{-3}$                       | $3 \times 10^{-3}$                       |
| Polymerization time (h)           | 8  | 8  | 8  |
| Polymerization temp (°C)          | 70                                       | 70                                       | 70                                       |
| Particle diameter (nm)            | 560                                      | 438                                      | 440                                      |
| Δ                                 | —  | 7.1                                      | 9.6                                      |

TABLE II  
Preparation of P(St/HEMA/AA) Latex

| Latex                                    | P(St/HEMA <sub>1</sub> /AA <sub>2</sub> ) | P(St/HEMA <sub>2</sub> /AA <sub>2</sub> ) | P(St/HEMA <sub>4</sub> /AA <sub>2</sub> ) | PS                 |
|--|---|---|---|--------------------|
| Styrene ( <i>M</i> )                     | 1   | 1   | 1   | 0.9                |
| 2-Hydroxyethyl methacrylate ( <i>M</i> ) | 0.01                                      | 0.02                                      | 0.04                                      | —                  |
| Acrylic acid ( <i>M</i> )                | 0.02                                      | 0.02                                      | 0.02                                      | —                  |
| Potassium persulfate ( <i>M</i> )        | $3 \times 10^{-3}$                        | $3 \times 10^{-3}$                        | $3 \times 10^{-3}$                        | $3 \times 10^{-3}$ |
| Polymerization time (h)                  | 9   | 9   | 9   | 24                 |
| Polymerization temp (°C)                 | 70  | 70  | 70  | 70                 |
| Particle diameter (nm)                   | 447                                       | 454                                       | 440                                       | 498                |
| Δ (nm)                                   | 6.6                                       | 11.7                                      | 12.1                                      | —                  |

## Methods

### *Conductometric and Potentiometric Titrations*

Conductometric titrations of the latexes were done immediately after purification with NaOH solution in a stirred vessel under N<sub>2</sub> atmosphere. The conductivity was measured using a conductivity dip cell and a TOA Model CM 30 ET conductivity meter. Potentiometric titrations were carried out using a Hitachi-Horiba Model F-7SS meter. The titrations were performed on the latexes containing  $10^{-3}$  mol dm<sup>-3</sup> HCl.

### *Colloidal Stability*

The rapid-mixing flocculation experiments were performed by the stopped-flow method using a JASCO UVIDEK 610 spectrophotometer with a SFC-333 flow cell device. In this apparatus, equal volumes of latex dispersion and electrolyte solution were taken into the two syringes and then rapidly mixed by depressing the plunger. The transmittance of the mixture was recorded on an attached recorder. The wavelength used was 680 nm by a tungsten lamp.

### *ζ-Potential*

Electrophoretic mobilities of the latex particles were measured with a Rank Brothers microelectrophoresis apparatus, Mark II, and the ζ-potentials were calculated according to the Henry equation.<sup>9</sup>

### *Viscosity*

Viscosities of latex dispersions were measured with an Ostwald viscosimeter at various volume fractions of latex particles. The measurements were carried out at  $10^{-2}M$  NaCl and 25°C.

## RESULTS AND DISCUSSION

Figure 1 shows the conductometric titration curves of P(St/HEMA/AA) latexes. The titration of P(St/AAM/AA) latexes gave the similar curves. As shown in Figure 1, the end points for strong acid groups are clearly observed.

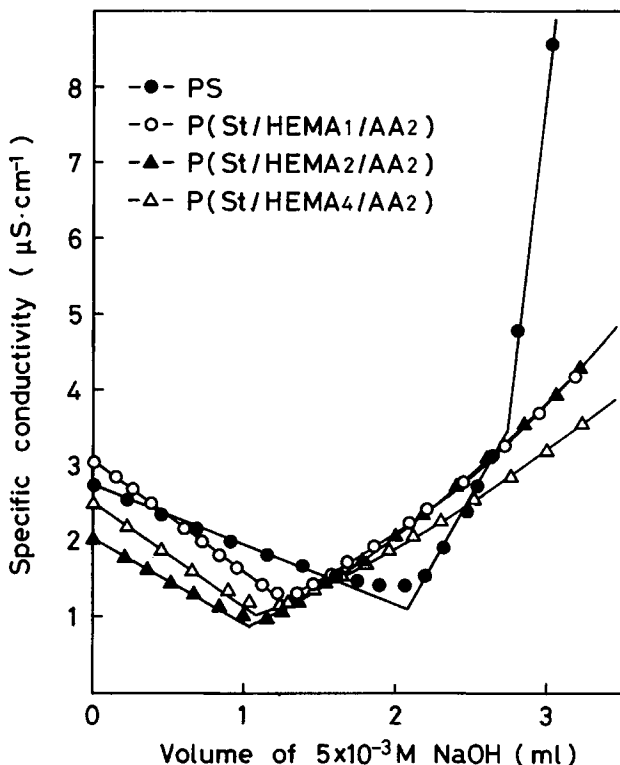


Fig. 1. Conductometric titration curves for the latexes at 25°C: (●) PS; (○) P(St/HEMA<sub>1</sub>/AA<sub>2</sub>); (▲) P(St/HEMA<sub>2</sub>/AA<sub>2</sub>); (△) P(St/HEMA<sub>4</sub>/AA<sub>2</sub>).

These end points are due to sulfate ( $-\text{OSO}_3^-$ ) groups derived from initiator. In the case of polymer latexes prepared using potassium persulfate as initiator, some authors have reported that the end points for weak acid groups such as carboxyl groups are detected by conductometric titration, in addition to those for strong acid groups.<sup>10-12</sup> Carboxyl groups have been considered to be generated by hydrolysis of  $-\text{OSO}_3^-$  groups from initiator and oxidation.<sup>13</sup> P(St/AAm/AA) and P(St/HEMA/AA) latex particles contain a number of carboxyl groups derived from copolymerized acrylic acid in addition to carboxyl groups from initiator. Nevertheless, the titration end points for weak acid groups are ambiguous as shown in Figure 1.

Furthermore, in order to consider the surface groups of P(St/AAm/AA) and P(St/HEMA/AA) latex particles, the potentiometric titrations were carried out. The results on P(St/AAm/AA) latex are shown in Figure 2. In comparison with blank titration without latex particles, the amount of NaOH consumed for the latexes increased with increasing pH. Its increase is remarkable at alkaline pH. From the amount of titrant against pH, the surface charge density  $\sigma$  of the latexes were calculated as a function of pH. The  $\sigma$  of P(St/AAm/AA) latex and P(St/HEMA/AA) latex are shown in Figures 3 and 4, respectively. The surface charge density of the latex particles steeply and continuously increases with increasing pH. These results are similar to those on styrene/acrylic acid copolymer latex reported by Shirahama and Suzawa.<sup>14</sup> On the other hand, the increase in the surface charge density with pH is scarcely dependent on the amount of AAm and HEMA copolymerized.

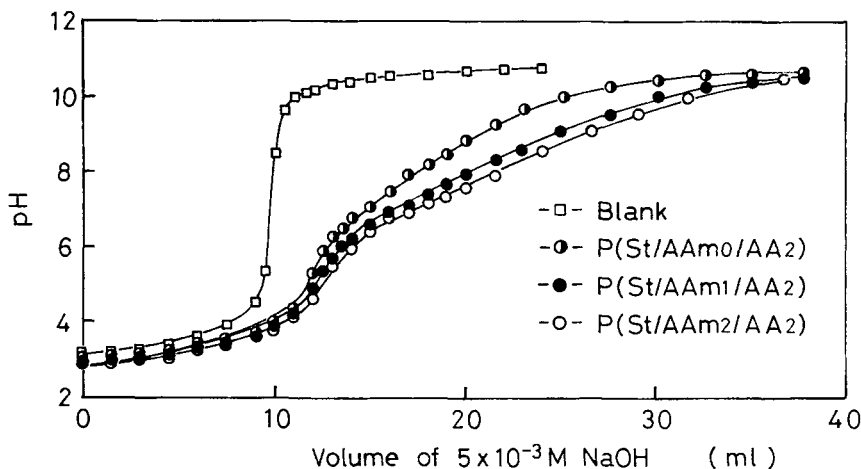


Fig. 2. Potentiometric titration curves for P(St/AAM/AA) latex at 25°C, 10<sup>-2</sup>M NaCl: (□) blank; (●) P(St/AAM<sub>0</sub>/AA<sub>2</sub>); (●) P(St/AAM<sub>1</sub>/AA<sub>2</sub>); (○) P(St/AAM<sub>2</sub>/AA<sub>2</sub>).

Regarding the conductometric titration of acrylic acid copolymer latex prepared by potassium persulfate, Egusa and Makuuchi<sup>15</sup> observed that the acidic groups detected by the direct titration with NaOH were smaller than those by the back titration with HCl. Their results were explained by a particle model<sup>16</sup> consisting of the core and its surrounding polymer layer which contains a part of buried acid groups in addition to surface-bound acid groups. Similarly to the interpretation given by Egusa and Makuuchi,<sup>15</sup> it is suggested that water-soluble polymer layer, which contracts at acidic pH and expands by the electrostatic repulsion due to the dissociated acid groups at alkaline pH, surrounds P(St/AAM/AA) and P(St/HEMA/AA) latex particles as shown in Figure 5. The acid groups exposed freshly by expansion of the water-soluble polymer layer are considered to increase the surface charge densities of P(St/AAM/AA) and P(St/HEMA/AA) latex particles with increasing pH.

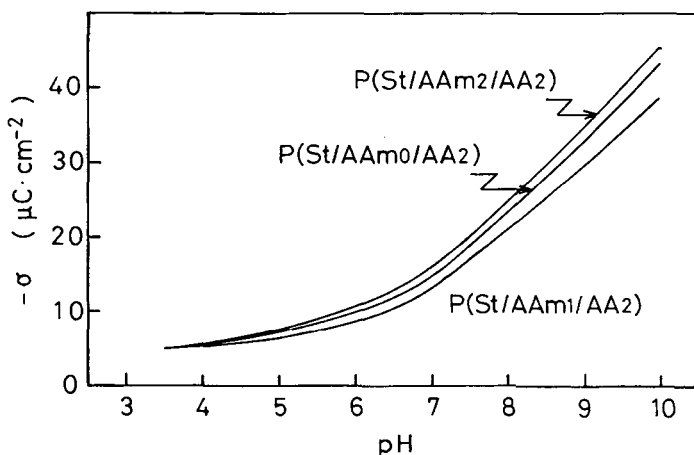


Fig. 3. Surface charge density of P(St/AAM/AA) latex.

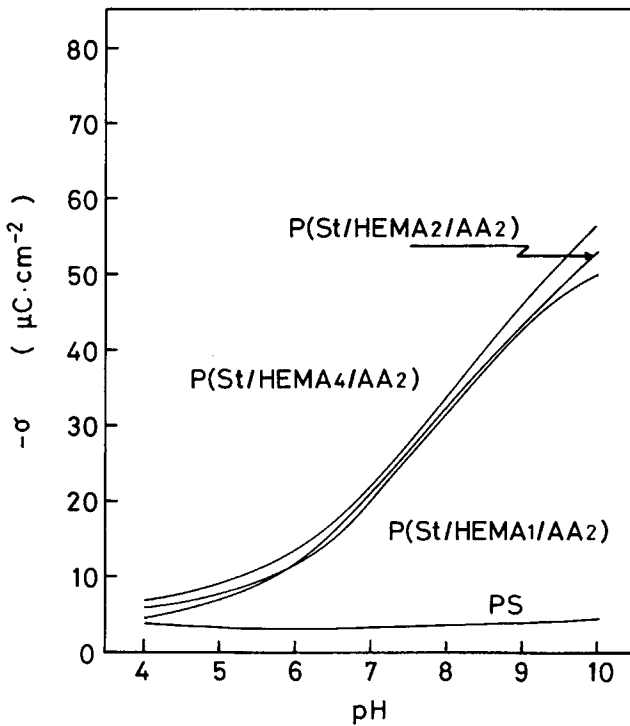


Fig. 4. Surface charge density of P(St/HEMA/AA) latex.

Figure 6 shows the  $\zeta$ -potentials of P(St/HEMA/AA) latex as a function of NaCl concentration. The  $\zeta$ -potentials of P(St/AAm/AA) latex showed the similar behaviors. The negative  $\zeta$ -potentials of the latexes decrease through the maximum with increasing NaCl concentration, similarly to those of PS latex. Regarding the  $\zeta$ -potential of PS latex particles, the effect of water-soluble short polystyrene chains (hairs), which have  $-\text{OSO}_3^-$  groups as end group at the particle surface, has been considered.<sup>17</sup> The shrinkage of this hairy layer due to the increase in NaCl concentration has been thought to cause the location of the slipping plane in electrical double layer to come close to the surface of latex particles, and consequently the negative  $\zeta$ -potential of PS latex increases. Since the surface of P(St/AAm/AA) and P(St/HEMA/AA) latex particles is thought hairy, as described in the results of potentiometric titration and shown in Figure 5, the maximum of the negative  $\zeta$ -potential for pH would be due to the shrinkage of this layer. On the other hand, both the

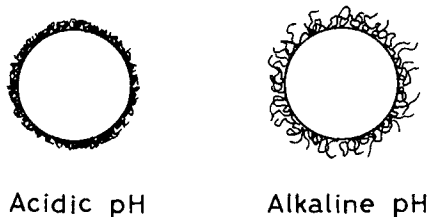


Fig. 5. Schematic representation of the latex particles.

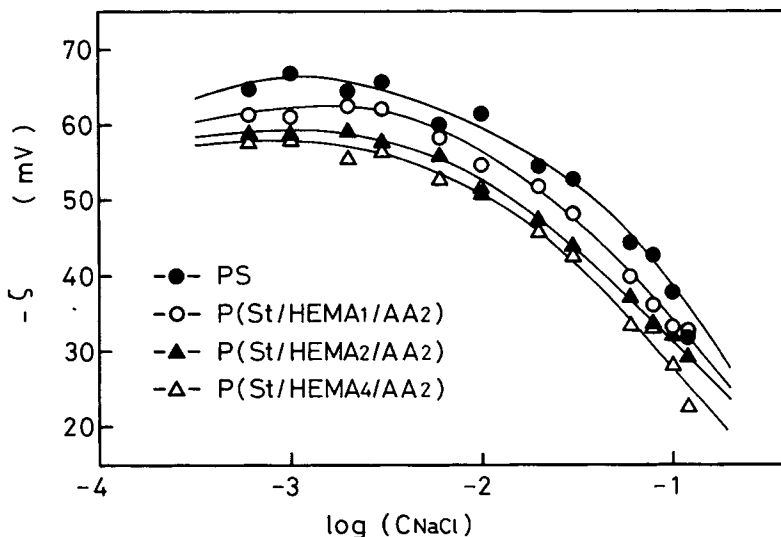


Fig. 6.  $\zeta$ -Potentials of P(St/HEMA/AA) latex as a function of NaCl concentration at 25°C: (●) PS; (○) P(St/HEMA<sub>1</sub>/AA<sub>2</sub>); (▲) P(St/HEMA<sub>2</sub>/AA<sub>2</sub>); (△) P(St/HEMA<sub>4</sub>/AA<sub>2</sub>).

negative  $\zeta$ -potentials of P(St/AAm/AA) and P(St/HEMA/AA) latexes decreases with increasing the amount of AAm and HEMA copolymerized. It is generally known that the  $\zeta$ -potential decreases due to an outward shift of the slipping plane when the surface potential is kept constant. The fact that the  $\zeta$ -potentials of P(St/AAm/AA) and P(St/HEMA/AA) latexes decrease with increase in the amount of AAm and HEMA can be explained by the increase in the thickness of surrounding water-soluble polymer layer described above, that is, the increase in outward shift of the slipping plane.

In order to consider the water-soluble polymer layer which is thought to surround the particles of P(St/AAm/AA) and P(St/HEMA/AA) latexes, the dispersion property of the latexes was investigated by viscosimetry. The relation between the reduced viscosity of P(St/HEMA/AA) latex dispersion,  $\eta_{sp}/\phi$  and volume fraction of latex particles,  $\phi$ , is given in Figure 7. The intercepts increase with increasing the amount of HEMA, in spite of the fact that the particle diameters determined by electron microscopy are almost the same ( $\approx 440$  nm). This indicates that the dispersed particle size is larger than that of the dried particle.

The similar results were obtained for P(St/AAm/AA) latexes. According to the procedure described in the previous paper,<sup>3,18</sup> the thickness of water-soluble polymer layer,  $\Delta$ , was calculated. The relation between  $\Delta$  and the amount of AAm and HEMA are shown in Tables I and II. The  $\Delta$  of P(St/AAm/AA) and P(St/HEMA/AA) latex particles increases with increasing the amount of AAm and HEMA, and the  $\Delta$  of P(St/HEMA<sub>4</sub>/AA<sub>2</sub>) latex particles is more than 12 nm. These results substantiate the assumption of water-soluble polymer layer surrounding the particle and the interpretation described above for the results of  $\zeta$ -potential and potentiometric titration.

The variation of the turbidity ( $\Delta\tau$ ) of the latex dispersion with time was measured immediately after mixing the latex with an electrolyte solution.

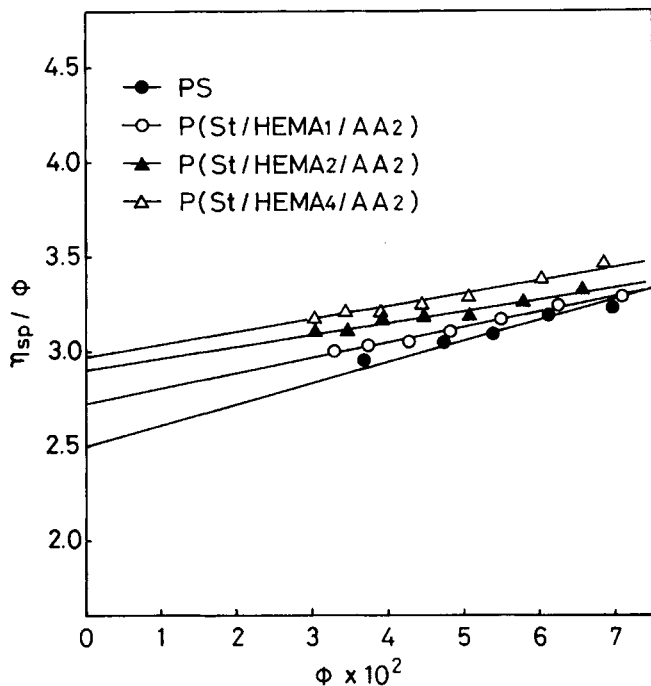


Fig. 7. Relation between  $\eta_{sp}/\phi$  and  $\phi$  for P(St/HEMA/AA) latex at  $10^{-2}M$  NaCl and  $25^{\circ}C$ : (●) PS; (○) P(St/HEMA<sub>1</sub>/AA<sub>2</sub>); (▲) P(St/HEMA<sub>2</sub>/AA<sub>2</sub>); (△) P(St/HEMA<sub>4</sub>/AA<sub>2</sub>).

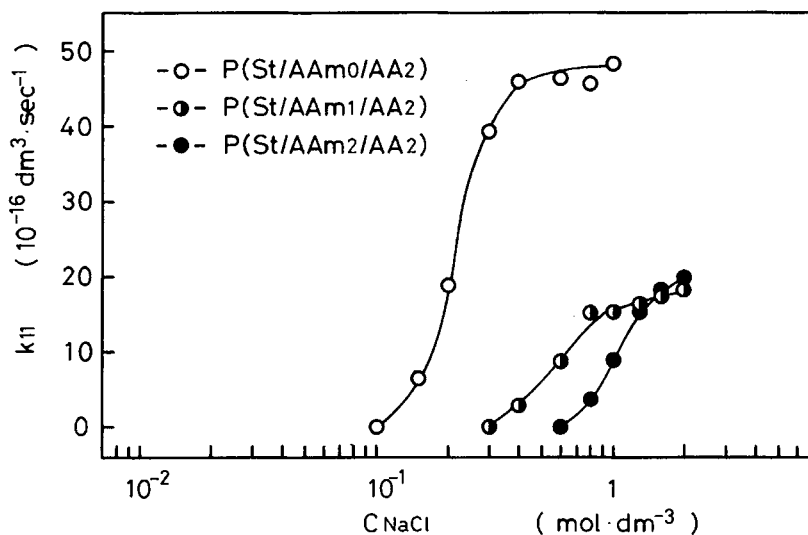


Fig. 8. Rate constant for the coagulations of P(St/AA/AA) latex as a function of NaCl concentration at pH 5.7 and  $25^{\circ}C$ : (○) P(St/AAm<sub>0</sub>/AA<sub>2</sub>); (◐) P(St/AAm<sub>1</sub>/AA<sub>2</sub>); (●) P(St/AAm<sub>2</sub>/AA<sub>2</sub>).



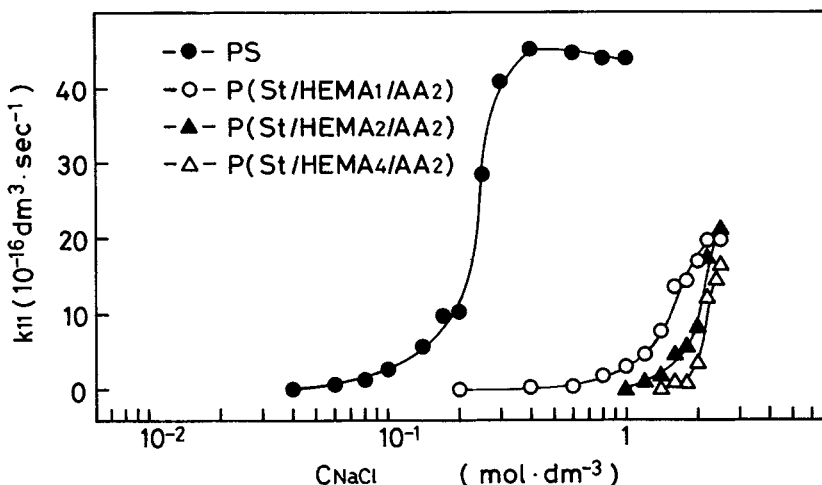


Fig. 9. Rate constant for the coagulations of P(St/HEMA/AA) latex as a function of NaCl concentration at pH 5.7 and 25°C: (●) PS; (○) P(St/HEMA<sub>1</sub>/AA<sub>2</sub>); (▲) P(St/HEMA<sub>2</sub>/AA<sub>2</sub>); (Δ) P(St/HEMA<sub>4</sub>/AA<sub>2</sub>).

Since the  $\Delta\tau$  increased linearly with time ( $\sim 100$  s) at the initial stage of coagulation, the rate constant ( $k_{11}$ ) of coagulation between singlet particles was calculated from the initial slope of  $\Delta\tau$  vs. time according to Lichtenbelt et al.<sup>19</sup> Figures 8 and 9 show the  $k_{11}$  of P(St/AAm/AA) latex and P(St/HEMA/AA) latex, respectively, as a function of NaCl concentration at pH 5.7. The coagulation was observed above certain NaCl concentrations and the  $k_{11}$  steeply increased with increasing NaCl concentration above these NaCl concentrations (slow coagulation). As shown in Figures 8 and 9, the minimum NaCl concentration (mcc) at which the slow coagulation takes place increases with increasing the amount of AAm and HEMA. The colloidal stabilities of P(St/AAm/AA) and P(St/HEMA/AA) latexes for electrolyte concentration are enhanced with increasing the amount of hydrophilic monomer AAm and HEMA at pH 5.7.

At pH 3, the NaCl concentration range where the coagulation of P(St/HEMA/AA) latex was observed was almost the same as that of PS latex, even if the amount of copolymerized HEMA increased. At acidic pH, HEMA scarcely contributes to the enhancement in colloidal stability of P(St/HEMA/AA) latex. At pH 10.5, no coagulation of P(St/HEMA/AA) latex was observed even at high NaCl concentration. On the other hand, the coagulation behavior, e.g. ccc and mcc, of PS latex for NaCl concentration in an alkaline solution is almost the same as those in neutral and acidic solutions. This indicates that the colloidal stability of P(St/HEMA/AA) latex remarkably increases with increasing pH. We interpreted the opposite relation between the surface charge density and the  $\zeta$ -potential of P(St/HEMA/AA) latex (Fig. 10) for the increase in pH, by an outward shift of the slipping plane due to expansion of water-soluble polymer layer surrounding the particle. On the same grounds, the enhancement in colloidal stability of P(St/HEMA/AA) latex with increase in pH can be considered. That is, the increase in steric repulsion between latex particles due to expan-

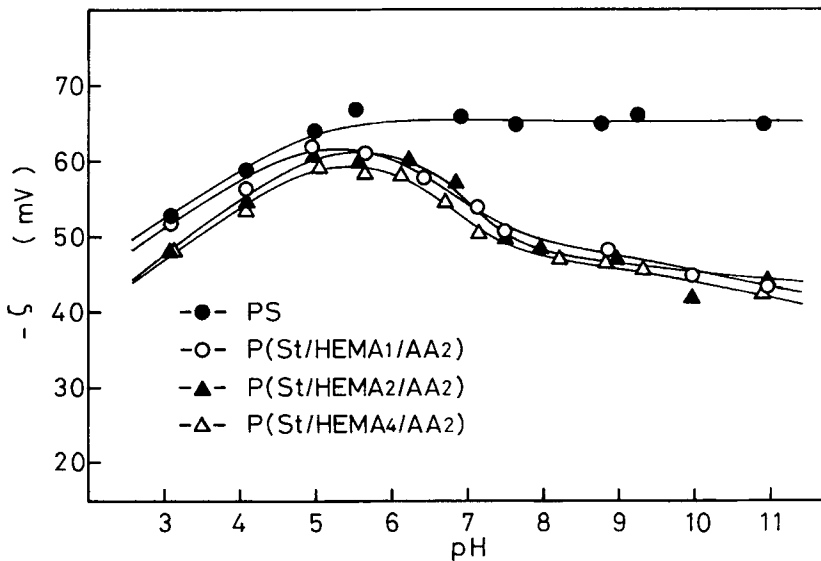


Fig. 10.  $\zeta$ -Potentials of P(St/HEMA/AA) latex as a function of pH at  $10^{-3}$  ionic strength and  $25^{\circ}\text{C}$ : (●) PS; (○) P(St/HEMA<sub>1</sub>/AA<sub>2</sub>); (▲) P(St/HEMA<sub>2</sub>/AA<sub>2</sub>); (△) P(St/HEMA<sub>4</sub>/AA<sub>2</sub>).

sion of water-soluble polymer layer enhances the colloidal stability of P(St/HEMA/AA) latex, in addition to electrostatic repulsion. From the point that the colloidal stability depends on the amount of AAm and HEMA at pH 5.7, it is suggested that the water-soluble polymer layer consists of mixed polymers generated from AA and AAm or HEMA.

### References

1. T. Suzuta, *Kobunshi*, **29**, 112 (1980).
2. J. M. Singer, *Am. J. Med.*, **31**, 766 (1961).
3. H. Tamai, T. Murakami, and T. Suzawa, *J. Appl. Polym. Sci.*, **30**, 3857 (1987).
4. H. Tamai, A. Fujii, and T. Suzawa, *J. Colloid Interface Sci.*, **116**, 37 (1987).
5. A. Rembaum and S. Margel, *Br. Polymer J.*, **10**, 275 (1978).
6. A. Rembaum, S. P. S. Yen, E. Cheong, S. Wallace, R. S. Molday, I. L. Gordon, and W. J. Dreyer, *Macromolecules*, **9**, 328 (1976).
7. R. S. Molday, W. J. Dreyer, A. Rembaum, and S. P. S. Yen, *J. Cell Biology*, **64**, 75 (1975).
8. K. Marumoto, T. Suzuta, H. Noguchi, and Y. Uchida, *Polymer*, **19**, 867 (1978).
9. D. C. Henry, *Proc. Roy. Soc.*, **A133**, 105 (1931).
10. B. H. Bijsterbosch, *Colloid Polymer Sci.*, **256**, 343 (1978).
11. H. Ono, E. Jidai, and K. Shibayama, *Br. Polymer J.*, **7**, 109 (1975).
12. A. R. Goodall, J. Hearn, and M. C. Wilkinson, *J. Polym. Sci. Chem. Ed.*, **15**, 2193 (1977).
13. J. W. Goodwin, J. Hearn, C. C. Ho, and R. H. Ottewill, *Br. Polym. J.*, **5**, 347 (1973).
14. H. Shirahama and T. Suzawa, *Polym. J.*, **16**, 795 (1984).
15. S. Egusa and K. Makuuchi, *J. Colloid Interface Sci.*, **79**, 350 (1981).
16. K. L. Hoy, *J. Coatings Technol.*, **51**, 27 (1979).
17. A. G. Van der Put and B. H. Bijsterbosch, *J. Colloid Interface Sci.*, **92**, 499 (1983).
18. G. J. Fleer, L. K. Koopal, and J. Lyklema, *Kolloid Z. Z. Polym.*, **250**, 689 (1972).
19. J. W. Th. Lichtenbelt, H. J. M. C. Ras, and P. H. Wiersema, *J. Colloid Interface Sci.*, **46**, 522 (1974).

Received May 4, 1988

Accepted July 20, 1988