

# Surface Properties of Polymethylenediamine-Fixed Styrene/Acrylic Acid Copolymer Latex

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## SYNOPSIS

Surface charge density,  $\zeta$ -potential, and dispersion stability of polymethylenediamine (PMD)-fixed styrene/acrylic acid copolymer [P(St/AA)] latex were investigated. PMD-fixed P(St/AA) latices are amphoteric and have isoelectric points at pH 4–7. Though the flocculations were observed at neutral pH, the pHs where the flocculation rates were maximum are slightly higher than were the isoelectric points. This result suggests the influence of the expansion of PMD-fixed polymer layer surrounding the particles on the flocculation. The fixation of PMD to the surface of P(St/AA) latex lowers the dispersion stability for high electrolyte concentration.

## INTRODUCTION

Highly spherical and monodispersed polymer latex particles have been widely used in many serological tests such as in the detection of rheumatoid arthritis factor.<sup>1</sup> In these applications, the agglutination behavior of antigen- and antibody-fixed latex particles is utilized, based on the antigen-antibody reaction. Since proteins such as antigens and antibodies are generally fixed to the surface of latex particles by physicochemical adsorption, the detachment of antigens or antibodies from the latex particles occasionally interfere with the detection. Rembaum et al.<sup>2–5</sup> reported on the fixation of antibodies to latex particles by chemical bonding, such as covalent bonding, using the latices having functional groups, e.g., carboxyl, amino, and hydroxy groups. They suggested that in fixation of antibodies by chemical bonding the introduction of a short chain, called a spacer, between antibodies and the surface of the latex particles was effective in keeping the antibodies fixed to the latex particles.

From these points of view, we investigated the surface characteristics and dispersion stability of the spacer introduced into styrene/acrylic acid copolymer [P(St/AA)] latex particles. For spacers,

polymethylenediamines (PMD) of different carbon chain lengths were used.

## EXPERIMENTAL

### Materials

Styrene and acrylic acid from Wako Pure Chemical Industries were distilled under reduced pressure in N<sub>2</sub> atmosphere. Potassium persulfate was recrystallized from water. Polymethylenediamine, viz. ethylenediamine (ETD), tetramethylenediamine (TMD), hexamethylenediamine (HMD), and octamethylenediamine (OMD) from Tokyo Kasei and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) from Wako were used without further purification. Sodium chloride (NaCl), sodium hydroxide (NaOH), and hydrochloric acid (HCl) were all analytical grade. Distilled and deionized water was used throughout the experiments.

### Preparation of P(St/AA) latex and PMD-fixed P(St/AA) latex

P(St/AA) latex was prepared in the absence of an emulsifier using potassium persulfate.<sup>6</sup> Particle size was determined by electron microscopy. More than 30 particles were sized. The number-average particle diameter was 476 nm. The uniformity ratio ( $U$ ) cal-

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culated from the ratio of the volume diameter to the number-average diameter was 1.0004. The latex was dialyzed for over 1 week using well-boiled Visking dialysis tubing. Then, the latex was centrifuged and the sedimented particles were redispersed in water by ultrasonics. The above procedure was repeated three times, and, finally, the latices were purified by ion exchange.

The introduction of PMD into the surface of P(St/AA) latex particles was carried out by carbodiimide reaction.<sup>2,3</sup> EDC was used as carbodiimide. The fixation conditions are shown in Table I. With respect to HMD, the concentration of HMD was varied. Immediately after the reaction, PMD-fixed latex dispersions were centrifuged to remove unreacted PMD and EDC. Sedimented particles were redispersed in water. Then, PMD-fixed P(St/AA) latex was dialyzed for over 1 week using well-boiled Visking dialysis tubing. Furthermore, the latices were purified by ion exchange. Diaion PK 212-sulfonic acid type and PA 312-trimethylammonium type (Mitsubishi Chemical Industries) were used as the cationic ion exchange resin and the anionic ion exchange resin, respectively.

## METHODS

### Potentiometric and Conductometric Titrations

Potentiometric titration of P(St/AA) latex was carried out at 25°C using a Hitachi-Horiba Model F-7SS pH meter. The titrations were performed on  $5 \times 10^{-2} \text{ dm}^3$  of the latex dispersion containing  $10^{-3} \text{ mol dm}^{-3}$  HCl. NaOH solution,  $5 \times 10^{-3} \text{ mol dm}^{-3}$ , was obtained.

Conductometric titrations were performed on PMD-fixed P(St/AA) latex particles dispersed in  $10^{-3} \text{ mol dm}^{-3}$  NaOH solution. The titrations were done with  $5 \times 10^{-4} \text{ mol dm}^{-3}$  HCl solution in a stirred vessel under  $\text{N}_2$  atmosphere. The conductivity was measured using a conductivity dip cell and a TOA Model CM-30ET conductivity meter.

### $\zeta$ -Potential

The  $\zeta$ -potential of PMD-fixed P(St/AA) latex particles was obtained by microelectrophoresis. The electrophoretic mobilities were measured with a Rank Brothers Mark II. The electrophoretic mobility was converted to the  $\zeta$ -potential by the Henry equation.<sup>7</sup>

### Flocculation

The flocculation rates of PMD-fixed latex were obtained as a function of pH and NaCl concentration. The flocculation rates were measured by the rapid mixing and stopped flow method, using a JASCO UVIDEK 610 spectrophotometer with an SFC-333 flow cell device (light path length 10 mm) connected to a Union MX-7 sample mixing device. Equal volumes of PMD-fixed latex and electrolyte solution were taken into the two syringes and then rapidly mixed by depressing the plunger. The change of turbidity ( $\Delta\tau$ ) of the mixture with time was recorded on an attached recorder. Since the  $\Delta\tau$  increased linearly with time ( $\sim 100 \text{ s}$ ) at the initial stage of flocculation, the rate constant ( $k_{11}$ ) of flocculation between singlet particles was calculated from the initial slope of  $\Delta\tau$  vs. time according to Lichtenbelt et al.<sup>8</sup>

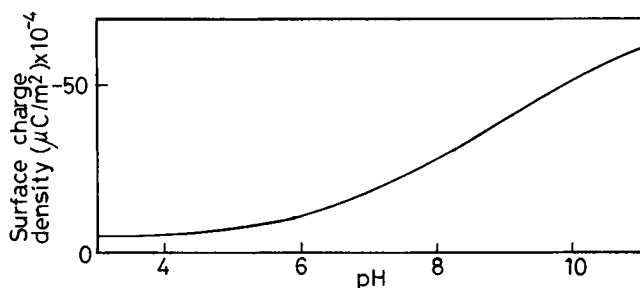
**Table I** Bonding of PMD to P(St/AA) Latex

|                                    | Latex                 |                       |                      |                      |                       |                       |
|------------------------------------|-----------------------|-----------------------|----------------------|----------------------|-----------------------|-----------------------|
|                                    | L(ETD <sub>10</sub> ) | L(TMD <sub>10</sub> ) | L(HMD <sub>1</sub> ) | L(HMD <sub>5</sub> ) | L(HMD <sub>10</sub> ) | L(OMD <sub>10</sub> ) |
| Dried weight of P(St/AA) latex (g) | 5                     | 5                     | 5                    | 5                    | 5                     | 5                     |
| EDC (mol/dm <sup>3</sup> )         | 0.01                  | 0.01                  | 0.01                 | 0.01                 | 0.01                  | 0.01                  |
| ETD (mol/dm <sup>3</sup> )         | 0.01                  | —                     | —                    | —                    | —                     | —                     |
| TMD (mol/dm <sup>3</sup> )         | —                     | 0.01                  | —                    | —                    | —                     | —                     |
| HMD (mol/dm <sup>3</sup> )         | —                     | —                     | 0.001                | 0.005                | 0.01                  | —                     |
| OMD (mol/dm <sup>3</sup> )         | —                     | —                     | —                    | —                    | —                     | 0.01                  |
| Temperature (°C)                   | 25                    | 25                    | 25                   | 25                   | 25                    | 25                    |
| Time (h)                           | 2                     | 2                     | 2                    | 2                    | 2                     | 2                     |
| Total volume (dm <sup>3</sup> )    | 0.2                   | 0.2                   | 0.2                  | 0.2                  | 0.2                   | 0.2                   |

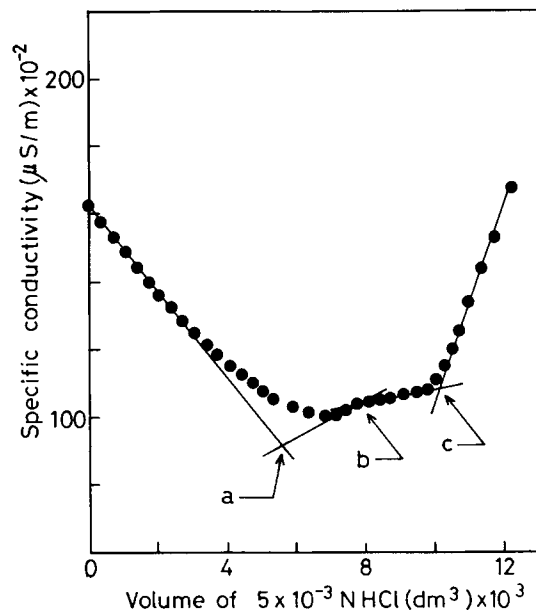
## RESULTS AND DISCUSSION

The change of surface charge density ( $\sigma$ ) of P(St/AA) latex, determined by potentiometric titration, is shown in Figure 1. The  $\sigma$  of P(St/AA) latex greatly increases with increasing pH in the alkaline pH region. From the result of the conductometric titration of P(St/AA) latex prepared by radiation-initiated emulsion polymerization, Egusa and Makuuchi<sup>9</sup> proposed a particle model consisting of the core and its surrounding polymer layer that contains a part of buried acid groups in addition to surface-bound acid groups. This surrounding polymer layer expands by the electrostatic repulsion due to the dissociated acid groups at alkaline pH. Accordingly, the increase of  $\sigma$  of P(St/AA) latex with increasing pH is supposed to be due to carboxyl groups exposed freshly by expansion of the surrounding polymer layer.

Figure 2 shows the conductometric titration curve of L(HMD<sub>10</sub>) latex. The titrations of other PMD-fixed latices gave similar curves. Three endpoints were observed. These titration curves of PMD-fixed P(St/AA) latex are analogous to those of amphoteric latices. The first endpoint is due to excess NaOH added to the latex. Ozaki et al.<sup>10</sup> obtained a similar result on the conductometric titration curve for styrene/diethylaminoethyl methacrylate/methacrylic acid copolymer latex with barium hydroxide. According to Ozaki et al.,<sup>10</sup> the region from point a to b in Figure 2 is regarded as the titration of carboxyl groups, and the region from b to c, as the titration of amino groups. From the titration curves, the surface charge densities due to amino groups derived from PMD and acidic groups were obtained from the endpoints in Figure 2. The results are shown in Table II. As shown in Table II, the surface charge density due to amino groups slightly increases with increasing HMD concentration and methylene chain length. This suggests that the



**Figure 1** Surface charge density of P(St/AA) latex as a function of pH.

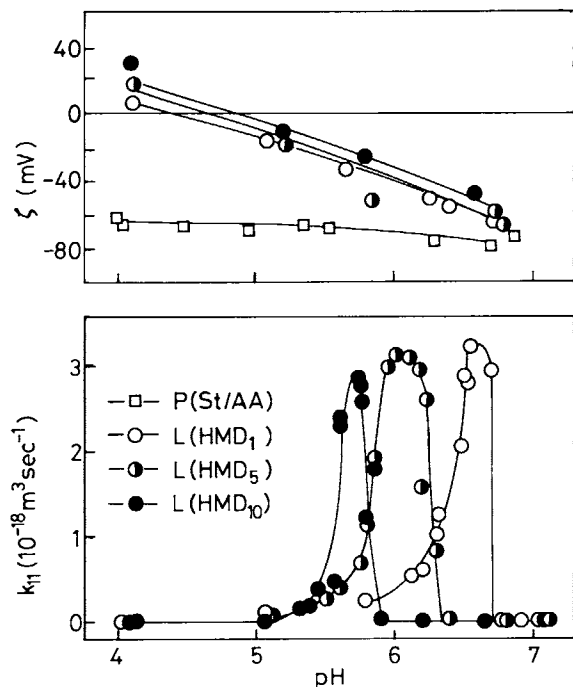


**Figure 2** Conductometric titration curve for L(HMD<sub>10</sub>) latex.

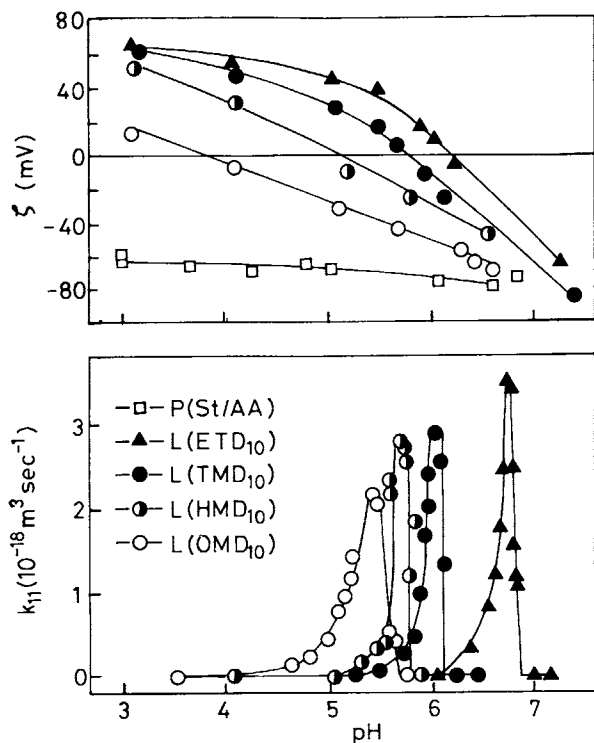
amount of PMD fixed to the particle surface slightly increases with increasing both the PMD concentration and methylene chain length. On the other hand, the surface charge density due to acidic groups also slightly increases with increasing methylene chain length. Because the longer methylene chain diamine has a higher energy of adsorption, the amount of longer PMD fixed to the particle surface would be higher. Therefore, the higher electrostatic repulsion between the charged loose ends could create a greater expansion of the surface polymer layer. Consequently, a greater number of acid groups will be exposed and the surface charge densities due to acidic groups is supposed to increase.

**Table II** Surface Charge Density ( $\sigma$ ) of PMD-fixed P(St/AA) Latex

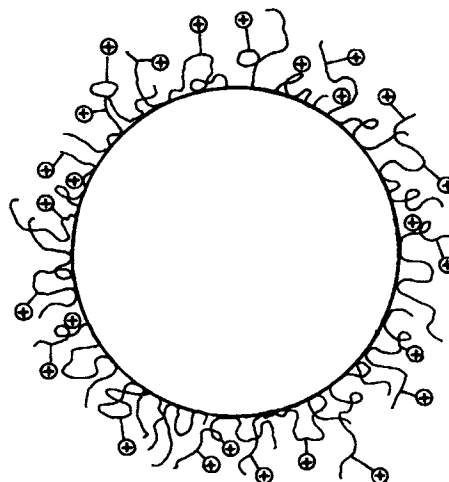
| Latex                 | Surface Charge Density<br>( $\mu\text{C}/\text{m}^2$ ) $\times 10^{-4}$ |                           |
|-----------------------|---|---------------------------|
|                       | $\sigma_{\text{acidic}}$  | $\sigma_{-\text{NH}_3^+}$ |
| L(ETD <sub>10</sub> ) | 19.7  | 16.5                      |
| L(TMD <sub>10</sub> ) | 20.1  | 16.4                      |
| L(HMD <sub>1</sub> )  | 22.1  | 18.9                      |
| L(HMD <sub>6</sub> )  | 21.9  | 19.9                      |
| L(HMD <sub>10</sub> ) | 26.6  | 22.9                      |
| L(OMD <sub>10</sub> ) | 27.0  | 24.4                      |



**Figure 3**  $\zeta$ -Potential and flocculation rate constant of L(HMD) latex as a function of pH (ionic strength  $1 \times 10^{-3}$ ).



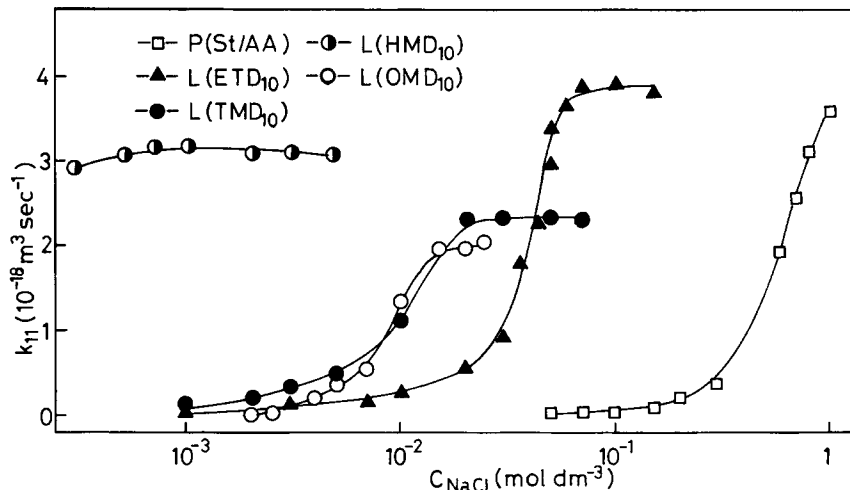
**Figure 4**  $\zeta$ -Potential and flocculation rate constant of PMD-fixed latices as a function of pH (ionic strength  $1 \times 10^{-3}$ ).



**Figure 5** Schematic representation of PMD-fixed latex.

Figure 3 shows the flocculation rate constants ( $k_{11}$ ) and the  $\zeta$ -potential of L(HMD<sub>x</sub>) ( $x = 1, 5, 10$ ) latices as a function of pH. The  $\zeta$ -potential of P(St/AA) latex is negative at all pH tested. On the other hand, L(HMD<sub>x</sub>) latices have isoelectric points at pH 4–5. The HMD-fixed latex is obviously amphoteric. The point that the  $k_{11}$  of HMD-fixed P(St/AA) latices give the maximum values at pH 5.5–6.5 indicates that HMD-fixed latices are colloiddally unstable at neutral pH. The pH where the  $k_{11}$  give the maximum values is slightly higher than the isoelectric point and shifts to acidic pH with increasing HMD concentration.

Figure 4 shows the flocculation rate constants ( $k_{11}$ ) and the  $\zeta$ -potential of PMD-fixed latices as a function of pH. The PMD-fixed latices have the isoelectric points at the neutral pH region. The isoelectric points shift to acidic pH with increasing methylene chain length. This could be attributed to the stronger adsorption at the particle surface of the longer methylene chains, leading to a steric hindrance of the amino groups toward protons. The PMD-fixed latices flocculate in the region of pH 5–7. In general, the maximum flocculation rate of amphoteric latex is observed at the isoelectric point of the latex.<sup>11</sup> However, the pH where the maximum flocculation rates of the PMD-fixed latices were observed are slightly higher than the isoelectric points. The slight difference between the isoelectric points and the pH where the flocculation rates are maximum indicates the influence of the expansion of the PMD-fixed polymer layer surrounding the particles on the flocculation in addition to the electrostatic repulsion between latex particles. The PMD-fixed



**Figure 6** Flocculation rate constant of PMD-fixed latex as a function of NaCl concentration at pH 5.7.

P(St/AA) latex particle is schematically represented in Figure 5. However, the flocculation mechanism is not clear in this work.

Figure 6 shows the flocculation rate constants of PMD-fixed latices as a function of NaCl concentration at pH 5.7. The flocculations of L(ETD<sub>10</sub>), L(TMD<sub>10</sub>), and L(OMD<sub>10</sub>) latices were observed at about  $5 \times 10^{-3}$  mol dm<sup>-3</sup> NaCl, and the flocculation rate increases with increasing NaCl concentration. The flocculation rate is supposed to increase with increasing NaCl concentration since the electrical double layer surrounding the latex particle is compressed. The L(HMD<sub>10</sub>) latex flocculates even at very low NaCl concentration because the pH tested is in the vicinity of the isoelectric point of the latex.

The results on flocculation of PMD-fixed latices, on the whole, indicate that the introduction of PMD into the surface of P(St/AA) latex lowers the dispersion stability for high electrolyte concentration.

## CONCLUSION

Polymethylenediamine (PMD)-fixed P(St/AA) latices are amphoteric and the isoelectric points are at pH 4–7. The surface charge densities due to amino groups slightly increase with increasing methylene

chain length. The fixation of PMD to the surface of P(St/AA) latex lowers the dispersion stability for high electrolyte concentration.

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