

## Method for the Determination of Surface Basic Groups in Cationic Polystyrene Latexes

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### Synopsis

The method for the determination of basic groups chemically bound to the surface of particles (surface basic groups) in cationic polystyrene latexes has been investigated. It is clarified that surface basic groups such as amidino groups resulting from 2,2'-azobis(2-amidinopropane) hydrochloride used as initiator and amino groups resulting from dimethyl aminoethyl methacrylate copolymerized can be determined accurately by the following method. First, latexes are cleaned and surface basic groups are converted into unneutralized form by ion exchange; then, latexes are titrated conductometrically with strong acid. By this method, however, surface amidino groups and surface amino groups cannot be determined separately.

### INTRODUCTION

The authors have recently investigated the preparation of cationic polystyrene latexes in the absence of soaps and clarified that stable latexes can be obtained by two processes, that is, by using a cationic initiator such as 2,2'-azobis(2-amidinopropane) hydrochloride (AAP) (initiator process) or by copolymerizing cationic monomers such as dialkyl aminoethyl methacrylates (copolymerization process).<sup>1</sup> The stability of these latexes may be attributed to basic groups chemically bound to the surface of particles (surface basic groups) such as amidino groups resulting from AAP and amino groups resulting from dialkyl aminoethyl methacrylates. It is of interest to determine surface basic groups in these latexes. It seems, however, that the method for the determination of surface basic groups has not previously been established.

On the other hand, the method for the determination of surface groups in anionic latexes has already been established. It has been demonstrated that surface carboxyl groups in carboxylated latexes<sup>2,3,4</sup> and surface sulfate groups in polystyrene latexes<sup>3,5,6,7</sup> prepared by using potassium persulfate as initiator can be determined accurately by conductometric titration after ion exchange. This method seems to be applicable also to the determination of surface basic groups in cationic latexes.

In this paper, the authors attempted to establish the method for the determination of surface basic groups in the above-described cationic polystyrene latexes.

TABLE I  
Polymerization Recipe and Properties of Cationic Polystyrene Latexes

Latex	Polymerization recipe, g					Properties of latex	
	Water	St	DM <sup>a</sup>	DPC	AAP	pH	Particle diameter, $\mu$
S-1482	100	27.27	0.00	0.50	1.00	4.61	0.078
S-1486	100	24.47	2.80	1.00	1.00	3.09	0.096

<sup>a</sup> Neutralized with HCl.

## EXPERIMENTAL

### Materials

Water, dimethyl aminoethyl methacrylate (DM), AAP, dodecyl pyridinium chloride (DPC), and poly(oxyethylene nonylphenyl ether) (PNE) have been described in the previous paper.<sup>1</sup> CP-grade ethylenediamine (EDA) and tetraethylenepentamine (TEPA) were used.

As ion exchange resins, quaternary ammonium resin (IRA-402; Rohm & Haas Co., Ltd.) and sulfonic acid resin (IR-120B; Rohm & Haas Co., Ltd.) were used after purification by the method described by Vanderhoff et al.<sup>8</sup> The exchange capacities of these resins were 0.85 meq/g (wet) and 1.85 meq/g (wet) for IRA-402 and IR-120B, respectively.

Cationic polystyrene latexes have been described in detail in the previous paper.<sup>1</sup> The polymerization recipe and properties of these latexes are shown in Table I.

### Procedures

The particle diameter was determined as number-average by electron microscopy.

The ion exchange of the latexes was carried out as follows using the batchwise procedure reported by Vanderhoff et al.<sup>8</sup> A latex diluted to the solids content of about 0.5–5% (wt) and stabilized, if necessary, by the introduction of PNE was mixed with an excess amount of ion exchange resins and stirred until constant pH and conductance were observed. After that, the latex was filtered and the solids content determined gravimetrically.

The potentiometric and conductometric titrations of purified latexes and model compounds were performed at room temperature by monitoring pH and conductance. Aqueous solutions of hydrogen chloride, *N*/10 and *N*/100, were used as titrant.

## RESULTS AND DISCUSSION

### Determination of Basic Groups in Model Compounds

The cationic polystyrene latexes in Table I are believed to contain two types of surface basic groups such as amidino groups resulting from AAP and amino groups resulting from DM, which are represented by the following formulas:

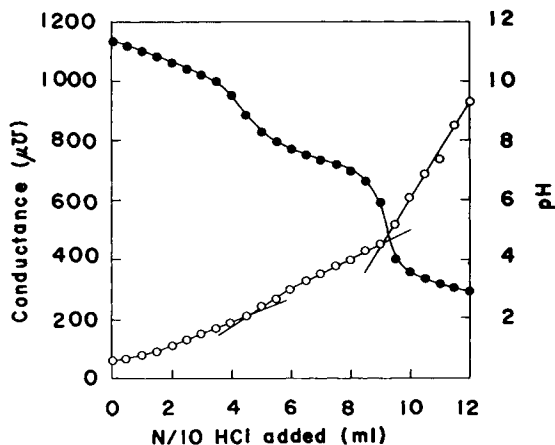


Fig. 1. Potentiometric and conductometric titration curves of EDA: (O) conductance; (●) pH.

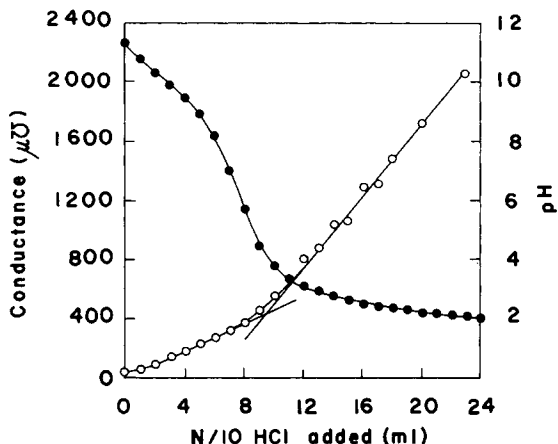
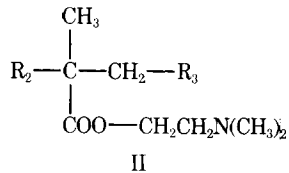
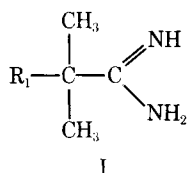


Fig. 2. Potentiometric and conductometric titration curves of TEPA: (O) conductance; (●) pH.



where  $R_1$ ,  $R_2$ , and  $R_3$  are polymer chains. Although the basicity of these surface basic groups cannot be determined definitely,  $pK_a$  values of their homologous model compounds such as acetamidine, N,N-dimethylethylamine, and ethanolamine are reported<sup>9,10,11</sup> to be 12.40, 9.99, and 9.5, respectively. This indicates that these surface basic groups function as weak bases. Therefore, the determination of weak base by potentiometric and conductometric titration<sup>10</sup> was investigated, using water-soluble amines as model compounds.

The titration curves of EDA and TEPA with the aqueous solution of hydrogen chloride are shown in Figures 1 and 2. Figure 1 shows that EDA gives two

TABLE II  
Effect of PNE on Determination of Amino Groups in EDA<sup>a</sup>

Equivalence point	Volume of <i>N</i> /10 HCl, ml	
	Theoretical	Observed
First	4.53	4.45
Second	9.06	9.15

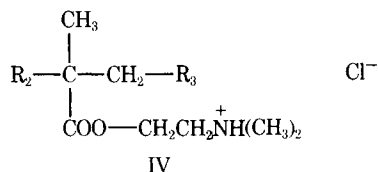
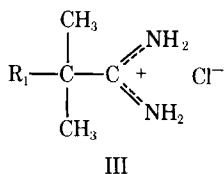
<sup>a</sup> Concentration of PNE is 0.31 g/l.

equivalence points which correspond to two amino groups in the molecule, whereas Figure 2 shows that TEPA gives only one equivalence point which corresponds to all the amino groups in the molecule. On the other hand, since surface basic groups are chemically bound to the surface of particles and adjacent to each other, they will function as polyamine. This indicates that cationic polystyrene latexes in Table I show at most two equivalence points corresponding to surface amidino groups and surface amino groups.

Next, the effect of nonionic soap PNE which is introduced to avoid the reversible coagulation<sup>1</sup> of latex through ion exchange was investigated. Amino groups in EDA were determined in the presence of PNE by conductometric titration, and the result is shown in Table II. It is apparent from Table II that PNE has little effect on the determination of amino groups, and this may also be the case for amidino groups.

### Ion Exchange of Latexes

The surface basic groups in cationic polystyrene latexes in Table I have already been represented by formulas I and II. In practice, however, these surface basic groups are at least partially neutralized by hydrogen chloride and dissociate to form cations represented by the following formulas:<sup>12</sup>



where  $\text{R}_1$ ,  $\text{R}_2$ , and  $\text{R}_3$  are polymer chains. Therefore, these surface basic groups must be converted to unneutralized form prior to the determination by conductometric titration. Further, these latexes contain low molecular weight compounds such as cationic soap DPC, unreacted cationic initiator AAP, and unreacted cationic monomer DM, which must affect the determination of the surface basic groups. In this section the removal of low molecular weight com-

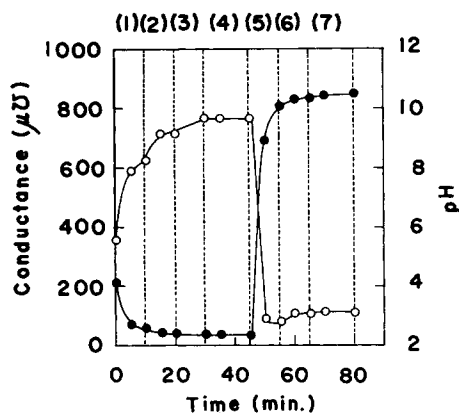


Fig. 3. Ion exchange behavior of cationic polystyrene latex S-1486: (O) conductance; (●) pH. Amount of solids in the latex is 1.06 g; amount of ion exchange resins added is as follows: (1) IR-120B, 3.31 g; (2) IR-120B, 2.77 g; (3) IR-120B, 1.82 g; (4) IR-120B, 2.12 g; (5) IRA-402, 2.55 g; (6) IRA-402, 2.03 g; (7) IR-120B, 1.54 g, and IRA-402, 1.36 g.

pounds and the conversion of surface basic groups into unneutralized form with ion exchange were investigated.

The aqueous solutions of DPC, AAP, and DM, the concentrations of which are 35.3, 36.9, and 44.6 mmole/l., respectively, were ion exchanged with the excess amount of ion exchange resins and filtered. The filtrates exhibited the same pH and conductance as pure water, and no basic species was found by conductometric titration with the aqueous solution of hydrogen chloride. This indicates that these low molecular weight compounds can be completely removed by ion exchange.

The ion exchange of the cationic polystyrene latex in Table I was investigated. Ion exchange was carried out in the following order to avoid the precipitation of above-described low molecular weight compounds. First, IR-120B, then IRA-402 was added stepwise until constant pH and conductance were observed. After that, IR-120B and IRA-402 were added simultaneously until constant pH and conductance were observed. A typical ion exchange behavior is shown in Figure 3. It is apparent from this figure that the ion exchange has been completed within 60 minutes in the sixth step, where the total amount of ion exchange resins added reaches to about 4–10 times that of solids in the latex. The fairly high pH at the end of the ion exchange indicates that surface basic groups have been converted to unneutralized forms. Cationic polystyrene latexes with low concentrations of surface basic groups show reversible coagulation<sup>1</sup> through ion

TABLE III  
Effect of Ion Exchange on Number-Average Particle Diameter and Coefficient of Variation of Particle Diameter of Cationic Polystyrene Latex S-1486

Latex	Particle diameter, $\mu$	Coefficient of variation, %
Original	0.096	9.8
Ion exchanged	0.099	10.6

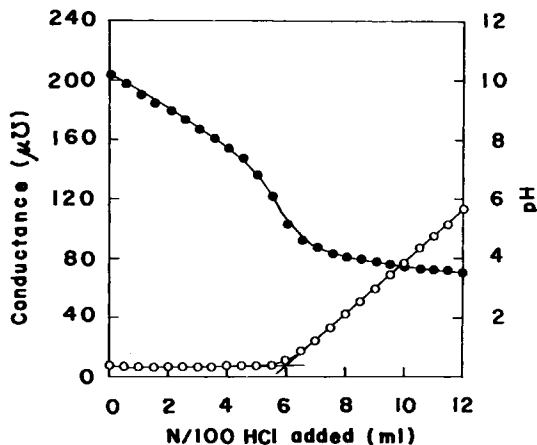


Fig. 4. Potentiometric and conductometric titration curves of ion-exchanged cationic polystyrene latex S-1482: (○) conductance; (●) pH.

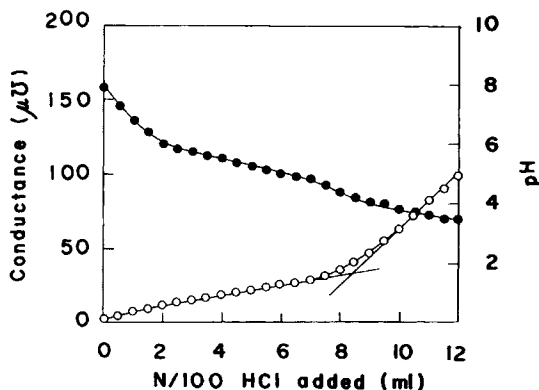


Fig. 5. Potentiometric and conductometric titration curves of ion-exchanged cationic polystyrene latex S-1486: (○) conductance; (●) pH.

exchange, which prevents the following filtration and titration. This may be ascribed to the poorer stability of particles with unneutralized surface basic groups than that of particles with neutralized surface basic groups. These latexes must be stabilized prior to ion exchange by the introduction of nonionic soap PNE of about 2–15% (wt) to total solids.

Further, the fractionation of particles with ion exchange<sup>13</sup> which may affect the determination of surface basic groups was investigated. In Table III the number-average particle diameter and particle diameter distribution of a cationic polystyrene latex before and after the ion exchange are shown. It is apparent from Table III that the ion exchange causes little fractionation of particles and does not affect the determination of surface basic groups.

#### Determination of Surface Basic Groups

Typical potentiometric and conductometric titration curves of the ion-exchanged cationic polystyrene latexes in Table I are shown in Figures 4 and 5. Since the latex in Figure 4 contains only amidino groups as surface basic groups,

TABLE IV  
Accuracy of Determination of Surface Basic Groups in Cationic Polystyrene Latexes

Latex	Ion exchange		Concentration of surface basic groups, meq/g <sup>b</sup>	
	Concentration of PNE, wt-% <sup>a</sup>	Reversible coagulation	Observed value	Mean value
S-1482	9.5	not observed	0.041	0.039
	9.3	not observed	0.038	
	9.3	not observed	0.038	
S-1486	0.0	observed	0.547	0.543
	1.9	observed	0.563	
	4.9	not observed	0.520	

<sup>a</sup> Concentration of PNE to total solids in the latex.

<sup>b</sup> Milliequivalents of surface basic groups found per 1 g polymer.

the equivalence point in Figure 4 corresponds to surface amidino groups. On the other hand, although the latex in Figure 5 contains both amidino groups and amino groups as surface basic groups, Figure 5 shows only one equivalence point corresponding to both surface amidino groups and surface amino groups. This means that separate determination of both groups is impossible by this method.

In Table IV the reproducibility of the determination of surface basic groups in cationic polystyrene latexes in Table I based on the above-described procedure are shown. From Table IV it is clear that the concentration of surface basic groups in these latexes can be determined within an error of  $\pm 5\%$ . It is particularly interesting that the reversible coagulation<sup>1</sup> observed during ion exchange does not affect the determination of surface basic groups. This indicates that the coagulation is literally reversible and particles can easily be dispersed with the neutralization of surface basic groups which enhances the stability of particles.

## CONCLUSIONS

Surface basic groups such as amidino groups resulting from AAP and amino groups resulting from DM in cationic polystyrene latexes can be determined accurately by the following method. First, the latexes are cleaned and surface basic groups are converted to unneutralized form by ion exchange; then, the latexes are titrated conductometrically with strong acid. Although latexes with low concentration of surface basic groups cause reversible coagulation through ion exchange, addition of a small amount of the nonionic soap PNE effectively avoids this trouble.

Since both surface amidino groups and surface amino groups function as weak bases, they cannot be determined separately by this method. It seems that a more detailed investigation is necessary to settle this difficulty.

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