

## Electrolyte Stability of Carboxylated Latexes Prepared by Several Polymerization Processes

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### Synopsis

Carboxylated isoprene/styrene copolymer or polystyrene latexes have been prepared by several polymerization processes. The density of carboxyl groups chemically bound to the surface of particles (surface carboxyl groups), and the electrolyte stability of these carboxylated latexes was determined to elucidate the relationship between them. The critical coagulation concentration (CCC), which represents the electrolyte stability of latex, decreases considerably with increasing valency of the cation, as expected from theory. The CCC increases remarkably with increase in the density of surface carboxyl groups or increase in the degree of neutralization of surface carboxyl groups. The electrolyte stability of these carboxylated latexes seems to be governed substantially by the density of carboxylate ions on the surface of particles irrespective of the polymerization process or the composition of polymers in the interior of particles.

### INTRODUCTION

Carboxylated latexes stabilized with chemically bound carboxyl groups are excellent in mechanical stability,<sup>1,2</sup> freeze-thaw stability,<sup>3</sup> and electrolyte stability<sup>4</sup> compared with latexes stabilized only with physically adsorbed soaps. Among these properties, the last one, which is closely related to the compatibility with pigments containing polyvalent ions,<sup>5,6</sup> seems to be of great practical value. Recently, Greene et al.<sup>4,7</sup> have demonstrated that the electrolyte stability of carboxylated butadiene/styrene copolymer latexes can be determined by the measurement of the coagulation rate.

In previous papers,<sup>8,9</sup> the authors have demonstrated that stable carboxylated isoprene/styrene copolymer or polystyrene latexes can be obtained in the absence or presence of soaps by several polymerization processes. It was clarified that the density of carboxyl groups chemically bound to the surface of particles (surface carboxyl groups) as well as the size and uniformity of particles are greatly dependent on the polymerization process. It seems to be of great interest to elucidate the relationship between the electrolyte stability and the density of surface carboxyl groups of the carboxylated latexes obtained by different polymerization processes.

In the present paper, the electrolyte stability of the above-described carboxylated latexes has been determined by the method of Greene et al. to elucidate the relationship between the electrolyte stability and the density of surface carboxyl groups.

## EXPERIMENTAL

### Materials

The monomers isoprene (IP), styrene (St), acrylic acid (AA), and methacrylic acid (MAA) used for preparation of the latexes have been described in a previous paper.<sup>8</sup> The soaps sodium dodecylbenzene sulfonate (SDBS), sodium poly(oxyethylene) nonylphenyl sulfate [average number of moles of ethylene oxide per one molecule is 10—POE(10)], and sodium dodecyl sulfate (SDS) used for preparation of the latexes have been described in the previous papers.<sup>8,9</sup> Potassium chloride (KCl), potassium persulfate (KPS), sodium hydroxide (NaOH), sodium hydrogen carbonate (NaHCO<sub>3</sub>), and *tert*-dodecyl mercaptan (*t*-DDM) used for preparation of the latexes have also been described in the previous papers.<sup>8,9</sup>

Deionized water and extrapure-grade sodium chloride (NaCl), barium chloride–water (1/2) (BaCl<sub>2</sub>), and lanthanum chloride–water (1/7) (LaCl<sub>3</sub>) were used for the determination of the electrolyte stability of the latexes.

### Preparation of the Latexes

The latexes were prepared by three polymerization processes, that is, the initial-charge process, the shot process, and the soap-free process.

In the initial-charge process, IP and St were copolymerized with the carboxylic monomer in the presence of soaps, and the polymerization was substantially completed.

The shot process is composed of three steps. In step 1, IP and St were copolymerized in the presence of soaps to a conversion of 60–70%. In step 2, the latex was stabilized with an additional amount of soaps; and in step 3, the mixture of the carboxylic monomer and St was introduced (shot) along with additional initiator at a conversion higher than 80%, and the polymerization was substantially completed.

In the soap-free process, St was copolymerized with the carboxylic monomer at a degree of neutralization of 0.80 in the presence of the slight amount of soaps, and the polymerization was substantially completed. In the case of the two-step polymerization, after the completion of the first step, the mixture of IP and St was introduced dropwise, and the polymerization was substantially completed.

Detailed procedures of these polymerization processes have been described in the previous papers.<sup>8,9</sup>

### Characterization of the Latexes

The particle diameter of the latexes was determined as number average by electron microscopy, after hardening the particles, if necessary, with osmium tetroxide.

The determination of surface carboxyl groups was performed by conductometric titration of the latex cleaned with ion-exchange as has been described in detail in the previous paper.<sup>8</sup> The distribution of carboxyl groups in particles was calculated as the ratio of equivalent of surface carboxyl groups found to total carboxyl groups charged as carboxylic monomers. The surface area occupied

by a surface carboxyl group was calculated by the following procedure and expressed in terms of square angstrom. First, the total surface area of particles per unit mass of polymers was calculated regarding the density of polymer as  $1 \text{ g/cm}^3$ . Next, the number of surface carboxyl groups per unit mass of polymers was calculated from the results of the determination of surface carboxyl groups. Then the surface area occupied by a surface carboxyl group was calculated dividing the former by the latter.

### Determination of Electrolyte Stability

The latexes were diluted for the measurement of the coagulation rate by the following procedure. First, the latex was ion exchanged, if necessary, by the method described in detail in the previous paper.<sup>8</sup> Next, the latex was diluted with water to a particle concentration of 0.01% (wt) and neutralized, if necessary, with sodium hydroxide. The degree of neutralization of surface carboxyl groups, defined as the ratio of equivalent of base to surface carboxyl groups, was calculated on the assumption that the base initially charged is not occluded in the interior of particles. The pH of the latex diluted to a particle concentration of 0.005% (wt) was measured at which the coagulation rate was measured.

The measurement of the coagulation rate was carried out as follows. The diluted latex was mixed with the aqueous solution of electrolyte to give a particle concentration of 0.005% (wt) and the prescribed concentration of electrolyte, and the change in optical density with time was recorded continuously. The measurement was made at  $25^\circ\text{C}$  on a Shimadzu-Kotaki 5D photoelectric colorimeter equipped with an optical cell 5 cm long using incident light with a wavelength of  $5461 \text{ \AA}$ . The coagulation rate was obtained from the initial slope of the optical density-time curve.<sup>4</sup> The critical coagulation concentration was determined from the relationship between the logarithms of the stability ratio calculated from the coagulation rate and the concentration of electrolyte as the point of intersection of the two linear parts.<sup>4,10</sup>

## RESULTS AND DISCUSSION

### Preparation and Characterization of the Latexes

The polymerization recipe and characterization results of the latexes obtained by the initial-charge process, the shot process, and the soap-free process are shown in Tables I, II, and III, respectively. It is apparent from the tables that the size and uniformity of particles are strongly dependent on the polymerization process, which suggests that the particle formation processes in these polymerization processes differ from one another. The coefficient of variation of particle diameter of the latexes obtained by the initial-charge process or the shot process is fairly large. In this case the formation of particles may be explained by the usual emulsion polymerization theory.<sup>11</sup> On the contrary, the coefficient of variation of particle diameter of the latexes obtained by the soap-free process is fairly small. This is consistent with the fact that in this case particles are formed by the precipitation of growing radicals formed in the aqueous phase and are uniform in size, as has been described in the previous paper.<sup>9</sup>

It is also apparent from Tables I, II, and III that the distribution of carboxyl

TABLE I  
Polymerization Recipe and Characterization Results of the Initial-Charge Process Latex<sup>a,b</sup>

Latex	Particle diameter, $\mu$	Coefficient of variation of particle diameter, %	Distribution of carboxyl groups, surface/total <sup>c</sup>	Surface area occupied by a surface carboxyl group, $\text{\AA}^2$
S-1061	0.102	10.5	0.131	128

<sup>a</sup> Data cited in part from ref. 8.

<sup>b</sup> Polymerization recipe, g: water/IP/St/MAA/POE(10)/KPS/KCl/t-DDM = 110/45/50/5/7/0.5/0.5/0.09.

<sup>c</sup> Ratio of equivalents of surface carboxyl groups to total carboxyl groups.

TABLE II  
Polymerization Recipe and Characterization Results of Shot Process Latexes<sup>a</sup>

Latex	Amount of AA or MAA, g <sup>b</sup>	Particle diameter, $\mu$	Coefficient of variation of particle diameter, %	Distribution of carboxyl groups, surface/total <sup>c</sup>	Surface area occupied by a surface carboxyl group, $\text{\AA}^2$
S-1105	AA 1.2	0.100	—	0.763	93.3
S-1113	AA 2.4	0.090	13.6	0.737	54.1
S-1100	AA 3.6	0.099	15.9	0.765	31.9
S-1102	MAA 2.8	0.100	16.7	0.698	51.7

<sup>a</sup> Data cited in part from ref. 8.

<sup>b</sup> Polymerization recipe, g: step 1, water/IP/St/POE(10)/SDBS/KPS/NaOH/t-DDM = 120/48/62.4/1.7/2.4/0.6/0.2/0.3; step 2, water/POE(10)/SDBS = 20/0.57/0.8; step 3, water/St/AA or MAA/KPS = 10/7.2/variable/0.6.

<sup>c</sup> Ratio of equivalents of surface carboxyl groups to total carboxyl groups.

TABLE III  
Polymerization Recipe and Characterization Results of the Soap-Free Process Latexes

Latex	Polymerization recipe <sup>a</sup>	Particle diameter, $\mu$	Coefficient of variation of particle diameter, %	Distribution of carboxyl groups, surface/total <sup>b</sup>	Surface area occupied by a surface carboxyl group, $\text{\AA}^2$
S-1372	A	0.236	5.4	0.292	20.0
S-1180	B	0.244	3.8	0.294	19.2

<sup>a</sup> A, g: step 1, water/St/AA/NaHCO<sub>3</sub>/SDS/KPS = 100/9.09/5/4.66/0.05/1.32; step 2, IP/St = 40.2/41.8; B, g: water/St/AA/NaHCO<sub>3</sub>/SDS/KPS = 100/90.9/5/4.66/0.05/1.32.

<sup>b</sup> Ratio of equivalents of surface carboxyl groups to total carboxyl groups.

groups in particles as well as the density of surface carboxyl groups are strongly dependent on the polymerization process. The initial-charge process localizes only approximately 13% of total carboxyl groups on the surface of particles, whereas the shot process localizes more than 70% of total carboxyl groups on the surface of particles irrespective of the amount and species of the carboxylic

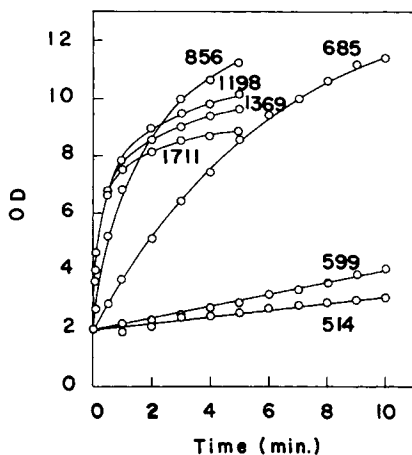


Fig. 1. Change in optical density-time curve of ion-exchanged shot process latex S-1113 with concentration of electrolyte:  $OD = \text{optical density, } \times 10^{-2}$ . Figures on curves indicate concentration of sodium chloride in mmole/l.

monomer, which means that the method of introduction of the carboxylic monomer has a considerable effect on the distribution of carboxyl groups in particles.<sup>8</sup> The soap-free process localizes approximately 29% of carboxyl groups on the surface of particles. Consequently, it may be concluded that the shot process is the most effective in localizing carboxyl groups on the surface of particles.

The change in density of surface carboxyl groups with the polymerization process is as follows. The surface area occupied by a surface carboxyl group is larger than  $100 \text{ \AA}^2$  for the initial-charge process latex and in the range of about  $30\text{--}90 \text{ \AA}^2$  for the shot process latexes. On the contrary, the surface area occupied by a surface carboxyl group for the soap-free process latexes is only approximately  $20 \text{ \AA}^2$ , which is much smaller than the molecular area of  $48 \text{ \AA}^2$  reported for SDS on the surface of particles in a polystyrene latex.<sup>12</sup> Consequently, it may be concluded that the soap-free process is the most effective to enhance the density of surface carboxyl groups.

#### Method for the Determination of Electrolyte Stability

The applicability of the method for the determination of the electrolyte stability proposed by Greene et al.<sup>4</sup> to the latexes described in the previous section was investigated. The change of the optical density-time curve of the ion-exchanged shot process latex with the concentration of electrolyte is shown in Figure 1. It is apparent from this figure that at the initial stage of the coagulation the curve is linear irrespective of the concentration of electrolyte, which indicates that the reaction occurring is bimolecular, as expected from theory.<sup>13</sup> In this case, the initial slope of the curve is directly proportional to the coagulation rate or inversely proportional to the stability ratio.<sup>10</sup> It is also apparent from Figure 1 that with increase in concentration of electrolyte, the initial slope of the curve increases until a maximum slope is reached which is independent of electrolyte concentration.

The relationship between the logarithms of the stability ratio and the electrolyte concentration obtained from Figure 1 is represented by the left-hand

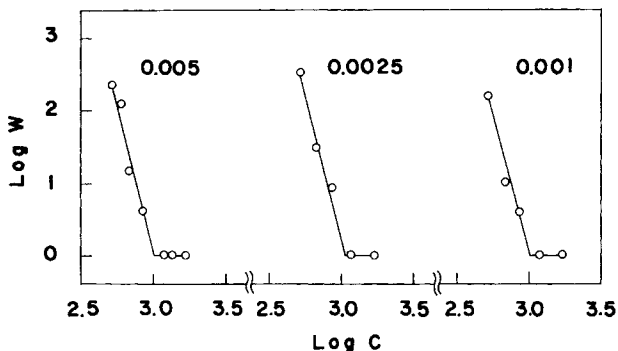


Fig. 2. Relationship between logarithms of the stability ratio and the concentration of electrolyte for ion-exchanged shot process latex S-1113 at various particle concentrations:  $W$  = stability ratio;  $C$  = concentration of sodium chloride, mmole/l. Figures on curves indicate concentration of particles in % (wt).

curve in Figure 2. It is apparent that the curve consists of two approximately linear parts, as expected from theory.<sup>10</sup> In the first part, the stability of the latex decreases rapidly with increase in concentration of electrolyte, whereas in the second part, it is independent of electrolyte concentration. The point of intersection of the two linear parts corresponds to the transition from the region of slow coagulation to that of rapid coagulation. Consequently, the critical coagulation concentration ( $CCC$ ) which represents the electrolyte stability of the latex can be obtained from the point of intersection of the two linear parts.<sup>4</sup>

Figure 2 shows the effect of the concentration of particles on the relationship between the logarithms of the stability ratio and the concentration of electrolyte. The constancy of the slopes of the curves in Figure 2 indicates that the relative coagulation rate of the latex is virtually independent of the concentration of particles. The  $CCC$  values obtained from Figure 2 are 1000 mmole/l., 1070 mmole/l., and 1020 mmole/l. for the concentrations of particles of 0.005% (wt), 0.0025% (wt), and 0.001% (wt), respectively. The differences between them are small enough to fall within the experimental error.

Almost similar results were obtained for both the initial-charge process latex and the soap-free process latexes. Consequently, it may be concluded that the electrolyte stability of the latexes described in the previous section can be determined by the above-described procedure.

### Electrolyte Stability of the Latexes

The electrolyte stability of the initial-charge process latex was examined, and the results are shown in Table IV. It is apparent from Table IV that the  $CCC$  for sodium chloride decreases considerably with ion exchange. This may be attributed to the removal of soaps, which are adsorbed on the surface of particles and enhance the stability of latex, with ion exchange. It is also apparent from Table IV that the  $CCC$  of the ion-exchanged latex is strongly dependent on the valency of the electrolyte cation. Table V shows the relationship between the cation valency and the relative value of the  $CCC$ . Table V shows that the  $CCC$  observed is approximately proportional to the inverse sixth power of the cation valency, as expected from theory.<sup>4,14</sup>

TABLE IV  
Electrolyte Stability of Initial-Charge Process Latex

Latex	Measurement conditions		Electrolyte stability	
	Degree of neutralization <sup>a</sup>	pH <sup>b</sup>	Electrolyte	CCC, mmole/l.
S-1061 (original)	0.00	5.2	NaCl	1180
S-1061 (ion exchanged)	0.00	5.3	NaCl	347
			BaCl <sub>2</sub>	20.0
			LaCl <sub>3</sub>	0.381

<sup>a</sup> Degree of neutralization of surface carboxyl groups.

<sup>b</sup> Observed pH for latex diluted to a particle concentration of 0.005% (wt).

TABLE V  
Relationship Between Cation Valency and Relative CCC Value

Cation valency	Relative value of CCC	
	Observed <sup>a</sup>	Theoretical
1	1	1
2	0.058	0.016
3	0.0011	0.0014

<sup>a</sup> Calculated from data in Table IV.

The electrolyte stability of the shot process latexes was examined, and the results are shown in Table VI. It is apparent from Table VI that the CCC of latex S-1113 for sodium chloride decreases remarkably with ion exchange. This may be attributed to the conversion of surface carboxyl groups from the partially neutralized form to the unneutralized form with ion exchange, which is believed to reduce the stability of latex as will be described below as well as the removal of soaps with ion exchange described above. It is also apparent from Table VI that the CCC of the ion-exchanged latex S-1113 decreases remarkably with increasing cation valency. In this case, however, the relationship between the cation valency and the relative value of the CCC is not closely consistent with that expected from theory.<sup>4,14</sup>

It is clear from Table VI, in comparison with Table II, that the CCC of the ion-exchanged shot-process latexes for sodium chloride increases remarkably with decrease in the surface area occupied by a surface carboxyl group, irrespective of the amount and species of the carboxylic monomer. This may indicate that the stability of carboxylated latex is substantially governed by the density of carboxylate ions on the surface of particles.<sup>4</sup> In this case, however, the density of carboxylate ions on the surface of particles does not seem to be proportional to the density of surface carboxyl groups because it has been demonstrated by Vanderhoff et al.<sup>12</sup> that the apparent degree of dissociation of surface sulfate groups, which are much stronger in acidity than surface carboxyl groups, is dependent on the density of these surface sulfate groups and is in the range of 0.05 to 0.39.

To confirm the above considerations, the effect of the degree of neutralization of surface carboxyl groups on the electrolyte stability of latex was examined.

TABLE VI  
Electrolyte Stability of Shot Process Latexes

Latex	Measurement condition		Electrolyte stability	
	Degree of neutralization <sup>a</sup>	pH <sup>b</sup>	Electrolyte	CCC, mmole/l.
S-1105 (ion exchanged)	0.00	5.6	NaCl	700
S-1113 (original)	0.20	5.3	NaCl	1870
S-1113 (ion exchanged)	0.00	5.3	NaCl	1000
			BaCl <sub>2</sub>	9.34
			LaCl <sub>3</sub>	0.132
	0.20	6.0	NaCl	1090
	0.50	6.4	NaCl	1170
	1.00	7.0	NaCl	1410
S-1100 (ion exchanged)	0.00	5.6	NaCl	2225 <sup>c</sup>
S-1102 (ion exchanged)	0.00	5.6	NaCl	955

<sup>a</sup> Degree of neutralization of surface carboxyl groups.

<sup>b</sup> Observed pH for latex diluted to a particle concentration of 0.005% (wt).

<sup>c</sup> Larger than 2225 mmole/l.

Figure 3 shows the change of the optical density–time curve of the ion-exchanged shot process latex with the degree of neutralization of surface carboxyl groups. The figure shows that the coagulation rate decreases remarkably with increasing degree of neutralization. As shown in Table VI, the CCC also increases remarkably with increasing degree of neutralization of the surface carboxyl groups. It has been demonstrated by some workers<sup>15,16</sup> that surface carboxyl groups have an apparent  $pK_a$  in the range of about 4.0–4.6, which means that the degree of dissociation of surface carboxyl groups is approximately consistent with their degree of neutralization.<sup>17</sup> Consequently, in this case, it may be concluded that

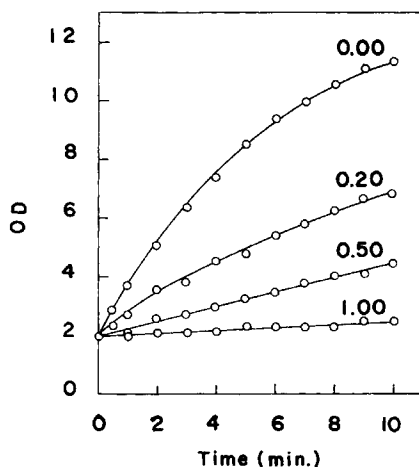


Fig. 3. Change in optical density–time curve of ion-exchanged shot process latex S-1113 with degree of neutralization of surface carboxyl groups: concentration of sodium chloride = 685 mmole/l. Figures on curves indicate degree of neutralization of surface carboxyl groups.



TABLE VII  
Electrolyte Stability of Soap-Free Process Latexes

Latex	Measurement condition		Electrolyte stability	
	Degree of neutralization <sup>a</sup>	pH <sup>b</sup>	Electrolyte	CCC, mmole/l.
S-1372 (original)	0.80	6.2	NaCl	1711 <sup>c</sup>
S-1372 (ion exchanged)	0.00	5.6	BaCl <sub>2</sub>	9.12
			NaCl	1711 <sup>c</sup>
			BaCl <sub>2</sub>	11.3
S-1180 (original)	0.80	6.4	LaCl <sub>3</sub>	0.151
			NaCl	1711 <sup>c</sup>
S-1180 (ion exchanged)	0.00	5.6	NaCl	1711 <sup>c</sup>
			BaCl <sub>2</sub>	11.5

<sup>a</sup> Degree of neutralization of surface carboxyl groups.

<sup>b</sup> Observed pH for latex diluted to a particle concentration of 0.005% (wt).

<sup>c</sup> Larger than 1711 mmole/l.

the stability of carboxylated latex is substantially governed by the density of carboxylate ions on the surface of particles.

The electrolyte stability of the soap-free process latexes was examined, and the results are shown in Table VII. It is apparent from Table VII that the CCC for sodium chloride or barium chloride does not show any substantial change with ion exchange, which is consistent with the fact that the soap-free process latexes do not contain appreciable amounts of soap. It is also apparent from Table VII that the CCC of the ion-exchanged latex S-1372 decreases remarkably with increasing cation valency. Also, in this case the relationship between the cation valency and the relative value of the CCC is not closely consistent with that expected from theory.<sup>4,14</sup>

It is clear from Table VII, in comparison with Table III, that the ion-exchanged soap-free process latexes which have approximately the same particle diameter and density of surface carboxyl groups show approximately the same CCC for barium chloride, in spite of the difference in the composition of polymers in the interior of the particles. This indicates that the Hamaker constant of polystyrene is not so much different from that of isoprene/styrene copolymer because it is expected from theory<sup>4,14</sup> that the CCC is inversely proportional to the square of the Hamaker constant. At the present stage, however, further discussion is difficult.

The results in Tables IV, VI, and VII show that, in general, the electrolyte stability of the latexes obtained by the initial-charge process, the shot process, and the soap-free process increases in this order, which corresponds to the increase in the density of surface carboxyl groups.

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