

Polymerization Behavior and Distribution of Carboxyl Groups in Preparation of Soap-Free Carboxylated Polystyrene Latexes

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Synopsis

Soap-free carboxylated polystyrene latexes have been prepared by copolymerizing acrylic acid (AA) in a wide range of the degree of neutralization using a slight amount of soap; and the distribution of carboxyl groups was investigated from the determination of carboxyl groups localized on the surface of particles (surface carboxyl groups). It appears that the degree of neutralization of AA or the amount of AA has a considerable effect on the rate of polymerization as well as the stability of the polymerization system. At a degree of neutralization of approximately 0.80, stable latexes are obtained at a sufficient rate of polymerization. It is also clarified that the distribution of carboxyl groups is governed substantially by the degree of neutralization of AA. At a degree of neutralization of 0.80, approximately 30% of the total carboxyl groups are localized on the surface of particles. The amount of AA or the particle diameter seems to have little effect on the distribution of carboxyl groups.

INTRODUCTION

Carboxylated latexes that are of importance in industrial use are, in general, prepared by copolymerizing carboxylic monomers.¹ It seems that the properties of these latexes are greatly dependent on the distribution of carboxyl groups in the particles because these latexes are stabilized substantially with carboxyl groups chemically bound to the particle surface (surface carboxyl groups).^{2,3,4} Some workers^{5,6,7,8} have demonstrated that the distribution of carboxyl groups in the preparation of carboxylated latexes is governed substantially by the hydrophilic nature of the carboxylic monomer, the concentration of the carboxylic monomer, and the degree of neutralization of the carboxylic monomer.

The authors⁹ have recently demonstrated that stable soap-free carboxylated polystyrene latexes can be obtained by copolymerizing carboxylic monomers at the appropriate degree of neutralization and that the distribution of carboxyl groups is dependent on the degree of neutralization of the carboxylic monomers. In the previous paper, however, a comprehensive interpretation of the distribution of carboxyl groups has not been achieved because of the presence of two kinds of carboxylic monomers and the poor stability of the polymerization system. In the present paper, soap-free carboxylated polystyrene latexes have been prepared using only acrylic acid (AA) as carboxylic monomer to elucidate the distribution of carboxyl groups more precisely.

EXPERIMENTAL

Materials

Deionized water was used. Extrapure-grade styrene (St) and AA were used after distillation under reduced pressure. Extrapure-grade sodium hydrogen carbonate (NaHCO_3), sodium dodecyl sulfate (SDS; Tokyo Chemical Industry Co., Ltd.), and potassium persulfate (KPS) were used without further purification.

Procedures

Preparation of latexes was carried out at 70°C in a 500-ml glass vessel equipped with a stirrer. The prescribed amounts of water, SDS, sodium hydrogen carbonate, AA, and St were placed in the reactor and heated to, and kept at, the polymerization temperature. Then, the prescribed amount of KPS dissolved in water was introduced. Polymerization was continued until it was substantially completed.

Conversions were determined gravimetrically. The rate of polymerization was calculated from the linear part of the conversion-time curves.

The particle diameter was determined as number average by electron microscopy. The number of particles in the polymerization system were calculated assuming the density of polymers to be 1 g/cm^3 .

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.¹⁰ The distribution of carboxyl groups was calculated as the ratio of equivalents of surface carboxyl groups found to total carboxyl groups charged as the carboxylic monomer. The surface area occupied by a surface carboxyl group was calculated by the following procedure and expressed in terms of square angstroms. First, the total surface area of particles per unit mass of polymer was calculated assuming the density of polymers to be 1 g/cm^3 . Next, the number of surface carboxyl groups per unit mass of polymer 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.

The concentration of SDS was calculated assuming the density of the aqueous phase in the polymerization system to be 1 g/cm^3 .

RESULTS AND DISCUSSION

Polymerization Behavior

A polymerization recipe was established as shown Table I based on that adopted in the previous paper.⁹ Polymerization was carried out in the range of the degree of neutralization of AA defined as the ratio of equivalents of sodium hydrogencarbonate to AA from 0.00 to 1.00. The concentration of SDS was maintained at 1.60 mmole/l. , which effectively enhances the rate of polymerization as will be described below.

Table II shows the effect of the degree of neutralization of AA on the polymerization behavior. It is apparent from Table II that the degree of neutral-

TABLE I
Polymerization Recipe

Ingredient	Amount, g
Water	100
St	90.9
AA	variable (0.5–5)
NaHCO ₃	variable (0–5.83)
SDS	variable (0–2)
KPS	1.32

TABLE II
Effect of Degree of Neutralization of Carboxylic Monomer
on Polymerization Behavior^a

Degree of neutralization of AA	Stability of polymerization system	Rate of polymerization, %/hr	Particle diameter, μ
0.00	poor (coagulated)	48.8	—
0.30	poor	34.8	0.308
0.50	poor	33.3	0.391
0.60	poor	32.9	0.393
0.70	poor	42.1	0.295
0.75	good	44.3	0.257
0.80	good	44.6	0.244
0.85	good	35.5	0.271
0.90	poor	12.8	0.422
1.00	poor	10.6	0.439

^a Polymerization recipe, g: water/St/AA/NaHCO₃/SDS/KPS = 100/90.9/5/variable/0.05/1.32.

ization strongly affects the stability of the polymerization system as follows: with increase in the degree of neutralization from lower than 0.75 via 0.75–0.85 to higher than 0.85, the stability of the polymerization system changes from poor via good to poor, respectively. The change in the rate of polymerization with degree of neutralization of AA can be described as shown Figure 1. Although

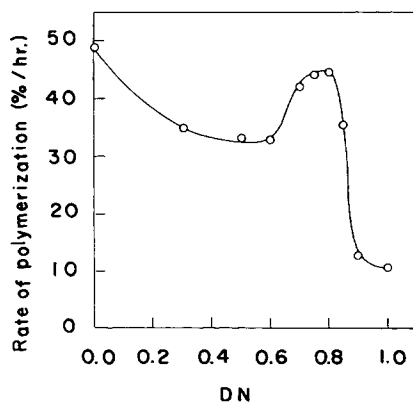


Fig. 1. Change in rate of polymerization with degree of neutralization of the carboxylic monomer: DN = degree of neutralization of AA.

TABLE III
Effect of Amount of Carboxylic Monomer on Polymerization Behavior^a

Amount of AA, g	Stability of polymerization system	Rate of polymerization, %/hr	Particle diameter, μ
0.50	poor	20.0	0.324
1.00	poor	19.5	0.325
2.50	good	19.6	0.273
3.75	good	37.2	0.264
4.50	good	36.9	0.261
5.00 ^b	good	44.6	0.244

^a Polymerization recipe, g: water/St/AA/NaHCO₃/SDS/KPS = 100/90.9/variable/variable/0.05/1.32.

^b Corresponds to seventh run in Table II.

the rate of polymerization decreases with increase in the degree of neutralization, it becomes maximum at a degree of neutralization of approximately 0.80. It is also apparent from Table II that the particle diameter changes remarkably with degree of neutralization, which means that the number of particles formed in the polymerization system is strongly dependent on the degree of neutralization.

At a degree of neutralization of AA of 0.80, which gives stable latexes at a sufficient rate of polymerization as described above, polymerization was carried out in the range of an amount of AA from 0.50 to 5.00 g. The concentration of SDS was maintained at 1.60 mmole/l. as described above. In Table III is shown the effect of the amount of AA on the polymerization behavior. Table III shows that the stability of the polymerization system is poor in the range of an amount of AA smaller than 2.50 g, whereas it is good in the range of an amount of AA larger than 2.50 g. It is apparent from Table III that with increasing amount of AA, the rate of polymerization increases. It is also apparent from Table III that the particle diameter decreases with increase in the amount of AA. This means that the number of particles formed in the polymerization system is dependent also on the amount of AA, which is believed to play an important role in the formation of particles.

Polymerization was carried out in a wide range of SDS concentrations. The degree of neutralization of AA was maintained at 0.80 as described above. The effect of the SDS concentration on the polymerization behavior is shown in Table IV. The stability of the polymerization system was good irrespective of the SDS concentration. It is apparent from Table IV that the rate of polymerization increases with increasing concentration of SDS from 0.000 to 1.60 mmole/l., remains almost constant with increasing SDS concentration from 1.60 to 31.8 mmole/l., and increases gradually with increasing SDS concentration from 31.8 to 63.0 mmole/l. This means that a concentration of SDS of 1.60 mmole/l. is appropriate to enhance the rate of polymerization effectively. In this case, the latex may virtually be defined as soap free because the amount of SDS relative to that of polymers is less than 0.06% (wt). Figure 2 shows the relationship between the logarithms of the rate of polymerization per particle and the particle diameter. The figure indicates that the rate of polymerization per particle is almost constant in the range of particle diameter from 0.215 to 0.240 μ , whereas

TABLE IV
Effect of Soap Concentration on Polymerization Behavior^a

Concentration of SDS, mmole/l.	Rate of polymerization, %/hr	Rate of polymerization per particle, $\times 10^{-15}\%/hr^b$	Particle diameter, μ
0.000	33.3	8.00	0.353
0.160	33.8	5.24	0.305
0.321	33.8	4.74	0.295
0.642	35.9	4.12	0.276
1.60 ^c	44.6	3.51	0.244
3.21	43.8	3.45	0.244
6.41	48.4	3.87	0.245
16.0	46.6	3.53	0.240
31.8	45.7	3.01	0.229
63.0	57.0	3.10	0.215

^a Polymerization recipe, g: water/St/AA/NaHCO₃/SDS/KPS = 100/90.9/5/4.66/variable/1.32.

^b Obtained dividing the rate of polymerization by the number of particles in the polymerization system.

^c Corresponds to seventh run in Table II.

it is proportional to the 2.5 power of the particle diameter in the range of particle diameter from 0.240 to 0.353 μ . This means that in a particle diameter range smaller than 0.240 μ , the polymerization proceeds according to the theory of emulsion polymerization,¹¹ whereas for a particle diameter larger than 0.240 μ , the polymerization rather proceeds according to the theory of bulk polymerization as reported by Vanderhoff et al.¹² However, the accuracy of the determination of the critical particle diameter or the slope may not be sufficient for a detailed discussion because the points in Figure 2 show some scatter.

The above-described results are somewhat similar to those obtained in the previous paper⁹ where two kinds of carboxylic monomers were used. Detailed discussions on the particle formation process which seems to be governed by the

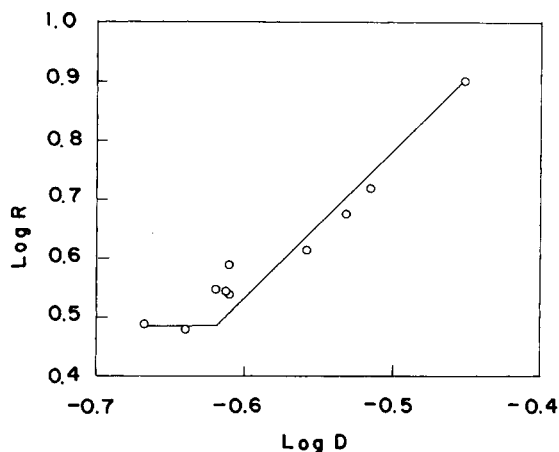


Fig. 2. Relationship between logarithms of rate of polymerization per particle and particle diameter: R = rate of polymerization per particle, $\times 10^{-15}\%/hr$; D = particle diameter, μ .

TABLE V
Effect of Degree of Neutralization of Carboxylic Monomer on Distribution of Carboxyl Groups

Degree of neutralization of AA	Distribution of carboxyl groups, surface/total ^a	Surface area occupied by a surface carboxyl group, Å ²
0.30	0.476	9.4
0.50	0.274	12.8
0.60	0.276	12.7
0.70	0.265	17.6
0.75	0.271	19.7
0.80	0.294	19.2
0.85	0.248	20.4
0.90	0.174	18.8
1.00	0.171	18.4

^a Ratio of equivalents of surface carboxyl groups to total carboxyl groups.

degree of neutralization or the amount of the carboxylic monomer as well as soap concentration will be described elsewhere.

Distribution of Carboxyl Groups

The effect of the degree of neutralization of AA on the distribution of carboxyl groups is shown in Table V. The change in distribution of carboxyl groups with degree of neutralization of AA is described in Figure 3. It is apparent that the fraction of carboxyl groups localized on the surface of the particles decreases remarkably with increasing the degree of neutralization from 0.30 to 0.50, remains almost constant with increasing the degree of neutralization from 0.50 to 0.80, and decreases gradually with increasing the degree of neutralization from 0.80 to 1.00. This means that the distribution of carboxyl groups is greatly dependent on the degree of neutralization. The change in surface area occupied by a surface carboxyl group (which is determined by both the distribution of carboxyl groups

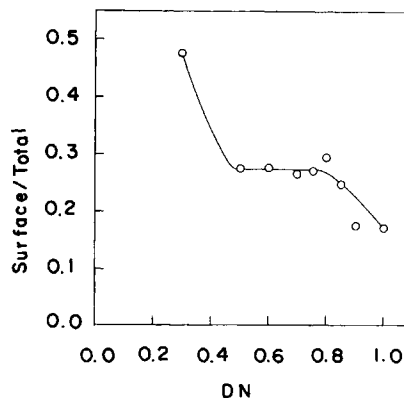


Fig. 3. Change in distribution of carboxyl groups with degree of neutralization of the carboxylic monomer: surface/total = ratio of equivalents of surface carboxyl groups to total carboxyl groups; DN = degree of neutralization of AA.

TABLE VI
Effect of Amount of Carboxylic Monomer on Distribution of Carboxyl Groups

Amount of AA, g	Distribution of carboxyl groups, surface/total ^a	Surface area occupied by a surface carboxyl group, Å ²
1.00	0.260	78.4
2.50	0.227	43.5
3.75	0.222	30.8
4.50	0.238	24.5
5.00	0.294	19.2

^a Ratio of equivalents of surface carboxyl groups to total carboxyl groups.

TABLE VII
Effect of Soap Concentration on Distribution of Carboxyl Groups

Concentration of SDS, mmole/l.	Distribution of carboxyl groups, surface/total ^a	Surface area occupied by a surface carboxyl group, Å ²
0.000	0.283	13.8
0.160	0.262	17.2
0.321	0.292	16.0
0.642	0.253	19.6
1.60	0.294	19.2
3.21	0.270	20.8
6.41	0.271	20.7
31.8	0.262	23.0
63.0	0.289	22.2

^a Ratio of equivalents of surface carboxyl groups to total carboxyl groups.

and the particle diameter that is inversely proportional to the total surface area of particles in the polymerization system) with degree of neutralization is rather complicated, as shown in Table V. The data in Tables II and V show that the stability of the polymerization system is not closely related to the density of surface carboxyl groups. This may indicate that the stability of the polymer-

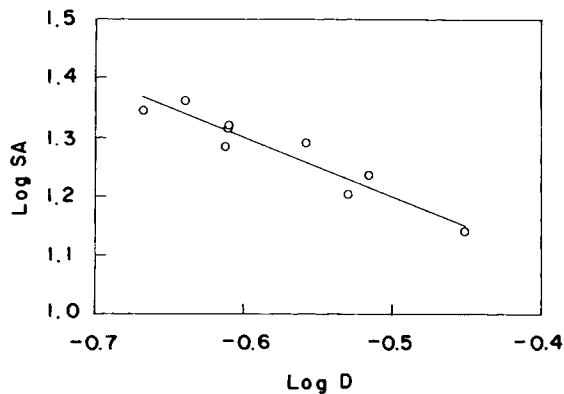


Fig. 4. Relationship between logarithms of surface area occupied by a surface carboxyl group and particle diameter: SA = surface area occupied by a surface carboxyl group, Å²; D = particle diameter, μ.

ization system is governed by the density of carboxylate ions on the surface of particles which is dependent on both the density of surface carboxyl groups and the degree of neutralization of surface carboxyl groups.

In Table VI is shown the effect of the amount of AA on the distribution of carboxyl groups. It is apparent from Table VI that the amount of AA has little effect on the distribution of carboxyl groups, which indicates that the distribution of carboxyl groups is governed substantially by the degree of neutralization of AA. The surface area occupied by a surface carboxyl group decreases remarkably with increase in the amount of AA, as shown in Table VI. This can reasonably be explained by the change of both the total amount of carboxyl groups in the polymerization system and the particle diameter that is inversely proportional to the total surface area of particles in the polymerization system. The data in Tables III and VI show that the stability of the polymerization system is closely related to the density of surface carboxyl groups. This may also indicate that the stability of the polymerization system is governed by the density of carboxylate ions on the surface of particles, because in this case it is believed that the density of carboxylate ions on the surface of particles is proportional to the density of surface carboxyl groups.

Table VII shows the effect of the concentration of SDS on the distribution of carboxyl groups. It is apparent from Table VII that the fraction of carboxyl groups localized on the surface of particles is almost constant irrespective of the concentration of SDS. On the other hand, the particle diameter is strongly dependent on the concentration of SDS and decreases from 0.353 to 0.215 μ with increase in SDS concentration from 0.000 to 63.0 mmole/l. This means that the distribution of carboxyl groups is governed substantially by the degree of neutralization of AA as described above and is independent of the particle diameter. The surface area occupied by a surface carboxyl group increases gradually with increase in SDS concentration as shown in Table VII. This may be attributed to the change of the particle diameter which is inversely proportional to the total surface area of particles in the polymerization system.

In Figure 4 the relationship between the logarithms of the surface area occupied by a surface carboxyl group and the particle diameter is shown. The points in Figure 4 approximately fit a straight line with a slope of -1 as expected from the above-described consideration. It is apparent from Table VII that the surface area occupied by a surface carboxyl group is in the range of approximately 14–23 \AA^2 , which is much smaller than the molecular area of 48 \AA^2 reported by Vanderhoff et al.¹³ for SDS on the surface of particles in a polystyrene latex. This means that the latexes in Table VII are sufficiently stabilized with surface carboxyl groups because it is believed that in this case the degree of neutralization of surface carboxyl groups is fairly high.

Based on the above considerations, it may be concluded that the distribution of carboxyl groups is governed substantially by the degree of neutralization of the carboxylic monomer and is independent of both the amount of the carboxylic monomer and the particle diameter.

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