

Preparation and Characterization of Soap-Free Carboxylated Polystyrene Latexes

KAZUYUKI SAKOTA and TAKUJI OKAYA, *Central Research Laboratories, Kuraray Co., Ltd., Kurashiki, Okayama, Japan*

Synopsis

Soap-free carboxylated polystyrene latexes have been prepared by copolymerizing carboxylic monomers in a wide range of degree of neutralization using a slight amount of soap. In this polymerization system, the formation of particles seems to be explained by the precipitation of growing radicals formed in the aqueous phase. The degree of neutralization of carboxylic monomers has a great effect on the formation of particles, which may be attributed to a change in the hydrophilic nature of growing radicals formed in aqueous phase that governs the number and uniformity of particles. The number of particles increases remarkably with increasing the amount of soap to some extent, which may be attributed to the stabilization of primary particles formed by the precipitation of growing radicals with the adsorption of soap. The localization of carboxyl groups on the surface of particles seems to be governed by the electrostatic repulsion between carboxyl groups. The surface area occupied by a surface carboxyl group, however, is fairly small irrespective of the degree of neutralization of carboxylic monomers or the amount of soap, which indicates that the latexes are sufficiently stabilized with surface carboxyl groups.

INTRODUCTION

Carboxylated latexes stabilized with chemically bound carboxyl groups are excellent in mechanical stability,¹ freeze-thaw stability,² and compatibility with pigments^{3,4} compared with latexes stabilized only with physically adsorbed soaps. Consequently, carboxylated latexes have become very important in industrial use.

Recently, Ceska^{5,6} has obtained soap-free carboxylated butadiene/styrene copolymer latexes by copolymerizing carboxylic monomers and demonstrated that the formation of particles can be explained by the combination and nucleation of highly carboxylated oligomers formed in the aqueous phase. This indicates that the neutralization of carboxylic monomers has a great effect on the formation of particles. Fitch et al.⁷ have investigated the formation of particles in polymer colloids and clarified that, although the formation of particles can predominantly be attributed to the precipitation of growing radicals formed in aqueous phase, the number of particles is much enhanced in the presence of a slight amount of soap. It seems also to be the case for the formation of particles in the above-mentioned soap-free carboxylated latexes.

In this paper, the authors intended to prepare soap-free carboxylated polystyrene latexes by copolymerizing carboxylic monomers in a wide range of the degree of neutralization using a slight amount of soap. Furthermore, carboxyl groups chemically bound to the surface of particles (surface carboxyl

groups) were determined to elucidate the distribution of carboxyl groups in particles.

EXPERIMENTAL

Materials

Deionized water was used. EP-grade styrene (St) and acrylic acid (AA) were used after purification by the usual method. GR-grade potassium persulfate (KPS) and EP-grade fumaric acid (FA), sodium hydrogencarbonate (NaHCO_3), and sodium dodecyl sulfate (SDS) (Tokyo Chemical Industry Co., Ltd.) 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 hydrogencarbonate, FA, 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.

Characterization of latexes was carried out as follows. The particle diameter was determined as number average by electron microscopy. The determination of surface carboxyl groups was performed by the method previously described.⁸ The rate of polymerization was calculated from the linear part of conversion-time curves. The number of particles per gram polymer and the surface area occupied by a surface carboxyl group was calculated assuming the density of polymers to be 1 g/cm³.

RESULTS AND DISCUSSION

Formation of Particles

Effect of the Degree of Neutralization of Carboxylic Monomers

St was copolymerized with carboxylic monomers AA and FA in the presence of a minimum amount of soap SDS which effectively enhances the number of particles, as will be described in the following section. Carboxylic monomers were neutralized with sodium hydrogencarbonate to the degree of neutralization ranging from 0.00 to 1.00. The degree of neutralization was defined for convenience as the ratio of equivalents of sodium hydrogencarbonate to carboxyl groups in AA and FA, although the degree of dissociation of carboxylic monomers in the actual polymerization system seems to be much more complicated because of the difference in the dissociation constants of AA and two carboxyl groups in FA⁹ and, presumably, the difference in the partition coefficients of AA and FA between water and St.

In Table I is shown the effect of the degree of neutralization of carboxylic monomers on the polymerization behavior. It is apparent from Table I that the degree of neutralization of carboxylic monomers strongly affects the sta-

TABLE I
Effect of Degree of Neutralization of Carboxylic Monomers
on Polymerization Behavior^a

Degree of neutralization	Stability of polymerization system	Rate of polymerization, %/hr
0.00	low (coagulated)	54.5
0.50	low (coagulated)	35.9
0.70	low (coagulated)	26.2
0.80	high	25.0
0.83	high	32.1
0.84	high	32.2
0.85	high	35.9
0.86	high	31.9
0.87	high	28.2
0.90	low	9.8
0.95	low	8.3
1.00	low	6.2

^a Polymerization recipe, g: water/St/AA/FA/NaHCO₃/SDS/KPS = 100/90.9/5/2.5/variable/0.05/1.32.

bility of polymerization system as follows: with increasing the degree of neutralization from less than 0.80 via 0.80–0.90 to higher than 0.90, the stability of the polymerization system changes from very low via high to low, respectively. At a degree of neutralization less than 0.80, the latex coagulates through phase inversion from O/W emulsion to O/W/O emulsion.¹⁰ The change of the rate of polymerization with the degree of neutralization of carboxylic monomers can be described as in Figure 1. Although the rate of polymerization decreases remarkably with increase in the degree of neutralization, it becomes maximum at a degree of neutralization of about 0.85. These results show that a degree of neutralization of carboxylic monomers of about 0.85 is preferable for obtaining stable soap-free carboxylated latexes at a sufficient rate of polymerization.

In Table II is shown the effect of the degree of neutralization of carboxylic monomers on the formation of particles. It is apparent from Table II that

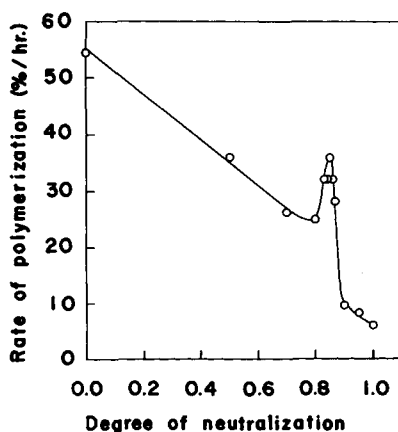


Fig 1. Change of rate of polymerization with degree of neutralization of carboxylic monomers.

TABLE II
Effect of Degree of Neutralization of Carboxylic Monomers on Formation of Particles

Degree of neutralization	Number of particles per gram polymer $\times 10^{12}$	Coefficient of variation of particle diameter, %	Rate of polymerization per particle, $10^{-13}\%/hr^a$
0.00	170 ^b	—	—
0.50	112 ^b	—	—
0.70	81.9 ^b	—	—
0.80	54.2	2.6	4.6
0.83	80.8	1.8	4.0
0.84	92.9	2.3	3.5
0.85	112	2.1	3.2
0.86	98.2	3.2	3.3
0.87	80.8	1.6	3.5
0.90	25.6	9.8	3.8
0.95	21.3	16.0	3.9
1.00	13.7	12.8	4.5

^a Obtained dividing the rate of polymerization in Table I by the number of particles per gram polymer.

^b Calculated assuming the rate of polymerization per particle to be $3.2 \times 10^{-13}\%/hr$.

the rate of polymerization per particle is almost constant irrespective of the degree of neutralization, which indicates that the change of the rate of polymerization with degree of neutralization can predominantly be attributed to the change in the number of particles, as is generally recognized in emulsion polymerization.¹¹ From Table II, the change in the number and uniformity of particles with degree of neutralization will be described as follows. Although the number of particles decreases remarkably with increase in the degree of neutralization, it becomes maximum at a degree of neutralization of about 0.85. The coefficient of variation of particle diameter is small at a degree of neutralization ranging from 0.80 to 0.90, whereas it is fairly large at a degree of neutralization ranging from 0.90 to 1.00. These results show that, as was expected, the neutralization of carboxylic monomers has a great effect on the formation of particles. In this polymerization system, growing radicals formed in the aqueous phase will be composed of St, carboxylic monomers, and the neutralized form of carboxylic monomers, the hydrophilic nature of which will be strongly affected by the degree of neutralization of carboxylic monomers. Consequently, the effect of the degree of neutralization of carboxylic monomers on the formation of particles may predominantly be attributed to a change in the hydrophilic nature of growing radicals formed in aqueous phase which governs the number and uniformity of particles. The change in pH and ionic strength which governs the decomposition of initiator¹² and the stability of primary particles¹³ with the degree of neutralization of carboxylic monomers may also affect the formation of particles.⁷ It seems that the above-described factors, as a whole, explain the complicated relationship between the number or uniformity of particles and the degree of neutralization of carboxylic monomers.

A detailed discussion on the formation of particles in a simplified polymerization system will be given elsewhere.

TABLE III
Effect of Amount of Soap on Formation of Particles^a

Amount of SDS, g	Particle diameter, μ	Number of particles per gram polymers $\times 10^{12}$	Coefficient of variation of particle diameter, %	Rate of polymerization per particle, $10^{-13}\%/hr^b$
0.00	0.277	89.9	5.1	3.6
0.01	0.264	104	5.3	3.4
0.02	0.259	110	4.2	3.4
0.03	0.216	190	—	2.5
0.05	0.204	225	2.8	2.2
0.07	0.210	206	—	2.4
0.09	0.198	246	2.7	2.0
0.10	0.210	192	—	2.6
0.50	0.202	232	3.9	2.1
1.00	0.197	250	8.5	2.0
3.50	0.140	696	10.6	2.0

^a Polymerization recipe, g: water/St/AA/FA/NaHCO₃/SDS/KPS = 100/90.9/5/2.5/8/variable/1.32.

^b Obtained dividing the rate of polymerization by the number of particles per gram polymer.

Effect of the Amount of Soap

At a degree of neutralization of carboxylic monomers of 0.85 which gives stable soap-free carboxylated latexes at a sufficient rate of polymerization, as was described in the previous section, the effect of the amount of soap on the formation of particles was examined. The results are shown in Table III. The change of the number of particles with the amount of soap can be described as in Figure 2, which shows that the number of particles increases remarkably with increasing the amount of SDS from 0.00 to 0.05 g, remains almost constant with increasing the amount of SDS from 0.05 to 0.5 g, and increases gradually with increasing the amount of SDS from 0.5 to 3.5 g. It is apparent from Table III that the coefficient of variation of particle diameter is small in the range of an amount of SDS from 0.00 to 0.5 g, whereas it is fair-

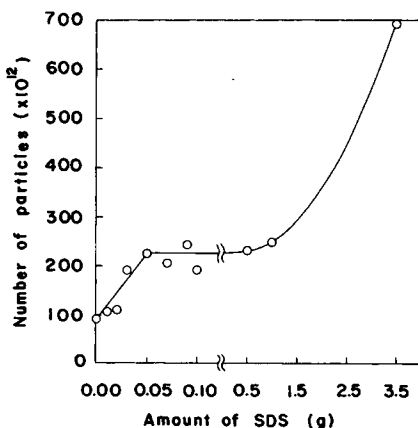


Fig. 2. Change of number of particles per gram polymer with amount of soap.

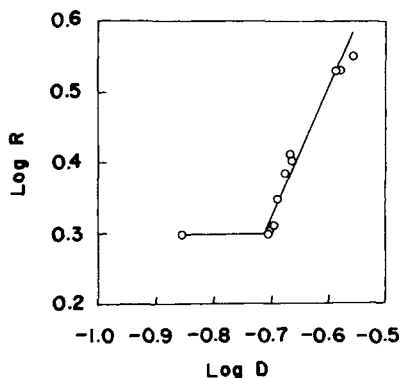


Fig. 3. Relationship between rate of polymerization per particle and particle diameter: R = rate of polymerization per particle, $10^{-13}\%$ /hr; D = particle diameter, μ .

ly large in the range of an amount of SDS larger than 0.5 g, which strongly suggests a difference in the particle formation process between these two ranges.

From these results, the role of soap in the formation of particles may be described as follows. In the range of an amount of SDS from 0.00 to 0.5 g, the formation of particles may predominantly be attributed to the precipitation of growing radicals formed in aqueous phase, and soap will adsorb on the surface of primary particles to stabilize them.⁷ Consequently, the number of particles increases remarkably with increasing the amount of SDS from 0.00 to 0.05 g, which is sufficient to stabilize primary particles, and remains constant with increasing the amount of SDS from 0.05 to 0.5 g because of the presence of the excess amount of soap to stabilize primary particles. In the range of an amount of SDS larger than 0.5 g, the formation of particles may predominantly be attributed to the initiation of polymerization in soap micelles. Consequently, the number of particles increases gradually with increasing the amount of soap, and the uniformity of particles is fairly low, as is generally recognized in emulsion polymerization.¹¹

The relationship between the rate of polymerization per particle and the particle diameter is shown in Figure 3. It is apparent from Table III and Figure 3 that the rate of polymerization per particle is almost constant in the range of particle diameter from 0.140 to 0.195 μ , whereas it is proportional to the 2.3 power of the particle diameter in the range of the particle diameter from 0.195 to 0.277 μ . This indicates that in the range of particle diameter smaller than 0.195 μ , the polymerization proceeds according to the theory of emulsion polymerization,¹¹ whereas in the range of a particle diameter larger than 0.195 μ , the polymerization rather proceeds according to the theory of bulk polymerization as reported by Vanderhoff et al.¹⁴ In this case, however, the critical particle diameter is not in good agreement with that of Vanderhoff et al., which may be ascribed to a difference in the definition of the particle diameter.

Distribution of Carboxyl Groups

Surface carboxyl groups were determined to elucidate the distribution of carboxyl groups in particles. In Table IV, the effect of the degree of neutral-

TABLE IV
Effect of Degree of Neutralization of Carboxylic Monomers on Distribution of Carboxyl Groups

Degree of neutralization	Distribution of carboxyl groups, surface ^a /total ^b	Surface area occupied by a surface carboxyl group, Å ²
0.80	0.150	17.8
0.83	0.178	17.1
0.85	0.179	19.0
0.87	0.186	16.3
0.90	0.123	16.9
0.95	0.087	22.4
1.00	0.077	22.0

^a Amount of carboxyl groups found on the surface of particles.

^b Amount of carboxyl groups initially charged.

ization of carboxylic monomers on the distribution of carboxyl groups is shown. It is clear from Table IV that the distribution of carboxyl groups is dependent on the degree of neutralization, whereas the surface area occupied by a surface carboxyl group is almost constant irrespective of the degree of neutralization. At a degree of neutralization of about 0.85, about 18% of carboxyl groups are localized on the surface of particles, and the surface area occupied by a surface carboxyl group is less than 20 Å², which is much smaller than the molecular area of 48 Å² reported by Vanderhoff et al.¹⁵ for SDS on the surface of particles in a polystyrene latex. This indicates that the latexes in Table IV are sufficiently stabilized with surface carboxyl groups.

In Table V is shown the effect of the amount of soap on the distribution of carboxyl groups. It is clear from Table V that the distribution of carboxyl groups is almost constant irrespective of the amount of soap, except for the run where a large amount of soap was used and about 18% of carboxyl groups are localized on the surface of particles. The surface area occupied by a surface carboxyl group also is almost constant irrespective of the amount of soap and is in the range of 18 to 27 Å², which is much smaller than the above-mentioned molecular area for SDS.

From the above-described results, the procedure of the distribution of car-

TABLE V
Effect of Amount of Soap on Distribution of Carboxyl Groups

Amount of SDS, g	Distribution of carboxyl groups, surface ^a /total ^b	Surface area occupied by a surface carboxyl group, Å ²
0.00	0.173	18.2
0.01	0.159	20.8
0.05	0.199	21.6
0.09	0.179	24.6
0.50	0.175	24.8
1.00	0.167	26.6
3.50	0.258	24.2

^a Amount of carboxyl groups found on the surface of particles.

^b Amount of carboxyl groups initially charged.

boxyl groups in particles may be described as follows. During the growth of particles, although carboxyl groups of polymer chains in particles may prefer to be localized on the surface of particles because of their hydrophilic nature, the number of carboxyl groups per unit surface area will not exceed the specific value determined by the electrostatic repulsion between carboxyl groups. Consequently, only a small portion of carboxyl groups, which gives a number of carboxyl groups per unit surface area lower than the specific value, is localized on the surface of particles, and a large portion of carboxyl groups is buried in the interior of particles.

The authors wish to express their thanks to Dr. T. Yasui and Dr. K. Fujii for their encouragement and helpful suggestions.

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Received September 23, 1975

Revised October 30, 1975