

Formation of Particles in the Preparation of Carboxylated Polystyrene Latexes

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Synopsis

Carboxylated polystyrene latexes have been prepared by copolymerizing acrylic acid at the appropriate degree of neutralization in the absence or presence of sodium dodecyl sulfate (SDS), and the particle formation process was investigated from the number and uniformity of particles. In the absence of SDS or in a concentration range of SDS lower than 6.41 mmole/l., the formation of particles can predominantly be attributed to the precipitation of growing radicals formed in the aqueous phase; whereas in a concentration range of SDS higher than 6.41 mmole/l., the formation of particles can predominantly be attributed to the initiation of polymerization in the interior of SDS micelles containing solubilized styrene by the collision of growing radicals formed in the aqueous phase. In the former range, the number of particles increases linearly with increasing concentration of SDS below the critical concentration of 1.60 mmole/l., which is sufficient to stabilize particles formed by the precipitation of growing radicals, and remains constant above the critical concentration. The effect of initiator concentration as well as amount of styrene on the formation of particles also supports the particle formation process described above.

INTRODUCTION

The particle formation process in emulsion polymerization has been studied intensively since Smith and Ewart¹ proposed a fundamental theory in 1948. Recently, some workers^{2,3} have studied emulsion polymerization of styrene in the presence of soaps ranging in concentration from below to above the critical micelle concentration (*CMC*) and demonstrated that particles can be formed in the absence of soap micelles. Furthermore, a number of workers⁴⁻⁹ have investigated the aqueous polymerization of styrene or methyl methacrylate and demonstrated that particles are formed even in the absence of soaps and that the precipitation of growing radicals formed in the aqueous phase plays an important role in the formation of particles. It seems, however, that there have been few earlier published studies on the particle formation process in the preparation of carboxylated latexes. Only Ceska^{10,11} has studied the particle formation process in the preparation of soap-free carboxylated butadiene/styrene copolymer latexes; he demonstrated that the formation of particles can be explained by the combination and nucleation of highly carboxylated oligomers formed in the aqueous phase.

The authors¹² 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 number of particles is greatly enhanced by the presence of a slight amount of soap. This indicates that,

although the formation of particles can predominantly be attributed to the precipitation of growing radicals formed in the aqueous phase, the slight amount of soap plays an important role in the formation of particles.

It is of great interest to clarify the particle formation process in the preparation of the above-described carboxylated polystyrene latexes. The polymerization system used in the previous paper,¹² however, is considerably complicated because of the presence of two kinds of carboxylic monomers which makes it difficult to elucidate the particle formation process. In the present paper, the authors intended to elucidate the particle formation process in a simplified polymerization system where only acrylic acid (AA) was used as carboxylic monomer.

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.), potassium persulfate (KPS), and potassium sulfate (K_2SO_4) 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 amount of water, SDS, potassium sulfate, 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.

The particle diameter was determined as number average by electron microscopy. The number of particles in the polymerization system was calculated assuming the density of polymers to be 1 g/cm³. The concentration of SDS or KPS and the ionic strength were calculated assuming the density of the aqueous phase in the polymerization system to be 1 g/cm³.

RESULTS AND DISCUSSION

Effect of Soap Concentration on the Formation of Particles

In the previous paper,¹² it was shown that stable, soap-free carboxylated polystyrene latexes can be obtained by copolymerizing AA and fumaric acid at a degree of neutralization of about 0.85. In fact, however, stable, soap-free carboxylated polystyrene latexes can be obtained also by copolymerizing only AA at a degree of neutralization of about 0.80, as will be described in a subsequent paper.¹³ Consequently, in the present paper, a polymerization recipe was established as in Table I, where the degree of neutralization of AA, defined as the ratio of equivalent of sodium hydrogen carbonate to AA, was maintained at 0.80. Potassium sulfate was introduced, if necessary, to adjust the ionic strength.

TABLE I
Polymerization Recipe

Ingredient	Amount, g
Water	100
St	variable (2.73–90.9)
AA	5
NaHCO ₃	4.66
SDS	variable (0–2)
KPS	variable (0.132–2.64)
K ₂ SO ₄	variable (0–1.7)

TABLE II
Effect of Soap Concentration on the Formation of Particles^a

Concentration of SDS, mmole/l.	Number of particles, × 10 ^{15b}	Coefficient of variation of particle diameter, %
0.000	4.16	9.8
0.160	6.45	1.2
0.321	7.13	1.9
0.642	8.72	3.9
1.60	12.7	3.8
3.21	12.7	3.7
6.41	12.5	2.0
16.0	13.2	3.7
31.8	15.2	6.0
63.0	18.4	14.9

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

^b Number of particles in the polymerization system.

According to the polymerization recipe in Table I, polymerization was carried out in the absence of SDS or in the presence of SDS ranging widely in concentration. The effect of the concentration of SDS on the formation of particles is shown in Table II. The change of the number of particles in the polymerization system with SDS concentration can be described as in Figure 1. It is apparent from Table II that a considerably large number of particles is formed even in the absence of SDS, which indicates that in this polymerization system particles are formed predominantly by the precipitation of growing radicals formed in the aqueous phase.^{5,10,11} It is also apparent from Table II that the coefficient of variation of particle diameter is particularly large in the absence of SDS. This suggests that the formation of particles proceeds over a fairly long period of time because particles formed by the precipitation of growing radicals are not stabilized with the adsorption of soaps and may flocculate with each other.^{5,6}

The CMC for SDS in this polymerization system is 0.173 mmole/l., as has been described in the previous paper.¹⁴ Consequently, it is apparent from Figure 1 that with an increase in SDS concentration from 0.000 to 1.60 mmole/l., the number of particles increases almost linearly irrespective of the absence or presence of SDS micelles. It is also apparent from Table II that the coefficient of variation of particle diameter is fairly small in this range of SDS concentration.

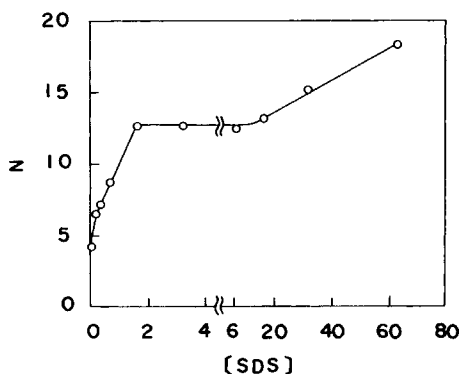


Fig. 1. Change in number of particles in the polymerization system with soap concentration: N = number of particles in the polymerization system $\times 10^{15}$; [SDS] = concentration of SDS, in mmole/l.

This indicates that in this range of SDS concentration particles are formed predominantly by the precipitation of growing radicals formed in the aqueous phase and that SDS micelles do not play an important role in the formation of particles. In this case, however, the number of particles seems to be enhanced by the presence of SDS because particles formed by the precipitation of growing radicals are stabilized with adsorption of SDS.⁵

In the range of SDS concentration from 1.60 to 6.41 mmole/l., which is much higher than the above-described *CMC*, it is apparent from Figure 1 and Table II that the number of particles is almost constant and the coefficient of variation of particle diameter is fairly small. This also indicates that in this range of SDS concentration, particles are formed predominantly by the precipitation of growing radicals formed in the aqueous phase and that SDS micelles do not play an important role in the formation of particles. It seems that in this case, the SDS concentration is higher than the critical concentration which is sufficient to stabilize particles formed by the precipitation of growing radicals and that the number of particles is independent of the concentration of SDS. The critical concentration of SDS can be determined from Figure 1 and Table II to be approximately 1.60 mmole/l., which is nearly consistent with that reported by Fitch et al.⁵ for the aqueous polymerization of methyl methacrylate.

In the range of SDS concentration from 6.41 to 63.0 mmole/l., it is apparent that the number of particles increases gradually with increasing SDS concentration and that the coefficient of variation of particle diameter is fairly large. Moreover, in this range the relationship between logarithms of the number of particles in the polymerization system and the SDS concentration can be described as in Figure 2. The linear relationship in Figure 2 is consistent with that expected from the theory of emulsion polymerization proposed by Smith and Ewart,¹ although the slope is somewhat different from that expected from the theory. This indicates that in this range of SDS concentration, particles are formed predominantly by the initiation of polymerization in the interior of SDS micelles.¹ The critical SDS concentration at which the transition of the particle formation process occurs, that is, the transition from the precipitation of growing radicals in the aqueous phase to the initiation of polymerization in the interior of SDS micelles, can be determined from Figure 1 and Table II to be approximately 6.41 mmole/l., which is much higher than the above-described *CMC*.

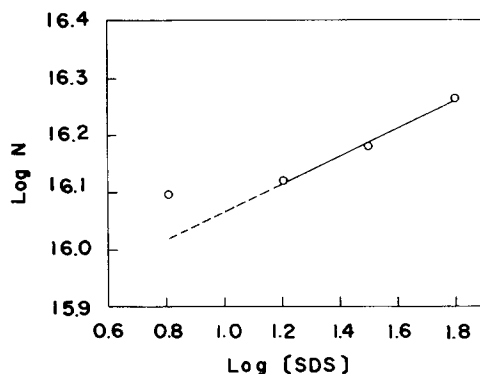


Fig. 2. Relationship between logarithms of number of particles in the polymerization system and SDS concentration: N = number of particles in the polymerization system $\times 10^{15}$; $[SDS]$ = concentration of SDS, in mmole/l.

On the basis of the above-described considerations, the particle formation process in this polymerization system is believed to be as follows. First, polymerization is initiated in the aqueous phase, and growing radicals are formed; then the growing radicals form particles by precipitating out at the critical degree of polymerization above which growing radicals exceed their solubility⁵ or by colliding with SDS micelles to initiate the polymerization of St solubilized in the interior of SDS micelles.¹⁴ In the range of SDS concentration lower than 6.41 mmole/l., growing radicals substantially precipitate out to form particles before they collide with SDS micelles because the theoretical maximum degree of polymerization reached by growing radicals during the period of time from the initiation in the aqueous phase to the collision with SDS micelles is larger than the above-described critical degree of polymerization. On the other hand, in the range of SDS concentration higher than 6.41 mmole/l., growing radicals collide with SDS micelles to form particles before they precipitate out because the theoretical maximum degree of polymerization is smaller than the critical degree of polymerization. This means that the theoretical maximum degree of polymerization at an SDS concentration of 6.41 mmole/l. represents the critical degree of polymerization of growing radicals formed in this polymerization system.

It has been demonstrated by Fitch et al.⁵ that in the polymerization system where particles are present, the growing radical formed in the aqueous phase will precipitate out to form a particle at the critical degree of polymerization above which the growing radical exceeds its solubility, or collide with particles. In the latter case, the displacement L experienced by the growing radical during the period of time from the initiation in the aqueous phase to the collision with particles is given by the following equation:

$$L = 1/(\pi N a^2) \quad (1)$$

where N is the number of particles per unit volume and a is the radius of particles. The relationship between L and the degree of polymerization D.P. reached by the growing radical is represented by the following equation:

$$\text{D.P.} = L^2 k_p [M] / (2D) \quad (2)$$

where k_p is the propagation rate constant of the growing radical, $[M]$ is the concentration of monomer, and D is the diffusion constant of the growing radical. From eqs. (1) and (2) it is possible to calculate the theoretical maximum degree of polymerization reached by the growing radical during the period of time from the initiation in the aqueous phase to the collision with particles. Consequently, it also seems to be possible to calculate the theoretical maximum degree of polymerization reached by growing radicals in this polymerization system during the period of time from the initiation in the aqueous phase to the collision with SDS micelles by substituting SDS micelles for particles in the above-described theory.

In this polymerization system, the number and radius of SDS micelles containing solubilized St can be calculated as has been described in the previous paper.¹⁴ At an SDS concentration of 6.41 mmole/l., the number of SDS micelles in the polymerization system is calculated to be 5.82×10^{17} , and the radius of SDS micelles is calculated to be approximately 4.7×10^{-7} cm. Although the accurate k_p value in this polymerization system is unknown because the terpolymerization of undissociated AA, dissociated AA, and St will proceed in the aqueous phase, it may be assumed¹⁵ to be approximately 1×10^4 l./mole-sec. As will be described in a subsequent paper,¹³ $[M]$ is approximately 6.3×10^{-1} mole/l. In this manner, by assuming¹⁶ D to be 1×10^{-6} cm²/sec, the theoretical maximum degree of polymerization reached by growing radicals during the period of time from the initiation in the aqueous phase to the collision with SDS micelles can be calculated from eqs. (1) and (2). The calculation result was approximately 230, which is much larger than the 65 and 50 reported respectively for poly(methyl methacrylate)⁵ and poly(vinyl acetate).¹⁷ This is consistent with the fact that the hydrophilic nature of growing radicals formed in this polymerization system is predicted to be fairly high from the calculation result of the composition of growing radicals.¹³ At the present stage, however, direct determination of the critical degree of polymerization of growing radicals is difficult. Furthermore, the termination of growing radicals in the aqueous phase has not been taken into account in the above-described discussions. A detailed study from this point of view seems to be necessary.

Effect of Ionic Strength and Concentration of Initiator on the Formation of Particles

At the critical SDS concentration of 1.60 mmole/l., which is sufficient to stabilize particles formed by the precipitation of growing radicals as has been described in the previous section, the effect of the ionic strength and the concentration of potassium persulfate (KPS) on the formation of particles was examined. The results are shown in Tables III and IV. It is apparent from Table III that the ionic strength has little effect on the number of particles or the coefficient of variation of particle diameter. This indicates that at the critical SDS concentration of 1.60 mmole/l., particles formed by the precipitation of growing radicals are sufficiently stabilized with SDS adsorbed on the surface of particles⁵ as well as carboxyl groups^{10,11,12} and sulfate endgroups^{5,6,8} localized on the surface of particles and do not flocculate with each other.^{5,6} Because the flocculation of particles formed by the precipitation of growing radicals is strongly affected by the ionic strength,⁶ in this case the number of particles and the coefficient

TABLE III
Effect of Ionic Strength on the Formation of Particles^a

Ionic strength	Number of particles, $\times 10^{15b}$	Coefficient of variation of particle diameter, %
0.646 ^c	12.7	3.8
0.711	12.0	3.6
0.775	13.6	4.1
0.901	11.0	2.6

^a Polymerization recipe, in g: water/St/AA/NaHCO₃/SDS/KPS/K₂SO₄ = 100/90.9/5/4.66/0.05/1.32/variable.

^b Number of particles in the polymerization system.

^c Corresponds to the fifth run in Table II.

TABLE IV
Effect of Initiator Concentration on the Formation of Particles^a

Concentration of KPS, mmole/l.	Ionic strength	Number of particles, $\times 10^{15b}$	Coefficient of variation of particle diameter, %
4.54	0.531	2.89	2.6
9.08	0.543	3.12	2.5
22.6	0.582	8.62	1.5
33.8	0.614	8.72	2.3
40.5	0.633	11.0	3.6
44.9 ^c	0.646	12.7	3.8
56.0	0.678	15.9	2.9
67.0	0.709	14.9	3.5
88.8	0.772	15.2	2.2

^a Polymerization recipe, in g: water/St/AA/NaHCO₃/SDS/KPS = 100/90.9/5/4.66/0.05/variable.

^b Number of particles in the polymerization system.

^c Corresponds to the fifth run in Table II.

of variation of particle diameter are believed also to be strongly affected by the ionic strength. The change of the *CMC* for SDS caused by the change of the ionic strength^{14,18} seems to have little effect on the formation of particles because in the range of SDS concentration lower than 6.41 mmole/l., the particle formation process is governed by the total concentration of SDS.

The change of the number of particles in the polymerization system with the concentration of KPS can be described as in Figure 3. It is apparent from the figure that in the range of concentration of KPS lower than 56.0 mmole/l., the number of particles increases linearly with increasing KPS concentration, whereas in the range of concentration of KPS from 56.0 to 88.8 mmole/l., the number of particles is independent of the concentration of KPS. Although the change in KPS concentration causes also a change in ionic strength, these results may substantially be attributed to the former because the latter has little effect on the formation of particles. This is consistent with the fact that the coefficient of variation of particle diameter is fairly small and is independent of the concentration of KPS, as shown in Table IV. The linear relationship between the

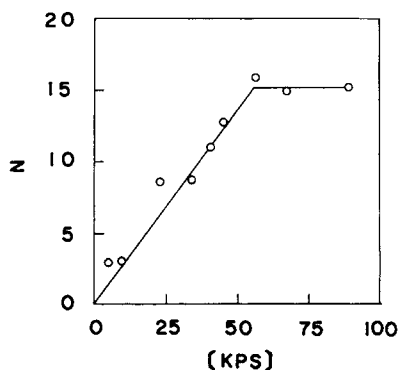


Fig. 3. Change in number of particles in the polymerization system with initiator concentration: N = number of particles in the polymerization system $\times 10^{15}$; [KPS] = concentration of KPS, in mmole/l.

number of particles and the concentration of KPS in Figure 3 may indicate that at the critical concentration of SDS of 1.60 mmole/l., the formation of particles is governed by the homogeneous nucleation and particle capture theory proposed by Fitch et al.⁵ which predicts that the rate of particle formation is proportional to the rate of initiation in the aqueous phase. The fact that at the high concentration of KPS the number of particles is independent of the concentration of KPS seems to be attributed to the enhanced probability of termination of growing radicals in the aqueous phase. At the present stage, however, further quantitative discussions are difficult.

Effect of Amount of Monomer on the Formation of Particles

The effect of the amount of St on the formation of particles was examined at the critical SDS concentration of 1.60 mmole/l., which is sufficient to stabilize particles formed by the precipitation of growing radicals as has been described in the previous section. The results are shown in Table V. It is apparent from Table V that the number of particles and the coefficient of variation of particle diameter are almost independent of the amount of St.

The concentration of St dissolved in the aqueous phase of this polymerization system has been determined in the previous paper¹⁴ to be 4.52 mmole/l. This

TABLE V
Effect of Amount of Monomer on the Formation of Particles^a

Amount of St, g	Number of particles, $\times 10^{15b}$	Coefficient of variation of particle diameter, %
2.73	12.2	4.5
9.09	11.3	2.0
27.27	9.3	1.9
90.9 ^c	12.7	3.8

^a Polymerization recipe, in g: water/St/AA/NaHCO₃/SDS/KPS = 100/variable/5/4.66/0.05/1.32.

^b Number of particles in the polymerization system.

^c Corresponds to the fifth run in Table II.

corresponds to approximately 0.051 g in the polymerization recipe shown in Table I, which is much smaller than the amount of St used in Table V. This indicates that the change in the amount of St in Table V does not affect the concentration of St dissolved in the aqueous phase. The change of the concentration of AA in the aqueous phase with change in the amount of St in Table V may also be negligibly small because the partition coefficient of AA between St and water is fairly small.¹⁹ Consequently, it may be concluded that the change in the amount of St causes no substantial change in the concentration of St, undissociated AA, and dissociated AA in the aqueous phase and does not affect the formation of particles. This is consistent with the above-described observation.

The results in Table V indicate that the formation of particles is completed during the initial short period of time where at most 2.73 g of St are polymerized and after the completion of the formation of particles polymerization proceeds substantially in the interior of particles. A detailed study on the effect of an amount of St smaller than 2.73 g is in progress, which is believed to give useful information about the critical stage of polymerization where the formation of particles is completed.

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