

Effect of the Hydrophilic Nature of Growing Radicals on the Formation of Particles in the 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 degree of neutralization using a slight amount of soap, and the particle formation process was investigated from the number and uniformity of particles. It was found that the degree of neutralization of AA as well as the amount of AA have a great effect on the formation of particles. On the basis of the calculation results of the composition of the growing radical formed in the aqueous phase at the initial stage of the polymerization, the results can reasonably be explained by a change in the hydrophilic nature of growing radicals which are formed in the aqueous phase and precipitate out to form particles. It was also established that the introduction of α -methylstyrene or methyl methacrylate has a great effect on the formation of particles, which is consistent with the above-described considerations.

INTRODUCTION

The particle formation process in the preparation of soap-free polystyrene or poly(methyl methacrylate) latexes has so far been investigated by a number of workers.¹⁻⁶ It seems, however, that there have been few published studies on the particle formation process in the preparation of carboxylated latexes. Only Ceska^{7,8} 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 authors⁹ have recently demonstrated that stable soap-free carboxylated polystyrene latexes can be obtained by copolymerizing carboxylic monomers at an appropriate degree of neutralization and that the number and uniformity of particles are strongly dependent on the degree of neutralization of the carboxylic monomers. This indicates that the hydrophilic nature of the growing radicals formed in the aqueous phase and precipitate out to form particles has a great effect on the formation of the particles.

It is of great interest to clarify the particle formation process in the preparation of the above-described soap-free carboxylated polystyrene latexes more precisely. The polymerization system used in the previous paper,⁹ however, is very 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 effect of the hydrophilic nature of growing radicals formed in the aqueous phase on the formation of particles will be dealt with using a simplified polymerization system which contains only acrylic acid (AA) as carboxylic monomer.

EXPERIMENTAL

Materials

Deionized water was used. Extrapore-grade styrene (St), α -methylstyrene (AMS), methyl methacrylate (MMA), and AA were used after distillation under reduced pressure. Extrapore-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.

Procedure

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, and monomers were placed in the reactor and heated to and kept at the polymerization temperature. The prescribed amount of KPS dissolved in water was then introduced. Polymerization was continued until it was substantially completed.

The pH measurement of the polymerization system was carried out at 70°C for the modified polymerization system where St was excluded and equimolar potassium sulfate was substituted for KPS to avoid the initiation of polymerization during the measurement without affecting the ionic strength.

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 the polymers to be 1 g/cm^3 .

RESULTS AND DISCUSSION

Effect of Degree of Neutralization of the Carboxylic Monomer

The authors¹⁰ have recently investigated the role of soaps in the preparation of carboxylated polystyrene latexes by copolymerizing AA at the appropriate degree of neutralization and demonstrated that, although a considerably large number of particles are formed even in the absence of soaps, the number of particles is effectively enhanced at the critical concentration of SDS of approximately 1.60 mmole/l. , which is sufficient to stabilize particles formed by the precipitation of growing radicals in the aqueous phase. At this critical SDS concentration, the amount of SDS relative to that of polymers is less than 0.06% (wt), which means that the latex can substantially be defined as soap free. Consequently, in the present paper, a polymerization recipe was established as shown in Table I, where the concentration of SDS was maintained at 1.60 mmole/l.

According to the polymerization recipe in Table I, polymerization was carried

TABLE I
Polymerization Recipe

Ingredient	Amount, g
Water	100
St ^a	90.9
AA	variable (0.5–5)
NaHCO ₃	variable (0–5.83)
SDS	0.05
KPS	1.32

^a Partially replaced, if necessary, by AMS or MMA.

out in the range of the degree of neutralization of AA defined as the ratio of equivalent of sodium hydrogen carbonate to AA from 0.00 to 1.00. The effect of the degree of neutralization of AA on the formation of particles is shown in Table II. The change on number of particles in the polymerization system with the degree of neutralization of AA can be described as in Figure 1. It is apparent from this figure that, although the number of particles decreases considerably with increase in the degree of neutralization, it reaches a maximum at the degree of neutralization of approximately 0.80. It is also apparent from Table II that the coefficient of variation of particle diameter is small in the range of a degree of neutralization below 0.90, whereas it is fairly large in the range of a degree of neutralization above 0.90. Such a remarkable effect of the degree of neutralization on the formation of particles may predominantly be attributed to a change in the hydrophilic nature of the growing radicals formed in the aqueous phase because, at this concentration of SDS, it is believed that particles are formed by the precipitation of growing radicals formed in the aqueous phase as has been described in the precious paper.¹⁰

In this polymerization system, the growing radical will be formed in the aqueous phase by the terpolymerization of undissociated AA, dissociated AA, and St. Consequently, the composition of the growing radical which governs the hydrophilic nature of the growing radical is dependent on the concentrations of these species. The concentration of St in the aqueous phase of the polymerization system will be approximately 4.52 mmole/l., as has been reported in a

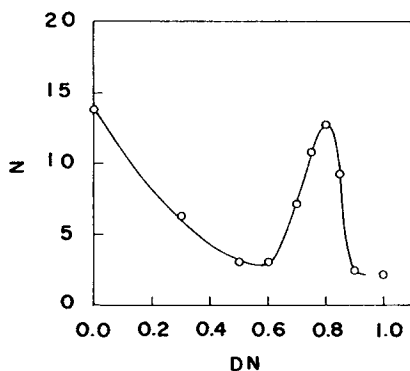


Fig. 1. Change in number of particles in the polymerization system with degree of neutralization of carboxylic monomer: N = number of particles in the polymerization system, $\times 10^{15}$; DN = degree of neutralization of AA.

TABLE II
Effect of Degree of Neutralization of Carboxylic Monomer
on the Formation of Particles^a

Degree of neutralization of AA	Number of particles $\times 10^{15b}$	Coefficient of variation of particle diameter, %
0.00 ^c	13.8 ^d	—
0.30	6.27	3.2
0.50	3.07	1.8
0.60	3.02	4.0
0.70	7.13	3.2
0.75	10.8	3.1
0.80	12.7	3.8
0.85	9.21	1.5
0.90	2.44	7.5
1.00	2.17	11.4

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

^b Number of particles in the polymerization system.

^c The latex coagulated.

^d Calculated assuming the rate of polymerization per particle is equal to that at the degree of neutralization of 0.80; see reference 9.

previous paper.¹¹ The concentration of the carboxylic monomer will be determined by the partition of AA between St and the aqueous phase and the dissociation of AA in the aqueous phase.

The partition and dissociation equilibrium of AA in the polymerization system is described by the following equations^{12,13} as reported in a previous paper:¹⁴

$$K = [\text{H}^+]_W [\text{A}^-]_W / [\text{HA}]_W \quad (1)$$

$$[\text{Na}^+]_W + [\text{H}^+]_W = [\text{OH}^-]_W + [\text{A}^-]_W \quad (2)$$

$$\alpha = [\text{HA}]_S / [\text{HA}]_W \quad (3)$$

$$C = ([\text{HA}]_W + [\text{A}^-]_W) V_W + [\text{HA}]_S V_S \quad (4)$$

where K , α , C , V_S , and V_W are the dissociation constant of AA, the partition coefficient of AA between St and water, the moles of total AA in the polymerization system, the volume of St, and the volume of the aqueous phase in the polymerization system, respectively. The symbols HA, A⁻, []_S, and []_W represent undissociated AA, dissociated AA, the concentration in St, and the concentration in aqueous phase of the polymerization system, respectively.

On the other hand, the relationship between the pH of the polymerization system observed and the degree of neutralization of AA is described as in Figure 2. It is apparent from Figure 2 that in the polymerization system where AA is not neutralized, $[\text{H}^+]_W$ is much higher than $[\text{OH}^-]_W$. In this case, eq. (2) becomes eq. (5) and the concentration of the carboxylic monomer can be determined from eqs. (1), (3), (4), and (5):

$$[\text{H}^+]_W = [\text{A}^-]_W \quad (5)$$

It is also apparent from Figure 2 that in the polymerization system where AA is appreciably neutralized, $[\text{Na}^+]_W$ is much higher than $[\text{H}^+]_W$ or $[\text{OH}^-]_W$. In

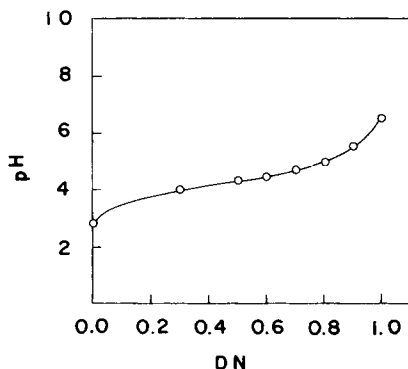


Fig. 2. Relationship between pH of polymerization system and degree of neutralization of carboxylic monomer: $DN =$ degree of neutralization of AA. Formulation for polymerization system, in g: water/AA/NaHCO₃/SDS/K₂SO₄ = 100/5/variable/0.05/0.85.

this case, eq. (2) becomes eq. (6) and the concentration of the carboxylic monomer can be determined from eqs. (3), (4), and (6):

$$[Na^+]_w = [A^-]_w \quad (6)$$

In eqs. (1) and (3), K and α are reported^{14,15} to be 5.66×10^{-5} and 0.102, respectively; and in eq. (4), V_S and V_W can be calculated by assuming the density of St to be 0.909 g/cm³ and the density of the aqueous phase to be 1 g/cm³. In this manner, the concentrations of undissociated AA and dissociated AA in the aqueous phase of the polymerization system are obtained.

On the other hand, the monomer reactivity ratios for the terpolymerization of undissociated AA, dissociated AA, and St can be calculated¹⁴ as in Table III from the Q and e values reported by Ito et al.¹⁶ Consequently, it is possible to calculate the composition of the growing radical formed in the aqueous phase at the initial stage of the polymerization by the use of the equation represented by Alfrey et al.¹⁷ In Table IV the calculation results of the concentration of the carboxylic monomer in the aqueous phase of the polymerization system and the composition of the growing radical formed in the aqueous phase at the initial stage of the polymerization are shown. It is apparent from Table IV that the molar fraction of undissociated AA of the growing radical decreases with increasing degree of neutralization of AA, whereas the molar fractions of both dissociated AA and St of the growing radical increase with increasing degree of neutralization of AA. This means that the hydrophilic nature of the growing radical changes considerably with degree of neutralization because the increase in the molar fraction of undissociated AA or dissociated AA will enhance the

TABLE III
Calculation Results of Monomer Reactivity Ratios^a

Monomer	Notation	Q	e	Monomer reactivity ratio
Undissociated AA	M_1	0.40 ^b	0.25 ^b	$r_{12} = 3.29; r_{13} = 0.308$
Dissociated AA	M_2	0.11 ^b	-0.15 ^b	$r_{21} = 0.259; r_{23} = 0.121$
St	M_3	1.00	-0.80	$r_{31} = 1.08; r_{32} = 5.41$

^a See reference 13.

^b From reference 15.

TABLE IV
Calculation Results of Change in Concentration of the Carboxylic Monomer and Composition of Growing Radical with Degree of Neutralization of the Carboxylic Monomer^a

Degree of neutralization of AA	Concentration of carboxylic monomer, mole/l. ^b		Composition of growing radical, molar fraction ^c		
	Undissociated AA	Dissociated AA	Undissociated AA	Dissociated AA	St
0.00	0.596	0.006	0.973	0.003	0.024
0.30	0.414	0.194	0.854	0.118	0.028
0.50	0.294	0.322	0.733	0.234	0.033
0.60	0.235	0.386	0.655	0.309	0.036
0.70	0.176	0.449	0.560	0.401	0.039
0.80	0.117	0.511	0.435	0.522	0.043
0.90	0.058	0.574	0.262	0.691	0.047
1.00	0.000	0.636	0.000	0.945	0.055

^a Formulation for polymerization system, in g: water/St/AA/NaHCO₃/SDS/KPS = 100/90.9/5/variable/0.05/1.32.

^b The concentration of the carboxylic monomer in the aqueous phase of the polymerization system.

^c The composition of the growing radical formed in the aqueous phase of the polymerization system at the initial stage of the polymerization.

hydrophilic nature of the growing radical, whereas the increase in molar fraction of St will reduce the hydrophilic nature of the growing radical. The change in the hydrophilic nature of the growing radical will affect the critical degree of polymerization above which the growing radical exceeds its solubility as well as the stability of the particle formed by the precipitation of the growing radical, which govern the number and uniformity of particles.^{10,18}

The change in the ionic strength of the polymerization system with degree of neutralization of AA seems to have little effect on the formation of particles, as has been described in a previous paper.¹⁰ On the other hand, the change in the pH of the polymerization system with degree of neutralization of AA may affect the formation of particles because the mode of decomposition of the initiator KPS is dependent on pH.^{19,20} Consequently, it seems that the above-described factors, as a whole, explain the complicated relationship between the number and uniformity of particles and the degree of neutralization of AA. At the present stage, however, the direct determination of the composition of the growing radical formed in the aqueous phase of the polymerization system has not successfully been established. Further investigations from this point of view seem to be necessary.

Effect of Amount of the Carboxylic Monomer

At a degree of neutralization of AA of 0.80, where the number of particles reaches a maximum, as has been described in the previous section, the effect of the amount of carboxylic monomer on the formation of particles was examined. The results are shown in Table V. The change in the number of particles in the polymerization system with amount of AA can be described as in Figure 3, which shows that the number of particles increases almost linearly with increasing

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

Amount of AA, g	Number of particles, $\times 10^{15b}$	Coefficient of variation of particle diameter, %
0.50	5.14	8.2
1.00	5.12	7.7
2.50	8.77	2.1
3.75	9.84	3.8
4.50	10.2	2.5
5.00 ^c	12.7	3.8

^a Polymerization recipe, in g: water/St/AA/NaHCO₃/SDS¹/KPS = 100/90.9/variable/variable/0.05/1.32.

^b Number of particles in the polymerization system.

^c Corresponds to the seventh run in Table II.

amount of AA. It is apparent from Table V that the coefficient of variation of particle diameter is fairly large in the range of an amount of AA smaller than 1.00 g, whereas it is small in the range of an amount of AA larger than 1.00 g. These results may also be explained by a change in the hydrophilic nature of the growing radicals formed in the aqueous phase.

To confirm this, the composition of the growing radical formed in the aqueous phase at the initial stage of the polymerization was calculated by the above-described procedure. In Table VI the calculation results of the concentration of the carboxylic monomer in the aqueous phase of the polymerization system and the composition of the growing radical formed in the aqueous phase at the initial stage of the polymerization are shown. It is apparent from Table VI that the molar fractions of both undissociated AA and dissociated AA of the growing radical increase gradually with increase in the amount of AA, whereas the molar fraction of St of the growing radical decreases significantly with increase in the amount of AA. This means that the hydrophilic nature of the growing radical increases considerably with increase in the amount of AA because the increase in the molar fraction of undissociated AA or dissociated AA as well as the decrease in the molar fraction of St enhance the hydrophilic nature of the growing radical. Such a remarkable effect of the amount of AA on the hydrophilic nature of the

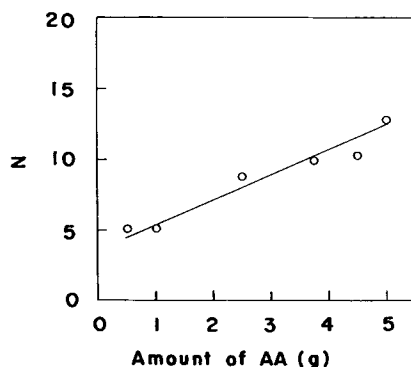


Fig. 3. Change in number of particles in the polymerization system with amount of carboxylic monomer: N = number of particles in the polymerization system $\times 10^{15}$.

TABLE VI
 Calculated Results of the Change of the Concentration of the Carboxylic Monomer
 and the Composition of the Growing Radical with the Amount
 of the Carboxylic Monomer^a

Amount of AA, g	Concentration of carboxylic monomer, mole/l. ^b		Composition of growing radical, molar fraction ^c		
	Undissociated AA	Dissociated AA	Undissociated AA	Dissociated AA	St
0.50	0.012	0.054	0.343	0.388	0.269
1.00	0.025	0.108	0.392	0.444	0.164
2.50	0.060	0.264	0.421	0.500	0.079
3.75	0.089	0.390	0.430	0.515	0.055
4.50	0.106	0.463	0.431	0.521	0.048
5.00	0.117	0.511	0.435	0.522	0.043

^a Formulation for polymerization system, in g: water/St/AA/NaHCO₃/SDS/KPS = 100/90.9/variable/variable/0.05/1.32.

^b The concentration of the carboxylic monomer in the aqueous phase of the polymerization system.

^c The composition of the growing radical formed in the aqueous phase of the polymerization system at the initial stage of the polymerization.

growing radical may at least qualitatively explain the change in the number and uniformity of particles with the amount of AA described above.

Effect of Introduction of AMS or MMA

The effect of the introduction of AMS or MMA on the formation of particles was examined at a degree of neutralization of AA of 0.80, where the number of particles reaches a maximum, as has been described in the previous section. The results are shown in Table VII. In Figure 4 the change in the number of particles in the polymerization system with amount of AMS or MMA is shown. It is apparent from Figure 4 that, with increasing amount of AMS, the number of particles increases gradually, whereas with increasing amount of MMA, the number of particles decreases remarkably in the range of an amount of MMA smaller

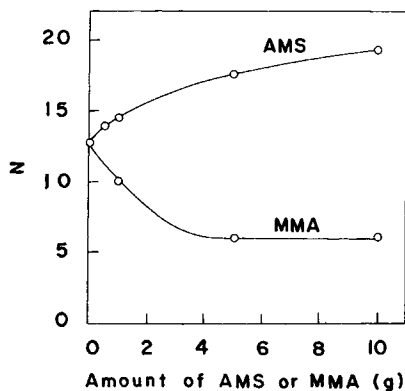


Fig. 4. Change in number of particles in the polymerization system with amount of AMS or MMA: N = number of particles in the polymerization system $\times 10^{15}$.

TABLE VII
Effect of Introduction of AMS or MMA on the Formation of Particles^a

Amount of AMS or MMA, g	Number of particles, $\times 10^{15b}$	Coefficient of variation of particle diameter, %
0.0 ^c	12.7	3.8
AMS 0.5	13.9	3.3
AMS 1.0	14.5	0.6
AMS 5.0	17.6	4.5
AMS 10.0	19.3	1.1
MMA 1.0	10.1	2.1
MMA 5.0	6.03	3.1
MMA 10.0	6.15	2.7

^a Polymerization recipe, in g: water/St/AA/NaHCO₃/SDS/KPS = 100/90.9(variable)/5/4.66/0.05/1.32. St was partially replaced by AMS or MMA.

^b Number of particles in the polymerization system.

^c Blank test; corresponds to the seventh run in Table II.

than 5 g and remains constant in the range of an amount of MMA from 5 g to 10 g. It is also apparent from Table VII that the coefficient of variation of particle diameter is fairly small irrespective of the amount of AMS or MMA.

The solubility of AMS or MMA in water at 20°C is reported²¹ to be approximately 0.056% (wt) or 1.6% (wt), respectively, which is somewhat larger than that of St, reported²¹ to be approximately 0.032% (wt). This means that in the presence of these monomers, the growing radical is formed in the aqueous phase by the multicomponent polymerization of undissociated AA, dissociated AA, St, and one of these monomers; and that the molar fraction of these monomers in the growing radical is considerably high. Consequently, the above-described effect of the introduction of AMS or MMA on the formation of particles may predominantly be attributed to a change in the hydrophilic nature of the growing radical formed in the aqueous phase because, at this concentration of SDS, it is believed that particles are formed by the precipitation of growing radicals formed in the aqueous phase.¹⁰

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