

## ***Polymerization Behavior of Carboxylic Monomers in the Preparation of Carboxylated Latexes***

### **INTRODUCTION**

Carboxylated latexes that are of great importance in the industrial use are, in general, prepared by copolymerizing carboxylic monomers.<sup>1</sup> The properties of these latexes are greatly dependent on the method of introduction of the carboxylic monomer,<sup>2,3</sup> which indicates that this method has a great effect on the polymerization behavior. Recently, the authors<sup>4</sup> have investigated the preparation and characterization of carboxylated isoprene/styrene copolymer latexes and demonstrated that the distribution of carboxyl groups is governed by the method of introduction of the carboxylic monomer. The introduction of the carboxylic monomer prior to the initiation of polymerization (initial-charge process) localizes only 12–13% of the total carboxyl groups on the surface of particles, whereas the introduction of the carboxylic monomer at the last stage of polymerization (shot process) localizes more than 60% of the total carboxyl groups on the surface of particles, though the percentage is greatly dependent on the shot conversion. It is of interest to clarify the reason why such a distribution of carboxyl groups takes place.

In this paper, the authors investigated the polymerization behavior of the carboxylic monomer in the initial-charge process and the shot process to elucidate the effect of the method of introduction of the carboxylic monomer on the distribution of carboxyl groups.

### **EXPERIMENTAL**

**Materials.** Deionized water was used. Extrapure-grade styrene (St), acrylic acid (AA), and methacrylic acid (MAA) were used after distillation under reduced pressure.

**Procedure.** The determination of the partition coefficients of carboxylic monomers was carried out as follows. Water, 100 ml, and the prescribed amount of the carboxylic monomer were placed in a 500-ml flask equipped with a stirrer. After the completion of dissolution, 100 ml St was introduced and stirred vigorously at 25°C. Then the mixture was kept at 25°C and the aqueous phase was separated and titrated with 1*N* aqueous solution of sodium hydroxide using phenolphthalein as indicator.

### **RESULTS AND DISCUSSION**

#### **Partition Coefficients of Carboxylic Monomers**

It is essential for the elucidation of the distribution of the carboxylic monomer in the polymerization system to determine the partition coefficient of the carboxylic monomer.

The partition coefficients of AA and MAA between St and water were determined by measuring the amount of the carboxylic monomer partitioned in water on the assumption that the association and dissociation of the carboxylic monomer in both phases can almost be neglected. The change of the amount of AA partitioned in water with the equilibration time is shown in Table I. It is apparent from Table I that the equilibration has been completed within 1 min. This was also the case for MAA. In Table II are shown the partition coefficients of AA and MAA thus obtained.

#### **Distribution of Carboxylic Monomers**

The distribution of carboxylic monomers in the polymerization system of the shot process was investigated. This process is composed of three steps.<sup>4</sup> In step 1, the emulsion copolymerization of isoprene (IP) and St is initiated and reacted to a conversion of 60–70%; in step 2, the latex is stabilized with an additional amount of soaps; and in step 3, the mixture of the carboxylic monomer and St is introduced (shot) at various conversions higher than 80% and the polymerization is substantially completed.

TABLE I  
Effect of Equilibration Time on the Partition of AA between St and Water at 25° C

Run no.	Equilibration time, min	Amount of AA partitioned in water, mmole
P-5 <sup>a</sup>	—	11.88
P-11	1/30	10.96
P-10	1/6	11.00
P-9	1	10.76
P-7	30	10.72
P-8	60	10.78

<sup>a</sup> Blank test without St.

TABLE II  
Partition Coefficients of AA and MAA Between St and Water Observed at 25° C

Carboxylic monomer	Partition coefficient
AA	0.102
MAA	1.01

The standard polymerization recipe of the shot process is shown in Table III, where POE(10), SDBS, KPS, NaOH, and t-DDM represent sodium polyoxyethylene nonylphenyl sulfate ( $n = 10$ ), sodium dodecylbenzenesulfonate, potassium persulfate, sodium hydroxide, and *tert*-dodecyl mercaptan, respectively. At the shot conversion of 90%, the unreacted monomer in the polymerization system may substantially be St because of the higher monomer reactivity ratio of IP than St.<sup>5</sup> Since St is sparingly soluble in water,<sup>6</sup> most of the unreacted St must be occluded in particles. Although we have no experimental results concerning the distribution of the unreacted St, with the aid of the encapsulation theory presented by Williams et al.<sup>7</sup> we may assume that it is localized in the outer layer of the particles. On the other hand, IP/St copolymers formed in steps 1 and 2 will be localized in the center of particles.

The mixture of the carboxylic monomer and St introduced in step 3 will distribute in this polymerization system as follows. St will be localized mainly in the outer layer of the particles, whereas the carboxylic monomer will be partitioned between St and water. The partition and dissociation equilibrium of the carboxylic monomer HA in this polymerization system is represented by the following equations<sup>8,9</sup>:

$$K = [\text{H}_3\text{O}^+]_w [\text{A}^-]_w / [\text{HA}]_w \quad (1)$$

$$[\text{Na}^+]_w + [\text{OH}_3^+]_w = [\text{OH}^-]_w + [\text{A}^-]_w \quad (2)$$

$$\alpha = [\text{HA}]_s / [\text{HA}]_w \quad (3)$$

$$(\text{HA}) = V_s [\text{HA}]_s + V_w ([\text{HA}]_w + [\text{A}^-]_w) \quad (4)$$

where  $K$ ,  $\alpha$ ,  $(\text{HA})$ ,  $V_s$ , and  $V_w$  are the dissociation constant of HA, the partition coefficient of HA between St and water, the total amount of HA, the volume of St, and the volume of water, respectively. The symbols  $[ ]_s$  and  $[ ]_w$  represent the concentrations in St and water, respectively. Taking into account the titration curve of a weak acid with a strong base,<sup>9</sup> it is apparent that in this polymerization system,  $[\text{Na}^+]_w$  is much higher than  $[\text{OH}_3^+]_w$  and  $[\text{OH}^-]_w$ . Therefore, eq. (2) becomes eq. (5):

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

Consequently, the distribution of the carboxylic monomer can be determined by using eq. (3), (4), and (5) and the partition coefficients in Table II.

From these considerations, the polymerization system of the shot process after the shot may be represented as follows. Particles are composed of 84.4% (wt) of IP/St copolymers localized in the center (core) and 15.6% (wt) of St localized in the outer layer (shell). The carboxylic monomer is partitioned between the shell and water. In Table IV are shown the calculation results of the dis-

TABLE III  
Standard Polymerization Recipe of the Shot Process<sup>a</sup>

Ingredient	Amount, g		
	Step 1	Step 2	Step 3
Water	120	20	10
IP	48	—	—
St	62.4	—	7.2
AA or MAA	—	—	2.4 or 2.87
POE(10)	1.7	0.57	—
SDBS	2.4	0.8	—
KPS	0.6	—	0.6
NaOH	0.2	—	—
t-DDM	0.3	—	—

<sup>a</sup> See ref. 4.

TABLE IV  
Calculation Results of the Distribution of Carboxylic Monomers  
in the Polymerization System

Carboxylic monomer	Concentration of carboxylic monomer, mmole/l.		
	[HA] <sub>W</sub>	[A <sup>-</sup> ] <sub>W</sub>	[HA] <sub>S</sub> <sup>a</sup>
AA	186	33	19
MAA	166	33	169

<sup>a</sup> The concentration of the carboxylic monomer in the unreacted St in the shell.

TABLE V  
Calculation Result of Monomer Reactivity Ratio for AA

Monomer Notation		Q	e	Monomer reactivity ratio
St	M <sub>1</sub>	1.00	-0.80	r <sub>12</sub> = 1.08; r <sub>13</sub> = 5.41
HA	M <sub>2</sub>	0.40 <sup>a</sup>	0.25 <sup>a</sup>	r <sub>21</sub> = 0.308; r <sub>23</sub> = 3.29
A <sup>-</sup>	M <sub>3</sub>	0.11 <sup>a</sup>	-0.15 <sup>a</sup>	r <sub>31</sub> = 0.121; r <sub>32</sub> = 0.259

<sup>a</sup> From ref. 11.

tribution of the carboxylic monomer in the polymerization system, where the densities of aqueous phase and the shell were regarded as 1 g/cm<sup>3</sup> and 0.909 g/cm<sup>3</sup>, respectively.

#### Polymerization Behavior of Carboxylic Monomers

The polymerization behavior of carboxylic monomers in the polymerization system of the shot process was investigated. The thermal decomposition of KPS in water gives sulfate radicals and hydroxyl radicals<sup>10</sup> which will add to monomers dissolved in water to form growing radicals. Since the monomers dissolved in water are HA, A<sup>-</sup>, and St, growing radicals formed in water will be the terpolymer of these monomers. The concentrations of HA and A<sup>-</sup> have already been shown in Table IV, and the concentration of St becomes 2.9 mmole/l. on the assumption that the solubility of St in water is 0.03% (wt).<sup>6</sup> In the case where AA is used as HA, the monomer reactivity ratio can be calculated as in Table V from the Q and e values reported by Ito et al.<sup>11</sup> The composition of the terpolymer formed immediately after the shot was calculated using the equation represented by Alfrey et al.,<sup>12</sup> and the result is shown in Table VI. The molar fraction of St in the terpolymer is lower than 0.05, which indicates that the growing radical is water soluble unless its degree of poly-

TABLE VI  
Calculation Result of Composition of Terpolymer for AA

Monomer unit	Concentration in aqueous phase, mmole/l.	Molar fraction in terpolymer
St	2.9	0.044
HA	186	0.908
A <sup>-</sup>	33	0.048

TABLE VII  
Calculation Results of Maximum Degree of Polymerization

Case no	$k_p$ , l./mole·sec	$L$ , cm	D.P. <sup>a</sup>
1	$1 \times 10^3$	$1.5 \times 10^{-5}$	$2.3 \times 10^{-2}$
2	$1 \times 10^3$	$7.5 \times 10^{-5}$	$5.6 \times 10^{-1}$
3	$1 \times 10^3$	$1.5 \times 10^{-4}$	2.3
4	$1 \times 10^4$	$1.5 \times 10^{-5}$	$2.3 \times 10^{-1}$
5	$1 \times 10^4$	$7.5 \times 10^{-5}$	5.6
6	$1 \times 10^4$	$1.5 \times 10^{-4}$	$2.3 \times 10$

<sup>a</sup> Maximum degree of polymerization reached by the growing radical during the period from initiation to collision.

merization has reached so high. In the case where MAA is used as HA, although the monomer reactivity ratio is unknown, the composition of the terpolymer may not differ so much from that of the first case because of the low concentration of St.

It has been demonstrated by Fitch et al.<sup>13</sup> that the growing radical formed in water will precipitate out to form a particle at a critical degree of polymerization or collide with particles. In the latter case, the maximum displacement  $L$  experienced by the growing radical during the period from the initiation to the collision is given by the following equation<sup>13</sup>:

$$L = 1/(\pi Na^2) \quad (6)$$

where  $N$  is the number of particles per unit volume and  $a$  is the radius of the particles. On the other hand, the relationship between the displacement  $L$  experienced by the growing radical and the degree of polymerization D.P. reached by the growing radical is represented by the following equation<sup>13</sup>:

$$\text{D.P.} = L^2 k_p [\text{M}]/(2D) \quad (7)$$

where  $k_p$  is the propagation rate constant of the growing radical,  $[\text{M}]$  is the concentration of the monomer, and  $D$  is the diffusion constant of the growing radical.

Consequently, from eq. (6) and (7), it is possible to calculate the maximum degree of polymerization reached by the growing radical during the period from the initiation to the collision. In the polymerization system after the shot, since  $a$  is about  $5 \times 10^{-6}$  cm and  $N$  is calculated to be  $8.4 \times 10^{14}$  particle/cm<sup>3</sup>,  $L$  becomes  $1.5 \times 10^{-5}$  cm from eq. (6). Although the accurate value of  $k_p$  for the terpolymerization of HA, A<sup>-</sup>, and St is unknown, it may be assumed to be in the range of  $1 \times 10^3$  to  $1 \times 10^4$  l./mole·sec.<sup>14</sup> In this manner, by assuming  $[\text{M}]$  and  $D$  to be  $2 \times 10^{-1}$  mole/l. and  $1 \times 10^{-6}$  cm<sup>2</sup>/sec, respectively,<sup>15</sup> D.P. was calculated from eq. (7) for the overestimated value of  $L$  ranging from  $1.5 \times 10^{-5}$  to  $1.5 \times 10^{-4}$  cm. The results are shown in Table VII. It is apparent from Table VII that, in spite of the overestimation of  $L$ , the maximum degree of polymerization reached by the growing radical during the period from the initiation to the collision is remarkably low in all cases. It is believed that the growing radical is water soluble at such a low degree of polymerization because the growing radical is very hydrophilic as described above. This means that, in this polymerization system, the growing radical collides with particles before it precipitates out to form a particle.

The above-described considerations lead us to the conclusion that, in the polymerization system of the shot process, the growing radical formed in water collides with particles immediately after the initiation and does not precipitate out to form a particle. After the collision, the growing radical will continue to propagate or be terminated with the other growing radical to yield the copolymer

of the carboxylic monomer and St in the shell. The carboxylic monomer must be supplied to the shell from water during the copolymerization process. Consequently, although the carboxylic monomer is partitioned between St in the shell and water, the fraction of the carboxylic monomer polymerized in water is negligibly small and most of the carboxylic monomer copolymerizes with St in the shell. This is consistent with the result in the previous paper<sup>4</sup> that the shot process does not give any water-soluble copolymers containing carboxyl groups.

### Distribution of Carboxyl Groups

The relationship between the polymerization behavior of the carboxylic monomer and the distribution of carboxyl groups was investigated. In the polymerization system of the shot process, since most of the carboxylic monomer copolymerizes with St in the shell, the shell is filled with carboxylic monomer/St copolymers. For example, after the completion of polymerization by the standard polymerization recipe, a particle about 500 Å in radius will be comprised of a core about 470 Å in radius filled with IP/St copolymers and a shell only 30 Å in thickness filled with carboxylic monomer/St copolymers. In contrast, in the polymerization system of the initial-charge process, the carboxylic monomer introduced prior to the initiation of polymerization will give terpolymers comprised of the carboxylic monomer, IP, and St, which will distribute rather uniformly in the particle.

The difference in the polymerization behavior of the carboxylic monomer between these two processes may reasonably explain the remarkably high percentage of carboxyl groups localized on the surface of particles in the shot process and the low percentage in the initial-charge process. In the former process, the polymerization behavior of the carboxylic monomer may explain also the strong effect of the shot conversion on the percentage of carboxyl groups localized on the surface of particles on the basis of the ratio of the thickness of the shell to the radius of the particle. Thus, the effect of the method of introduction of the carboxylic monomer on the distribution of carboxyl groups has been interpreted qualitatively, but it seems to be desirable to clarify the structure of the surface of particles more precisely.

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