

# Preparation of Carboxylated Polymer Emulsion Particles in Which Carboxyl Groups Are Predominantly Localized at Surface Layer by Using the Seeded Emulsion Polymerization Technique

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## Synopsis

It was studied how to localize carboxyl groups at the particle surface in a preparation of styrene (S)/butyl acrylate (BA)/methacrylic acid (MAA) polymer emulsion. The relative distribution of carboxyl groups in the emulsion was determined by conductometric titration method: in serum, at surface, and inside particle. By seeded (two-stage) emulsion polymerization that S-BA-MAA terpolymer emulsion was first prepared at low pH and then second stage polymerization of S-BA was continued at high pH, S/BA/MAA polymer emulsion particles in which carboxyl groups are localized predominantly at the surface could be prepared.

## INTRODUCTION

In order to give chemical reactivity to polymer particles and to improve various stabilities of polymer emulsion, carboxyl groups are generally introduced into polymer particles by emulsion copolymerization of such an unsaturated acid monomer as acrylic acid (AA) and methacrylic acid (MAA). In some cases, only carboxyl groups distributed at surface layer were useful.<sup>1-4</sup> A lot of workers reported that carboxyl groups tend to be distributed predominantly at the surface rather than inside the particles. This tendency is more remarkable in the case of AA than MAA, because AA is more hydrophilic than MAA.<sup>5-7</sup> However, even in the case of AA the absolute amount of carboxyl groups is more inside the particle than at the surface, because the volume of the inside is absolutely larger than that of surface layer. Moreover, in the case of AA, water-soluble polymers which have carboxyl groups are produced in serum in the process of copolymerization.<sup>5-7</sup> The production frequently results in various inexpediences. For the purpose of localizing carboxyl groups at the particle surface, there has been some experiments, for instance, post-addition<sup>8</sup> and neutralization<sup>9,10</sup> of the unsaturated monomer in the process of emulsion copolymerization. However, it seems that desirable results are not obtained in these experiments.

We have also studied this problem and succeeded in it by direct alkali hydrolysis of ester group at the surface of poly(ethyl acrylate) emulsion particles<sup>11</sup> or by redistribution of carboxyl groups in the carboxylated polymer particles from the inside to the surface.<sup>12</sup> The latter was induced by the

following treatment. Carboxyl groups in S-MAA copolymer emulsion were neutralized with alkali and then organic solvent, e.g., methyl ethyl ketone (MEK), was absorbed into the particles. After a certain time of standing, the organic solvent was removed by steam stripping. However, both of the methods described above are post-treatment and so need more than two processes.

In this work we tried to localize carboxyl groups predominantly at polymer surface layer in the process of emulsion polymerization on the basis of the knowledge obtained from the latter treatment described above. Thus emulsifier-free seeded (two-stage) emulsion polymerization for styrene (S) and butyl acrylate (BA) was carried out at high pH in the presence of S-BA-MAA terpolymer particles, which were formed at low pH in the absence of emulsifier. Although similar polymerization technique has already been applied to prepare a stable emulsifier-free polymer emulsion by Ceska,<sup>7</sup> the variation of relative acid distribution before and after the polymerization was not discussed therein.

## EXPERIMENTAL

### Materials

S, BA, and MAA were purified by distillation under reduced pressure in a nitrogen atmosphere and stored in a refrigerator. Analytical-grade potassium persulfate were purified by recrystallization. Analytical-grade MEK, hydrochloric acid, and potassium hydroxide were used without further purification.

### Seeded Emulsion Polymerization

S-BA-MAA (83.1/8.9/8, mol ratio) terpolymer seed emulsion was prepared in a reaction flask under conditions of no. 1 listed in Table I. Seeded emulsion copolymerization for S and BA (90.3/9.7, mol ratio) under conditions of no. 2 was carried out at alkali or acidic condition, where the

TABLE I  
Recipes of Emulsion Polymerization<sup>a</sup>

Sample no.	1	2
No. 1 Emulsion <sup>b</sup> (mL)		100
BA <sup>c</sup> (g)	27.1	2.9
S <sup>d</sup> (g)	205.5	21.5
MAA <sup>e</sup> (g)	16.4	
Water (g)	750	95.0
KPS <sup>f</sup> (mg)	1250	122
pH	2.2	9.5 <sup>g</sup> → 9.0

<sup>a</sup> Conducted at 70°C for 7 h under nitrogen atmosphere.

<sup>b</sup> Polymer concn, 24.4 g/100 mL.

<sup>c</sup> Butyl acrylate.

<sup>d</sup> Styrene.

<sup>e</sup> Methacrylic acid.

<sup>f</sup> Potassium persulfate.

<sup>g</sup> Adjusted with KOH.

monomers were added by two methods. (1) Absorption method: all monomers were preliminary absorbed in the seed particles at 2°C for 24 h before the seeded emulsion polymerization were started. (2) Dropwise method: all monomers were slowly added to the reaction flask from a micro feeder by dripping at the constant rate of 4.75 mL/h. It was confirmed by electron microscope observation that the second stage feed monomers were polymerized in the seed particles without forming new particles.

### Determination of Carboxyl Groups

Prior to the titration of carboxyl groups, the pH values of sample emulsions, which were above 9, were adjusted to 2 by addition of 0.2*N* HCl, and they were stirred for 2 h at room temperature. These emulsions were ultra-centrifuged at 20,000 rpm for 2 h to separate the serum and polymer particles, and then the latter were redispersed with a distilled deionized water. This process was repeated three times, and all supernatants were collected for the measurement of carboxyl groups in serum.

Conductometric titration was carried out at room temperature with 0.02*N* KOH by auto titrator (Hiranuma sangyo Co., Ltd., RAT-II). One drop of titrant was 0.1 mL and conductance of the system was measured after standing for 20 s. This procedures were repeated. The amounts of carboxyl groups distributed in three loci were determined as follows. In serum: The amount of carboxyl groups in serum was measured by titration of the supernatant collected as described above. At particle surface: It at particle surface was calculated by subtracting that in serum from that titrated in sample emulsion. Inside particle: It inside particle was calculated by subtracting that in sample emulsion from total amount of carboxyl groups calculated from the polymerization recipe.

## RESULT AND DISCUSSION

### Preliminary Experiments

Prior to the seeded emulsion polymerization which will be carried out to localize carboxyl groups at particle surface in the following section, the effect of each condition at the polymerization, that is, increasing of affinity against water by ionization of carboxyl groups, on redistribution of carboxyl groups at particle surface was investigated. Three kinds of treatments of the S-BA-MAA terpolymer emulsion were carried out: "heat treatment," "alkali treatment," and "alkali-organic liquid treatment." In the heat treatment, the emulsion was stirred at 70°C for 7 h, of which pH was about 3. In the alkali treatment, the emulsion, of which pH was adjusted to about 9.5 with KOH was stirred at 70°C for 7 h. In the alkali-organic liquid treatment, the emulsion, of which pH value was adjusted to about 9.5 with KOH, was absorbed the same volume of MEK to polymer solid at 70°C for 7 h, and then all MEK absorbed into particle was removed by steam stripping.

Figure 1 shows the distribution of carboxyl groups in three loci after various treatments. In the control, the percentage of carboxyl groups distributed inside the particle was 87% and that at the surface was only 10%. By the alkali treatment, the percentage inside the particle decreased to 71% and that

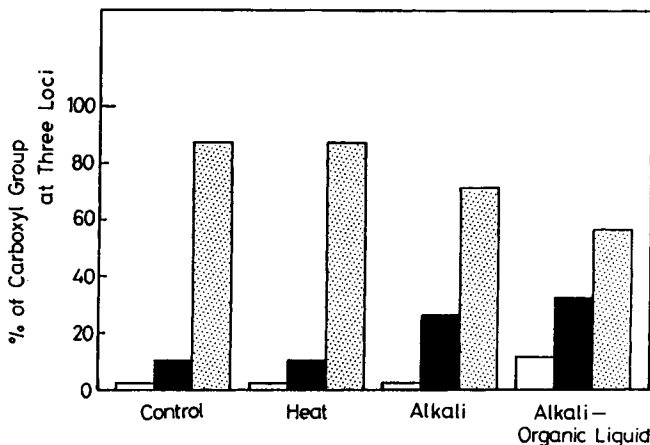


Fig. 1. Modes of distribution of carboxyl groups in S-BA-MMA (82.8/9.2/8.0, mol ratio) terpolymer seed emulsion after various treatments: heat, treated at 70°C, pH 3 for 7 h; alkali, treated at 70°C, pH 9.5 (by KOH) for 7 h; alkali-organic liquid, treated at 70°C, pH 9.5 (by KOH) for 7 h after absorbing the same volume of methyl ethyl ketone into the particles. (□) In serum; (■) on surface; (▨) inside particle.

at the particle surface increased to 26%. Further, by the alkali-organic liquid treatment, the percentage inside the particle decreased to 56% and that at the particle surface increased to 32%, although a little amount of carboxyl groups were distributed in the serum.

These results will be explained as follows. In the case of the heat treatment, there was no driving force to move polymer segments having carboxyl groups from the inside to the surface. In the case of the alkali treatment, although affinity of carboxyl groups against water was increased by ionization, the mobility of polymer segments were not enough, because treating temperature was nearly equal to the glass-transition temperature of this polymer (calculated value 78°C). In the case of the alkali-organic liquid treatment, polymer segments having ionized carboxyl groups inside the particles will easily move to the surface because MEK is absorbed in the particles once the viscosity is reduced therein.

The result of these preliminary experiments, especially the result of the alkali-organic liquid treatment, indicates that there is a possibility of attaining the purpose of this investigation because the situations of the treatment resembles those in the seeded emulsion polymerization for S and BA in the presence of S-BA-MAA terpolymer particles under alkali condition. The difference may be only that monomer operates the function of MEK.

Here, in order to clarify whether the hydrolysis of ester groups in BA unit occurred or not, the solution consisting of 0.7 g of nonionic emulsifier, 14 g of BA, 290 g of water, of which pH was adjusted to 9.5 with KOH, was stirred at 70°C for 7 h. Amount of carboxyl groups titrated in the solution was less than that 0.05% of feed BA. This result indicates that the influence of the hydrolysis of BA component on the distribution of carboxyl groups in the emulsion can be negligible and will be also ignored in seeded emulsion polymerization conducted in the following section.

### Seeded Emulsion Polymerization

The emulsifier-free S-BA-MAA terpolymer emulsion used in the above preliminary experiment was used as seed emulsion. Emulsifier-free seeded emulsion polymerization for S and BA was carried out at 70 °C under alkali or acid condition by batch or dropwise monomer addition method.

Figure 2 shows the relative distribution of carboxyl groups in three loci in the produced emulsion. In the case of seeded emulsion polymerization under alkali condition, the amount of carboxyl groups at the surface increased as follows, although the amount in the serum also increased somewhat: Using the dropwise method, the percentage of carboxyl groups inside the particle decreased from 87 to 51% and that at the surface increased from 10 to 37%. Moreover, using the absorption method, it inside the particle sharply decreased to 30% and that at the surface remarkably increased to 56%. The difference between these monomer addition methods seems to be due to the difference of viscosity in the particles. Thus, in the case of the absorption method the viscosity was lower than that in the case of dropwise method. On the other hand, the effect that localizes carboxyl groups at the surface in the case of the seeded emulsion polymerization under acidic condition was not observed. These results indicate that polymer segments including carboxyl groups move from the inside to the surface by ionization of carboxyl groups and by swelling with monomers as presuming from the above preliminary experiment.

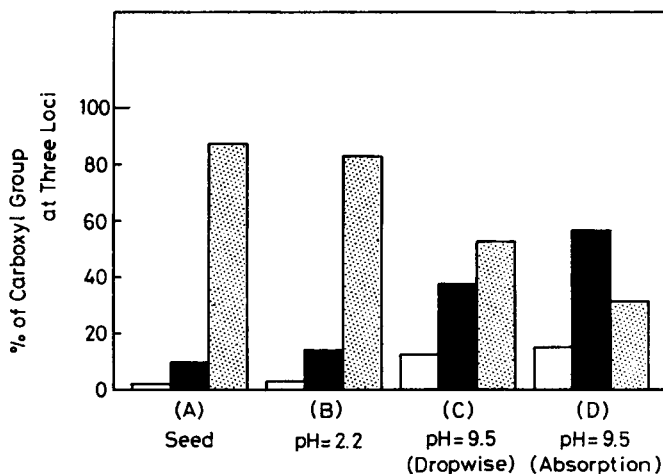


Fig. 2. Modes of distribution of carboxyl groups in S/BA/MAA (86.7/9.3/4.0, mol ratio) polymer emulsion (B, C, D) prepared by seeded emulsion polymerization (no. 2 in Table I) for S and BA with S-BA-MAA (83.1/8.9/8.0, mol ratio) terpolymer seeded emulsion (A) at pH 9.5 (C, D) or 2.2 (B) and at 70 °C using absorption (B, D) or dropwise (C) monomer addition method. (□) In serum; (■) on surface; (▨) inside particle.

In this way, by the emulsifier-free seeded (stage-type) emulsion polymerization in which carboxylated seed polymer emulsion is first prepared at low pH and, subsequently, second-stage polymerization without unsaturated acid monomer is continued at high pH, we have succeeded in preparing carboxylated polymer emulsion particles in which carboxyl groups are localized predominantly at the surface layer.

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