

## The Effect of Carboxylic Monomers on Surfactant-Free Emulsion Copolymerization

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### Synopsis

A study was made of the effect of carboxylic monomers on the surfactant-free emulsion polymerization of styrene and styrene-butadiene. Acid monomers, such as acrylic acid, methacrylic acid, and itaconic acid, were shown to play a critical role in particle formation and particle stabilization in such systems. In the emulsion polymerization of styrene, methacrylic acid forms particles more efficiently than acrylic acid. This difference is attributed to the more hydrophobic nature of the methacrylic monomer which allows it to diffuse more rapidly to the particle surface where it acts to prevent agglomeration. The ability of carboxyl groups to orient at the particle-water interface was studied by acid-base and soap titrations of carboxylated styrene-butadiene latices. The polymerization of itaconic acid onto the particle surface of a styrene-butadiene latex produces a surface carboxyl density much higher than is obtainable with classically adsorbed surfactants. This result is used to explain the greater stability of carboxylated versus noncarboxylated emulsion polymers. During the polymerization of styrene-butadiene latices, carboxyl groups derived from methacrylic acid are shown to be buried more deeply into the particle as compared to carboxyls derived from the more hydrophilic acrylic acid which orient more at the particle-water interface.

### INTRODUCTION

Many papers have been written comparing the emulsion polymerization of partially water-soluble monomers to the polymerization of relatively water-insoluble monomers.<sup>1-3</sup> For example, particle formation in emulsion polymerizations involving vinyl acetate, acrylonitrile, or methyl methacrylate is influenced by the solubility of monomer in the aqueous phase.<sup>4-7</sup> However, little quantitative work has been reported on the effect of water-soluble, functional monomers polymerized in combination with relatively water-insoluble monomers.<sup>8</sup>

Considering the technological importance of functionally modified hydrophobic emulsion polymers, the lack of reported data in this field (except for patent literature) is surprising. Carboxyl, amide, and sulfo monomers have been exploited extensively in the preparation of styrene, acrylate, and vinyl acetate-based latices. In the production of emulsion polymers for use in formulations in the paint, paper, and textile fields, functional monomers have in part or in some cases totally replaced conventional surfactants. Charge stabilization produced by copolymerized, chemically bound stabilizers has been found more effective than charge obtained by physically adsorbed surface active agents.<sup>9,10</sup>

The mechanism of particle formation in nonmicellar emulsion systems has been an area of considerable interest in recent years.<sup>11</sup> This article explores the effects of carboxylic monomers on particle formation and stabilization in the surfactant-free emulsion polymerization of styrene and copolymers containing styrene.

## EXPERIMENTAL

### Materials

Sinclair-Koppers' polymer-grade styrene and Arco's butadiene were used in all polymerizations. The persulfate used was Baker reagent grade. Sapon WD, a low-salt sodium lauryl sulfate from Alcolac Chemical, was used in the soap titrations.

### Procedures

The polymerizations were run in quart bottles in a rotary bottle polymerizer. The runs were followed gravimetrically by driving off water and monomers from a weighed sample in an oven set at 175°C.

The soap titrations were carried out using the procedures of Maron et al.<sup>12</sup> Photomicrographs were taken with a Philips EM-75B electron microscope calibrated with a carbon replica grading having 54,864 lines per inch. Samples were hardened with bromine water before using.

## RESULTS AND DISCUSSION

### The Generation of Particles by Acid Monomers

The classical Smith-Ewart theory was the first successful interpretation of the kinetics of emulsion polymerization. The theory argues that polymerization proceeds inside monomer swollen particles which originated from micelles formed from surfactant molecules. Hence, the rate of polymerization is directly proportional to the number of particles present and therefore to some function of the concentration of surface-active agent.

Table I describes surfactant-free emulsion polymerization recipes containing varied amounts of methacrylic acid. Figure 1 illustrates the effect of the methacrylic acid on the polymerization rate of styrene. The polymerization rates are a direct, monotonic function of the concentration of methacrylic acid. The function of the acid monomer is twofold. It induces the formation of polymer particles, thereby increasing polymerization rate, and lends stability to the polymer particles. Table II and Figure 2 describe the same phenomena with acrylic acid substituted for methacrylic acid.

Figure 3 depicts the effect of equal mole-% methacrylic, acrylic, and itaconic acids on polymerization rate and hence particle formation (see also Table III). The ability of the carboxylic monomers to generate particles is inversely related to their hydrophilicity, with the most hydrophilic, itaconic acid, being least effective. It is known that the distribution of acid monomer

TABLE I  
Surfactant-Free Formulations with Varied Methacrylic acid<sup>a</sup>

	Sample 1	2	3	4	5
Styrene, g	60	60	60	60	60
Methacrylic acid, g	0	1	2	3	4
Potassium persulfate, g	0.40	0.40	0.40	0.40	0.40
Water, g	220	220	220	220	220

<sup>a</sup> Temperature 70.0°C.

TABLE II  
Surfactant-Free Formulation with Varied Acrylic Acid<sup>a</sup>

	Sample 1	2	3	4	5
Styrene, g	60	60	60	60	60
Acrylic acid, g	0	1	2	3	4
Potassium persulfate, g	0.40	0.40	0.40	0.40	0.40
Water, g	220	220	220	220	220

<sup>a</sup> Temperature 70.0°C.

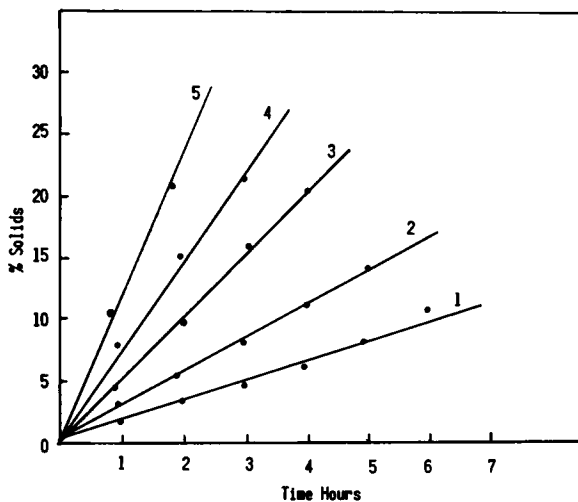


Fig. 1. Rates of polymerization as a function of methacrylic acid content: (1) 0% acid; (2) 1.6% acid; (3) 3.3% acid; (4) 5% acid; (5) 6.7% acid.

between styrene and water is in the order methacrylic acid > acrylic acid > itaconic acid. Therefore, the acid monomer with the greatest concentration in the styrene monomer is most effective in generating particles. The surface tensions of the three latices at approximately 20% solids are: methacrylic acid = 72, acrylic acid = 55, and itaconic acid = 56. The more hydrophobic monomer, methacrylic acid, does not produce any "free" surface-active components as do the more hydrophilic acrylic and itaconic acids.

Of interest in comparing the three curves in Figure 3 and the curves in Figures 1 and 2 is the linear rates exhibited by methacrylic acid as compared

TABLE III  
Surfactant-Free Formulations with Equivalent Amounts of Acrylic,  
Methacrylic, and Itaconic Acid.<sup>a</sup>

	Sample 1	2	3
Styrene, g	60	60	60
Methacrylic acid, g	2.40	—	—
Acrylic acid, g	—	2.00	—
Itaconic acid, g	—	—	3.64
Potassium persulfate, g	0.40	0.40	0.40
Water, g	220	220	220

<sup>a</sup> Temperature 70.0°C.

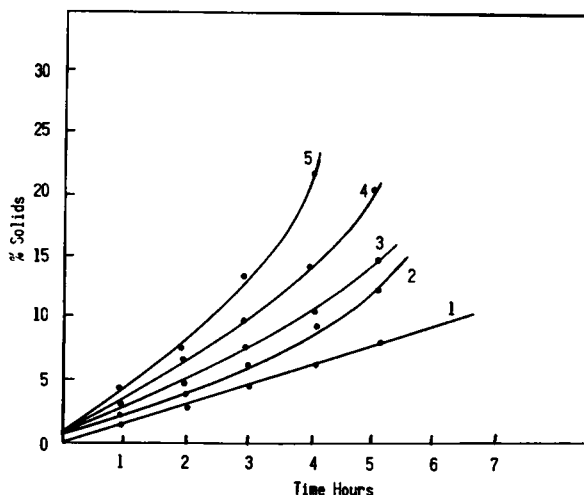


Fig. 2. Rates of polymerization as a function of acrylic acid content: (1) 0% acid; (2) 1.6% acid; (3) 3.3% acid; (4) 5% acid; (5) 6.7% acid.

to the increasing rate-time curves in the acrylic acid-itaconic acid runs. Acrylic and itaconic acids lead to particle generation at high conversion not evidenced with methacrylic acid.

The ability of acid monomers to induce the generation of particles in emulsion polymerization is clearly illustrated by the data in Figures 1-3. To more thoroughly investigate this phenomenon, a series of surfactant-free styrene-butadiene latices containing varied amounts of itaconic acid was prepared with formulations as described in Table IV. Table V shows the average particle diameters of the resulting latices as determined by electron microscopy. The decrease in particle size with increasing itaconic acid correlates with the increase in rates shown in Figure 4. After a short induction period, the styrene-butadiene runs, unlike the styrene polymerization with itaconic acid, display a linear rate. A log-log plot of particle number  $N$  versus weight-% itaconic acid, as shown in Figure 5, produces a line with slope approximating 0.6, the same slope expected ideally from

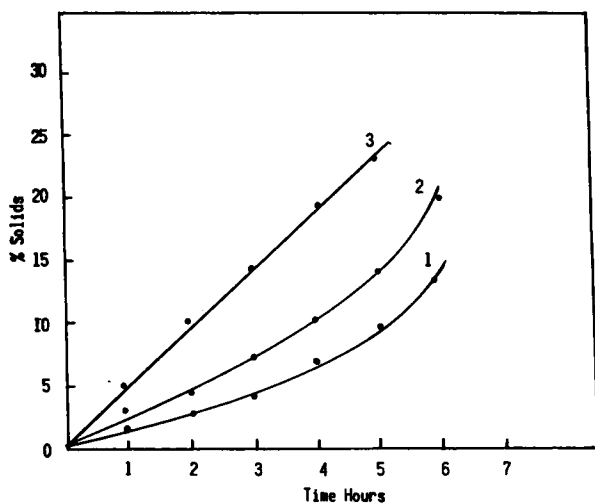


Fig. 3. Effect of equimolar amounts of acrylic, methacrylic, and itaconic acids on polymerization rates: (1) itaconic acid; (2) acrylic acid; (3) methacrylic acid.

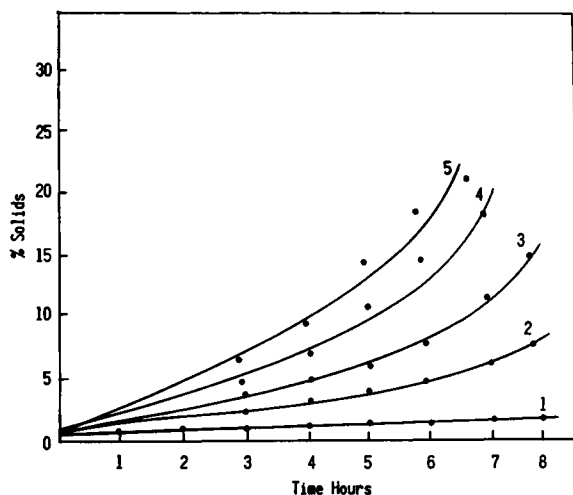


Fig. 4. Rates of polymerizations of styrene-butadiene latices as a function of itaconic concentration: (1) 0%; (2) 0.82%; (3) 1.62%; (4) 3.2%; (5) 4.70%.

Smith-Ewart theory for the dependence of particle number on soap concentration.

Qualitatively, the ability of acid monomers to induce particle formation can be explained by the theory of Fitch and co-workers.<sup>13,14</sup> Persulfate radicals induce polymerization in the aqueous phase producing highly carboxylated oligomers which combine and nucleate to form particles. Particle growth continues inside the particle. The particle maintains its stability from the hydrophilic shell provided by the carboxyl groups which concentrate at the particle-water interface. The concept of a micelle is un-

TABLE IV  
Surfactant-Free Formulations Containing Varied Amounts of Itaconic Acid<sup>a</sup>

	Sample 1	2	3	4	5	6
Styrene, g	36	36	36	36	36	36
Butadiene, g	25	25	25	25	25	25
Water, g	220	220	220	220	220	220
Itaconic acid, g	0	0.50	1.0	2.0	3.0	4.0
Potassium persulfate, g	0.40	0.40	0.40	0.40	0.40	0.40

<sup>a</sup> Temperature 70.0°C.

TABLE V  
Particle Sizes of Styrene-Butadiene Latices Containing Varied Amounts of Itaconic Acid

Itaconic acid, wt-%	Number of particles counted	Arithmetic average diameter, $\mu$	Surface average diameter, $\mu$
0.82	617	0.1336	0.1534
1.62	946	0.1121	0.1134
3.20	542	0.0946	0.0957
4.70	788	0.0805	0.0812

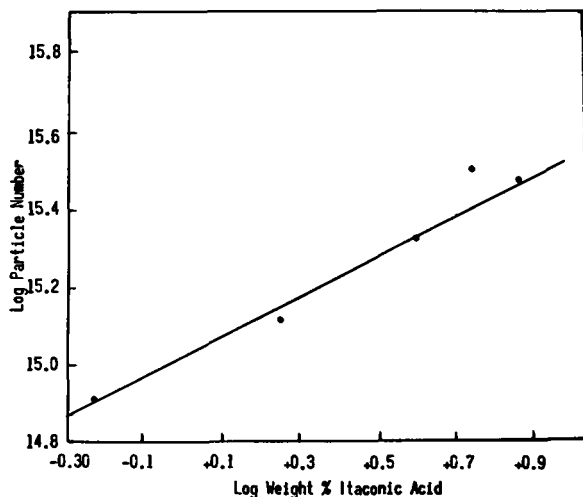


Fig. 5. Number of particles as a function of itaconic acid concentration.

necessary in this explanation of particle formation. The highly carboxylated oligomers formed in situ during the polymerization are similar to the carboxylated polymeric soaps reported by Graham and Roe.<sup>15,16</sup>

It is of interest to comment on the differences observed between the nature of the copolymeric carboxylic monomer and its effect on particle formation. These differences must relate to varied reactivities of the acids and their distributions between monomer droplets and aqueous phase. In the polymerization of styrene, as shown in Figure 3 for equimolar amounts of acid, rates fall in the order methacrylic acid > acrylic acid > itaconic acid.

The more hydrophobic the monomer, the faster the rate. Particle nucleation begins in the aqueous phase with the generation of oligomers containing sulfate and carboxyl moieties. These oligomers agglomerate and nucleate when they become water insoluble.

To support polymerization, these newly formed particles become rapidly swollen with styrene monomer. In its initial stages, accompanied by a large increase in surface area, the particle will agglomerate to form new, larger particles until it achieves sufficient stabilization from entering hydrophilic carboxyl and sulfate groups. There are two mechanisms by which the carboxyl group can reach the existing particle. One mechanism is the diffusion of functional oligomers or functional oligomeric radicals formed in the aqueous phase onto the particle surface. The other possible source of functional monomer incorporation onto the particle surface involves the diffusion of polar monomer, alone or in combination with hydrocarbon monomer, onto the growing particle where it then polymerizes and orients on the particle surface.

The data of Figure 3 indicates that the monomer diffusion mechanism is most important. Polymerization rates in the presence of equimolar amounts of acid monomer fall in the order methacrylic acid > acrylic acid > itaconic acid. As the carboxyl monomer becomes more hydrophobic, the polymerization rate becomes greater because of the smaller particle size that is generated. The more hydrophobic monomer can diffuse into the particle, polymerize, and thereby stabilize the growing particle more readily than the hydrophilic itaconic acid that must wait to be carried to the particle surface by means of oligomeric radicals formed in the aqueous phase. If aqueous oligomer diffusion predominated as the major mechanism for functional group incorporation and particle stabilization, the more hydrophilic monomer, being more concentrated in the aqueous phase, would be expected to produce the smallest particle-size latex having the fastest rate of polymerization. The lower reactivity of itaconic acid as compared to acrylic or methacrylic acid must also be considered as a hindrance to its incorporation onto the particle surface.

No attempt has been made in this study to assess the role in particle formation of sulfate radical ions generated by persulfate initiator. Sulfated radical ions transported to the particle surface by oligomeric radical ions undoubtedly serve a function in the generation and stabilization of latex particles.

### **Copolymerized, Carboxylic Monomers at the Particle-Water Interface**

The nature of the particle-water interface is the determining factor in many of the colloidal and application properties of emulsion polymers. Mechanical and chemical stability, adhesion, and rheological properties are just a few of the properties that are directly related to the composition of the particle surface and the interaction of this surface with the surrounding media. Unlike bulk properties, properties related to surface phenomena

TABLE VI  
Results of Soap Titration Data on Styrene-Butadiene Latices with Varied  
Itaconic Acid at Low pH

Itaconic acid, wt-%	pH	Total area/g polymer, $\times 10^{-21}$ , $\text{\AA}^2$ <sup>a</sup>	Moles soap/g polymer, $\times 10^{16}$ <sup>b</sup>	Free area/g polymer, $\times 10^{-21}$ , $\text{\AA}^2$	Coverage by itaconic carboxyl, %
0.82	2.80	4.40	1.19	4.37	0
1.60	2.80	5.25	0.698	2.56	51
3.20	2.70	6.21	0.725	2.66	57
4.70	2.70	7.39	0.678	2.49	66

<sup>a</sup> Total surface area calculated using surface average diameter.

<sup>b</sup> Effective surface area of sodium lauryl sulfate,  $61 \text{\AA}^2$  molecule.

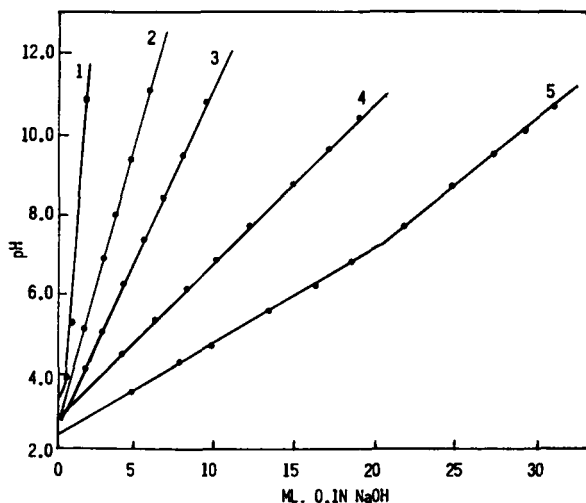


Fig. 6. Acid-base titration of latices with varied itaconic acid content: (1) 0%; (2) 0.82%; (3) 1.62%; (4) 3.20%; (5) 4.70%.

can undergo extreme variations with only small changes in the composition of a colloidal system. The success or failure of the preparation or application of an emulsion polymer may be dependent on the presence or absence of as little as 0.5% of an ingredient at the particle-water interface. This work is concerned with the effect of placing anionic charge at a latex particle-water interface by copolymerizing hydrophilic acidic monomers onto a hydrophobic surface.

Styrene-butadiene latices prepared as described in Table IV with varied itaconic acid were subjected to soap titration and base titration as shown in Tables VI and VII and Figure 6. The base titrations of Figure 6 indicate an increasing acidity of the particle surface as more itaconic acid is polymerized onto the particle. The only break in the straight-line relationships between pH and added base occurs at approximately pH 6.5, for the latex containing



TABLE VII  
Results of Soap Titration Data on Styrene-Butadiene Latices with Varied  
Itaconic Acid at High pH

Itaconic acid, wt-%	pH	Total area/g polymer, $\times 10^{-21} \text{ \AA}^2$ <sup>a</sup>	Moles soap/g polymer $\times 10^4$ <sup>b</sup>	Free area/g polymer, $\times 10^{-21} \text{ \AA}^2$	Coverage by itaconic carboxyl, %
0.82	10.2	4.40	0.698	2.56	42
1.60	10.2	5.25	0.459	1.68	68
3.20	10.2	6.21	0.341	1.25	80
4.70	10.2	7.39	0.315	1.16	83

<sup>a</sup> Total surface area calculated using surface average diameter.

<sup>b</sup> Effective surface area of sodium lauryl sulfate,  $61 \text{ \AA}^2$  molecule.

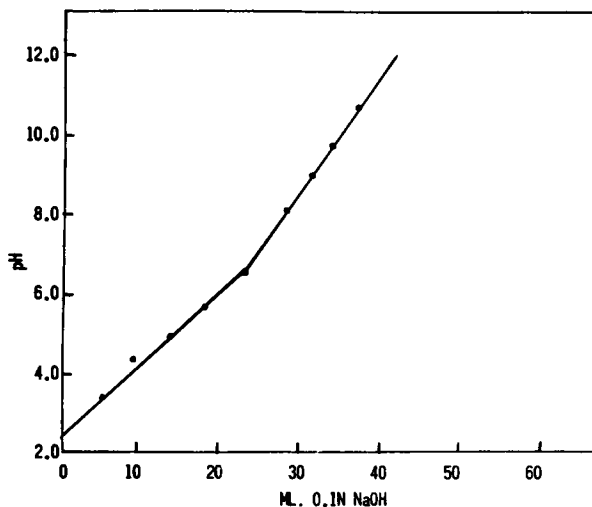


Fig. 7. Acid-base titration of monomeric itaconic acid.

the highest itaconic acid content. However, the titration curve for monomeric itaconic acid shown in Figure 7 indicates that this change in slope is due to unpolymerized acid monomer. The curves of Figure 6 reveal that there are no carboxyl groups on the particle surface which have a distinct  $pK_a$  value. The acidity of the particle surface can only be described as being less acidic as the pH of the emulsion system is raised. As the pH is raised, the increasing concentration of negative carboxyl groups acts through inductive and field effects to weaken the acidity of un-ionized carboxyls in their vicinity. Similar behavior is found in the base titration of polycarboxylic acids.<sup>17</sup>

Soap titrations were carried out to ascertain how effectively the copolymerized itaconic acid accumulates at the particle-water interface. These data are shown in Tables VI and VII. The particle size data of Table V were used to determine the total surface area of the styrene-

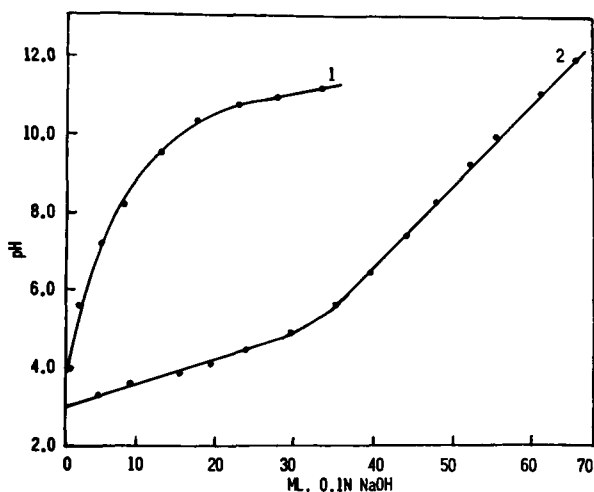


Fig. 8. Acid-base titration of styrene-butadiene latices containing methacrylic and acrylic acids: (1) methacrylic acid (6.15 milliequiv.); (2) acrylic acid (8 milliequiv.).

butadiene latices of varied itaconic acid content. The soap titration results were used to calculate the area covered by soap using the effective molecular area for sodium lauryl sulfate as  $61 \text{ \AA}^2/\text{molecule}$ .<sup>18</sup> The "free area" not protected by surface carboxyl was calculated from the difference between total area and the soap-covered area. The per cent area shielded by carboxyl groups was determined as "free area" per gram of polymer divided by total area per gram of polymer. As the concentration of polar carboxyl groups increases at the particle surface, the amount of surfactant per gram of polymer adsorbed by the surface decreases. The ability of the carboxyl moieties to effectively cover or "protect" the particle surface is enhanced at high pH due to the increased charge imposed on the particle by neutralized carboxyl groups.

At high pH and approximately 3% itaconic acid content, very little adsorbed surfactant is required to saturate the particle surface. The enhanced stability of carboxylated emulsion polymers compared to more classical noncarboxylated emulsions stabilized by adsorbed surfactants can be explained by the high carboxyl content that can be placed on the particle surface by carboxyl monomer. For example, the equivalent weights per carboxyl group of stearic acid, abietic acid, and itaconic acid are 284, 302, and 65, respectively. The particle surface of the latex of Table VII containing 3.2% itaconic acid would require 15% abietic acid to achieve an equal concentration of carboxyl moieties. However, the surface would be saturated with surfactant at much lower soap concentrations. Therefore, conventional surfactants cannot provide emulsion polymers with the surface charge density and hence the stability of polymers prepared with carboxylic monomers.

TABLE VIII  
Styrene-Butadiene Latices Carboxylated with Acrylic and  
Methacrylic Acids

	Sample 1	Sample 2
Styrene, g	60	60
Butadiene, g	40	40
Potassium persulfate, g	0.32	0.32
Methacrylic acid, g	5.0	—
Acrylic acid, g	—	5.0

Figure 8 depicts the acid-base titration of two styrene-butadiene latices whose composition is shown in Table VIII. The latex prepared with acrylic acid has a distinctly more acidic surface than the latex containing methacrylic acid. The increased hydrophobic character of methacrylic acid compared with acrylic acid causes the methacrylic carboxyls to become buried inside the polymer particle where they cannot be titrated with aqueous base. In this system, acrylic acid will be much more effective than methacrylic acid in producing negative charge density at the particle-water interface.

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