

Role of Itaconic Acid in Latex Particle Nucleation

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SYNOPSIS

Itaconic acid, a carboxylated water-soluble monomer, was examined in terms of its role in latex particle nucleation when copolymerized with acrylate monomers. From emulsion polymerizations in which the particle number concentrations were followed as a function of monomer conversion, it was found that the greater the amount of itaconic acid present, the larger the final latex particle diameter. This was interpreted as the result of the lower number of primary particles being initially nucleated. The above observations can be explained by the incorporation of the hydrophilic itaconic acid into acrylate oligomeric radicals that initially form. This incorporation increases the water-solubility of the radicals such that a lower proportion of these radicals is likely to precipitate to form primary particles.

INTRODUCTION

Itaconic acid (IA) is a dicarboxylated vinyl monomer that finds occasional use in the preparation of carboxylated latexes. This type of latex, generally produced from the emulsion copolymerization of a base hydrophobic monomer and a small amount of hydrophilic carboxylated monomer, tends to exhibit improved colloidal and mechanical properties,¹ making them useful in commercial applications.

In an emulsion copolymerization, itaconic acid residues mainly in the aqueous phase, owing to its polar nature.² It is also known that this monomer is slow to polymerize in both solution homopolymerization³ and emulsion copolymerization.⁴⁻⁶ These factors are likely to affect the final properties of latexes made with itaconic acid.

Our previous paper on itaconic acid described the induced decomposition of potassium persulfate initiator by this acid monomer, as well as its emulsion copolymerization with acrylate esters.⁷ One of the major goals of our continuing study of the emulsion copolymerization of this carboxylated monomer with *n*-butyl (BA) and methyl acrylates (MA) is to better understand the role that itaconic acid plays in latex particle nucleation and growth.

This goal was achieved by experimental determination of the particle number concentration as a function of the monomer conversion, rather than just considering the final latex particle sizes. Taking the latter approach may lead to simplistic explanations of the nucleation process, as well as a neglect of important events that contribute to the final particle size.

EXPERIMENTAL

Reagents

The itaconic acid (Pfizer, Inc. refined grade) was used as supplied. The butyl and methyl acrylate monomers (BASF) were purified by distillation under reduced pressure. The 4,4'-azobis(4-cyanopentanoic acid) (ACPA) (Wako Pure Chemical Industries Ltd., U.S.) initiator was neutralized with an equivalent amount of NaOH to make it water soluble just prior to use. The sodium lauryl sulfate (Henkel) and *n*-dodecyl mercaptan (Pennwalt) were used without further purification.

Latex Preparation

Table I gives the polymerization recipe, in which the concentration of itaconic acid in the aqueous phase was varied from 0.0 to 16.7 mM. The percent

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Table I Recipe for Batch Latex Polymerizations

Compound	Weight (g)
<i>n</i> -Butyl acrylate	9.13
Methyl acrylate	1.13
Itaconic acid	0.0–0.90
Sodium lauryl sulfate	0.09
ACPA initiator	0.18
<i>n</i> -Dodecyl mercaptan	0.03
Distilled, deionized water	415

solids were at 3% to avoid coagulation problems. The latexes were polymerized in batch for 2 h at 60°C. Ten-ml samples were withdrawn periodically for gravimetric determination of the percent conversion by drying the latex samples for 24 h at 50°C. One-ml portions of each sample were reserved for particle size analysis.

Particle Number Concentrations

The particle size of each sample was measured by transmission electron microscopy using the negative staining technique developed by Shaffer et al.⁸ Approximately 500 particles were measured for each sample to calculate the average diameter in nanometers. To estimate the particle number concentration at any one point in the polymerization, the total volume of polymer formed at that time (known from the percent conversion) was divided by the average particle volume (known from the average particle diameter) at that time. The number of particles was then divided by the total volume of latex to yield the particle number concentration.

Copolymerization Reactivity Ratios

These values were determined experimentally for the pairs butyl acrylate/itaconic acid and methyl acrylate/itaconic acid. Solution copolymerizations were carried out in 50/50 mixtures of water and dioxane at 60°C. This solvent mixture was chosen to ensure that the monomers and the resultant copolymers remained soluble during the polymerizations. ACPA initiator was used and the weight ratios of itaconic acid to acrylate ester were varied from 4/10 to 12/10. The polymerizations were allowed to proceed to less than 10% conversion. The copolymer compositions were determined by analysis of the percentages of each monomer converted. For the acrylate esters, this was done gravimetrically. For itaconic acid, this was done by a reversed-phase HPLC method⁹ in which the copolymer solutions

were diluted with water, the copolymer was precipitated with aluminum sulfate solution, and then the mixture was centrifuged. The serum was recovered and injected into the HPLC detector for analysis at 210 nm.

The copolymer composition data were subsequently analyzed using the Fineman and Ross equations¹⁰ to calculate the r_1 and r_2 values.

Aqueous Monomer Concentrations

The concentrations of the monomers in the aqueous phase before emulsion polymerization were measured. Monomer/water mixtures were prepared in the same proportions given in the recipe of Table I and allowed to equilibrate for 6 h; the aqueous phase in each sample was then sampled using a hypodermic syringe. The acrylate ester concentrations were determined by capillary gas chromatography. The itaconic acid concentration was determined by HPLC as described in the previous section, with the exception that no aluminum sulfate solution was used.

RESULTS

The four latexes, containing 0.0, 4.18, 8.35, or 16.7 mM itaconic acid, were prepared, and their particle number concentrations were determined as a function of conversion. Figure 1 shows the particle number-conversion curves from these experiments. It is readily apparent from the earliest stages of polymerization (< 10% conversion) that the number of particles formed decreases significantly as the amount of itaconic acid is increased. During the

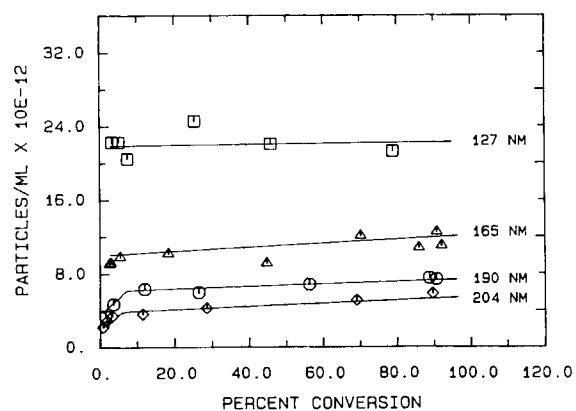


Figure 1 Particle number concentrations vs. conversion for latexes containing various amounts of itaconic acid, prepared at 60°C. □, 0.0 mM IA; △, 4.18 mM IA; ○, 8.35 mM IA; ◇, 16.7 mM IA. Numbers at right of each curve are diameters of final latexes.

course of polymerization, no significant change in the particle number occurs, indicating that no new particles form and that no flocculation of existing particles takes place.

The numbers to the right of each curve are the average diameters of the final latex particles. As the number of particles decreases with increasing itaconic acid content, the particle sizes become larger. From these curves, it can be concluded that the major effect of itaconic acid is to decrease the number of particles nucleated. Further, the presence of this carboxylated monomer does not cause flocculation of the primary particles by some destabilization process, as is sometimes thought to occur.

For the latexes that contained itaconic acid, the pH of the aqueous phase was 2.8–3.2; that of the latex made without itaconic acid was 6.8. To determine whether the acidity of itaconic acid had any effect on the particle number concentration, a control experiment was performed in which no itaconic acid was used, but the pH of the aqueous phase was lowered to 3.0 by the addition of HCl. Again, the particle number concentration was determined as a function of conversion.

Figure 2 shows the results of this experiment, as well as the previous one without itaconic acid at neutral pH. Essentially, there is no discernible difference in the data of either curve. The final particle size for the latex made at neutral pH is 127 nm, while that of the latex made at acidic pH is 130 nm. One can therefore conclude that an acidic pH does not influence the number of particles initially formed or cause any flocculation and coalescence throughout the course of the polymerization.

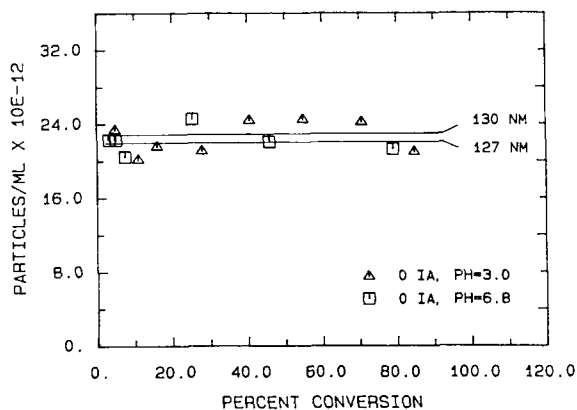


Figure 2 Particle number concentrations versus conversion for latexes made without itaconic acid at either neutral or acidic pH, prepared at 60°C. Δ , pH = 3.0; \square , pH = 6.8. Numbers at right of each curve are diameters of final latexes.

DISCUSSION

To understand the effect of itaconic acid on particle nucleation, as well as the results of Figure 1, it is helpful to first examine the process whereby dissolved acrylate esters polymerize to form particles in an emulsion polymerization without carboxylated monomer.

For acrylate esters, particle nucleation is generally held to occur by "homogeneous nucleation," first conceptualized by Jacobi¹¹ and Priest¹² in 1952 and later developed mathematically by Fitch in 1965.¹³ This process is generally applicable to vinyl monomers that have water solubilities greater than 0.1%.¹⁴ Therefore, this process is applicable to monomers such as methyl methacrylate, *n*-butyl acrylate, ethyl acrylate (EA), and methyl acrylate, which have water solubilities of 1.5, 0.18, 1.2, and 5.2%, respectively.

Water-soluble initiators are generally used in emulsion polymerization; consequently, in the earliest stages of polymerization, their radicals react with monomer dissolved in the aqueous phase to form soluble oligomeric radicals. These oligomeric radicals grow to some critical molecular weight, above which they precipitate to form primary particles. These new particles are stabilized by the adsorption of surfactant and the presence of ionic groups derived from initiator fragments residue.

After the formation of primary particles, the soluble oligomeric radicals that subsequently form undergo three possible processes: (1) growth to the critical molecular weight followed by precipitation, as described in the previous paragraph, causing more primary particles to form; (2) "capture" by adsorption onto the surface of preexisting particle; or (3) termination with another solute radical. As the particle formation continues, the probability of capture by preexisting particles increases until, ultimately, most oligomeric radicals are captured and, thereafter, no new primary particles are formed. Once captured, the oligomeric radical propagates inside the monomer-swollen latex particle.

The change in the number of particles present during the course of an emulsion polymerization in which homogeneous nucleation is operative is defined by the following equation¹⁴:

$$dN/dt = R_i - R_c - R_t, \quad (1)$$

where R_i is the effective rate of oligomeric radical formation in the aqueous phase, R_c is the rate of oligomeric radical capture by preexisting particles,

and R_f is the rate at which particles flocculate with each other. During the earliest stages of polymerization, no particles are present, so dN/dt is essentially equal to R_i . At later stages, the preexisting particles capture oligomeric radicals from solution so $dN/dt = R_i - R_c$. As long as the R_c term is approximately equal to the term R_i , all oligomeric radicals that form are captured, and no new primary particles are formed.

Flocculation of particles can occur if the preexisting particles reach a size at which they are no longer stable. This flocculation will not occur during polymerization if there is sufficient adsorbed surfactant and bound sulfate end groups present on the latex particle surface, and if the percent solids of the latex is kept relatively low.

Fitch and Tsai¹⁴ have developed the following mathematical expression to describe the distance L that an oligomeric radical travels in the aqueous phase before it reaches the critical molecular weight and precipitates to form a primary particle.

$$L = \left\{ \frac{2D_f DP_{\max}}{k_p(M)} \right\}^{0.5}, \quad (2)$$

where D_f is the diffusion coefficient of the oligomeric radical in the water phase, DP_{\max} is the critical molecular weight at which the oligomeric radical precipitates from solution, k_p is the propagation rate constant for the oligomeric radical in water, and M is the molar concentration of monomer in the water phase. The greater the value of L , the longer the time that the oligomeric radical remains soluble in the aqueous phase.

This equation points out the important parameters that affect the value of L . For example, if the propagation rate constant or the concentration of monomer are increased, the distance L is decreased, so that it takes a shorter time for the oligomeric radical to precipitate. On the other hand, if the diffusion coefficient or DP_{\max} are increased, L is correspondingly increased, so that it takes a longer time for the oligomeric radical to precipitate.

Fitch and Tsai¹⁵ also developed the following expression for the rate of capture of oligomeric radicals by these particles by a diffusion mechanism:

$$R_c = R_i \pi r^2 N L = R_i \pi r^2 N \left\{ \frac{2D_f DP_{\max}}{k_p(M)} \right\}^{0.5}, \quad (3)$$

where r is the radius of the preexisting particles and N is the number concentration of particles. Increas-

ing either the particle size or the particle number concentration, or the distance L , increases the probability that an oligomeric radical will be captured by a particle rather than precipitating to form a new particle.

In the case of copolymer oligomers, the above mathematical expressions still hold for the most part. In these cases, k_p is the overall composite of the propagation rate constants and M is the overall concentration of all vinyl monomers in the aqueous phase. DP_{\max} will be increased if a more water-soluble monomer is introduced into an emulsion polymerization containing only a base monomer of low solubility. Also, if DP_{\max} is increased to a high enough degree, the copolymer oligomeric radicals will spend so much time diffusing through the aqueous phase that the likelihood of cotermination with each other also increases. This event results in the formation of water-soluble copolymer that never precipitates to form a particle.

One interesting investigation of the nucleation of BA and EA and MA emulsion polymerization¹⁶ did not deal with measuring DP_{\max} per se, but determined the growth of the latex particles during the earliest stages of polymerization. A complex light-scattering apparatus was constructed that detected the presence of the very small particles (< 20 nm) formed during the first few minutes of emulsion polymerization. It was observed that the rate of increase of scattering intensity increased in the order BA $>$ EA $>$ MA, meaning that BA formed particles more quickly than EA, which in turn formed particles more quickly than MA. Again, this was attributed to an increase in the DP_{\max} of these monomers with the increase in their respective water solubilities, so particles are nucleated first for BA, next for EA, and last for MA.

For latexes made with both acrylate esters and itaconic acid, the major role of itaconic acid is in the earliest stages of emulsion polymerization, when the particles are just forming by the precipitation of oligomeric radicals (homogeneous nucleation). It is proposed that itaconic acid affects the propagation and subsequent precipitation of copolymer oligomeric radicals in two ways. First, because itaconic acid is slower to polymerize than the acrylate esters, its presence is likely to reduce the rate of propagation in the aqueous phase (smaller k_p). Second, the incorporation of even small amounts of itaconic acid into the copolymer oligomers significantly increases their water solubility, so DP_{\max} is also increased.

Both of these factors cause the value of L to be larger when itaconic acid is present so the copolymer

oligomeric radicals spend more time diffusing through the aqueous phase before precipitation occurs. Therefore, the probability that two oligomeric radicals coterminate with each other in the aqueous phase also increases with the possible formation of water-soluble polymer.

The sequence of events taking place during particle nucleation involving acrylate esters alone and acrylate esters with itaconic acid is shown in Figure 3. In the case of the acrylate ester alone (part A), an initiator radical in the water phase adds solute monomer molecules until one of two events occurs: The oligomeric radical reaches the critical molecular weight (DP_{max}), whereupon it precipitates to form a primary particle, or the oligomeric radical coterminates with another oligomeric radical to form acrylate ester polymer. If this new species has a high enough molecular weight, it will also precipitate to form a primary particle.

When itaconic acid is present in the aqueous phase (part B), each oligomer adds both acrylate ester and itaconic acid units. DP_{max} becomes larger owing to the inclusion of the itaconic acid, and the copolymer oligomeric radical must grow to a higher molecular weight before it precipitates to form a primary particle; thus, the oligomeric radical re-

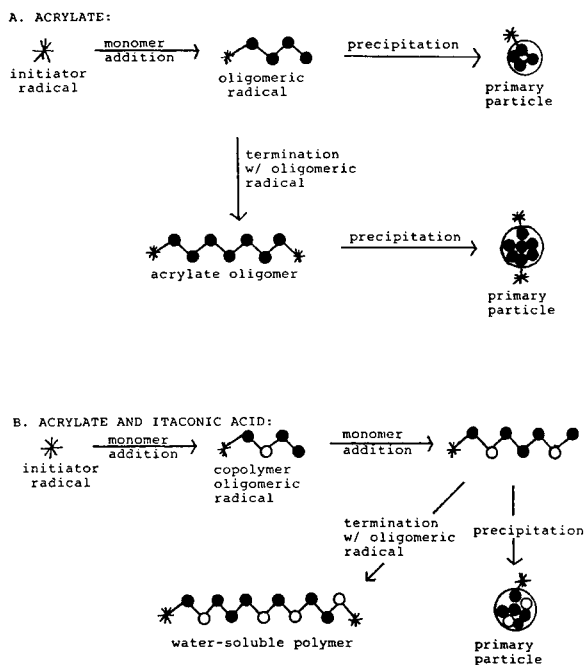


Figure 3 Schematic representation of nucleation events occurring in (A) the case of acrylate esters alone and (B) the case of acrylate esters and itaconic acid. ●, acrylate ester unit; ○, itaconic acid unit.

Table II Copolymerization Reactivity Ratios

Monomer 1	Monomer 2	r_1	r_2
BA	MA	0.73	1.28
BA	IA	1.10	0.23
MA	IA	1.29	0.34

mains dissolved in the aqueous phase for a longer time. Because of this longer time, the probability that two copolymer oligomeric radicals coterminate with each other is also increased. And, if this copolymer contains enough itaconic acid, it remains dissolved in the aqueous phase rather than precipitating to form a new particle.

Thus, for the latexes made with acrylate esters alone, nearly all of the oligomeric radicals formed early in the polymerization generate primary particles. However, when itaconic acid is present, a smaller proportion of the oligomeric radicals eventually become particles; the others generate water-soluble copolymer. So, in this case, fewer particles are formed; hence, for the same percent solids latex, larger particles should result. This larger particle size is observed experimentally. Further, the greater the amount of itaconic acid in the recipe, the smaller should be the proportion of copolymer oligomeric radicals that precipitate to form primary particles, so the final particles should be larger. This trend is also observed experimentally, verifying the validity of this proposed mechanism.

CALCULATIONS ON THE COMPOSITION AND SEQUENCE LENGTH DISTRIBUTIONS OF INITIAL COPOLYMER OLIGOMERIC RADICALS

To better understand this nucleation process involving itaconic acid, it would be useful to know more about the nature of the initial oligomeric radicals that form in the aqueous phase. It would be difficult to analyze these species directly since they make up such a small part by weight of the total emulsion polymerization system. However, it is possible to carry out statistical calculations that predict both the monomer compositions and the sequence of monomers in the initial oligomeric radicals. The results of these calculations are useful in understanding the nucleation events so important to this study.

To perform these calculations, it is necessary to know the copolymerization reactivity ratios for all

pairs of monomers, as well as the aqueous monomer concentrations at the beginning of polymerization. The copolymerization reactivity ratios of the three monomer pairs are given in Table II; the values for the pair BA and MA were calculated using the Q-e scheme while the values for the two pairs involving itaconic acid were determined as described in the experimental section.

The values for the acrylate ester-itaconic acid pairs show the copolymerization behavior of itaconic acid. From the r_1 values, the homopolymerization of either acrylate ester is slightly more favorable than copolymerization with itaconic acid. From the r_2 values, the copolymerization of itaconic acid with either acrylate ester is three to four times more favorable than its homopolymerization.

The aqueous monomer concentrations, determined by gas chromatography for acrylate ester, and HPLC for itaconic acid, are given in Table III. It was found that the presence of itaconic acid did not effect the water solubility of either acrylate ester. Further, the concentrations found for itaconic acid represent 99% of the amount charged, demonstrating that it was partitioned almost entirely in the aqueous phase rather than in the acrylate ester phase.

The predicted terpolymer compositions calculated using the equations developed by Ham¹⁷ and Mirabella¹⁸ are given in Table IV. Small but significant amounts of itaconic acid are predicted to become incorporated into the copolymer oligomeric radicals. This incorporation would indeed be expected to increase the water solubility of these oligomeric radicals and hence increase DP_{max} .

It is also possible to calculate the sequence length distributions of itaconic acid and the acrylate esters in the copolymer oligomeric radicals¹⁹ formed early in the polymerization using the data given in Tables II and III. The acrylate ester concentration used in these calculations was the sum of the concentrations of the *n*-butyl and methyl acrylates.

Table III Aqueous Monomer Concentrations at the Beginning of Emulsion Copolymerization

Latex	BA	MA (mM/L)	IA
1	8.27	22.5	0.0
2	8.27	22.5	4.20
3	8.27	22.5	8.35
4	8.27	22.5	16.7

Table IV Calculated Terpolymer Compositions (in mole percent) for Initial Oligomeric Radicals

Latex	% BA	% MA	% IA
1	22.1	77.9	0
2	20.6	73.7	5.7
3	19.4	70.4	10.1
4	17.7	65.5	16.7

Figures 4–6 show the sequence length distributions for the three latexes containing 4.18, 8.35, and 16.7 mM itaconic acid, respectively; the horizontal axis represents sequence lengths from 1–20 and the vertical axis represents the probabilities (or mole fractions) of a given sequence length. The probabilities for itaconic acid are given by the broken lines (placed slightly to the left of the actual sequence length) and the probabilities for the acrylate esters are given by the solid lines (placed slightly to the right). In the upper right corner of each figure are the values for the average acrylate block length, as well as the average itaconic acid block length.

For the lowest concentration of itaconic acid (4.20 mM) (Fig. 4), 96% of the itaconic acid is found in blocks of one unit in length, demonstrating that ev-

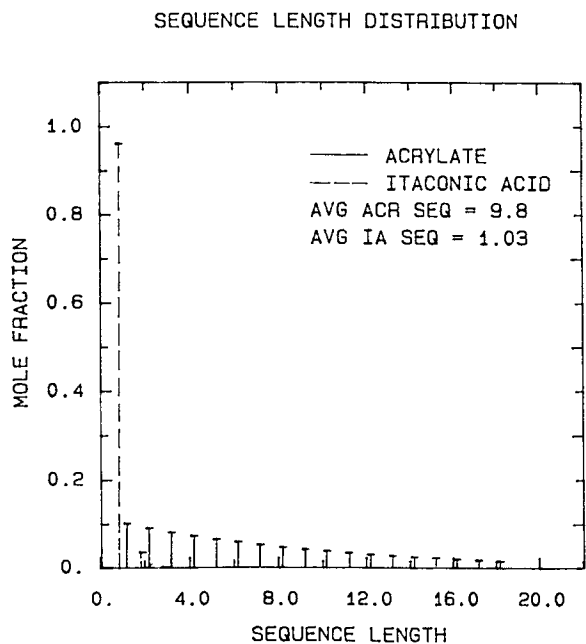


Figure 4 Monomer sequence length distribution for aqueous oligomeric radicals formed at the beginning of emulsion copolymerization for latex containing 4.18 mM itaconic acid. ---, IA; —, BA/MA.

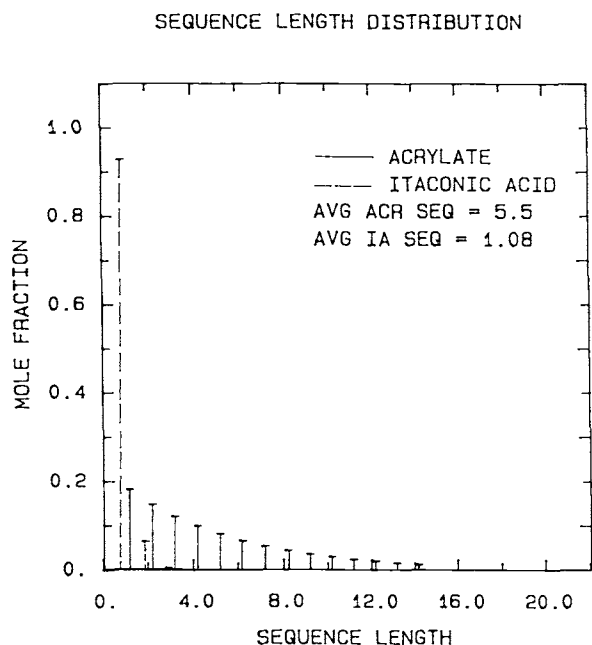


Figure 5 Monomer sequence length distribution for aqueous oligomeric radicals formed at the beginning of emulsion copolymerization for latex containing 8.35 mM itaconic acid. ---, IA; —, BA/MA.

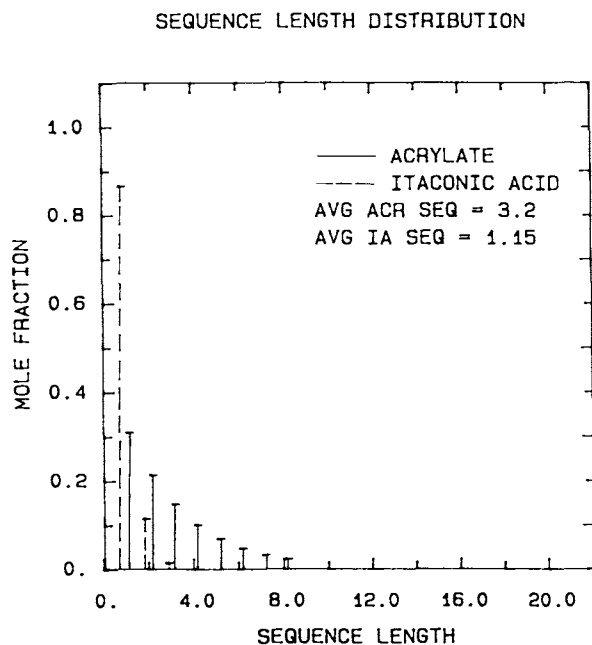


Figure 6 Monomer sequence length distribution for aqueous oligomeric radicals formed at the beginning of emulsion copolymerization for latex containing 16.7 mM itaconic acid. ---, IA; —, BA/MA.

ery time an itaconic acid molecule adds to a propagating radical, there is a 96% chance that the next molecule to add will be an acrylate ester. The acrylate esters form blocks which range in length from 1–18 acrylate ester units and average approximately 10 units long. This wide range in block length means that, when an acrylate ester radical is at the end of a propagating copolymer chain, it has a good chance of adding either another acrylate ester molecule or an itaconic acid molecule.

Similarly, Figures 5 and 6 show that most of the itaconic acid is found in blocks of only one unit in length. This is a consequence of the low probability of itaconic acid adding to its own radical. Still, the higher the concentration of itaconic acid in the recipe, the shorter on average are the acrylate ester blocks. For instance, when IA = 8.35 mM, the acrylate blocks range from 1–14 units in length, the average being near 6. When IA = 16.7 mM, the acrylate ester blocks range from one to eight units in length, with the average being approximately three.

Figure 7 shows the average copolymer structure, based on these statistical calculations. It is expected that these copolymers will be comprised mainly of individual itaconic acid units interspersed between acrylate ester blocks of widely differing lengths, these block lengths diminishing as the itaconic acid concentration is raised. This means that some copolymer oligomeric radicals will contain more acrylate ester units than others, so they will have lowered degrees of water solubility. This, of course, will result in these more hydrophobic oligomeric radicals precipitating and forming primary particles more quickly than other radicals that contain higher amounts of itaconic acid.

These predictions of the composition and micro-

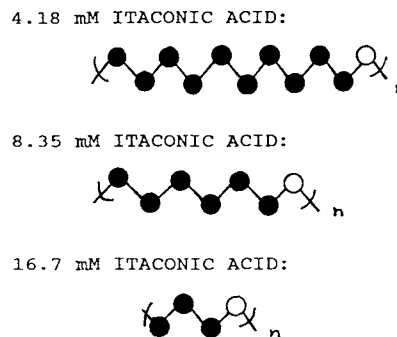


Figure 7 Average copolymer microstructures for oligomeric radicals formed at the beginning of emulsion copolymerization, based on statistical calculations. ●, acrylate ester unit; ○, itaconic acid unit.

structure of the initial oligomeric radicals are consistent with both the mechanism presented earlier and the experimental curves of Figure 1. The predictions demonstrate that increasing the concentration of itaconic acid should lead to the formation of more polar oligomeric radicals. These more hydrophilic radicals will be less likely to precipitate to form primary particles and thus should ultimately result in smaller particle number concentrations, as observed experimentally in Figure 1.

CONCLUSIONS

Examination of the nucleation and particle growth of acrylate ester latexes containing various amounts of itaconic acid as a function of conversion has shown that the major effect of the itaconic acid is the decrease of the number of particles formed in the earliest stage of emulsion polymerization. The more itaconic acid present, the smaller the number of particles formed, and the larger final particle size of the latex. Consideration of the mechanism of particle nucleation shows that the most likely reason for the above observation is that the incorporation of the polar itaconic acid into oligomeric radicals increases their water solubility such that a small proportion of these radicals eventually precipitate to form primary particles. In addition, statistical calculations show that itaconic acid copolymerizes in the aqueous phase to give oligomeric radicals with single itaconic acid units interspersed with acrylate ester blocks of various sequence lengths.

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