Investigation of the Persulfate/Itaconic Acid Interaction and Implications for Emulsion Polymerization

MICHELE R. LOCK, MOHAMED S. EL-AASSER, ANDREW KLEIN, and JOHN W. VANDERHOFF, *Departments of Chemical Engineering and Chemistry, Emulsion Polymers Institute and Center for Polymer Science and Engineering, Lehigh University, Bethlehem, Pennsylvania 18015*

Synopsis

Itaconic acid, a carboxylated water-soluble vinyl monomer, is shown to greatly induce the thermal decomposition of potassium persulfate initiator. From decomposition rate studies carried out at 50, 60, and 70°C, the rate constants for this interaction are found to be increased eight to 15 times as much over the values of rate constants from uninduced decompositions. The induction is found to be particularly sensitive to the concentration of the first anion of itaconic acid and is thought to lead to wastage of initiator radicals. As the polymerization temperature is increased from 50 to 70°C, this interaction between itaconic acid and persulfate leads to worsening monomer conversion levels in acrylate latexes made with both compounds. Employing a water-soluble azo initiator in the presence of itaconic acid does not result in any induced decomposition of the former. Acrylate latexes prepared with these two compounds have monomer conversion levels which rise as the polymerization temperature is increased, as is expected in conventional emulsion polymerizations.

INTRODUCTION

Carboxylated latexes are generally produced from the emulsion copolymerization of a base hydrophobic monomer and small amounts of a hydrophilic carboxylated monomer. Such latexes tend to exhibit improved colloidal and mechanical properties,[1] which make them useful in industrial applications. Itaconic acid (IA) is a dicarboxylated vinyl monomer that finds occasional use in preparing this type of latex.

Figure 1 shows the structure of this monomer as well as its first ionization equilibrium, which has a K_a of 1.4×10^{-4}. It is approximately twice as acidic as the commonly used methacrylic or acrylic acid. Due to its highly polar nature, itaconic acid resides mainly in the water phase during emulsion polymerization, rather than partitioning between the monomer and water phases as do the above two acids.[2]

It is known that itaconic acid is slow to react in both solution[3] and emulsion copolymerization.[4-6] The goals of our work in copolymerizing it with butyl acrylate are to elucidate the factors which lead to reduced polymerization rates and low incorporation of itaconic acid into latex particles. It is expected that a better understanding of these factors, such as interactions of this functional monomer with other compounds found in latex systems, will allow us to optimize its copolymerization with the acrylate monomer. Furthermore,
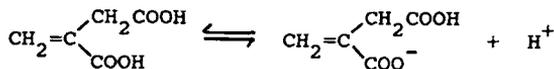
Fig. 1. First ionization equilibrium of itaconic acid to yield the itaconate anion.

these findings should be relevant to latex systems involving itaconic acid with other classes of conventional monomers.

In this regard, the interaction between itaconic acid and the widely used potassium persulfate (KPS) initiator was examined. It has been reported that several conventional monomers with appreciable water solubility such as methyl acrylate,[7] acrylonitrile,[8] and vinyl acetate[9] do cause a small increase in the rate of thermal decomposition of KPS. It seemed likely that itaconic acid, with its propensity for the aqueous phase, could be similarly involved in an induced decomposition of this water-soluble initiator. The magnitude of this interaction was explored by us, as well as its effects on batch latex preparation.

EXPERIMENTAL

Reagents

Potassium persulfate (Cert. A.C.S.) was used as received from Fisher Scientific. 4,4'-Azobis(4-cyanopentanoic acid) from Wako Pure Chemical Industries Ltd. (U.S.A.) was neutralized with an equivalent amount of NaOH to make it water-soluble; it was prepared just before use. Itaconic acid (refined grade) was provided by the chemical division of Pfizer. Butyl and methyl acrylate were purified through distillation under reduced pressure. Sodium lauryl sulfate (Henkel), n-dodecyl mercaptan (Pennwalt), and sodium styrene sulfonate (DuPont) were used without further purification.

Latex Preparation

The general recipe used is shown in Table I, in which the weight percent of itaconic acid varied from 0 to 10% of the total monomer phase. The latexes were prepared in batch at 300 g levels and were allowed to polymerize for 20 h. Three series of latexes were prepared at 50, 60, and 70°C. Final conversion of the volatile acrylate monomers was determined gravimetrically; conversion of the nonvolatile itaconic acid was measured using a reversed-phase HPLC method in which the latex was diluted with water, coagulated with aluminum sulfate solution, and then centrifuged to recover the serum which was then injected for analysis.

TABLE I
Latex Recipe for Batch Polymerizations

Compound	Weight (g)	Percent
Butyl acrylate	27–30	9–10
Itaconic acid	0–3	0–1
Sodium lauryl sulfate	0.09	0.03
Potassium persulfate	0.09	0.03
n-Dodecyl mercaptan	0.06	0.02
DDI water	270	90

Initiator Decomposition Rate Studies

The rate of KPS decomposition in water under various conditions was monitored using a redox titration based on ceric oxidimetry.[10] The initial concentration of KPS was 3.0 mM, and the log of the ratio of instantaneous over initial concentration was plotted vs. time to yield straight lines whose slopes gave the decomposition rate constants. For the azo initiator, decomposition was monitored by the decrease in the azo group's UV absorbance at 365 nm; rate constants were calculated as above.

RESULTS

Batch latexes prepared using the general recipe at either 50, 60, or 70°C revealed some interesting features with respect to monomer conversion. Figures 2 and 3 show the final percent conversions of both itaconic acid and butyl acrylate as a function of the weight percent IA in the monomer phase. For both monomers, the conversion levels decreased with increasing amounts of itaconic acid present, which is at least partly attributable to the latter's slow rate of polymerization. More unexpected is the trend of lower itaconic conversion with the higher reaction temperatures, which is not generally seen in conventional emulsion polymerization. As for the butyl acrylate, its conversion increased on going from 50 to 60°C; then on going to 70°C, the final
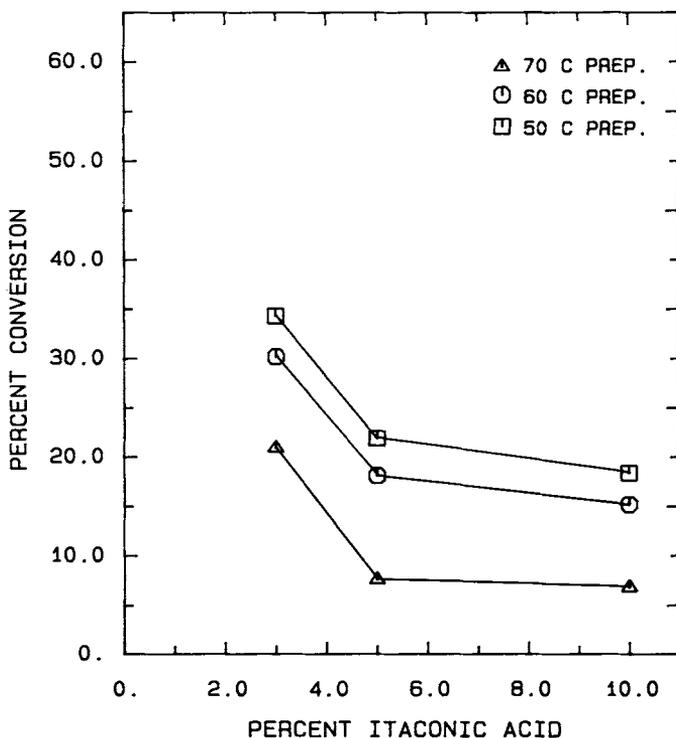
Fig. 2.   Effect of the weight percent of itaconic acid in the monomer phase on the final itaconic acid conversion during emulsion copolymerization with butyl acrylate at various temperatures, and using KPS as initiator: (△) 70°C; (○) 60°C; (□) 50°C.
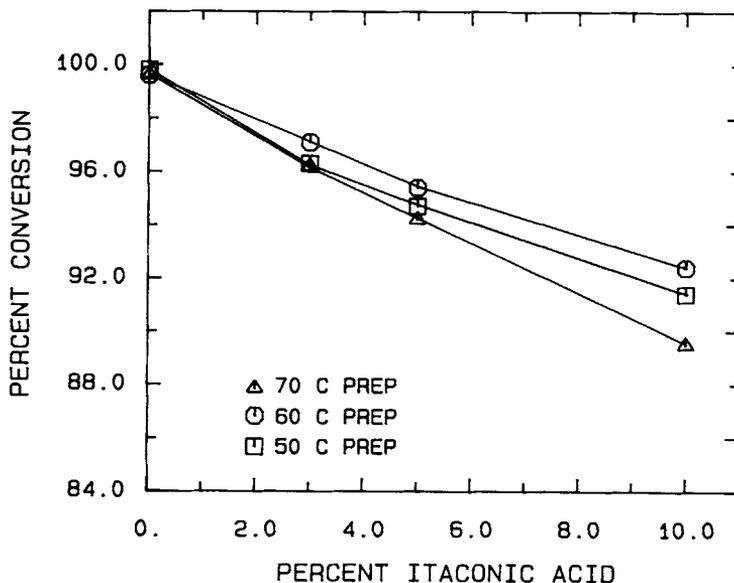
Fig. 3.   Effect of the weight percent of itaconic acid in the monomer phase on the final butyl acrylate conversion during emulsion copolymerization with itaconic acid at various temperatures, and using KPS as initiator: (△) 70°C; (○) 60°C; (□) 50°C.
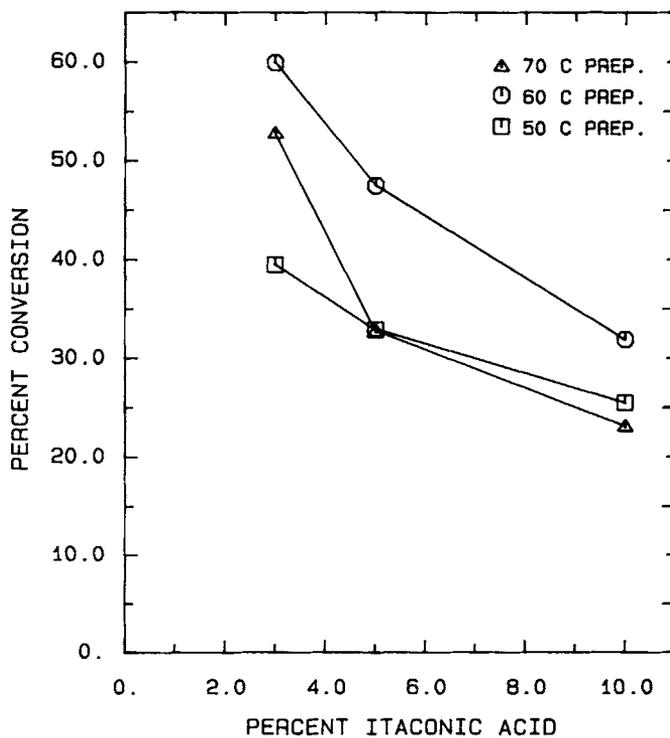
Fig. 4.   Effect of the weight percent of itaconic acid in the monomer phase on the final itaconic acid conversion during emulsion copolymerization with butyl acrylate/methyl acrylate at various temperatures, and using KPS as initiator: (△) 70°C; (○) 60°C; (□) 50°C.
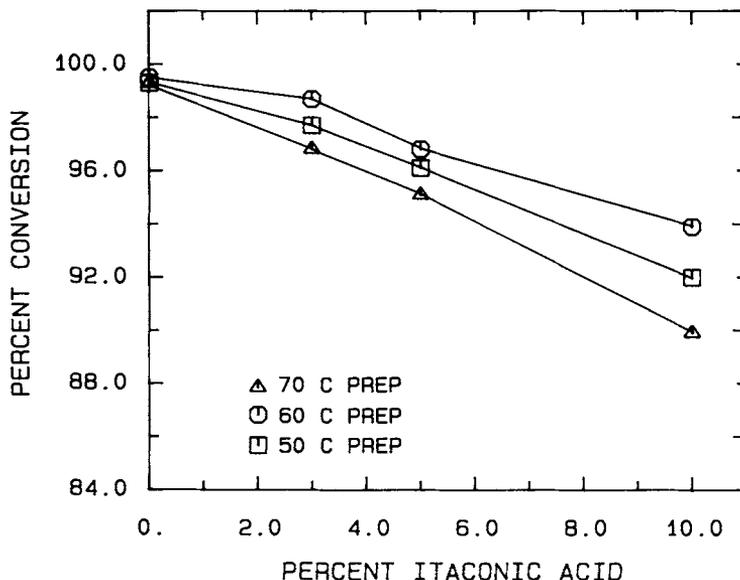
Fig. 5.   Effect of the weight percent of itaconic acid in the monomer phase on the final butyl acrylate/methyl acrylate conversion during emulsion copolymerization with itaconic acid at various temperatures, and using KPS as initiator: ($\triangle$) 70°C; ($\bigcirc$) 60°C; ($\square$) 50°C.

conversions were decreased to below those found at the two lower temperatures.

It was thought that replacing a small portion of butyl acrylate with the more water-soluble methyl acrylate would promote the incorporation of itaconic acid, due to the greater chance of copolymerization occurring in the aqueous phase. Indeed, when 10% of the butyl acrylate was replaced with methyl acrylate, the conversion of the acid monomer to polymer was increased significantly, as seen in Figure 4. However, there was essentially no change in the overall conversion of the acrylate monomers (Fig. 5). In addition, although the monomer conversions levels in both cases were raised on going from 50 to 60°C, the levels dropped off again on going to 70°C.

It appeared possible that the above trends with respect to reaction temperature were the result of an interaction between the itaconic acid and persulfate initiator. This could result in a decrease in the amount of initiator available to complete polymerization that would be more noticeable as the temperature is raised. To test this, kinetic studies of the rate of persulfate decomposition were carried out in the presence of 1% itaconic acid, which has a pH of 2.6. As controls, studies at pH 7.5 and pH 2.5 due to HCl addition were carried out.

Figure 6 gives the kinetic curves for the above three cases at 50°C. There is only a slight increase in the rate on going from a pH of 7.5 to 2.5. However, in the presence of itaconic acid, the rate (as seen by the steeper slope) is greatly enhanced. The same experiments were carried out at 60 and 70°C; the decomposition rate constants and activation energies from all these experiments are gathered in Table II. These data show that itaconic acid is causing
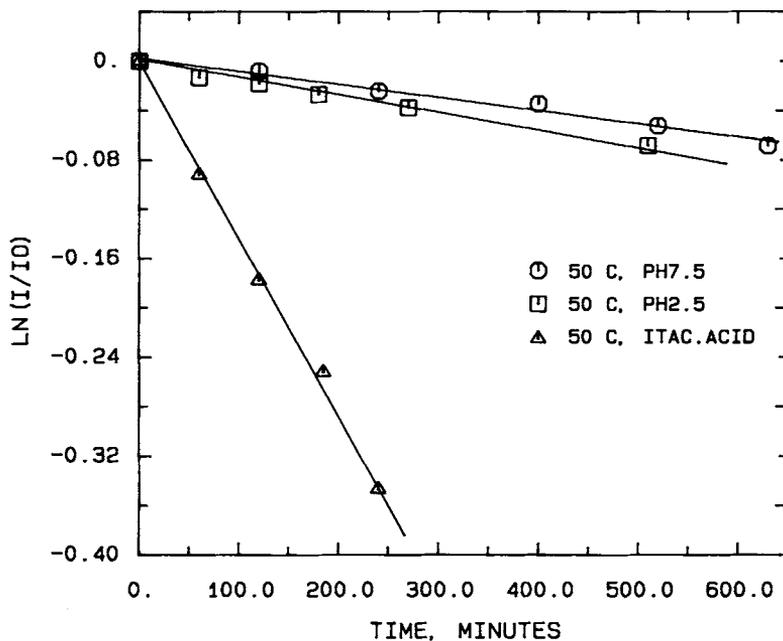
Fig. 6. Plot of the log fraction of remaining persulfate as a function of time under three conditions at 50°C: (○) pH 7.5; (□) pH 2.5 using HCl; (△) pH 2.6 using 1% itaconic acid.

an eight- to 15-fold increase in the rate of decomposition of the initiator. Likewise, the activation energy is lowered by 17%.

To more fully understand the mechanism of this interaction, the kinetic order was determined experimentally. From the log–log plot of Figure 7, it was found that the induced decomposition is first order with respect to persulfate concentration. However, the solid curve of Figure 8 shows that, as the concentration of itaconic acid was raised, the decomposition rate was lowered, which is rather uncommon kinetically. On comparing the rate data with the degree of ionization of the itaconic acid (dashed curve), a good correlation between the two is apparent. This signifies that the interaction is particularly sensitive to the presence of the itaconate anion (see Fig. 1). Indeed, with kinetic experiments in which the concentrations of persulfate and itaconic acid were held constant and the amount of itaconate varied by adjusting the pH between 2.5 and 3.2, the order of the interaction was found

TABLE II

Potassium Persulfate Decomposition Rate Constants and Activation Energies as a Function of Temperature and Acid Conditions

Condition	k_d (50°C) (min^{-1} × 10^4)	k_d (60°C) (min^{-1} × 10^4)	k_d (70°C) (min^{-1} × 10^4)	E_{act} (KJ/mol)
pH = 7.5	1.07	4.20	15.8	125
pH = 2.5 (HCl)	1.30	5.53	19.2	124
1% Itaconic acid				
(pH = 2.6)	14.1	48.5	131.0	103
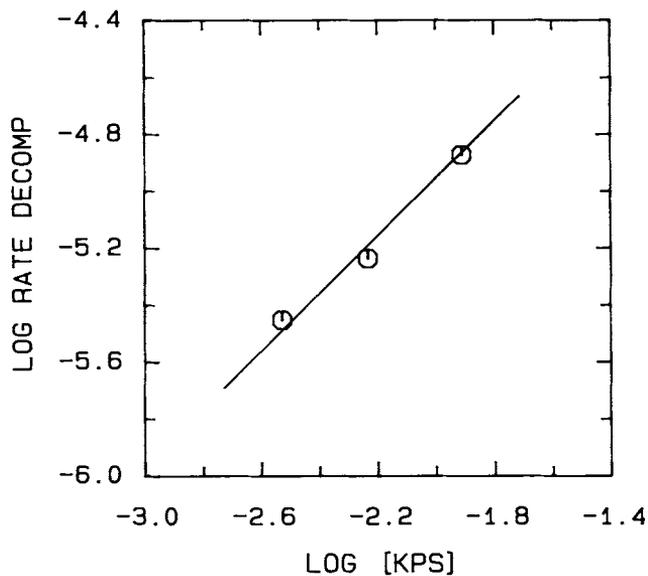
Fig. 7. Log–log plot of rate of KPS decomposition vs. KPS concentration at 50°C: [IA] = 76.0 mM; slope = 0.94.
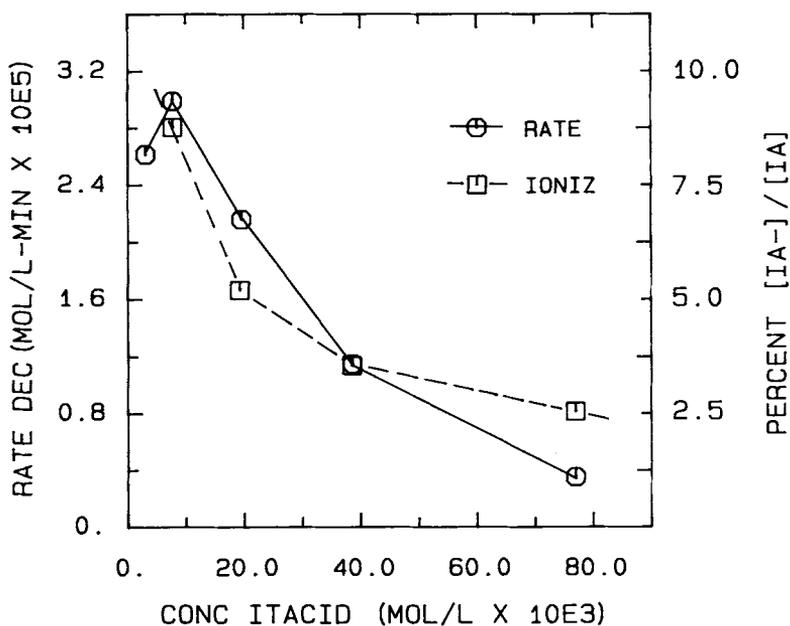
Fig. 8. Effect of itaconic acid concentration on the rate of KPS decomposition (solid curve) and on the degree of ionization (dashed curve), both at 50°C. [KPS] = 3.0 mM.
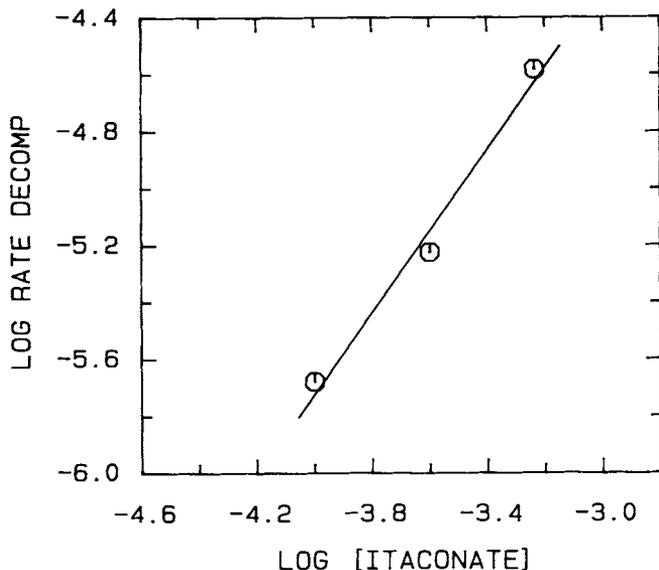
Fig. 9. Log–log plot of rate of KPS decomposition vs. itaconate concentration at 50°C. [KPS] = 3.0 mM; [IA] = 2.4 mM. Slope = 1.43.

to be three-halves with respect to itaconate concentration (see Fig. 9). Therefore, one can write the following kinetic expression:

$$d[\text{KPS}]/dt = -k[\text{KPS}][\text{IA}^-]^{3/2}.$$

The important point with the above findings is that the persulfate decomposition rate will be variable, depending on both the amount and degree of ionization of itaconic acid present in the polymerization system, which is undesirable. This has necessitated our choosing to use another water-soluble initiator for latex preparation. It has been reported that azo initiators tend not to be involved in unexpected side reactions, because the tertiary radicals formed from these initiators are well stabilized.[11] Therefore, the water-soluble disodium salt of 4,4′-azobis(4-cyanopentanoic acid) (ACPA) was chosen for our work.

The rate constants of ACPA decomposition in the presence of 1% itaconic acid were determined and compared to literature values for neutral conditions at 50, 60, and 70°C. Table III shows the results, and it appears that this azo

TABLE III
Effect of Itaconic Acid on ACPA Decomposition Rate
Constants and Activation Energies

Condition	k_d (50°C) (min^{-1} × 10^4)	k_d (60°C) (min^{-1} × 10^4)	k_d(70°C) (min^{-1} × 10^4)	E_{act} (KJ/mol)
1% Itaconic acid	1.06	3.50	17.8	130
Literature value	1.11	5.30	21.4	136
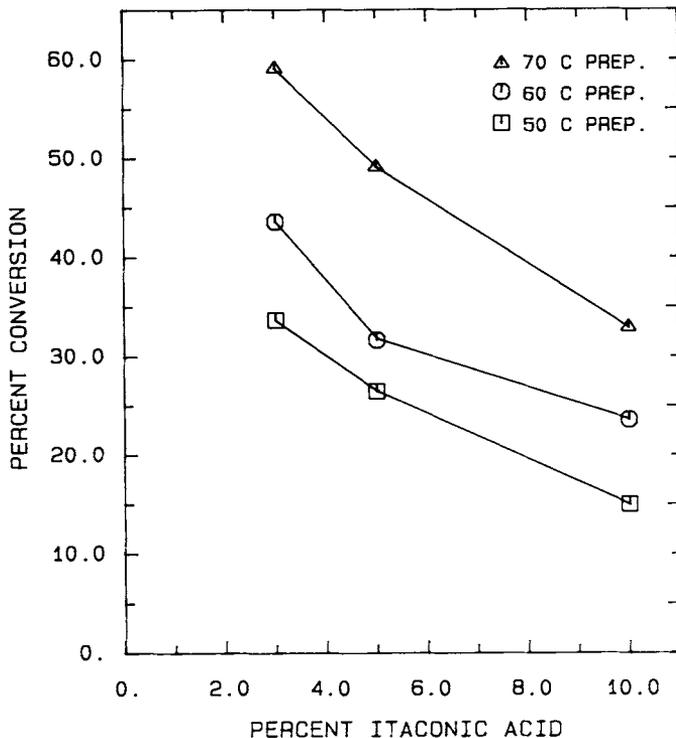
Fig. 10. Effect of the weight percent of itaconic acid in the monomer phase on the final itaconic acid conversion during emulsion copolymerization with butyl acrylate/methyl acrylate at various temperatures, and using ACPA as initiator: (△) 70°C; (○) 60°C; (□) 50°C.
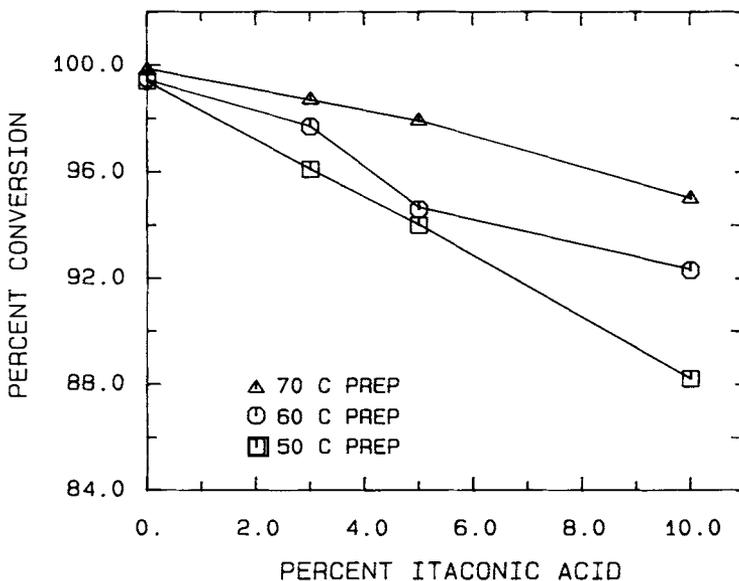
Fig. 11. Effect of the weight percent of itaconic acid in the monomer phase on the final butyl acrylate/methyl acrylate conversion during emulsion copolymerization with itaconic acid at various temperatures, and using ACPA as initiator: (△) 70°C; (○) 60°C; (□) 50°C.

initiator is behaving similarly in both environments, meaning that the itaconic acid is not interacting with ACPA, as is desired.

Another series of latexes made with ACPA instead of KPS was prepared at the three reaction temperatures used previously. The only other change made with the general recipe of Table I is that 0.06% sodium styrene sulfonate was also added so as to stabilize the latexes, which now lack the stabilizing sulfate group derived from KPS.

In Figure 10, it can be seen that the itaconic acid conversion now rises as the temperature is raised. The same behavior is seen with regards to the final acrylate conversion (Fig. 11). These more conventional conversion results are attributable to the ability of the azo initiator to initiate polymerization without being encumbered with wasteful side reactions. In fact, employing ACPA leads to having the best combination of high conversions for both kinds of monomers. However, there still remains the trend of lowered conversions as the amount of itaconic acid present is increased. Possible reasons for this will be discussed further on.

DISCUSSION

The induced decomposition of KPS by itaconic acid gives rise to several implications for emulsion polymerizations employing both of these compounds. First, the persulfate decomposes so rapidly that radicals are produced only up to the first two-thirds or so of the 20-h reaction period. With increasing temperatures, this radical-production time is reduced even further. Moreover, some of the radicals formed from the interaction of these compounds may not be reactive enough to initiate polymerization, thus lowering the initiator efficiency. It is even possible that these unwanted radicals persist in the aqueous phase and prematurely terminate polymerization there, thus reducing the radical flux into the growing latex particles. The reduction in monomer conversion levels with increasing reaction temperature can be traced to the above probable events.

In cases where it is not possible to substitute an azo initiator for the persulfate when preparing a latex containing itaconic acid, the data of Figures 4 and 5 suggest that it is better to work at lower reaction temperatures in order to achieve higher monomer conversions. The above most likely explains the tendency in the literature (Refs. 3–6) to polymerize systems containing itaconic acid and persulfate at 50°C. Although the KPS/IA interaction would still be taking place, its detrimental affects would be lessened at the lower temperatures.

It is not clear at this point what the exact free radical mechanism is for the interaction of persulfate and itaconic acid. It has been reported in the literature that persulfate is capable of oxidizing carboxylic acids via a free radical pathway.[12] Moreover, this oxidation has been exploited synthetically to decarboxylate phenylacetic acids[13] as well as to effect intramolecular rearrangements leading to dimerization of aromatic acids[14] and lactonization of alkanoic acids.[15]

In all of the above cases, the major reaction between the persulfate radical and the carboxylic acid is the removal of an electron from one of the oxygens of the latter. In a study of the interaction of persulfate radical with oxalic

acid,[16] it was found that the rate of the interaction was increased when a greater amount of the acid was neutralized with base prior to oxidation; this agrees with the results found in this study concerning the reactivity of the itaconate anion. It appears that when the electron density is increased on the oxygens of the acid group via neutralization, this electron removal is enhanced.

No decarboxylation appears to be occurring with the itaconate anion, as evidenced by the absence of CO_2 evolution during the course of our work. It seems likely that a rearrangement mechanism is probable during this interaction with persulfate. A reasonable pathway for this may be the following:

$$CH_2{=}C\overset{CHCOOH}{\underset{C-\ddot{O}:^{-1}}{\Big\langle}} \quad + \quad \cdot SO_4^{-1} \rightarrow CH_2{=}C\overset{CHCOOH}{\underset{\underset{O}{\overset{\|}{C}}-\dot{\ddot{O}}:}{\Big\langle}} \quad + \quad :SO_4^{-2}$$

$$CH_2{=}C\overset{CHCOOH}{\underset{\underset{O}{\overset{\|}{C}}-OH}{\Big\langle}} \quad \leftrightarrow \quad \cdot CH_2{-}C\overset{CHCOOH}{\underset{\underset{O}{\overset{\|}{C}}-OH}{\Big\langle}}$$
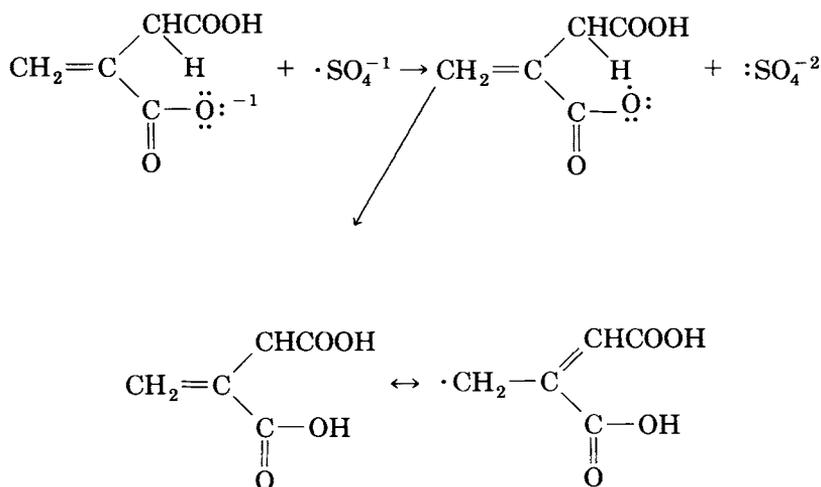
The first step is for the sulfate radical to remove an electron from the carboxylate group, forming a sulfate anion and a carboxylate radical. The latter can rearrange intramolecularly to form a stable allylic radical, which is unlikely to initiate polymerization, although it can terminate the propagation step. Of course, this proposed scheme would only be a portion of the complete mechanism, which may involve multiple pathways.

Use of the azo initiator avoids the above unwanted side reactions which interfere with the role of the initiator during polymerization. In fact, with ACPA, radicals are produced throughout the 20-h reaction period. With raising the temperature, more radicals are produced so that the final conversions of all monomers are higher.

There still remains to be explained the phenomenon of lowered monomer conversions with increasing amounts of itaconic acid in the recipe. There are several points which can shed light on these results. First, oligomeric radicals in the water phase containing significant amounts of the polar IA may terminate in this phase before capture by the growing latex particles, thus decreasing the flux of radicals into the particles. This would manifest itself in lowered rates of monomer conversion during polymerization. Second, towards the final stage of polymerization, the concentration of carboxyl groups on the particle surface may increase to such a level that it becomes difficult for any further carboxylated oligomeric radicals to be adsorbed by the particles. This again would result in a lowered radical flux into the latex particles. To address

this problem, kinetic studies throughout the polymerization are being conducted, and will be reported in a later publication.

CONCLUSIONS

Itaconic acid causes a significant induced decomposition of potassium persulfate, which leads to reduced monomer conversion that becomes worse with increasing reaction temperature when preparing carboxylated latexes. This interaction between the two was found to be first-order with respect to persulfate and three-halves order with respect to itaconate anion. Use of the azo initiator ACPA avoids these complications and leads to more conventional conversion behavior with regard to temperature.

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