

# A Study of Inverse Dispersion Polymerization of Acrylic Acid Using Water-Soluble Redox Initiators

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**ABSTRACT:** Inverse dispersion polymerizations of acrylic acid were conducted by using a water-soluble redox initiation system under both isothermal and nonisothermal conditions. The polymerizations were monitored by measuring residual monomer by high-performance liquid chromatography for isothermal polymerizations or by monitoring the temperature variation inside the dispersion for nonisothermal polymerizations. The aqueous drop behavior was examined throughout the course of polymerization by scanning electron microscopy with freeze-fracture equipment. The agitation intensity had a significant effect on polymerization, drop size, and distribution. The volume of aqueous reductant affected the polymerization rate and limiting conversion. A second shot of aqueous reductant induced a further initiation of reaction. The rate of dispersion polymerization was slower than that of solution polymerization with surfactant. A hypothesis was proposed that polymerization occurred in aqueous drops. Coalescence and breakup of aqueous drops took place simultaneously and played an important role in polymerization. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 2191–2197, 1997

**Key words:** acrylic acid; inverse dispersion polymerization; redox initiators; drop coalescence; breakup

## INTRODUCTION

Inverse dispersion polymerization has been of great importance in producing water-soluble polymer lattices and colloids. The products can be used directly or recovered easily by inversion. In comparison with bulk and solution polymerizations, it has the advantages of low viscosity and good heat removal. Nevertheless, dispersion polymerization is a unique technique for producing high-molecular-weight polymers at a high reaction rate. Previously, attempts have been made to obtain an understanding of individual systems and different mechanisms have been developed.<sup>1–8</sup> So far, the most intensively studied

systems have been those that use a one-component initiator including oil-soluble and water-soluble initiators. Water-soluble redox initiation systems have been used in inverse dispersion polymerizations.<sup>9–11</sup> However, no detailed studies have been found in the literature concerning the mechanistic aspects in this specific system.

In inverse dispersion polymerizations using water-soluble redox initiators, the two components of a redox pair have to be introduced separately. Normally, the oxidizing part is dissolved in the aqueous monomer, which is then dispersed in an oil stabilized with surfactant, and the reducing part is then added to start polymerization. An alternative way is that both oxidant and reductant are added separately to the dispersion of aqueous monomer in an agitated oil phase. Therefore, the polymerization system may consist of either two or three different droplets and the distribution of initiator(s) is heterogeneous in nature.

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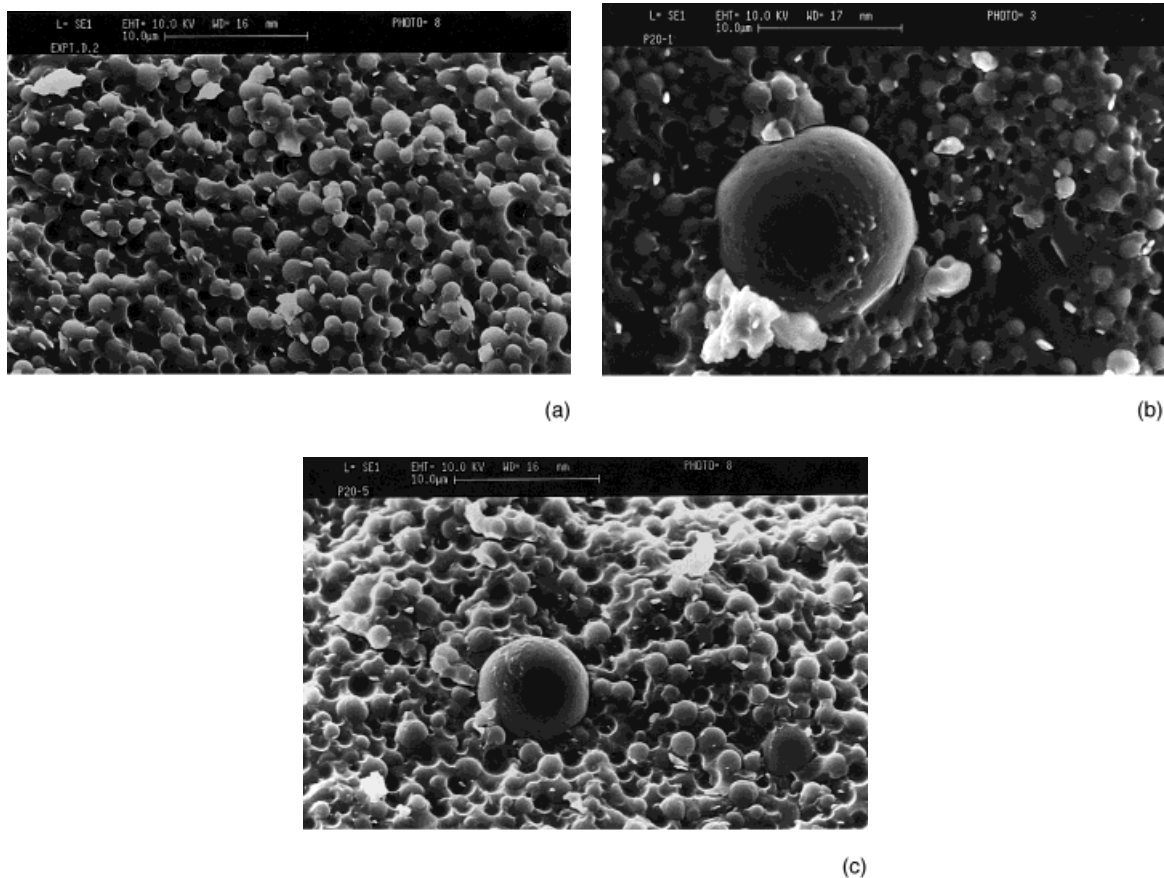
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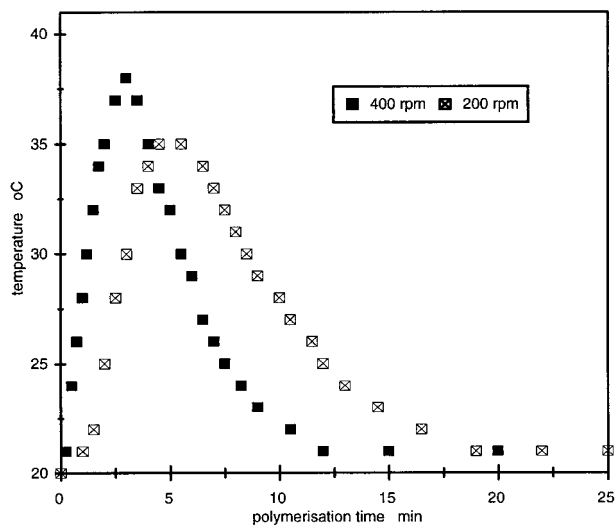
**Figure 1** Dispersion SEM images at different polymerization stages (a) before adding aqueous reductant, (b) 1.5 minutes after adding aqueous reductant, (c) 30 minutes after adding aqueous reductant. Experimental conditions: 23°C, crossed paddle stirrer at 500 rpm. Reactant concentrations:  $[M] = 4.243$  mol/L of aqueous phase,  $[I_{ox}] = 1.769 \times 10^{-3}$  mol/L of aqueous phase,  $[I_r] = 7.698 \times 10^{-4}$  mol/L of aqueous phase,  $[S] = 10$  wt % of oil phase. See Nomenclature.

In our current research work, inverse dispersion polymerization of aqueous acrylic acid in hydrocarbon oil stabilized with nonionic surfactant using water-soluble redox initiators has been studied. The objective is to obtain an understanding of the mechanism for this polymerization process.

## EXPERIMENTAL

Acrylic acid was purified by vacuum distillation before polymerization. Other materials were used as received without further purification. Isopar M (an isoparaffinic mixture) and *N, N*-bishydroxyethyl tall oil amide were used as oil and surfactant, respectively. Polymerizations were conducted in a 500-mL glass jacketed reactor with

a mechanical stirrer, baffles, and nitrogen inlet. Dispersions were prepared by adding the aqueous monomer containing the oxidizing half of the redox pair (potassium bromate) to the oil phase under agitation. The monomer contained a small amount of methylene bisacrylamide crosslinking agent; this did not affect the polymerization rate. Ammonium hydroxide was used for neutralization. The mole ratio of acrylic acid to ammonium hydroxide was about 1 : 1. The ratio of aqueous phase to oil phase was about 3 : 1. The dispersion was then emulsified at an agitation speed of 1000 rpm under nitrogen purge. After this, the agitation was set to the designated speed and the reductant (sodium metabisulfite) in aqueous solution was injected. For isothermal polymerizations, the dispersion temperature was automatically controlled at  $23 \pm 1^\circ\text{C}$  and the monomer conversion was



**Figure 2** Polymerization temperature profiles at different agitation speeds. Experimental conditions: crossed paddle stirrer at two different speeds. Reactant concentrations were the same as in Figure 1.

monitored by using high-performance liquid chromatography. For nonisothermal polymerizations, the reaction was followed by monitoring the temperature inside the dispersion. The drop size was examined with a scanning electron microscope (SEM) with freeze-fracture equipment. Fourier transform infrared spectroscopy (FTIR) was used for monomer partition analysis, and flame atomic emission spectrometry was used for analyzing the solubility of initiators in the oil phase.

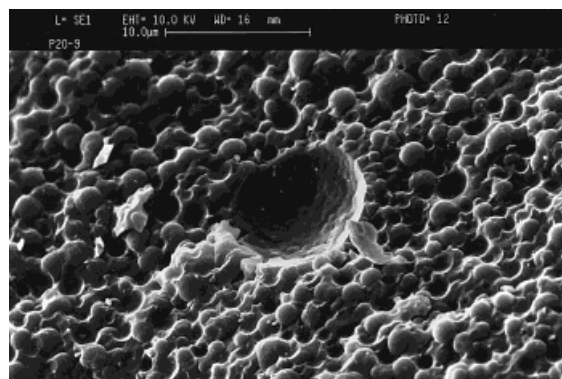
## RESULTS AND DISCUSSION

The two components of the redox initiators in our system are inorganic compounds. Flame atomic emission spectrometry analysis indicated their insolubility in the oil phase. No polymer was produced during the nitrogen purge of the aqueous monomer containing the oxidant. Therefore, the reaction which produces primary radicals can only take place in the aqueous phase as a result of the intermixing of the redox pair by coalescence between the added reductant drops and the dispersed aqueous monomer drops. In nonisothermal experiments, a rapid temperature rise indicated that the polymerization occurred as soon as the reductant solution was introduced to the dispersion. This suggests that the coalescence could be very quick in this case.

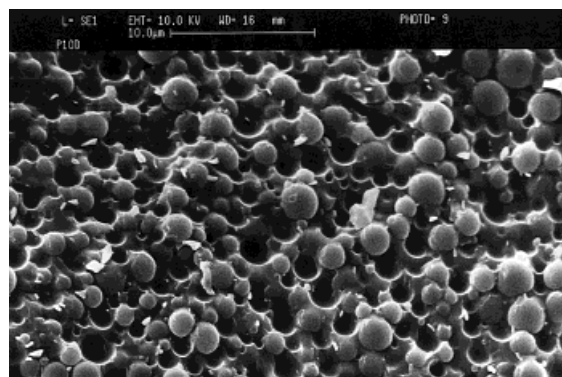
Figure 1 shows a series of SEM images of the

dispersion at different polymerization stages. The aqueous monomer drop size was in a range of 0.6–2.0  $\mu\text{m}$  before the addition of the aqueous reductant. Big drops appeared after a shot of reductant solution was added to the dispersion. Obviously, they were derived from the newly introduced reductant solution. It is clear that the big drop size was getting smaller as polymerization proceeded, indicating a breakup of these drops under the agitation. Apart from this, no significant size change was observed for the small drops throughout the course of polymerization.

In an inverse dispersion polymerization of aqueous acrylamide in toluene using a blend of surfactants as the emulsifying system and azobisisobutyronitrile (AIBN) as the oil-soluble initiator, Graillat and coworkers found two populations of droplets/particles in both the initial dispersion and the final inverse latex.<sup>5</sup> The large

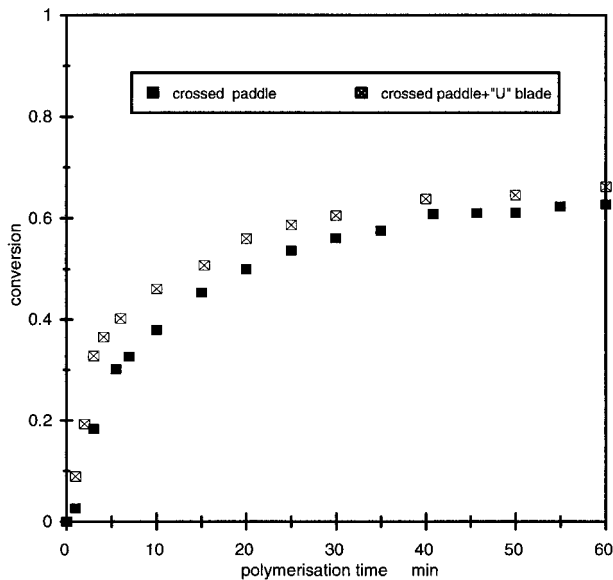


(a)



(b)

**Figure 3** SEM images of final lattices prepared at different agitation speeds. Experimental conditions: 23°C, crossed paddle stirrer. (a) At 500 rpm, (b) at 700 rpm. Reactant concentrations were the same as in Figure 1.



**Figure 4** Polymerization conversion curves using different stirrers. Experimental conditions: 23°C, two types of stirrer at 1000 rpm. Reactant concentrations were the same as in Figure 1.

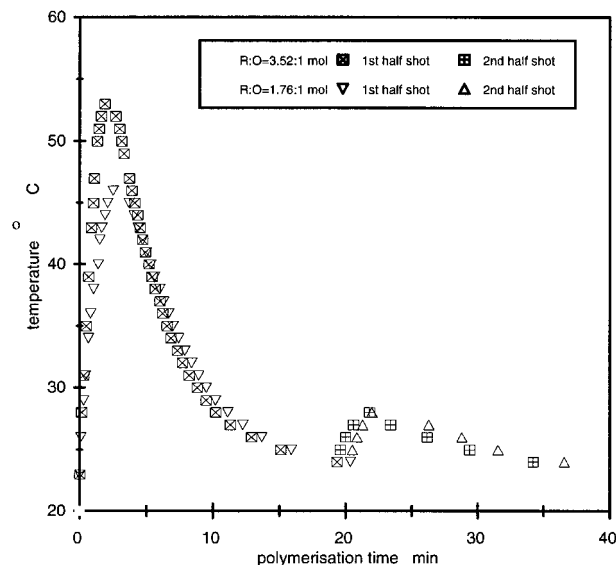
droplets underwent a sharp size decrease at a certain percent conversion depending on the agitation. Those authors believed that the polymerization locus was the aqueous phase and attributed the evolution of the droplet size distribution to a balance between coalescence and dispersion of the droplets under the effect of prevailing shear rate due to agitation. Using sodium persulfate and sodium metabisulfite as a water-soluble redox initiation system, *Texter et al.* reported a change of droplet size from 5 nm in the initial dispersion to 37–39 nm in the final latex in the polymerization of tetrahydrofurfuryl methacrylate using Aerosol-OT as emulsifier.<sup>11</sup> They assumed that this phenomenon was due to the proximity of the polymerization initiation point to the boundary of the isotropic single-phase region or due to the lengthy polymerization time and low temperature.

Because the reductant was added as a water solution in our system, it seems reasonable to postulate that the reductant drops were unstable at the beginning and tended to reduce their interfacial tension by adsorbing the surfactant molecules. They could acquire stabilizer either by adsorbing the free surfactant molecules in the oil phase or by coalescing with the surrounding aqueous monomer drops. Therefore, the tendency to reduce the interfacial tension of the aqueous reductant drops could promote their coalescence with the stabilized aqueous monomer drops. This

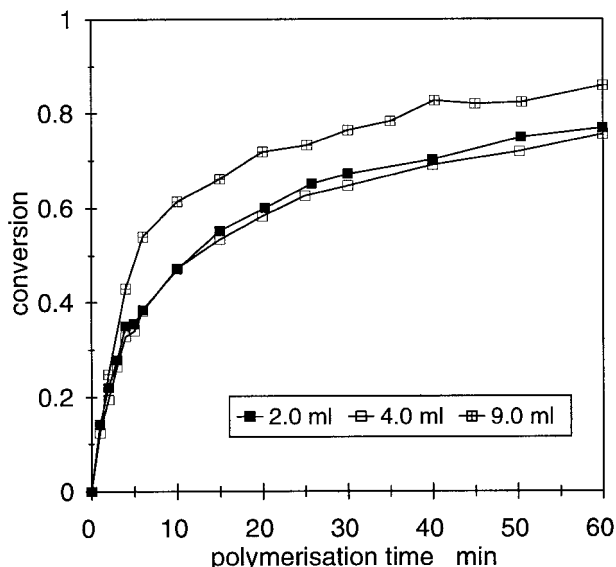
may account for the instantaneous polymerization which occurred when the reductant solution was added. So, the big drops observed early in the polymerization were likely to have acquired some monomer by coalescence and to act as polymerization loci. These coalesced drops could undergo breakup under the agitation stress and, simultaneously, participate in further coalescence.

It was found that agitation speed has a significant influence on the polymerization rate. Figure 2 shows the temperature profiles of polymerizations conducted at two agitation speeds. The faster agitation resulted in a sharper increase in dispersion temperature and a higher maximum value. The higher polymerization rate could be the result of an increase in both coalescence and breakup at higher agitation speed. SEM images of the final lattices provided evidence for this suggestion (Fig. 3). Some big drops (about 8.0  $\mu\text{m}$  in diameter) existed in the final latex produced at 500 rpm agitation, although they were barely observable when agitation at 700 rpm was used.

A difference in polymerization rate was also observed when two different stirrers were used (Fig. 4). A modification of the crossed-paddle stirrer by fixing a "U" blade clearly increased the polymerization rate. This is probably attributed to the same effect on coalescence and breakup by improving agitation intensity. In addition, the higher agitation intensity using the modified stir-



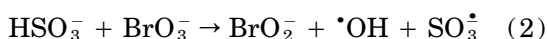
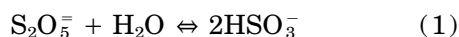
**Figure 5** Further initiation by adding second shot of aqueous reductant. Experimental conditions: crossed paddle stirrer at 1000 rpm. Reactant concentrations were the same as in Figure 1.



**Figure 6** Polymerization conversion curves using different aqueous reductant volumes (same reductant mass). Experimental conditions: 23°C, crossed paddle plus “U” blade stirrer at 1000 rpm. Reactant concentrations were the same as in Figure 1.

rer produced a larger number of smaller aqueous monomer drops in the dispersion. Because the total interfacial area was increased, the coalescence between the aqueous monomer drops and the aqueous reductant drops could be enhanced.

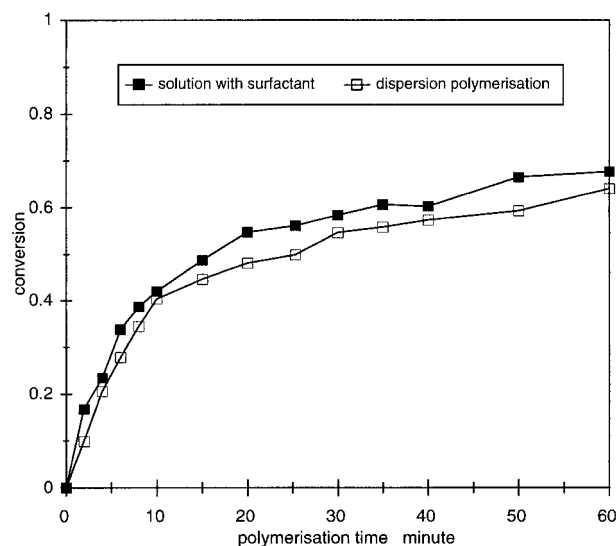
It is interesting that a second shot of the aqueous reductant induced further initiation of polymerization, as indicated by another temperature rise in the nonisothermal polymerization (Fig. 5). However, no significant temperature change was detectable by adding a second shot of the aqueous oxidant. One possible explanation is that the reductant molecules were used up before the second shot of the reductant was added. On the basis of the literature search, the reaction between sodium metabisulfite and potassium bromate could be as follows<sup>12</sup>:



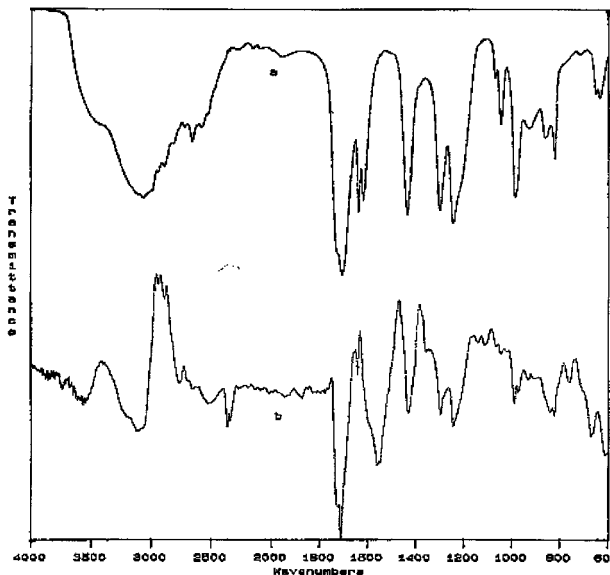
In the polymerizations shown in Figure 5, the mole ratio of reductant to oxidant was in excess of the value required for the above chemical reaction scheme. Therefore, complete exhaustion of the reductant is unlikely and there must be another reason for a diminishing polymerization rate.

According to the foregoing hypothesis, polymer-

ization proceeded in coalesced drops as a result of the simultaneous coalescence and breakup of the drops. The drop coalescence and breakup are very complicated procedures and dependent not only on mixing conditions, but also on system internal properties.<sup>13</sup> The further coalescence and breakup of the coalesced drops could be restrained by the increase in the fluid viscosity inside the drops, owing to the formation of polymer molecules. However, the volume ratio of the reductant solution to the aqueous monomer is quite low (about 1 : 66), so that the aqueous reductant drops are unlikely to intermix with all aqueous monomer drops. As a result, both the reductant and the oxidant molecules might not be completely consumed at the end of polymerization; the oxidant remains in uncoalesced aqueous monomer drops, while the reductant is “trapped” in highly polymerized drops. With the addition of the second shot of aqueous reductant, which has a low viscosity, the coalescence could take place again and further polymerization could proceed. In contrast, further coalescence, which could occur by the addition of a second shot of oxidant, cannot initiate significant polymerization because the newly formed coalesced drops will lack either the reductant or the monomer.



**Figure 7** Comparison of dispersion and solution (with surfactant) polymerizations. Experimental conditions: 23°C, crossed paddle plus “U” blade stirrer at 1000 rpm for dispersion polymerization and at 600 rpm for solution polymerization (with surfactant). Reactant concentrations:  $[M] = 1.993$  mol/L of aqueous phase,  $[I_{ox}] = 1.377 \times 10^{-3}$  mol/L of aqueous phase,  $[I_r] = 2.268 \times 10^{-3}$  mol/L of aqueous phase,  $[S] = 10$  wt % of oil phase. See Nomenclature.



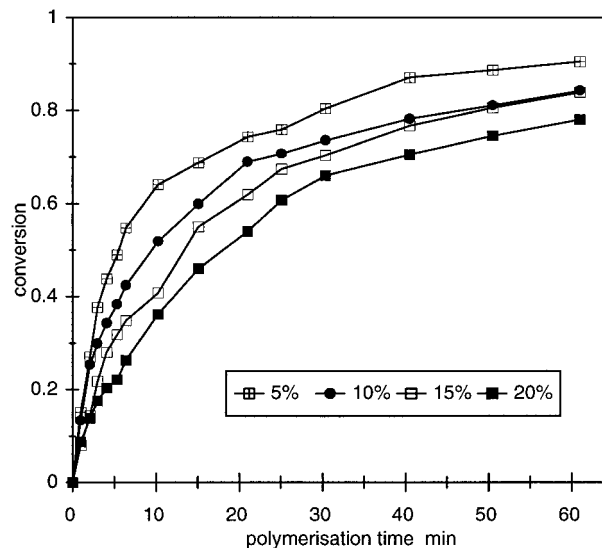
**Figure 8** FTIR spectra. (a) Spectrum of acrylic acid, (b) subtracted spectrum.

The effect of changing aqueous reductant volume on polymerization was also in agreement with the hypothesis. Figure 6 shows the conversion curves using different volumes of the reductant solution while the reductant mass was kept constant. The small increase in the volume seems not to change polymerization significantly. However, pronounced increases in both polymerization rate and limiting conversion were evident when a larger volume was used. This is probably attributed to a combination of two conflicting factors affecting polymerization. An increase in the volume will obviously produce a larger number of the aqueous reductant drops and increase the opportunity of coalescence between different drops. On the other hand, the reductant concentration in these drops decreases with increased volume, so that the polymerization rate in each coalesced drop could be reduced.

Solution polymerization in the presence of surfactant was conducted for comparison. Figure 7 shows the conversion curves of two different polymerizations conducted using the same formulation, except for the absence of Isopar M in the solution polymerization, under identical conditions. It can be seen that the polymerization rate is slightly lower in the dispersion polymerization than in the solution polymerization. This is contrary to results reported by Vanderhoff et al.<sup>1</sup> In the inverse dispersion polymerization of sodium *p*-vinylbenzene sulfonate in oxylene stabilized with Span 60 with potassium persulfate as wa-

ter-soluble initiator, they found that the rate of the dispersion polymerization was remarkably higher than that of the solution polymerization. The authors attributed the higher rate in dispersion polymerization to initiation in both aqueous drops and inverse micelles. In the polymerization of acrylamide with water-soluble azoisobutyro (*N*-hydroxyethyl-2) amidin as initiator, Baade and Reichert reported that the initiation occurred in the aqueous drops by decomposition of the initiator, so that each aqueous drop acted as an individual batch solution polymerization.<sup>3</sup> The difference between the dispersion and solution polymerizations reported here suggested a different mechanism and could be interpreted as evidence for the drop mixing hypothesis. Because the polymerization only occurred in the coalesced drops and the generation of the coalesced drops is a function of time, the aqueous monomer drops cannot all be initiated at the same time. Because of its specific features, discussed above, our inverse dispersion polymerization cannot be described simply as an emulsion polymerization or as a suspension polymerization.

FTIR characterization of the oil phase separated from the unpolymersed dispersion indicated a small amount of acrylic acid molecules in the oil phase. In Figure 8, plot b is the FTIR



**Figure 9** Polymerization conversion curves at different surfactant concentrations. Experimental conditions: 23°C, crossed paddle stirrer at 1000 rpm. Reactant concentrations:  $[M] = 4.243$  mol/L of aqueous phase,  $[I_{ox}] = 1.789 \times 10^{-3}$  mol/L of aqueous phase,  $[I_r] = 7.888 \times 10^{-4}$  mol/L of aqueous phase. See Nomenclature.

spectrum obtained by subtracting the spectrum of the oil phase before dispersion from the spectrum of the separated oil phase after dispersion. The subtracted FTIR spectrum is in good agreement with that of pure acrylic acid. This suggested a transfer of monomer between the two phases. It may be possible that some oligomer radicals formed in the coalesced drops might also transfer to the oil phase and then be captured by the aqueous monomer drops. This would provide another kind of initiation mechanism, but the polymerization experiments show that any such mechanism is of minor importance.

It was found that there is an inverse relationship between polymerization rate and surfactant concentration (Fig. 9). Hunkeler and coworkers reported a similar phenomenon and attributed it to a chain transfer reaction which involved the surfactant molecules.<sup>6</sup> In our system, this transfer might take place through the double bonds in the surfactant molecules. The new surfactant radicals could initiate monomer polymerization if they were not inactive. As discussed above, the coalescence and breakup of drops would result in a redistribution of the surfactant molecules which were located on the interface. Therefore, chain transfer could lead to another kind of initiation.

## CONCLUSION

Our research results suggest that, in an inverse dispersion polymerization using water-soluble redox initiators, the initiation of polymerization is generated by coalescence between two different types of drop. Coalescence and breakup of aqueous drops take place simultaneously under a continuous agitation and have a significant effect on polymerization, drop/particle size, and distribution. Particles with different percent conversion were produced as polymerization proceeded. The mechanism differs from both conventional emulsion polymerization and suspension polymerization. The migration of the monomer through the

oil phase and chain transfer to the surfactant molecule might provide other ways for initiation.

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## NOMENCLATURE

$M$	monomer
$S$	surfactant
$I_{ox}$	oxidizing half of redox initiation system
$I_r$	reducing half of redox initiation system
[ ]	concentration
wt %	weight percentage

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