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Inverse dispersion polymerisation of acrylic acid initiated by a water-soluble redox pair: the role of drop mixing

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Abstract

Polymerisation of acrylic acid has been initiated by the sodium metabisulphite/potassium bromate redox pair. The reaction occurred in aqueous drops dispersed in a paraffinic oil and stabilised by a non-ionic surfactant. Characterisation of drop/particle behaviour throughout the course of polymerisation, using a freeze-fracture technique with a scanning electron microscope, suggested a mechanism of drop polymerisation that included continuous and simultaneous drop coalescence and break-up. The important role of drop mixing in the polymerisation was investigated by conducting polymerisations with some varied experimental parameters. It has been found that the agitation speed, the composition of the reductant aqueous solution and the method of adding the aqueous reductant had significant effects on polymerisation rate, limiting monomer conversion, particle size and size distribution in the final latexes. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Inverse dispersion polymerisation; Redox initiators; Drop mixing

1. Introduction

Vanderhoff et al. reported a pioneering investigation on the preparation of water-soluble polymers through polymerisation of some vinyl monomers in water-in-oil dispersion in 1962 [1]. They introduced a term ‘inverse’ to distinguish this kind of heterophase polymerisation from the conventional direct heterophase polymerisation in oil-in-water dispersion. The proposed schematic representation of the polymerisation (termed inverse emulsion polymerisation) was almost an exact ‘mirror-image’ of a conventional direct emulsion polymerisation. From the 1980s, the rapid growth in the application of water-soluble polymeric materials in a wide variety of fields has brought increasing interest in polymerisations in inverse dispersions from both academia and industry. In the literature, the majority of attention so far has been focused on the polymerisations using single-component initiators [2–13]. Various mechanisms have been suggested for these polymerisations in order to identify the reaction locus and to describe the nucleation of polymer particles. Redox initiators have been extensively used in low-temperature conventional direct emulsion polymerisations because they have relatively low activation energies for free-radical generation [14]. Kurenkov et al. reported a successful polymerisation of aqueous acrylamide in toluene using potassium persulphate/sodium metabisulphite redox pair as initiators, but gave no details concerning the mechanism of the process [15]. Dimonie et al. reported a polymerisation of aqueous acrylamide in inverse dispersion initiated by potassium persulphate/sodium bisulphite redox pair [16,17]. Gel formation occurred in the very early stages, on addition of the initiator(s), followed by the break-up of the gel into small particles under vigorous agitation as the polymerisation proceeded. The authors correlated this unusual polymerisation behaviour with the physical-chemical interface phenomenon and with the fact that the gel had a rather complex heterogeneous structure.

For polymerisations in inverse dispersions, the aqueous monomers are initially dispersed in organic liquids (oil) in the presence of surfactants. In the case of using single-component initiators, the polymerisations can be initiated by the decomposition of initiators in the oil phase, aqueous phase or in both phases depending on the partition of the initiators in the two phases. When using a water-soluble redox pair, at least one of the two components has to be segregated from the monomer to prevent polymerisation before the inverse dispersion is established. The oxidant goes more commonly with the aqueous monomer in the initial inverse dispersion whilst the reductant is introduced later as an aqueous solution to start polymerisation. Alternatively, both oxidant and reductant in aqueous solutions

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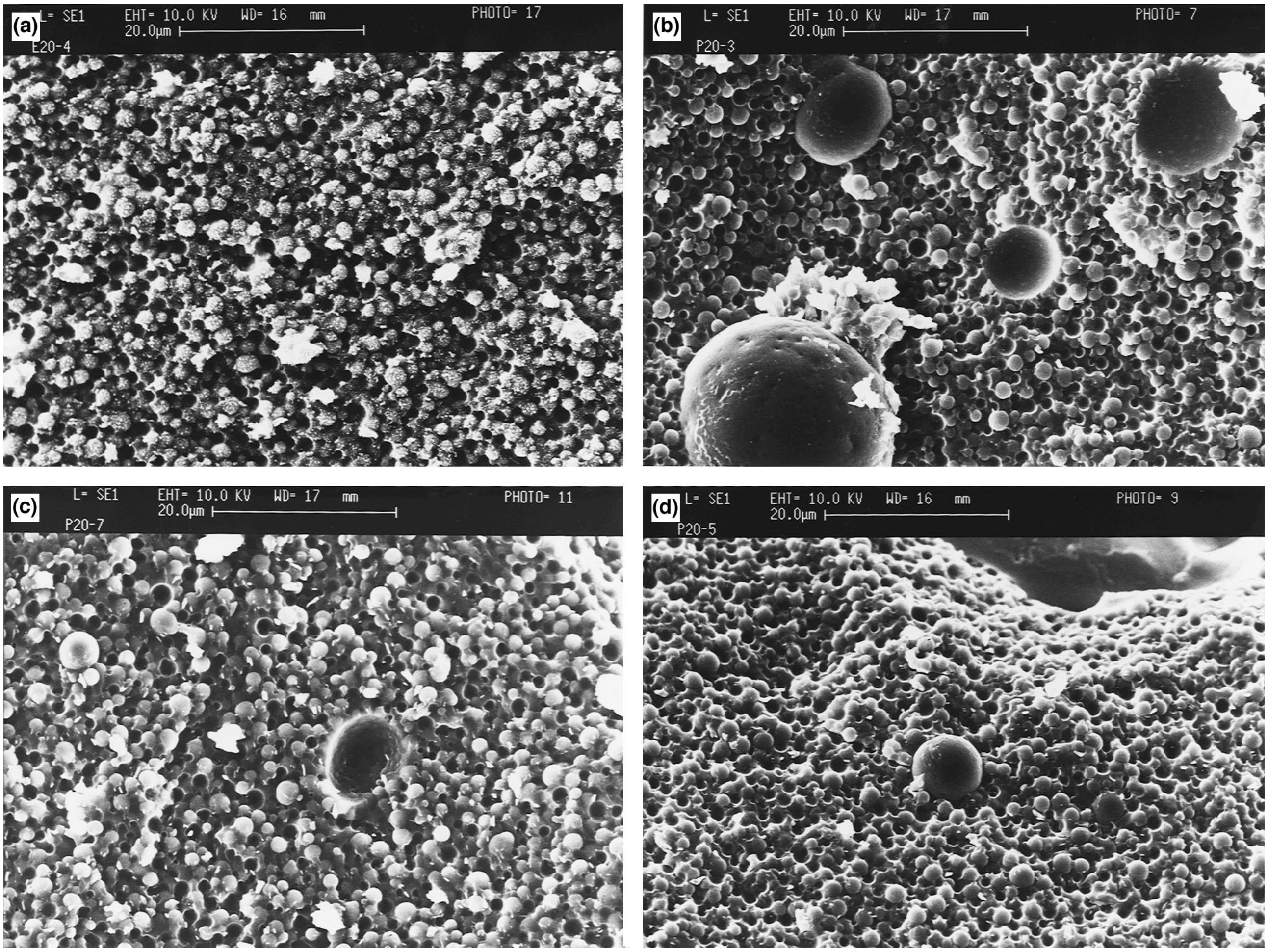

Fig. 1. Freeze-fracture SEM images of inverse dispersion at various polymerisation times. Time after adding aqueous reductant: (a) 0 min; (b) 2 min; (c) 30 min; (d) 60 min. $[AA]_o = 4.24$ mol l^{-1}, $[Na_2S_2O_5]_o = 7.70 \times 10^{-4}$ mol l^{-1}, $[KBrO_3]_o = 1.77 \times 10^{-3}$ mol l^{-1}, 500 rpm agitation, 23°C.

are introduced separately to the dispersion of aqueous monomer in an agitated oil phase. Therefore, the reaction system initially consists of two or three different types of aqueous drops in which the reactants are segregated from each other. Some specific features of inverse dispersion polymerisation of aqueous acrylic acid using potassium bromate/sodium metabisulphite redox initiators has been reported in a previous paper [18]. The research reported in this paper concerns investigation of drop behaviour and its influence on this kind of polymerisation.

2. Experimental

Acrylic acid (AA), supplied by Scott Bader, was purified by distillation prior to polymerisation. Distilled and de-ionised water (DI water) was used as solvent. Other chemicals (commercial grade) were used as received without further purification.

Polymerisations were conducted with a 500 ml glass-jacketed reactor fitted with mechanical stirrer, baffles, nitrogen inlet and outlet. The design and operation of this apparatus were described elsewhere [19]. For isothermal polymerisations, the temperature of inverse dispersion was automatically controlled at a designated value within a fluctuation of ±1°C by circulating warm water or ice water through the jacket. For non-isothermal polymerisations, water of the same temperature as the designated reaction starting temperature was pumped through the jacket at a constant rate throughout the course of polymerisation. The dispersed aqueous phase was initially prepared by mixing acrylic acid, potassium bromate (oxidant) and a small amount of *N*,*N*′-methylene-bisacrylamide (cross-linking agent) in an aqueous solution. Ammonium hydroxide was employed as buffer for maintaining the aqueous solution at pH 5.1 ± 0.1. This solution was then dispersed in Isopar M (a mixture of paraffinic liquids) containing *N*,*N*-bis-hydroxyethyl tall oil amide (a non-ionic surfactant) under 1000 rpm agitation. The amount of surfactant was 10 wt% of oil phase and the overall phase weight ratio of aqueous phase to oil phase was about 3:1. After about 1 h emulsification with a surface nitrogen

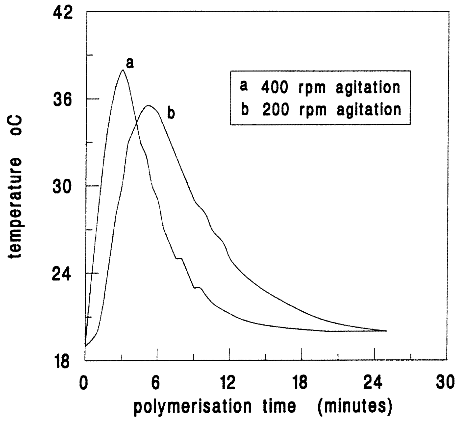

Fig. 2. Temperature profiles of polymerisation at different agitation speeds. $[AA]_o = 4.24$ mol l^{-1}, $[Na_2S_2O_5]_o = 7.85 \times 10^{-4}$ mol l^{-1}, $[KBrO_3]_o = 1.73 \times 10^{-3}$ mol l^{-1}.

purge at a constant slow flow, the agitation was adjusted to the designated speed and sodium metabisulphite (reductant) in aqueous solution was introduced and the time was recorded as polymerisation starting time. Unless stated otherwise, the aqueous reductant was injected as a shot using a glass syringe. The volume of the aqueous reductant was about 1.4% of the total aqueous volume. The instantaneous rise of temperature in non-isothermal polymerisations indicated that the polymerisations proceeded with no induction period.

Small samples of the inverse dispersion/latex were frozen rapidly and the aqueous drops/particles in the inverse dispersion/latex were examined by using a scanning electron microscope (SEM) with freeze-fracture equipment. The isothermal polymerisations were followed by measuring residual monomer level using high-performance liquid chromatography while the non-isothermal polymerisations were monitored by measuring the variation of inverse dispersion temperature.

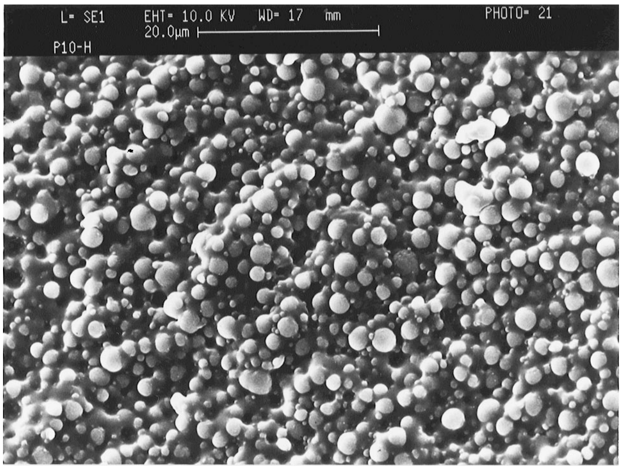

Fig. 3. Freeze-fracture SEM image of final latex produced at 700 rpm agitation. Reactant concentrations are the same as in Fig. 1, 23°C.

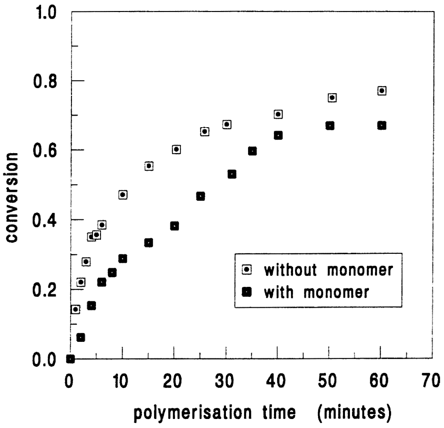

Fig. 4. Monomer conversion curves for polymerisations with and without monomer in reductant aqueous solution. $[AA]_o = 4.24$ mol l^{-1}, $[Na_2S_2O_5]_o = 7.94 \times 10^{-4}$ mol l^{-1}, $[KBrO_3]_o = 1.77 \times 10^{-3}$ mol l^{-1}, 1000 rpm agitation, 23°C.

3. Results

3.1. Evolution of aqueous drop size and size distribution

Fig. 1 shows a series of SEM images of the inverse dispersion at various polymerisation stages. Image (a) clearly reveals that the aqueous monomer-oxidant drops (AMODs) are fairly uniform with a range of diameter from 0.6 to 2.0 μm before the addition of the aqueous reductant. After adding the aqueous reductant as a shot, some big aqueous drops are observed (image (b)). It must be mentioned that in the very early stages of polymerisation, the big aqueous drops did not distribute uniformly in the system. It is reasonable to postulate that these big aqueous drops are originally derived from the newly introduced aqueous reductant solution under the rotation stress of agitation. It is also evident that the size of the big aqueous drops decreases with time, an implication of their further break-up (images (c) and (d)).

3.2. Effect of agitation speed

Inverse dispersion polymerisations were performed at various agitation speeds. Fig. 2 shows temperature profiles of non-isothermal polymerisations at agitation speeds of 200 and 400 rpm, respectively. It is seen that the agitation speed has a significant effect on polymerisation rate. The maximum temperature was reached in about 3.0 min at 400 rpm agitation whereas it was reached in about 4.5 min at 200 rpm agitation. The maximum temperature at 400 rpm (about 38°C) was higher than that at 200 rpm agitation (about 35°C). The influence of agitation speed on particle size and size distribution in the final latexes was also examined using the freeze-fracture SEM. Some big particles were observed in the final latex produced at 500 rpm agitation (see Fig. 1(d)), whereas the particle size in the final latex produced at 700 rpm agitation was rather uniform (Fig. 3).

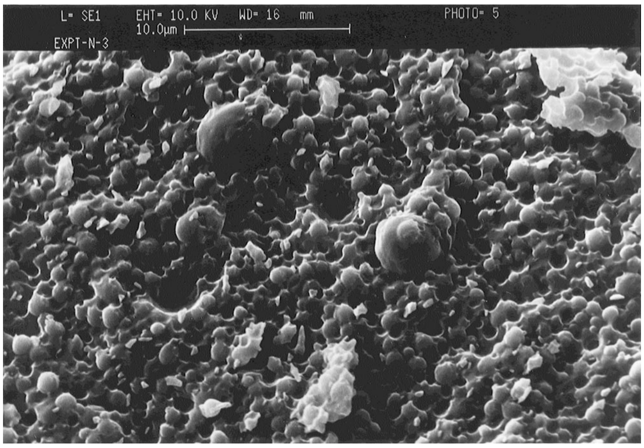

Fig. 5. Freeze-fracture SEM image of final latex produced in the presence of monomer in reductant solution. For reactant concentrations and experimental conditions see Fig. 4.

3.3. Effect of monomer in an aqueous reductant

An inverse dispersion polymerisation was conducted by adding an aqueous reductant solution containing acrylic acid at the same concentration as that in the AMODs. Fig. 4 shows the variations of monomer conversion with polymerisation time in the presence and in the absence of acrylic acid in the aqueous reductant solution. The total acrylic acid concentrations remained the same in these two polymerisations. It is evident that the presence of acrylic acid in the aqueous reductant solution results in decreases in both polymerisation rate at early stages and limiting monomer conversion. The freeze-fracture SEM image reveals the existence of some big particles in the final latex although the polymerisation was performed at 1000 rpm agitation (Fig. 5). These results indicate the importance of the acrylic acid distribution in the initial aqueous phase and imply that the polymerisation is influenced by its heterogeneous nature.

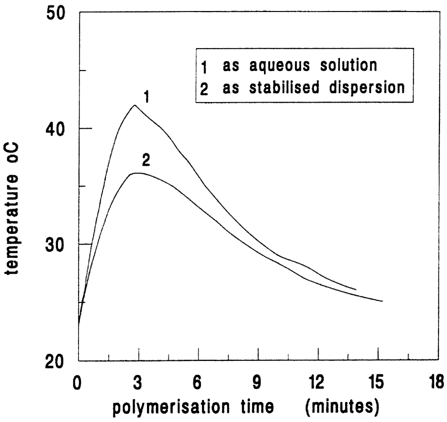

Fig. 6. Temperature profiles of polymerisations by adding aqueous reductant in different ways. $[AA]_o = 4.24\ \mathrm{mol\ l^{-1}}$, $[Na_2S_2O_5]_o = 8.05 \times 10^{-4}\ \mathrm{mol\ l^{-1}}$, $[KBrO_3]_o = 1.79 \times 10^{-3}\ \mathrm{mol\ l^{-1}}$, 1000 rpm agitation.

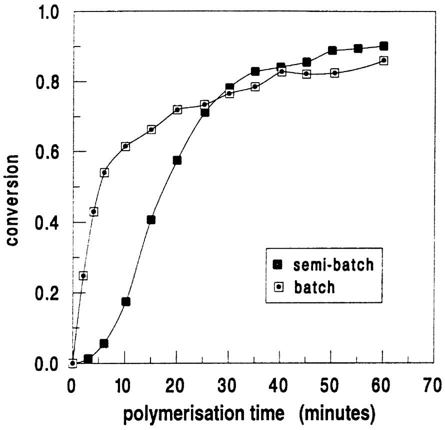

Fig. 7. Monomer conversion curves for batch and semi-batch polymerisations. Reactant concentrations and experimental conditions are the same as in Fig. 4.

3.4. Adding aqueous reductant as stabilised dispersion

In some inverse dispersion polymerisation experiments, the aqueous reductant was pre-dispersed in Isopar M which contained surfactant and the stabilised drops were then added to the aqueous monomer-oxidant dispersion. The phase ratio and the concentration of the surfactant in the dispersion of the aqueous reductant were the same as those in the aqueous monomer-oxidant dispersion. Fig. 6 shows a pronounced difference in the temperature profiles of non-isothermal polymerisations between adding the reductant as an aqueous solution and adding the reductant as a stabilised dispersion. This suggests that the polymerisation is retarded by pre-dispersing the aqueous reductant in the stabilised oil.

3.5. Continuous addition of aqueous reductant

A semi-batch inverse dispersion polymerisation was carried out by adding the aqueous reductant continuously within 25 min at an approximately constant rate. Fig. 7 shows the monomer conversion curves of batch polymerisation (adding the aqueous reductant as a shot) and semi-batch polymerisation conducted under identical experimental composition and conditions. The initial rate of the batch polymerisation was evidently higher than that of the semi-batch polymerisation. This is obviously because more reductant molecules, in the former case, were present in the system for initiation at the early polymerisation stages. However, the rate of the semi-batch polymerisation increased gradually with the continuous addition of the aqueous reductant and then levelled off. In addition, it seems that a somewhat higher limiting monomer conversion was attained in the semi-batch polymerisation.

4. Discussion

In Vanderhoff's schematic representation of an inverse emulsion polymerisation, it was postulated that the

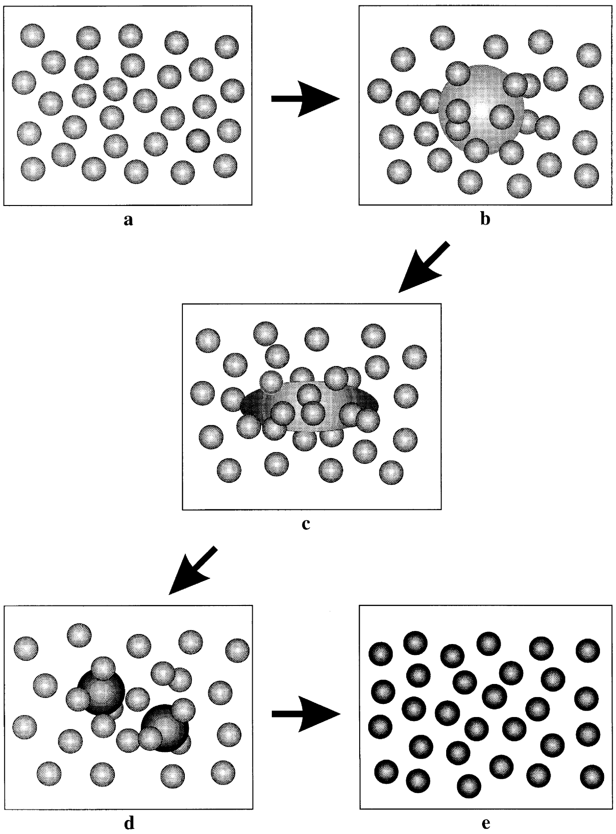

Fig. 8. Illustration of inverse dispersion polymerisation process. Diagrams refer to different stages of polymerisation (see text). Increase in shading intensity represents increase in monomer conversion.

dispersed aqueous phase was present in inverse micelles apart from in the aqueous droplets [1]. However, there is no direct evidence to date for the formation of polymer particles from this kind of inverse micelle [20]. Most of the research concerning polymerisations in inverse dispersions has demonstrated, so far, that the polymerisation loci are aqueous droplets, regardless of the solubility of initiators in water [2,3,7,12]. It is not clear whether the non-ionic surfactant molecules form inverse micelles in Isopar M at the experimental surfactant concentration in the present polymerisation system. The evolution of aqueous drop size and size distribution indicates little importance of micellar nucleation. In the case of micellar nucleation, as demonstrated in the conventional direct emulsion polymerisations [14], the dispersed monomer droplets act as reservoirs and their size decreases as polymerisation proceeds, predominantly in the monomer-swollen micelles. However, no significant decrease in the size of AMODs was observed during the present polymerisation. This implies that only a small amount of acrylic acid diffuses through the oil phase. In addition, the significant effect of agitation speed on the particle size in the final latexes suggests that the nucleation of particles could not be attributed to initiation in inverse micelles or in the continuous oil phase because the size of micelles is usually insensitive to agitation intensity.

Although most researchers assume the polymerisation loci to be in the aqueous monomer droplets, when single-component initiators are used, different hypotheses have been proposed in the literature for the initiation modes, depending on the solubility of initiators in the aqueous phase. When using a water-soluble single-component initiator, Baade and Reichert demonstrated that each aqueous droplet acted as a tiny solution polymerisation reactor and the polymerisation kinetics were the same as those of polymerisation in aqueous solution [3,4]. When using the initiators with limited solubility in water, two possible initiation modes are possible. One is the initiation by the primary free-radicals formed by the decomposition of initiator molecules dissolved in the aqueous droplets [2]. In the other mode, the primary free-radicals, formed in the continuous oil phase, diffuse through the interfacial boundary layer into the aqueous droplets to initiate polymerisation [3,12]. These two initiation modes may occur simultaneously in some cases [4]. In a redox pair initiated polymerisation, the primary free-radicals are generated via an oxidation–reduction reaction. It has been confirmed that both the oxidant and the reductant in the present polymerisation cannot initiate the polymerisation of aqueous acrylic acid alone and they are hardly soluble in the oil phase [19]. Therefore, the generation of primary free-radicals can only be in the dispersed aqueous drops when the two components of the redox pair come together. The segregation of the two redox components in the two different aqueous drops makes the initiation mode different from that when using single-component initiators. The most probable way for initiation is the coalescence between the AMODs and the aqueous reductant drops (ARDs). The pronounced dependence of polymerisation rate on agitation speed (Fig. 2) also shows a characteristic feature of drop initiation [2].

As soon as the primary free-radicals are produced by redox reaction in the coalesced aqueous drops, polymerisation will take place and hence, aqueous polymer-monomer particles (APMPs) form. The instantaneous rise of temperature after adding the aqueous reductant, as shown in Fig. 2, indicates that the coalescence is very quick. Therefore, the big aqueous drops in the SEM images, even at very early stages of the polymerisation, are probably the APMPs rather than the real ARDs. Because the aqueous reductant was added as an unstabilised aqueous solution, the newly formed ARDs could be rather unstable until they acquire surfactant molecules for stabilisation. In addition to adsorbing the free surfactant molecules in the oil phase, they could acquire surfactant molecules by coalescing with the stabilised AMODs which collide with them in the turbulent field. In fact, the drop collision frequency in the system is expected to be high due to the relatively high volume ratio of the aqueous phase to the oil phase and the fast movement of the aqueous drops/particles under agitation. This could account for the quick initiation of polymerisation by drop coalescence.

It is clear that the size of these APMPs reduced with time. This suggests a continuous breakup of them under the agitation. The drop breakup will create more unstabilised interface and induce further coalescence. In this way, more and more AMODs are initiated. Therefore, the polymerisation probably proceeds as a result of simultaneous and continuous drop-coalescence and breakup. This process can be illustrated diagrammatically in Fig. 8. The separate parts of this figure relate to the various stages of the reaction system, from before the addition of the aqueous reductant up to complete conversion. At stage (a), an inverse dispersion is established. The monomer and oxidant in aqueous solution are present as aqueous drops in the oil and stabilised with the surfactant. These AMODs are moving and colliding with one another in the turbulent field of agitation. They may experience coalescence and breakup, but an equilibrium between the drop coalescence and breakup has been established. Therefore, the size of the AMODs is fairly uniform. At (b) the addition of the aqueous reductant to the system is shown. Because the aqueous reductant is added as a shot, it must be initially present as aqueous drops, much larger than the AMODs. These ARDs are unstable and tend to acquire surfactant for stabilisation. At (c) the deformation of the ARDs under the rotational stress is shown. At the same time, the ARDs will collide with the AMODs. Some AMODs may stick with the ARDs after collision and subsequently join together (coalescence). As soon as coalescence occurs, the two components of the redox pair mix together and primary free radicals are generated within these coalesced aqueous drops. In consequence, some ARDs disappear and some APMPs are now formed. At (d) the breakup of big ARDs or APMPs into smaller aqueous drops or particles is shown. It must be mentioned that there is probably no sharp distinction between stages (c) and (d). The coalescence and breakup of the ARDs are more likely to take place simultaneously. The time which elapses between the addition of the big ARDs and their breakup into the same size aqueous drops as the AMODs is anticipated to be lengthy, relative to the time for the coalescence and the initiation of polymerisation. Therefore, the big ARDs will soon become APMPs before they are all broken into small aqueous drops. These APMPs are still too big to exist in the system and will undergo further breakup. At the same time, they will coalesce with the remaining AMODs. Provided that the reductant is added in an amount equal to or larger than that required for the redox reaction, polymerisation will continue within the newly formed APMPs derived from the coalescence between the AMODs and the APMPs. In an ideal system, all the AMODs experience coalescence with the ARDs or with the APMPs and, eventually, the polymerisation within every APMP is complete. Finally, the system comprises an inverse dispersion of small polymer particles stabilised with the surfactant molecules. This is represented at the end stage (e).

Here it is assumed that the diffusion of all kinds of free radicals through the oil phase is negligible.

From the above hypothesis, it is not difficult to expect that the composition in each individual APMPs could vary as reactions and drop mixing proceed. The polymer content in APMPs will increase with time. This will raise the internal fluid viscosity, which would, in turn, influence drop mixing [21]. Graillat et al. investigated the effects of acrylamide conversion on the viscosity of polymer-monomer solution and on the dispersibility of this solution in toluene [7]. It was found that the viscosity of the polymer-monomer aqueous solution simulating 10% monomer conversion was so high that it could not be dispersed in toluene regardless of the agitation intensity. A very quick increase in the viscosity of the aqueous polymer-monomer solution was also observed in the present polymerisation. Therefore, it is reasonable to postulate that an APMP could not undergo further coalescence and breakup when a certain monomer conversion in it had been attained. If the drop breakup is not fast enough to split up the relatively big APMPs to give particles with the same size as the AMODs before their internal fluid viscosity increases to a certain value, some big particles would remain in the final latex. This could account for the effect of agitation intensity on the particle size and size distribution in the final latexes (Figs 1, and 3).

On the other hand, once an AMOD and an ARD coalesce, the concentration of monomer in the coalesced aqueous drops should be diluted because the reductant is normally added as an aqueous solution without monomer. This dilution effect will be eliminated by adding an aqueous solution containing both the reductant and the monomer. It has been found that the higher monomer concentration resulted in a faster polymerisation rate [22]. However, the experimental result indicates a lower overall polymerisation rate in this case (Fig. 4). This is also probably due to the effect of drop mixing on the polymerisation. From the preceding mechanistic model, it is not difficult to predict that the overall polymerisation rate is a function of two terms: the polymerisation rate in individual polymerising APMPs and the volume percentage of the aqueous phase undergoing polymerisation. The faster polymerisation rate in the APMPs resulted in more significant growth in the fluid viscosity and hence, restricted their further coalescence and breakup. As a consequence, the overall polymerisation rate reduced because less AMODs were initiated in unit time, although the polymerisation rate in individual APMPs might increase. In addition, the faster polymerisation rate in the APMPs could lead to earlier stoppage of their further coalescence and breakup. The broadening in the particle size distribution in the final latex provides further evidence (see Fig. 5).

In the case of adding the aqueous reductant as a stabilised dispersion, the opportunity for collision between the ARDs/APMPs and the AMODs should increase, at least at the early stages of polymerisation, because of the greater number of ARDs/APMPs. However, the experimental results reveal that the polymerisation rate was retarded rather than being promoted (Fig. 6). This can probably be attributed to the effect of the interfacial surfactant molecules on drop coalescence. It is well established that, in an agitated two-phase liquid–liquid system, some colliding drops could rebound owing to the elastic properties of the interfacial film entrapped between them. Coalescence only occurs when the colliding drops remain together for a long enough time to enable the rupture of the interfacial film. The strength of this film can be increased by the presence of surfactant molecules [21]. By adding the reductant as a stabilised dispersion, the coalescence frequency between the unlike aqueous drops would be reduced due to the stabilisation function of the interfacial surfactant molecules. However, the presence of the surfactant molecules on the surface of the ARDs did not completely inhibit their coalescence with AMODs, in spite of retardation. This is clearly indicated by the immediate rise of the inverse dispersion temperature once the stabilised dispersion of the aqueous reductant was introduced (Fig. 6). This suggests that the coalescences not only involve the unstabilised aqueous drops, but also take place between the stabilised aqueous drops. This supports the hypothesis that the generation of polymerising APMPs could continue through simultaneous coalescence and breakup between the polymerising APMPs and the uncoalesced AMODs provided the fluid viscosity in the former is not too high.

According to the foregoing hypothesis, the only way to initiate the AMODs is by their coalescence with the ARDs or the APMPs containing the reductant molecules. It has been demonstrated that the ARDs could become APMPs very soon after being introduced to the dispersion of AMODs. Thereafter, the initiation of residual monomer is via further coalescence and breakup of these APMPs with the AMODs. Because of the statistic feature of drop coalescence and breakup in a turbulence field, the drop mixing history of the individual APMPs is different and hence, particles with various composition may co-exist within a certain duration. If this coalescence and breakup process is not quick enough to convert all the aqueous drops/particles to uniform ones before it completely stops, owing to the increase in the fluid viscosity, aqueous drops/particles with various monomer conversions would remain in the final latex. Therefore, the overall limiting monomer conversion is dependent not only on the limiting monomer conversion in the individual particles, but also on the drop mixing. Any factors promoting quick and uniform drop mixing would benefit the increase in the limiting monomer conversion, and vice versa. In the case of adding the reductant aqueous solution containing the monomer (Fig. 4), the relatively quick increase in the fluid viscosity in the APMPs restricts their further drop mixing with remaining AMODs. This is probably why lower limiting monomer conversion was achieved. The difference in the limiting monomer conversion between the batch and semi-batch polymerisations is probably also attributed to the same important role of drop mixing in the polymerisation. Compared with the batch polymerisation, a lesser number of ARDs are present in the dispersion at the initial stage of semi-batch polymerisation, i.e., the number ratio of the AMODs to the ARDs is higher. Therefore, the opportunity for the coalescence between a big ARDs and the AMODs is larger. This would facilitate the quick distribution of the reductant molecules in the aqueous phase and reduce the possibility of trapping them in the APMPs with high fluid viscosity. By adding the aqueous reductant continuously, the newly introduced ARDs would prefer to coalesce with the remaining AMODs or the APMPs with lower monomer conversion because of the influence of the internal fluid viscosity on drop coalescence and breakup. Therefore, the overall residual monomer level could be reduced in this way.

5. Conclusions

A mechanistic model has been proposed for the process of polymerisation in inverse dispersion using water-soluble redox initiators. The polymerisation takes place in the aqueous drops as a result of continuous simultaneous drop coalescence and breakup. The composition in individual drops/particles depends on their drop-mixing history, which, in turn, influences the drop mixing. These specific features have important consequences for the polymerisation rate, limiting monomer conversion, particle size and size distribution in the final latexes.

Acknowledgements

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