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On the Evolution of Particle Size Average and Size Distribution in Suspension Polymerization Processes

Fatemeh Jahanzad,[1] *Shahriar Sajjadi,*[2] *Brian W. Brooks**[1]

[1]Department of Chemical Engineering, Loughborough University, Loughborough, Leicestershire, LE11 3TU, UK
E-mail: b.w.brooks@lboro.ac.uk
[2]Division of Engineering, King's College London, London, WC2R 2LS, UK

Summary: The dispersion of methyl methacrylate (MMA) and its suspension polymerization were used as models to elaborate the evolution of particle size average and size distribution in the course of suspension polymerization. The underlying mechanisms for the occurrence of the dynamic and static steady states in the population of drops were defined and their effects on the evolution of drop/particle size average and size distributions were examined. The characteristic intervals of suspension polymerizations (transition, steady-state, growth, and identification) were elaborated. The formation of satellite droplets and their evolution in the course of polymerization were also discussed.

Keywords: dispersion; drop break up and coalescence; particle size distribution; steady-state; suspension polymerization

Introduction

In suspension polymerization, drops of monomer (containing initiator) are dispersed in an aqueous phase, which contains a stabilizer or suspending agent, with the aid of mechanical agitation. As polymerization reactions proceed in the dispersed monomer drops they are gradually converted to polymer particles. The suspending agent prevents excessive coalescence of drops. The product of this process is polymer particles or beads with diameters in the range of 1-5000 μm, depending on the process conditions.

The size of polymer beads is a complex function of drop break up and coalescence rates during the polymerization process. Those rates are affected by several parameters such as the densities and viscosities of each phase, interfacial tension, type and concentration of suspending agent, dispersed-phase hold up, type of impeller and stirring speed[1-3].

A suspension polymerization can be described as a reactive liquid-liquid dispersion in which the

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nature of the drops change continuously with time. In a typical liquid-liquid dispersion, the average drop size at first decreases quickly because of a high rate of drop break up in comparison with drop coalescence. Eventually a point is reached when the rates of drop break up and drop coalescence become equal. That leads to the establishment of a so called quasi steady state in drop size and size distribution[4,5].

The evolution of drop size in suspension polymerization is more complex because drop viscosity increases continuously. As the drop viscosity increases, in the course of reaction, the tendency of drops to break up[6-9] and coalesce[10-12] is reduced. This will affect the balance of the rates of the break up and coalescence and may lead to an increase in the size of drops.

Suspension polymerization reactions produce particles with a broad size distribution. This is because different mechanisms for particle formation might coexist in suspension polymerization[13]. Three size classes of particles can be obtained from a suspension polymerization reactor. They are bead particles, satellite particles, and emulsion particles. Satellite particles are the result of the drop break up mechanism and/or nonhomogenities of the system[3]. Experimental evidence and model predictions have been presented to show that drops deform and burst into daughter drops and a number of satellite droplets[14-16]. Emulsion particles are the result of partial dissolution of the initiator in the water phase that gives free radicals that propagate to form new particles in the aqueous phase. These particles are usually smaller than the satellite particles.

In this paper, the characteristics of a model MMA suspension polymerization in the presence of polyvinyl alcohol (PVA) as stabilizer are studied. The evolution of drop/particle size and size distribution is compared with those in the corresponding MMA-water dispersion and some general conclusions are made.

Experimental

MMA (analytical grade from Aldrich) was distilled at reduced pressure. PVA (Mw = 85000-146000, degree of hydrolysis = 87-89% from Aldrich) and lauroyl peroxide (LPO) (97%, from Aldrich) were used as stabilizer and initiator, respectively, without any further purification. Distilled water was used as continuous phase. The monomer volume fraction was 0.20 and different PVA concentrations were used. The suspension polymerization and dispersion used similar formulation, with the exception that in the suspension polymerization experiments an initiator concentration of 1.0 wt% (based on the monomer phase) was used.

The experiments were carried out using a one-litre jacketed glass reactor equipped with four 90° baffles. A four-paddle impeller was used for agitation. The stirring speed was 500 rpm for all experiments. The temperature of the vessel content was continuously monitored using a thermocouple and controlled within ± 0.5°C of the desired reaction temperature (70 °C). In suspension polymerization experiments nitrogen purging of the aqueous phase was carried out for 30 minutes before the monomer phase was added. Samples were withdrawn at the desired time intervals from the reaction vessel, using a hypodermic syringe, to measure the monomer conversion gravimetrically. Drop/particle size distributions were determined by using a laser diffraction particle sizer (Coulter LS130).

Results and Discussion

Dynamic Steady State

The evolution of the Sauter mean diameter (d_{32}) of the MMA-water dispersion with 0.5 g/l PVA is shown in Figure 1. In the dispersion process (without polymerization), the evolution of drop size can be divided into two stages; *transition* and *steady state*. The steady state drop size distribution in liquid-liquid dispersions will mainly depend on the relative magnitude of the rates of drop break up and coalescence. At steady state, when the rates of drop break up and coalescence are balanced, coalescence removes as many drops from the dispersion as are made via the break up mechanism. This has been called a *dynamic steady state* where individual drops do not retain a unique identity but undergo continuous break up and coalescence.

Figure 1 also illustrates the evolution of d_{32} in the corresponding suspension polymerization with 0.5 g/l PVA. Similar to the dispersion process, during the *transition stage* drops are reduced in size, until they reach an almost constant average size. It can be seen that drops are less severely broken up during the transition stage for the suspension polymerization process in comparison with the dispersion process. This implies that the formation of even a very small amount of polymer in monomer drops, during the first few minutes of suspension polymerization, suppresses the rate of drop break up and as a result larger drop sizes are formed at the end of this interval. The quasi steady-state drop size is established at a higher value for the suspension polymerization. Enhanced drop stability with adding a very small amount of polymer has been reported by Dowding et al.[11].

According to Figure 1, the particles start to grow at the time of 45 min and a steep rise in the drop size is observed at 60 min. Conversion-time data for this polymerization system shows a steep rise in the rate of polymerization at the time of 60 min, corresponding to the conversion of 0.50 (see the small graph in Figure 3). The acceleration in the rate of polymerization is the result of the gel effect which is caused by the increase in the drop viscosity. It should be noted here that the PVA concentration was found to have no effect on the rate of polymerization or conversion-time curve.

Based on the variations of drop size, as shown in Figure 1, the pattern of variation in drop size with time after the end of the transition stage can be characterised by up to three intervals depending on the polymerization conditions. The first interval is the *steady-state stage* during which a rather constant drop size is maintained by balanced rates of drop break up and coalescence despite an increase in the drop viscosity. A short quasi steady-state stage can be seen for the conditions given in Figure 1. The presence of a quasi steady state for suspension polymerization is not always certain and sometimes that condition is never reached. Even for the dispersion processes there is some reduction in the size of drops with time during the steady-state stage. However, such variations are relatively limited.

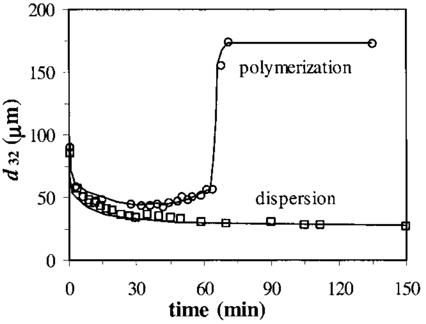

Figure 1- Comparison of evolution of d_{32} in the suspension polymerization of MMA and in the corresponding dispersion ([PVA]=0.5 g/l).

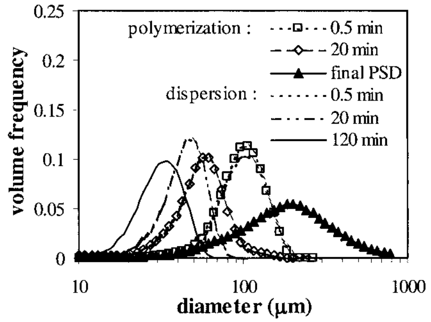

Figure 2- Evoluion of drop/paerticle size distribution for the systems shown in Figure 1.

As the drop viscosity increases, a point is reached where drops can not be easily broken up but they can still undergo coalescence. As a result, drops start growing by coalescence. This interval can be called *growth stage*. This stage has been called the *sticky stage* in the literature perhaps because of the impression that drop coalescence increases with the drop viscosity due to increasing drop tackiness. However, the present authors believe that this is a misleading title because, during this interval, particles are usually more stable against coalescence than in the earlier stage because of reduced mobility of the surface of drops. The viscosity increase in the drops reduces the rate of drop break up more significantly than drop coalescence resulting in an increase in the size of particles [17]. The abrupt increase in the size of drop during the growth stage is a direct result of a sudden viscosity build up in the drops because of the gel effect.

At the end of the growth stage, drops have a very high viscosity and behave like solid particles. These drops cannot coalesce with each other and they keep their identity for the remainder of the process. This has been called *identification point*. Variations in average drop size occur in both the transition stage and the growth stage but sizes remain almost constant during the steady state and during the *identification stage* (i.e., after the indentification point is reached); although some limited flocculation may occur during the identification stage.

Figure 2 shows that the size and size distribution of the reacting and non-reacting drops in the first minutes are similar. Later, during the transition period, the size distribution of both types of drops narrow significantly with time, due to a higher rate of drop break up in comparison with drop coalescence, until a steady-state value is reached. For the dispersion, the size distribution of drops does not change appreciably after the steady-state, but the size distribution of the reacting drops broadens with time when d_{32} changes as shown in Figure 1.

Static Steady State

Figure 3 illustrates the evolution of d_{32} in the suspension polymerization of MMA and in the corresponding MMA dispersion with 10 g/l PVA. For the dispersion process, a similar trend as to that found for 0.5 g/l PVA was obtained. For the suspension polymerization, however, the pattern was different from the suspension polymerization with 0.5 g/l PVA, but it was very similar to that found for the dispersions. In a liquid-liquid dispersion if drops are reduced to a size that cannot be further broken by agitation and if they are also sufficiently protected against drop coalescence, then drops do not undergo any transformation during mixing and a *static steady-state* may be established. Such a dispersion has been called a *turbulent-stabilized* dispersion by Church and Shinnar[4]. Static steady-state can actually be achieved, or approached, if a high concentration of stabilizer, for example, is used. The resulting drops from such dispersions would be very small. Figure 3 shows that the increase in drop size is very small in the growth stage for the polymerizing drops despite the large increase in the drop viscosity.

Figure 4 depicts the evolution of drop/particle size distribution for conditions corresponding to those shown in Figure 3. For the suspension polymerization, particle growth and PSD broadening occurred to a very limited extent. It is expected that, at a higher PVA concentration, coalescence can be completely removed from the system and the evolution of drop size average and size distribution in suspension polymerizations follow similar trends to those in the corresponding dispersions. The experimental data from Konno et al.[18] for the suspension polymerization of styrene with 10 g/l PVA provides an evidence for such a claim. Although the size measurements with optical microscopy, as used by Konno et al.[18], may not be sufficiently sensitive to small variations in particle size.

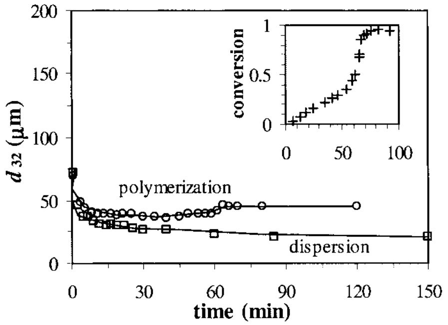

Figure 3- Comparison of evolution of d_{32} in the suspension polymerization of MMA and in the corresponding dispersion ([PVA]=10 g/l).

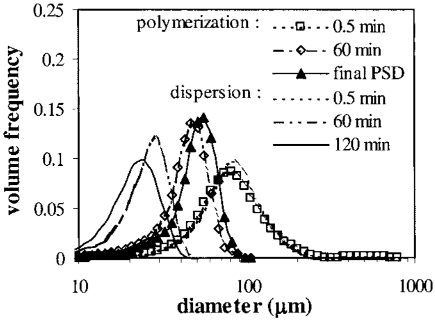

Figure 4- Evolution of drop/particle size distribution for the systems shown in Figure 3.

Satellite Droplets

The size distributions of drops/particles from the suspension polymerizations and dispersions were all bimodal. Figure 5 illustrates a typical PSD measured by using laser diffraction. The drop/particle size distributions included a main or primary peak corresponding to bead drops/particles within the size range of 10-300 μm. That was accompanied by a small secondary peak given by drop/particles with diameters less than 10 μm. The secondary peak is mainly the cumulative result of satellite droplet formation from drop break up but there is a partial contibution from particle formation via dispersion and/or emulsion polymerization mechanisms. Study on the secondary peak has been rarely reported in the literature[19,20]. We used an initiator with very limited water solubility, lauroyl peroxide, to minimize the formation of emulsion particles. The secondary peaks are not shown in Figures 2 and 4 and were ignored in the calculation of d_{32} for simplicity.

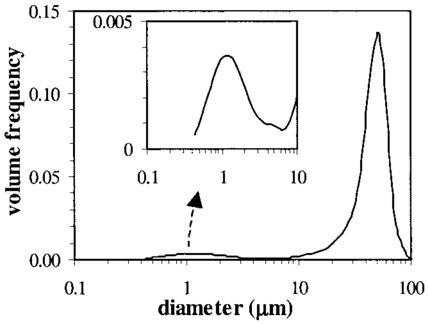

Figure 5- A typical drop size distribution in Suspension polymerization of MMA (t=60 min, [PVA]=10 g/l).

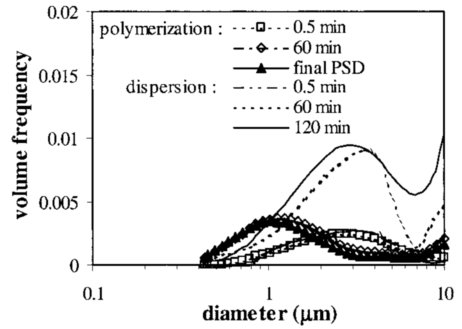

Figure 6- Evolution of satellite size distribution for the systems shown in Figure 5.

Figure 6 illustrates evolution of the size distribution of secondary particles for suspension polymerization of MMA with 10 g/l PVA and for the corresponding dispersion. Satellite droplets were continuously formed with time in the dispersion system. For the polymerization system the satellite size distribution is narrower and smaller in comparison with the corresponding dispersion which can be the result of increasing viscosity in polymerizing drops. In suspension polymerizations with lower PVA concentration the population of satellite droplets dropped significantly during the growth stage because of coalescence and/or flocculation.

Conclusion

The evolution of drop/particle size distribution in suspension polymerization may pass through four intervals; transition, steady-state, growth and identification stages. As the stability of drops in a suspension polymerization is enhanced, by increasing stabilizer concentration for example, the evolution of drop size distribution approaches that in the corresponding dispersion. That evolution is characterized by a transition stage followed by a steady-state stage. That can only occur if the dynamic steady state can transform to a static one. The size average and distribution of satellite particles obtained via suspension polymerization were smaller and narrower, respectively, than those found in the corresponding dispersion at the conditions of this study. The results suggest that tracking of the evolution of satellite particles could lead to a better understanding of the mechanism of drop formation in suspension polymerization.

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