

Unsteady Stirring Method Used in Suspension Polymerization of Styrene

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ABSTRACT: An unsteady stirring method, that is, coreverse rotation with different periodic intervals, was adopted to the suspension polymerization of styrene. Experiments were carried out in a 0.5-L flat-bottom flask with a six-blade Rushton turbine. Parameters affecting the final particle size and the particle size distribution under the unsteady stirring conditions, such as the agitation speed and the periodic interval, had been studied in detail, and the results were compared with those under a steady stirring one. The experimental results showed that the average particle size decreased and the uniformity final particle size distribution could be significantly improved when unsteady stirring approach is used. These were explained as the result of the decrease of the coalescence rate during the suspension polymerization when the unsteady stirring method was used. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1431–1438, 2000

Key words: suspension polymerization; steady stirring; unsteady stirring; particle size distribution; coalescence rate

INTRODUCTION

Suspension polymerization is an important industrial process in which monomer(s), relatively insoluble in water, is(are) dispersed as liquid droplets with steric stabilizer and vigorous stirring, starting with the addition of an initiator that is soluble in the monomer phase, to produce polymer particles as a dispersed solid phase. The particle size and particle size distribution (PSD) affects important product quality attributes, for instance, bead impregnability and morphology after expansion, insulation capability, processability, and mechanical resistance.¹ Thus, forming as uniform as possible a final particle size product is the most important issue in the industrial suspension polymerization.

Many technologies have been used to produce polymers of narrow particle size distribution, such as using an encapsulation step of monomer droplets,² carrying out a suspension polymerization in a “gelled” solution of water and agarose,³ using a Shirasu porous glass (SPG) membrane emulsifier to generate styrene drops of uniform size that would later polymerize in an agitated tank reactor,⁴ etc. Although these technologies increase the uniformity of the final particle size to some degree, they complicate the suspension polymerization operations. In this work, instead of traditional steady stirring of the impeller, a simple unsteady stirring technology was used in the suspension polymerization of styrene to improve the uniformity of final particle size.

The suspension polymerization reactor is usually a stirred vessel. The monomer phase is subjected to either turbulent pressure fluctuations or viscous shear forces, which break it into small droplets that assume a spherical shape under the influence of the interfacial tension. The individual

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drops undergo continuous breakage and coalescence. Eventually, a dynamic equilibrium is established in which individual drops maintain their identities over prolonged periods of time and lead to a stationary average particle size. Thus, the breakage-coalescence of the polymerization process can be looked at as a liquid-liquid turbulent dispersion in which the physical properties (viscosity, interfacial tension, density, etc.) of the monomer drops change dramatically. For the liquid-liquid turbulent dispersions there are four types of energy: turbulent energy, interfacial energy, viscous energy, and the elastic energy. The turbulent energy is determined by the agitation intensity, and usually does not change if the agitation speed is not changed in the polymerization process. The interfacial energy, viscous energy, and the elastic energy change continuously with the polymerization proceeding due to the variation of the physical properties of the dispersed phase; thus, the relative quantities among them also vary continuously. According to the difference of the energy that dominates the polymerization process, the particle formation can be divided into three stages: formation of the monomer droplets, drop coalescence, and formation of the final particles (Fig. 1).⁵ 0% ~ X*: formation of the monomer droplets, interfacial energy domination; X* ~ X**: drop coalescence, viscous energy domination; X** ~ 100%: formation of the final particles, elastic energy domination.

Formation of the Monomer Drops (Interfacial Energy Domination)

At the beginning of the polymerization, the monomer phase is dispersed in the continuous phase, under the effect of the agitation and the suspending agent, to form a stable turbulent dispersion system in which the stabilizer concentration is higher than a critical concentration of the drops surface to be covered totally. With the polymerization proceeding, the polymer begins to be formed. Because, for a bead suspension polymerization (e.g., the suspension polymerization of styrene), the polymer is soluble in the monomer drops, the viscosity and interfacial tension of the drops change gradually; thus, the original dynamic equilibrium of the drop breakage-coalescence is broken and the drop sizes are changing constantly. In this stage, the effects of the elastic energy and the viscous energy can be nearly neglected due to the low viscosity of the dispersed phase, so the drop dispersion is dominated by the

action of the interfacial energy, and the average drop size is proportional to $We^{-0.6}$ and is independent of the dispersed phase viscosity. In this process, the interfacial tension decreases due to the addition of the suspending agent, which causes the breakage of the drops to be accelerated and the coalescence held back. So, the average drop size in this process does not increase much.

Drop Coalescence (Viscous Energy Domination)

Upon proceeding with the polymerization, the viscosity of the dispersed phase, μ_d , increases, and with an increase in the conversion it increases more and more quickly. By degrees, the viscous energy is superior to the interfacial energy, affecting the breakage and coalescence behaviors of the drops, which raises the resistance against the breakage of the drops; thus, the breakage rate becomes slower and slower. When μ_d increases to a critical value of d_{c1} ($X = X_{C1}$), the breakage will cease to occur, whereas coalescence continues. The dispersion will, therefore, coalesce completely, which leads to the particle size increasing sharply. Thus, it is very important to control the coalescence behavior at this stage. Once the dispersion loses stability, the viscous drops may agglomerate with the force of an avalanche and lead to the polymerization stopping.

Formation of the Final Particles (Elastic Energy Domination)

With the continuous increase of the conversion, the viscoelasticity of the drop increases rapidly at the same time that the drop viscosity is increasing, and the drops begin to appear hard. Enhancement of the elasticity will hold back the coalescence of the drops, thereby slowing the growth of the drops. At a certain conversion ($X = X_{C2}$), the elastic energy overcomes the viscous energy to dominate the suspension process, in which the drops become so hard that coalescence between them becomes impossible. At that time, the particles size does not change any more, and the polymerization only occurs within the fixed particles, and the dispersion system looks like a solid-liquid suspension. The function of the agitation then only lies in keeping the solid-liquid suspension and removing reaction heat.

From the analysis above we can see that the final particle size, in fact, has been determined before the end of the polymerization, and, in the second stage, the drop size increase is greater.

Many researchers showed that the coalescence behavior during the polymerization process, especially during the second stage, was the most important to determine the final particle size, and it was the coalescence that made the particle size distribution broad.⁶ Therefore, if the coalescence rate during the polymerization process can be retarded efficiently, the final particle size distribution may be narrowed down.

It has long been recognized that the extent of the drop breakup and coalescence during suspension polymerization, which will determine the final PSD, is affected by geometric factors (agitator type;⁷ vessel dimensions^{8,9}), operating parameters (the hold-up fraction,¹⁰ the agitator speed^{11–13}), and physical characteristics of the suspension polymerization. In practice, the geometric factors of the reactor and the stirrer are mainly determined by the productivity requirements, while the operating parameters, in principle, are determined by the polymerization kinetics. Thus, the remaining control factors for the breakage and coalescence rate are the intensity of stirring and the type and concentration of the stabilizer. The latter is out of our research, and here we only discuss the effect of the stirring.

There has been much research on the effect of the stirring speed on the final particle size distribution, but little research on efficient stirring methods to increase the uniformity of the PSD, except for the work of reducing the agitation speed at some stages of the suspension polymerization, which showed that the particle size distribution obtained was narrowed down efficiently due to the coalescence rate being retarded.¹⁴ Recently, it has been demonstrated by experiments that the mixing time can be significantly reduced, at a relatively low Reynolds number of less than 50, by adopting unsteady stirring.¹⁵ On the other hand, in the case of turbulent conditions, work, including the publications by Ogawa et al.¹⁶ and Yoshida et al.,^{17,18} which indicates that unsteady agitation could improve gas–liquid mixing. Tanaka¹⁹ reported that the dispersion degree of polymer particles in a suspension polymerization reactor could decrease to 50% if a forward–reverse rotation, where the rotational direction was changed periodically at an angle of 90°, is used. We tried to use an unsteady stirring method in which the rotational direction of the impeller was changed at periodic time intervals during the suspension polymerization of styrene. By studying the coalescence behavior in the polymerization process we found that the coalescence rate was

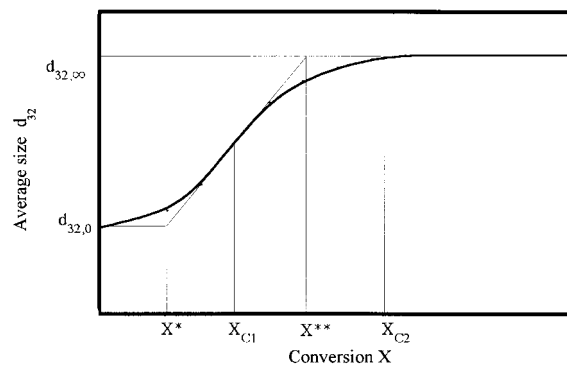


Figure 1 Particle formation process of suspension polymerization (Pan et al., 1997).

low compared with that of the steady stirring method used; moreover, with the periodic interval decrease, the coalescence rate decreased.²⁰ Thus, according to the analysis of the particle formation process above, the decrease of the coalescence would lead to uniform final PSD. The experimental result was in good agreement with this. Note that the energy dissipation under the unsteady stirring condition has been investigated during the suspension polymerization, and it was found that the energy dissipation was the same as that under the steady stirring condition.

EXPERIMENT

Reactor and Impeller

The suspension polymerization experiments were performed in a 0.5-L flat-bottom flask with an inside diameter of 0.085 m. The flask was fitted with a reflex condenser, a nitrogen inlet, and two equally spaced stainless steel baffles, each 1/10th the flask diameter. To ensure an inert atmosphere and to prevent inhibition effect from oxygen, a continuous flow of nitrogen purged the reactor at least half an hour before the reaction. The impeller was a six-blade Rushton turbine made of stainless steel. The reactor flask was put in a thermal water vessel, and the temperature was kept at 85°C. The experimental setup is shown in Figure 2.

Unsteady Stirring of the Impeller

The unsteady stirring used here was a coreverse stirring of the impeller with periodic intervals, and the relation of the agitation speed with time as shown in Figure 3. A RTM control box (HEI-

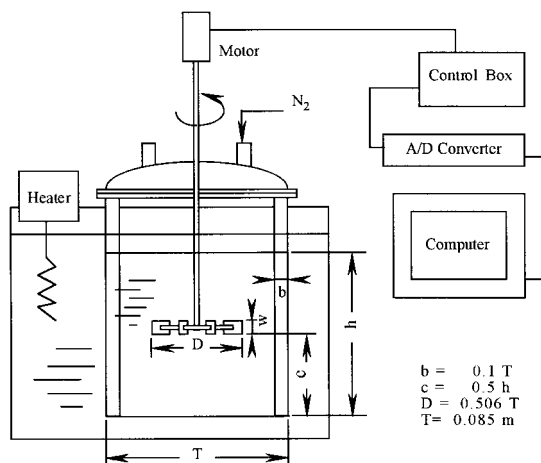


Figure 2 Experimental setup of suspension polymerization.

DON) controlled by a computer program was used to adjust the agitation speed, N , and the periodic time interval, t' . The impeller rotating speed and the periodic time interval were easily controlled within 1 rpm and 0.01 s, respectively.

Reactants

The continuous phase was deionized water. The initiator for the styrene suspension polymerization was benzoyl peroxide (BPO), purified by precipitation with methanol out of a chloroform solution, and a mixture of poly(vinyl alcohol) (PVA) and tribasic calcium phosphate (TCP) was used as the stabilizer. All of the chemical reactants were provided by Kanto Chemical Co., Inc. The recipe for styrene suspension polymerization experiments is shown in Table I.

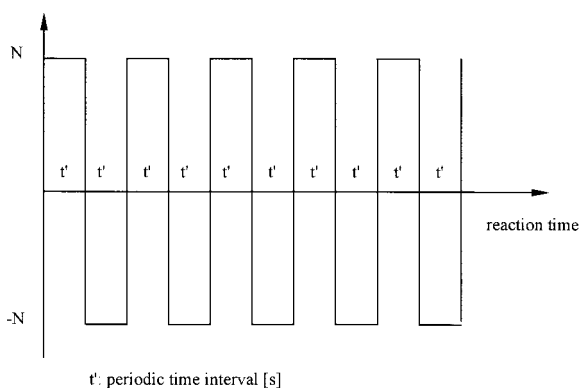


Figure 3 Variation of agitation direction with time the coreverse stirring method.

Table I Recipe for Suspension Polymerization

Water	305 g
Styrene	91.5 g
Styrene/water	0.3
TCP ^a	0.1525 g
TCP/water	0.05%
PVA ^b	0.0153 g
PVA/water	0.005%
BPO ^c	0.915 g
BPO/styrene	1.0%
Temperature	85°C
Agitation speed	200–500 rpm
Periodic interval	2–60 s

TCP^a: tribasic calcium phosphate.

PVA^b: poly(vinyl alcohol) [average $M_w = 15,000$].

BPO^c: benzoyl peroxide [purified by precipitation].

Particle Size Measurement

At the end of the polymerization, the product was washed by water, then filtered, and dried. After that, photographs of the particles (about 300–400 droplets) were taken by a microscope camera [Olympus-PM-10-M(C-35)], and from those, the particle diameters were measured and the mean particle size and size distribution were calculated. Here, the particle diameter is the Sauter mean diameter.

RESULTS AND DISCUSSIONS

Effect of the Agitation Speed on the Average Particle Size

The agitation speed was equal to 200, 250, 300, 350, 400, 450, and 500 rpm, respectively, under both steady and unsteady stirring condition, and the periodic interval of the unsteady stirring was equal to 2, 10, 30, and 60 s, respectively. The final mean particle sizes of the suspension polymerization are shown in Figure 4.

From Figure 4 we can learn that, in the case of steady stirring, with an increase in impeller speeds, the average particle size decreases. This observation probably lies in the greater breakage rate at the high agitation speed than at the low one. It must be remembered that the drop (particle) size is the dynamic result of two competing processes—breakage and coalescence. Although an increase of the impeller speed may result in not only an increase of breakage rate tending to decrease the drop size, but also a rising in coalescence rate tending to increase the drop size; the

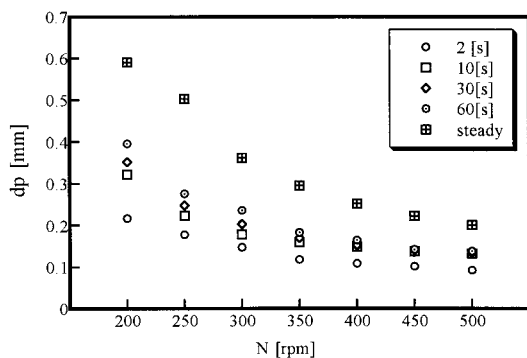


Figure 4 Effect of agitation speed on average particle size.

increase of breakage rate will outweigh the latter, thus producing a smaller size particle. This result is in agreement with many other works.¹⁰ In the case of unsteady stirring, when the periodic interval is constant, the larger the agitation speed, the smaller the average particle size, which can be explained the same way as the above. The most interesting phenomenon is that when the impeller speed is kept constant, the final particle sizes obtained under the unsteady stirring condition are all smaller than those obtained under the steady one; moreover, when the periodic interval decreases, for instance, from 60 to 2 s, the final particle size becomes small. The shortest periodic interval in our experiments, 2 s, gives the smallest particle size at every impeller speed investigated. These phenomena resulted from the effects of the unsteady stirring on the coalescence rate of drops during the suspension polymerization. It is well known that the coalescence behavior dominates the growth of the drop during the polymerization process. When unsteady stirring was used, the coalescence rate was slower than that when steady stirring was used; therefore, the growth of the drops was slow, leading to the final particle sizes being smaller than that under the steady one. In addition, because under the unsteady stirring condition the coalescence rate was found to decrease with the decrease of periodic time, so the final particles size obtained under the short interval was smaller than that under the long one.

The dependence of the mean particle size on the agitation speed with different time interval can be expressed as:

$$d_p = 29.5t'^{0.123}N^{-0.945}$$

$$t' \leq 30 \text{ s}, 200 \text{ rpm} \leq N \leq 500 \text{ rpm}$$

Effect of the Agitation Conditions on the Particle Size Distribution

The particle size distributions of the suspension polymerization, under steady stirring and unsteady stirring with a periodic intervals of 2, 10, 30, and 60 s, were investigated, and Figures 5 and 6 show the particle size distribution at agitation speeds of 300 and 500 rpm, respectively. Figure 7 shows the dependence of the particle size distribution on the impeller speed at different time intervals. Here, the particle size distribution is assessed by the ratio of the standard deviation to the mean diameter, σ/d_p . This means that the smaller the value of the σ/d_p , the higher the degree of the uniformity of the particle size. The standard deviation was calculated by:

$$\sigma = \sqrt{\frac{1}{n} \sum_{i=1}^n (d_i - d_p)^2}$$

From Figure 5 we can see that when the agitation speed is equal to 300 rpm, under the steady stirring condition, the particle size distribution is broad, while under the unsteady stirring condition the particle size distribution is obviously narrower. Moreover, with the periodic interval varying from 60 to 2 s, the particles size distribution becomes clearly narrower: when the periodic interval is 2 s, the particle size distribution is the narrowest. From Figure 6 we can see that when the agitation speed is 500 rpm, the variation of the particle size distribution is the same as that shown in Figure 5, that is, the particle size distributions obtained under the unsteady stirring condition are all more uniform than those obtained under steady stirring, and when the interval time becomes short, the distribution becomes more uniform. The same observation can also be found in Figure 7.

These phenomena probably result from the great differences of the coalescence rate when the different stirring methods were used. It has been pointed out that the coalescence behavior during suspension polymerization is the most important factor for the particle formation, and a high coalescence rate always lead to broad PSD.⁶ If the coalescence rate can be hindered to some degree, the PSD will become uniform.⁵ Thus, because under the unsteady stirring condition the coalescence rates are lower than that under steady stirring, so the final particle size distributions under unsteady stirring are more uniform. Moreover,

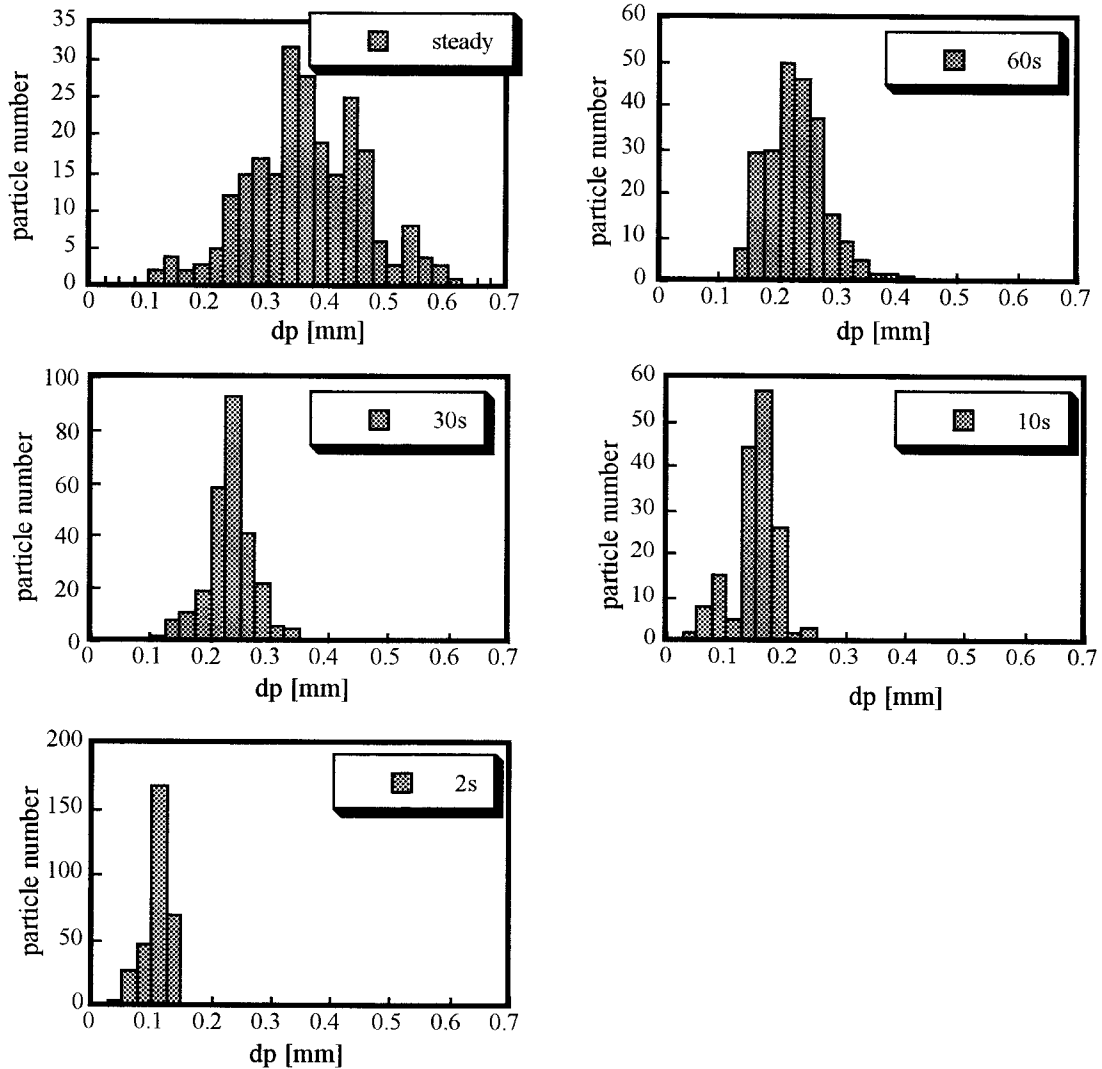


Figure 5 Particle size distribution at different periodic intervals ($n = 300$ rpm).

due to the decrease of the periodic interval resulting in the decreasing coalescence rate under the unsteady stirring condition, the particle size distribution becomes uniform with a decrease in the periodic interval decrease. So the uniformity of the particles size distributions can be improved dramatically when the unsteady stirring method with the periodic interval of 2 s is used, in which the coalescence rate was retarded most efficiently.

CONCLUSIONS

An unsteady stirring method was adopted for the suspension polymerization of styrene, and the results were compared with that under steady stir-

ring conditions. The experimental results show that the final particles size decreases and the particle size distribution becomes more uniform with the periodic interval decrease, compared to the steady stirring method. When the unsteady stirring method with the periodic interval of 2 s is used, the uniformity of the particle size distribution can be improved efficiently. This results from the effect of the unsteady stirring method on the coalescence rate.

NOMENCLATURE

b width of baffles (m) c impeller clearance (m) d_p mean particle diameter (mm) d_i particle diameter (mm) $d_{32,0}$ Sauter diameter of drops at the begin-

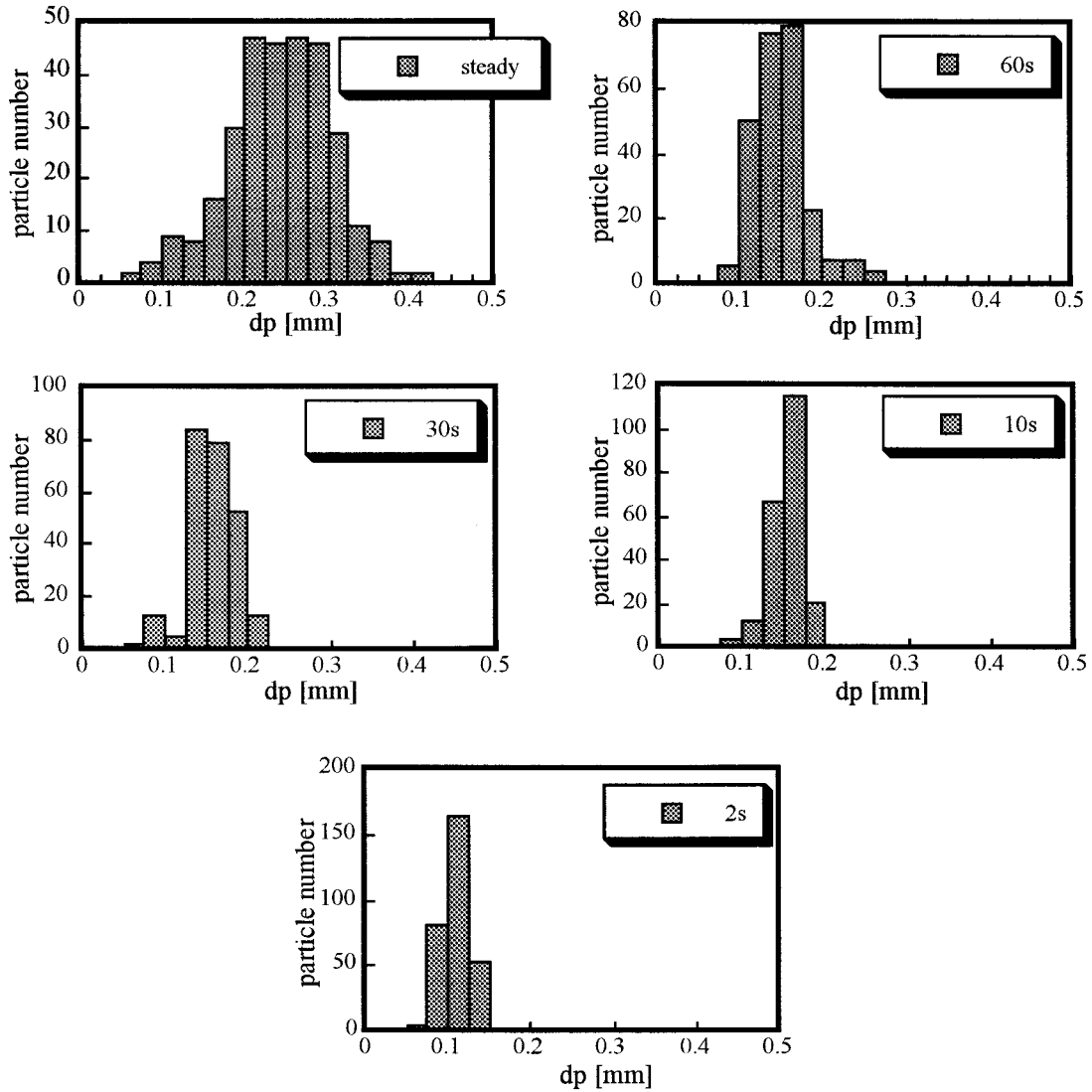


Figure 6 Particle size distribution at different periodic intervals ($n = 500$ rpm).

ning of polymerization $d_{32,\infty}$ Sauter diameter of particles D impeller diameter (m) N impeller speed (rpm) t' periodic time interval, (s) T reactor diameter (m) We Weber number X, X^*, X^{**} conversion of suspension polymerization X_{c1} critical conversion at which the breakage rate decreases to zero X_{c2} critical conversion at which the coalescence rate decreases to zero σ standard deviation μ° viscosity of dispersed phase $\mu_{d,c1}$ viscosity of dispersed phase at the critical conversion of X_{c1}

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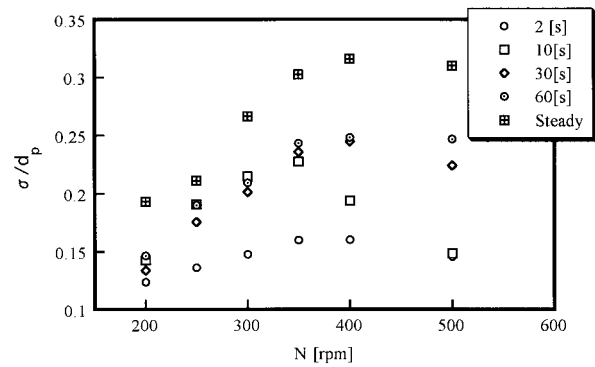


Figure 7 Particle size distribution at different periodic intervals.

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