

Unsteady Stirring Method *Staged* Used in Suspension Polymerization of Styrene

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Received 30 August 2000; accepted 7 December 2000

ABSTRACT: The results of an unsteady stirring method *staged*, used in the suspension polymerization of styrene in a lab-scale batch reactor, are presented. Variation of droplet size during the whole polymerization process under the unsteady stirring condition, compared with that under a steady stirring condition, was found to be small. According to the variable droplet size character, two methods were used to divide the polymerization process into four stages and the unsteady stirring method was used in only one stage of each experimental run. By these operations, the optimum operation of obtaining large particle product with uniform particle size distribution was achieved. The results suggest that controlling the droplet coalescence process is more important than controlling the initial droplet size distribution to obtain uniform final particle products. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1873–1881, 2001

Key words: unsteady stirring; staged; droplet; particle size; particle size distribution

INTRODUCTION

In suspension polymerization, particle size, particle size distribution (PSD), and particle morphology affect the polymer's handling, storage, processing, and application characteristics. Thus, to form a product whose final particle size is as uniform as possible is the most important issue in industrial suspension polymerization. The particle size distributions are determined by breakage and coalescence of polymer droplets in the course of polymerization. The rates of droplet breakage and coalescence are strongly controlled not only by the physical properties of the dispersion systems concerned but also by the agitation conditions. Many technologies, such as using an encapsulation step of monomer droplets,¹ carrying out a suspension polymerization in a "gelled"

solution of water and agarose,² and the use of a Shirasu porous glass (SPG) membrane emulsifier to generate styrene drops of uniform size that would later polymerize in an agitated tank reactor,³ have been used to produce polymers of narrow particle size distribution (PSD). However, these technologies complicate the operation.

A simple, unsteady stirring technology has been reported to be used in suspension polymerization of styrene, and the final PSDs were improved dramatically because the droplet breakage processes were strengthened and the coalescence processes were retarded for the coreverse rotating of the impeller. By this method, however, the final particles were small.^{4,5} Because the properties of the dispersion system (such as dispersed phase viscosity, density, etc.) vary continuously during the suspension polymerization process, the droplet breakage and coalescence rate vary correspondingly. As shown in many investigations the droplet breakage rate decreased with the poly-

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Journal of Applied Polymer Science, Vol. 82, 1873–1881 (2001)
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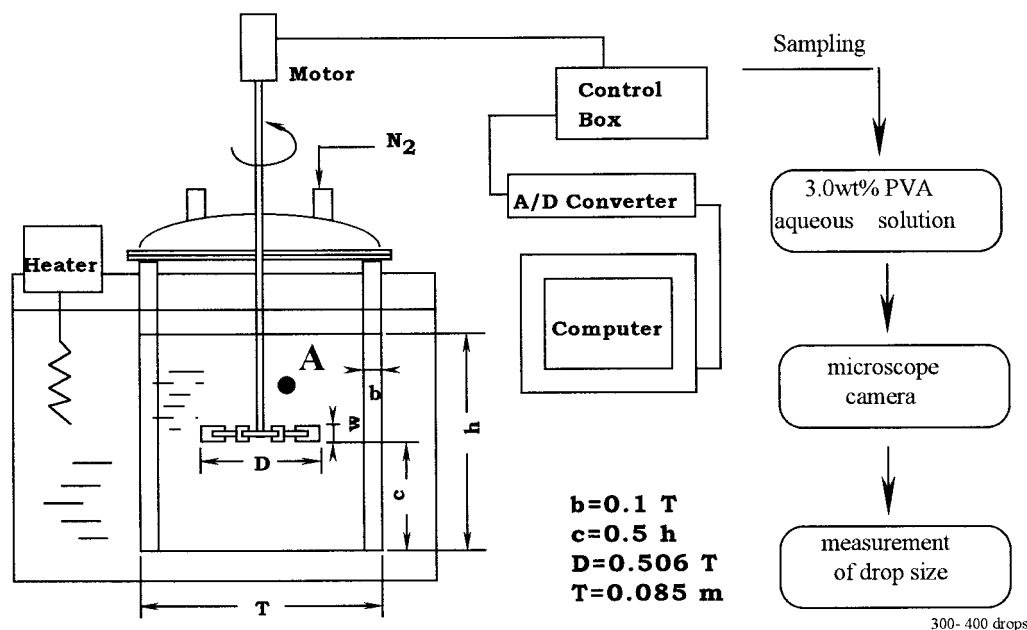


Figure 1 Experimental setup of styrene suspension polymerization.

merization evolution and at a conversion reached zero, and at the same conversion only the droplet coalescence occurred, which then also progressively decreased and then also reached zero at another conversion.⁶ Therefore if the unsteady stirring method is used in different reaction stages, the effects on droplet breakage and coalescence should be different, and thus the final particle size and PSD should also be different.

The purpose of this study was to investigate how the unsteady stirring method staged, used in the course of polymerization, affects the final particle sizes and PSDs, and whether the final particle sizes can be increased and at the same time the uniformity of particle size can be improved by this operation.

In the present study, first the conversions of the styrene monomer and the evolution of droplet size during styrene suspension polymerization under both the steady and the unsteady stirring method were investigated. Then, according to results of these investigations the polymerization processes were divided into four stages using two methods, respectively. In every experimental run the unsteady stirring method was used separately in only one of the four stages and the steady stirring method was used in the other three stages. The droplet evolution, final particle sizes, and particle size distributions of every run were investigated, respectively.

EXPERIMENTAL

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 reflux condenser, a nitrogen inlet, and two equally spaced stainless-steel baffles, each one-tenth the flask diameter. To ensure an inert atmosphere and to prevent the inhibition effect from oxygen, a continuous flow of nitrogen purged the reactor at least 0.5 h 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 1.

Unsteady Stirring of the Impeller

The unsteady stirring used here was a coreverse stirring of the impeller at periodic intervals and the relation of the agitation speed with time is shown in Figure 2. An RTM control box (Heidon BL600, provided by Shinto Scientific Co., Ltd., Japan) 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.

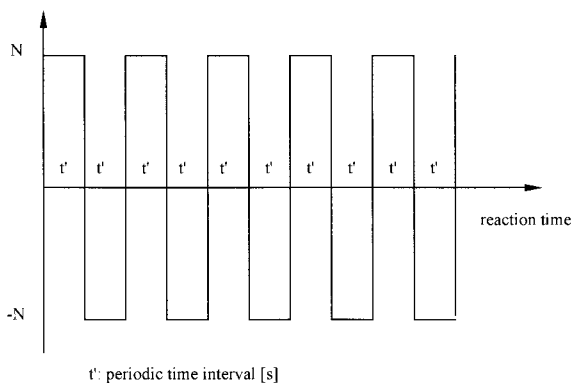


Figure 2 Variation of agitation direction with time in the unsteady stirring method.

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. (Japan). The recipe for styrene suspension polymerization experiments is the same as previously reported.⁴

Droplet Size Measurement

In this work the drop size measurements were conducted by the sampling method. As shown in Figure 1, at constant time intervals from the beginning of the experiment, 0.3 mL of sample liquid was drawn off with a glass pipette from point A. The sampled droplets were transferred to a laboratory dish containing 3.0 wt % aqueous solution of PVA (average polymerization degree = 15,000) to prevent the droplets from coalescing. The entire sampling procedure took about 1 s. After the sample was collected, photographs of the droplets (about 300–400 droplets) were taken by a microscope camera [Olympus-PM-10M (C-35), provided by Olympus Optical Co., Ltd., Japan], from which the transient droplet diameters were measured and the Sauter average diameter d_{32} was calculated.

Particle Size Measurement

At the end of the polymerization, the product was washed with water, then filtered and dried. After that, photographs of the particles (about 300–400

droplets) were taken by a microscope camera [Olympus-PM-10M(C-35)], from which the particle diameters were measured and the Sauter mean particle size and size distribution were calculated.

RESULTS AND DISCUSSION

Profiles of Conversion and Dispersed-Phase Viscosity

The monomer conversion was calculated by gravimetric analysis of samples taken from the reactor at the chosen sampling times by pipettes (0.8 mm i.d.) and put into aluminum dishes. Toward the end of the reactions representative sampling of the suspending particles became more difficult. Figure 3 shows fair experimental reproducibility for the styrene conversion profiles at the same temperature and initiator level, despite agitation speed and agitation method ($N = 300, 400, 500$ rpm and $t' = 10$ s). A simple calculation shows that monomer droplets are large enough to contain a very large number of free radicals ($\sim 10^8$).⁷ Therefore the kinetic mechanism is the same as that of bulk polymerization, and the same kind of dependence of the polymerization rate on initiator concentration and temperature is observed. Thus the change of agitation speed and agitation method did not have a significant effect on the polymerization rate.

The dispersed phase viscosity η_d was calculated by the following equation:

$$\eta_d = \eta_{d0} \left(1 + \gamma \frac{X/X_m}{1 - X/X_m} \right)^2 \quad (1)$$

where X is the monomer conversion, X_m is the conversion of the particle identity point (PIP), η_{d0} is the viscosity of the styrene monomer (3.71×10^{-4} Pa/s at 85°C), and γ is a constant of 19.9.⁶

Figure 3 shows that the viscosity of dispersed phase increases dramatically as the polymerization proceeds and at the end of polymerization, it increases to more than 30 Pa/s, which is nearly 10^5 times the value of the monomer viscosity. It is just this increment that easily allows the droplets to agglutinate, and only a suitably protective agent and agitation can prevent it.

Evolution of Droplet Size

Average particle size and particle size distribution of the final product from suspension polymer-

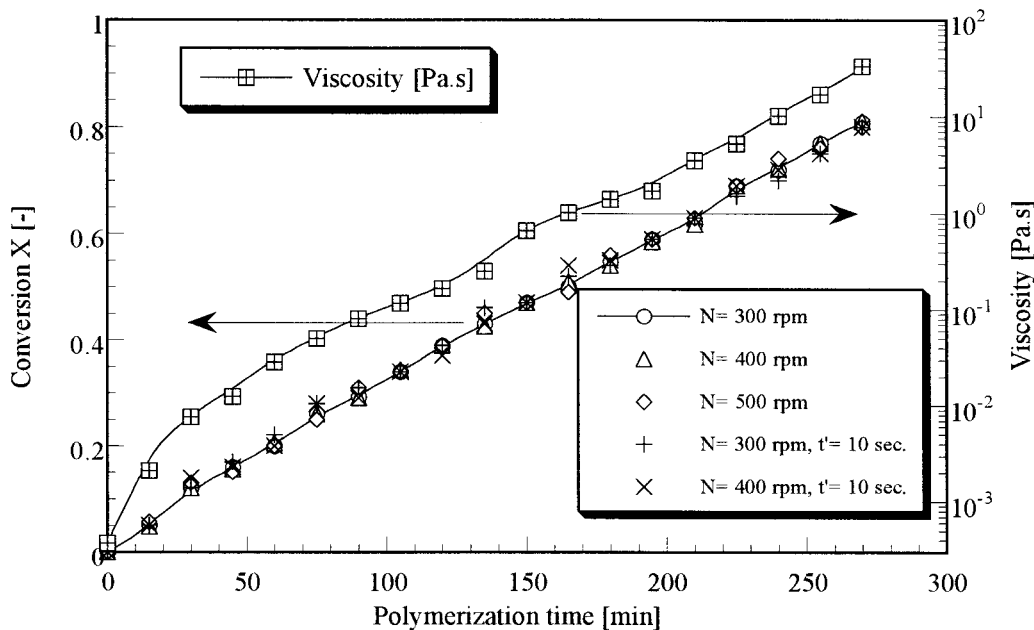


Figure 3 Styrene conversion profiles and viscosity variation of the dispersed phase.

ization reactors are important for certain applications. Keeping constant the average particle size during reactor scale-up is a challenging practical issue. Prediction and control of the final particle size distribution are associated with the evolution of the droplet size distribution of the monomer dispersion in the aqueous continuous phase.

The steady and unsteady stirring method were used, respectively, with the agitation speed N of 300 rpm and period time interval t' of 10 s; the evolution of droplet size with polymerization time is shown in Figure 4. From Figure 4 we can see the following in the case of the steady stirring method: d_{32} varied with an "S" shape, that is, at

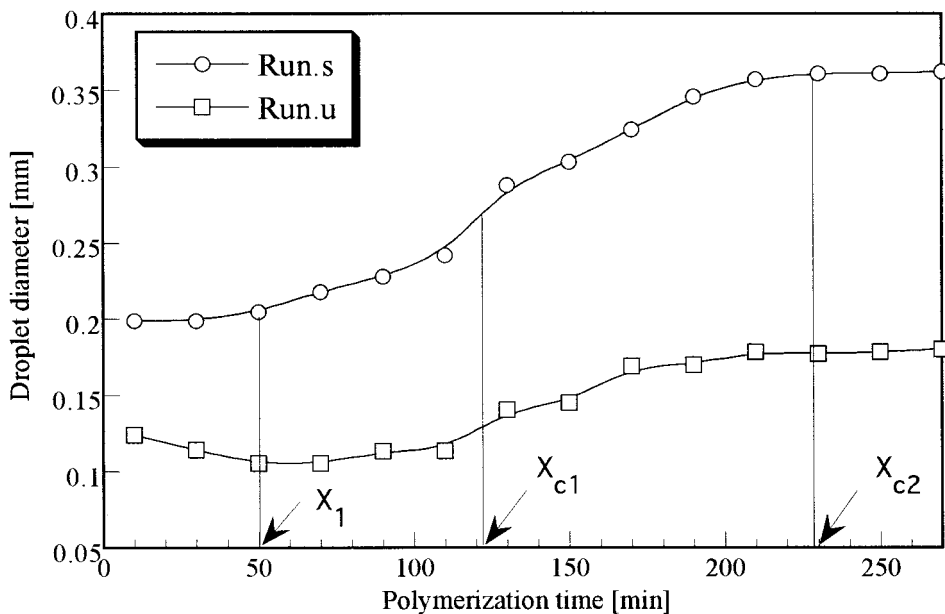


Figure 4 Evolutions of droplet size with polymerization time under steady and unsteady stirring ($N = 300$ rpm, $t' = 10$ s).

the beginning of the polymerization ($X = 0$ to X_1), the droplet size increases slowly, but as the reaction proceeds ($X = X_1$ to X_{c2}) the droplet size obviously increases and there is a maximum increment of droplet size ($X = X_{c1}$); and at the end of the reaction ($X = X_{c2}$ to the end) the droplet size remains constant because the viscosity at that time is too high, so droplets cannot be broken up. The point of X_{c2} is called particle identity point (PIP).⁸ As explained in many other studies, the appearance of X_{c1} shows at that conversion, the droplet breakage process stops, and only the droplet coalescence process exists in the polymerization system, thus leading to the maximum increase of the droplet size; the appearance of X_{c2} shows at that conversion and even the droplet coalescence process stops, and thus the droplet size no longer changes. From Figures 3 and 4, we can confirm that X_1 is about 0.17, and X_{c1} and X_{c2} are about 0.45 and 0.72, respectively.

Also from Figure 4 we can see the following in the case of the unsteady stirring method. Although the variation of d_{32} appears as the "S" shape, there are some differences from that of the steady stirring case: at the beginning of the polymerization, d_{32} is smaller than that of the steady stirring case, and as polymerization proceeds ($X = 0$ to X_1), the d_{32} did not increase but decreased slightly. As polymerization proceeds further, d_{32} stops decreasing and begins to increase, undergoing a maximum increment point ($X = X'_{c1}$); at a conversion ($X = X'_{c2}$) the d_{32} stops increasing and remains constant until the end of reaction. The two characteristic conversions X'_{c1} and X'_{c2} are about 0.44–0.5 and 0.71–0.73, respectively.

By comparing the d_{32} variation curves under the two stirring methods, we can see that the increment of d_{32} during the whole polymerization process under unsteady stirring is smaller than that under steady stirring because the coalescence rate was inhibited.⁴ We also can see that, although the unsteady stirring method affects the droplet breakage and coalescence rate, thus leading to the d_{32} variation, the conversions at which the maximum increases of d_{32} appear (X_{c1} and X'_{c1}) and the PIPs appear (X_{c2} and X'_{c2}) are almost same. This confirms that the two conversions do not depend on the agitation method.

Effect of Unsteady Stirring Staged Used on the Evolution of Droplet Size, Particle Size, and Particle Size Distribution

From the preceding results, two methods were used to divide the polymerization process into

stages, as outlined below: one (a) is dividing the whole polymerization time, 270 min, equally into four stages, using Run.1, Run.2, Run.3, and Run.4, respectively, to express the time stage in which the unsteady stirring method is used; another (b) is dividing the polymerization into four stages according to the two characteristic conversions (X_{c1} or X'_{c1} , X_{c2} or X'_{c2}), using Run'.1, Run'.2, Run'.3, and Run'.4, respectively.

(a) $n = 4$	(b) $n = 4$
Run.1: $t = 0\text{--}67.5$ min	Run'.1: $X = 0\text{--}0.17$
Run.2: $t = 67.5\text{--}135$ min	Run'.2: $X = 0.17\text{--}0.45$
Run.3: $t = 135\text{--}202.5$ min	Run'.3: $X = 0.45\text{--}0.72$
Run.4: $t = 202.5\text{--}270$ min	Run'.4: $X = 0.72\text{--}0.81$

Note that at every experimental run, only in the time range expressed is the unsteady stirring method used, and at other polymerization times, the steady stirring methods are still used. For example, Run.2: $t = 67.5\text{--}135$ min expresses an operation as the following:

- when polymerization time = 0–67.5 min, the steady stirring method is used;
- when polymerization time = 67.5–135 min, the unsteady stirring method is used;
- when polymerization time = 135–270 min, the steady stirring method is used.

The agitation speed N is 300 rpm and the period time interval of the impeller coreverse rotating t' is 10 s.

In every experimental run, the variation of droplet size, final particle size, and final PSD are investigated and the results are shown in Figure 5 and Figure 6, respectively.

Effect on the Evolution of Droplet Sizes

From Figure 5 we can see the evolutions of droplet size are very different because of the unsteady stirring method used in the different stages of polymerization. For Run.1 and Run'.1, in which unsteady stirring was used at the beginning of polymerization, because the viscosities of the dispersed phase at that time were small, and the dispersions were dominated by droplet breakage (under the strong breakage function caused by the unsteady stirring of the impeller), the droplet sizes were smaller than those of Run.s, Run.2–Run.4, and Run'.2–Run'.4. Then, after converting

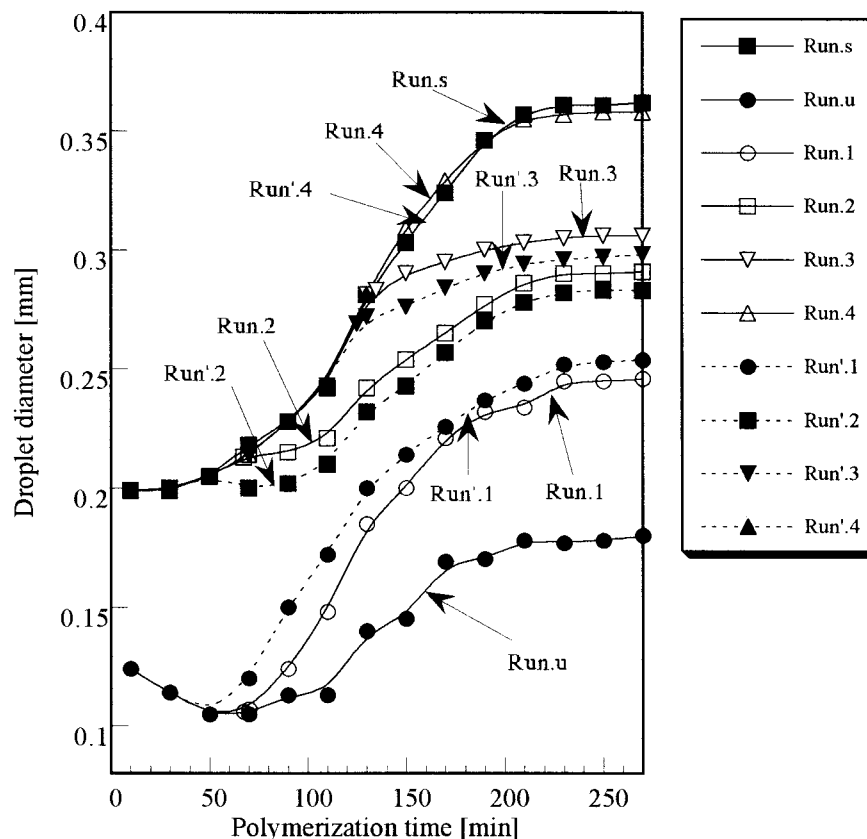


Figure 5 Evolutions of droplet size with polymerization time.

to the steady stirring method, the droplet sizes increase quickly, undergoing a maximum increasing point, then reaching the constant point. The final particles formed under these operations are relatively small (as shown in Fig. 6).

For Run.2 and Run'.2, before converting to the unsteady stirring method in the polymerization, the droplets were evolving for periods of time under steady stirring conditions, and the droplet sizes began to appear with an increasing tendency (as a result of the droplet coalescence function) to overcome the breakage function, allowing the droplets to increase in size. After converting to the unsteady stirring method, the droplet sizes appear either somewhat decreased (for Run'.2) or slowly increased (for Run.2). When converting to the steady stirring method again, the droplet sizes increase quickly and, over the PIP, reach a constant size.

For Run.3 and Run'.3, in which the unsteady stirring method is used in the time range in which only droplet coalescence occurs, we can see upon conversion to the unsteady stirring method in the polymerization reaction that the increasing drop-

let sizes during this period are not so obvious as those under the steady stirring condition, which shows that the droplet coalescence action is not strong. The final particle sizes are also smaller than those under steady stirring conditions.

For Run.4, in which unsteady stirring is used only at the last stage of polymerization, the droplet sizes at that range vary only slightly. For Run'.4, the drop variation is not affected by the unsteady stirring method because at that range the drop coalescence had been stopped. Thus from Figure 5 we conclude that the use of the unsteady stirring method leads to a strengthening of drop breakage and a weakening of the degree of coalescence; however, because the drop breakage and coalescence characteristics vary during the different stages of polymerization, the degree of effects of the unsteady stirring method also varies dramatically, thus causing variations in droplet size.

Effect on Final Particle Sizes and PSD

Figure 6 shows the variation of the final particle size d_p and particle size distribution with the

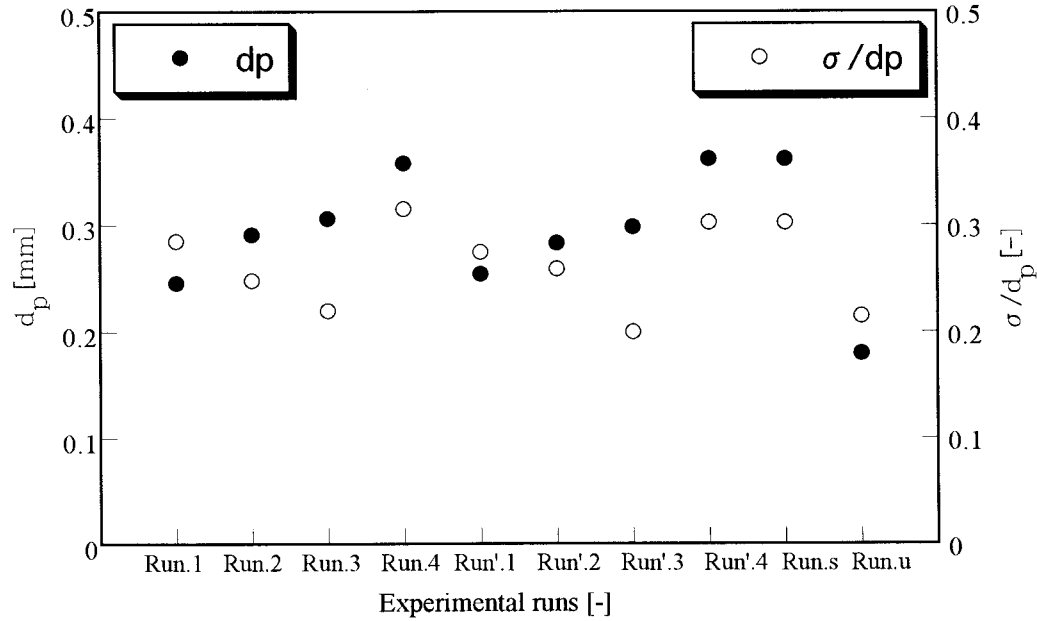


Figure 6 Final particle size and particle size distribution of different experimental runs.

unsteady stirring method used in the different polymerization stages, where d_p is the Sauter mean diameter and PSD is assessed by the ratio of the standard deviation to the mean diameter σ/d_p . This means that the smaller the value of σ/d_p , the higher the degree of particle size uniformity. The standard deviation was calculated by

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

In Figure 6 the d_p and PSD, obtained under the conditions of the steady and the unsteady stirring methods used in the whole polymerization process (expressed by using Run.s and Run.u, respectively), are also presented.

From Figure 6 we can see the final particle sizes and PSD are obviously different because the unsteady stirring method was used in the different polymerization stages. As to the particle size, the d_p of Run.1 is the smallest, the d_p of Run.4 is the largest, and all of the d_p , obtained under the unsteady stirring method staged conditions, are larger than that of the unsteady stirring condition (Run.u), but smaller than that of the steady stirring condition (Run.s). As to the particle size distribution, the PSD of Run'.3 is the most uniform (the σ/d_p of which is the smallest), the PSD of Run.3 is the next most uniform, and the PSD of

Run.4 is the worst. Thus the operation of Run'.3 is run under the optimum conditions to obtain a uniform PSD. By further analysis, three determinations can be obtained.

First, compared with Run.u we can see that, although the d_p of Run'.3 is much larger than that of Run.u, the PSD of Run'.3 is more uniform than that of Run.u, which shows (1) that the control of the drop coalescence process can efficiently improve the uniformity of PSD, and (2) that large as well as uniform final particle products can be obtained if the unsteady stirring method is used in the polymerization stage in which only the droplet coalescence occurs, instead of being used during the whole polymerization process.

Second, from Figure 7 which shows the droplet size distributions (DSD) and the PSD of Run.1, Run'.1, Run.3, and Run'.3, we can see at the initial polymerization stage (t is about 67.5 min) the DSD of Run.1 and Run'.1 are more uniform than the DSD of Run.3 and Run'.3, although at the end of polymerization, the PSD of Run.1 and Run'.1 become nonuniform, whereas the PSD of Run.3 and Run'.3 appear relatively more uniform than that of Run.1 and Run'.1. Although some researchers have concluded that the dispersion uniformity of the initial droplets plays an important role in determining the final PSD, and many techniques have been focused on improving the

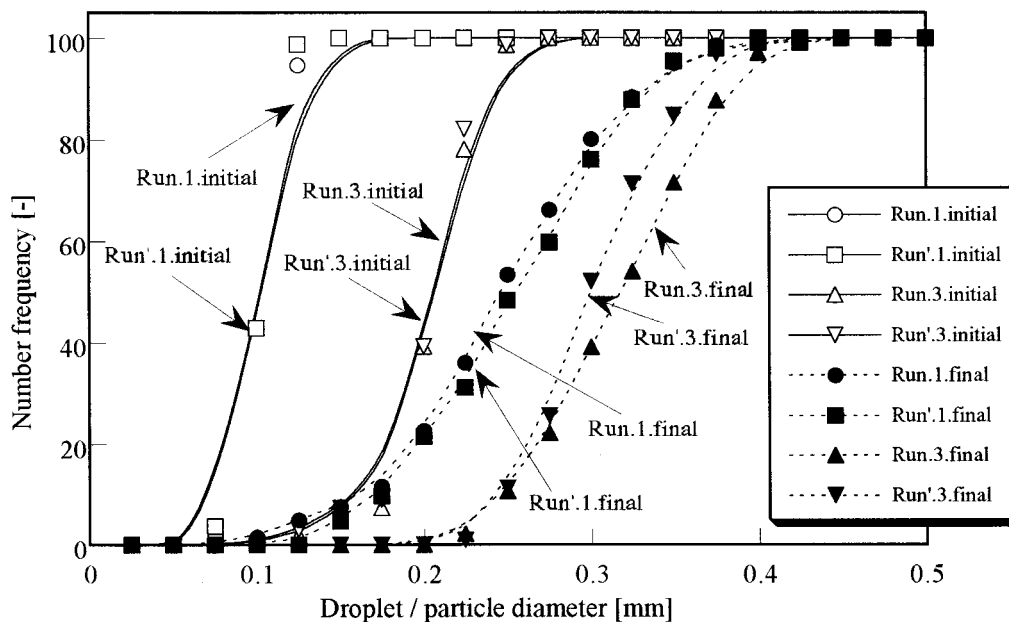


Figure 7 Drop size distribution and particle size distribution of Run.1, Run'.1, Run.3, and Run'.3.

initial droplet size uniformity,³ from the experimental results obtained here, we find that controlling the droplet coalescence processes is more important than controlling the dispersion uniformity of the initial droplets, to obtain uniform final particle size distribution.

Finally, from Figure 6, by comparing the two dividing methods [method (a): simply by polymerization time; method (b): by the characteristic conversions], we can see when the polymerization processes were divided by the characteristic conversions, thus obtaining the optimum operation (Run'.3). Therefore method (b) is better than method (a) to divide polymerization into stages to obtain uniform PSD, which is not difficult to understand because the stirring method affects both the droplet breakage and the coalescence characteristics. Thus dividing the polymerization process with regard to the differences of the breakage and coalescence characteristics should be reasonable.

CONCLUSIONS

1. By investigating the evolution of droplet size during styrene suspension polymerization, we find the variation of d_{32} during the whole polymerization process under the unsteady stirring condition is smaller than

that under the steady stirring condition, although the conversions at which the maximum increases of d_{32} appear (X_{c1} and X'_{c1}) and the PIPs appear (X_{c2} and X'_{c2}) are independent of the stirring method.

2. By investigating the unsteady stirring method staged, used in styrene suspension polymerization (with agitation speed of 300 rpm and period time interval of 10 s), we can see the evolution of droplet size, the final particle size, and PSD are affected dramatically as a result of the unsteady stirring method used in different stages of polymerization. The operation condition of Run'.3 is the optimum one to obtain not only uniform PSD but also relatively large particle size. By analysis of the droplet breakage and coalescence characteristics we find that controlling the droplet coalescence process is the most efficient way to improve PSD uniformity.

Concerning the unsteady stirring method staged, used in the suspension polymerization process, there are many other approaches that are worth trying, such as using different agitation speeds at the different stages, using this method in other suspension polymerization systems, and so forth. No matter what combination of agitation method and agitation speed is used, the use of the

unsteady agitation method will bring new results in the suspension polymerization products.

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