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SHORT COMMUNICATION

Agitation requirement for synthesis of micron-sized monodisperse polymer particles in soap-free polymerization method

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Abstract Single-stage polymerization recently proposed for producing micron-sized polymer particles in aqueous media by Gu, Inukai and Konno (2002) was carried out under the control of agitation with styrene monomer, an amphoteric initiator, 2,2′-azobis [*N*-(2-carboxyethyl)-2-methylpropionamidine] tetrahydrate and a pH buffer NH_3/NH_4Cl at a monomer concentration of 1.1 kmol/m^3 H_2O, an initiator concentration of 10 mol/m^3 H_2O and a buffer concentration of $[NH_3]=[NH_4Cl]=10$ mol/m^3 H_2O. In the polymerizations, impeller speed was ranged from 300 to 500 rpm to satisfy complete dispersion of the monomer phase and not to introduce the gas phase from the free surface. Polymerization experiments under steady agitation indicated that impeller speed was an important factor for size distribution of polymer particles. An increase in impeller speed promoted particle coagulation during the polymerization to enlarge the average size of polymer particles but widen the size distribution. To produce polymer particles with narrow size distribution, stepwise reduction in impeller speed was examined in the polymerization experiments. It was demonstrated that this method was more effective than the steady agitation. The impeller speed reduction could produce highly monodisperse particles with an average size of 2 μm and a coefficient of variation of size distributions of 2.2% that was much smaller than typical monodispersity criterion of 10%.

Keywords Soap-free polymerization · Stirring speed · Particle size distribution · Monodisperse · Polystyrene particles

Introduction

The development of techniques for producing micron-sized polymer particles has long been an important subject in the field of heterogeneous polymerization. Seeded growth techniques [1–4] and two-step swelling techniques [5] are typical methods developed in the past. These methods were successful and have been applied in industry. However, a drawback of the methods is the requirement of multistage polymerization. Dispersion polymerization that was more recently developed is another successful technique that enables single-stage polymerization with the use of hazardous solvents [6–8]. Furthermore, the existing techniques have a common problem: that is the use of considerable amounts of surfactants or stabilizers, which is undesirable from the points of product impurity and environmental restriction.

To meet the demand for the use of a nonhazardous solvent without any use of surfactants or stabilizers, the authors proposed a novel type of soap-free emulsion polymerization with an amphoteric initiator, 2,2′-azobis [*N*-(2-carboxyethyl)-2-methylpropionamidine] tetrahydrate [9–12]. Since polymer particles formed in the system have ionizable groups arising from the amphoteric initiator, the electric surface potential of the particles can be varied with

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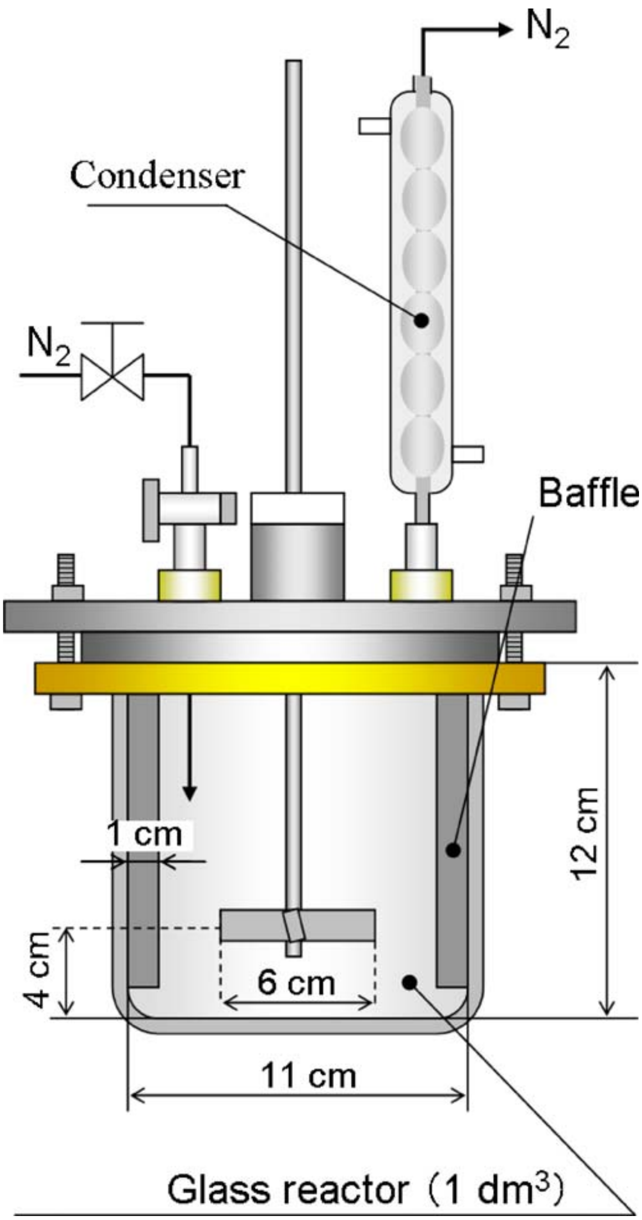


Fig. 1 Schematic diagram of reactor used for polymerization

pH, which controls the particles' coagulation, eventually affecting the final particle sizes. Previous reports verified that highly monodisperse, micron-sized polymer particles could be produced with this method in a single-stage polymerization of styrene at a fixed impeller speed of 300 rpm [9, 10, 12].

If sizes of particles in liquid are in the colloidal range (less than 100 nm), coagulation of the particles is mainly controlled by Brownian motion and scarcely depends on impeller speed. However, since sizes of particles produced with the present polymerization method attain micron meters, particle coagulation can be affected by impeller speed. The purpose of this work is to examine the effects of impeller speed on size distributions of polymer particles in the polymerization and find better control of agitation for producing monodisperse and large particles.

Experimental

All materials were special grades of Wako Pure Chemical Industry (Osaka, Japan). Styrene (99%, with 0.003% *p-t*-butyl catechol stabilizer) was distilled at reduced pressure under a nitrogen atmosphere after inhibitor removal. The initiator VA057 [$HOOC(CH_2)_2HN(HN{=})C(CH_3)_2CN{=}NC(CH_3)_2C({=}NH)NH(CH_2)_2COOH$], NH_3 (25% aqueous solution), and NH_4Cl (99%) were used without further purification. Water was deionized and distilled to have an electric resistance higher than 18 MΩ·cm.

Soap-free polymerizations were carried out in a batch reactor (11 cm inside diameter and 12 cm height) equipped with four baffles (1 cm in width) and a six-blade pitched paddle impeller (6 cm in diameter and 1 cm in width). Figure 1 shows a schematic diagram of the reactor used for the polymerization. The impeller was located at one-third of the liquid height from the bottom. Styrene, water, NH_3, and NH_4Cl were charged into the reactor, and deoxygenated by bubbling with nitrogen for 30 min under stirring. Then, the bubbling was stopped, and aqueous initiator solution was added to the reaction mixture to start polymerization. Concentrations of initiator and monomer were 1.1 $kmol/m^3H_2O$ and 10 mol/m^3H_2O, respectively. Both concentrations of NH_3 and NH_4Cl were 10 $mol/m^3 H_2O$ corresponding with pH=8.3. All runs were conducted at an initial volume of the reactants, 9×10^{-4} m^3, under nitrogen atmosphere at 65 °C. Impeller speed was set above

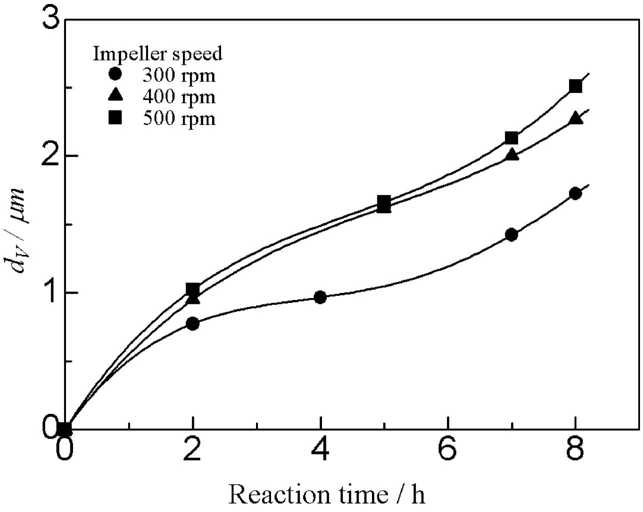


Fig. 2 Evolution of volume-averaged diameter during polymerizations at different impeller speeds

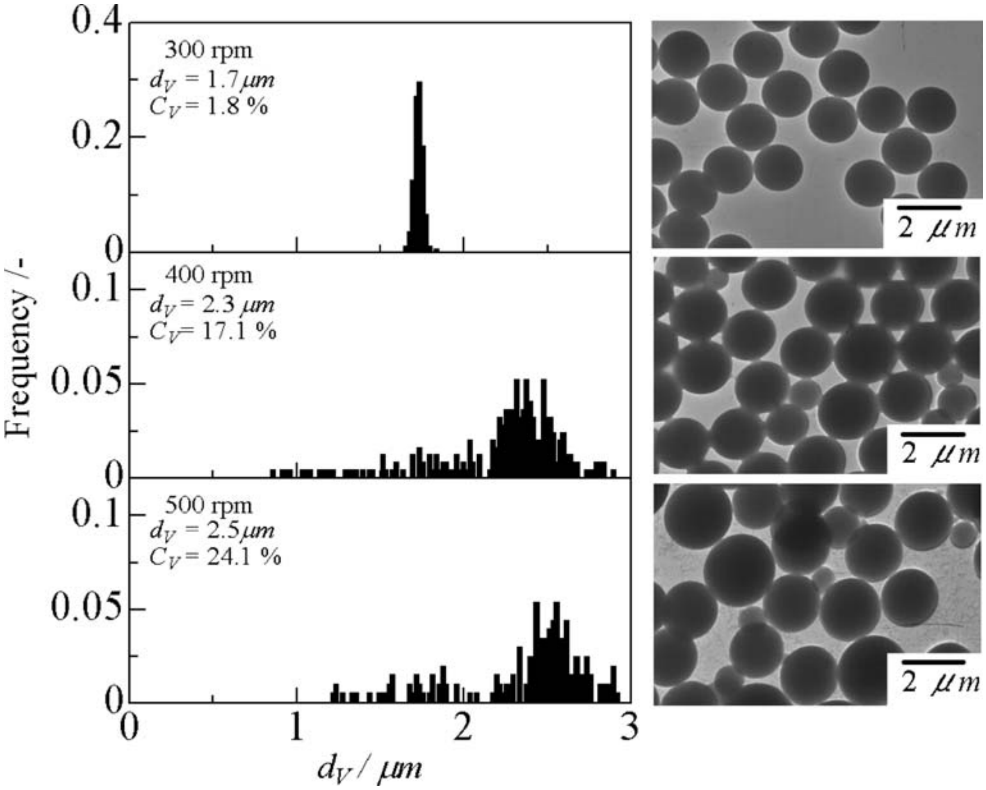


Fig. 3 Particle size distributions and micrographs of final particles at different impeller speeds

the minimum speed for complete liquid–liquid dispersion and below minimum speed for introduction of gas phase from the free surface. The minimum speed predicted from the correlation equation of Skelland and Ramsay [13] was 200 rpm, which was almost consistent with the observed result of 220 rpm.

During the polymerization, small amounts of reactant solutions (less than 2 cm^3) were withdrawn from the reactor to determine monomer-to-polymer conversion and particle size distributions. Hydroquinone was added to the solution to terminate the polymerization. Polymer yield was determined from the weight of polystyrene contained in the solution. More than two hundred particle diameters were measured with a transmission electron microscope (LEO 912 OMEGA) to determine particle size distribution, which was used to calculate the number-averaged diameter, d_n, the volume-averaged diameter, d_V, the standard deviation, σ, and the coefficient of variation of particle size distribution, C_V, defined as follows:

$$d_\mathrm{n} = \left(\sum n_i d_i \Big/ \sum n_i\right) \tag{1}$$

$$d_\mathrm{V} = \left(\sum n_i d_i^3 \Big/ \sum n_i\right)^{1/3} \tag{2}$$

$$\sigma = \left(\sum (d_i - d_\mathrm{n})^2 \Big/ \sum n_i\right)^{1/2} \tag{3}$$

$$C_\mathrm{V} = \frac{\sigma}{d_\mathrm{n}} \times 100 \tag{4}$$

where n_i is the number of particles with a diameter d_i.

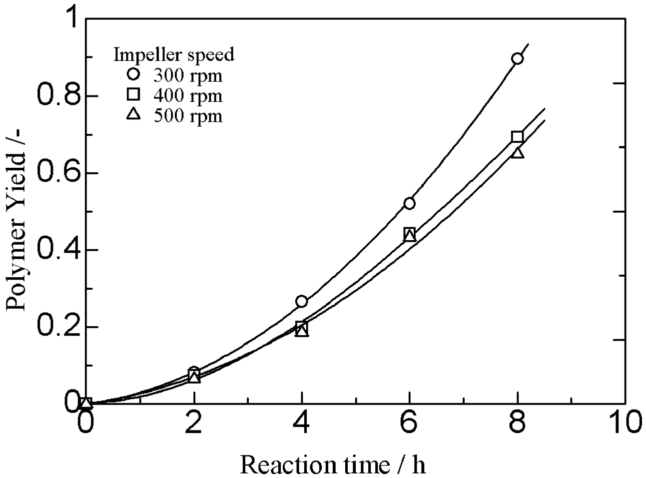


Fig. 4 Polymer yield during the polymerizations at different impeller speeds

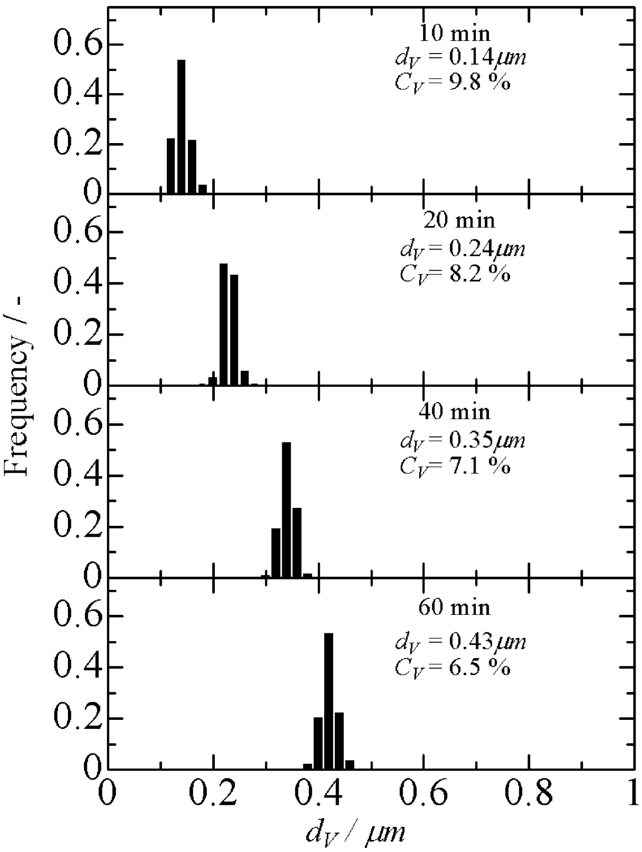


Fig. 5 Transient particle size distributions during polymerizations at an impeller speed of 300 rpm

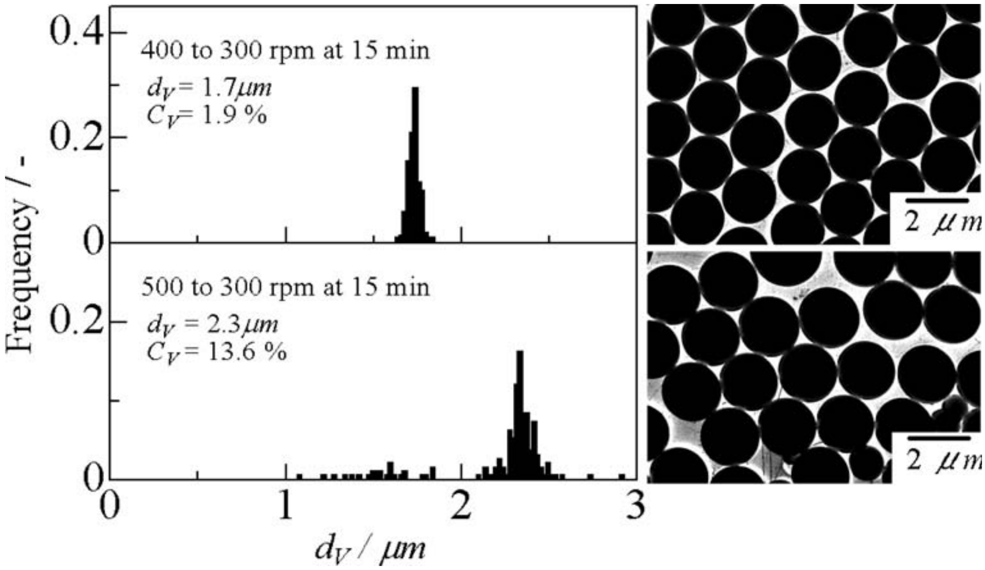
Result and discussion

In the initial stage of soap-free emulsion polymerizations of styrene, most of the styrene monomer disperses as droplets in water phase and a small part of the styrene dissolves in the water phase. Ionic radicals are generated from decomposition of initiator molecules, react with monomer in the water phase, and grow their chain length. Oligomers with long chains are thought to precipitate out of the water phase and coagulate to form polymer particles, which increase their sizes, absorbing monomer and radicals. Particle formation terminates when all oligomer radicals are caught, before precipitation, by existing polymer particles. The polymer particles have ionic surface groups and can be stabilized by an electric double layer.

Promotion of particle coagulation during the polymerization brings about the generation of large particles. An increase in impeller speed may promote particle coagulation. Figure 2 shows plots of d_V against reaction time at different impeller speeds of 300 to 500 rpm. An increase in impeller speed gave rise to a significant increase in the average diameter. The final value of d_V was increased with an increase in stirring speed, attaining a d_V value of 2.5 μm at 500 rpm. Figure 3 shows the size distributions and micrographs of final particles in the polymerizations. The distribution at 300 rpm was highly monodisperse, while the distributions at 400 and 500 rpm were quite broad. Polymer yields in the polymerizations are presented in Fig. 4. Polymer yields at 400 and 500 rpm were similar at each reaction time, but somewhat smaller than that at 300 rpm. In the polymerizations at 400 and 500 rpm adhesion of polymer to the reactor was observed in the late stage of the reaction, while no adhesion was observed in the polymerization at 300 rpm throughout the reaction.

The larger d_V at higher impeller speed in Fig. 2 implies that the number of polymer particles decreased with impeller speed. Ionic groups originating from the decomposition of initiator molecules accumulate on the particle

Fig. 6 Particle size distributions and micrographs of final particles in the experiments for stepwise reduction of impeller speed



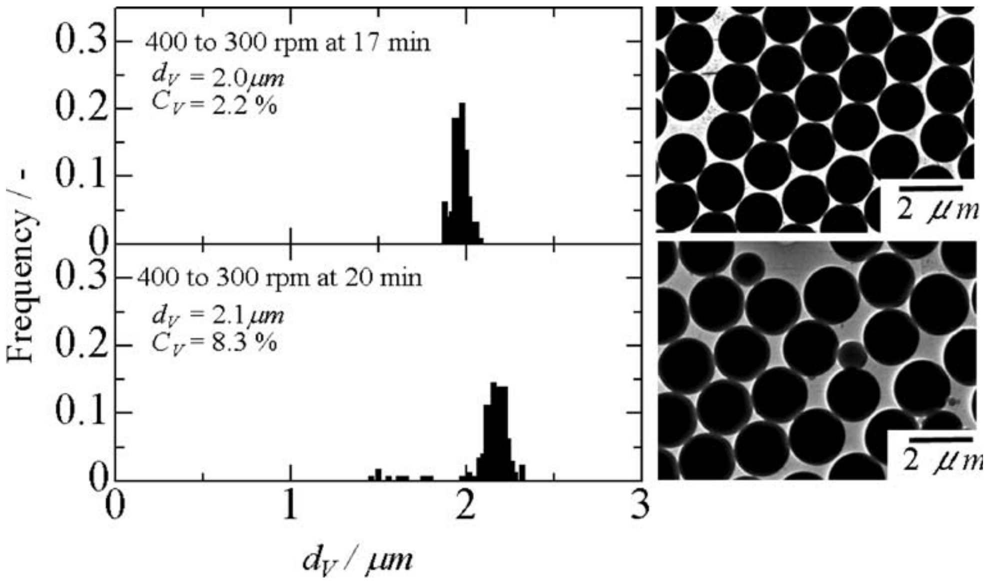


Fig. 7 Particle size distributions and micrographs of final particles in the experiments for stepwise reduction of impeller speed

surface with reaction time. Accordingly, the electric surface potential of the particles increases with time. Since the higher impeller speed promotes particle coagulation in the early reaction stage, a higher electric surface potential can take place at the higher impeller speed due to reduction in the total surface area of the particles. This might cause the successive generation of secondary particles, eventually broadening the size distribution of the particles. In addition, the generation of the secondary particles reduces the diffusion rate of the ionic radicals into the existing primary particles that have a major part of reaction loci. This can be considered to decrease the polymerization rate, appearing as the reduction in polymer yields in Fig. 4. It can also be considered that the surface potential of the primary particles decreased after the appearance of the secondary particles. Because the reduction of the diffusion rate of ionic radicals into the primary particles can decrease the charge density of the particle surface, the primary particles might adhere to the reactor surface and coagulate to further broaden their size distribution.

Figure 5 shows transient particle size distributions in the early stage of the polymerization at 300 rpm that brought about the highest monodispersity of distribution in Fig. 3. Figure 5 indicates that particles grew with reaction time, keeping a similar width of size distribution. The sizes of particles already exceeded 100 nm at the reaction time of 10 min. Therefore, the growth of particles may be changed if the impeller speed is changed after 10 min.

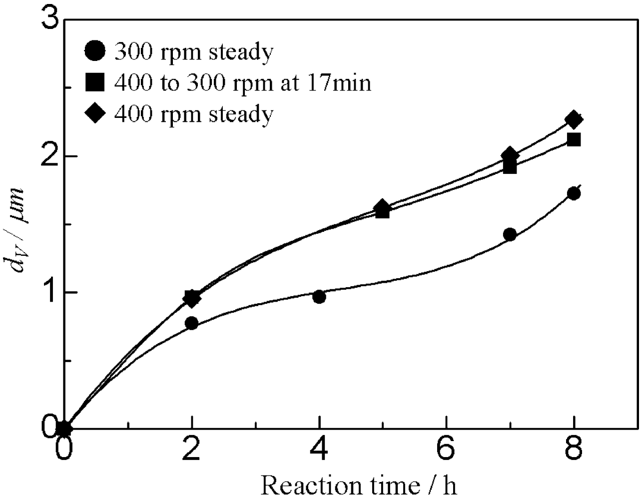


Fig. 8 Evolution of d_V during the polymerizations for the stepwise reduction of impeller speed from 400 to 300 rpm at 17 min (*squares*) and steady impeller speeds at 300 (*circles*) and 400 rpm (*diamonds*)

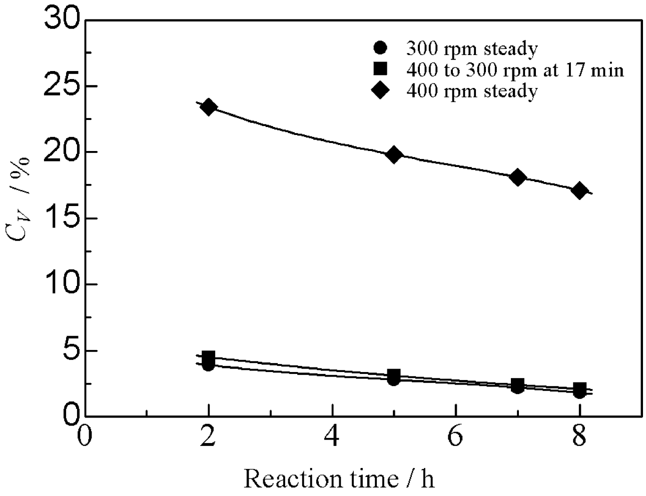


Fig. 9 Evolution of C_V during the polymerizations for the stepwise reduction of impeller speed

Figure 6 shows the size distributions and micrographs of final particles in polymerizations in which impeller speed was changed from 400 or 500 rpm to 300 rpm at 15 min. No significant difference was observed between the size distributions at the first impeller speed of 400 rpm in Fig. 6 and the steady impeller speed of 300 rpm in Fig. 3. On the other hand, a significant difference was observed between the size distributions at the first impeller speed of 500 rpm in Fig. 6 and the 300-rpm speed in Fig. 3. Raising the first impeller speed to 500 rpm increased d_V to 2.3 μm, generating a small amount of secondary particles, which increased C_V to 13.6%. However, it should be noted that, whereas the d_V at the first impeller speed of 500 rpm in Fig. 6 was the same as the one at the constant impeller speed of 400 rpm in Fig. 3, the C_V in the former case was considerably small compared with the latter case of the constant impeller speed. Thus, the impeller speed change brought about the favorable result to the distribution.

Figure 7 shows the size distributions and micrographs of final particles in polymerizations in which the impeller speed was changed from 400 to 300 rpm at reaction times that were little bit later. The impeller speed change at 20 min generated secondary particles so that the C_V value of the distribution was larger than the one for the impeller speed change at 17 min.

In Figs. 8 and 9, the d_V and the C_V for this change at 17 min are compared with those obtained at the steady speeds of 300 and 400 rpm. Interestingly, the impeller speed reduction enlarged the d_V to the level for the steady speed of 400 rpm but lowered the C_V to the level for the steady speed of 300 rpm. Thus, the impeller speed change in the very early stage of the polymerization was effective to adjust the size distribution with large d_V and small C_V.

Conclusion

Polymerization experiments at steady impeller speeds indicated that impeller speed was an important factor for controlling particle size distribution. Although the average size of final particles was enlarged under the steady agitation of high impeller speed, the C_V value of the size distribution was increased. Stepwise reduction in impeller speed was examined as another choice for the polymerization. It was demonstrated that the impeller speed reduction was more effective than the steady agitation in order to produce large particles with narrow size distribution.

Notation

C_V	Coefficient of variation of particle sizes (%)
d_i	Diameter of polymer particle (m)
d_n	Number-averaged diameter of polymer particle (m)
d_V	Volume-averaged diameter of polymer particle (m)
n_I	Number of particles (−)
σ	Standard derivation of particle sizes (m)

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