Suspension Polymerization of Styrene with Circular Loop Reactor

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Synopsis

A circular loop reactor was devised and applied to the suspension polymerization of styrene. The transient droplet diameter distribution and the final particle size distribution are measured by changing widely the impeller speed, the dispersed phase volume fraction, and the stabilizer concentration. The effects of these conditions on the size distribution and mean size of the final polymer particle are investigated. An expression correlating the mean particle size with the operating conditions is derived. The circular loop reactor is found to be superior to the production of the polymer particle of uniform size.

INTRODUCTION

In the practical operation of suspension polymerization, the most important issue is how to control the mean size and the size distribution of the final polymer beads. Namely, it is strongly required to produce the polymer particles of the desired and uniform size.

Until now, a number of investigations have been performed to improve the degree of the uniformity of the polymer particle sizes. These works may be substantially classified by the methods adopted as follows.

(i) Method by utilizing the stabilizing effect of inorganic and polymeric chemical species for the suspension polymerization system.[1-4]

(ii) Method by forming the monomer droplets of uniform diameter at the beginning of polymerization.[5-8]

(iii) Method by utilizing the effects of geometry of the reactor.[9-12]

The first method is based on controlling coalescence and breakup of the polymer droplets in the course of polymerization by an addition of many kinds of chemical species because the size distribution and mean size of the final polymer particles are determined as a result of coalescence and breakup of the polymer droplets.

The second method is based on completing polymerization in individual droplets which have the uniform diameter and no experience of coalescence and breakup throughout the polymerization process.

The third method is based on controlling such dispersing behavior of the polymer droplets as coalescence and breakup due to the modification of geometry of the reactor.

At all events, the methods described above are ascribable to how to pertinently control coalescence and breakup of the polymer droplets in the course of polymerization.

The present authors devised the loop reactor, which was constructed from four straight pipes and three elbows connecting the pipes, and applied this reactor to suspension polymerization of styrene.[12] However, the data obtained are not practical, because they used only the dispersed phase volume fraction of 0.1. Moreover, the large pressure drop was found to take place at the elbow and to affect dispersing behavior of the polymer droplets.[13]

And so, the present authors devised a circular loop reactor without any elbows and tried to apply this reactor to suspension polymerization of styrene by changing widely the operating conditions. The advantages of the loop reactor were described in the previous paper.[12]

The purpose of this paper is to investigate the effects of such operating conditions as the dispersed phase volume fraction, the impeller speed, and the stabilizer concentration on the size distribution and mean sizes of the final polymer particles and to compare the results with those obtained in the conventional stirred tank reactor.

EXPERIMENTAL

Apparatus and Procedure

Figure 1 shows the schematic diagram of experimental apparatus. The circular loop reactor consists of two parts of the semicircular glass pipe, the inner diameter of which is 5×10^{-2} m. The essential volume of the reactor is 2.3×10^{-3} m^3. The impeller is three pitched (45°) blade paddle impeller, the diameter of which is 3.2×10^{-2} m. The details of the impeller are also shown in Figure 1.

The reactor was filled with the predetermined volume of the continuous phase, in which the given concentrations of stabilizer and substabilizer were dissolved. In order to keep the reaction temperature at 70°C, the reactor was immersed into the thermostated water bath. Then, the continuous phase water was bubbled with N$_2$ gas under an agitation at the predetermined impeller speed.
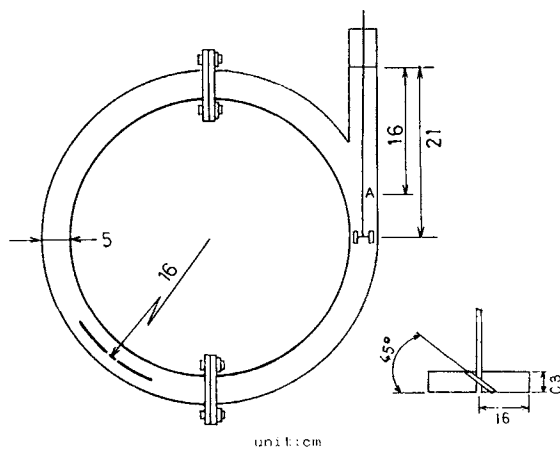

unit : cm

Fig. 1. Schematic diagram of experimental apparatus.

The inhibitor for polymerization dissolving in styrene monomer was removed by contacting three times with sodium hydroxide aqueous solution of a concentration of 1.0 kmol m^{-3}. After this, the styrene monomer of predetermined volume dissolving the initiator for polymerization was poured into the reactor, and then polymerization was started. At constant time intervals from the beginning of polymerization, a portion of the reaction mixture was drawn off with a glass pipet from a point (A point) as shown in Figure 1. The sampled droplets were transferred to a laboratory dish containing 1.0 wt % aqueous solution of poly(vinyl alcohol) (the number average degree of polymerization, 500) to prevent the droplets from coalescing. Photographs of these droplets were taken, and from these the transient droplet diameter distribution and mean diameter were measured. Here, the mean diameter is the Sauter mean diameter. The operation as described above was performed by changing the impeller speed, the dispersed phase volume fraction, and the stabilizer concentration.

Experimental Conditions

The experimental conditions adopted here are as follows:
continuous phase: ion-exchanged water
dispersed phase: styrene monomer
dispersed phase volume fraction ϕ: 0.1–0.5
initiator for polymerization: benzoyl peroxide
    (concentration: 1.0×10^{-1} kg mol m^{-3} for styrene)
stabilizer: calcium tertiary phosphate
stabilizer concentration C_T: 0.25–0.6 wt % for continuous
    phase water
substabilizer: sodium dodecylbenzenesulfonate
    (concentration: 30 ppm for continuous phase water)
impeller speed N_T: 15–50 s^{-1} (rps)
reaction temperature: 70°C

RESULTS AND DISCUSSION

Transient Droplet Diameter Distribution

Figure 2 shows the transient droplet diameter distributions (cumulative volume fraction) measured by changing the impeller speed under the dispersed phase volume fraction of $\phi = 0.3$ and the stabilizer concentration of $C_T = 0.3$ wt %. From this figure, the distributions are found to shift toward the large diameter with the reaction time t (min). This means that the polymer droplets coalesce with each other to grow in the course of polymerization. Also, at the high impeller speed, a more remarkable shift of the diameter distribution is observed after the middle stage than from the early stage to the middle stage of polymerization. This may be considered as follows. As the smaller droplets are formed at the beginning of polymerization with increasing the impeller speed, the suspension may be kept comparatively stable to the middle stage of polymerization. After the middle stage of polymerization, where the viscosity of the polymer droplet phase increases extremely, the higher the impeller speed increases, the more frequent coalescence between the polymer droplets
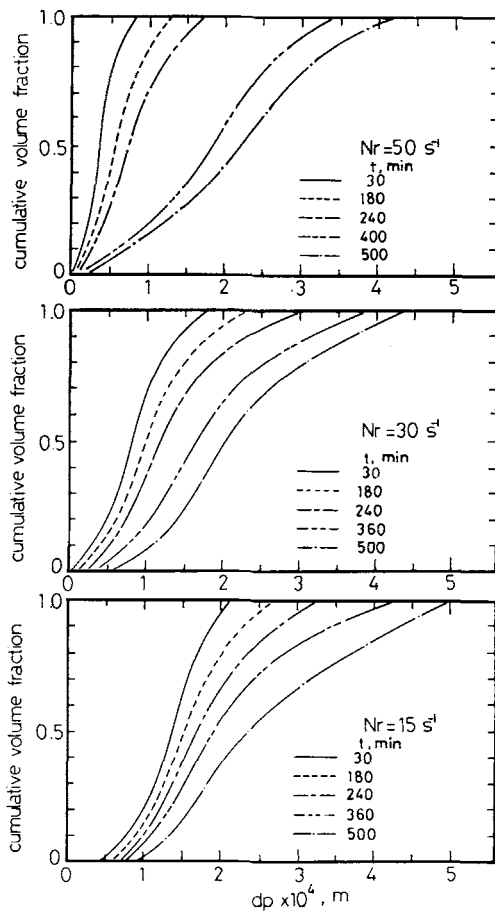
Fig. 2. Transient droplet diameter distribution measured by changing impeller speed.

becomes. Accordingly, the shift of the diameter distribution may become remarkable.

Figure 3 shows the transient droplet diameter distributions measured by changing the dispersed phase volume fraction under the impeller speed of $N_r = 20 \text{ s}^{-1}$ and the stabilizer concentration of $C_T = 0.3$ wt %. The higher the dispersed phase volume fraction becomes, the more remarkable the distributions shift toward the large diameter. This is considered to be attributable to the reason why coalescence between droplets becomes vigorous with increasing the dispersed phase volume fraction, in other words, the droplet number concentration.

Figure 4 shows the transient droplet diameter distributions measured by changing the stabilizer concentration under the impeller speed of $N_r = 20 \text{ s}^{-1}$ and the dispersed phase volume fraction of $\phi = 0.3$. As the stabilizer concentration increases, the degree of the shift of the distribution toward the large diameter becomes smaller, namely, the stabilizing effect increases. At the stabilizer concentration of $C_T = 0.6$ wt %, no shift of the diameter distribution is almost observed.
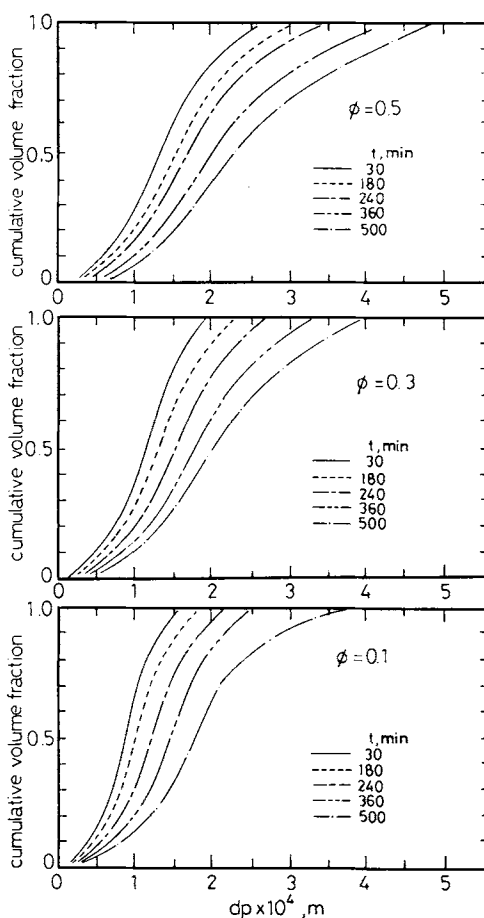
Fig. 3. Transient droplet diameter distribution measured by changing dispersed phase volume fraction.

Transient Mean Droplet Diameter

Figure 5 shows the transient mean droplet diameters measured by changing the impeller speed, the dispersed phase volume fraction, and the stabilizing concentration.

With respect to the effect of the impeller speed, the mean diameters continue to keep nearly constant in the early stage of polymerization and then start to grow due to coalescence. Conversion (reaction time), at which the mean diameters start to increase, becomes higher with the impeller speed. Also, the mean diameter at the beginning of polymerization becomes smaller with increasing the impeller speed, but the mean diameter at the late stage of polymerization becomes minimal under an agitation of the middle impeller speed. This result is considered to be attributable to the fact that coalescence and breakup of the polymer droplet are controlled by the impeller speed, the physical properties of liquids concerned, and the mean diameter at that conversion.[1]
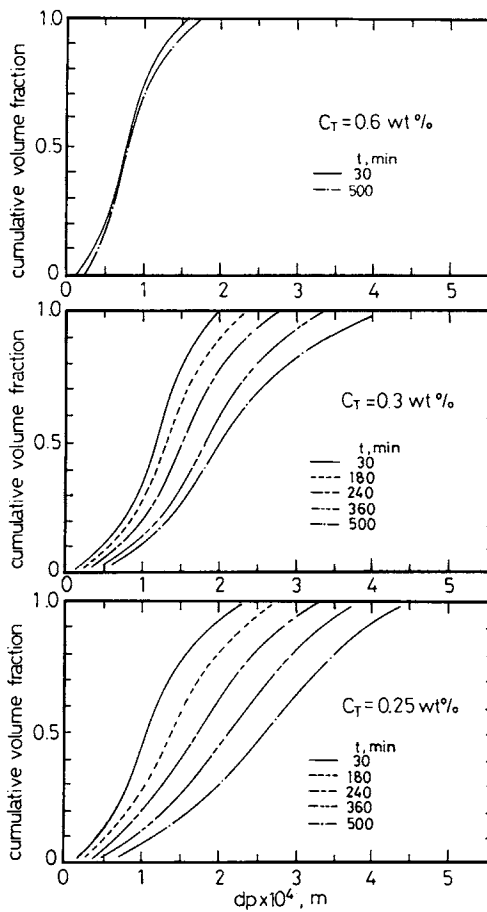
Fig. 4. Transient droplet diameter distribution measured by changing stabilizer concentration.

With respect to the effect of the dispersed phase volume fraction, the transient mean diameters show the same features as those measured by changing the impeller speed and the degree of growth of the droplets due to coalescence becomes remarkable with increasing the dispersed phase volume fraction. With respect to the effect of the stabilizer concentration, at the concentration of $C_T \geq 0.4$ wt %, the mean diameters continue to keep constant.

In the conventional stirred tank reactor, Konno et al.[3] and Hirose and O'shima[14] observed the shift of the diameter distributions and the growth of the polymer droplet according to such operating conditions as the impeller speed, the dispersed phase volume fraction, and the stabilizer concentration.

Accordingly, the transient features of the diameter distributions and mean diameters of the droplets in the circular loop reactor are found to be almost similar to those in the conventional stirred tank reactor.

Transient Dispersity

Figure 6 shows the dependencies of the transient dispersities on the impeller speed, the dispersed phase volume fraction, and the stabilizer concentration.
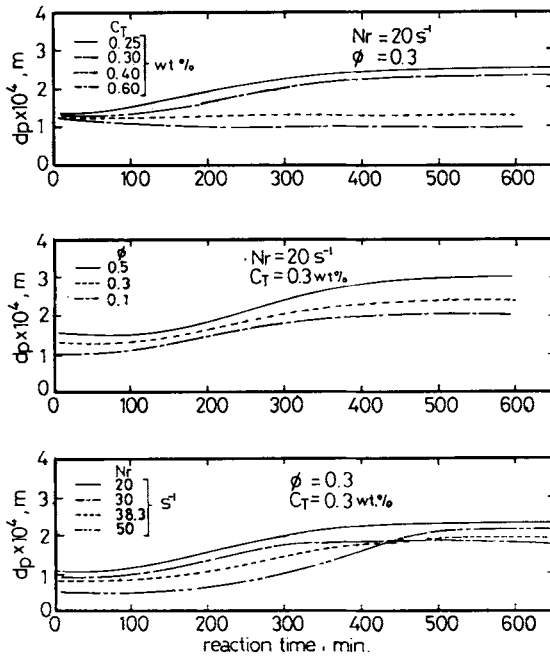
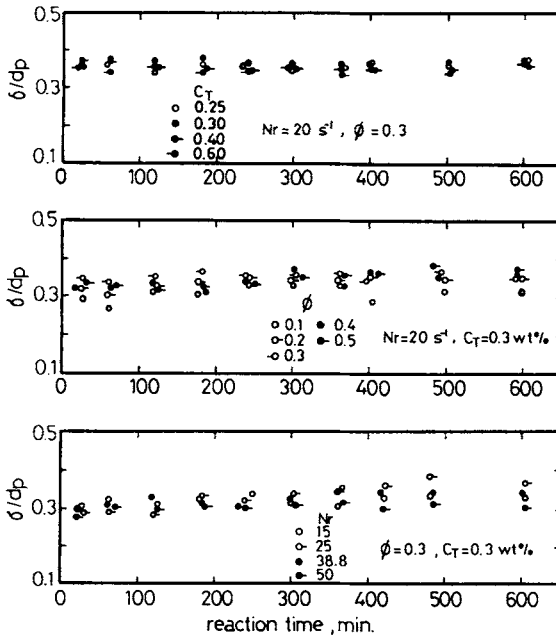Fig. 5.   Transient mean droplet diameter.

Fig. 6.   Transient dispersity.

TABLE I
Comparison of Dispersity between Circular
Loop Reactor and Stirred Tank Reactor

Circular loop reactor					Stirred tank reactor			
N_r	ϕ	C_T	σ/d_p		N_r	ϕ	C_T	σ/d_p
20	0.5	0.3	0.19		4.2	0.5	0.3	0.55
25	0.5	0.3	0.18		5.0	0.5	0.3	0.6
30	0.5	0.3	0.20		6.0	0.5	0.3	0.62
40	0.5	0.3	0.21		7.5	0.5	0.3	0.65
50	0.5	0.3	0.24		8.2	0.5	0.3	0.66

Here, the dispersity is used to elucidate the degree of the uniformity of the droplet diameters and is defined as the ratio of the standard deviation to the mean diameter, σ/d_p. This means that the smaller the value of the dispersity, the higher the degree of the uniformity of the droplet diameter.[12]

With respect to the effect of the impeller speed, the dispersity continues to be ca. 0.3 irrespective of the impeller speed. This is considered to be attributable to the reason why the degree of growth of the droplet due to coalescence becomes equal to that of broadening of the diameter distribution. However, after the middle stage of polymerization, the dispersity increases slightly under an agitation of the middle impeller speeds. This may be considered to be attributable to the fact that the mean diameters at the late stage of polymerization become smaller at middle impeller speeds than at lower and higher impeller speeds, as seen from Figure 5. The value of the dispersity is largely affected by the change in mean diameter.

With respect to the effect of the dispersed phase volume fraction, the dispersity increases slightly in the range from 0.26 to 0.4. Also, the dispersity shows a trend to become smaller at the lower dispersed phase volume fraction, but this trend is not systematic. With respect to the effect of the stabilizer concentration, the dispersity shows a trend to become smaller at the higher stabilizer concentration.

Table I shows the comparison of the final dispersities with those obtained by using the same polymerization system in the conventional stirred tank reactor. From Table I, the circular loop reactor is found to be superior to the production of the polymer particle of more uniform size. This is considered as follows. In the loop reactor, such dispersing behavior of the polymer droplets as coalescence and breakup can be unified in comparison with the conventional stirred tank reactor; in other words, the numbers of coalescence and breakup of which individual droplets have experience can be averaged.[12] This must repress broadening of the size distribution. However, investigations over extensive experimental conditions must be made to discuss more precisely the superiority of the loop reactor.

Critical Coverage of Stabilizer

As shown in Figures 4 and 5, at a certain concentration of the stabilizer, no diameter distributions shift toward the large diameter and no polymer droplets grow. This must mean that there is a critical concentration of the stabilizer at which no coalescence between the polymer droplets occurs.
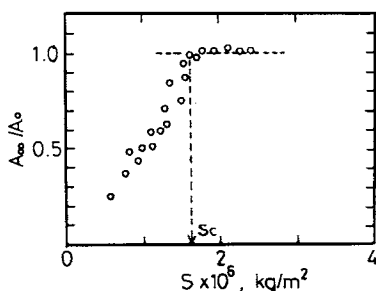
Fig. 7. Critical surface coverage.

So, in order to estimate the critical concentration or the critical surface coverage of the stabilizer used here, the following manipulation is performed. First, the surface coverage S is calculated from the initial mean droplet diameter and the stabilizer concentration by assuming that all powders of the stabilizer added adhere on the surface of the droplets. Then, at each surface coverage calculated thus, the initial and the final surface areas per unit volume, A_0 and A_∞, are calculated. Second, how the ratio of two surface areas, A_0/A_∞ changes according to the surface coverage is investigated for all the results obtained.

Figure 7 shows how the ratio changes according to the surface coverage. In this figure, the value of the ratio smaller than unity means that at the given surface coverage the droplets coalesce to grow in the course of polymerization. Accordingly, the surface coverage, by which the values of the ratios come to unity, must be the critical surface coverage S_c. From Figure 7, the critical surface coverage is found to be ca. 1.6×10^{-6} kg m^{-2}. The critical surface coverage and concentration, S_c and C_{Tc}, and the mean droplet diameter can be correlated as

$$C_{Tc} = \frac{6\phi}{(1-\phi)d_p}S_c \tag{1}$$

From eq. (1), the critical concentration of the stabilizer at each dispersed phase volume fraction and droplet diameter can be calculated.

Leng and Quarderer[15] performed suspension polymerization of styrene by use of poly(vinyl alcohol) as stabilizer in the conventional stirred tank reactor and reported that $S_c = 8 \times 10^3$ m^2/kg for the critical surface coverage.

It should be noticed that the critical surface coverage of the stabilizer is different according to the reaction temperature and the substabilizer concentration, etc.

Correlation of Final Mean Particle Sizes with Operating Conditions

Figure 8 shows the dependence of the final mean particle size on the impeller speed. With increasing the impeller speed, the final mean particle sizes first decrease, become minimal at the impeller speed of ca. $N_r = 30$ s^{-1},
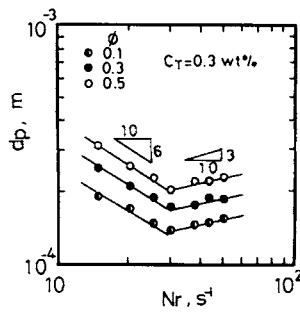
Fig. 8. Dependence of final mean particle size on impeller speed.

and then increase. This dependence can be expressed as follows:

$$\ln d_p = \ln A + a \ln N_r \tag{2}$$

$$a = -0.6 \quad \text{at} \quad 15 \leq N_r < 30 \text{ s}^{-1}$$

$$a = 0.3 \quad \text{at} \quad 30 < N_r \leq 50 \text{ s}^{-1}$$

The positive dependence on the impeller speed is considered to be attributable to the reason why coalescence between the polymer droplets extremely prevails over breakup at the impeller speed larger than some critical impeller speed in the late stage of polymerization.

In the conventional stirred tank reactor, in general, the dependence of the mean size on the impeller speed is reported to be between -0.3 and -3.3, according to the experimental conditions and the polymerization system.[16-19] Moreover, the positive dependence has been also observed in the conventional stirred tank, where the value of a was 0.70 at $N_r > 23$ s^{-1}.[20] In this case, however, most polymer particles were found to include a number of tiny bubbles which were entrained from the free liquid surface by the high impeller speed. Accordingly, these polymer particles are considered to become large as a result of inclusion of bubbles. In contrast with this, no polymer particles formed in the circular loop reactor include any bubbles. This is considered to be the reason why the air is scarcely entrained owing to the narrow free liquid surface. This must be the structural characteristic of the circular loop reactor.

Langner et al.[19] reported that the dependence of the mean size on the impeller speed changed from $a = -3.3$ at $N_r < 5$ s^{-1} to $a = -0.3$ at $N_r > 7.5$ s^{-1}, where they performed suspension polymerization of styrene in the conventional stirred tank reactor. For this reason, they explained it to be attributable to the fact that the balance between coalescence and breakup varied due to the change in physical properties of liquids and the impeller speed.

Figure 9 shows the dependence of the final mean particle size on the dispersed phase volume fraction. The dependence can be expressed as

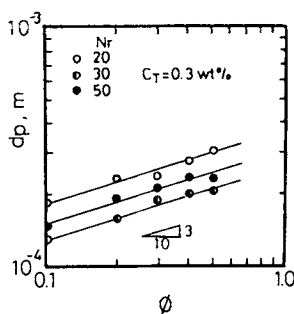$$\ln d_p = \ln B + b \ln \phi \tag{3}$$

$$b = 0.3$$

Fig. 9. Dependence of final mean particle size on dispersed phase volume fraction.

Moritz et al.[21] reported that the dependence of the mean size on the dispersed phase volume fraction changed from 0.21 to 0.40 according to the stabilizer concentration, where they investigated by use of a nonpolymerizing two-phase system in the conventional stirred tank reactor. There are no comparable data obtained in the stirred tank with respect to the dependence on the dispersed phase volume fraction.

Figure 10 shows the dependence of the final mean size on the stabilizer concentration. The dependence can be expressed as

$$\ln d_p = \ln C + c \ln C_T \tag{4}$$

$$c = -1.0$$

In general, as the effect of polymeric stabilizer on the particle size is mainly based on the change in interfacial tension, the dependence on the interfacial tension has been investigated. However, the inorganic powder stabilizes the suspension due to the protective layer formed on the droplet surface. Accordingly, as the results obtained here cannot be compared with other results, eq. (4) is used to elucidate the effect of the stabilizer as it is. From eqs. (2)–(4), eq. (5) can be derived by use of the least squares method:

$$\ln d_p = \ln A' + a \ln N_r + 0.3 \ln \phi - 1.0 \ln C_T \tag{5}$$

$$A' = 6.5 \times 10^{-3}, \quad a = -0.6 \quad \text{at} \quad 15 \leqq N_r < 30 \, \text{s}^{-1}$$

$$A' = 9.8 \times 10^{-3}, \quad a = 0.3 \quad \text{at} \quad 30 < N_r \leqq 50 \, \text{s}^{-1}$$
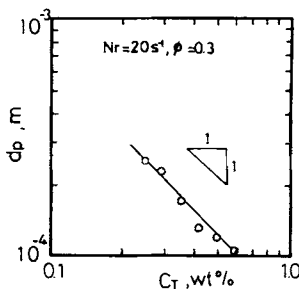

Fig. 10. Dependence of final mean particle size on stabilizer concentration.

Hopff et al.[16] derived an expression similar to eq. (5) for the results obtained in the conventional stirred tank reactor, where they assumed that no coalescence between the polymer droplets occurred in the course of polymerization.

CONCLUSION

A circular loop reactor was applied to suspension polymerization of styrene. The effects of the operating conditions, the impeller speed, the dispersed phase volume fraction, and the stabilizer concentration on the polymer particle size were investigated. An expression correlating the mean size of the polymer particle with the operating conditions was derived.

$$\ln d_p = \ln A' + a \ln N_r + 0.3 \ln \phi - 1.0 \ln C_T$$

$$A' = 6.5 \times 10^{-3}, \qquad a = -0.6 \quad \text{at} \quad 15 \leq N_r < 30 \, \text{s}^{-1}$$

$$A' = 9.8 \times 10^{-3}, \qquad a = 0.3 \quad \text{at} \quad 30 < N_r \leq 50 \, \text{s}^{-1}$$

References

1. E. O'shima and M. Tanaka, *Kagaku Kogaku Ronbunshu*, **8**, 188 (1982).
2. M. Tanaka and E. O'shima, *Kagaku Kogaku Ronbunshu*, **8**, 734 (1982).
3. M. Konno, K. Arai, and S. Saito, *J. Chem. Eng. Jpn.*, **15**, 131 (1982).
4. M. Tanaka and T. Morishima, *Kagaku Kogaku Ronbunshu*, **12**, 231 (1986).
5. A. C. Edward, U.S. Patent, 57-102905 (1982).
6. H. Kato, K. Uhisa and H. Morikawa, Jpn. Pat. 58-91701 (1983).
7. H. Noguchi, S. Noda, and H. Baba, Jpn. Pat. 59-30801 (1984).
8. H. Noguchi, T. Morishita and H. Baba, Jpn. Pat. 61-115902 (1986).
9. M. Tanaka and E. O'shima, *Kagaku Kogaku Ronbunshu*, **9**, 72 (1983).
10. M. Tanaka and E. O'shima, *Kagaku Kogaku Ronbunshu*, **11**, 376 (1985).
11. M. Tanaka and T. Izumi, *J. Chem. Eng. Jpn.*, **18**, 354 (1985).
12. M. Tanaka and E. O'shima, *Can. J. Chem. Eng.*, **66**, 29 (1988).
13. Y. Sato, Y. Murakami, T. Hirose, Y. Hashiguchi, S. Ono, and M. Ichikawa, *J. Chem. Eng. Jpn.*, **12**, 448 (1979).
14. M. Hirose and E. O'shima, *Kagaku Kogaku*, **34**, 181 (1970).
15. D. E. Leng and G. J. Quarderer, *Chem. Eng. Sci.*, **14**, 177 (1982).
16. H. Hopff, H. Lussi, and P. Gerspacher, *Makromol. Chem.*, **78**, 37 (1964).
17. H. Hopff, H. Lussi, and E. Hammer, *Makromol. Chem.*, **84**, 274 (1965).
18. H. Hopff, H. Lussi, and E. Hammer, *Makromol. Chem.*, **84**, 282 (1965).
19. F. Langner, H. U. Moritz, and K. H. Reichert, *Ger. Chem. Eng.*, **2**, 329 (1979).
20. M. Tanaka, S. Hasegawa, and E. O'shima, *Kagaku Kogaku Ronbunshu*, **13**, 693 (1987).
21. H. U. Moritz, F. Langner, and K. H. Reichert, *Ger. Chem. Eng.*, **2**, 112 (1979).