

Effect of Stirring on the Emulsion Polymerization of Styrene

MAMORU NOMURA, MAKOTO HARADA,* WATARU EGUCHI,*
and SHINJI NAGATA, *Department of Chemical Engineering, Kyoto
University, Kyoto, Japan*

Synopsis

The purpose of this paper is to clarify the effect of stirring on the course of emulsion polymerization of, for example, styrene. It establishes the existence of an optimum range of stirring speed and three important factors which must be considered in carrying out emulsion polymerization. (1) Stirring significantly affects the course of reaction in the presence of an imperfectly purified nitrogen atmosphere. Consequently, the number of polymer particles produced and the polymerization rate per particle will be affected. (2) At higher stirring speeds, polymer particles coagulate and coalesce. At lower stirring speeds, the reaction rate is controlled by the monomer transport rate from monomer droplets to the aqueous phase. (3) Stirring contributes to the reduction of the number of micelles because emulsifier molecules are adsorbed onto the surfaces of monomer droplets finely dispersed by the stirring. At low emulsifier concentrations near the critical micelle concentration, this effect cannot be neglected.

INTRODUCTION

Stirred tank reactors are widely used for emulsion polymerization on an industrial scale. It is often observed that the reaction rate and the quality of the polymer produced are affected by the stirring conditions, but as this effect is very complicated, it has not been well understood. Therefore, from the standpoint of reactor design and reactor scale-up, it is very important to know what kind and degree of stirring is required for emulsion polymerization.

Shunmukham¹ studied the effect of stirring on the emulsion polymerization of styrene and concluded that violent agitation diminished the polymerization rate. Schoot² criticized Shunmukham's results because the agitation effects that he observed might have been due to traces of oxygen contained in the nitrogen atmosphere under which the reaction was carried out. Evans et al.³ reported that the emulsion polymerization of vinylidene chloride was influenced by stirring from the very beginning of the reaction, and they suggested two factors to explain their results. The first was the effect on the reduction of the emulsifier effective for the formation of polymer particles caused by the adsorption of emulsifier molecules onto mono-

* Present address: Engineering Research Institute, Kyoto University, Uji, Japan.

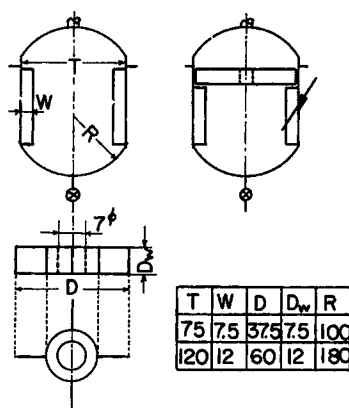


Fig. 1. Details of the reaction vessel and impeller.

mer droplets finely dispersed by stirring. The other was the effect upon monomer transport from monomer droplets to polymer particles.

However, Omi et al.⁴ came to the contrary conclusion that emulsion polymerization of styrene was not affected by stirring, as long as emulsification conditions were the same. They considered that stirring influenced the reaction only through the first of the above factors suggested by Evans.

As mentioned above, their conclusions were derived only from observations of the reaction rate without determining other physical factors which would ensure that their conclusions are correct. Their conclusions appear to be inconsistent with each other. Further research is therefore required to clarify the effect of stirring.

The purpose of this report is to illustrate the effects of stirring in more detail by showing how agitation affects emulsion polymerization, what steps of the reaction are affected by stirring, and whether a suitable range of agitation exists in emulsion polymerization.

EXPERIMENTAL

Emulsion polymerization of styrene was carried out using sodium lauryl sulfate as emulsifier and potassium persulfate as initiator. The materials used were purified in the same way as described in the previous paper.⁵ The reactor used was a cylindrical glass vessel with a dished bottom, fitted with four baffle plates located at 90° intervals and a four-bladed turbine-type impeller. When required, a float on the surface of the reaction mixture was used to prevent surface aeration. The reactors used were 75 mm and 120 mm in diameter and were geometrically similar. The dimensions are shown in Figure 1, and the schematic diagram of the experimental apparatus is shown in Figure 2. The liquid depth was made equal to the diameter of the reactor. The reactions were carried out at 50°C under a nitrogen atmosphere which was purified by two different methods. One

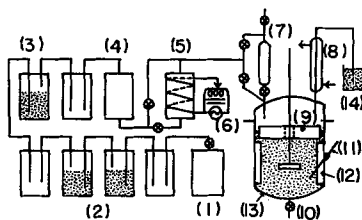


Fig. 2. Schematic diagram of experimental apparatus: (1) N_2 gas cylinder; (2) pyrogallol solution; (3) H_2SO_4 ; (4) $CaCl_2$; (5) electric furnace; (6) voltage regulator; (7) feeder for initiator; (8) reflux condenser; (9) float; (10) sampling cock; (11) thermometer; (12) baffle; (13) reaction vessel; (14) pressure regulator.

was purified by passing nitrogen gas (industrial cylinder nitrogen of 99.9% purity) through an alkaline pyrogallol solution, and the other, by passing it through both an alkaline pyrogallol solution and an electric furnace with copper gauze. Polymerizations carried out with the former were called A, those with the latter were called B, and those with high-purity cylinder nitrogen (better than 99.99% purity) without further purification were called C.

The number of polymer particles, the monomer weight fraction in the polymer particles, and the average degree of polymerization were determined in the same way as described in the previous paper.⁵ Monomer conversions were determined gravimetrically. When a monomer layer separates from the emulsion phase, the ratio of monomer to water is not always uniform throughout the reactor, so that samples withdrawn from the bottom of the reactor do not represent the mean composition of the reaction mixture. Thus, monomer conversion may be determined from $(a/b)/M_0$, where a and b represent the amounts of polymer and aqueous solution (water + emulsifier + initiator) in the sample, and M_0 is the initial ratio of monomer to aqueous solution. In these experiments, the values of a and b were determined by the following procedure. Monomer was added to the sample withdrawn from the reactor. After the polymer particles in the sample were fully saturated with the monomer, monomer droplets in the sample were separated by a centrifuge. The amount of the polymer, a , in the sample was determined gravimetrically. The total weight of polymer and monomer in the sample was known to be $2.33 \times a$ because the polymer particles were saturated with monomer.⁵ The amount of aqueous solution, b , in the sample was found by subtracting $2.33 \times a$ from the weight of the sample.

The average diameter of the emulsified monomer droplets was determined by the following procedure. Monomer droplets in a sample withdrawn from the reaction mixture were separated as a cream by centrifugation. The emulsifier concentration in the aqueous phase of the sample was measured by the Epton method.⁸ The average diameter of the monomer droplets was determined from the decrease in emulsifier concentration in the aqueous phase assuming that the emulsifier molecules were adsorbed on

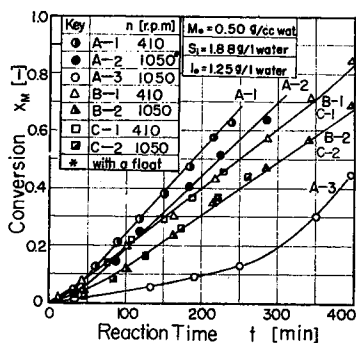


Fig. 3. Effect of stirring on the course of emulsion polymerization under nitrogen atmospheres having different purities A, B, and C.

monomer droplets in a monomolecular layer and using a_s equal to 35×10^{-16} cm²/molecule, the area per adsorbed emulsifier molecule.⁵

RESULTS AND DISCUSSION

Effect of Stirring in the Presence of Imperfectly Purified Nitrogen

Emulsion polymerization was carried out under nitrogen atmospheres of three purities, A, B, and C. The experimental results are shown in Figure 3.

The series of experiments denoted by A-1, A-2, and A-3 were carried out under nitrogen atmosphere A, and those denoted by B-1 and B-2, under nitrogen atmosphere B. It is clear from the results that the stirring action is very marked under nitrogen atmosphere A. In general, emulsion polymerization proceeds according to a zero-order mechanism after a short induction period. Run A-1, which was carried out at a stirring speed of 410 rpm, has a similarly shaped conversion time curve to run B-1 at the same stirring speed of 410 rpm, the induction period or retardation period being short in both cases. On the other hand, run A-3, carried out at a stirring speed of 1050 rpm, showed a prolonged retardation period, and it took much longer before polymerization proceeded according to a zero-order mechanism.

From visual inspection of the state of the reaction mixture, the surface of the reaction mixture was slightly undulating at a stirring speed of 410 rpm, but violent motion and fine dispersion of the nitrogen atmosphere into the reaction mixture occurred at 1050 rpm. It was therefore supposed that the prolonged retardation period at higher stirring speed was due to surface aeration by the nitrogen atmosphere, i.e., the absorption of trace impurities in the nitrogen into the reaction mixture. To prove the above supposition, emulsion polymerization was carried out at 1050 rpm using a reactor equipped with a float covering the surface of the emulsion to prevent surface aeration by the nitrogen atmosphere. This experimental result is denoted by A-2 in Figure 3. This time there was no prolonged retardation

period, and the progress of polymerization was similar to A-1. It may be concluded from the experimental results given above that the variation of the progress of polymerization with agitation under nitrogen atmosphere A can be attributed to the variation of the amount of trace impurity absorbed into the reaction mixture. Run B-2, which was carried out at a stirring speed of 1050 rpm, did not show such a prolonged retardation period as seen in A-3. On the other hand, polymerizations were carried out under high-purity cylinder nitrogen atmosphere (better than 99.99% purity) without further purification at 410 rpm and 1050 rpm, respectively. The progress of the polymerizations denoted by C-1 and C-2 in Figure 3 was quite similar to that under nitrogen atmosphere B. These results deny the possibility that the purification procedures introduce a contaminant in the form of entrained droplets of the reagents used, pyrogallol solution or sulfuric acid, and that these may themselves affect the rate of polymerization. Therefore, it is estimated that almost all of the impurity in the nitrogen that passed through an alkaline pyrogallol solution was then removed by passing it through copper gauze kept at about 500°C. The differences between A-1 and A-2 or B-1 and B-2 will be discussed later.

Under the imperfectly purified nitrogen atmosphere A, violent stirring significantly affected the progress of emulsion polymerization, causing a long retardation period. The effects of stirring on emulsion polymerization under nitrogen atmosphere A are shown in Figure 4. The retardation period was prolonged by increasing the degree of agitation. It was often noted that the reaction rate after a longer retardation period became greater than after a shorter retardation period. This may be explained by the authors' theory⁵

$$N_{Tc} \propto \left(\frac{r_i}{\mu}\right)^{2/7} (S_0)^{5/7} \quad (1)$$

$$\frac{dX_M}{dt} = \left[\frac{k_p M_p M_w}{M_0 N_A} \right] \frac{N_T}{2} \quad (2)$$

where r_i , S_0 , t , X_M , k_p , M_p , M_w , M_0 , and N_A denote the number of radicals produced in 1 cc of water per second; emulsifier concentration effective for micelle formation (g/l. water); reaction time, monomer conversion; rate constant of propagation (l./g-mole·sec); monomer concentration in polymer particles (g-mole/l.); molecular weight of monomer (g/g-mole); initially charged monomer weight per unit volume of water; and Avogadro's number, respectively. If polymerization is retarded in the region where polymer particles are being generated, the average volumetric growth rate of a polymer particle μ is decreased, and hence according to eq. (1), the number of polymer particles N_{Tc} (particles/cc water) becomes greater than in the situation without a retardation period. When impurities in the nitrogen gas are consumed and the supply of them to the reaction mixture is not sufficient for restraining polymerization, the polymerization rate will increase in proportion to an increase in N_{Tc} . Under a nitrogen atmosphere

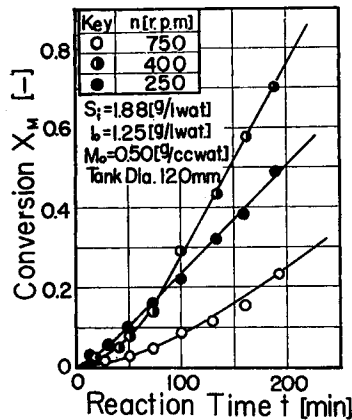


Fig. 4. Typical courses of emulsion polymerization affected by stirring under an imperfectly purified nitrogen atmosphere A.

that is contaminated with impurities, presumably oxygen, the progress of emulsion polymerization is greatly affected by the degree of agitation. It is difficult to estimate these effects quantitatively because of the complexity of the behavior of the impurities and its transport mechanism. To prevent emulsion polymerization from being affected by stirring, the space in a reactor over the surface of the emulsion must be minimized.

Effect of Stirring in the Presence of Well-Purified Nitrogen Atmosphere

It was pointed out in the previous section that stirring had a great influence upon the course of polymerization under imperfectly purified nitrogen atmosphere. Therefore, in this section, all experiments were carried out under nitrogen which was deoxygenized by passing it through both an alkaline pyrogallol solution and an electric furnace with copper gauze. As shown in Figure 3, there is some difference between the reaction rates of B-1 and B-2 from the beginning of the reaction, even though the reactions were carried out under a well-purified nitrogen atmosphere.

The reaction rate in run B-1 (410 rpm) is greater than that in run B-2 (1050 rpm) by about 15%. The number of polymer particles observed was 1.6×10^{14} particles/cc water in B-1 and 1.4×10^{14} particles/cc water in B-2. The number of polymer particles in run B-1 is also higher than that of run B-2 by the same degree as the reaction rates. Although the accuracy of measurement of N_{Tc} is not always satisfactory, it is considered that the difference between the reaction rates corresponds to the difference between the numbers of polymer particles.

As pointed out by Evans et al.³ and Omi et al.,⁴ the reason why the number of polymer particles formed decreases when the degree of agitation is increased may be due to the fact that the effective emulsifier concentration for micelle formation varies with stirring speed because the amount of emulsifier adsorbed onto the surfaces of the monomer droplets varies with

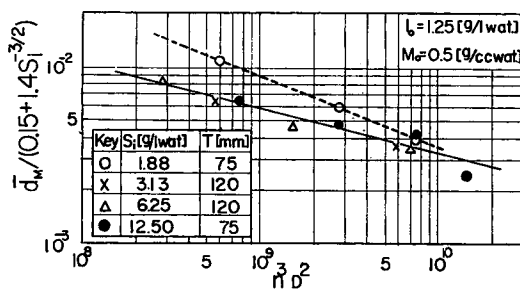


Fig. 5. Relation between mean diameter of monomer droplets and degree of stirring. stirring speed. To verify the validity of this supposition, the mean diameter of monomer droplets in an emulsion was observed. Figure 5 shows the mean diameter, \bar{d}_M (cm), of monomer droplets emulsified in the same mixture of monomer, water, emulsifier, and initiator as used in the reaction experiments, small quantities of inhibitor being added to the emulsion to stop the reaction. The amount of emulsifier adsorbed on the surfaces of monomer droplets, S_a (g/l. water), is calculated by assuming that emulsifier molecules are adsorbed onto the surfaces of monomer droplets in a monomolecular layer:

$$S_a = \left\{ \left(\frac{6M_0M_G}{\rho_M a_s N_A} \right) / \bar{d}_M \right\} \times 10^3 \quad (3)$$

where ρ_M and M_G denote monomer density (g/cc) and molecular weight of the emulsifier (g/g-mole), respectively. In the case of the initial emulsifier concentration, $S_i = 1.88$ g/l. water, the value of S_a calculated by eq. (3) with the aid of \bar{d}_M in Figure 5 is 0.085 g/l. water at a stirring speed of 410 rpm and 0.274 g/l. water at a stirring speed of 1050 rpm. The value of the effective emulsifier concentration for micelle formation, $S_0 = S_i - S_a - S_{CMC}$ at $S_i = 1.88$ g/l. water is about 14.5% greater at a stirring speed of 410 rpm than that at 1050 rpm, where S_{CMC} , the critical micelle concentration, is 0.50 g/l. water under these conditions. N_{Tc} may be about 10% greater at 410 rpm than at 1050 rpm according to eq. (1). Although the calculated difference does not agree exactly with the observed one, it is concluded that stirring contributes to the reduction of the effective emulsifier for micelle formation and therefore causes a reduction in the number of polymer particles formed. The empirical equation for \bar{d}_M is given by the following equation in the range $S_i \geq 3.13$ g/l. water:

$$\bar{d}_M = 1.05 (0.15 + 1.4S_i^{-3/2})(n^3D^2)^{-1/4} \quad (4)$$

where S_i , n , and D denote the initial emulsifier concentration (g/l. water), stirring speed (rpm), and impeller diameter (cm), respectively. In the range $S_i \geq 3.13$ g/l. water, the dependence of n upon the mean diameter of monomer droplets coincides with the results obtained by Rodgers⁶ and Shinnar.⁷ The term $(0.15 + 1.4S_i^{-3/2})$ may represent the effect of a preventive action against the coalescence of monomer droplets.

At $S_i = 6.25$ g/l. water, N_{Tc} is only 5% less at 1050 rpm than at 410 rpm, according to calculations using eqs. (1), (3), and (4). However, this difference is too small to be distinguished by the methods of measurement used in this study as shown in Figures 6, 7, and 9. Therefore, it is concluded that the stirring effect is negligible as long as the initially charged emulsifier concentration is much larger than the critical micelle concentration.

Figures 6 and 7 show the stirring effect over the whole range of conversion. The experiments were carried out at an emulsifier concentration $S_i = 6.25$ g/l. water. The courses of polymerization at stirring speed of 410 to 600 rpm coincided with each other over the whole range of monomer conversion, and the polymerizations proceeded according to a zero-order mechanism with respect to monomer concentration at monomer conversion between 3% and 43% where monomer droplets exist. At stirring speeds of 200 and 300 rpm, the courses of polymerization were the same as those at 410 and 600 rpm when $X_M < 0.07$, the reaction rates decreasing gradually thereafter with increasing reaction time t , falling below those at 410 and 600 rpm. On the other hand, at stirring speeds greater than 800 rpm, the course of polymerization was the same as those at 410 and 600 rpm until substantial monomer conversion had taken place, and then the rate of polymerization again fell below those at 410 and 600 rpm.

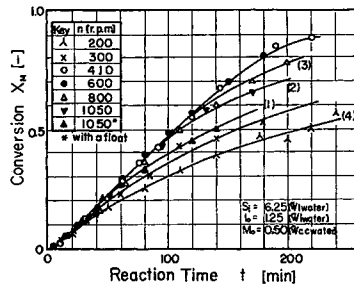


Fig. 6. Effect of stirring on the course of emulsion polymerization under a well-purified nitrogen atmosphere B.

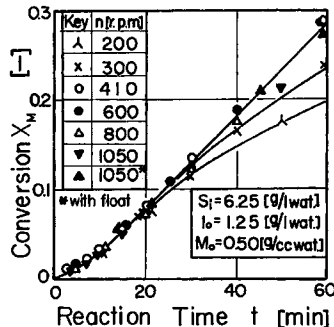


Fig. 7. Details of early stages of polymerizations shown in Figure 6.

The variation of the average degree of polymerization with monomer conversion tends to be the same as that of the reaction rates, as shown in Figure 8. The values of \bar{p}_μ obtained experimentally at 410 rpm remained almost constant in the range $0.05 < X_M < 0.43$, but at stirring speeds of 200 to 300 rpm, the values of \bar{p}_μ gradually decreased with reaction time t after monomer conversion reached about 0.07, by which time the rate of polymerization had also started to decrease. At a stirring speed of 800 rpm, the degree and the rate of polymerization deviated from the experimental values obtained at 410 rpm at a monomer conversion of $X_M \cong 0.6$ (refer to Figures 6 and 8).

It is estimated from the previous paper⁵ that the factors which may be affected by agitation are the number of polymer particles N_{Tc} and the monomer concentration in the polymer particles M_p , as shown by eq. (2).

Figure 9 shows the number of polymer particles N_{Tc} observed in the series of experiments. At a stirring speed of 410 to 600 rpm, N_{Tc} remained constant in the range of conversion $0.03 < X_M < 1.0$. At a stirring speed of 800 to 1050 rpm, the values of N_{Tc} began to decrease from the constant value when the course of polymerization deviated from that at 410 rpm. The broken lines, 1, 2, and 3 in Figure 9, were obtained by differentiating

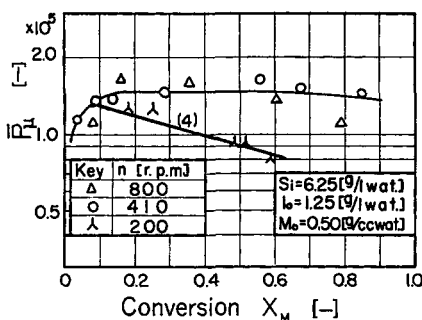


Fig. 8. Effect of stirring on the degree of polymerization of polymer produced under a well-purified nitrogen atmosphere B.

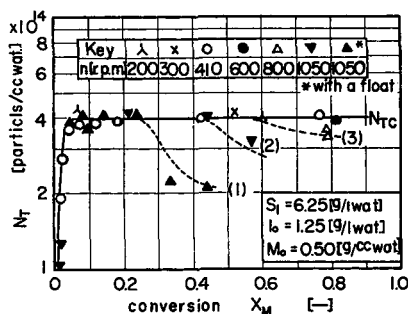


Fig. 9. Effects of stirring on the number of polymer particles formed and its variation in the course of polymerization.

the smoothed conversion time curves shown in Figure 6 with the aid of eq. (2), $k_p = 212$ l./mole·sec and $M_p = 5.48$ moles/l. in the range $X_M < 0.43$ where monomer droplets exist or $M_p = 9.61(1 - X_M)$ mole/l. in the range $X_M \geq 0.43$ where monomer droplets disappear. Since the observed values of N_{Tc} agree well with those calculated, it is concluded that the decrease in the reaction rate observed at a stirring speed of 1050 rpm was due to a decrease in the number of polymer particles. The distribution of diameters of polymer particles which were obtained in the experiment carried out at a stirring speed of 1050 rpm with a reactor equipped with a float are compared with those at 410 rpm in Figure 10. Comparing the distribution curves at 1050 rpm with those at 410 rpm, it is clear that the distribution at 1050 rpm and $X_M < 0.25$ follows a similar pattern to that at 410 rpm, except that the distribution is broader when $X_M > 0.25$. This is particularly true at large particle diameters. This means that polymer particles collide with each other and coalesce at the higher stirring speed. As can be seen in Figure 9, coalescence occurred appreciably more in the experiment with a float in the reactor.

Now let us consider the reason why the reaction rate decreased at stirring speeds of 200 to 300 rpm. Even at these stirring conditions, the number of polymer particles was the same as that obtained in the experiments at 410 and 600 rpm, as shown in Figure 9. Therefore, the decrease in reaction rates could not be ascribed to the reduction of N_{Tc} . By visual inspection, the monomer was seen to be perfectly dispersed at stirring speeds greater than 410 rpm as long as some monomer droplets remained. At a stirring speed of 200 rpm, the emulsified monomer droplets started to separate from the emulsion phase at about $X_M = 0.07$. The monomer conversion was 0.035 when the micelles disappeared at these experimental conditions.⁵ Monomer separation occurred after the disappearance of the micelles, and

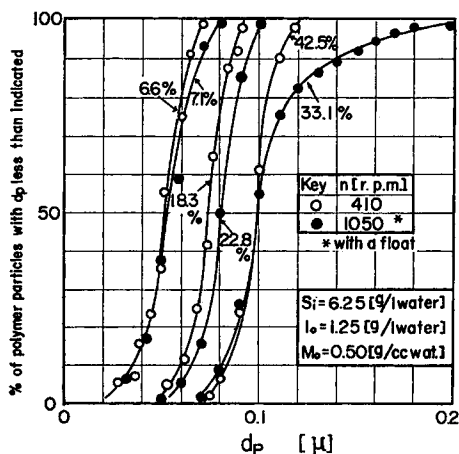


Fig. 10. Effect of stirring on particle size distribution with per cent conversion as parameter.

the conversion when monomer separation occurred agreed approximately with the conversion at which the rate of polymerization started to decrease. Therefore, the decreased reaction rate at the lower stirring speeds of 200 and 300 rpm was caused by monomer separation from the emulsion phase in the course of the polymerization.

Figure 11 shows the relation between the monomer weight fraction in the polymer particles, ϕ , and monomer conversion. In the experiment at a stirring speed greater than 410 rpm, ϕ remained constant until all the monomer droplets disappeared. However, in the experiment at 200 rpm, ϕ decreased as monomer conversion increased, even though monomer droplets still remained. The solid lines, 4 in Figures 8 and 11, were obtained from eqs. (5) and (6), using the value of M_p predicted by differentiating the smoothed conversion time curve 4 in Figure 6:

$$\phi = \frac{1}{1 + \frac{10^3 \cdot \rho_p}{M_p \cdot M_w} - \frac{\rho_p}{\rho_M}} \quad (5)$$

where ρ_p means polymer density (g/cc), and

$$\left(\frac{\bar{P}_\mu}{\bar{P}_{\mu X_M = X_c}} \right)^a = \frac{\int_{X_c}^{X_M} \left(\frac{M_p}{M_{p X_M = X_c}} \right)^a dX_M + X_c}{X_M}, \quad (X_c = 0.07) \quad (6)$$

where a denotes the power number in Mark-Houwinks' equation. The calculated curves agree well with the observed values. Therefore, it is concluded that the resistance to monomer transfer from monomer droplets to the polymer particles causes a decrease in M_p , and hence a decrease in reaction rates and in the degree of polymerization.

Let us consider the resistance of monomer transport to the polymer particles. Since the solubility of styrene in water is very slight, the quantities of monomer dissolved in the aqueous phase are negligible com-

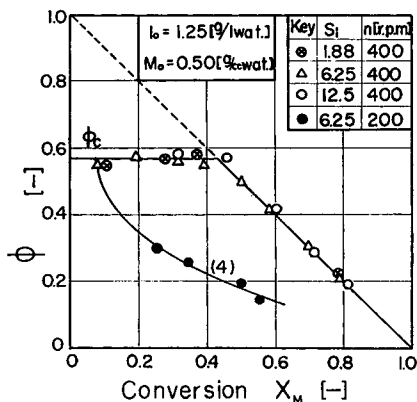


Fig. 11. Variation of ϕ with conversion when polymerized at a lower stirring speed.

pared with the total amount of monomer initially charged. Thus, the rate of polymerization is given by the following equation:

$$\frac{dX_M}{dt} = \left(\frac{k_p \frac{C_M^*}{m} M_w}{2M_0 N_A} \right) N_T \left\{ \frac{1}{1 + (k_p N_T / 2k_L A m) + (k_p / 4\pi \bar{d}_p D m N_A)} \right\} \quad (7)$$

where k_L , A , m , and D denote the mass transfer coefficient around a monomer droplet; the total area of monomer droplets per unit volume of water; the partition coefficient of monomer between the aqueous phase and polymer particles; and the diffusion coefficient of monomer in the aqueous phase, respectively; \bar{d}_p denotes the mean diameter of the polymer particles; C_M^* denotes the saturation concentration of monomer in the aqueous phase; and C_M^*/m represents the monomer concentration in the polymer particles when the system is reaction controlling.

The third term on the right-hand side of the denominator represents the contribution of the monomer transport resistance from the aqueous phase to the polymer particles, and the second term represents the contribution of the monomer transport resistance from the monomer droplets to the aqueous phase. Since the former is negligible, the latter represents the main resistance to monomer transport. Figure 12 shows the variation of capacity coefficient $k_L A$ with monomer conversion calculated by eq. (8):

$$k_L A = \frac{\left\{ M_0 \left(\frac{1}{1 - \phi} \right) + M_0 X_M \frac{(2 - \phi)}{(1 - \phi)^2} \right\} \frac{dX_M}{dt}}{C_M^* (1 - \phi/\phi_c)} \quad (8)$$

where ϕ_c denotes the monomer weight fraction in the polymer particles when the resistance to monomer transport is negligible in comparison with the resistance of the reaction, the value of ϕ_c being 0.571 as shown in Figure 11. The capacity coefficient $k_L A$ was higher at lower conversions, but decreased rapidly with the progress of polymerization, as shown in Figure 12. The rate of coalescence of unstabilized monomer droplets became faster with

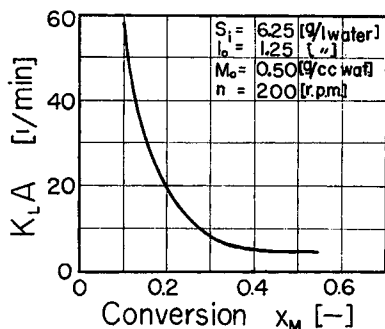


Fig. 12. Variation of $k_L A$ with conversion X_M at a lower stirring speed.

increase in monomer conversion because the emulsifier was insufficient for stabilizing the monomer droplets, this insufficiency being caused by an increase in the number of emulsifier molecules adsorbed on the surfaces of the growing polymer particles. Therefore, increasing monomer conversion leads to an increase in the size of monomer droplets and hence leads to a rapid decrease in the interfacial area A . Thus, the variation of $k_L A$ is considered to correspond to the variation of interfacial area of the monomer droplets A .

CONCLUSIONS

The effects of stirring on emulsion polymerization have been studied. From the experiments and discussion described in this paper, the following conclusions can be derived: (1) Emulsion polymerization is greatly influenced by impurities (perhaps trace of oxygen) contained in the nitrogen atmosphere in contact with the emulsion; this effect is very complicated and varies widely with degree of stirring. (2) Even under pure nitrogen atmosphere, emulsion polymerization is affected by the degree of stirring. At higher speeds of stirring, polymer particles coagulate and coalesce. At lower speeds of stirring, the polymerization rate is controlled by the monomer transport rate from the monomer droplets to the aqueous phase. Therefore, there exists an optimum degree of agitation where emulsion polymerization is not affected. For the scaling up of stirred tank reactors for emulsion polymerization, the two factors mentioned above should be considered. (3) At low emulsifier concentrations near the critical micelle concentration, stirring affects the reaction such that an increase in agitation causes a reduction of the effective emulsifier for the formation of micelles and therefore a decrease in the number of polymer particles formed.

One of the authors (M. Harada) wishes to thank the Sakko Kai Foundation for their (financial) support. The authors wish to express their thanks to Prof. Magari for allowing the use of the electronmicroscope in his laboratory, and to Mr. Kojima and Mr. Nakagawara for carrying out the experimental work.

References

1. S. R. Shunmukham, V. L. Hallenbeck, and R. L. Guile, *J. Polym. Sci.*, **6**, 691 (1951).
2. C. J. Schoot, J. Baker, and K. H. Klassens, *J. Polym. Sci.*, **7**, 657 (1951).
3. C. P. Evans, P. M. Hay, L. Marker, R. W. Murray, and O. J. Sweeting, *J. Appl. Polym. Sci.*, **5**, 39 (1961).
4. S. Omi, Y. Shiraishi, H. Sato, and H. Kubota, *J. Chem. Eng. Japan*, **2**, 64 (1969).
5. M. Harada, M. Nomura, H. Kojima, W. Eguchi, and S. Nagata, *J. Appl. Polym. Sci.*, **16**, 811 (1972).
6. W. A. Rodger, V. G. Trice, and J. H. Ruchton, *Chem. Eng. Prog.*, **52**, 515 (1956).
7. R. Shinnar and J. M. Church, *Ind. Eng. Chem.*, **52**, 253 (1960).
8. A. S. Weatherburn, *J. Amer. Chem. Soc.*, **28**, 233 (1951).

Received December 12, 1969

Revised July 29, 1970; October 21, 1971