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THE EFFECT OF AGITATION ON THE RATE OF EMULSION POLYMERIZATION OF STYRENE*

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The effect of agitation on the reaction rate of emulsion polymerization of styrene was experimentally studied. The agitation intensity in preparing the emulsion affects the polymerization rate. This is because the amount of soap molecules adsorbed on monomer droplets decrease the number of soap micells which produce polymer particles in the induction reaction region.

Once the emulsion is prepared in a specified condition, the agitation intensity during reaction does not affect the polymerization rate.

The amount of soap adsorbed on monomer droplets was estimated from the reaction rate in the zero-order region by assuming Smith and Ewart's theory, and was correlated empirically with the surface area of monomer droplets at the moment of emulsion preparation.

Introduction

Although the kinetics of emulsion polymerization of styrene has been frequently studied, little has been known about the influences of agitation or emulsified conditions of reactant mixture on the rate of polymerization and the average degree of polymerization.

Using a glass apparatus, Shunmukham et al.⁶⁾ tried to evaluate the effect of agitation on the rate of emulsion polymerization of styrene, and reported that the rate of polymerization decreased with increasing agitation intensity. As pointed out by Schoot⁵⁾, however, in their experiment oxygen was not completely eliminated and it was probably introduced into the polymerization system. Therefore the retardation effect of the oxygen played an important role in their experimental results. For the emulsion polymerization of vinylidene chloride, Evans et al.¹⁾ recognized that the rate of polymerization decreased with the increase of agitation intensity of the system. They propose that the quantity of adsorbed emulsifiers on monomer droplets may reduce the number of micelles from which polymer particles are formed.

These studies are intended for the emulsion polymerization of hydrophobic monomer. In this case the number of polymer particles is kept constant in

the ordinary reaction condition of batch operation. For the case when hydrophilic monomer is used this may not occur and coalescence of polymer particles will be taken into consideration.

In the present paper the effect of agitation on the rate of emulsion polymerization of styrene, which is a typical hydrophobic monomer, is studied.

Experimental Procedure

Experimental apparatus is the same as was used in our previous work⁴⁾. The polymerization reaction was carried out in isothermal batch operation. The experimental procedure is also the same as that in the previous work⁴⁾ except agitation procedures.

Preparation of Emulsion: Reactant mixtures of specified composition were transferred into the reactor and emulsified with selected agitation rates of the stirrer: 350, 700 and 1500 r.p.m., for one hour at the temperature of 60°C. A high speed family mixer, which has four blades with knife-edged shape and the agitation rates of 16,000 r.p.m., was also used. When this mixer was used, the emulsified mixture was obtained after one minute's agitation at room temperature.

Agitation Conditions during Polymerization Reaction:

When the emulsion was prepared at 350, 700 or 1500 r.p.m., the same agitation was employed during the reaction. On the other hand, when the family mixer

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was used for emulsification, it was transferred into the reactor after the emulsion was prepared, and then the reaction was carried out with a specified agitation rate.

Determination of Average Diameters of Monomer Droplets:

The diameters of monomer droplets were measured by the microscopic technique. The average diameter \bar{d}_M was determined by surface equivalent one which was calculated from

$$\bar{d}_M = \left[\frac{\sum_{i=1}^N d_i^2}{n} \right]^{1/2} \quad (1)$$

The number of monomer droplets n was taken from 200 to 600 in each sample.

Effect of Agitation during Reaction

In Fig. 1 and 2 the effect of agitation intensity during the reaction are shown. The results shown in Fig. 1 were obtained for the cases where the emulsions of reactant mixtures were prepared with the same method, i. e. using the family mixer, but the agitation intensities during reaction in the reactor are different. No remarkable difference between these results obtained in either case was observed. These results show that, once the reaction mixture is sufficiently emulsified, the polymerization reaction proceeds in-

dependently of the agitation intensity during reaction.

In the results shown in Fig. 2, the situation is different. Emulsions were prepared in the reactor with the same agitation rate as that used in the reaction that followed. It seems that monomer conversions in both cases almost coincide at the beginning of the zero-order reaction region (for the reaction region, refer to the authors' previous paper¹). After the end of the zero-order reaction region, a clear difference between the two cases is observed, i. e. the lower agitation rates give much lower monomer conversion at the same elapsed time.

These results will be explained as follows. There must be some difference in size of monomer droplets dispersed in water, depending on the difference of agitation conditions when the emulsions are prepared. When the family mixer was used (this corresponds to the case shown in Fig. 1), monomer is fully dispersed to smaller size droplets and a stable dispersion of monomer droplets will remain until the end of the zero-order reaction region, when the monomer droplets disappear completely. Therefore, the agitation conditions during reaction have no effect on the polymerization rate.

On the other hand, when the agitation velocity in preparing the emulsion is weak, as is the case shown in Fig. 2, monomer droplets dispersed in water will

Fig. 1 Effect of agitation rate during reaction

(I) Emulsions were prepared by using family mixer (16,000 r.p.m.)

Experimental conditions:

Water 640 ml, Styrene 160 ml, Sodium oleate 1.50 g, Potassium persulfate 0.55 g, 60°C

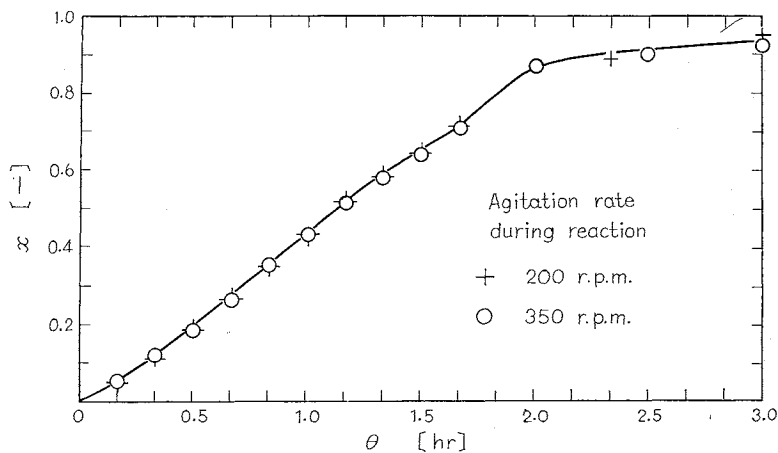
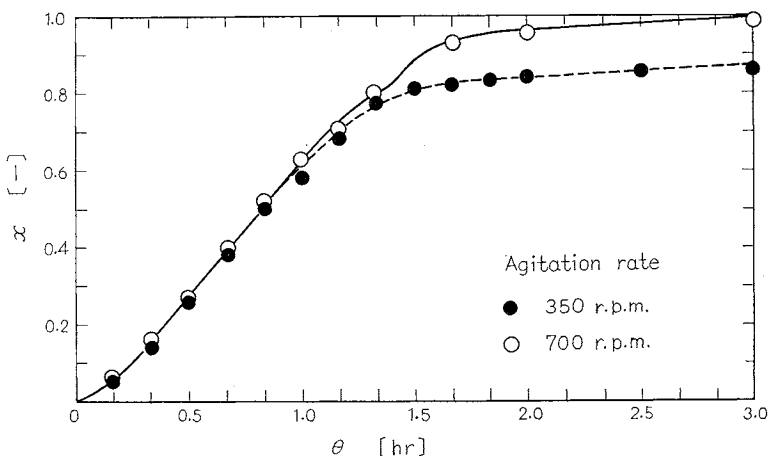


Fig. 2 Effect of agitation velocity during reaction

(II) Emulsions were prepared under the same condition as that of during reaction

Experimental conditions:

water 640 ml, Styrene 160 ml, Sodium oleate 1.50 g, Potassium persulfate 0.55 g, 60°C



have larger diameters and a stable dispersion cannot be obtained. Therefore, separation into two phases, i.e. monomer and water phases, will easily occur during reaction. The result for the agitation velocity of 350 r. p. m. shown in Fig. 2 corresponds to this case. This phase separation is considered to take place for the following reason. In emulsion polymerization, soap molecules adsorbed on the surface of monomer droplets prevent the coalescence of monomer droplets and give a stable emulsion. However, this dispersion state of monomer droplets gradually becomes unstable as the reaction proceeds, because the soap molecules on the monomer droplets transfer to the surface of polymer particles, which are newly produced and are growing to have quite a larger surface area. The monomer droplets which have lost soap molecules will become unstable and easily coalesce with each other. If the agitation velocity is too weak to keep monomer in droplets as observed in the case of 350 r. p. m., the separation of phase will finally take place.

In this situation, the diffusion of monomer into a polymer particle is strongly prevented, thus the transition from the zero-order to the first-order reaction region appears at the lower value of the monomer conversion and it will become difficult to have complete conversion of the monomer within the usual reaction time.

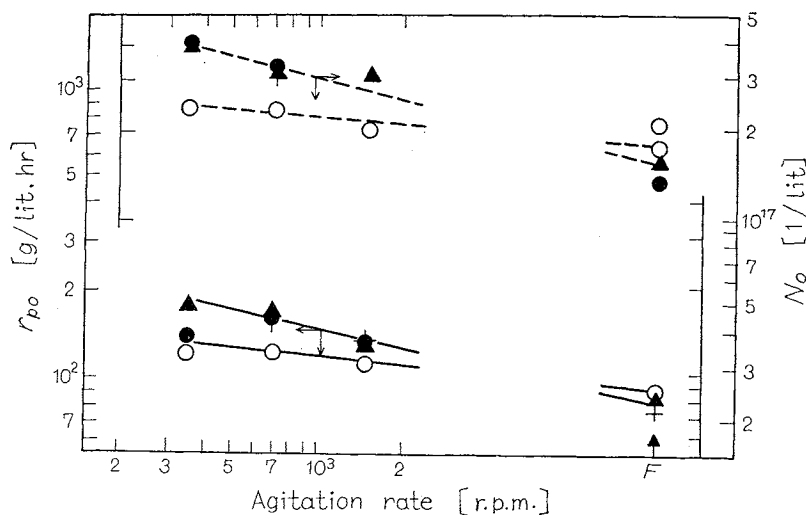
From the results mentioned above, it can be concluded that when agitation conditions are kept constant during emulsion preparation, the polymerization rate is independent of the agitation condition during reaction unless phase separation occurs.

Agitation Effect during Emulsion Preparation

When the concentration of emulsifier is constant, the state of dispersion of monomer droplets in emulsion will depend on the agitation intensity and the monomer concentration. The experimental results for emulsions prepared under different agitation conditions and monomer concentrations are shown in Fig. 3. In this figure, polymerization rate and also number of polymer particles per unit volume of the reactant mixture were plotted against changing agitation rate and phase ratio of monomer to water for the case where sodium oleate was used as the emulsifier. In Fig. 3, 4, 5, 9, 11 the observed values designated by the agitation rate of F indicates the case where the family mixer was used for emulsion preparation. Fig. 3 shows that the polymerization rate decreases as the agitation intensity increases. It is also observed that at lower agitation intensity, as the phase ratio of monomer to water in the reactant mixture increases, polymerization rate tends to increase, while the opposite effect appears when the agitation is more rigorous. Where sodium stearate was used as the emulsifier, the results are shown in Fig. 4. The results are similar to those of sodium oleate. In this case, the dispersion of monomer droplets is a little more unstable, and this may result in slightly larger experimental error.

When N. N. LT-221 was used as the emulsifier, as is shown in Fig. 5, the polymerization rate is independent of the agitation intensity and decreases as the monomer concentration decreases.

Quantitative Treatment of Reaction Rate : In accordance



	Water	Styrene
○	640 ml	160 ml
●	560	240
▲	480	320
+	400	400

Fig. 3 Effect of emulsification condition (agitation rate) for zero-order reaction rate and number of polymer particles (1) Sodium oleate as emulsifier

Experimental conditions :
Sodium oleate 1.50g, Potassium persulfate 0.55g, 60°C

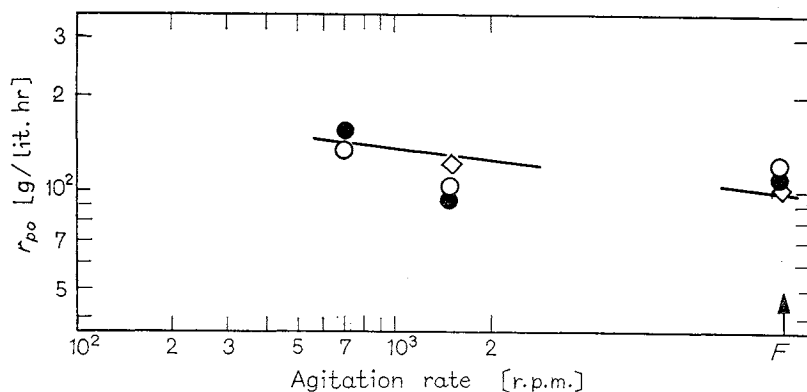


Fig. 4 Effect of emulsification condition for zero-order reaction rate

(II) Sodium stearate as emulsifier

Experimental conditions:

Sodium stearate 1.50g, Potassium persulfate 0.55g, 60°C

	Water	Styrene
○	640 ml	160 ml
◇	560	240
●	480	320

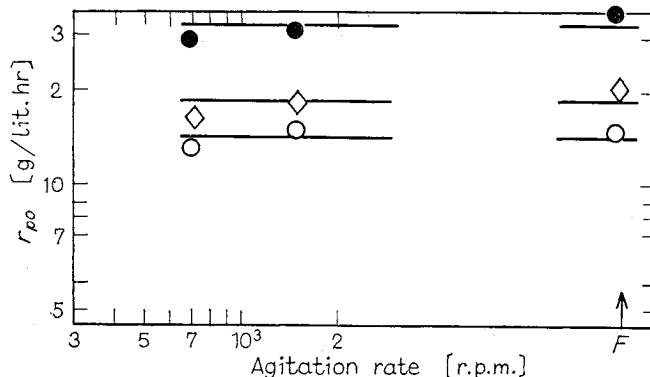


Fig. 5 Effect of emulsification condition (agitation rate) for zero-order reaction rate

(III) N. N. LT-221 as emulsifier

Experimental conditions:

N. N. LT-221 30.0g, Potassium persulfate 0.55g, 60°C

	Water	Styrene
●	480 ml	320 ml
◇	560	240
○	640	160

with the authors' previous articles⁴⁾, only in the cases where sodium oleate and sodium stearate were used as emulsifiers was the following relation, proposed by Smith and Ewart⁷⁾, satisfied.

$$r_{p0} \propto N_0 \quad (2)$$

Where r_{p0} is the zero-order reaction rate and N_0 is the number of polymer particles. However, the dependence of polymerization rate on agitation intensity and also on monomer concentration cannot be explained.

As already described, in the case of emulsion polymerization of vinylidene chloride, Evans et al¹⁾ observed similar results as were obtained here, and proposed the following explanation. The decrease of polymerization rate accompanying the increase of agitation intensity may be due to the increase of the amount of adsorbed emulsifier molecules on monomer droplets. This leads to the decrease of the number of soap micelles, from which polymer particles are

formed. This explanation is considered sufficient to interpret the results obtained here and will be extended quantitatively.

Now the authors assume that the theory proposed by Smith and Ewart will be satisfied only when the amount of adsorbed soap on monomer droplets is negligible. Then, let S_M be this amount of soap adsorbed on monomer droplets. Suppose that the concentration of initiator is constant, the equations derived by Smith and Ewart will be modified as follows,

$$N_0 = k_N(S_0 - S_M)^{0.6} \quad (3)$$

$$r_{p0} = k(S_0 - S_M)^{0.6} \quad (4)$$

where S_0 is the concentration of the emulsifier initially added. k_N and k are proportional constants.

k and S_M will be determined from the experimental data obtained in the following trial and error manner. The polymerization rate is measured for different values of S_0 , under the conditions of a constant monomer concentration and agitation intensity. Assuming

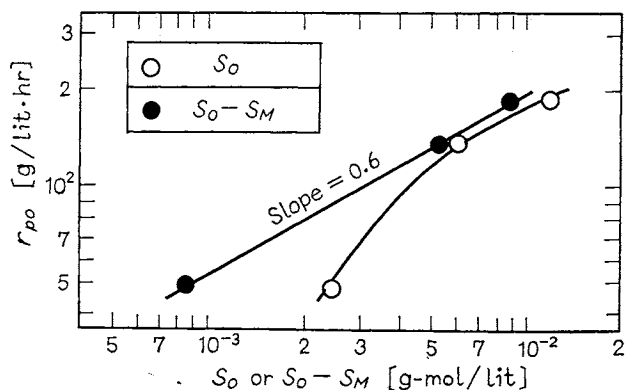


Fig. 6 Relation between zero-order reaction rate and emulsifier concentration

(I) Sodium oleate as emulsifier

Experimental conditions:

Water 640 ml, Styrene 160 ml, Potassium persulfate 0.55g, 60°C, 700 r.p.m.

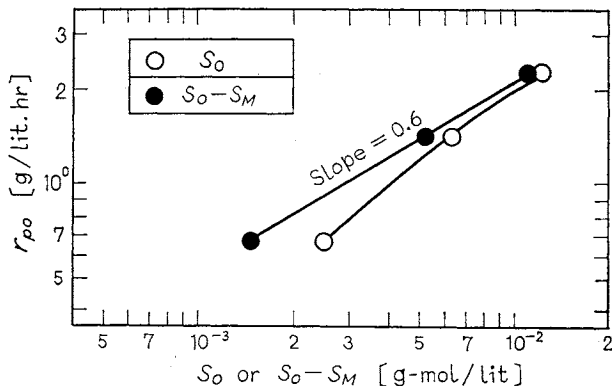
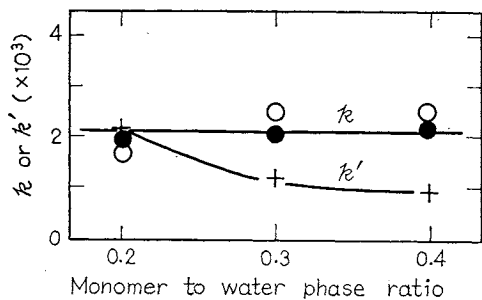


Fig. 7 Relation between zero-order reaction rate and emulsifier concentration

(II) Sodium stearate as emulsifier

Experimental conditions:

Water 640 ml, Styrene 160 ml, Potassium persulfate 0.55g, 60°C, 700 r.p.m.



Emulsifier :

- Sodium oleate
- Sodium stearate
- + N.N.LT-221

Fig. 8 Relation between k or k' and monomer to water phase ratio

a constant value of S_M , now k will be obtained from the values of r_{p0} and S_0 in accordance with Eq. (4). Using this value of k obtained at the same monomer concentration, S_M will be corrected for each agitation intensity. The trials are repeated to obtain converted values of S_M and k . This supposes that the existence of S_M causes the deviation from a straight line of which slope is 0.6 in Fig. 6 and 7, where $\log r_{p0}$ is plotted against $\log S_0$. In another words, this deviation can be corrected by S_M .

If S_0 is very large compared with S_M , the effect of S_M becomes negligible and the theory predicted by Smith and Ewart will be strictly satisfied. The results presented by Nagata et al.³⁾, who studied the rate of emulsion polymerization of styrene with sodium lauryl sulfate as the emulsifier, may belong to this case. i. e. $S_0 \gg S_M$.

In the case when N.N.LT-221 was used as the emulsifier, it was observed that N_0 is proportional to the emulsifier concentration as mentioned in previous article by the authors⁴⁾, therefore the following equation will be used instead of Eq. (3).

$$N_0 = k_N' S_0 \quad (5)$$

and Eq. (4) converts also to

$$r_{p0} = k' S_0 \quad (6)$$

In this case S_M is negligible in comparison with S_0 as shown in Fig. 5, because a large amount of emulsifier is required to obtain a measurable reaction rate.

Values of S_M determined from the data by the method described above will be shown later in connection with the surface area of monomer droplets. The values of k and k' are shown in Fig. 8. When sodium oleate and sodium stearate are used as emulsifiers, the values of k agree fairly well with the calculated value, $k = 2.12 \times 10^{-3}$ which is obtained from Eqs. (2) and (3) in the authors' previous paper⁴⁾. The relation of Eqs. (3), (4), (5) and (6) shows that the agitation intensity during emulsion preparation and the monomer concentration affect only the number of polymer particles N_0 . Therefore, once N_0 is determined, the procedure to predict the polymerization rate will be accomplished in the same manner that is presented in the authors' previous articles⁴⁾.

Surface Area of Monomer Droplets and S_M : Diameters of monomer droplets in the emulsion just before addition of initiator were determined by the microscopic technique. An example of the relation between the average diameter of monomer droplets \bar{d}_M and agitation rate is shown in Fig. 9. The total surface area of monomer droplets a_M (cm^2/cm^3) can be calculated from the following equation.

$$a_M = \frac{6}{\bar{d}_M} (V_M - v_M) \quad (7)$$

Where v_M is the monomer volume solubilized in soap micelles per unit volume of the reactant mixture and V_M is the total volume of monomer in the reactant mixture at the initiation of reaction. Under the conditions of present experiments for sodium oleate and sodium stearate, v_M will be negligible compared with V_M .

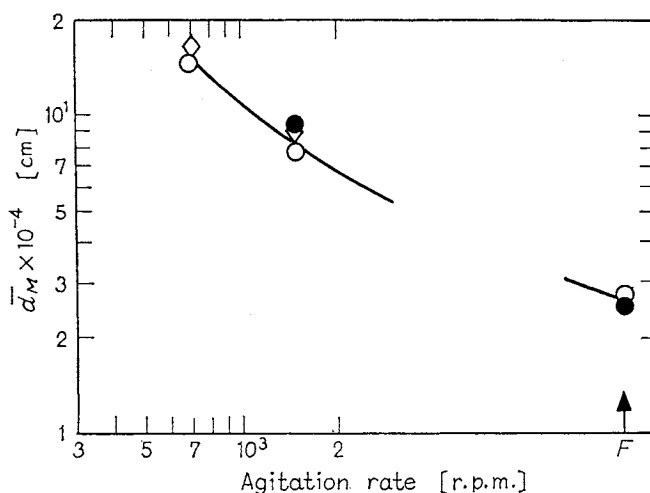


Fig. 9 Relation between agitation rate in emulsion preparation and average diameter of monomer droplets
Experimental conditions: Sodium oleate 1.50g, 60°C

	Water	Styrene
○	640 ml	160 ml
◇	560	240
●	480	320

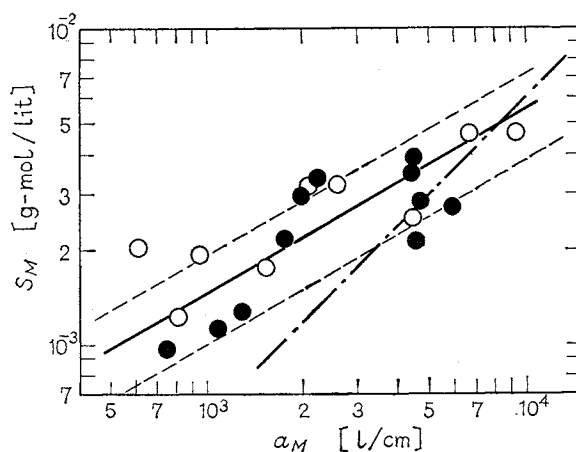


Fig. 10 Relation between emulsifier concentration occupied by monomer droplets and total surface area of monomer droplets

Emulsifier :	
○	Sodium oleate
●	Sodium stearate
—	Eq. (8)
- - -	Theoretical line for sodium oleate

The values of S_M obtained in the way described above are plotted against a_M in Fig. 10, which gives the following empirical relation.

$$S_M = 4.49(10^{-5})a_M^{0.57} \quad (8)$$

At the agitation rate of 350 r.p.m., monomer droplets tend to coalesce with each other when microscopic samples are taken. Therefore, calculation of the surface area in this case cannot be made.

As the value of S_M was defined to be the amount of adsorbed emulsifier molecules on monomer drop-

lets, then S_M will be proportional to the first power of a_M . Assuming the surface area, which will be occupied by unit molecule of sodium oleate is 28 \AA^2 ²¹, the theoretical relation between S_M and a_M is obtained as shown in the dashed line in Fig. 10. A difference between the theoretically and the experimentally determined lines is not made clear.

Effect of Agitation on the Average Degree of Polymerization: Fig. 11 shows the change of the average degree of polymerization within the zero-order re-

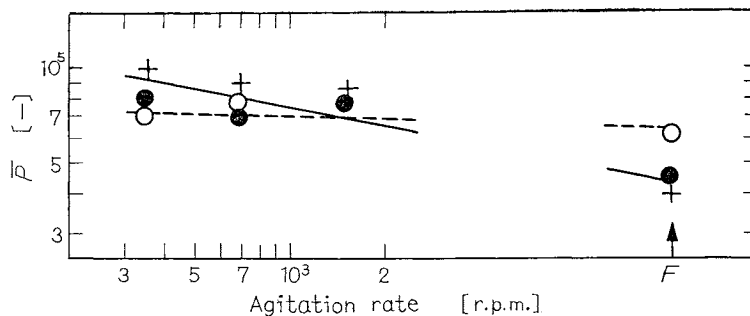


Fig. 11 Effect of emulsification condition (agitation rate) for average degree of polymerization, \bar{P}

	Water	Styrene
○	640 ml	160 ml
●	560	240
+	480	320

action region. Comparing this with Fig. 3, it is noted that the theory proposed by Smith and Ewart which states the proportional relation between the average degree of polymerization and the polymerization rate, i. e. $r_{po} \propto \bar{P}$, will be satisfied. Thus the effect of agitation conditions on the average degree of polymerization will be the same as that on the polymerization rate. This is well illustrated in Fig. 11.

Consideration for Agitation in Practical Operation

As described above, when emulsion polymerization of styrene is proceeding, the surface of the growing polymer particles begins to lack monomer droplets and it robs soap molecules from the surface of monomer droplets. Therefore the state of dispersion of monomer droplets may become unstable. This will continue until the end of the zero-order reaction region, when all monomer droplets are consumed by the reaction. The stabilization of monomer droplets up to this moment is required. To stabilize the emulsion it was experimentally found that intensified agitation while preparing the emulsion is effective. However, it should be noticed that the intensified agitation at this moment causes a reduction of the polymerization rate.

On the other hand the agitation condition has almost no effect on reaction rate as far as a sufficient dispersion of monomer is kept during reaction. Also it had been reported that intensified agitation sometimes causes inhibition of reaction³⁾. In practical batch operations, after a desirable emulsion of the reactant mixture is obtained, agitation during reaction should be enough to keep a stable dispersion of monomer droplets until the end of the zero-order reaction

region. Practically of course the effect of agitation on heat transfer to the cooling medium through the wall or cooling coils must be also taken into consideration.

Nomenclature

a_M	= surface area of monomer droplets per unit volume of reactant mixture	[1/cm]
d_M	= diameter of monomer droplets	[cm]
\bar{d}_M	= average value of d_M	[cm]
k, k', k_N, k_N'	= proportional constants	
N_0	= number of polymer particles per unit volume of reactant mixture	[1/lit]
n	= number of monomer particles sampled	[—]
r_{po}	= polymerization rate, moles of monomer converted to polymer per unit time per unit volume of reactant mixture	[g-mol/lit·hr]
S_0	= concentration of emulsifier initially added	[g-mol/lit]
S_M	= concentration of emulsifier molecules adsorbed on monomer droplets	[g-mol/lit]
V_M	= volume of monomer per unit volume of reactant mixture	[—]
v_M	= volume of monomer solubilized in soap micelles per unit volume of reactant mixture	[—]

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