

# Emulsion Polymerization of Water-soluble Monomers

By

Seizo OKAMURA and Takuhiko MOTOYAMA

(Department of Textile Chemistry)

(Received April, 1955)

## Synopsis

The rate and the degree of polymerization are measured and compared in the mass- and emulsion- polymerization of styrene, methyl methacrylate, methyl acrylate, vinyl caproate and vinyl acetate in the presence of soap molecule.

Vinyl caproate is found to resemble vinyl acetate at the rate and the degree of polymerization in the mass-polymerization, but to resemble styrene in the emulsion-polymerization.

Therefore, it is concluded that the solubility behavior is the matter claiming settlement prior to that of the reactivity.

## 1. Introduction

It is generally conceived that the reaction locus of emulsion polymerization is the monomer phase in soap micelle. This conception has been introduced by W. Harkins<sup>1)</sup> and confirmed quantitatively by W. V. Smith and R. H. Ewart.<sup>2)</sup> One of the quantitative expressions of the Harkins' theory seems to be that the over-all rate of emulsion polymerization is proportional to  $3/5$  power of soap concentration. This relationship has been confirmed by the results of the emulsion polymerization of styrene reported by Smith.<sup>3)</sup> The degree of polymerization, on the other hand, is expected to increase as the soap concentration increases. This relationship has been also justified in the emulsion polymerization of styrene reported by S. Okamura et al.,<sup>4)</sup> and E. A. Hauser and G. E. Perry.<sup>5)</sup> These investigations are frequently limited to styrene or butadiene, i. e. one of water-insoluble monomers and no experiments have been reported in the cases of water-soluble monomers such as methyl acrylate or vinyl acetate.

In the work reported here, the rate and the degree of polymerization are measured and compared in the emulsion polymerization of styrene, methyl methacrylate, methyl acrylate, vinyl caproate and vinyl acetate.

## 2. Experimental

### a) Materials:

Sodium dodecylsulphate is used as the emulsifier in the turbidity measurements.

This soap was not easily soluble in monomers and so was not suitable for the comparison of emulsion- and mass-polymerization. Polyethyleneoxide dodecylether is used as the emulsifier in polymerization, for it is very easily soluble into each monomer. The anionic soap is recrystallized in the ethanol solution and the nonionic is freed from impurities by the extraction by ether, both followed by the drying in vacuum.

The monomeric styrene (*St*) is distilled in vacuum, and the monomers, methyl methacrylate (*MMA*), methyl acrylate (*MA*) and vinyl acetate (*VAc*) are distilled in the presence of benzoyl peroxide according to the report of Bartlett and Nozaki,<sup>6)</sup> and Matsumoto.<sup>7)</sup>

The vinyl caproate (*VCp*) is obtained by the ester-exchange reaction between vinyl acetate and caproic acid, mentioned in "Organic Synthesis".<sup>8)</sup>

The ammonium persulphate (*APS*) and 2-azobisisobutyronitrile (*Az*), used as initiators in emulsion- and mass-polymerization are recrystallized from the aqueous and the methanol solution of commercial C. P. grades.

b) Solubility determination of monomers into the aqueous soap solution :

The mixture of monomer and water or aqueous soap solution is filled into a separation funnel, and agitated vigorously in the thermostatt at 30°C. After the stand-still for about three days, the aqueous phase is saponified by alkaline solution. The solubility in water of such ester-type monomers as *MMA*, *MA*, *VAc* and *VCp* are calculated from the saponification values. The solubilization determination into the aqueous soap solution is performed by the turbidity measurement, reported by Klevens.<sup>9)</sup> The equilibrium of solubilization is attained after about fifty minutes in the case of *VAc* and *MA*, but only after about fifty hours in the case of *St* and *MMA*.

c) Experiments in mass polymerization :

The Foord-type viscometer<sup>10)</sup> is filled with the 10 ml mixture of monomer, the initiator and soap, cooled by the mixture of dry ice and methanol, and sealed under 2 mm Hg pressure.

The yields of polymerization are calculated from the viscosity of the reaction mixture by the Baker's equation. The temperature of polymerization is  $60 \pm 0.2^\circ\text{C}$ .

d) Experiments in emulsion polymerization :

The mixture of 8 ml monomer, 0.1 g initiator and 100 ml aqueous soap solution is polymerized into emulsion state at  $70 \pm 0.2^\circ\text{C}$ . The yields of polymerization are obtained by the usual methods in the procedure of emulsion polymerization, *i. e.* coagulation, washing and drying.

e) Determination of the degree of polymerization ( $\bar{P}$ ) :

$\bar{P}$  is determined at about 10% yield in mass polymerization and also at about 20% yield in emulsion polymerization respectively. It is calculated from the viscosity

of the dilute solution using the following equations,

$$\begin{aligned}
 [\eta] &= 0.50 \cdot 10^{-4} \bar{P}, && \text{for polystyrene in toluene solution,}^{11)} \\
 [\eta] &= 0.47 \cdot 10^{-4} \bar{P} + 0.0095 && \text{for polymethyl methacrylate in chloroform solution}^{12)} \\
 [\eta] &= 0.239 \cdot \log(1 + \bar{P}/2000) && \text{for polymethyl acrylate in acetone solution}^{13)} \\
 [\eta] &= 0.280 \cdot \log(1 + \bar{P}/2000) && \text{for polyvinyl acetate and polyvinyl caproate in acetone solution}^{14)}
 \end{aligned}$$

### 3. Experimental results

a) Solubilization experiments:

The solubility of monomers into pure water is represented in Table 1.

Table 1. The solubility of four monomers into pure water at 30°C.

MA	VAc	MMA	(St)	VCp
4.05	2.33	0.91	(0.03)	0.004

(Value in St is in the reference<sup>15)</sup>)

In Table 1, the order of the solubility into pure water is found to be,

$$VCp < St < MMA < VAc < MA$$

The turbidity in the aqueous soap solution are shown in Figure 1.

As represented in Fig. 1, the concentrated soap solution is already turbid without the addition of monomer. To compare the relative values, the turbidity of the aqueous soap solution itself is normalized to unity and the change of turbidity by the addition of monomer is shown in Figure 2.

As shown in Figure 2, the order of the solubilization into the soap solution is found to be,

$$VCp < St < MMA < VAc < MA.$$

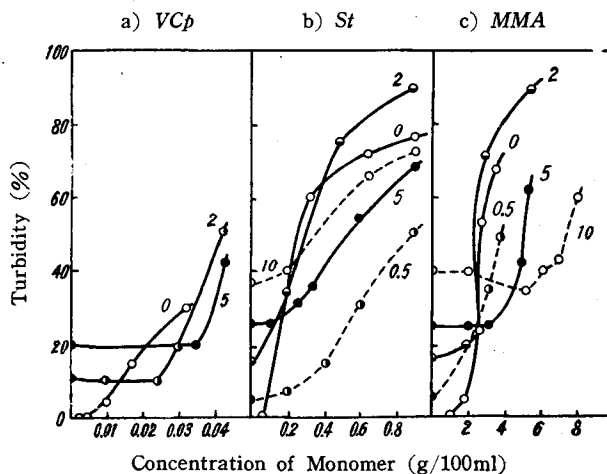


Fig. 1. Turbidity of three monomers in the sodium dodecylsulphate solution.

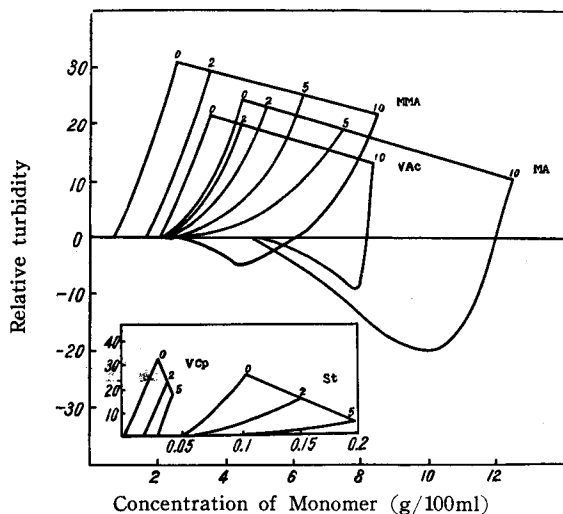


Fig. 2. Relative turbidity of five monomers in sodium dodecylsulphate solution (schematic drawings).

In the water-soluble monomers, *e.g.* VAc or MA, the turbidity decreases first by the addition of monomer into the concentrated soap solution. Recently it was recognized by Mc. Bain and Gupta<sup>16)</sup> that the turbidity of the aqueous solution of K-laurate decreased first by the addition of benzene. In their experiments, the competitive solubilization was found to occur between the soap used and the acidic soap formed after dissociation. Some of the higher alcohols retained in the soap as unreacted components seems to

be competitive with the monomer in our solubilization experiments. As already reported in the X-ray investigations<sup>17)</sup>, the polar compounds were found to be solubilized into the palisade layer, and not into the core part of the soap micelle. It is worth mentioning that the circumstances of solubilization are not the same in different monomers and will play different roles against the behavior of the emulsion polymerization.

As clarified by H. B. Klevens<sup>18)</sup>, the amount of solubilized oil into the solution of the soap-salt mixture decreases with the salt concentration, in the case of the strongly hydrophilic oil. The change of solubilization by the addition of sodium sulphate are determined in ethyl acetate, MMA and VAc, and are shown in Table 2.

Table 2. The solubilization of two monomers by the addition of sodium sulphate (the concentration of sodium dodecylsulphate, used as soap is 2.0%).

Concentration of sodiumsulphate (% to soap concentration)	Oil solubilized (g/100 ml) (Numbers in brackets show the relative values normalized to pure soap solution)		
	Ethyl acetate	MMA	VAc
0	9.8 (1.0)	2.2 (1.0)	4.0 (1.0)
20	10.5 (1.07)	2.2 (1.0)	3.6 (0.90)
50	10.6 (1.08)	2.1 (0.96)	3.2 (0.80)
100	11.2 (1.09)	1.95 (0.89)	3.0 (0.75)

In the views of Klevens, *VAc* seems to be more hydrophilic to the solubilization behavior than *MMA* also in the salt effect.

b) Mass polymerization experiments;

The reaction rate of five monomers in mass polymerization using *Az* as initiator is represented in Figure 3.

For the qualitative consideration it seems to be enough to compare the rate of polymerization from the straight lines shown in Figure 3. Results are summarized with the induction period and also the degree of polymerization in Table 3.

As shown in Figures 3 and Table 3, the decrease of the rate and the degree of polymerizations are comparatively slight in *St* and *MMA*, but clearly large in such monomers as *VCp* and *VAc*. These are considered to be due to the reactivity or the sucesibility of growing polymer radicals toward the soap molecule.

The order of the decreasing rates or degrees of polymerization is,

$$St \leq MMA < MA < VCp < VAc.$$

c) Emulsion polymerization experiments;

The reaction rate of four monomers in emulsion polymerization using *APS* as initiator is shown in Figure 4.

In many reference papers, the typical rate-curves of emulsion polymerization are known to be in the shape of S-type in the whole range of polymerization. But here the straight lines obtained in a more limited range as given in Figure 4 are compared, and the apparent rates of emulsion polymerization thus obtained are summarized together with the degree of polymerization in Table 4,

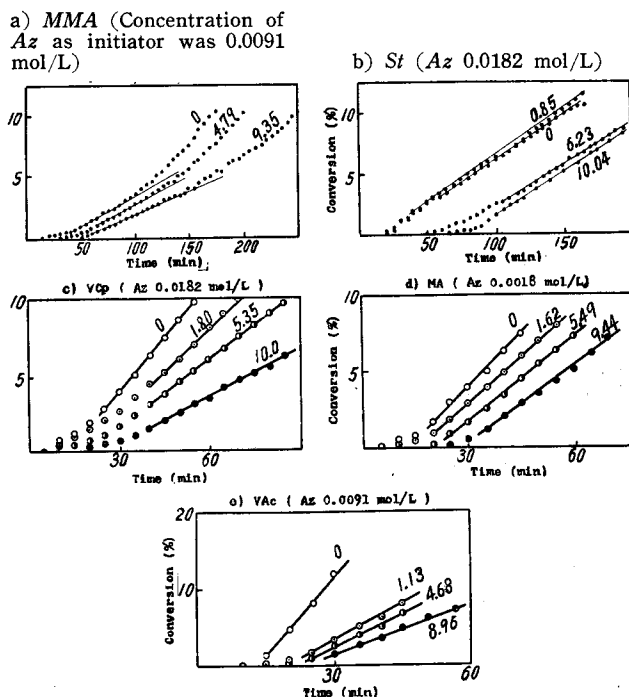


Fig. 3. The rate-curves of mass polymerization (Numbers in Figures show the concentration of polyethyleneoxide dodecylether added into the polymering mixture).

Table 3. The results of mass polymerization.

Monomer	Conc. of initiator (mol/L)	Conc. of soap resolved (g/100 ml)	Rates of polym. (mol/L/sec. $10^{-4}$ )	Induction period (minutes)	Degree of polym.
			(Numbers in brackets are relative values normalized to unity in the case without soap addition)		
MMA	0.0091	0	0.87 (1.00)	32	1170 (1.00)
"	"	4.79	0.76 (0.87)	41	1110 (0.95)
"	"	9.35	0.66 (0.76)	50	1030 (0.88)
St	0.0182	0	1.2 (1.00)	27	230 (1.00)
"	"	0.85	1.2 (1.00)	25	240 (1.04)
"	"	6.23	1.1 (0.92)	60	230 (1.00)
"	"	10.04	1.1 (0.92)	74	240 (1.04)
VAc	0.0182	0	2.5 (1.00)	13	600 (1.00)
"	"	1.80	1.9 (0.76)	15	590 (0.98)
"	"	5.35	1.5 (0.60)	19	520 (0.87)
"	"	10.00	1.2 (0.48)	28	490 (0.82)
MA	0.0018	0	4.2 (1.00)	12	4000 (1.00)
"	"	1.62	3.6 (0.86)	16	3580 (0.90)
"	"	5.49	3.5 (0.83)	20	2500 (0.63)
"	"	9.44	3.1 (0.74)	28	2170 (0.54)
VAc	0.0091	0	2.5 (1.00)	13	600 (1.00)
"	"	1.80	1.9 (0.76)	15	590 (0.98)
"	"	5.35	1.5 (0.60)	19	520 (0.87)
"	"	10.0	1.2 (0.48)	28	490 (0.82)

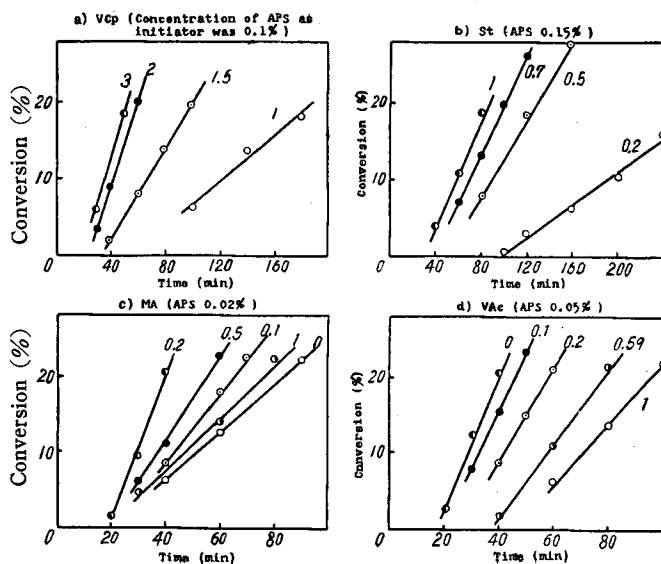


Fig. 4. The rate-curves of emulsion polymerization (Numbers in Figure show the concentration of polyethyleneoxide dodecylether added as emulsifier).

Table 4. The results of emulsion polymerization.

Monomer	Conc. of initiator (%)	Conc. of emulsifier (g/100 ml)	Rates of polym. (mol/L/sec. $10^{-5}$ ) (Numbers in brackets show relative values)	Degrees of polym.
<i>St</i>	0.15	0.2	1.3 (1.00)	780 (1.00)
"	"	0.5	3.2 (2.46)	970 (1.24)
"	"	0.7	3.9 (3.00)	1280 (1.64)
"	"	1.0	4.5 (3.46)	1590 (2.04)
"	"	1.5	6.4 (4.92)	3520 (4.50)
<i>VCp</i>	0.1	1.0	1.6 (1.00)	600 (1.00)
"	"	1.5	3.2 (2.00)	650 (1.08)
"	"	2.0	6.2 (3.88)	680 (1.13)
"	"	2.5	6.2 (3.88)	740 (1.23)
"	"	3.0	7.8 (4.88)	810 (1.35)
"	"	4.0	9.0 (5.61)	1030 (1.72)
<i>MA</i>	0.02	0	4.4 (1.00)	2440 (1.00)
"	"	0.1	6.7 (1.52)	2470 (1.01)
"	"	0.2	13.7 (3.11)	2630 (1.08)
"	"	0.5	8.5 (1.93)	2500 (1.02)
"	"	1.0	5.6 (1.27)	2500 (1.02)
<i>VAc</i>	0.05	0	14.4 (1.00)	3120 (1060)*(1.00) (1.00)*
"	"	0.1	10.5 (0.73)	2060 ( 990) (0.66) (0.93)
"	"	0.2	8.6 (0.60)	1690 ( 855) (0.54) (0.81)
"	"	0.5	7.2 (0.50)	1390 ( 800) (0.45) (0.75)
"	"	1.0	5.7 (0.40)	1020 ( 685) (0.33) (0.65)

(Values in \*-marks show the degree of polymerization as polyvinyl alcohol obtained by the saponification of polyvinyl acetate in the same lines of left column.)

As represented in Table 4, the rate of polymerization increases with the soap concentration in the case of *St* and *VCp*, but in the case of *MA* the maximum appears in curves and finally in the case of *VAc* the rate decreases. The relation is almost the same with the degree of polymerization. Comparing Table 3 with Table 4, it is recognized that *VCp* resembles *VAc* in mass polymerization, but resembles *St* in emulsion polymerization.

#### 4. Discussion

The recent works on the effect of soap concentration upon the rate and the degree of polymerization in emulsion polymerization are summarized in Table 5. It has been suggested that the less water-soluble monomers such as *St*, vinylidene chloride or *MMA* have shown ascending curves both in the rate and the degree of polymerization, but the more soluble monomers such as *MA* or *VAc* represented the maximum or descending.

Table 5. The relationship between the rates of emulsion polymerization or the degrees of polymerization and the soap concentration, reported in references.

Monomer	Emulsifier	Type of curves obtained with the soap concentration		References
		Rate of polymerization	Degrees of polymerization	
<i>St</i>	Sodium oleate	ascending	ascending	4) 5)
Vinylidene chloride	Pottasium laurate	ascending	constant	6)
<i>MMA</i>	S-F soap Na laurylsulphate Polyethyleneoxidedodecylether Cetyltrimethylammoniumbromide	ascending	ascending	7)
<i>MA</i>	Na laurylsulphate Polyethyleneoxidedodecylether S-F soap	maximum maximum maximum	maximum constant descending	8)
<i>VAc</i>	P-F soap Na laurylsulphate Polyethyleneoxidedodecylether	maximum descending	descending descending	9) 10)

In view of the fact that these works were performed under different conditions, the direct comparison made in Table 5 is subject to query. Therefore the relative values of the rates and the degrees of polymerization in Tables 3 and 4, are represented in Figures 5 and 6 respectively.

In Figure 6 the direct comparison under the same condition is possible. These curves are shown, therefore, to be of the ascending type in the case of *St* and *VCP*, of the descending type in the case of *VAc* and maximum appears in *MA*. In consideration of the solubility behaviors of monomers shown in Tables 1 and 2, and in Figures 1 and 2, it is to be seen with a certain degree of distinctness that the water-soluble monomers have certain different qualities toward the emulsion polymerization from what the less water-soluble monomers have. But it is not right to ascribe these phenomena only to the solubility characteristics because the reactivities of monomers or growing radicals differ widely from *St* to *VAc*.

As ordinarily accepted, the reactivities of monomer- or polymer- radicals seem

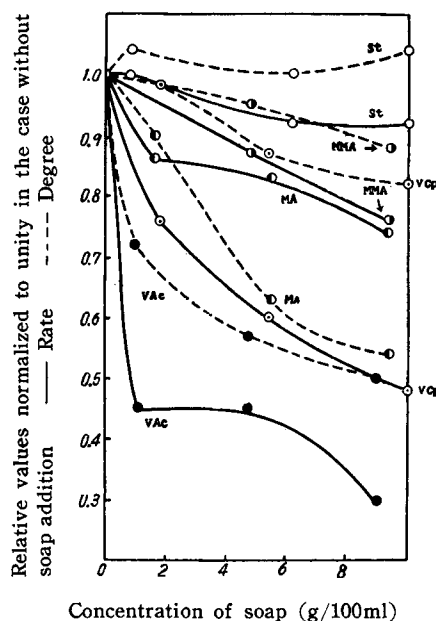


Fig. 5. The direct comparison of the rates and the degrees of polymerization under the influence of soap concentration (from the data in Table 3).



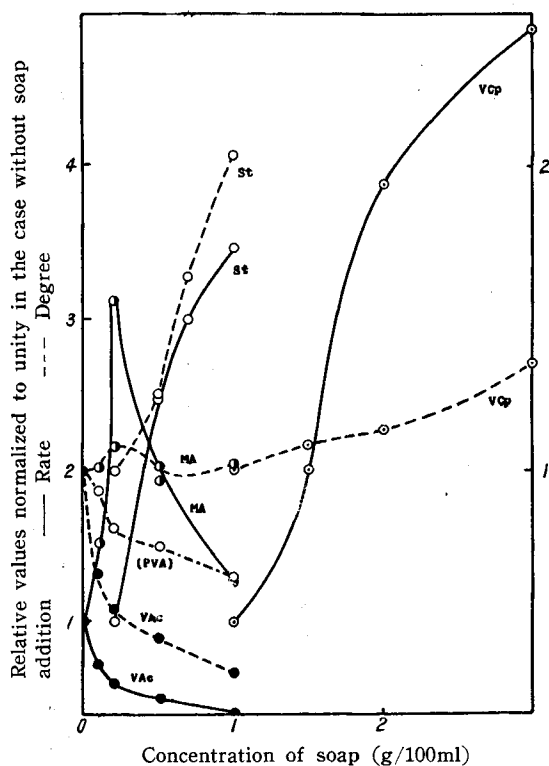
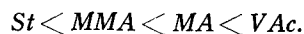


Fig. 6. The direct comparison of the rates and the degrees of emulsion polymerization under the influence of soap concentration (from the data in Table 4).

to increase in the following order,<sup>19)</sup>



*VAc* is presumed to be more sensitive than *St* toward the soap molecule added as one of retarders. As shown in Figure 5, it is recognized that the sensibility of soap molecule toward the rate of polymerization increases in the order of  $St < MMA < VCp < MA < VAc$ , and that toward the degree of polymerization is in the order of  $St < MMA < VCp < MA < VAc$ . The inversed order of *VCp* and *MA* toward the rate and the degree seems to be due to the low molecular weight formation of polyvinyl caproate. The order of reactivities of monomer- or polymer-radicals to the soap molecule can be assumed to be,



The immediate question which must be decided at this stage of inquiry is to determine which is the main factor in the behavior of emulsion polymerization, the solubility in water of monomers or the reactivity to the soap molecule. Here, *VCp* is found to be a clue to this determination. There is remarkable difference in characteristics between *VCp* and other monomers. *VCp* is considered, for instance, to resemble *VAc* in the reactivity characteristics.

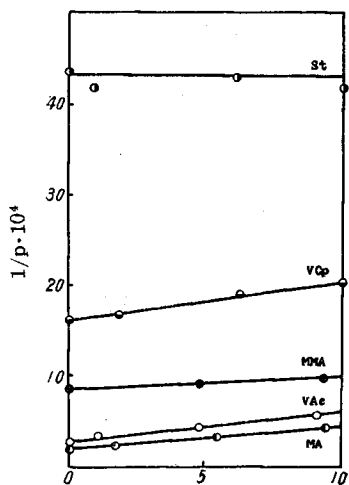
As shown in Figure 6 *VCp* is found to resemble *St* both in the rate and the degree of polymerization in emulsion polymerization.

Therefore, it is concluded that the solubility behavior is the matter claiming settlement prior to that of the reactivity.

The chain transfer action of soap molecules is shown in Figure 7 in mass polymerization, and Figure 8 in emulsion polymerization. The apparent chain transfer constants obtained from both these figures are also tabulated in the same figures. The chain transfer constants increase with the reactivity of monomer radicals.<sup>20)</sup> Thus the relations between these transfer constants

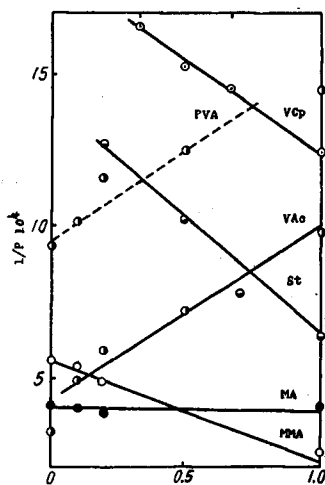
or rate depression ratios and the Alfrey-Price's P-values of monomers<sup>21)</sup> in mass polymerization are represented in Figure 9, and those in emulsion polymerization in Figure 10.

Assuming that the  $Q'$  value of  $VCp$  is about 0.01 (near to  $VAc$ ), the plot of  $VCp$  lies almost on the same line in mass polymerization, but diverges widely in emulsion polymerization.



Concentrations of soap (g/100ml)

Fig. 7. The chain transfer action of soap molecule in mass polymerization.



Concentration of soap (g/100ml)

Fig. 8. The chain transfer action of soap molecule in emulsion polymerization.

Fig. 9. Relations between transfer constants or rate depression ratios and the Alfrey-Price's P-values of monomers in mass polym.

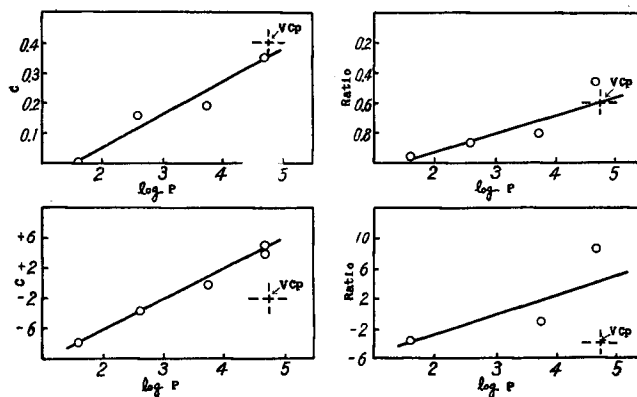


Fig. 10. Relations between transfer constants or rate depression ratios and the Alfrey-Price's P-values of monomers in emulsion Polymerization.

Acknowledgment— The authors gratefully acknowledge their indebtedness to the Ministry of Education of Japan for the financial support granted to them in executing

this work and also they wish to acknowledge their indebtedness to Professor Ichiro Sakurada.

#### References

- 1) W. D. Harkins; J. Am. Chem. Soc., **69**, 1428 (1947).
- 2) W. V. Smith a. R. H. Ewart; J. Chem. Phys., **16**, 592 (1948).
- 3) W. V. Smith; J. Am. Chem. Soc., **70**, 3695 (1948).
- 4) S. Okamura, M. Ohara, H. Sagawa a. M. Matsuoka; High Polymer Chem. (Japan), **3**, 125 (1946).
- 5) E. A. Hauser a. G. E. Perry; J. Phys. Coll. Chem., **52**, 1175 (1948).
- 6) P. D. Bartlett a. K. Nozaki; J. Am. Chem. Soc., **68**, 2377 (1946).
- 7) M. Matsumoto; High Polymer Chem. (Japan), **7**, 407 (1950).
- 8) Organic Synthesis; **30**, 106 (1950).
- 9) H. B. Klevens; Chem. Rev., **47**, 1 (1950).
- 10) S. G. Foord; J. Chem. Soc., **48**, (1940).
- 11) I. Sakurada; KOBUNSHI-GAIRON, p. 189.
- 12) I. Sakurada; High Polymer Chem. (Japan), **2**, 253 (1945).
- 13) I. Sakurada; KOBUNSHI-GAIRON, p. 196.
- 14) I. Sakurada; J. Chem. Ind. Japan, **47**, 135 (1944).
- 15) W. H. Lane; Ind. Eng. Chem., (analyt. ed.) **18** 295 (1946).
- 16) McBain a. S. G. Gupta; J. Coll. Sci., **8**, 474 (1953).
- 17) J. B. Schulman, A. H. Houghes, Biochem. J., **29**, 1243 (1935);  
R. S. Stearns a. W. D. Harkins, J. Chem. Phys. **15**, 496 (1947).
- 18) H. S. Klevens; J. Am. Chem. Soc. **72**, 3780 (1950).
- 19) T. Alfrey, Jr., J. J. Bohrer a. H. Mark; COPOLYMERIZATION, **66** (1952).
- 20) K. Katagiri, K. Uno a. S. Okamura; J. Polymer Sci., **15**, in press (1955).
- 21) " " " " in press (1955).