

A Study on the Soap-Free Emulsion Polymerization of Styrene

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Synopsis

A study on the soap-free emulsion polymerization of styrene has been accomplished in this work. The polymerization reaction was carried out in a batch reactor under isothermal condition. Potassium persulfate was used as an initiator. In our experiments, the effects of agitation speed, monomer concentration, and initiator concentration on the number and size of polymer particles, on the conversion of monomer and molecular weight of polymers were investigated. In addition, the systems in the presence of emulsifier or CaSO_3 were investigated and discussed in comparison with a system free of them.

INTRODUCTION

Emulsion polymerization is one of the most important processes for manufacture of polymers for coatings, adhesives, etc. Harkins¹ proposed a qualitative theory of emulsion polymerization in 1947, and later in 1948 the consequences were elaborated in kinetic terms by Smith and Ewart.² In 1968, Gardon³ had a series of discussions on the theory proposed by Smith and Ewart.

The concentrations of emulsifier in conventional emulsion polymerization are always above critical micelle concentration. But Roe⁴ in 1968 and Robb⁵ in 1969 have prepared polystyrene lattices under conditions when emulsifier concentrations were below critical micelle concentration. Matsumoto and Ochi⁶ also showed that stable polystyrene lattices could be prepared without any emulsifier.

For emulsifier-free emulsion polymerization in which no flocculation takes place, Fitch and Tsai⁷ in 1971 proposed a model of polymer particle formation, and developed a quantitative theory to predict the number of polymer particles formed. The effects of ionic strength, monomer concentration, initiator concentration, and temperature on the diameter of particles formed have been investigated by Goodwin et al.⁸ in 1973. Arai et al.⁹⁻¹¹ modified the theory proposed by Fitch and Tsai, and discussed the polymerization reaction rate and the effect of agitation speed on the reaction system in 1979-1981. In 1977, Goodall et al.¹² reported a study of the polymerization of styrene in water in the absence of emulsifier, and discussed the polymer particle size, particle number, molecular weight of polymer, and surface groupings of particles.

Several ways have been found to speed the reaction rate of emulsifier-free emulsion polymerization. By the addition of an alcohol to the reactants, Homola et al.¹³ has improved the polymerization reaction rates and yield.

Arai et al.¹⁴ speeded the reaction rates by adding inorganic substances, and expected to provide homogeneous dispersed composite materials. Sakota et al.,¹⁵ Ohtsuka et al.,¹⁶ and Zurkova et al.¹⁷ found the charge stability of polymer particles improved by copolymerization with ionic or hydrophilic monomers.

The present paper is to report a study of emulsifier-free emulsion polymerization of styrene. By changing the agitation speed, monomer concentration, and initiator concentration, the effects on the polymer particle number, particle size, monomer conversion and average molecular weight of polymers have been discussed and compared with the system including emulsifier or CaSO_3 .

EXPERIMENTAL

A. Materials

a. Styrene, chemical reagent grade, was purified through vacuum distillation (10 mmHg) twice before it was used as the monomer in polymerization reaction.

b. Potassium persulfate, chemical reagent grade, was used as an initiator directly without any further purification.

c. Sodium lauryl sulfate, chemical reagent grade, was used as an emulsifier directly without any further purification.

d. Calcium sulfite (CaSO_3) was prepared from the reaction of NaSO_3 with CaCl_2 in aqueous solution at 70°C for 24 hours. The precipitate formed (i.e., CaSO_3) was then purified through water washing, filtering, and drying several times, and milled into powder for use in the polymerization reaction.

B. Emulsion Polymerization

Emulsion polymerization was carried out in a four-neck flask reactor with thermometer, nitrogen inlet, agitator, and condenser. The temperature was kept at 70°C during polymerization reaction.

a. Conversion (X): The monomer conversion was determined by conventionally gravimetric method.

b. Size and number of polymer particles: Particle sizes were determined from shadowgraph examination of transmission electron micrographs. The mean particle size and particle number were calculated by:

$$\bar{d} = \left(\frac{\sum_{i=1}^N d_i^3}{N} \right)^{1/3} \quad (1)$$

and

$$N = \frac{6[M_o] X}{\pi \rho_p \bar{d}^3} \quad (2)$$

where

\bar{d} is the mean diameter of polymer particles

\tilde{N} is the number of particles measured

ρ_p is the density of polymer (= 1.06 g/cm³)

$[M_o]$ is the initial concentration of monomer

N is the particle number in unit volume

c. Concentration of monomer in polymer particles ($[M_p]$): Stop the polymerization reaction of sampling latex by adding hydroquinone aqueous solution (0.5 g/ℓ) and cooling. The monomer droplets in latex were removed by centrifugal method. Then the residual latex was divided into part A and part B. Part A was filtered and dried after adding hydroquinone methanol solution (0.5 g/ℓ). Part B was heated to 100°C in a closed vessel for 30 hours after adding K₂S₂O₈ aqueous solution (1 g/ℓ), and then dried. The weight fraction of monomer in particles was given by:

$$X_M = 1 - \frac{\left(\begin{array}{c} \text{weight of dried} \\ \text{part A} \end{array} \right) \times \left(\begin{array}{c} \text{weight of part B before} \\ \text{adding K}_2\text{S}_2\text{O}_8 \\ \text{aqueous solution} \end{array} \right)}{\left(\begin{array}{c} \text{weight of dried} \\ \text{part B} \end{array} \right) \times \left(\begin{array}{c} \text{weight of part A before} \\ \text{adding methanol} \\ \text{solution} \end{array} \right)} \quad (3)$$

Assuming the volumes of monomer and polymer in monomer swollen particles additive, then

$$[M_p] = \frac{X_M}{\frac{X_M}{\rho_M} + \frac{1 - X_M}{\rho_p}} \times \frac{1000}{M_w} \quad (4)$$

where

$[M_p]$ is the monomer concentration in a polymer particle

ρ_M is the density of monomer (= 0.902 g/cm³)

M_w is the molecular weight of monomer (= 104.2 g/mole)

d. Viscosity average molecular weight (\bar{M}_v): The viscosity average molecular weight of polymers was measured by Ubbelohde Capillary Viscometer with toluene as the solvent, and calculated by Mark-Houwink equation:

$$[\eta] = K\bar{M}_v^a \quad (5)$$

where $[\eta]$ is the intrinsic viscosity, the values of a and K are 0.72 and 0.92×10^{-5} , respectively, at 30°C.¹⁸

RESULTS AND DISCUSSION

In emulsion polymerization, the agitation speed is one of the important operation conditions to influence the monomer conversion, molecular weight of polymers, etc. Figure 1 shows the effect of agitation speed on monomer conversion. The conversion was almost the same initially and then gradually diverged from each other when the agitation speed changed from 250 rpm to 400 rpm. A lower conversion obtained at higher agitation

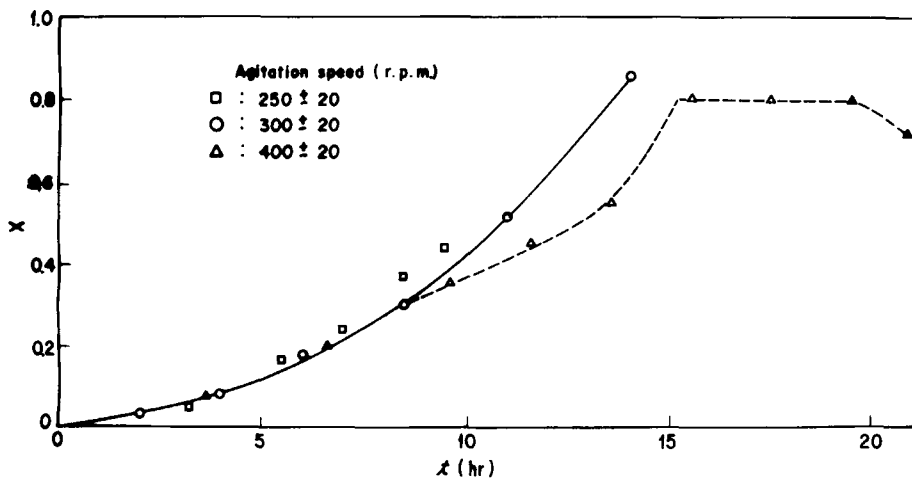


Fig. 1. Conversion-time curves: $[M_o] = 1.0$ mole/ ℓ -H₂O, $[I_o] = 1.0 \times 10^{-3}$ mole/ ℓ -H₂O.

speed resulted from the fact that some of the polymers in emulsion stuck on the agitator. The agitation speed was set on 300 rpm in this work where the amount of polymers stuck on agitator was negligible under all experimental conditions. Figure 2 shows the concentration of monomer in polymer particles as a function of conversion under various experimental conditions. From which the polymerization reaction was demonstrated to be a chemical-controlling reaction. The saturated concentration of monomer in polymer particles was read as 5.5 mol/ ℓ before the disappearance of monomer droplet. A corresponding conversion ($X = 0.41$) was indicated in the figure also. Figure 3 showed the electron micrograph of polymer particles in emulsions. Where the particles grew rather uniformly with varying the reaction time. Figure 4 showed the relationship between average diameter of particles and conversion for different concentrations of monomer $[M_o]$ and initiator $[I_o]$ in feed. Larger particles formed in the system with low initiator concentration and high monomer concentration as expected.

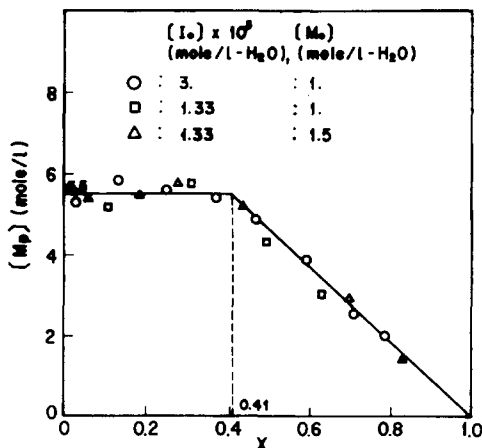


Fig. 2. Concentration of styrene in polymer particles as a function of conversion.

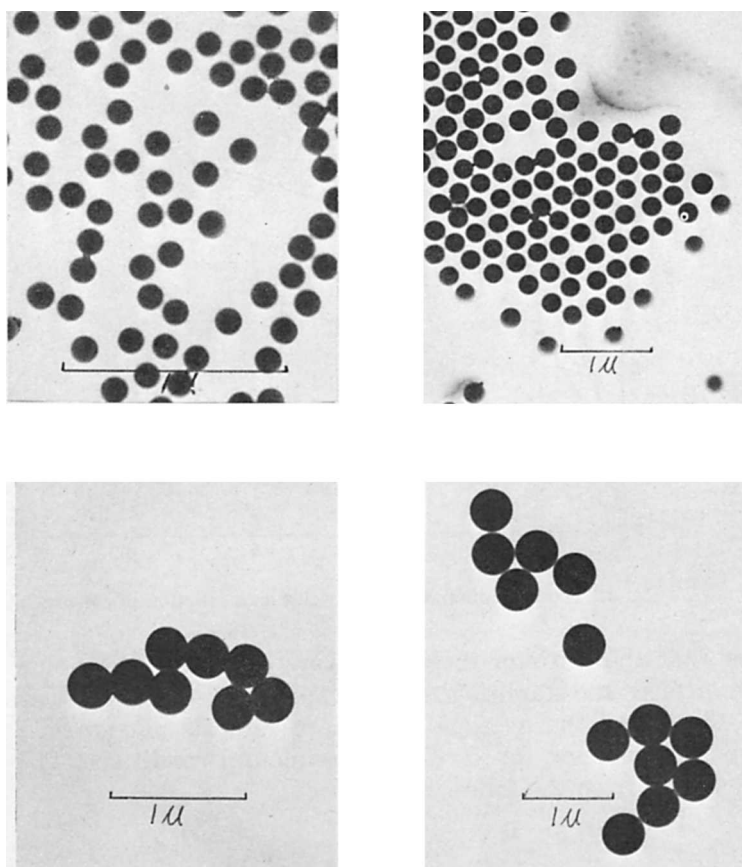


Fig. 3. Electron micrograph of latex: $[M_0] = 1.0 \text{ mole/}\ell\text{-H}_2\text{O}$, $[I_0] = 3.0 \times 10^{-3} \text{ mole/}\ell\text{-H}_2\text{O}$,

	$t(\text{h})$	$X(\%)$	$\bar{d}(\text{nm})$
(A)	1.0	3.5	129
(B)	3.0	13.6	241
(C)	5.0	25.3	330
(D)	9.9	70.5	477

From the plots of conversion versus time in soap-free emulsion polymerization shown in Figures 5 and 6, it was found that there existed a limiting conversion ($= 90\%$) in each case, the higher initiator concentration resulted in higher conversion because more particles would generate in the system with higher initiator concentration as in Figure 9. Figures 7 and 8 showed the effect of monomer concentration in feed on the conversion-time curve. A lower conversion was obtained in the case of higher monomer concentration because fewer polymer particles would form as shown in Figure 9. These results might be explained as follows: In the system with more initiator, it of course generated more radicals, which were the main source in forming polymer particles. But in the system with high monomer concentration, the initiator molecules did not increase, so the particle number would reduce to some extent to decrease the surface area of total particles

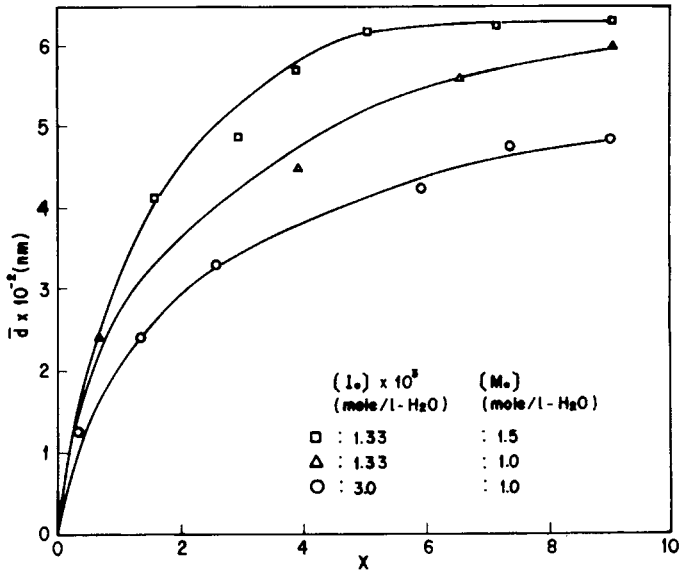


Fig. 4. Average diameter of particles as a function of conversion.

in order that the initiator molecules were enough to distribute over all particle surfaces and stabilize them through a balance of electrical strength. Figure 10 showed the average number of radicals per particle (\bar{n}) as a function of conversion for various experimental conditions. The \bar{n} value was calculated from the following equation:

$$[M_o] \frac{dx}{dt} = k_p [M_p] \frac{\bar{n}}{N_A} N \quad (6)$$

where N_A is Avogadro number, k_p is the rate constant for propagation ($= 316 \ell/g\text{-mole-sec}$), and other symbols have been mentioned above. A

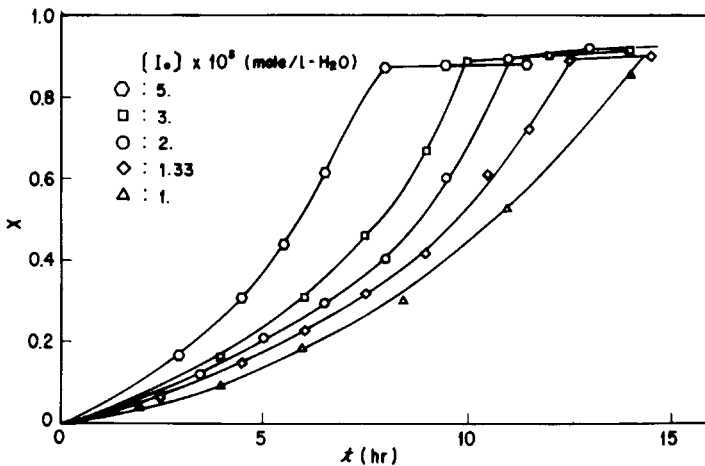


Fig. 5. Conversion-time curves: $[M_o] = 1.0 \text{ mole}/\ell\text{-H}_2\text{O}$.

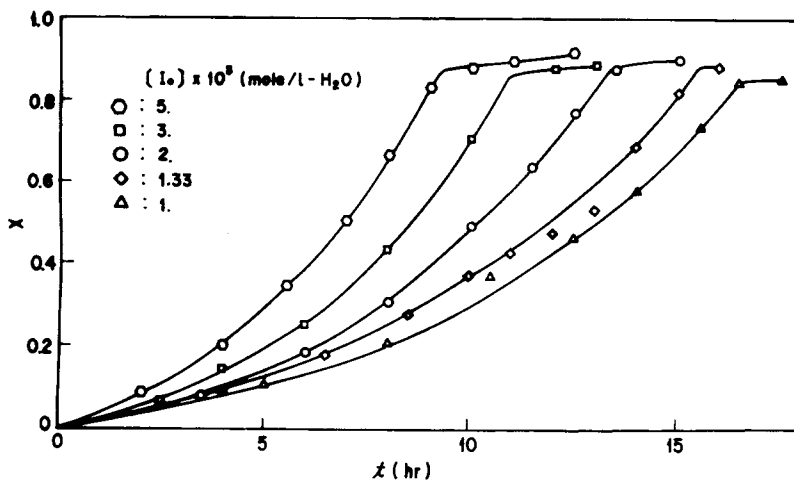


Fig. 6. Conversion-time curves: $[M_0] = 1.25 \text{ mole/l-H}_2\text{O}$.

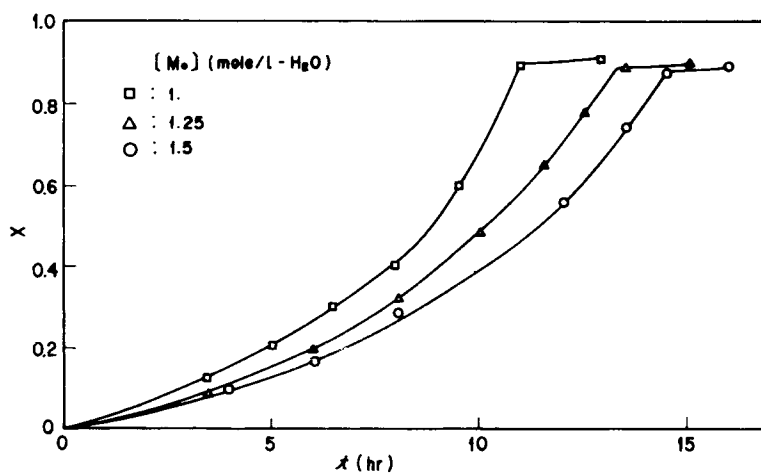


Fig. 7. Conversion-time curves: $[I_0] = 2.0 \times 10^{-3} \text{ mole/l-H}_2\text{O}$.

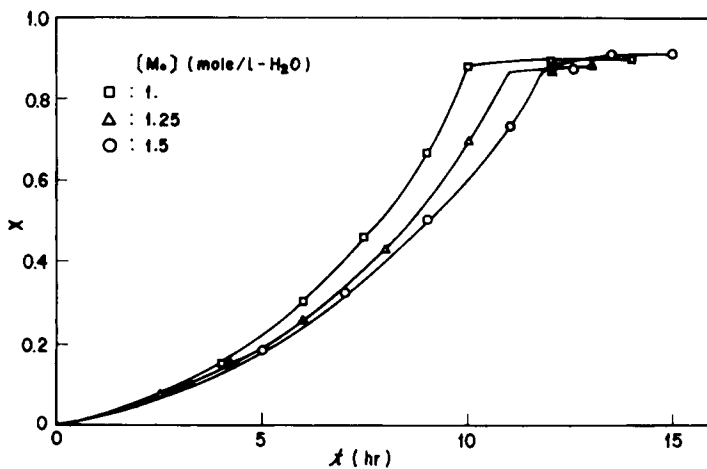


Fig. 8. Conversion-time curves: $[I_0] = 3.0 \times 10^{-3} \text{ mole/l-H}_2\text{O}$.

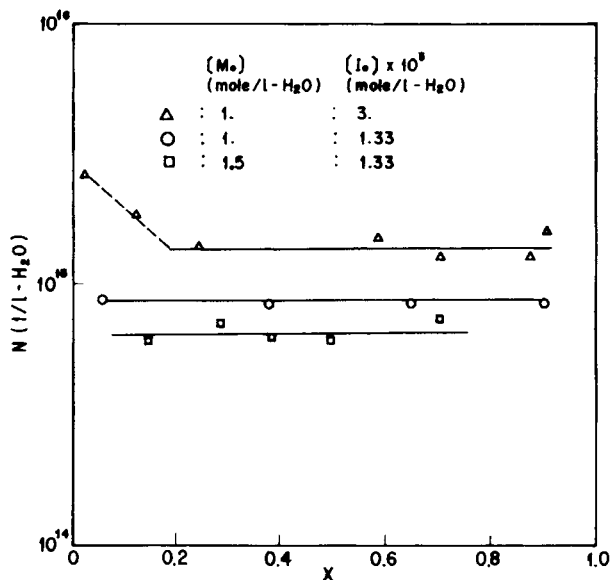


Fig. 9. Number of polymer particles per liter water as a function of conversion.

higher \bar{n} value was obtained in the case of high monomer concentration or low initiator concentration. Because termination reaction became more difficult to achieve in larger particles especially when the viscosity (or conversion) of the system was high. It was referred to the "gel effect." All the \bar{n} values obtained in our experiments were much higher than 0.5 as proposed by Smith-Ewart in emulsion polymerization. The effect of monomer

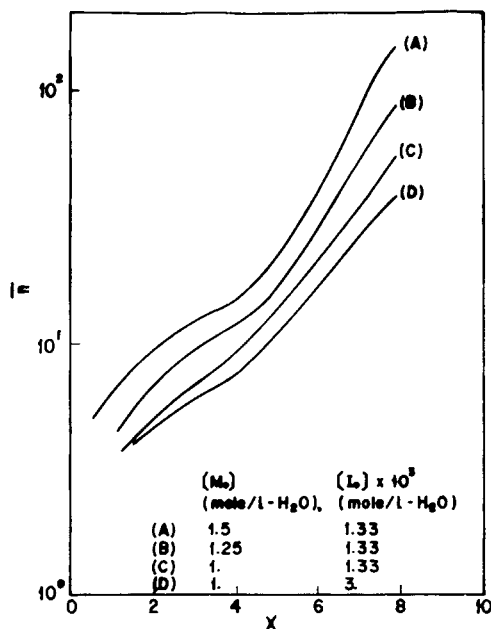


Fig. 10. Average number of radicals in a polymer particle as a function of conversion.

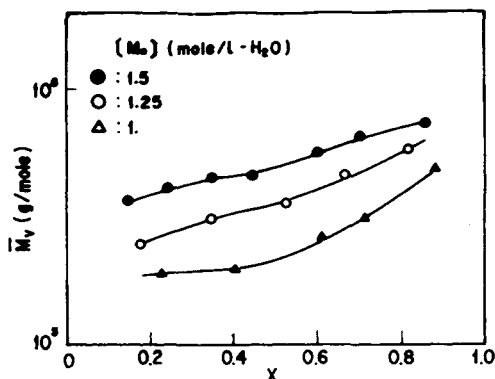


Fig. 11. Viscosity average molecular weight of polymer as a function of conversion, $[I_0] = 1.33 \times 10^{-3}$ mole/l- H_2O .

concentration on molecular weight of polymer (M_v) was shown in Figure 11. The higher the monomer concentration, the higher the molecular weight of polymer would be. Also \bar{M}_v increased slightly with increasing the conversion. The effect of initiator concentration on molecular weight of polymer was shown in Figure 12. Conversely, the lower the initiator concentration, the higher the molecular weight of polymer would be. These results were attributed to the gel effect. The system with high gel effect (i.e., high \bar{n} value) would produce polymers with higher molecular weight.

With all the above results, the soap-free emulsion polymerization could be characterized by low reaction rate, large size, and uniform size distribution of polymer particles, lower molecular weight of polymers, and fewer particles formed in comparison with the system including emulsifier. Table I showed the difference of some properties for soap-free and soap with emulsion polymerizations. Figure 13 showed the conversion-time curves for the systems without or with emulsifier.

In order to accelerate the reaction rate, a certain amount of $CaSO_3$ was added in the system as proposed by Arai et al.,¹⁴ who studied the effect of $CaSO_3$ on the soap-free emulsion polymerization of MMA. From which the reaction rate was found to be accelerated significantly. And it was explained

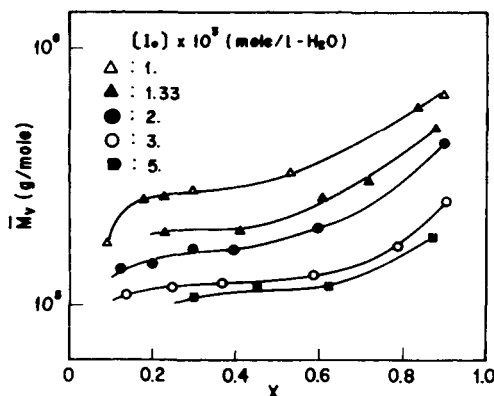


Fig. 12. Viscosity average molecular weight of polymer as a function of conversion, $[M_0] = 1.0$ mole/l- H_2O .

TABLE I
 Properties of Emulsion System at Different Concentrations of Emulsifier ($[E]$)
 $[M_o] = 1 \text{ mole/l-H}_2\text{O}$ $[I_o] = 3 \times 10^{-3} \text{ mole/l-H}_2\text{O}$

$[E]$ (g/l-H ₂ O)	X(%)	\bar{d} (nm)	N (1/l-H ₂ O)	\bar{M}_v (g/mole)
1	90.4	481	1.52×10^{16}	2.69×10^5
1	97.8	206	2.1×10^{16}	3.53×10^5
2	100	68	5.97×10^{17}	6.98×10^5
3	100	57	1.0×10^{18}	8.17×10^5

as: more radicals generated from a redox reaction of CaSO_3 with $\text{K}_2\text{S}_2\text{O}_8$ (initiator), therefore higher conversion was observed in the presence of CaSO_3 . Figure 14 showed the effect of CaSO_3 on the conversion-time curve of our system. Contradictory to our expectation, when the concentration of CaSO_3 was below $3 \times 10^{-4} \text{ mole/l-H}_2\text{O}$ (about the solubility of CaSO_3 in water at 70°C), the conversion curve did not change apparently. When the concentration of CaSO_3 was oversaturated ($1.0 \times 10^{-1} \text{ mole/l-H}_2\text{O}$), the conversion decreased largely. This observation was totally different from the case of Arai. From the observation of polymer particle size in Figure 15 for systems with different concentration of CaSO_3 , the particle size increased, and the particle number decreased with increased concentration of CaSO_3 . The flocculation among particles seemed to become more serious in the presence of CaSO_3 . Especially when the concentration of CaSO_3 was supersaturated, some CaSO_3 powder coexisted in the system, then not only serious flocculation among particles occurred, but also a large amount of radicals captured by the CaSO_3 powder. So we found the reaction mixture like a dispersion system instead of emulsion, and a very low conversion was obtained. From the above discussion, we might conclude that the ionic strength of styrene-water system increased by the addition of CaSO_3 , then

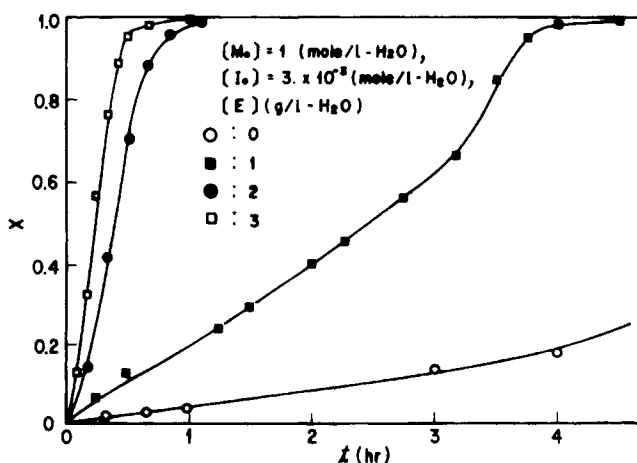


Fig. 13. Conversion-time curves: $[M_o] = 1.0 \text{ mole/l-H}_2\text{O}$.

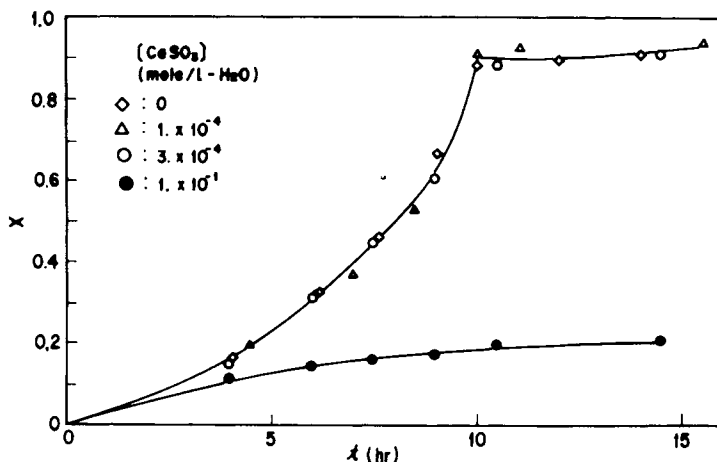


Fig. 14. Conversion-time curves: $[\overline{M}_0] = 1.0 \text{ mole/}\ell\text{-H}_2\text{O}$, $[I_0] = 3.0 \times 10^{-3} \text{ mole/}\ell\text{-H}_2\text{O}$.

each particle needed more hydrophilic groups from $\text{K}_2\text{S}_2\text{O}_8$ to stabilize itself, so the particle number would decrease through coalescence. Therefore, the reaction rate did not increase significantly by adding CaSO_3 although there have been more radicals generated from a redox reaction. Table II showed the difference of some properties in the system with or without CaSO_3 added. The molecular weight of polymer was almost unchanged when unsaturated CaSO_3 was added. But the molecular weight of polymer increased to some extent when supersaturated CaSO_3 was added in the system.

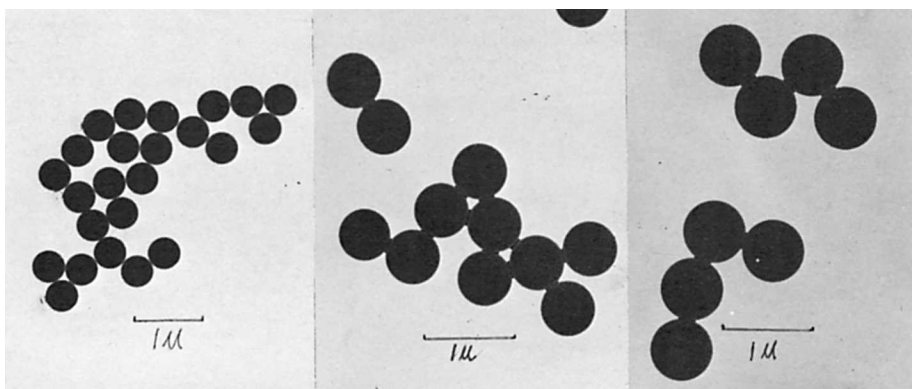


Fig. 15. Electron micrograph of latex: $[\overline{M}_0] = 1.0 \text{ mole/}\ell\text{-H}_2\text{O}$, $[I_0] = 3.0 \times 10^{-3} \text{ mole/}\ell\text{-H}_2\text{O}$, $[\text{CaSO}_3]$ (mole/ℓ-H₂O)

		X(%)	\bar{d} (nm)
(A)	0	90.4	481
(B)	1.0×10^{-4}	94.2	610
(C)	3.0×10^{-4}	91.0	690

TABLE II
 Properties of Emulsion System at Different Concentrations of CaSO_3
 $[\text{M}_0] = 1 \text{ mole/l-H}_2\text{O}$ $[\text{I}_0] = 3 \times 10^{-3} \text{ mole/lH}_2\text{O}$

$[\text{CaSO}_3]$ (mole/l-H ₂ O)	X(%)	\bar{d} (nm)	$N(1/l\text{-H}_2\text{O})$	$\bar{M}_v(\text{g/mole})$
0	90.4	481	1.52×10^{15}	2.69×10^{15}
1×10^{-4}	94.24	610	7.79×10^{14}	2.89×10^{15}
3×10^{-4}	91.0	690	5.2×10^{14}	3.34×10^{15}

References

1. W. D. Harkins, *J. Am. Chem. Soc.*, **69**, 1428 (1947).
2. W. V. Smith and R. H. Ewart, *J. Chem. Phys.*, **16**, 6, 592 (1948).
3. J. L. Gardon, *J. Polym. Sci.*, A-1, **6**, 623 (1968).
4. C. P. Roe, *Ind. Eng. Chem.*, **60**, 9, 20 (1968).
5. I. D. Robb, *J. Polym. Sci.*, A-1, **7**, 417 (1969).
6. T. Matsumoto and A. Ochi, *Kobunshi Kagaku*, **22**, 481 (1965).
7. R. M. Fitch and C. H. Tsai, *Polymer Colloids*, Plenum, New York, 1971.
8. J. W. Goodwin, J. Hearn, C. C. Ho, and R. H. Ottewill, *Br. Polym. J.*, **5**, 347 (1973).
9. M. Arai, K. Arai, and S. Saito, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 3655 (1979).
10. M. Arai, K. Arai, and S. Saito, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 2811 (1980).
11. K. Arai, M. Arai, S. Iwasaki, and S. Saito, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 1203 (1981).
12. A. R. Goodall, M. C. Wilkinson, and J. Hearn, *J. Polym. Sci., Polym. Chem. Ed.*, **15**(9), 2193 (1977).
13. A. M. Homola, M. Inone, and A. A. Robertson, *J. Appl. Polym. Sci.*, **19**, 3077 (1975).
14. M. Arai, K. Arai, and S. Saito, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 1021 (1982).
15. K. Sakota and T. Okaya, *J. Appl. Polym. Sci.*, **20**, 1725 (1976).
16. Y. Ohtsuka, H. Kawaguchi, and Y. Sugi, *J. Appl. Polym. Sci.*, **26**, 1637 (1981).
17. E. Zurkova, K. Bouchal, D. Zdenkova, Z. Pelzbauer, F. Svec, and J. Kalal, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 2949 (1983).
18. J. Brandrup, *Polymer Handbook*, Interscience Publishers, New York, 1966.

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