

The Emulsion Polymerization of Methyl Methacrylate

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The work of Harkins¹ and Smith² first put the mechanism and kinetics of emulsion polymerization on a firm basis. They showed that the equation

$$R_p = k_p N [M] / 2N_0 \quad (1)$$

(where R_p is the rate of polymerization in mole/liter sec., k_p is the propagation constant in liter/mole sec., N is the number of particles per liter H_2O , N_0 is Avogadro's number and $[M]$ is the monomer concentration in moles/liter in the monomer-polymer particles) agreed well with the observed rates of styrene polymerization for latices with particles less than 0.1μ in diameter. This equation can be derived by assuming initiation in the aqueous phase, the entry of single radicals into the monomer-polymer particle, no transfer of radicals out of the particle, and very rapid termination as soon as a radical enters a particle already containing a polymerizing radical.

The last assumption can become invalid for two reasons: the particle may grow to a volume sufficient to allow two radicals to grow simultaneously for an appreciable time, or the termination constant k_t could be so low as to prevent rapid termination, even in small particles. The first case, the volume effect, was discussed by Haward³ and recently by Roe and Brass⁴ and by Vanderhoff⁵ and co-workers. That k_t can decrease during the course of the polymerization was proposed by Norrish and Smith⁶ and by Trommsdorff⁷ and is sometimes known as the Trommsdorff or "gel" effect. Gerns⁸ has shown that the emulsion polymerization of styrene shows a weak gel effect at about 70% conversion and that several radicals per particle are polymerizing simultaneously. Since methyl methacrylate is subject to a strong gel effect in bulk polymerization, we have examined the kinetics of the emulsion polymerization of this monomer and compared them with the theories developed for styrene.

EXPERIMENTAL

In order to obtain reproducible results, an all-glass system, free of oxygen was used. Since the reaction is strongly exothermic, cooling as well as heating was provided. The apparatus is shown in Figure 1. The reaction vessel, a three-necked flask, was fitted with a stirrer, sampling tube, thermometer, nitrogen inlet, and catalyst addition tube. The sampling tube was arranged by means of a three-way stopcock so that no air was sucked into the reaction after a sample was taken. During its entire course, the reaction was kept under a positive pressure of 10 mm. Hg of oxygen-free nitrogen.

The polymerizations were run at $59.5 \pm 0.5^\circ C$. The usual charge was as follows: deionized water, 1200 g.; distilled monomer, 600 g.; Tergitol "7" (25% active), 4.5 g.; and $K_2S_2O_8$, 15 ml. of a 4% solution.

Some typical conversion vs. time curves are shown in Figure 2. Conversion was determined gravimetrically. As can be seen, only the curve for the polymerization that had an ultimate diameter of 0.11μ is linear. In the large particle runs (diameter greater than 0.2μ), a large portion of the polymerization occurs in a relatively short span of time, preceded by a period of slow reaction. That this period is not a retardation period can be shown by the rate of reaction per particle in the initial or linear part of the reaction as given in Table I. The observed rates agree well with those calculated from eq. (1) with a k_p of 1.2×10^3 l./mole-sec. This value was estimated from the data of Chinmayandan and Melville.⁹ The monomer concentration was calculated from the monomer/polymer ratio, which was 2.3 to 1 for large particles and 1.4 to 1 for small ones. These ratios were determined from the disappearance of the monomer layer during the polymerization and also by monomer analysis of samples removed during the polymerization by the bromine-pyridine sulfate method. Some increase in $[M]$ occurs as particles grow during the

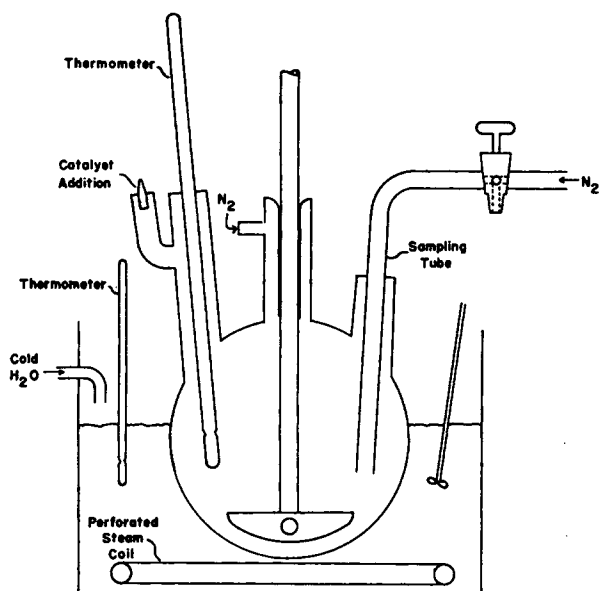


Fig. 1. Schematic diagram of the experimental apparatus.

polymerization, but an average value for each run was used in the calculations.

N was determined from the particle diameter, which was determined by light transmission measurements and electron microscopy.

Light transmission was measured on a Beckman DU spectrophotometer to which a collimator had been added between the sample and the photo cell to prevent false readings due to forward scattering. The equations and curves were calculated from the

TABLE I
Rate of Polymerization of MMA in Emulsion

Run	Monomer	Particle diameter, μ	Initial rate $\times 10^4$, moles/l. H_2O /sec.		Rate/particle $\times 10^{21}$
			Obs.	Calc.	
M-1	MMA	0.44	0.83	0.65	8.9
M-2	"	0.38	1.15	1.02	7.9
M-3	"	0.28	2.78	2.52	7.8
M-4	"	0.13	10.3	12.0	5.1
M-5	"	0.11	16.7	18.0	5.5
S-1	Styrene	0.15	2.10	2.4	0.74

Mie theory by Dr. S. Hochberg of this laboratory. More recently, similar calculations have been published by Heller.¹⁰ Agreement between particle sizes obtained by light transmission and electron microscopy on the same material was very good. The uniformity of the latex particles allowed us to assume that N was constant through most of the polymerization.

For the purpose of comparison one run was made with styrene as monomer (Fig. 3). The agreement between calculated and observed rates is good. The curve also shows a mild acceleration in rate at about 60% conversion, in agreement with the data of Gerrens.⁸ Thus, initially the polymerization of methyl methacrylate proceeds normally, and the predicted rates of polymerization are obtained under the conditions used.

At rates of stirring so low that the monomer col-

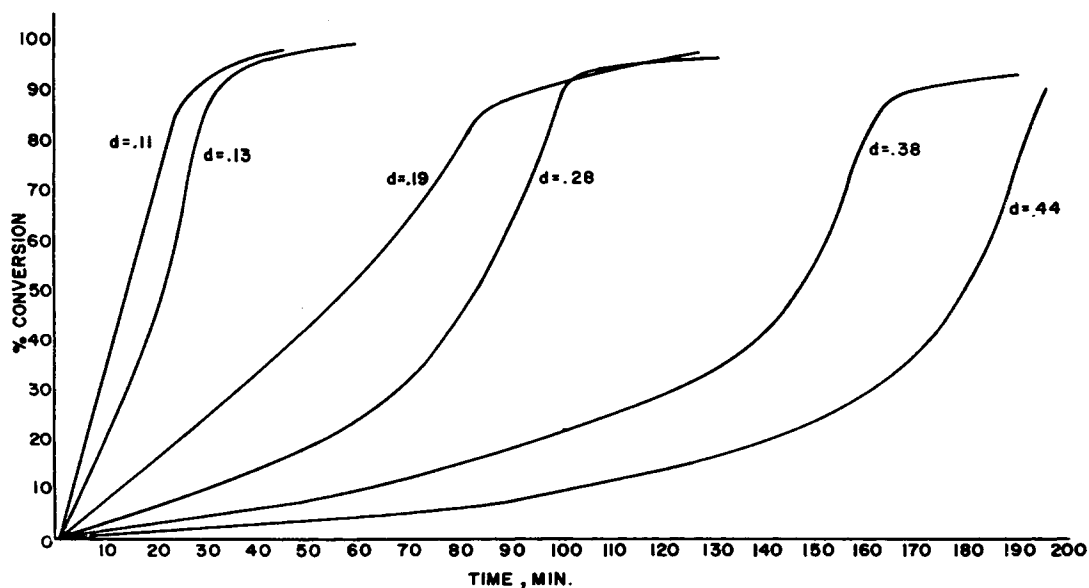


Fig. 2. Conversion-versus-time curves for the emulsion polymerization of methyl methacrylate. The final particle diameters (in microns) of the various experiments are shown.

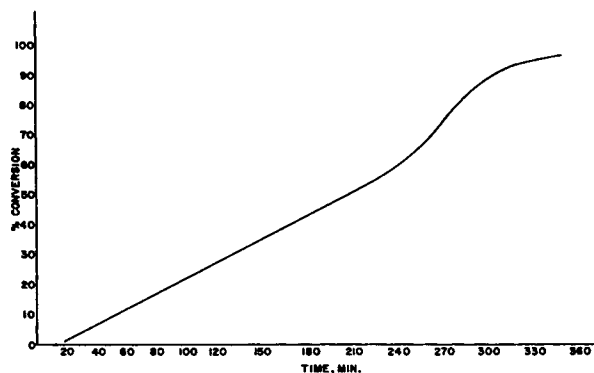


Fig. 3. Conversion-vs.-time curve for the emulsion polymerization of styrene.

lects on the top as a separate layer, the reaction kinetics change, and the square root of conversion is a linear function of time to better than 90% conversion. It seems likely that under these condi-

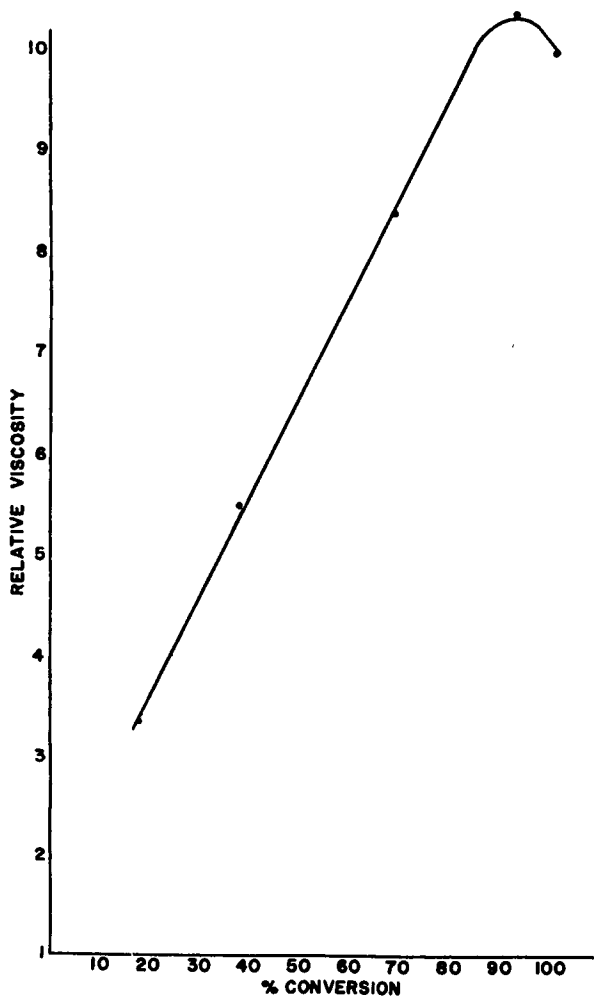


Fig. 4. Relative viscosity (at 0.5% solids) as a function of conversion for a single run.

TABLE II
Effect of Stirring Rate on Particle Size

Rate, rpm	Size, μ
75	0.29
125	0.33
200	0.32
300	0.32
400	0.31

tions the reaction is diffusion-controlled. At higher stirring rates, the effect of agitation on particle size is negligible (Table II).

When molecular weight is examined as a function of conversion, it is found that simultaneously with the increase in rate an increase in molecular weight takes place. Polymer prepared during the final slow stage of conversion is again lower in molecular weight (Fig. 4).

DISCUSSION

The most significant difference between the emulsion polymerization of styrene and of methyl methacrylate is probably the strong acceleration observed during the polymerization of the latter. As was shown, styrene shows some deviation from ideal kinetics at high conversion due to a weak gel effect. Since the polymerization of methyl methacrylate is subject to a strong gel effect in bulk,¹¹ it is not very surprising that the same behavior is observed in emulsion. It was expected that this would not appear, though, until all the free monomer had been used up, since the polymerization up to that point occurs in a fairly constant environment and k_t should be relatively constant. However, as can be seen (Fig. 2), deviations from standard kinetics already appear at less than 10% conversion, especially with larger particles. It was therefore suspected that the number of radicals was increasing earlier because of the volume effect. Since this work was started, papers by Roe and Brass⁴ and by Stockmayer¹² have been published, showing that such an effect must be expected to occur at lower particle sizes for low values of k_t . Since k_t for methyl methacrylate at 30% conversion is about two orders of magnitude lower than its initial value,¹³ the increase in the number of radicals per particle should occur at lower volumes than for styrene, as has actually been observed.

The average number \bar{n} of radicals per particle is:¹²

$$\bar{n} = R_p N_0 / k_p [M] N = a I_0(a) 4 I_1(a) \quad (2)$$

where I_0 and I_1 are hyperbolic Bessel functions and the parameter a is given by

$$a^2 = \frac{8}{k_t \tau} = \frac{16fk_d[I]N_0^2v}{k_t N} \quad (3)$$

in which v is the volume of growing particles (in liters), τ is the average time between successive entries of free radicals into a particle, f is efficiency of radical capture, $2fk_d[I]$ is the rate of radical capture (in mole/liter-second), and k_t , N_0 have the meanings given before.

For very small a , eq. (2) reduces to $\bar{n} = 1/2$, which corresponds to the ideal case of Smith and Ewart, as in eq. (1).

When a is not negligibly small, it has to be calculated from eq. (3). For this purpose, the values of the factors in the right side of eq. (3) must be known or estimated. The value for v , the volume of the growing particle, was calculated from the conversion and the monomer-polymer ratio as determined by analysis. The initiator concentration was known; k_d , the rate of decomposition, was obtained from the literature.¹⁴ The termination constant k_t is reported to be 8×10^7 at low conversion.⁹ Since the monomer, almost from the beginning of the reaction, polymerizes in an environment equivalent to about 30% conversion (as determined from the monomer/polymer ratio), we used the value 8×10^5 in the calculations. Since methyl methacrylate is soluble in water to about 0.15 moles/liter, we assumed that f was nearly 1 and constant.¹⁵

Our attempts to fit our data to these equations failed; the observed rates rose much more rapidly than the calculated rates. Roe and Brass⁴ have assumed that during the polymerization of styrene to large particles the efficiency of radical capture increases proportionally to $v^{2/3}$. We made the same assumption and also reasoned that if the efficiency is proportional to particle surface area it must be proportional to particle number, at least at low values of f . Thus, we took

$$f = ANv^{2/3} \quad (4)$$

where A is an experimental constant. By matching our data to one point of an experimental run we obtained the value $A = 1.4 \times 10^{-6}$. With this value we then calculated \bar{n} at various conversions for two polymerizations in which the final particle diameters were 0.28μ and 0.38μ . The agreement is good, as shown in the calculations of Table III for a particle diameter of 0.28μ . Thus, the equations of Stockmayer will predict the kinetics of the

TABLE III
Average Number of Growing Radicals per Particle as a Function of Conversion^a

Conversion, %	$v \times 10^{18b}$	f	a^2	\bar{n} (calc.) ^c	\bar{n} (obs)
6	2.46	0.09	0.568	0.52	0.50
10	4.10	0.12	1.33	0.57	0.57
14	5.95	0.16	2.48	0.64	0.66
18	7.7	0.19	3.92	0.71	0.69
22	9.4	0.22	5.34	0.77	0.80
26	11.1	0.24	6.98	0.85	0.85
30	12.8	0.27	8.88	0.92	1.50

^a Calculations based on the combination of eqs. (3) and (4): $a^2 = (16Ak_d[I]N_0^2v^{2/3}/k_t)$, for $k_d = 7 \times 10^{-6}/\text{sec.}$, $[I] = 1.8 \times 10^{-3}$ moles/l., and $k_t = 8 \times 10^5$.

^b v is determined from the diameter of the final particle, the density of the polymer (1.19), the monomer/polymer ratio, and the density of the monomer.

^c Calculation of \bar{n} from a^2 according to Stockmayer.¹²

emulsion polymerization of methyl methacrylate if one assumes that f is small. It is realized that eq. (4) is valid only in a limited region and will fail when the diameter of the final particles is less than 0.1μ .

According to Flory,¹⁶ if the primary radicals can diffuse freely to the surface of the particles, low efficiency of radical capture cannot be due to the competitive process of mutual termination in the aqueous phase. One possible explanation of low radical capture efficiency is the presence of sufficient oxygen or other inhibitor in the aqueous phase; it is known that methacrylate radicals react rapidly with oxygen in the aqueous phase.¹⁷ However, this mechanism cannot explain proportionality between efficiency and particle surface area.

Another possible fate for radicals in the aqueous phase is reaction with dissolved monomer and formation of new particles. This would result in a rapid increase in rate. It would also lead to broad particle size distribution, and electron micrographs show our particles to be remarkably uniform in size (Fig. 5).

A third and much more attractive explanation is that diffusion of the negatively charged primary radicals is greatly retarded by electrostatic repulsion due to the net negative charge on the particle surface caused by the anionic emulsifier used. If diffusion is sufficiently retarded and the number of particles is small enough, mutual termination in the aqueous phase can compete for the radicals. An exact calculation of the electrostatic effect is prohibitive, but approximate expressions^{18,19} suffice to show that the magnitude is adequate for the pur-

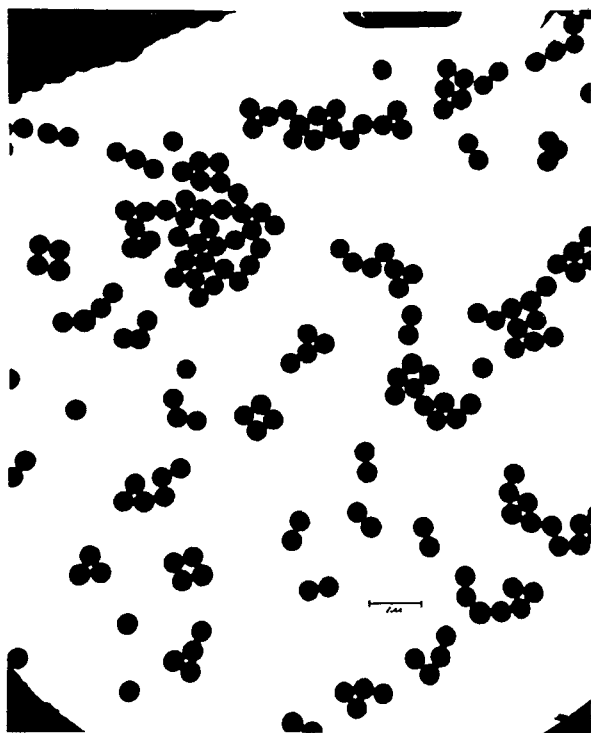


Fig. 5. Electron micrograph of a PMMA latex; enlargement, 17,500.

pose. Moreover, the dependence of the efficiency on the square (or still higher powers) of the particle radius can be understood.

CONCLUSION

The following conclusions can be drawn from this work. The emulsion polymerization of methyl methacrylate proceeds in accordance with the theories proposed by Harkins and Smith and recently extended by Roe and Brass and by Stockmayer, if one takes into account the special features encountered in polymerizing this monomer. Due to the gel effect the termination constant is low from the start of the polymerization, thus allowing the rate of polymerization to accelerate at smaller particle volumes or lower conversions than for styrene. Once the free monomer has been used up, constant conditions no longer prevail within the monomer-polymer particle, and the rate of polymerization becomes extremely rapid due to a continuous decrease of the rate of termination. However, up to the point at which free monomer disappears (the period of constant environment), existing theories can be used to predict the rate of reaction with considerable success.

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Synopsis

The kinetics of the emulsion polymerization of methyl methacrylate have been examined in the light of recent advances in theory. It has been found that, if allowance is made for the decrease in the termination rate, the kinetics of the reaction can be predicted up to the point where all monomer is absorbed by growing monomer-polymer particles. In order to do this it must be assumed that the efficiency of initiation is low and is a function of the size and number of growing particles in the latex. A possible explanation for these observations is discussed.

Résumé

La cinétique de la polymérisation en émulsion du méthacrylate de méthyle a été étudiée sur la base des théories nouvelles. Si on admet une diminution de la réaction de rupture, la vitesse de polymérisation peut être prédite avec précision jusqu'à disparition des gouttelettes de monomère. Il faut de toute façon admettre que le rendement de l'initiation est faible et dépend de la grandeur et du nombre des

particules de polymère. On essaie d'interpréter ces observations.

Zusammenfassung

Die Kinetik der Emulsionspolymerisation des Methylmethacrylats wurde mit Hinsicht auf die neuen Fortschritte der Theorie untersucht. Wenn die Verminderung der

Abbruchsreaction berücksichtigt wird, kann die Polymerisationsgeschwindigkeit bis zum Verschwinden der Monomerentropfen genau vorausgesagt werden. Man muss allerdings annehmen dass der Wirkungsgrad der Startreaction niedrig ist und von der Grösse und Zahl der Polymerteilchen abhängig ist. Es wird versucht diese Beobachtungen zu erklären.

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