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Some Observations on the Emulsion Polymerization of Ethyl Methacrylate Initiated by Potassium Persulfate at 50°C in a Phosphate Buffer Solution of pH 6.85 and at a Low Monomer/Water Ratio

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ABSTRACT

The emulsion polymerization of ethyl methacrylate initiated by the potassium persulfate (I) at 50° C in the presence of an anionic detergent (S), i.e., sodium lauryl sulfate at a low monomer/water ratio, has been investigated kinetically by the conventional dilatometric and gravimetric methods in a phosphate buffer solution of pH 6.85. The number of latex particles per mL of the aqueous phase has been estimated by the soap titration technique, and the average number of latex particles (N) per mL of the aqueous phase has been found to be 10^{14} to 10^{16}, depending upon the experimental conditions. At zero conversion, the rate of polymerization (V_p) may be written as

$$V_p \propto (I)^{0.56 \pm 0.03} \times (S)^{0.72 \pm 0.04}$$

where (I) and (S) denote initiator and soap concentrations, respectively. The viscosity-average molecular weight ($\overline{M}_v$) of the polymer at 28% conversion has been found to be

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$$(\overline{M}_v) \propto (I)^{-0.44 \pm 0.05}$$

At higher conversions (i.e., from 20 to 60%), the rate of polymerization (R_p), believed to be the steady-state rate in the light of the Harkins-Smith-Ewart-Gardon theory, has been found to be

$$(R_p) \propto (I)^{0.42 \pm 0.04} \times (S)^{0.62 \pm 0.06}$$

while the $(\overline{M}_v)$ of the polymers at 66% conversion is given by

$$(\overline{M}_v) \propto (I)^{-0.30 \pm 0.05}$$

At zero conversion,

$$(\overline{M}_v) \propto (I)^{-0.55 \pm 0.03}$$

Injection of initiator or detergent late in a run (i.e., between 20 to 40% conversion) has been found to increase the rate of polymerization. It is suggested that the primary initiation occurs in the aqueous phase by the primary radicals, viz., $SO_4^{\cdot -}$ and OH, and secondary initiation occurs in the detergent micelles by the olegomeric radicals.

INTRODUCTION

The emulsion polymerization of the sparingly water soluble monomer, viz., styrene, has been studied in detail and reviewed from time to time [1-8], but very little information is available of the emulsion polymerization of ethyl methacrylate. This monomer has very low solubility (about 0.5%, v/v, at 30°C), and so it may behave like styrene during emulsion polymerization. Here we report some of the observations made in the emulsion polymerization of ethyl methacrylate initiated by potassium persulfate at 50°C in a phosphate buffer solution of pH 6.85 and at low monomer/water ratio.

EXPERIMENTAL

The reagents were all AR/GR grade of BDH and E. Merck. Potassium persulfate was recrystallized thrice from the double distilled water. Soaps were purified by the methods of Paluch [9] and Dunn et al. [10]. The polymerization was carried out in a 4-necked 1 L round-bottomed flask fitted (with a Hg seal stirrer) to a dilatometer containing a magnetic stirrer via a 3-mm stopcock. The whole assembly could be housed in a large electrically heated and controlled water thermostat (t ± 0.20° C). All the reagents were mixed in the liter flask according to a given recipe in an atmosphere of pure nitrogen, and a part of the mixture was pushed into the dilatometer (made free of air by passing nitrogen) through the stopcock by the nitrogen gas pressure. The dilatometer was then isolated from the reactor by turning the stopcock. It was found that this procedure permitted us to study the kinetics of the polymerization reactions by the dilatometric and the gravimetric methods simultaneously. The details of the experimental procedure had been described elsewhere [11-14]. The number of the latex particles per mL of the aqueous phase (N), was estimated by the soap titration technique [15, 16]. Intrinsic viscosity $[\eta]$ of the polymers was determined in the ethyl acetate solvent at 35° C, and the viscosity-average molecular weights of the polymers ($\overline{M}_v$) were estimated from [17].

$$[\eta] = 8.60 \times 10^{-3} \times (\overline{M}_v)^{0.71}$$

The mixture in the reactor was stirred vigorously (rpm of the Hg-seal stirrer was 500) during the reaction. To get reproducible results, it was found that the reactant mixture must be stirred vigorously and continuously during the entire period of the polymerization reaction.

RESULTS

Typical dilatometric and gravimetric yield-time curves are shown in Figs. 1 and 2. It was noted that there was an induction period during which polymers were not formed in measurable quantities. The length of the induction period was found to decrease with the increase of the initiator concentrations. Initial rates (below 10% conversion) were estimated from the dilatometric data by plotting (volume contraction/capillary cross section)/time in (cm/min) versus time, and extrapolating the resulting straight line to zero time (Fig. 3). The intercept of Fig. 3 gave the initial rate. Figure 4 shows the conventional order plot for the initiator, and the order was found to be 0.56 ± 0.03 (by the least-squares method) at zero conversion. Figure 5 shows the initial rate determination when the detergent concentration was varied, while Fig. 6 gives the order plot for the soap, and this was found to be 0.72 ± 0.04 (by the least-squares method). The variation of the molecular weights ($\overline{M}_v$) of the polymers with the initiator concentrations is shown in Fig. 7 at two different conversions, 28 and 66%. It was found that the initiator order with respect to ($\overline{M}_v$) was -0.44 ± 0.03 at 28% conversion and -0.30 ± 0.05 at 66% conversion. The extrapolated value at zero conversion was -0.53 ± 0.03.

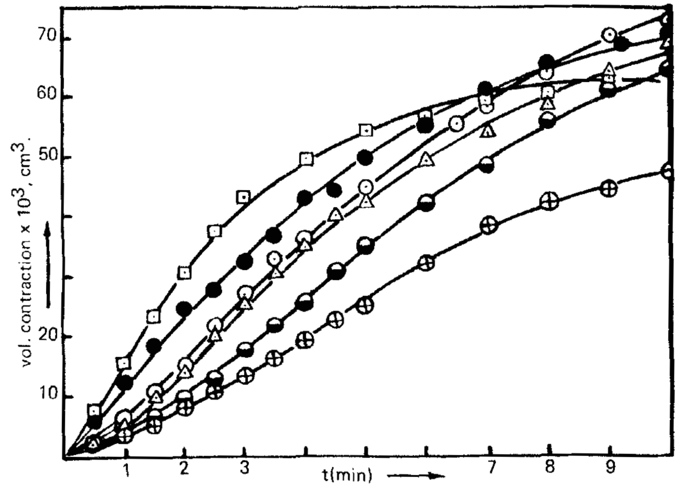

FIG. 1. Volume contraction as a function of time curves at different initiator concentrations. Recipe: Ethyl methacrylate 2.0% (v/v), detergent 0.60% (w/v), Phosphate buffer 0.01 M, pH 6.85 at 50°C. Initiator percent: (⊕) 0.005, (◒) 0.01, (△) 0.015, (⊙) 0.025, (●) 0.05, and (⊡) 0.075.

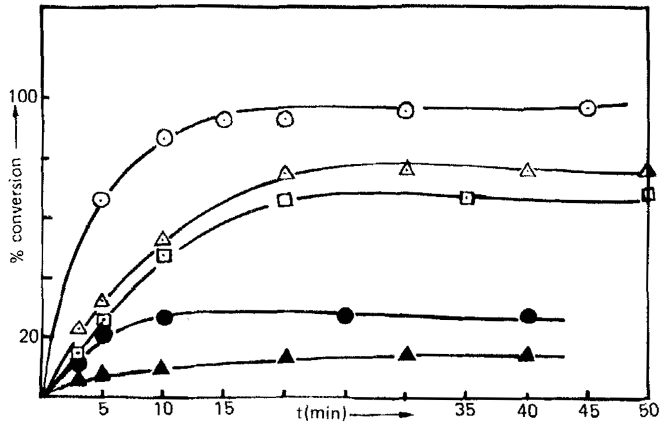

FIG. 2. Percent conversion-time curves at different initiator concentrations by the gravimetric method. Recipe same as in Fig. 1. Initiator percent: (▲) 0.005, (●) 0.01, (⊡) 0.015, (△) 0.025, and (⊙) 0.05.

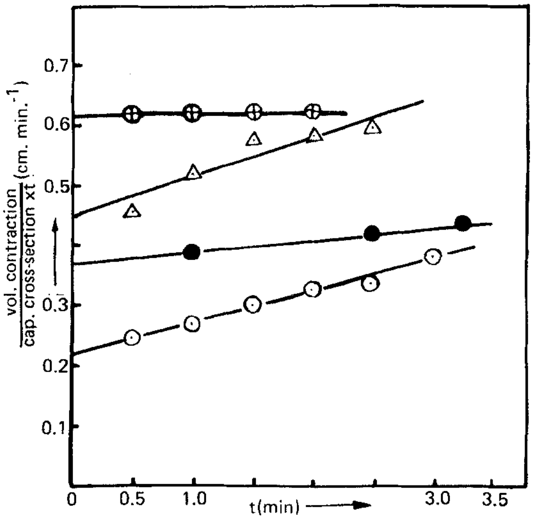

FIG. 3. Some plots for the determination of the initial rates from the analytical data of Fig. 1. The intercepts give the initial rates at different initiator concentrations. Initial rate is expressed as (volume contraction/capillary cross section)/time, in cm/min. Initiator concentrations (in %) are: (⊙) 0.005, (●) 0.01, (△) 0.015, and (⊕) 0.025.

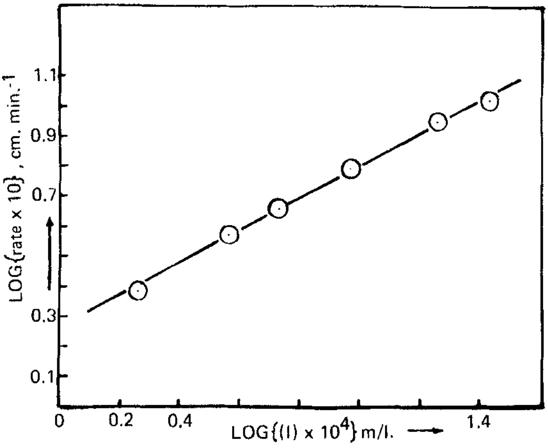

FIG. 4. Conventional order plot for the initiator. The slope of the line is 0.56 ± 0.03 (by the least-squares method). The rates are initial rates (in cm/min) from Fig. 3.

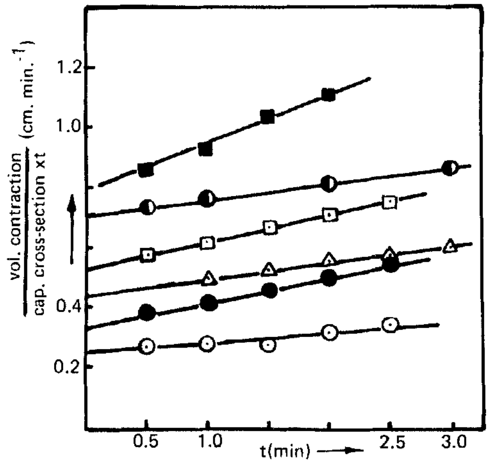

FIG. 5. Initial rate determination at various soap concentrations. Recipe: EMA 2.0% (v/v), initiator 0.025%, phosphate buffer 0.01 M. Soap % (w/v): (⊙) 0.4, (●) 0.6, (△) 0.8, (⊡) 1.0, (◐) 1.5, and (■) 2.0.

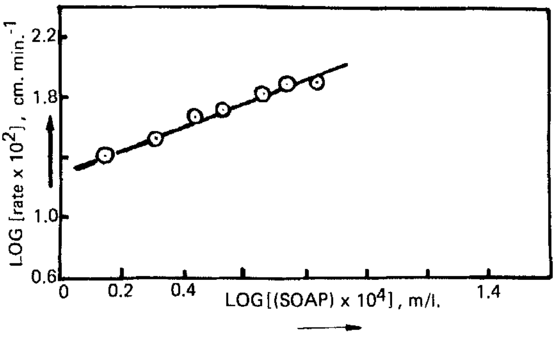

FIG. 6. Conventional order plot for the detergent. The least-squares slope of the line is 0.72 ± 0.04. The initial rates were taken from Fig. 5.

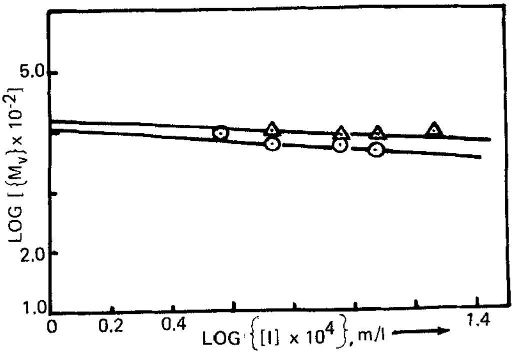

FIG. 7. Variation of the viscosity-average molecular weights (M_v) of the polymers with the initiator concentrations at a given conversion. Recipe same as in Fig. 1: (⊙) 28% and (▲) 66% conversion.

TABLE 1. Order of Initiator and of Soap at Different Conversions

Percent conversion	Order of initiator	Average	Order of soap	Average
20.0	0.45 ± 0.05		0.55 ± 0.05	
30.0	0.46 ± 0.04	0.42 ± 0.04	0.61 ± 0.06	0.62 ± 0.06
40.0	0.38 ± 0.03		0.68 ± 0.06	
60.0	0.38 ± 0.03		0.63 ± 0.04	

At higher conversions, viz., from 20 to 60%, where steady state in the light of Smith and Ewart theory is believed to occur, the polymerization rate (R_p) at a given conversion was estimated from Fig. 2, and the dependence on the soap and the initiator concentrations is shown in Table 1. Figures 8 and 9 show the rate curves when the concentrations of the soap were varied. Figures 10 and 11 show the effect of extra initiator and of extra soap when added late in a run. It was observed that in either case the rate of polymerization increased. Table 2 shows the number of latex particles per mL of the aqueous phase (N) as a function of the initiator concentrations.

DISCUSSION

It is generally assumed that in the emulsion polymerization of sparingly water-soluble vinyl monomers, the initiation occurs in the

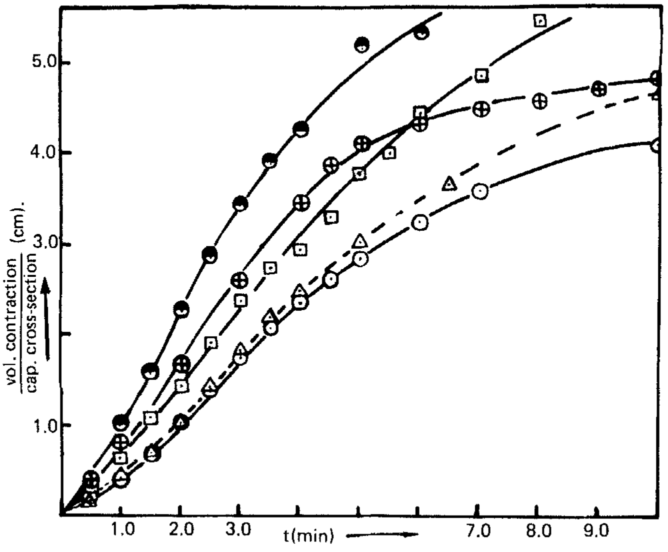

FIG. 8. Some of the (volume contraction/capillary cross section) versus time curves at various soap concentrations. Recipe same as in Fig. 5: (⊙) 0.6%, (△) 0.8%, (⊡) 1.0%, (⊕) 1.5%, and (◓) 2.0%.

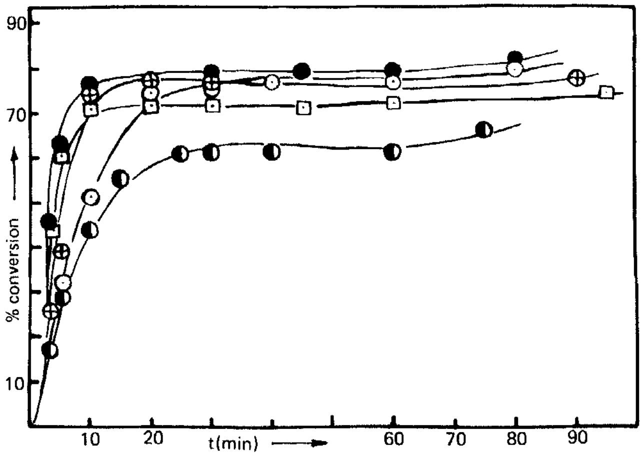

FIG. 9. Gravimetric yield-time curves at various soap concentrations. Recipe same as in Fig. 5. Soap percent: (◐) 0.4, (⊙) 0.6, (⊕) 0.8, (⊡) 2.0, and (●) 2.5.

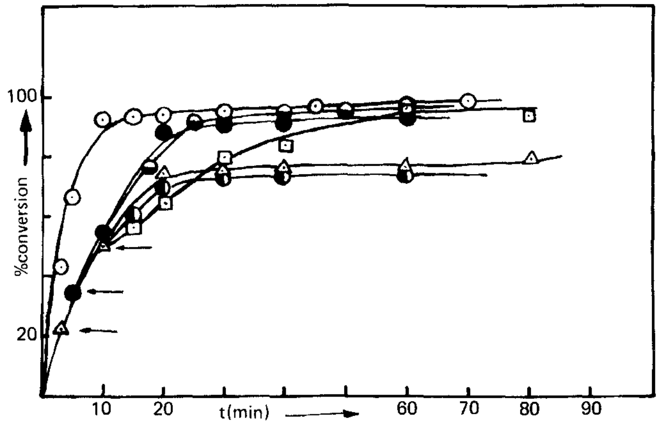

FIG. 10. Effect of the extra initiator when added late in a run. Recipe: EMA 2.0% (v/v), soap 0.6% (W/V), phosphate buffer 0.01 M. Initiator percent: (◬) 0.025 and (⊙) 0.05. Extra initiator (0.025%) added at 22.5% conversion (●), at 32% conversion (◒), and at 52% conversion (▣) to the system containing 0.025% initiator at the outset of polymerization. Oxygen-free distilled water (10 mL) was also injected to the system at 32% conversion (◐). Total volume of the mixture was kept constant at 400 mL in all cases before sampling.

monomer-swollen detergent micelles by the water-soluble initiators [1-6]. In the case of the ethyl methacrylate emulsion polymerization, we see that at zero conversion the initial rate of polymerization (v_p) is given by

$$v_p \propto (I)^{0.56 \pm 0.03} \times (S)^{0.72 \pm 0.04} \tag{1}$$

while the ($\overline{M}_v$) of the polymers is found to be

$$(\overline{M}_v) \propto (I)^{-0.53 \pm 0.03} \tag{2}$$

at zero conversion. Equations (1) and (2) show that the kinetics at zero conversion is the same as that of the homogeneous polymerization of ethyl methacrylate initiated by the free radicals and so we conclude that the initiation of the emulsion polymerization of the ethyl methacrylate takes place in the aqueous phase by the primary free radicals $SO_4^{\bullet -}$ and OH. It is only in the aqueous phase where homogeneous polymerization is possible at the very early stages of the reaction, because the monomer, the olegomers, the initiator, and

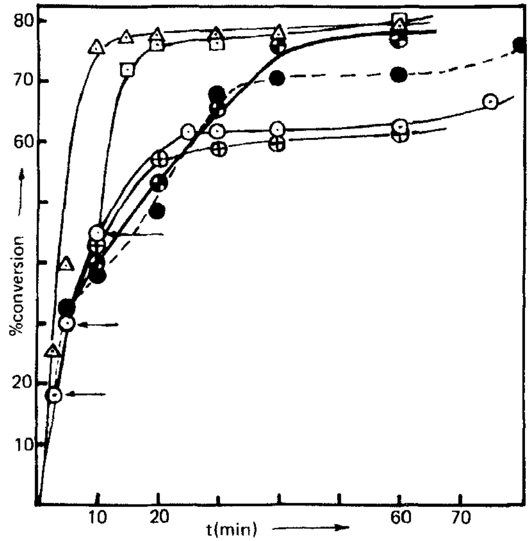

FIG. 11. Effect of extra soap when added late in a run. Recipe: EMA 2.0% (v/v), initiator 0.025%, phosphate buffer 0.01 M. Soap percent: (⊙) 0.4 and (△) 0.8. Extra soap (0.4%) added at various conversions [(●) 18.35%, (◉) 29.6%, and (⊡) 44.5%] to the system containing 0.4% soap initially. Oxygen-free distilled water (10 mL) was also injected to the system at about 29.6% conversion (⊕).

the soap are all water soluble. Secondary initiation may be occurring in the monomer-loaded detergent micelles by the water-soluble and -insoluble olegomeric radicals. Similar observations were noted in the emulsion polymerizations of styrene and methyl acrylate [12, 14].

At higher conversions, i.e., from 20 to 60%, the rate of polymerization (R_p) may be written as

$$R_p = Z(I)^{0.42 \pm 0.04} \times (S)^{0.62 \pm 0.06} \qquad (3)$$

where Z is a constant, (I) is the initial initiator concentration, and (S) is the initial soap concentration in the aqueous phase. Equation (3) agrees very well with the Smith-Ewart equation of Case II of the emulsion polymerization of styrene, where they assumed "steady state" in deriving the kinetic rate equations. From Fig. 2 it is very difficult to judge whether the steady-state assumption would be justified here. Figure 1 suggests a constant rate period only at the very early stages of the reaction, and so on the basis of the existence of the steady state, the kinetic parameters of (3) could be explained in the light of Smith and Ewart theory.

TABLE 2. Variation of the Latex Particles (N) per mL of the Aqueous Phase as a Function of the Initiator Concentrations, and Also as a Function of Conversion in a Given Run[a]

	Initiator concentration				
Time (min)	0.05%, $N \times 10^{-16}$	0.035%, $N \times 10^{-16}$	0.025%, $N \times 10^{-16}$	0.015% $N \times 10^{-16}$	0.01% $N \times 10^{-16}$
5.0	0.44 At 66.10%	0.90 35.30%	1.67 31.98%	1.03 25.87%	0.76 20.87% conversion
10.0	0.39 At 92.30%	0.42 67.50%	0.67 51.47%	0.39 46.48%	0.65 25.75%
20.0	0.39 At 92.50%	0.57 80.40%	0.40 74.39%	0.32 65.38%	0.61 25.97%
30.0	0.39 At 94.20%	0.57 81.00%	0.26 75.54%	X X	0.60 26.10%
40.0	0.38 At 95.10%	0.52 81.70%	0.25 76.26%	X X	0.58 26.25%
50.0	X At X	X X	X X	0.33 67.30%	X X
60.0	0.31 At 98.30%	0.49 82.30%	0.25 76.26%	X X	0.55 41.04%

[a] Recipe: Monomer = 2.0% (v/v); NaLS = 0.60% (w/v); $K_2S_2O_8$ = varies. Phosphate buffer (0.01 M); pH = 6.85; temp. = 50 ± 0.20°C. Note: The latex particles were subjected to extraction with cyclohexane before soap titration. Surface area of NaLS was taken as 46 $Å^2$ per molecule as recommended by J. W. VanderHoff in Polymer Colloids (R. M. Fitch, ed.), Plenum, New York, 1971.

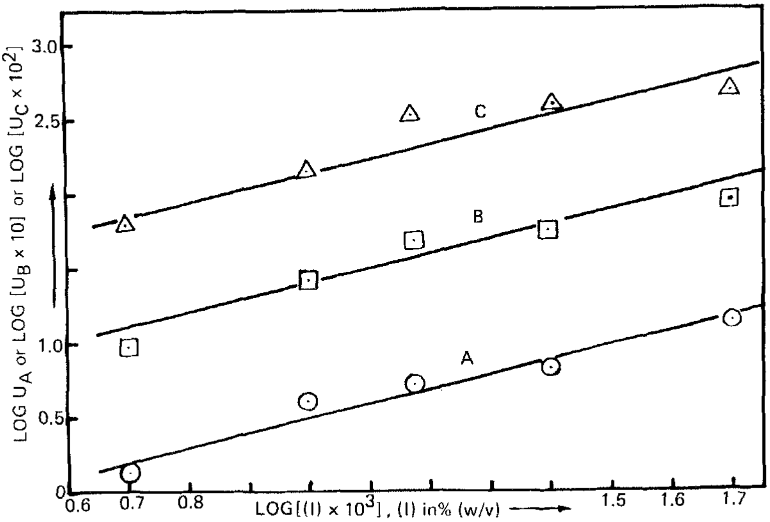

FIG. 12. Order plot for the initiator with respect to the time average rate U, in %/min from Fig. 2. Curve A with an average rate at 5 min, B with an average rate at 10 min, and C with an average rate at 20 min. Slopes of A, B, and C are 0.95 ± 0.11, 0.96 ± 0.16, and 0.91 ± 0.18, respectively.

Injection of the initiator or soap late in a run has been found to increase the rate of polymerization (Figs. 10 and 11). This observation is not consistent with the theory of Smith and Ewart. We also found the same phenomena when extra soap or initiator was added late in a run in the emulsion polymerization of styrene [11]. The increase in the polymerization rate due to the added extra initiator late in a run is probably due to the sustained coexistence of radicals in a particle when the particle volume is larger. This would slow down the termination rate inside the latex particles, and so the polymerization rate will increase [18]. In the case of the added soap late in a run, the increase in the polymerization rate is probably associated with the increase of N. This had been found in the case of styrene [11], where it was shown that new latex particles would be produced as long as the media contained emulsified oil droplets and was free of micellar soap. Gardon [18] observed the increase of polymerization rate of styrene in emulsion by injecting an additional quantity of initiator into the reactor late in a run.

Table 2 shows the formation of latex particles as a function of the initiator concentration. It is found that at a given conversion, N increases with the initiator concentration, attains a maximum at about 0.025% initiator concentration, and then decreases with a further increase of the initiator concentration, probably due to the coagulation

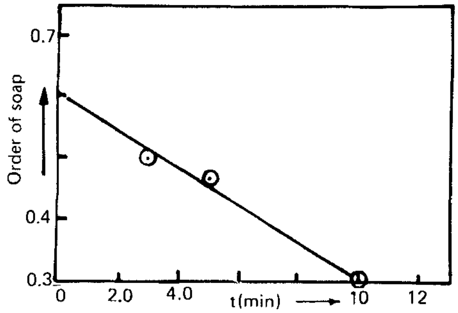

FIG. 13. Variation of soap order as a function of time. The extrapolated value at zero time is about 0.60.

of the colloidal latex particles. In a given run, N decreases with conversion and becomes almost constant after 40% conversion.

Incidentally, it may be pointed out that the determination of the reaction order from the time average rate (i.e., yield in time t/time t) and the initiator concentrations gave higher order for the initiator. For example, taking the time average rate from Fig. 2, we estimate the initiator order as 0.94 ± 0.11 (by least squares) when the average rate is yield of polymer in 5 min/5 min in % per min (Fig. 12); as 0.96 ± 0.16 when the average rate is yield of polymer in 10 min/10 min; and as 0.91 ± 0.18 when the average rate is yield of polymer in 20 min/20 min. This shows that the reaction is approximately first order with respect to the initiator concentration, but it must be noted that the conversion is about 6.5% in 5 min when the initiator concentration is 0.005%, while the conversion is 66% in 5 min when the initiator concentration is 0.05% (Fig. 2). If we use this initiator order in the rate expression, we have to ignore the effect of the monomer/polymer ratio in the latex particles. It is well known that this ratio will control the viscosity inside the latex particles, and this in turn will control the propagation (k_p) and the termination rate (k_t) constants [6]. At higher conversions, k_t will be diffusion controlled, and so the polymerization rate will increase [6]. Thus the extra (0.50 to 0.60) order of the initiator is probably associated with the gel effect of Norrish and Smith [6] and of Trommsdorff [6].

The order of the soap, however, when determined from the time average rate, decreases with conversion or time. The extrapolated value at zero time is about 0.60 ± 0.05, which is close to the value of about 0.70 at zero conversion, (Fig. 13). This decrease in the value of the detergent order is probably due to the fall in the polymerization rates as the monomer concentration at the reaction sites will decrease if N increases. Increase of soap concentrations will increase N and decrease the particle sizes. This will decrease the monomer concentration at the reaction site, particularly when the monomer/water ratio is small. The results obtained in this work are therefore consistent with the emulsion polymerization theory of Harkins-Smith-Ewart-Gardon (HSEG), at least qualitatively. The quantitative aspects of this work relative to HSEG theory will be published in a forthcoming publication.

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