Mechanism of the emulsion polymerization of methyl acrylate: 1. Initiation

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The emulsion polymerization of methyl acrylate (MA) has been carried out under two different experimental conditions so as to establish the mode of chain initiation. In the first system, the initiator was Fenton's reagent ($FeSO_4$ and H_2O_2 redox pair) in acid solution at 20°C in the presence of a cationic detergent, cetyltrimethyl – ammonium bromide (CTAB), while in the second system the initiator was potassium persulphate ($K_2S_2O_8$) at 50°C in the presence of an anionic detergent, sodium lauryl sulphate (NaLS). The polymerization was followed by the conventional dilatometric and gravimetric methods. Initial rates were determined by keeping the conversion below 10% and by plotting the (yield/time) *versus* time, and extrapolating the straight line to zero time. It was found that in either case, Initial rate (v) $\propto$ (Initiator)$^{0.50}$ while the viscosity average molecular weight ($\overline{M}_v$) of the polymers up to 20% conversion was found to be approximately inversely proportional to the square root of the initiator concentration (I), i.e. ($\overline{M}_v$) $\propto$ (I)$^{-0.50}$. The rate of polymerization up to 10% conversion was found to be approximately linear with the monomer concentration (from 0.5 to 5.0—, v/v) in the presence of detergents (above *CMC*) [critical monomer concentration] under the experimental conditions. Since the kinetics of the emulsion polymerization of MA at zero conversion are the same as that of the homogeneous polymerization of MA initiated by the free radicals, it is suggested that the initiation of the emulsion polymerization of MA takes place in the aqueous phase with little or no initiation in the detergent micelles containing monomer. If the polymerization is carried out within the solubility range of MA in the aqueous phase, then the initiation will take place entirely in the aqueous phase. Assuming homogeneous polymerization at zero conversion, the value of the termination rate constant (k_t) has been extracted from the experimental data at different initiator efficiencies.

INTRODUCTION

In the light of the Harkins[1], Smith and Ewart[2], and Gardon[3] theories of the emulsion polymerizations of the sparingly water soluble vinyl monomers, it is believed[4] that the initiation of the emulsion polymerization of vinyl monomers in general and of water insoluble or sparingly soluble monomer (such as styrene) in particular, would take place entirely in the monomer loaded detergent micelles with little or no initiation in the aqueous phase when the initiator (I) is soluble only in the aqueous phase. Recently[5] we have tested this hypothesis experimentally and found it incorrect.

In the persulphate–styrene–sodium lauryl sulphate (NaLS) system, we have shown that the primary initiation takes place in the aqueous phase by the primary ion radical ($SO_4^{\cdot -}$), while the secondary initiation takes place in the monomer loaded detergent micelles by the oligomeric free radicals. Very little information is available about the emulsion polymerization of the relatively water soluble methyl acrylate (MA) monomer[4]. When a monomer is added to an aqueous detergent solution containing micelles within its solubility range, it will distribute itself between the aqueous and micellar phases.

It has not yet been established whether the initiation of the emulsion polymerization of methyl acrylate will be entirely in the aqueous phase, or in the micellar phase, or in both the phases if the initiator is soluble only in the aqueous phase. We have used two initiators which are water soluble: (i) Fenton's reagent ($FeSO_4$ and H_2O_2) which gives neutral free radicals (OH),[6] in the presence of a cationic detergent, CTAB and dilute H_2SO_4 acid at 20°C, and (ii) $K_2S_2O_8$ which gives charged free radicals ($SO_4^{\cdot -}$) in the presence of an anionic detergent, NaLS at 50°C, to establish the mode of chain initiation. OH radicals will not face any electro static repulsion in entering a charged micelle and so can initiate polymerization either in the aqueous phase or in the charged micelles or in both the phases, whereas the SO_4^- ion radicals will face a repulsive energy barrier in entering negatively charged detergent micelles, and so micellar initiation by the primary $SO_4^{\cdot -}$ ion radicals would be highly unfavourable. We wished to see whether the two types of initiators used, would give the same or different kinetic results. Here we report some of the kinetic results obtained in the emulsion polymerization of MA at a low monomer/water ratio.

EXPERIMENTAL

The purification and fractionation of the monomers have been described elsewhere[5,7]. The reagents were BDH and E. Merck's AR/GR grade, and were used as such. Persulphate was recrystallized three times from double

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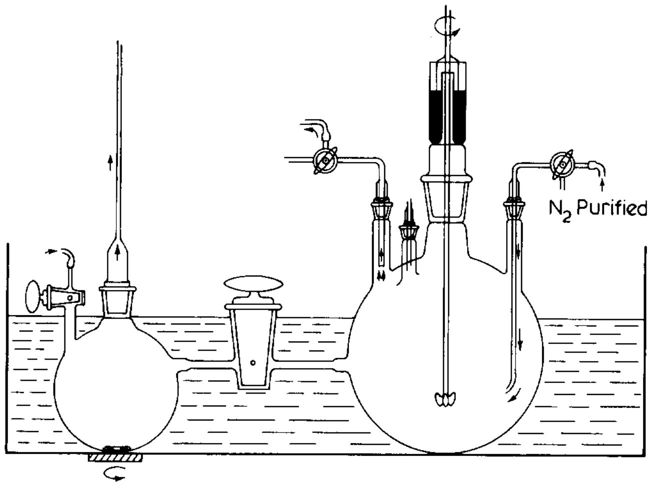

Figure 1 Diagrammatic representation of the reaction system. A 4-necked one litre round bottom pyrex (corning brand) flask is connected to a 100 ml dilatometer via a 3-mm stopcock

distilled water, while the detergents were further purified by recrystallization from organic solvents[8]. Reactions were carried out in a 4-necked one litre round bottom pyrex flask fitted (with a Hg-seal stirrer) to a dilatometer with a magnetic stirrer via a 3 mm stop cock (*Figure 1*). The whole apparatus could be housed in a large electrically heated and thermostatically controlled water bath ($t \pm 0.20°C$). The reactor was charged with the materials according to a given recipe in a nitrogen atmosphere[7] and the reagents were thoroughly mixed, and part of the emulsion was pushed to the dilatometer (made free of air by passing nitrogen) by the nitrogen pressure through the 3-mm stop cock. The dilatometer was then isolated from the flask by turning the stop cock. By using this procedure, it was possible to study simultaneously the kinetics dilatometrically and gravimetrically. We repeated experiments 10 times to check the reproducibility, and it was found that the results were reproducible within $\pm 3\%$, if the induction period of each run was similar. The onset of polymerization is signalled by the sudden appearance of turbidity in the system, and the corresponding time is taken as zero time for the emulsion polymerization.

In the dilatometric method, it was observed in the control experiments (either in the absence of monomer or initiator) that volume contractions occurred due to the evolution of oxygen (in the Fenton's reagent system) and of nitrogen trapped in the soap bubbles. The blank experiments (either without MA or without initiator) were repeated 10 times to estimate the average rate of nitrogen evolution, and necessary corrections were made in the volume contraction data obtained from the dilatometric method under the same experimental conditions. For the gravimetric determination of the polymerization rate, samples were withdrawn from the reactor at different times by the nitrogen pressure. Polymerization in the samples was stopped immediately by adding hydroquinone quencher. From a part of the sample, polymer was isolated by adding isopropyl alcohol, and a little dilute (N/20) HCl acid. It was then filtered in a tared gooch (No. G-4) crucible, washed with hot water thoroughly and finally dried in a vacuum oven (60°C) to a constant weight. The number of latex particles per ml (N) was determined by the soap titration technique[9,10]. The viscosity average molecular weights ($\bar{M}_v$) of the polymers were determined by measuring the intrinsic viscosities (η) of the polymers in benzene solvent at 30°C, and using the equation of Palit *et al.*[11]:

$$(\eta) = 1.282 \times 10^{-4} \times (\bar{M}_v)^{0.714}$$

The Fenton's reagent initiated polymerization was carried out in sulphuric acid solutions of pH in the range 3 to 4, following the procedure of Baxendale *et al.*[6]

RESULTS

Some typical results of the Fenton's reagent system and of persulphate system are shown in *Figures 2–5*. *Figure 2* shows the dilatometric and gravimetric rate curves obtained in the Fenton's reagent initiated system, in which the concentration of H_2O_2 has been varied, and the monomer is completely soluble in water under the experimental conditions. It is found that the rate increases with the increase of H_2O_2 concentrations. *Figure 3* gives the dilatometric volume contraction as a function of the time, curves obtained from the Fenton's reagent initiated system in which Fe^{2+} ion concentration has been varied, and also from the persulphate (KPS) initiated system. *Figures 4* and *5* show the gravimetric yield–time curves with KPS variation and Fe^{2+} ion concentration variation (Fenton's system) respectively. The shape of the yield–time curves appears to be a function of the composition of the recipe.

Initial rates (below 10% conversion) are determined by plotting the (volume contraction/time) *versus* time

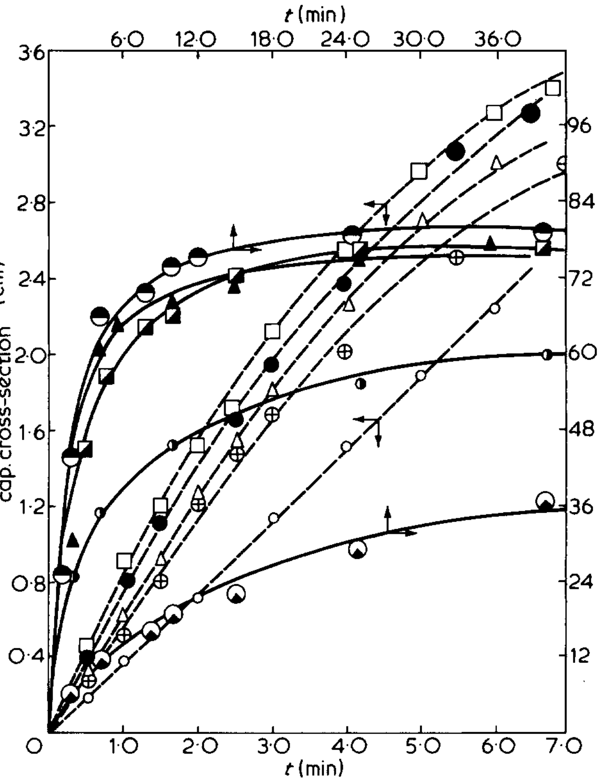

Figure 2 Dilatometric and gravimetric rate curves (i.e. conversion vs. time curves) in the Fenton's reagent system, when (H_2O_2) varies. (– – – –) broken lines show dilatometric results. Recipe given in *Table 1*. (H_2O_2) x 10^5 (M) = 0.247, ○; 0.511, ⊕; 0.92, △; 1.23, ●; and 1.65, □; (———) show gravimetric results. (H_2O_2) x 10^5 (M) = 0.247, ◉; 0.511, ◑; 0.92, ◪; 1.23, ▲; and 1.65, ◓

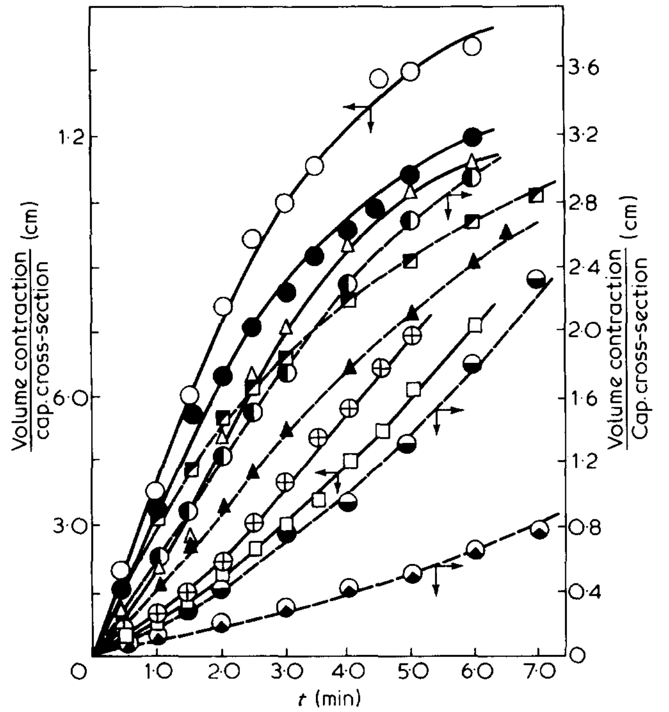

Figure 3 Dilatometric results from the Fenton's reagent system and from the persulphate system. (— — — —) Broken lines show volume contraction as a function of time when ($FeSO_4$) varies, (coordinates are shown in the Figure with arrows). Recipe given in *Table 1*. ($FeSO_4$) x10^4 (M) = 0.359, ◔; 0.719, ◒; 1.44, ▲; 2.88, ◐; and 5.76, ◪; (———) solid lines conversion time curves from the persulphate system, (coordinates shown with arrows). Recipe given in *Table 1* $K_2S_2O_8$ x 10^3 (M) = 1.029, □; 2.057, ⊕; 4.114, △; 6.174, ●; and 8.228, ○

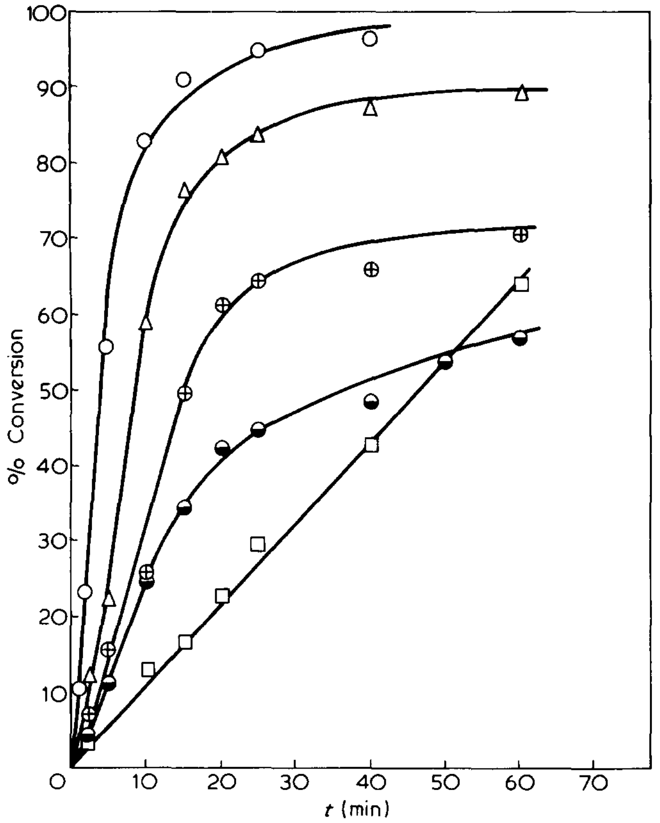

Figure 4 Gravimetric conversion time curves from the persulphate system. Recipe given *Table 1*. ($K_2S_2O_8$) x 10^3 = 0.514, □; 1.029, ◒; 2.057, ⊕; 4.114, △; 8.228, ○

(*Figure 6*), and extrapolating the resulting straight line to zero time. The intercept in *Figure 6* gives the initial rate. This apparent initial rate was corrected for nitrogen evolution during polymerization as described in the Experimental section, and the results are shown in *Table 1*. It is found that if the induction period is greater than 10 min, then correction for volume contraction due to nitrogen evolution is not significant. *Figure 7* shows the plot of $\log_{10}$ (initial rate) *versus* $\log_{10}$ (initiator) and from the slope of the line, the initiator exponent in the rate equation was estimated, and the results are shown in *Table 2*. The reaction orders by (i) the eye estimation and (ii) the least square method have been displayed. Some of the scattered data in the order plots were appeared to be in error, and they were ignored during the order determination by the eye estimation method; while all the data were thought to be correct when the orders were estimated by the least square method. That is why the least square results are slightly on the high side. The agreement however between the two sets of results seems to be satisfactory. The initiator exponent was found to be close to 0.50. *Figure 8* shows the plot of the initial rate *versus* $[(H_2O_2)(FeSO_4)]^{0.50}$ when the line passes through the origin. This indicates that the initial rate is proportional to the square root of the initiator concentration. In *Figure 8*, the initial rates at high initiator concentrations appear to be in error, as the reaction starts almost instantaneously when the initiator is injected into the system and consequently the short reaction time measured by a stop watch is not very accurate. The rate data at high initiator concentrations have therefore been ignored in *Figure 8*.

The viscosity average molecular weight ($\bar{M}_v$) as a function of the initiator concentrations at different conversions is shown in *Figure 9* and the results are summarised in *Table 3*. It is found that ($\bar{M}_v$) is

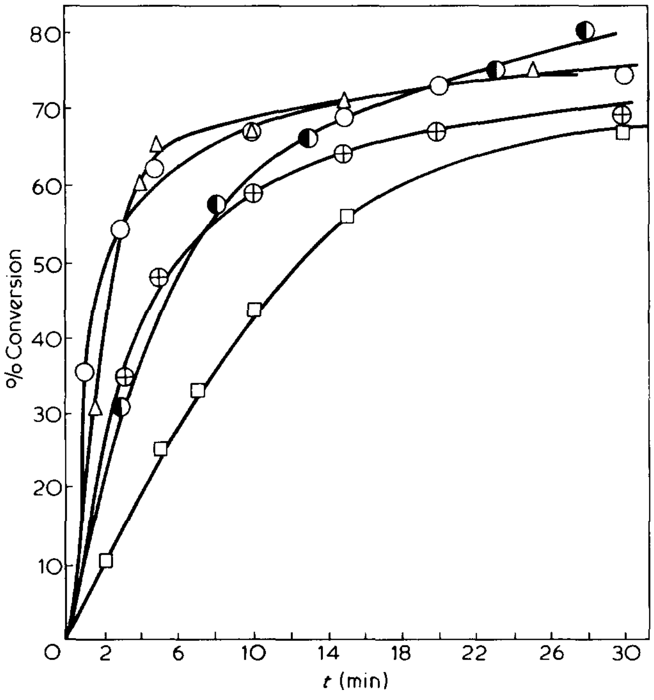

Figure 5 Gravimetric yield–time curves from the Fenton's reagent system with ($FeSO_4$) variations. Recipe given in *Table 1*. ($FeSO_4$) x 10^4 (M) = 0.359, □; 0.719, ◐; 1.44, ⊕; 2.88, △; and 5.76, ○

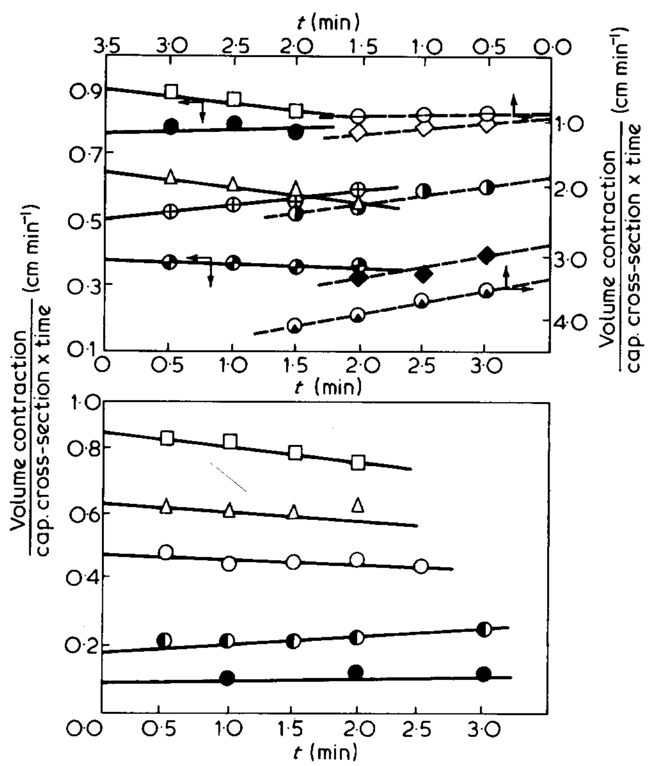

Figure 6 Determination of initial rates from the dilatometric results. (a) The (———) solid lines show results from the Fenton's system with (H_2O_2) variations: (H_2O_2) x 10^5 (M) = 0.247, ◕; 0.511, ⊕; 0.92, △; 1.23, ●; and 1.65, □; (— — — —) broken lines from the persulphate system: ($K_2S_2O_8$) x 10^3 (M) = 8.228, ◒; 6.174, ◆; 4.114, ◑; 2.057, ◇; and 1.029, ⊖. (b) The lines show results from the Fenton's reagent system with ($FeSO_4$) variations: ($FeSO_4$) x 10^4 (M) = 0.359, ●; 0.719, ○; 1.44, ◐; 2.88, △; and 5.76, □

approximately inversely proportional to the square root of the initiator (*I*) concentrations, i.e.

$$(\bar{M}_v) \propto (I)^{-0.50}$$

at the early stages of the reaction. It has been observed that the colloidal polymer is unstable if no detergent is added to the system, and the number of particles per ml of the aqueous phase, (*N*), is of the order of 10^{14} to 10^{16} by the soap titration technique[9,10] in the presence of detergents, and of 10^{12} to 10^{14} in the absence of detergents, and *N* depends on the composition of the recipe at a given temperature. Detergents also increase the rate of polymerization. Some results are shown in *Table 4*. It has also been observed that the initial rate of polymerization is proportional to the monomer concentration, i.e.

$$\text{Initial rate} \propto (\text{M})^{1.01 \pm 0.14} \text{ (by least square)}$$

below 10% conversion (*Figure 10*).

DISCUSSION

In the light of the Harkins–Smith–Ewart–Gardon, (HSEG) theory, the persulphate initiated emulsion polymerization of styrene in the presence of negatively charged detergent micelles would take place in the monomer swollen detergent micelles at the early stages of the reaction, and no initiation in the aqueous phase or in the emulsified oil droplets. It has been shown recently[5,12] that in the persulphate–styrene–NaLS system, the

Table 1a Initiation by Fenton's reagent. Recipe: MA 2% (v/v); CTAB = 0.02% (w/v); H_2O_2 = 0.92 x 10^{-5} (M) $FeSO_4$ varies; temperature = 20 ± 0.20°C

Apparent rate expressed as (volume contraction/capillary cross section) in cm min^{-1}	Corrected rate in cm min^{-1} (v)	$\log_{10}$ (*v* x 10)	$\log_{10}[(Fe^{++})10^5)$ where (Fe^{++}) in (m l^{-1})
0.86	0.58	0.7634	1.7601
0.65	0.37	0.5682	1.4580
0.48	0.24	0.3802	1.1579
0.18	0.18	0.2552	0.8569
0.10	0.10	0.0000	0.5558

** Correction due to N_2 evolution is necessary when the induction period is less than 5 min. Volume contraction due to N_2 evolution after 5 min. of mixing all the reagents, was found to be negligible

Table 1b Initiation by Fenton's reagent. Recipe: MA 2% (v/v); CTAB = 0.02% (w/v); $FeSO_4$ = 2.88 x 10^{-4} (M), H_2O_2 varies; temperature = 20 ± 0.20°C

Apparent rate in cm min^{-1}	Corrected rate in cm min^{-1} (*v*)	$\log_{10}$ (*v* x 10)	$\log_{10}[(H_2O_2)10^6]$ where (H_2O_2) in (m l^{-1})
0.90	0.58	0.7634	1.217
0.75	0.43	0.6330	1.089
0.65	0.37	0.5682	0.964
0.522	0.282	0.4500	0.708
0.380	0.210	0.3222	0.393

Table 1c Initiation by the potassium persulphate system. Recipe: MA 10% (v/v); NaLS = 0.333% (w/v); $K_2S_2O_8$ in (M) varies; temperature = 50 ± 0.20°C

Apparent rate in cm min^{-1}	Corrected rate in cm min^{-1} (*v*)	$\log_{10}$ (*v* x 10)	$\log_{10}[(K_2S_2O_8)$ x $10^4]$
3.35	3.05	1.484	1.915
2.95	2.70	1.431	1.790
1.85	1.73	1.238	1.614
1.01	1.01	1.004	1.313
0.85	0.85	0.929	1.013

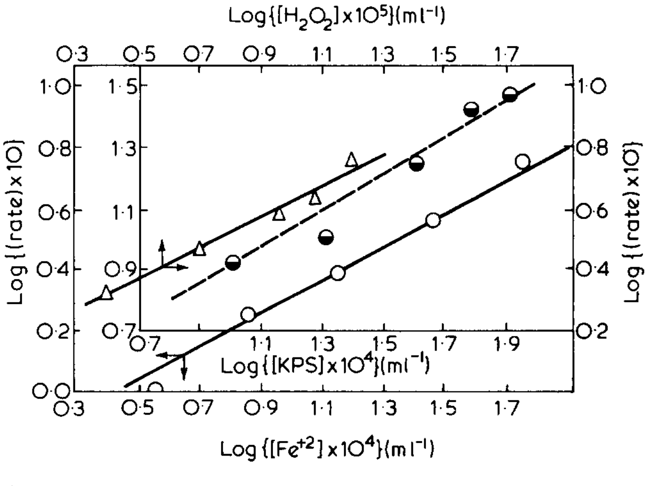

Figure 7 Order determination with respect to initiators. Inner rectangle shows coordinates of the persulphate system, while the outer one shows those of Fenton's reagent systems: ○, ($FeSO_4$); △, (H_2O_2) and ◒, ($K_2S_2O_8$)

Table 2 Determination of reaction order with respect to initiators

	Fenton's reagent system. Reaction order		Potassium persulphate system. Reaction order	
	Eye estimation	Least square	Eye estimation	Least square
$(FeSO_4)$	0.53 ± 0.07	0.61 ± 0.03	(0.56 ± 0.05)	(0.58 ± 0.05)
(H_2O_2)	0.505 ± 0.03	0.508 ± 0.05		

Note: Order determination by the eye estimation method has been made by ignoring the scattered data in the order plot, which seem to be in error; whereas that by the least square method has been done by considering all the data. The agreement between the two methods seems to be satisfactory. The true order appears to be very close to 0.50

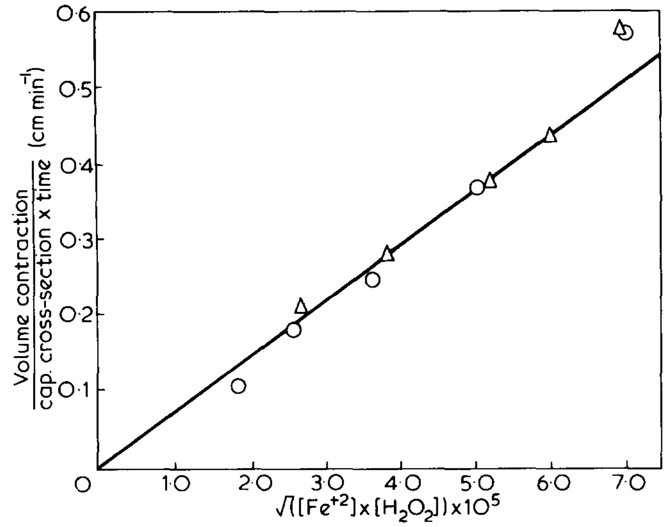

Figure 8 Plot of $[(FeSO_4)(H_2O_2)]^{1/2}$ *versus* initial rates from the Fenton's reagent systems: ○, $(FeSO_4)$ variations; △, $(H_2O_2$ variations

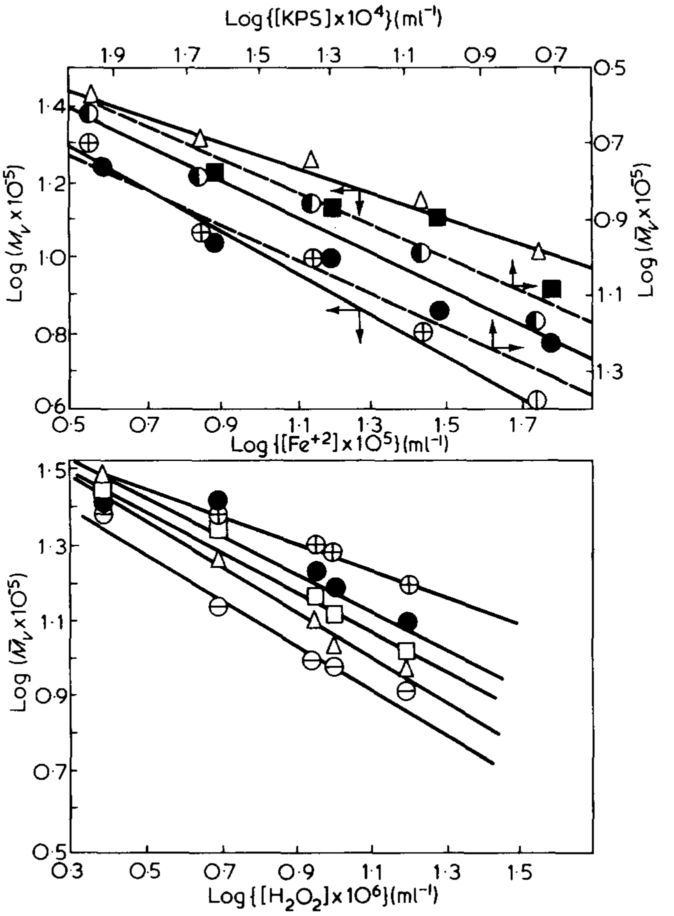

Figure 9 Plot of $\log_{10}(\bar{M}_v)$ *versus* $\log_{10}$ (Initiator) at various conversions. The upper diagrams show the results from the Fenton's Reagent system, (——) solid lines; and from the persulphate system, (— — — —) broken lines. $(FeSO_4)$ variation: ⊕, 10% conversion; ◐, 20% and △, 30%. $(K_2S_2O_8)$ variation: ●, 5% conversion, ■, 10%. The lower diagram shows the results of the Fenton's reagent system with the variation of (H_2O_2): ⊖, 10% conversion; △, 20%; □, 30%; ●, 40%; ⊕, 60%

initiation is a two step process. Primary initiation occurs in the aqueous phase while the secondary initiation takes place in the monomer swollen detergent micelles by the oligomeric radicals. It has also been shown[12] that the charged primary ion radicals, $SO_4^{\cdot-}$, cannot enter a negatively charged micelle or latex particle because of electrostatic repulsions. Smith and Ewart ignored this fact and allowed a negatively charged free radical to enter a negatively charged micelle freely to initiate polymerization inside the micelle. On this basis, they deduced a recursion formula from which the kinetics of the emulsion polymerization of styrene can be predicted. Roe[13] however got the same recursion formula for the emulsion polymerization of styrene by assuming initiation entirely in the aqueous phase. The two theories are therefore identical except in the mode of chain initiations[4a,13]. Experimental results support[12] the views of Roe[13].

In the case of the emulsion polymerization of methyl acrylate (MA), which is fairly soluble in water (about 5% w/v, at 50°C), it is generally believed[4] that the initiation would occur predominantly in the monomer swollen detergent micelles, and partly in the aqueous phase because of its water solubility. We have tested this hypothesis here experimentally. In the Fenton's reagent system, the primary free radical producing reaction is[4,6,14]

(i) $Fe^{2+}+H_2O_2\xrightarrow{k_1}Fe^{3+}+OH+OH^-$,

or $[Fe(OH)]^{2+}+OH$

where the rate constant $k_1=4.45\times10^{8}\times\exp(-9400/1.987\ T)$, l m^{-1} s^{-1}. In the second system, the primary free radical is a charged species[4,14,15]:

(ii) $S_2O_8^{2-}\xrightarrow{k_2}2SO_4^{\cdot-}$

where $k_2=10^{12.903}\times\exp(-27{,}600/1.987\ T)$ s^{-1}.[14] It is believed that some OH radicals are also produced by the reaction[4,14,15],

(iii) $SO_4^{\cdot-}+H_2O\rightarrow HSO_4^-+OH$

Table 3 Dependence of $(\bar{M}_v)$ of the polymers on the initiator concentrations at different conversions

Percent conversion* (P.C.)	Fenton's reagent system Value of x of equation 2 from *Figure 9*		Persulphate system** Value of x				
	Eye estimation	Least square	Eye estimation	Least square	P.C.***	Eye estimation	Least square
5.0	–	–	0.43 ± 0.05	0.41 ± 0.06	10.0	0.54 ± 0.04	0.60 ± 0.09
10.0	0.508 ± 0.05	0.54 ± 0.05	0.45 ± 0.05	0.44 ± 0.07	20.0	0.55 ± 0.04	0.61 ± 0.05
20.0	0.46 ± 0.03	0.43 ± 0.03	–	–	30.0	0.50 ± 0.05	0.52 ± 0.07
30.0	0.35 ± 0.03	0.33 ± 0.03	–	–	40.0	0.47 ± 0.06	0.42 ± 0.08
					60.0	0.35 ± 0.03	0.35 ± 0.03

* Recipe: MA 2% (v/v); CTAB = 0.02% (w/v); H_2O_2 = 0.92 x 10^{-5} (M); ($FeSO_4$) varies. Temperature 20°C
** Recipe: MA 10% (v/v); NaLS = 0.333% (w/v); Persulphate varies. Temperature 50°C
*** Recipe: MA 2% (v/v); CTAB = 0.02% (w/v); (H_2O_2) varies; ($FeSO_4$) = 2.88 x 10^{-4} (M)

Note: The value of x by the eye estimation method has been determined by ignoring the scattered points in the order plot of *Figure 9*, which seem to be in error, whereas that by the least square method has been done by considering all the data. The agreement between the two methods seems to be reasonable. It should be noted that the correct order between 0.5 and 0.6, or between 0.4 and 0.5 is hard to determine experimentally[4]. It appears that the true value of x at low conversion is close to 0.50

Table 4 Effect of detergents on N, $(\bar{M}_v)$ and the rate of polymerization: Recipe: MA 0.11 (m l^{-1}); $K_2S_2O_8$ = 4.114 x 10^{-3} (m l^{-1}); temperature = 50°C

	Detergent nil			Detergent 1.156 x 10^{-2} (m l^{-1}) NaLS		
Time (min)	Yield (Y) %	$(\bar{M}_v)$ x 10^{-5}	N x 10^{-14}	Y %	$(\bar{M}_v)$ x 10^{-5}	N x 10^{-16}
5.0	2.85	–	–	16.80	4.52	2.90
10.0	8.08	3.18	4.05	33.00	5.45	2.06
15.0	12.69	4.05	–	–	–	–
20.0	20.09	5.60	6.31	52.22	4.66	0.26
25.0	27.00	–	9.88	55.00	4.47	–
40.0	–	–	–	60.01	3.81	0.19
45.0	53.18	5.34	2.54	–	–	–
60.0	67.76	4.55	2.24	72.40	3.74	0.13

Note It is clear from the above Table that the soap increases the rate of polymerization, $(\bar{M}_v)$ and N at the initial stages of the reaction. Soaps also make the colloid stable as it was found by the coagulation value obtained by titrating the colloid with $MgSO_4$ (N/50) solution. Determination of N by the soap titration is not at all satisfactory because of oversimplified assumptions made in the estimation of N[10]. The values of N given here have only qualitative significance. It is difficult to judge whether N becomes constant after 50% conversion in the presence of detergents. In the absence of detergents in the system, there may be incipient coagulation all the time, and so N will be a function of time or conversion. N will increase as long as the polymerization will continue to occur in the aqueous phase, i.e. upto about 30 to 35% conversion[6,12], when the locus of polymerization will be shifted overwhelmingly in the latex particles, and so N will pass through a maximum during polymerization in the detergent free system, which is consistent with the data presented in *Table 4* above

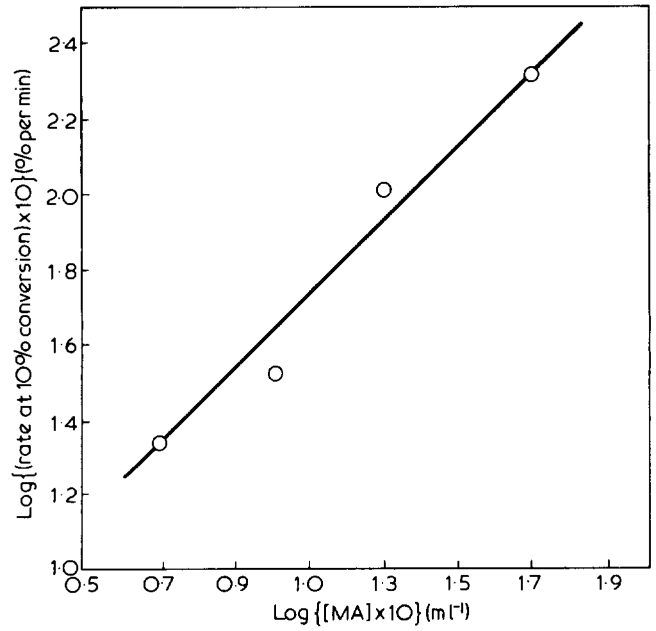

Figure 10 Plot of $\log_{10}$ (initial rate x 10) *versus* $\log_{10}$ (M) x 10 where the initial rate is expressed as % min^{-1}, and (M) as in percent, (v/v). Recipe:NaLS = 1.156 x 10^{-2} (M), persulphate = 2.057 x 10^{-3} (M). Monomer concentration varies in the range 0.056 to 0.56 ml^{-1}

The $SO_4^{\cdot -}$ ion radicals will however face a repulsive energy barrier in entering a negatively charged micelle[12], and so it is highly unlikely that they would initiate polymer chains inside the negatively charged micelles[27]. It was thought[4] that OH radicals might initiate polymerization inside the monomer swollen detergent micelles in the styrene–NaLS–persulphate system, since the polymers were found to contain hydroxyl end groups. However it has been shown by Vanderhoff *et al.*[27] that the hydroxyl endgroups of the polymers were due to the hydrolysis of sulphate endgroups. Further the reaction (iii) at 50°C would be a slow process as the activation energy of the reaction would be about 16 to 18 kcal mol^{-1}. It seems that OH radicals are not produced in the persulphate system significantly. In the present investigation, two initiators were used to produce OH and $SO_4^{\cdot -}$ radicals, so that the mode of chain initiation of the emulsion polymerization of MA could be traced.

The analytical data presented here (*Tables 1–4*) and *Figures 6–10*, show that the initial rate (v) of polymerization is approximately proportional to the square root of the initiator concentrations (I), i.e.

$$v = z.(I)^{0.50} \qquad (1)$$

where z is a constant, and the viscosity average molecular

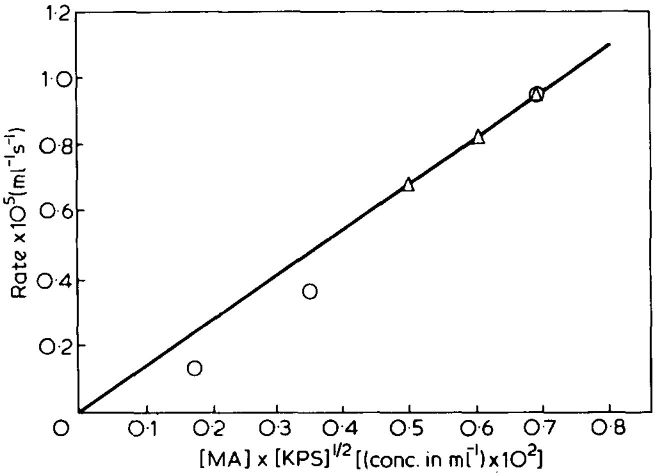

Figure 11 Plot of (initial rate x 10^5) in m l^{-1} s^{-1} *versus* $[(M)(I)^{1/2}]$ in $m^{3/2}$ $l^{-3/2}$. ○, Obtained when (M) was varied in the range 0.029 to 0.331 m l^{-1} and initiator (*I*) was 0.412 m l^{-1}; △, obtained when the initiator was varied in the range 0.206 to 0.411m l^{-1} and the monomer (M) was 0.110 m l^{-1}

weights ($\bar{M}_v$) is approximately inversely proportional to the square root of the initiator concentrations, i.e.

$$(\bar{M}_v) = P.(I)^{-x} \qquad (2)$$

where P is a constant and $x = 0.50$, up to 20% conversion. This clearly indicates that the emulsion polymerization of MA, at the early stages of the reaction, obeys the kinetics of free radical initiated homogeneous polymerization of MA, and is independent of the nature of the water soluble primary free radicals. We can think of homogeneous polymerization in the emulsion polymerization of vinyl monomers only at the very early stages of the reaction, when the monomer (within the solubility range), the polymer (i.e. oligomer) and the initiator are all water soluble. So we conclude, therefore, that the initiation of the emulsion polymerization of MA initiated by the water soluble initiators takes place in the aqueous phase. This is not surprising, since the MA has relatively higher solubility in water. In the aqueous polymerization of MA initiated by the redox pair, $K_2S_2O_8$ and $Na_2S_2O_4$, when the polymer separates as a stable colloid, Palit and Guha[16] found that the rate of polymerization at the initial stages of the reaction was approximately proportional to the square root of the initiator concentrations. Dainton *et al.*[17] made similar observations in the aqueous polymerization of acrylonitrile initiated by the Fenton's reagent, and this is of course a case of heterogeneous polymerization in the aqueous media. None of the authors[16,17], however, studied the dependence of ($\bar{M}_v$) of the polymers on (I) at a given conversion. Fitch *et al.*[18] found that the aqueous polymerization of methyl methacrylate obeyed homogeneous kinetics at low initiator concentrations at a given conversion.

It is not clear, however, whether the initiation of the emulsion polymerization of MA would take place entirely in the aqueous phase or whether there may be secondary initiation in the monomer loaded detergent micelles by the charged oligomeric radicals or by the neutral free radicals such as OH, particularly when MA would be present in the system beyond its solubility range. From the thermodynamic standpoint one would expect a thermodynamic equilibrium among the emulsified oil droplets, aqueous phase and micellar phase with respect to the distribution of monomer in these phases. As soon as the polymerization starts in the aqueous phase, the monomer in the oil droplets will immediately diffuse into the aqueous phase to maintain the thermodynamic equilibrium. In this case, secondary initiation in the monomer swollen detergent micelles by the oligomeric radicals or by the neutral primary free radicals (if soluble in the oil phase), would be possible. If however the emulsion polymerization is carried out within the solubility range of the monomer, there will be no emulsified oil droplets, and so when the polymerization starts in the aqueous phase, the monomer from the micelles will immediately diffuse out into the aqueous phase so as to maintain the thermodynamic equilibrium. This will make the monomer swollen micelles unstable as soon as polymerization starts in the aqueous phase, and so there would be hardly any reaction inside the micelles. Thus the importance of the secondary initiation in the detergent micelles will depend on (i) monomer solubility in the aqueous phase and (ii) experimental conditions. For the relatively water soluble vinyl monomers such as MA, acrylonitrile, vinyl acetate, etc. initiation would be entirely in the aqueous phase, particularly when there would be no emulsified oil droplets in the system.

Considering the homogeneous polymerization mechanism of MA in the aqueous media initiated by the $SO_4^{\cdot -}$ ion radicals:

$$\begin{array}{lcl} S_2O_8^{--} & \xrightarrow{k_d} & 2\,SO_4^{\cdot -} \\ SO_4^{\cdot -} + M & \xrightarrow{k_i} & M_1^{\cdot} \\ M_i^{\cdot} + M & \xrightarrow{k_p} & M_2^{\cdot} \\ M_j^{\cdot} + M & \xrightarrow{k_p} & M_{j+1}^{\cdot} \\ M_i^{\cdot}\ M_j^{\cdot} & \xrightarrow{k_t} & \text{Polymer} \end{array}$$

The steady state rate (R_p) expression is given by:

$$R_p = k_p(fk_d/k_t)^{0.5}(M)(S_2O_8{}^{--})^{0.50}$$

where f is the initiator efficiency. Assuming this steady state rate is the homogeneous initial rate in the emulsion polymerization of MA, the initial rates are plotted against $(M)(S_2O_8^{2-})^{1/2}$ in *Figure 11*, according to the above equation. The slope of the line is estimated by the least square method, considering the 6 experimental data and the origin, since the line has to pass through the origin, and is given by, slope $= (1.34 \pm 0.16)\ l^{\frac{1}{2}}\ m^{-\frac{1}{2}}\ s^{-1}$; while the intercept $= (0.07 \pm 0.02)$ m l^{-1} s^{-1}. Since the magnitude of the intercept is small, it was ignored and the line was made to pass through the origin (*Figure 11*)as required by the above equation.

Taking $k_p{}^{19} = 10^3$ l m^{-1} s^{-1} at 50°C, and $k_d = 1.70 \times 10^{-6}$ s^{-1} at 50°C,[14] it is possible to estimate k_t from the slope of the line of *Figure 11*, at a given initiator efficiency. There are two other literature values of k_d, i.e. 2.66×10^{-6} s^{-1} [20] at 50°C and 1.40×10^{-6} s^{-1}.[21] Morris and Parts[22] found that k_d increased by a factor of 4 to 6, when MA was added to the system at various concentrations. So, for our calculations, we took k_d as $(4 \times 1.70 \times 10^{-6}\ s^{-1})$ at 50°C. Taking $f = 1.0$,[2-4] we get k_t as $(3.79 \pm 0.03) \times 10^6$ l m^{-1} s^{-1} and if $f = 0.33$,[23,24] we get k_t as $(1.25 \pm 0.03) \times 10^6$ l m^{-1} s^{-1}. This value may be compared with that of k_t obtained in the homogeneous polymerization of MA in the non-aqueous media initiated by free radicals[25], i.e. $3.55 \times 10^6\ \mathrm{l\ m^{-1}\ s^{-1}}$ at 50°C, and also with that of k_t of the homogeneous acrylamide polymerization in the aqueous media initiated by free radicals[19,26], which was found to be pH dependent, i.e. $3.3 \times 10^6\ \mathrm{l\ m^{-1}\ s^{-1}}$ at pH 5.50. In the present investigation, pH was 6.0 ± 0.5. It seems that k_t value found here is quite reasonable in the homogeneous polymerization of MA in the aqueous media.

It may be pointed out here that persulphate has long life at 50°C, its half life being 4.05×10^5 s at 50°C if k_d is taken as $1.70 \times 10^{-6}\ \mathrm{s^{-1}}$, whereas the Fenton's reaction has a very short life, its half life at 20°C being only 23.05 s, if $(\mathrm{Fe^{2+}}) = (\mathrm{H_2O_2}) = 10^{-3}\ (\mathrm{m\ l^{-1}})$. Consequently the kinetic data obtained from the Fenton's reagent system will be meaningful only at zero conversion or zero time of the reaction.

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