# Mechanism of the emulsion polymerization of methyl acrylate: 2. Kinetics and growth of the polymers

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The emulsion polymerization of methyl acrylate (MA) was investigated in a batch reactor at 50°C using potassium persulphate (KPS) as an initiator with sodium lauryl sulphate (NaLS) acting as a micelle generator at a low monomer/water ratio (m/w). The rates of polymerizations, number of latex particles per ml ($N$), and colloid stability ($CS$) of the latex particles have been measured, while the molecular weights of the polymers ($\bar{M}_w$ and $\bar{M}_n$) have been estimated from the intrinsic viscosity ($\eta$) data, as a function of (m/w) ratio, detergent and initiator concentrations. It has been found that the steady state rate ($R_p$) obtained during the 10 to 40% conversions, may be written as:

$$R_p \propto (M)^0(\mathrm{KPS})^{0.46\pm0.04}(\mathrm{NaLS})^{0.30\pm0.03}$$

when the (m/w) ratio is higher, i.e. monomer concentration is above its solubility (0.58 moles per litre at 50°C), and

$$R'_p \propto (M)(\mathrm{KPS})^{0.42\pm0.04}(\mathrm{NaLS})^{0.25\pm0.05}$$

when the monomer concentration is less than 0.58 moles per litre. In the absence of detergents, the steady state rate ($R''_p$) is given by

$$R''_p \propto (M)(\mathrm{KPS})^{0.40\pm0.04}$$

when the monomer concentration is less than 0.58 moles per litre. The polymer phase was a very stable colloid in the aqueous medium even in the absence of detergents. At very high concentrations of detergents (i.e. above $3.5\times10^{-2}$ moles per litre) the rates of polymerizations were found to decrease. Injections of additional quantity of KPS late in a run did not alter the rates of polymerization, whereas injections of additional quantities of detergents late in a run always increased the polymerization rates. Injections of monomer late in a run increased the rates, if the (m/w) ratio was lower and detergent was present, and had no effect on the rates if the initial (m/w) ratio was higher. No experimental evidence was found in favour of the hypothesis that the chain termination in the latex particles would occur as a result of chain transfer to the monomer molecules. Injections of monomer late in a run always increased the polymer molecular weights. The ratio ($\bar{M}_w/\bar{M}_n$) was found to be about 1.30 to 1.50, but at higher (m/w) ratios lower KPS concentrations and higher soap concentrations (above $CMC$) the molecular weight ratio was found to be very close to unity. In a given run, the average rate of polymerizations ran approximately parallel with the rise and fall of the cumulative molecular weights of the polymers with time or conversion. It has been found that stirring always decreased the polymerization rates in the absence of detergents, but increased the rates in the emulsion systems containing detergents. The Harkins–Smith–Ewart theory of the emulsion polymerization of styrene has been tested with the analytical data, and it has been found that the theory gives only a qualitative description of the emulsion polymerization of methyl acrylate.

**(Keywords: emulsion; polymerization; methyl acrylate; kinetics; growth)**

## INTRODUCTION

We have recently reported the mode of chain initiation in the emulsion polymerization of methyl acrylate[1]. Little is known about the kinetics and mechanism of the emulsion polymerization of MA in static or batch systems[2]. Gerrens *et al.*[3] reported the kinetic results of the continuous and semi-continuous emulsion polymerizations of MA, where they found that the Smith–Ewart theory could not explain their experimental findings. Gerrens[4] also made a brief investigation of the emulsion polymerization of MA in batch systems and reported that there was no constant rate period. The rate of polymerization increased with conversion or time, attained a maximum at about 13% conversions, followed by a first order decrease with respect to the monomer. Deviations from the Smith–Ewart kinetics were ascribed in part to the water solubility of the monomer. Yeliseyeva[5] has recently reviewed the Russian work on the emulsion polymerizations of polar monomers at higher m/w ratios, and found that the surface area occupied by a detergent molecule on the

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polymer surface was dependent on the nature of the detergent and also on the polarity of the polymers. Here we report some detailed kinetic investigations of the emulsion polymerization of MA initiated by KPS at 50°C in a batch polymerization system.

## EXPERIMENTAL

The quality of chemicals used, their purifications and processing before use, and the experimental details of measuring rates of polymerizations, estimating the number of latex particles per ml, $N$, by the soap titration technique, determination of the colloidal stability ($CS$) of the latex particles, reproducibility of results and of estimation of $\bar{M}_w$ and $\bar{M}_n$ from the intrinsic viscosity $(\eta)$ measurements of polymers, have already been described in detail elsewhere[1]. The relationship between $(\eta)$ and $\bar{M}_w$ or $\bar{M}_n$ is given below[6]:

$$(\eta)\text{ in dl/g} = 3.56 \times 10^{-5} \times (\bar{M}_w)^{0.798}$$

and

$$(\eta)\text{ in dl/g} = 1.282 \times 10^{-4} \times (\bar{M}_n)^{0.7143}$$

## RESULTS

Results of the emulsion polymerizations of MA are shown in the following Tables and Figures. The solubility of MA in water[2-4] is about 50 grams per litre at 50°C, i.e. about 0.58 moles/litre, and polymerizations were carried out below and above the solubility of the monomer.

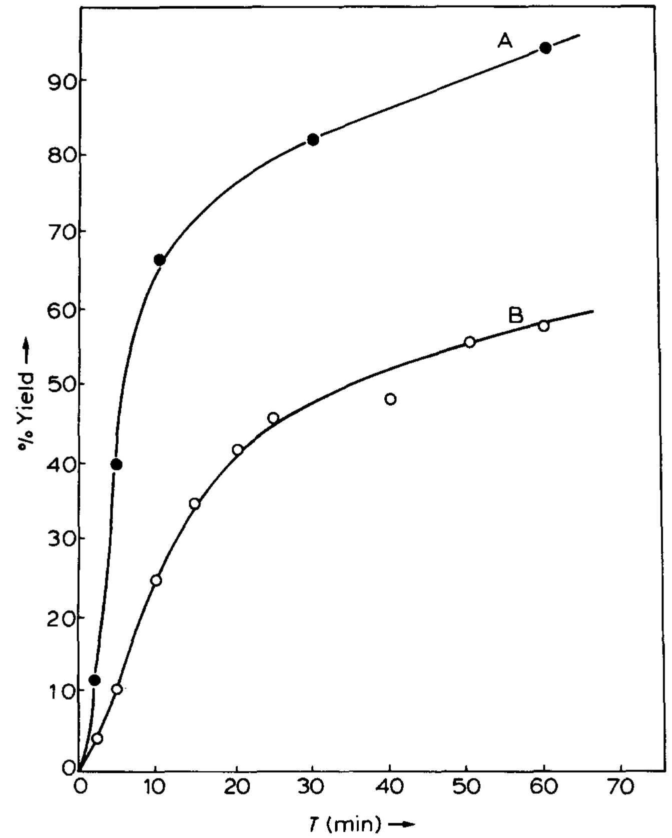

**Figure 1** Effect of stirring on conversions. Curve A (recipe: MA 10% (V/V), KPS $1.029 \times 10^{-3}$ M, NaLS $1.156 \times 10^{-2}$ M, stirrer speed 500 rpm, and stirring continued throughout the run). Curve B (recipe same as for curve A, but stirring discontinued after the initiation of polymerization reactions, i.e. at the end of the induction period which was about 15 min in this case)

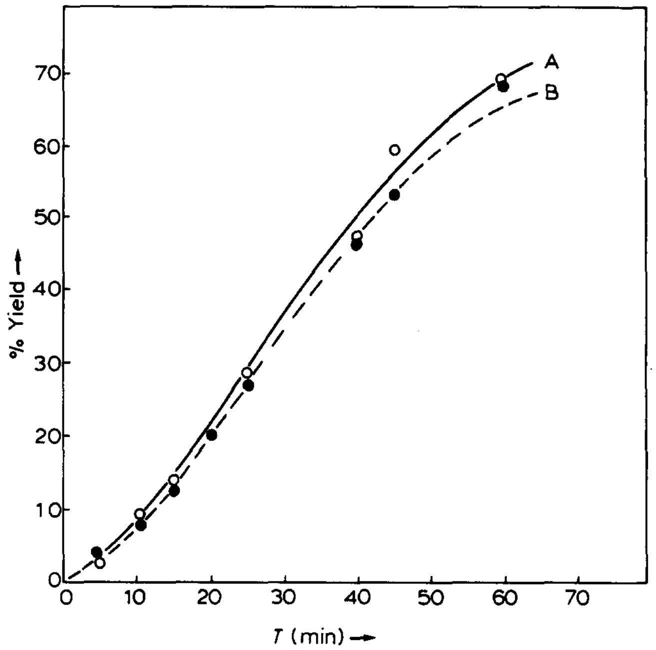

**Figure 2** Effect of stirring on conversion in the soapless system. Curve A (○) (recipe MA 1.0%, (V/V); KPS $4.114 \times 10^{-3}$ M; stirrer speed 200 rpm, and stirring discontinued at the end of the induction period which was about 3 min). Curve B (●) (recipe same as in A). Stirring continued throughout the run, stirrer speed 200 rpm. Curve A is the average of 5 runs. Curve B also average of 5 runs

### *Effect of stirring*

In *Figures 1* and *2*, some typical results of stirring during polymerizations have been shown. It was found that the stirring always decreased the rates of polymerization in the soapless systems, whereas it increased the rates in the soap-containing emulsion systems.

### *Rate dependence on the initiator concentrations*

The rates of polymerization were found to increase with the increasing initiator concentrations in the range (0.514 to 8.228) $\times 10^{-3}$ (m/l), with the rates being measured both dilatometrically and gravimetrically. Some results are shown in *Tables 1* to *3*.

The order plots for the initiator are shown in *Figure 3a*. The order of the initiator was found to be (0.46 ± 0.04) from the volume contraction data when the monomer/water ratio (m/w) was above (5/95, by weight), and about (0.70 ± 0.07) as determined by the gravimetric method. When the (m/w) ratio was less than (5/95), the initiator order was (0.42 ± 0.04). In the soapless system, the initiator order was (0.40 ± 0.04) under steady-state conditions.

Additional quantities of initiator were injected into the system late in a run (*Figures 4* and *5*), and it was found that the added initiators had no effect on the rates of polymerization within the experimental errors, as predicted by the Smith–Ewart theory.

### *Rate dependence on the monomer/water ratio*

The rate of polymerizations increased linearly with the increase in the monomer concentrations (below the solubility limit) in the presence and absence of soap. Above the solubility range, the rate below 50% conversions became independent of the (m/w) ratio (*Figure 6*). When an additional quantity of monomer was injected late in a run, i.e. in seeded systems, it was observed that the

**Table 1** Aqueous polymerization of methyl acrylate (MA) in the soapless systems. Recipe: MA 0.1105 M, NaLS nil, KPS $4.114 \times 10^{-3}$ M, temperature 50°C, stirrer speed 200 rpm

| Time, $t$ (min) | Per cent conversion ($y$) | ($y/t$) | $\bar{M}_w \times 10^{-6}$ | $\bar{M}_n \times 10^{-6}$ | ($\bar{M}_w/\bar{M}_n$) | $N \times 10^{-15}$ per ml | $CS$ |
|---|---|---|---|---|---|---|---|
| 5.0 | 2.85 | 0.57 | – | – | – | – | – |
| 10.0 | 8.08 | 0.81 | 0.42 | 0.32 | 1.31 | 0.41 | 15.0 |
| 15.0 | 12.69 | 0.85 | 0.52 | 0.40 | 1.30 | – | 10.0 |
| 20.0 | 20.09 | 1.00 | 0.69 | 0.56 | 1.23 | 0.63 | 15.0 |
| 25.0 | 27.00 | 1.08 | – | – | – | 0.99 | 8.5 |
| 45.0 | 53.18 | 1.18 | 0.68 | 0.53 | 1.24 | 0.25 | 5.0 |
| 60.0 | 67.76 | 1.13 | 0.59 | 0.46 | 1.28 | 0.22 | 4.5 |

Polymerization was carried out in the presence of purified nitrogen. Time ($t$) was measured after the induction period. $CS$ (in millimoles of $MgSO_4$ per litre) was determined by titrating 5 ml latex solution with a standard $MgSO_4$ solution following the standard procedure for coagulation value determination of colloids. The ratio ($\bar{M}_w/\bar{M}_n$) possibly indicates that the chain termination by combination of polymeric radicals in the latex particles or in the aqueous phase, is the major chain ending reactions. Since $\bar{M}_w$ or $\bar{M}_n$ has not been measured directly, their values shown here have to be accepted with some reservation

**Table 2** Emulsion polymerization of methyl acrylate (MA) in the absence of emulsified oil droplets. Recipe: MA 0.1105 M, NaLS $1.156 \times 10^{-2}$ M, KPS $4.114 \times 10^{-3}$ M, stirrer speed 200 rpm

| Time ($t$) (min) | Per cent conversion ($y$) | ($y/t$) | $\bar{M}_w \times 10^{-6}$ | $\bar{M}_n \times 10^{-6}$ | ($\bar{M}_w/\bar{M}_n$) | $N \times 10^{-15}$ | $CS$ in millimoles of $MgSO_4$ per litre |
|---|---|---|---|---|---|---|---|
| 5.0 | 16.80 | 3.36 | 0.58 | 0.45 | 1.29 | 29.00 | 62.6 |
| 10.0 | 33.00 | 3.30 | 0.68 | 0.55 | 1.26 | 20.0 | 66.7 |
| 20.0 | 52.22 | 2.61 | 0.59 | 0.47 | 1.25 | 2.60 | 64.9 |
| 25.0 | 55.00 | 2.20 | 0.57 | 0.45 | 1.26 | 1.90 | 56.3 |
| 40.0 | 68.01 | 1.70 | 0.49 | 0.38 | 1.28 | – | 46.5 |
| 60.0 | 77.40 | 1.29 | 0.48 | 0.37 | 1.29 | 1.30 | 44.4 |

*Note:* In comparing with the results of *Table 1*, it is evident that soap has increased the rates of the polymerizations, molecular weights of polymers at the early stages of the reaction, the values of $N$ and also the colloidal stability of the latex solution. The ($\bar{M}_w/\bar{M}_n$) ratio however remains unaffected in the presence of soap and this possibly indicates that the mode of chain termination does not alter in the presence of detergents

**Table 3** Emulsion polymerization of methyl acrylate (MA) in the presence of emulsified oil droplets. Recipe: MA 1.105 M, NaLS $1.156 \times 10^{-2}$ M, KPS $4.114 \times 10^{-3}$ M, stirrer speed 500 rpm, temperature 50°C

| Time ($t$) (min) | Per cent conversion ($y$) | ($y/t$) | $\bar{M}_w \times 10^{-6}$ | $\bar{M}_n \times 10^{-6}$ | ($\bar{M}_w/\bar{M}_n$) | $N \times 10^{-15}$ ($ml^{-1}$) | $CS$ in millimoles $MgSO_4$ per litre |
|---|---|---|---|---|---|---|---|
| 1.0 | 4.08 | 4.08 | 0.76 | 0.62 | 1.22 | – | – |
| 2.5 | 10.80 | 4.32 | 1.12 | 0.95 | 1.18 | – | 81.15 |
| 5.0 | 21.92 | 4.38 | 1.83 | 1.65 | 1.11 | 1.15 | 77.55 |
| 10.0 | 58.70 | 5.87 | 2.15 | 1.98 | 1.09 | 1.65 | 79.25 |
| 15.0 | 76.20 | 5.08 | 1.84 | 1.66 | 1.11 | 1.85 | 59.55 |
| 20.0 | 80.40 | 4.02 | 1.65 | 1.44 | 1.15 | 1.95 | 50.25 |
| 25.0 | 83.00 | 3.72 | 1.62 | 1.43 | 1.13 | 1.99 | 41.15 |
| 40.0 | 87.76 | 2.19 | 1.63 | 1.43 | 1.13 | 1.98 | 33.25 |
| 60.0 | 89.10 | 1.49 | 1.65 | 1.47 | 1.12 | – | – |

rates of polymerizations did not alter within experimental error in the systems where no soap was added, or where the m/w ratio was very high in the presence of soap (*Figures 7* and *8*). There was a slight fall in the rate initially when MA was added after 50% conversions (*Figure 8*). However in the systems where the m/w ratio was below 0.58 moles per litre water and soap was present, the rates of polymerization increased when an additional quantity of monomer was injected late in a run (*Table 4*). The molecular weights of polymers were, however, found to increase at a given conversion in all cases. Some results are shown in *Table 4*.

### *Rate dependence on the detergent concentrations*

The rates of polymerization were found to increase with increasing soap concentrations, however, at higher soap concentrations the rates were found to decrease. The results are shown in *Figure 9*. The order of soap in the concentration range (0.18 to 3.47) $\times 10^{-2}$ moles per litre was about 0.25 when the monomer concentration was below its solubility, and about 0.30 when the monomer concentration was above its solubility (*Figure 3b*). This small difference in soap order does not seem to be significant.

The rates of polymerizations were found to increase if additional quantity of soap was injected into the soap free

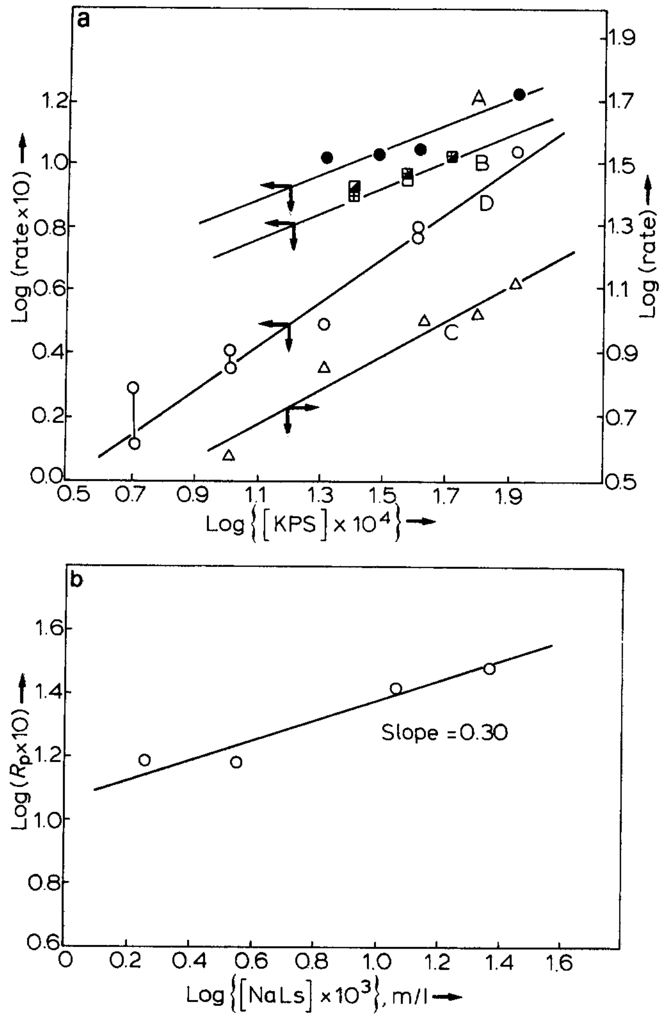

**Figure 3** (**a**) Determination of initiator order by gravimetric and dilatometric methods. In the gravimetric method, the rate is expressed as % polymerized (by weight) per minute, while in the dilatometric method the rate was first measured as volume contraction per minute and subsequently converted to % polymerized per minute. Data from curves A, B and D were from the gravimetric experiments, while those of C were from the dilatometric experiments. Curve A shows the order plot of the initiator in the range (2.057 to 8.529)$\times 10^{-3}$ M, MA 0.1105 M, and NaLS nil. Curve B shows the order plot of the initiator in the range (2.057 to 4.114)$\times 10^{-3}$ M, MA 0.1105 M and NaLS $1.156\times 10^{-2}$ M (above *CMC*). Rates were measured at various conversions viz. 15 to 40%, and the rates were found to be approximately independent of conversion in this range. Curve C shows the initiator order in the range (1.029 to 8.228)$\times 10^{-3}$ M, MA 1.105 M, i.e. above solubility, and NaLS $1.156\times 10^{-2}$ M. Curve D shows the order plot of the initiator when the rates were measured at a fixed time and the experimental condition was the same as for curve C. The initiator order from each curve was estimated by the least squares method and was found to be $0.40\pm 0.04$ (A); $0.42\pm 0.04$ (B); $0.46\pm 0.04$ (C) and $0.70\pm 0.07$ (D)

(**b**) Determination of the order of the micelle generator in the range, (0.18 to 3.47)$\times 10^{-2}$ M; KPS $1.029\times 10^{-3}$ M, and MA 1.105 M. By least square, the order was found to be $0.30\pm 0.03$

system late in a run (*Figure 10*), or into the emulsified system containing soap at the beginning of the polymerization (*Figure 11*). This observation, shown in *Figure 11*, is not consistent with the predictions of the Smith–Ewart theory.

*Growth of polymers*

At a given conversion, the molecular weights of the polymers were found to decrease with the increase in the

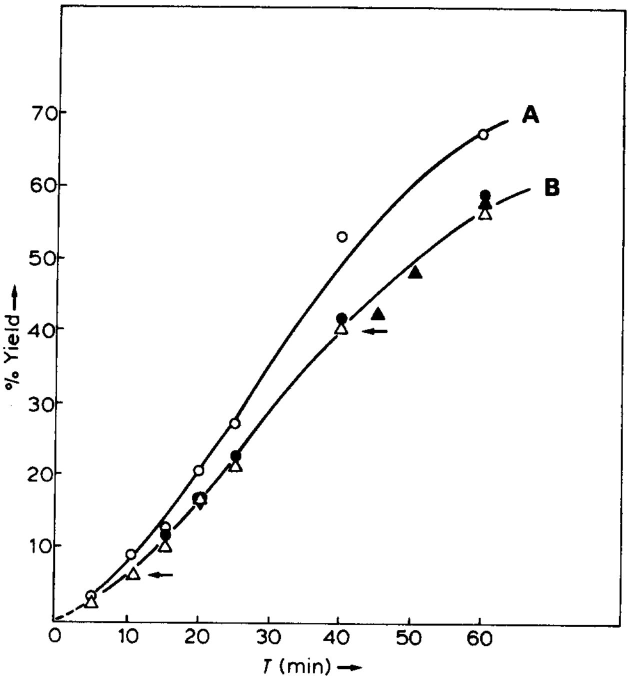

**Figure 4** Effect of initiator on the conversions when injected late in a run in the soapless system. Curve A (recipe: MA 0.1105 M, NaLS nil, KPS $4.114\times 10^{-3}$ M); curve B (recipe: MA 0.1105 M, NaLS nil, KPS $2.057\times 10^{-3}$ M). Additional quantity of initiator was injected at 5.50% and 40.9% conversions of curve B. Amount injected was $2.057\times 10^{-3}$ M. Arrows in the figure indicate the point of injections: (○), control run with $4.114\times 10^{-3}$ M KPS; (△), control run $2.057\times 10^{-3}$ M KPS; (●), $2.057\times 10^{-3}$ M KPS injected at 5.50% conversion; (▲), $2.057\times 10^{-3}$ M KPS injected at 40.90% conversion

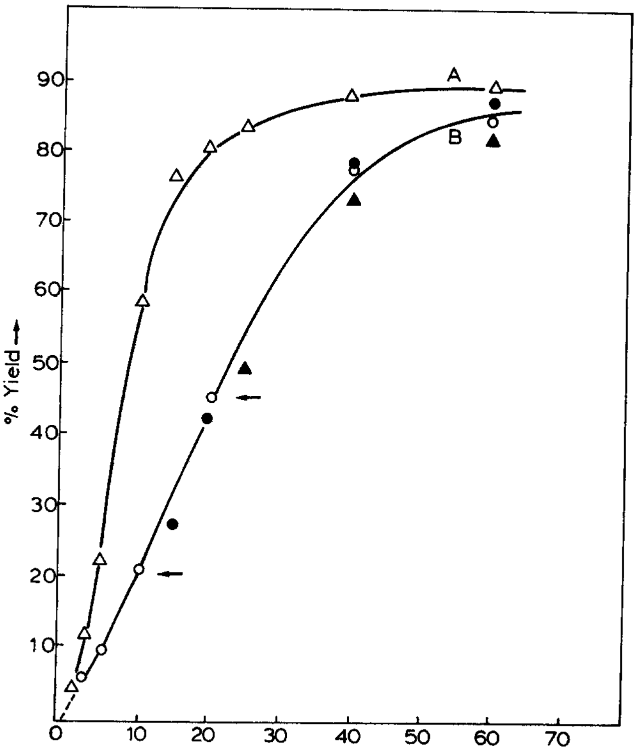

**Figure 5** Effect of initiator on conversions when injected late in a run in the presence of micelle generator (NaLS). Curve A (recipe: MA 0.1105 M, KPS $4.114\times 10^{-3}$ M, NaLS $1.156\times 10^{-2}$ M); curve B (recipe: MA 0.1105 M, KPS $1.225\times 10^{-3}$ M, NaLS $1.156\times 10^{-2}$ M). Extra $2.889\times 10^{-3}$ M KPS was injected at various conversions of B. Arrows indicate the injection points. (○) Control run with $1.225\times 10^{-3}$ M KPS, curve B. (△) Control run with $4.114\times 10^{-3}$ M KPS, curve A. (●) $2.889\times 10^{-3}$ M KPS injected at 20.90% conversion. (▲) $2.889\times 10^{-3}$ M KPS injected at 45.0% conversion

initiator concentrations. In a given run, the molecular weights of the polymers passed through a maximum when $\bar{M}_n$ or $\bar{M}_w$ was plotted against time or conversion (*Tables 1* to *3*). The rise and fall of $M_w$ or $M_n$ in a run were found empirically to run approximately parallel with the rise and fall of the average time rates (i.e. yield in time $t$/time $t$) of polymerizations with time or conversion (*Tables 1, 2* and *3*).

Molecular weights of the polymers were found to increase with the increase of soap concentrations at a given conversion, but decrease at higher soap concentrations (*Table 6*) when the rates of polymerizations were also found to decrease (*Figure 9*). Furthermore, the molecular weights of the polymers were also found to increase with the increase in monomer concentrations (*Tables 4* and *5*) at a given conversion in the presence and absence of detergents. The data in *Table 5* also show that the polymers became almost monodisperse if the soap concentration was above *CMC* and the m/w ratio was higher (i.e. above the solubility of the monomer), provided that the $\eta$ and $\bar{M}_w$ or $\bar{M}_n$ equations used here are correct.

## DISCUSSION

Since methyl acrylate (MA) is relatively water soluble, it is generally believed that the initiation of aqueous and

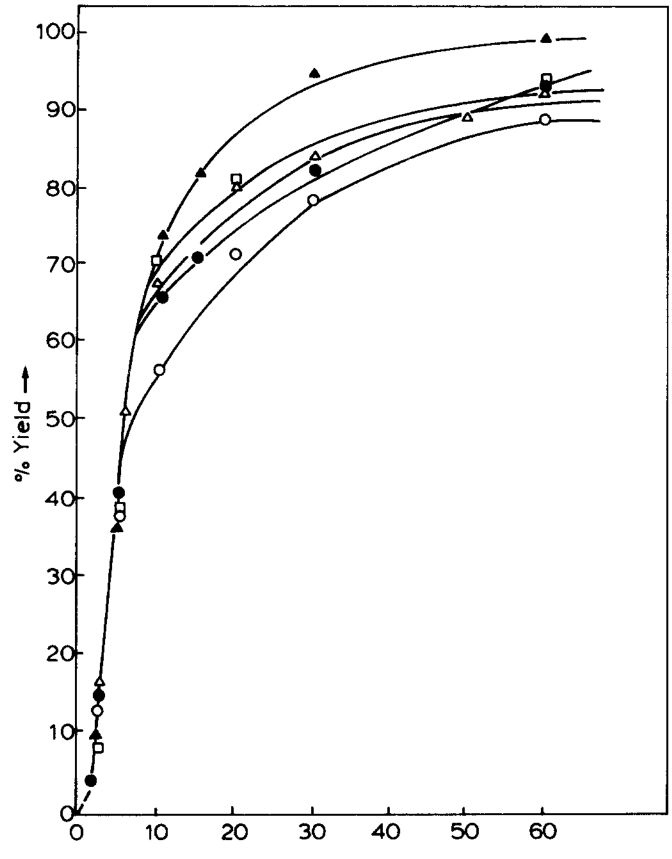

**Figure 6** Effect of (monomer/water) ratio on conversions as a function of time: (○), 5/95; (△), 7.5/92.5; (●), 10/90; (▲), 12.5/87.5; and (□), 15/85 (V/V). Recipe: KPS $1.029 \times 10^{-3}$ M, NaLS $1.156 \times 10^{-2}$ M, stirrer speed 500 rpm

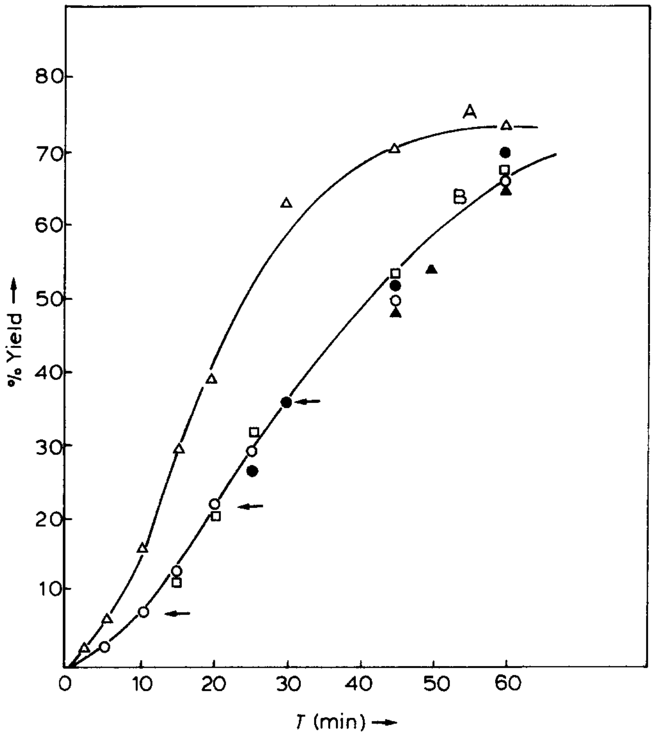

**Figure 7** Effect of additional quantity of monomer (0.1105 M) on conversions as a function of time, when injected late in a run in the soapless system. Recipe of curve A: MA 0.221 M, NaLS nil, KPS $4.114 \times 10^{-3}$ M; recipe of curve B: same as in A except MA was 0.1105 M. Arrows of curve B indicate the injection points at various conversions. Control run with 0.1105 M (○); control run with 0.221 M monomer (△); extra monomer (0.1105 M) injected at 22% conversion (●), and at 35% conversion (▲); 1.0% (V/V) oxygen free distilled water at about 6.0% conversions injected (□)

**Table 4** Effect of monomer on rates and molecular weights when injected late in a run. Recipe: KPS $2.057 \times 10^{-3}$ M, NaLS $1.156 \times 10^{-2}$ M, stirrer speed: 500 rpm

| Time ($t$) | Run 1 | | Run A | | Run B | | Run C | | Run 2 | |
|---|---|---|---|---|---|---|---|---|---|---|
| (min) | $Y$ | $Z$ | $Y$ | $Z$ | $Y$ | $Z$ | $Y$ | $Z$ | $Y$ | $Z$ |
| 5.0 | 12.67 | 0.42 | * | – | – | – | * | – | 30.45 | 0.85 |
| 10.0 | 28.78 | 0.44 | 47.68 | 0.91 | * | – | 24.45 | 0.46 | 52.92 | 1.10 |
| 15.0 | 42.07 | 0.33 | 65.02 | 0.85 | 49.68 | 0.89 | 39.21 | 0.38 | 61.47 | 1.00 |
| 20.0 | 49.13 | 0.30 | 72.72 | 0.75 | 63.21 | 0.94 | 46.21 | 0.32 | 65.77 | 0.98 |
| 25.0 | 56.50 | 0.26 | – | – | 72.73 | 0.91 | 51.15 | 0.28 | – | – |
| 40.0 | 65.23 | 0.18 | 87.58 | 0.76 | 83.40 | 0.89 | 65.35 | 0.24 | 80.01 | 0.95 |
| 60.0 | 72.09 | 0.20 | 89.64 | 0.69 | 87.79 | 0.86 | 71.41 | 0.22 | 85.68 | 0.92 |

Note: Runs 1 and 2 are control runs with initial monomer concentrations 0.1105 M and 0.2210 M, respectively. In runs A and B, some extra (0.1105 M) monomer was injected in the control Run 1 at various conversions indicated by (*) in the above Table. In Run C, 1.0% (V/V) oxygen free distilled water was injected after 12.0% conversions. $Y$ denotes per cent conversions, while $Z = \bar{M}_n \times 10^{-6}$

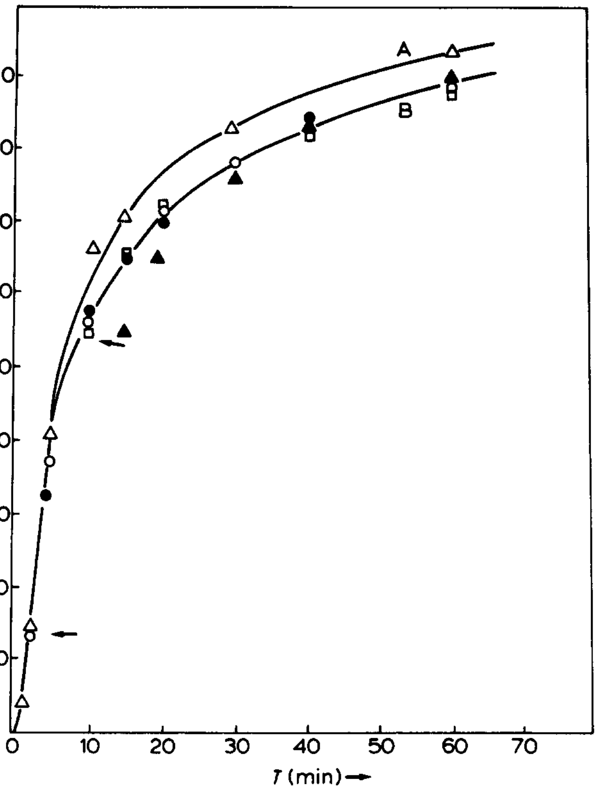

**Figure 8** Effect of additional quantity of monomer when injected late in a run where monomer/water ratios were relatively higher in the presence of detergents (above CMC). Curve A: (recipe: MA 10% (V/V), KPS $1.029 \times 10^{-3}$ M, NaLS $1.156 \times 10^{-2}$ M); curve B (same as in A except MA was 5.0% V/V). Arrows indicate the injection points of additional quantity of monomer (5.0% V/V). Stirrer speed 500 rpm, (□) 5.0% (V/V) oxygen free distilled water were injected at about 13.5% conversion. Curve A (△) with 10.0% (V/V) MA, (control run); curve B (○) with 5.0% (V/V) MA, (also control run); (●) 5.0% (V/V) MA injected at 13.5% conversion of curve B; (▲) 5.0% MA injected at about 53.0% conversion of curve B

emulsion polymerizations of MA takes place in the aqueous medium if the initiator (I) is water soluble. We have recently tested this hypothesis experimentally[1] with two different types of primary free radicals viz. $SO_4^{\bullet -}$ (from $K_2S_2O_8$) and OH (from Fenton's Reagent) generated in the system. The initial rate, $V_0$ (i.e. rate at zero time), was found to be:

$$V_0 \doteqdot k(I)^{0.5}(M)$$

in the soap free system. (M) denotes the monomer concentration in the aqueous phase at the beginning of the polymerization reactions. The above rate expression is the same as that for the free radical initiated homogeneous polymerization of MA.

In this work, it is found that the steady state rate ($R_p$) is given by:

$$R_p = k'(I)^{0.46 \pm 0.04}(\text{soap})^{0.30 \pm 0.03}(\text{m/w})^0 \qquad (1)$$

where the (m/w) ratio was above (5/95) by weight, and

$$R'_p = k''(I)^{0.42 \pm 0.04}(\text{soap})^{0.25 \pm 0.05}(M) \qquad (2)$$

where the m/w ratio was below (5/95) by weight, and (M) was the monomer concentration in the aqueous phase. In the absence of detergents, the separated polymer phase was also a very stable colloid and the steady state rate ($R''_p$) is given by:

$$R''_p = k'''(I)^{0.40 \pm 0.04}(M) \qquad (3)$$

where (M) was below the solubility of the monomer, and $k'$, $k''$ and $k'''$ are proportionality constants. According to the theory of Smith and Ewart for the emulsion polymerization of styrene, $R_p$ is given by (Case II of Smith and Ewart):

$$R_p = 0.5\, k_p C_M (N/N_A) \qquad (4)$$

$$= Z(I)^{0.40}(\text{soap})^{0.60}(\text{m/w})^0 \qquad (5)$$

where Z is a proportionality constant and $C_M$ denotes the monomer concentration in the latex particles, N = number of latex particles per unit volume of the aqueous phase, and $N_A$ is the Avogadro number. Comparing equations (1) and (5), it is evident that the initiator and monomer orders agree very well. Smith and Ewart assumed that the latex particles were produced only from the detergent micelles, whereas in the slightly water soluble monomer systems[2] and even in the styrene[7,8] system, latex particles are produced both in the aqueous and in the micellar phases. The slightly higher value of the initiator exponent viz. 0.46 found in this work may well be

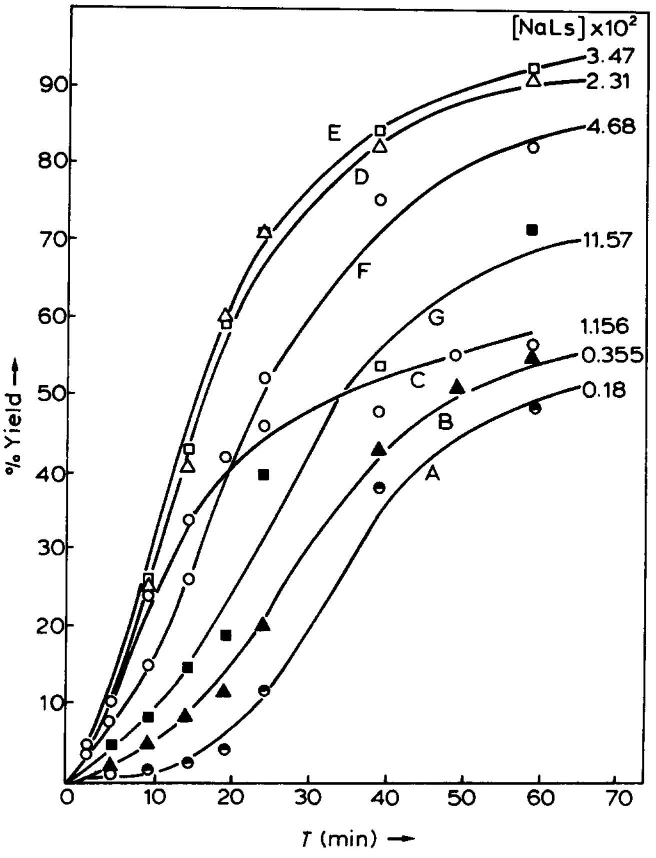

**Figure 9** Effect of soap on conversion as a function of time. Recipe: MA 10.0% (V/V), KPS $1.029 \times 10^{-3}$ M, NaLS varies in the range (0.18 to 11.57) $\times 10^{-2}$ M: NaLS: curve A: $0.180 \times 10^{-2}$ M, curve B: $0.355 \times 10^{-2}$ M, curve C: $1.156 \times 10^{-2}$ M, curve D: $2.310 \times 10^{-2}$ M, curve E: $3.470 \times 10^{-2}$ M, curve F: $4.680 \times 10^{-2}$ M, curve G: $11.57 \times 10^{-2}$ M

due to the simultaneous polymerizations in the aqueous phase and in the monomer–polymer particles.

The initiator order determined by the gravimetric method viz. 0.70 is rather high. This apparently high value seems to be an artefact due to the error in measuring time during sampling of the latex solution from the reactor. If we measure the rate at a given conversion, then there is uncertainty in time measurement if it is less than 5 min (where polymerization occurs at a rapid rate), whereas, if we measure the rate by keeping time fixed, then we see that the conversion was very high (above 80%) at the highest initiator concentration used, and was very low (below 5%) at the lowest initiator concentrations. In these cases order determination will be in error due to the 'gel effect' at higher conversions, leading to the higher value of the order of the initiator[9]. It seems to us that the higher order of the initiator (0.65) found by several workers[10] in the aqueous and emulsion polymerizations of vinyl acetate, may well be due to the gel effect at higher conversions. For reliable order determinations, the rates should be mea-

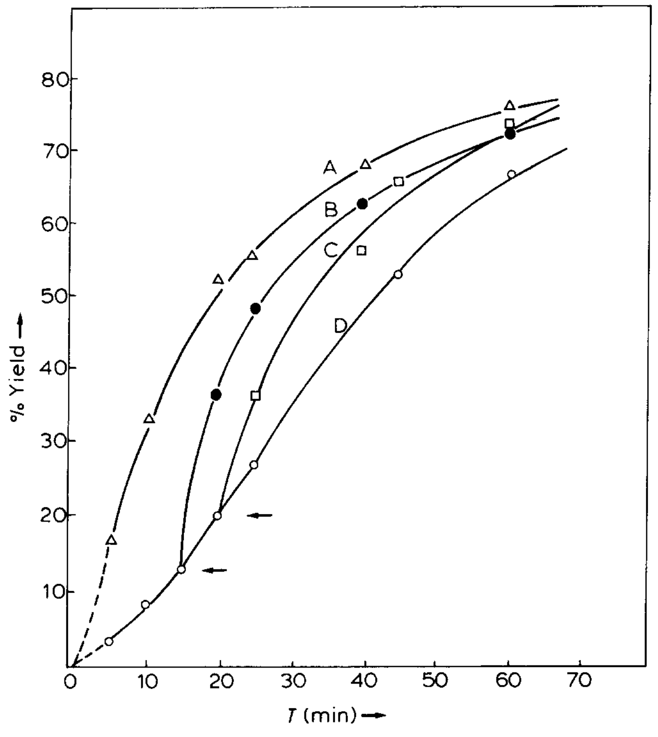

**Figure 10** Effect of soap on the conversions when injected late in a run. Recipe: MA 0.1105 M, KPS $4.114 \times 10^{-3}$ M. Curve A with NaLS $1.156 \times 10^{-2}$ M added at the outset of polymerization. Curve D with no soap. Curve B with 0.012 M NaLS injected at about 12.5% conversion of D, and curve C with 0.012 M NaLS injected at about 20% conversion of curve D. Arrows on D indicate the injection points: (△), curve A with NaLS ($1.156 \times 10^{-2}$ M) present initially. (○), curve D with no NaLS. (●), curve B with $1.156 \times 10^{-2}$ M NaLS injected at 12.5% conversion of curve D. (□), curve C with $1.156 \times 10^{-2}$ M NaLS injected at ~20% conversion of curve D

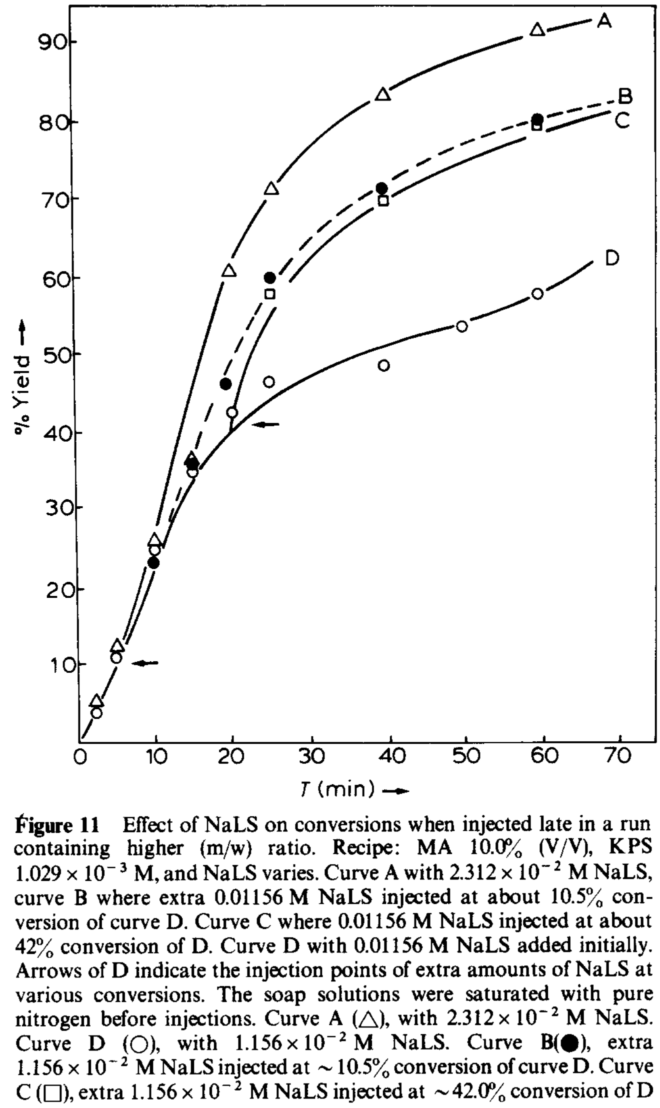

**Figure 11** Effect of NaLS on conversions when injected late in a run containing higher (m/w) ratio. Recipe: MA 10.0% (V/V), KPS $1.029 \times 10^{-3}$ M, and NaLS varies. Curve A with $2.312 \times 10^{-2}$ M NaLS, curve B where extra 0.01156 M NaLS injected at about 10.5% conversion of curve D. Curve C where 0.01156 M NaLS injected at about 42% conversion of D. Curve D with 0.01156 M NaLS added initially. Arrows of D indicate the injection points of extra amounts of NaLS at various conversions. The soap solutions were saturated with pure nitrogen before injections. Curve A (△), with $2.312 \times 10^{-2}$ M NaLS. Curve D (○), with $1.156 \times 10^{-2}$ M NaLS. Curve B(●), extra $1.156 \times 10^{-2}$ M NaLS injected at ~10.5% conversion of curve D. Curve C (□), extra $1.156 \times 10^{-2}$ M NaLS injected at ~42.0% conversion of D

**Table 5** Effect of high monomer/water (m/w) ratio on the molecular weights of polymers. Recipe: KPS $1.029 \times 10^{-3}$ M, NaLS $1.156 \times 10^{-2}$ M, monomer (MA) varies, stirrer speed: 500 rpm

| MA (mol $l^{-1}$) | Time (min) | Per cent conversion | $\bar{M}_w \times 10^{-6}$ | $\bar{M}_n \times 10^{-6}$ | $(\bar{M}_w/\bar{M}_n)$ | $N \times 10^{-15}$ per ml |
|---|---|---|---|---|---|---|
| 1.105 | 5.0 | 40.49 | 3.93 | 3.87 | 1.02 | 2.54 |
| | 10.0 | 66.95 | 3.24 | 3.12 | 1.04 | 2.32 |
| | 30.0 | 82.56 | 2.89 | 2.76 | 1.05 | 0.55 |
| | 60.0 | 94.36 | 2.66 | 2.45 | 1.06 | 0.54 |
| 1.657 | 5.0 | 38.50 | 4.77 | 4.82 | 0.99 | 2.55 |
| | 10.0 | 70.94 | 4.75 | 4.71 | 1.01 | 1.95 |
| | 30.0 | 83.01 | 4.28 | 4.26 | 1.00 | 0.75 |
| | 60.0 | 94.36 | – | – | – | – |

Note: At high (m/w), the polymer appears to be monodisperse under our experimental conditions. Since $\bar{M}_w$ and $\bar{M}_n$ have not been measured independently, this result has to be accepted with reservation. Further, the molecular weight of the polymer was found to increase with (m/w) at a given conversion, it seems that the termination due to chain transfer to monomer in the latex particles is not significant

**Table 6** Effect of soap (NaLS) on $\bar{M}_w$ at a given conversion (here 15%). Recipe: MA 1.105 M, KPS $1.029 \times 10^{-3}$ M, stirrer speed: 500 rpm

| $(NaLS) \times 10^2$ M | 0.18 | 0.355 | 1.156 | 2.312 | 3.47 | 4.63 | 11.57 |
|---|---|---|---|---|---|---|---|
| $\bar{M}_w \times 10^{-6}$ | 0.79 | 0.90 | 2.30 | 2.50 | 3.00 | 2.32 | 2.09 |

Note: $\bar{M}_w$ was found to be maximum when the rate of polymerization was found to be maximum (see *Figure 9*)

sured at a given conversion at various concentrations of the initiator, so as to avoid the complications due to the 'gel effect'.

The order of the initiator is however very close to 0.40 when the monomer concentration was below its solubility, i.e. emulsion polymerization in the absence of emulsified oil droplets. It seems that once the loci were shifted overwhelmingly into the monomer–polymer particles, polymerization would occur mainly in the monomer swollen latex particles as suggested by the Harkins–Smith–Ewart theory, and the unconverted monomer would distribute itself between the aqueous phase and the latex particles. The partition coefficient of the monomer distributing itself between the polymer phase and the aqueous phase, was found to be about 25 ($= C_M$ in polymer/$C_M$ in water) at 25°C. During the steady state rate period therefore the aqueous phase polymerization would be negligible when the initial monomer concentration was below its solubility.

The order of the monomer during the steady state rate period was found to be zero at high (m/w) ratio as predicted by the Smith–Ewart theory. Below the solubility of the monomer, solution polymerization would occur and also the particles would not remain saturated with monomer during the polymerizations. Under such conditions, the rate would clearly depend on the monomer concentrations in the aqueous and polymer phases.

The order of the soap was found to be 0.30, which is not consistent with the Harkins–Smith–Ewart theory. Zersberg[11] has pointed out that the order of the soap would decrease as the solubility of the monomer in water increased. It seems to us that the soap order would also depend on the nature of the interactions between a polymer molecule and a detergent molecule. If the soaps are strongly adsorbed by the polymer molecules or polymeric radicals (as is the case with the non-polar polymers viz. polystyrene, polybutadiene, polyethylene, etc.), the order of the soap was found to be very close to 0.60. If the polymers have partial polarity, as in the case of polyacrylates, the order would be less than 0.60 possibly because of poorer interactions between the soap and the polymer. For a given latex particle size, more soap molecules would be retained on the non-polar polymer particle surface, compared with those on the polar polymer particle surface. This means that the surface area covered by a soap molecule would vary with the nature of the polymer and this has been confirmed experimentally by Britenback *et al.*[12] and Russian workers[5]. The soap order has also been found to depend on the nature of the initiator[13].

Interesting results have been obtained from seeded polymerizations. By injecting an additional quantity of initiator (*Figures 4* and *5*) late in a run, it was found that the rates of polymerizations did not alter as predicted by the Smith–Ewart theory. However, the rates increased when an additional quantity of soap was injected late in a run (*Figures 10* and *11*). It appears that new latex particles were formed when soap was injected into the system, and also the colloidal stability of the latex particles increased. New micelles or mixed micelles would then be produced when an additional quantity of soap is injected into the system. The monomer in the latex particles or in the emulsified oil droplets would again distribute itself between the newly formed micelles and the latex particles, and as a result new particles would be formed which would increase the polymerization rates.

In the case of monomer injections, it was found that as long as the total monomer added to the aqueous phase did not exceed the solubility, and no soap was present, the rates of polymerizations did not increase. In the soap free system (*Figure 7*), any monomer being added late in a run was possibly absorbed by the existing particles because of the very high distribution coefficient of the monomer with respect to the polymer phase. Thus polymerization would occur mainly in the latex particles and to a much lesser extent in the aqueous phase, and so very few new particles would be formed, and the rates would not increase as long as the particles remained saturated with monomer. At higher m/w ratios, $N$ was found to be approximately independent of m/w (*Table 5*), and in these systems (*Figure 8*) injected monomer had no effect on the rates of polymerizations up to 50% conversions when the reaction order was zero with respect to the monomer.

The results shown in *Figure 10* are interesting. For a given monomer concentration (0.1105 M) and given initiator concentration ($4.114 \times 10^{-3}$ M), $N$ was of the order of $10^{14}$ per ml in the soap free system, whereas with monomer (0.1105 M) and a lesser amount of initiator ($2.057 \times 10^{-3}$ M), $N$ was found to be of the order of $10^{15}$ per ml in the presence of detergents above *CMC* (here soap concentration was $1.156 \times 10^{-2}$ M). Hence the relative concentration of monomer in the latex particles of the emulsion system containing detergents would be less compared with that of particles of the soap free system and so the particles of the former system would remain relatively unsaturated with monomer. When an additional quantity of monomer (0.1105 M) was injected into the system containing soap, the rate would increase possibly due to the increase of monomer concentration at the reaction site in the latex particles.

The rise and fall of the molecular weights of polymers in a run had been found to depend on the time average rates of polymerizations (*Tables 1* to *3*). Since the kinetic chain length is given by the ratio of the rate of polymerization/rate of termination or initiation in the steady state, the molecular weights of polymers would clearly depend on the average rate. At a given conversion, $\bar{M}_w$ decreased with the increase of initiator concentrations, but increased with the increase in the monomer concentrations or soap concentrations (*Table 6*). Since $N$ increases with increase in soap concentrations, so $\bar{M}_w$ increases with the soap concentrations as long as the rate increases with the soap concentrations, and this observation is consistent with the theory of Smith and Ewart. Since $\bar{M}_w$ always increases with the increase in the (m/w) ratios (*Tables 4* and *5*), it appears that the chain termination by transfer to monomer molecules in the latex particles, was not significant in this investigation.

It has been observed that when the soap concentrations were relatively higher (above $3.47 \times 10^{-2}$ M) in the system containing MA 1.105 M, KPS $1.029 \times 10^{-3}$ M, the rates decreased (*Figure 9*). It seems that under such conditions, the particles would be saturated with soap, and the excess soap might act as an electrolyte leading to the decrease of $N$ by coagulation. In addition degradative chain transfer to soap molecules may also occur on the polymer surface. All these could well account for the decrease in rates and in molecular weights of polymers at very high soap concentrations. It should be mentioned here that Fitch and Shih[25] observed that $N$ decreased at relatively higher soap concentrations in the emulsion polymerization of methyl methacrylate (recipe: MMA $9.51 \times 10^{-2}$ M, $K_2S_2O_8$ $8.46 \times 10^{-4}$ M, $NaHSO_3$ $1.30 \times 10^{-3}$ M, and ferrous ammonium sulphate $2.74 \times 10^{-6}$ M at 30°C) in the presence of various amounts of sodium dodecyl sulphate (SDS). Some of their results are shown here:

| (SDS) $\times 10^4$ (mol $l^{-1}$) | $N \times 10^{-16}$ per litre | $r_p \times 10^9$ (dm) (particle radius) |
|---|---|---|
| 13.9 | 81.3 | 136 |
| 17.4 | 102.0 | 126 |
| 20.8 | 131.0 | 116 |
| 27.8 | 90.5 | 131 |

Here $N$ is the number average, measured electron microscopically

At very high soap concentrations, it was not possible for us to estimate $N$ by the soap titration technique[1].

We have found empirically that in emulsion or in aqueous polymerizations, the number of latex particles per ml ($N$) in a given run increases with the increase in the colloidal stability ($CS$) of the latex particles, becomes a maximum when $CS$ reaches a maximum, and then decreases with the decrease in the $CS$ of the particles. The data of *Table 3* show that $N$ apparently remains constant after 60% conversion but $CS$ decreases with conversion. This suggests that there is always incipient coagulation in the system, and since $N$ remains approximately constant, new particles are also formed. This means that coagulation of the existing latex particles and formation of new particles in the aqueous phase occur simultaneously as stated previously by Alexander and Napper[18]. This in turn implies that the particle size distribution with time or conversion will be broadened as found by Robb[27] and by Gardon[16] in the emulsion polymerizations of styrene.

The material presented in this paper clearly shows that the results of this study can be explained qualitatively with the help of the Harkins–Smith–Ewart theory. Since $k_d$ (rate constant for $S_2O_8^{2-} \rightarrow 2SO_4^{\cdot -}$) increases with the increase in MA concentrations in the aqueous phase[2,14], and since $k_p$ and $k_t$ for the emulsion polymerizations of MA have not yet been measured experimentally, it is not possible at this stage to predict quantitatively the kinetics of the emulsion polymerization of MA. The normal practice in emulsion polymerization kinetics is to assume that $k_p$ for a particular monomer at a given temperature in the emulsion polymerization is the same as that for the homogeneous polymerization under identical experimental conditions, and $k_t$ (usually estimated from the Smith–Ewart theory, Case II) would not change as long as the particles remain saturated with monomer during the emulsion polymerizations. Melville[15] found in the homogeneous polymerization of vinyl acetate that $k_t$ decreased continuously with conversion from the outset of polymerization, and $k_p$ decreased after 46% conversion. After the theory of Smith and Ewart, many theories[16–21] have emerged dealing with emulsion polymerizations, but none gave a satisfactory quantitative description of the emulsion polymerization of styrene over the entire range of (m/w) ratios viz. from 0.50/99.50 to 40/60 by weight, because the theories are based on some assumptions which are not supported by the experimental data.

Recently it has been suggested that the mode of chain termination in the emulsion polymerization of styrene initiated by $K_2S_2O_8$ in the presence of sodium lauryl sulphate as micelle generator may well be due to the chain transfer to monomer in the latex particles[26]. If this hypothesis is correct, then the average number of 'end-groups' per polymer molecule should be much less than unity. The experimental data of VanderHoff *et al.*[22] and of others[23] indicate an average value of two end groups per chain. VanderHoff *et al.* think that the chain termination in the latex particles is due to the bi-polymeric radicals interaction, whereas Smith and Ewart[28] believed that it was due to the interaction of a primary free radical ($SO_4^{\cdot -}$) and a polymeric radical. Only Palit *et al.*[24] reported that the end-groups per polymer chain were much less than unity in the emulsion polymerization of styrene initiated by $K_2S_2O_8$, by the dye–partition technique, which was criticized by VanderHoff *et al.*[22]. However, if 20 to 30% of the chains are terminated by chain transfer to the monomer, and the rest by the interaction of two polymeric/oligomeric radicals in the monomer swollen polymer particles, then it would be difficult to find the contribution of chain termination by the transfer reactions by the end-group analysis of polymers. Chatterjee *et al*[27] showed by injecting monomer late in a run in the emulsion polymerization of styrene that the chain termination by transfer to monomer was not significant.

Furthermore, many authors[17,21,26] have assumed that the monomeric free radicals produced due to the chain transfer to the monomer in the latex particles in the emulsion polymerization of vinyl monomers (viz. styrene, methyl methacrylate, methyl acrylate, vinyl acetate, acrylonitrile, butyl acrylates, vinyl chloride, etc.) would distribute themselves between the aqueous phase and the polymer phase (latex particles) because of thermodynamic requirements. This may well happen if the monomeric radicals are produced on the surface of the latex particles or in the aqueous phase. However, if they are produced inside the latex particles having high viscosity ($\eta = 10^3$ poise or more), then would these radicals have extra energy to swim to the surface of the particles through the highly viscous path? The authors have tested their hypotheses by the curve fitting method for analysing the experimental data, assuming values for $k_p$, $k_t$, etc. in the emulsion polymerization system. If the monomeric radicals are produced only on the surface of the latex particles, it implies that polymerization would occur only on the surface of the particles as proposed by the Medvedev theory[2]. Such a hypothesis is difficult to prove experimentally for these monomers whose polymers are also soluble in their respective monomers.

We have tried to correlate the colloid stability ($CS$) with $N$ empirically (*Figure 12*) and it is found that $N$ is related

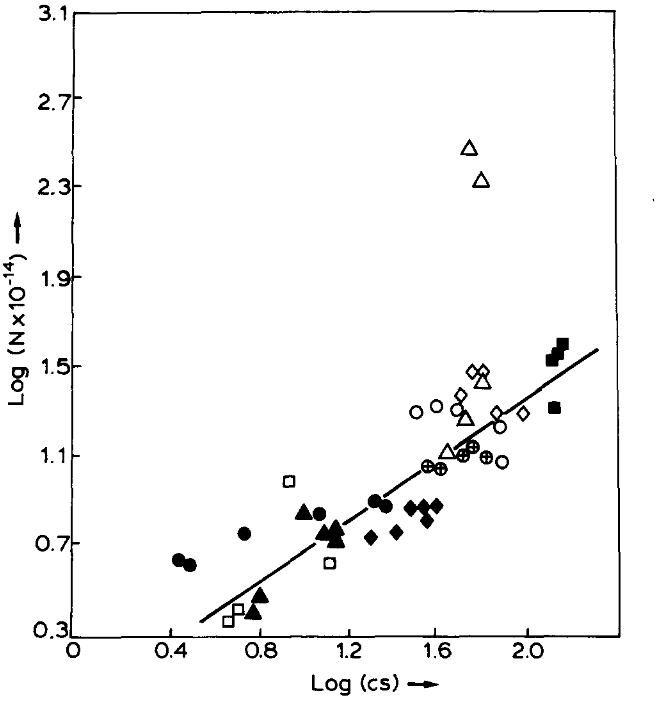

**Figure 12** Empirical correlation between the number of latex particles per ml, (*N*), and the colloidal stability (*CS*) of the latex particles. A linear relation has been found and the curve has been drawn by the least squares method. The slope of the line is about 0.80 (by least squares) in the plot of $\log_{10}$ ($N \times 10^{-14}$) *versus* $\log_{10}$ (*CS*)

to *CS* by the equation:

$$\log_{10}N = \log_{10}A + n\log_{10}(CS)$$

Least squares treatment of the data of *Figure 12* gives, $n = 0.80$ and $\log_{10}(A \times 10^{-14}) = -0.172$. Qualitatively, *N* is approximately proportional to the *CS* of the latex particles.

### *Effect of stirring*

It was observed that stirring decreased the rates of polymerizations in the soap free system (*Figure 2*), whereas it increased the rates in the soap containing system (*Figure 1*). Each run of *Figures 1* and *2* were repeated 5 times, and the average values are shown in the Figures. The standard error was found to be about 5% of the mean value. It seems that the small difference between curves A and B of *Figure 2*, is real and not due to experimental error. It appears that stirring brings about rapid coagulation of latex particles, as a result of which *N* decreased and so the rates fell in the soap free system, whereas it makes stable emulsions in the soap containing systems. Stable emulsions would enhance the values of *N* and also help rapid monomer transport to the latex particles from the emulsified oil droplets through the aqueous phase. All these would increase the rates in the soap containing system.

### *Average number of radicals per particle*

We have estimated the average number of radicals (*Q*) per particle assuming that the Smith–Ewart equations as modified by Gardon[16] would be applicable in this system from 10 to 60% conversion (case II of Smith and Ewart). Some results are shown in *Table 7*. It can be seen that *Q* is about 0.5 at low conversions, but increases continuously with conversion, i.e. with particle volume. This increase is not consistent with the predictions of the Smith–Ewart theory.

**Table 7** Average number of radicals per particle as a function of conversion. Recipe: MA 0.1105 M, NaLS $1.156 \times 10^{-2}$ M, KPS $2.057 \times 10^{-3}$ M, stirrer speed: 200 rpm

| Per cent conversion | 12.67 | 25.78 | 42.07 | 49.15 |
|---|---|---|---|---|
| *Q* | 0.54 | 0.58 | 0.60 | 0.63 |

Recipe: MA 1.105 M, KPS $1.029 \times 10^{-3}$ M, NaLS $2.312 \times 10^{-2}$ M, stirrer speed: 500 rpm

| Per cent conversion | 11.70 | 25.34 | 47.40 | 60.45 |
|---|---|---|---|---|
| *Q* | 0.59 | 0.69 | 0.78 | 0.88 |

The results presented here clearly show that the emulsion polymerization of MA can be described qualitatively by the Harkins–Smith–Ewart theory.

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