Kinetics and mechanism of potassium persulphate-initiated aqueous polymerization of methacrylonitrile at 50°C in an inert atmosphere of nitrogen gas

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The mechanism of persulphate-initiated aqueous polymerization of methacrylonitrile (MAN) has been investigated kinetically at 50 C in an inert atmosphere of nitrogen gas by the conventional gravimetric method within the solubility range of the monomer. It has been found that the rate of polymerization (R_p) of MAN is proportional to the square root of the initiator concentration [I] and the 1.6 power of the monomer concentration [M], i.e.

$$R_p \propto [I]^{0.50 \pm 0.05}[M]^{1.6 \pm 0.05}$$

It has been suggested that both the monomer and the water-soluble monomeric/oligomeric free radicals react with the persulphate ions in aqueous solutions (pH 4 to 7), viz. reactions C and D, which would then compete with the well established reactions A and B:

$$S_2O_8{}^{2-} \rightarrow 2SO_4^{\bullet\,-} \tag{A}$$

$$S_2O_8{}^{2-} + H_2O \rightarrow 2HSO_4{}^- + \tfrac{1}{2}O_2 \qquad \text{at pH 5 to 7} \tag{B}$$

$$S_2O_8{}^{2-} + M \rightarrow {}^{\bullet}M\text{–}O\text{–}SO_3{}^- + SO_4^{\bullet\,-} \tag{C}$$

$$S_2O_8{}^{2-} + (M_j^{\bullet})_w \rightarrow M_j\text{–}O\text{–}SO_3{}^- + SO_4^{\bullet\,-} \qquad j = 1 \text{ to } 10 \tag{D}$$

where $(M_j^{\bullet})_w$ is a water-soluble monomeric/oligomeric free radical. The separating polymer phase was in the aqueous solution as a stable colloid. The distribution coefficient of MAN between the polymer and the aqueous phase was found to be 1.8 ± 0.2 at 50°C in the presence and absence of electrolytes ($[K_2SO_4] = 7.5 \times 10^{-3}$ mol dm^{-3}). The termination rate constants in the aqueous phase (k_{tw}) and the polymer phase (k_{tp}) have been estimated as $k_{tw} = 1.29 \times 10^5$ dm^3 mol^{-1} s^{-1} and $k_{tp} = 1.90 \times 10^2$ dm^3 mol^{-1} s^{-1}, based on the literature value of k_p of MAN as 26 dm^3 mol^{-1} s^{-1} at 50°C. The locus of polymerization is partly in the aqueous phase and partly in the polymer phase.

(Keywords: free-radical polymerization; methacrylonitrile; kinetics)

INTRODUCTION

We have studied the mode of decomposition of potassium persulphate in aqueous solution of different monomers[1–3] and found that the kinetic data of the $S_2O_8{}^{2-}$–methacrylonitrile (MAN) system could be explained by the following elementary reactions[3]:

$$S_2O_8{}^{2-} \xrightarrow{k_1} 2SO_4^{\bullet\,-}$$

$$S_2O_8{}^{2\;\;} + H_2O \longrightarrow HSO_4{}^- + {}^{\bullet}OH + SO_4^{\bullet\,-}$$

$$\text{or } 2HSO_4{}^- + \tfrac{1}{2}O_2$$

$$S_2O_8{}^{2-} + M \xrightarrow{k_5} {}^{\bullet}M\;\;O\text{–}SO_3{}^- + SO_4^{\bullet\,-}$$

$$(M_j^{\bullet})_w + S_2O_8{}^{2-} \xrightarrow{k_{10}} M_j\;\;O\;\;SO_3{}^- + SO_4^{\bullet}$$

k_5 and k_{10} were estimated as 1.05×10^{-5} and 1.14×10^3 dm^3 mol^{-1} s^{-1} respectively at 50°C. While the aqueous polymerization of acrylonitrile has been studied extensively by Thomas *et al.*[4], Dainton *et al.*[5], Konar *et al.*[6] and others[7], no information is available on the aqueous and emulsion polymerization of methacrylonitrile. So we are reporting here the persulphate-initiated aqueous polymerization of methacrylonitrile in unbuffered aqueous solutions (pH = 3.5 to 7) at 50°C in the presence of nitrogen gas.

EXPERIMENTAL

Polymerization of MAN has been studied gravimetrically in a 1 litre round-bottomed Pyrex flask fitted with a Hg seal, stirrer and side tubes for passing nitrogen and for extracting solutions under nitrogen pressure for analysis. The details of the experimental procedure have been reported elsewhere[1]. To avoid complications during polymerizations, no buffer solutions were used. The pH of the medium was always above 3.5 and so the H^+-catalysed decomposition of persulphate ions was not significant[8,9]. We have found that K_2SO_4 (7.5×10^{-3} mol dm^{-3}) has no measurable effect on the rates of polymerization. The polymer formed was a stable colloid. Water was distilled twice from alkaline permanganate solutions[10]. Both the potassium persulphate (E. Merck,

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GR grade) and potassium sulphate (BDH, GR grade) were recrystallized three times from doubly distilled water. The monomer was supplied by Fluka (AG, stabilized by hydroquinone) and was washed with dilute sodium hydroxide (1%) solution, then thoroughly with distilled water to make it free from alkali. It was then dried over anhydrous calcium chloride, vacuum distilled and the distillate was passed over anhydrous calcium chloride and kept overnight. The monomer was then vacuum distilled and fractionated. The middle fraction (refractive index 1.401 at 25°C) was collected and stored at −5°C. The monomer was distilled before use to avoid peroxide formation. While acrylonitrile ($CH_2{=}CH{-}CN$) is highly soluble in water (8.5 wt% at 50°C)[11], methacrylonitrile ($CH_2{=}C(CH_3)CN$) is sparingly soluble in water. The measured solubility of MAN is found to be about 2.8 wt% at 50°C. Molecular weight was estimated from the intrinsic viscosity data in dimethylformamide (DMF) solvent at 30°C using the Mark Houwink equation[12], i.e.

$$[\eta] = K\bar{M}_v^{\alpha}$$

where $K = 0.306$ ml g^{-1} and $\alpha = 0.503$.

RESULTS

Table 1 shows the reproducibility of results of MAN polymerization under a given set of experimental conditions. The run was repeated 10 times, and the percentage conversion and the $\bar{M}_v$ of the polymer sample were measured as functions of time. It is seen that there is always an induction period (*IP*), which varies from run to run. The *IP* may be due to the presence of traces of dissolved O_2 in the system. It may also be due to the slow attack of $SO_4^{\cdot -}$ radicals on MAN molecules compared to those of acrylates[13]. The end of the induction period was signalled by the sudden appearance of haziness when scattered blue light was noticed (Tyndall scattering). This is taken as zero time for polymerization. It is seen that the uncertainty in percentage conversion in a given time is less than 2%. The results also indicate that in a given run, percentage conversion and $\bar{M}_v$ of polymers increased with time. It is seen that, if the induction period is identical from run to run, the results were highly reproducible (*Table 1*).

The results of the aqueous polymerization of methacrylonitrile initiated by $K_2S_2O_8$ are shown in *Figures 1* to *3*. *Figure 1* shows the conversion time curves at a given concentration of the monomer (0.30 mol dm^{-3}) and at various concentrations of the initiator (0.5×10^{-3} to 7.5×10^{-3} mol dm^{-3}). The ionic strength (μ =

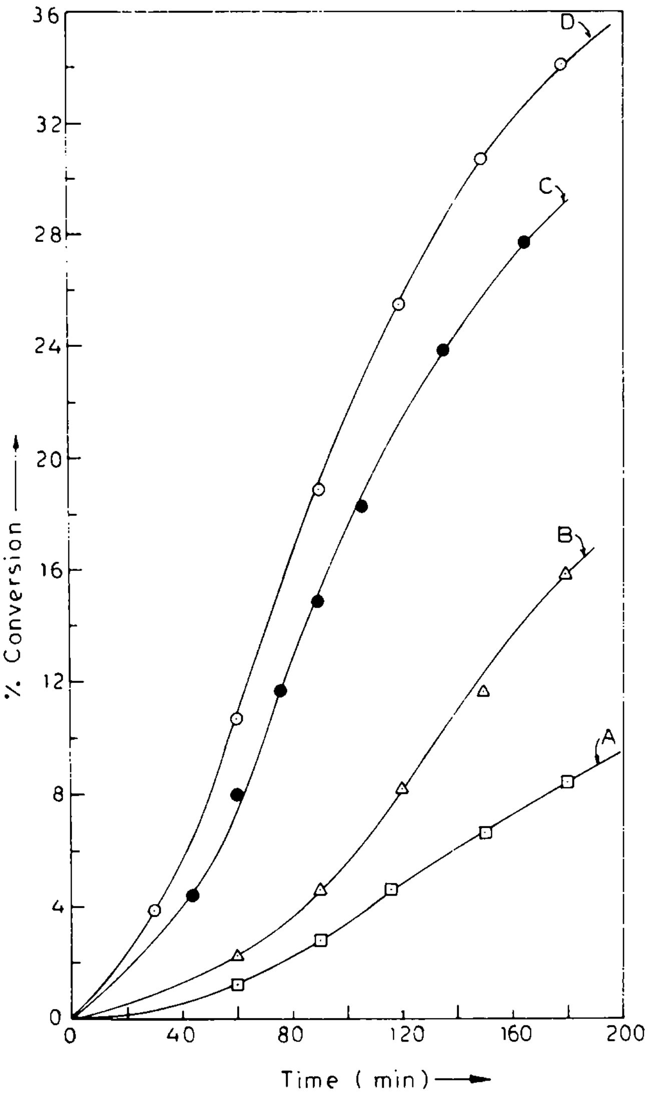

Figure 1 The conversion time (t) curves of methacrylonitrile (MAN) at 50°C in aqueous solution. [MAN] fixed at 0.30 mol dm^{-3}. [$K_2S_2O_8$] varies: (A) 0.5×10^{-3}, (B) 1×10^{-3}, (C) 5×10^{-3}, (D) 7.5×10^{-3} mol dm^{-3}. Ionic strength was kept constant by adding K_2SO_4

Table 1 Reproducibility of results[a]: [MAN] – 0.30 mol dm^{-3}; [$K_2S_2O_8$] – 5.0×10^{-3} mol dm^{-3}; temp. – 50°C

Time (min)		R_1 *IP* – 10m15s	R_2 9m	R_3 8m15s	R_4 7m30s	R_5 6m	R_6 9m25s	R_7 8m50s	R_8 8m30s	R_9 8m	R_{10} 9m5s	Average
45	*a* –	4.89	4.89	5.76	5.84	7.35	5.00	5.24	5.55		4.88	5.49 ± 0.79
	b –		-	–		3.60	2.99		2.79			3.13 ± 0.42
75	*a* –	11.13	11.83	12.48	13.07	15.94	11.40	11.40	9.96	12.80	11.60	12.16 ± 1.60
	b –	5.63		4.63		5.79	5.32		4.33		5.09	5.14 ± 0.57
105	*a* –	16.97	18.62	19.43	20.39	22.69	18.32	17.92	18.02	20.55	17.80	19.07 ± 1.71
	b –	7.40		6.11		6.60	6.61		6.77		6.43	6.65 ± 0.43
135	*a* –	22.14	23.92	24.44	26.75	26.55	23.85	23.33	24.03	25.60	23.13	24.37 ± 1.49
	b –	7.47	-	6.02		5.54	6.71		7.77		6.31	6.14 ± 0.86
165	*a*	26.47		26.91	30.17	30.09	27.54	27.74	28.12	30.36	26.93	28.26 ± 1.54
	b –	6.36		5.78	-	5.34	6.13		7.43		5.79	6.14 ± 0.72

[a] Time after induction period (*IP*); *a* – percentage conversion, *b* – $\bar{M}_v \times 10^{-5}$; m – minute, s – second; R_n denotes *n*th run

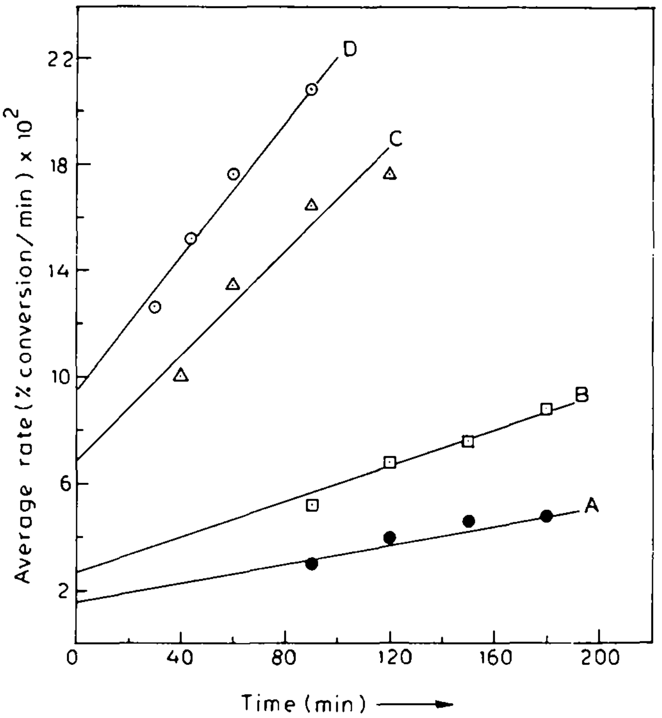

Figure 2 Estimation of rate at zero time $(R_p)_{t=0}$ or zero conversion from the intercept of the plot of time average rate (i.e. conversion at time *t*/time *t*) *versus* time *t* in the early stages of the reaction. Recipe same as in *Figure 1*. $[MAN] = 0.30\ mol\ dm^{-3}$. $[K_2S_2O_8] = 0.5 \times 10^{-3}$ (A), 1×10^{-3} (B), 5×10^{-3} (C) and $7.5 \times 10^{-3}\ mol\ dm^{-3}$ (D)

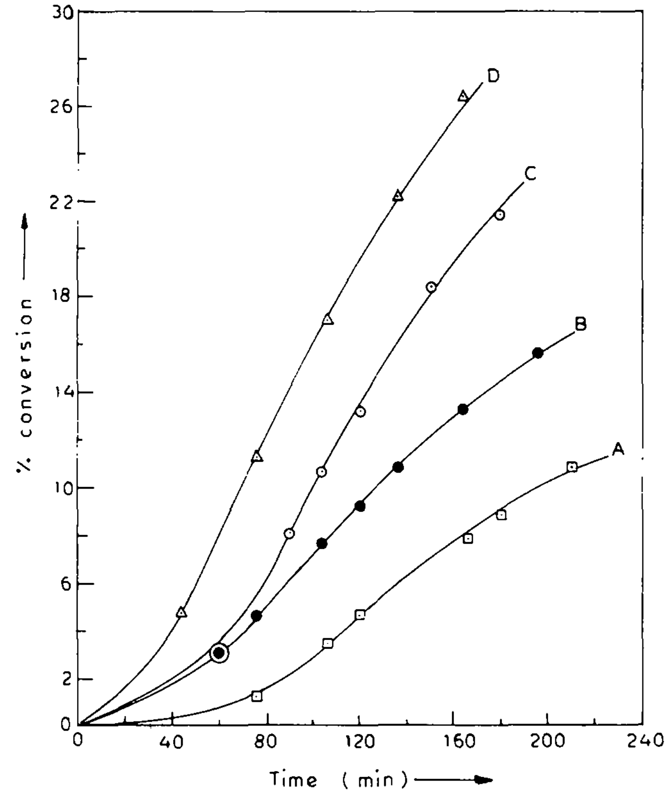

Figure 3 Conversion–time (*t*) curves of MAN polymerization at a given concentration of the initiator ($5.0 \times 10^{-3}\ mol\ dm^{-3}$) and at various concentrations of the monomer (MAN): (A) [MAN] = 0.16, (B) 0.20, (C) 0.24 and (D) 0.30 mol dm^{-3}

$22.5 \times 10^{-3}\ mol\ dm^{-3}$) was kept constant by adding K_2SO_4. Initial rates (below 10% conversion) were determined by plotting the average rate (percentage conversion/time) *versus* time (*Figure 2*) and extrapolating the resulting straight line to zero time. The intercept in *Figure 2* gives the initial rate. *Figure 3* shows the conversion–time curves at a given concentration of the initiator ($5.0 \times 10^{-3}\ mol\ dm^{-3}$) and at various concentrations of the monomer (0.30 to 0.16 mol dm^{-3}). *Figures 4* and *5* show the conventional order plots for the initiator and for the monomer respectively. The order of the initiator was found to be 0.5 ± 0.05 and that of monomer was found to be 1.6 ± 0.05. The effect of monomer injected late in a run on the rate of polymerization is shown in *Figure 6*, when the rate was found to

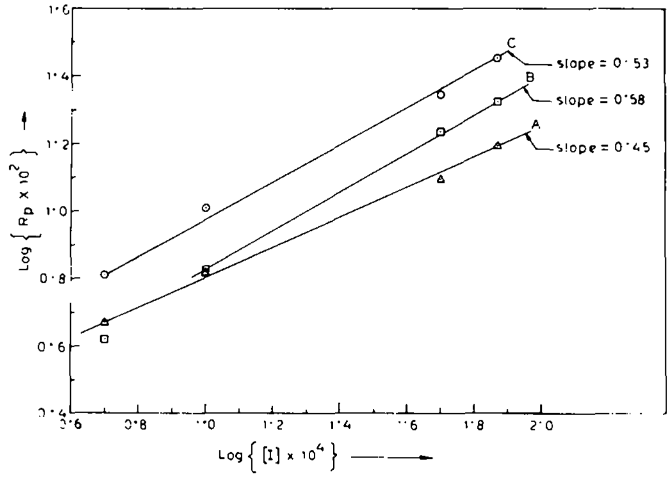

Figure 4 Order plot for the initiator from the rates of polymerizations: (A) rate (R_p) defined as [8% conversion/time (min)]; (B) rate (R_p) defined as per cent polymerized in 120 min; (C) rate (R_p) between 8% and 12% conversion at various initiator concentrations [I] (mol dm^{-3}) for a given MAN concentration, and the rates were estimated from the conversion–time curves

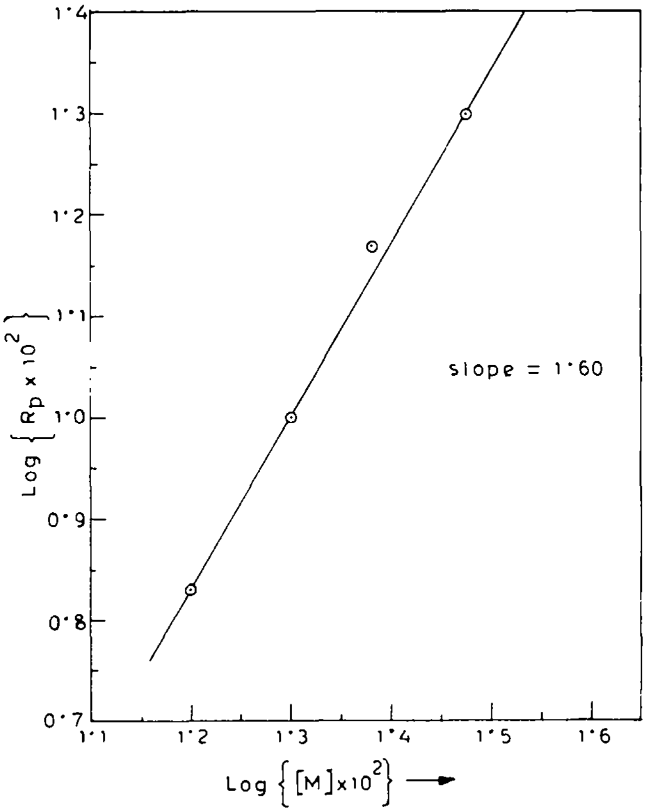

Figure 5 Order plot for the monomer from the rates of polymerizations: rate (R_p) defined as (percentage conversion/minute) and data taken from *Figure 3* for 8% to 12% conversion

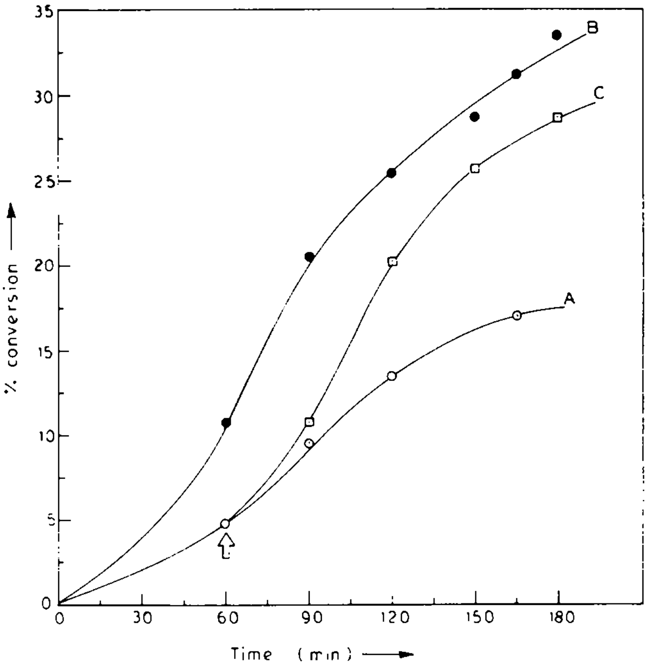

Figure 6 Effect of additional quantity of monomer when injected late in a run. Curve A: [MAN] = 0.20 mol dm^{-3}, [I] = 7.5 × 10^{-3} mol dm^{-3}. Curve B: [MAN] = 0.30 mol dm^{-3}, [I] = 7.5 × 10^{-3} mol dm^{-3}. Curve C: 0.10 mol dm^{-3} MAN injected in control run A at about 5% conversion. Arrow indicates the injection point of additional quantity of monomer

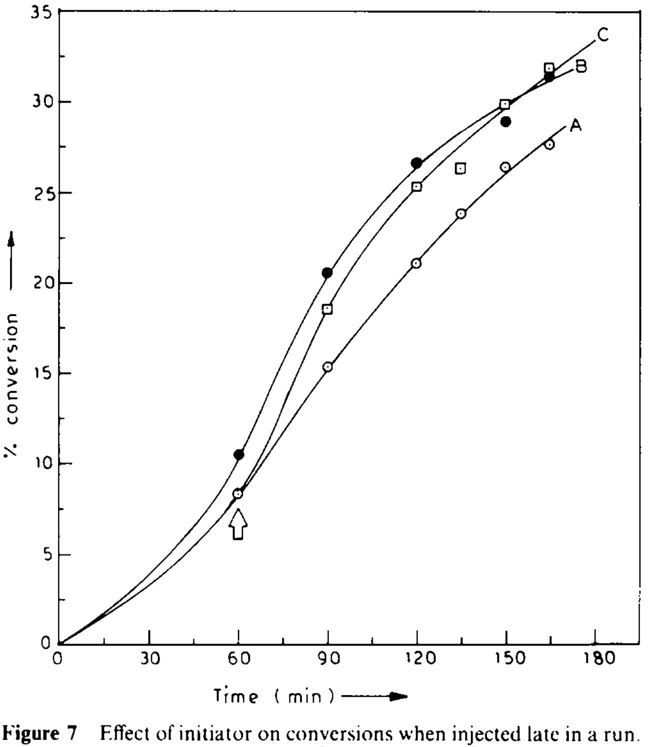

Figure 7 Effect of initiator on conversions when injected late in a run. Curve A: [MAN] = 0.30 mol dm^{-3}, [I] = 5 × 10^{-3} mol dm^{-3}. Curve B: [MAN] = 0.30 × 10^{-3} mol dm^{-3}, [I] = 7.5 × 10^{-3} mol dm^{-3}. Curve C: 2.5 × 10^{-3} mol dm^{-3} extra initiator injected in control run A at about 8.5% conversion. Arrow indicates the injection point of additional quantity of initiator

increase. *Figure 7* shows the effect of initiator injected late in a run on the rate of polymerization. Here, also, the rate was found to increase. The viscosity-average molecular weight ($\bar{M}_v$) of the polymers was found to increase in a given run up to 10 to 20% conversions (*Tables 1* and *2*). The molecular weights of polymers, however, at a given conversion, were found to decrease with increase of initiator concentrations (*Table 3*) but to increase with increase of monomer concentrations (*Table 2*). The molecular weight of polymers seems to be very high; it may be that K and α in the equation $[\eta] = K\bar{M}_v^{\alpha}$ are in error, or may not be applicable in this system. Very few data (for polymethacrylonitrile *N,N*-dimethylformamide at 30°C) are available. In the monomer injected experiments late in a run, $\bar{M}_v$ of polymers at a given conversion was found to increase (*Table 4*). There was no measurable change in $\bar{M}_v$ of polymers in the initiator injected experiments late in a run (*Table 5*).

DISCUSSION

To explain the results of the thermal decomposition of persulphate in aqueous solution in the presence of methacrylonitrile, the following mechanism has been suggested:

$$S_2O_8^{2-} \xrightarrow{k_1} 2SO_4^{\cdot -} \tag{1}$$

$$SO_4^{\cdot -} + H_2O \xrightarrow{k_2} HSO_4^- + {}^{\cdot}OH \tag{2}$$

$$2\dot{O}H \xrightarrow{k_3} H_2O_2 \text{ (or } H_2O + \tfrac{1}{2}O_2) \tag{3}$$

$$SO_4^{\cdot -} + M \xrightarrow{k_4} M_1^{\cdot} \ (= {}^-O_3S\text{–}O\text{–}\dot{M}) \tag{4}$$

$$SO_4^{\cdot -} + M\ (= RH) \xrightarrow{k_{4a}} HSO_4^- + R^{\cdot} \tag{4a}$$

$$S_2O_8^{2-} + M \xrightarrow{k_5} M_1^{\cdot} + SO_4^{\cdot -} \tag{5}$$

all in the aqueous phase;

$$M_j^{\cdot} + M(=RH) \xrightarrow{k_{trm}} M_jH + R^{\cdot} \tag{6}$$

$$M_j^{\cdot} + M \xrightarrow{k_p} M_{j+1}^{\cdot} \tag{7}$$

in water, in the particle and also at the particle–water interface;

$$(M_j^{\cdot})_w \rightleftharpoons (M_j^{\cdot})_p \tag{8}$$

at the particle–water interface, and when $j = 1$ to 10;

$$(M_j^{\cdot})_w + P \text{ (dead particle)} \leftrightharpoons P^* \text{ (active particle)} \tag{9}$$

at the particle water interface;

Table 2 Variation of molecular weights of polymers[a] as a function of monomer concentration [M]

Time (min)		[M] = 0.16 mol dm^{-3}	[M] = 0.20 mol dm^{-3}	[M] = 0.24 mol dm^{-3}	[M] = 0.30 mol dm^{-3}
60	a =		5.12	3.03	10.37
	b =	–	–		4.25
90	a =	5.44	8.52	7.85	20.43
	b =		0.85	2.49	6.75
120	a =	7.75	11.92	14.16	26.39
	b =		1.04	2.72	6.23
135	a =	8.64	13.29	17.29	28.81
	b =		0.89	2.79	6.27
165	a =	–	17.29	–	31.20
	b =	–	0.66	–	5.35
210	a =	14.31	–	–	–
	b =	0.30		–	–

[a] a = percentage conversion, $b = \bar{M}_v \times 10^{-5}$; [I] = 7.5 × 10^{-3} mol dm^{-3}

Table 3 Variation of the molecular weights of the polymers[a] as a function of the initiator concentration [I], at a given concentration of monomer, $[M] = 0.30\ \mathrm{mol\ dm^{-3}}$

Time (min)		$[I] = 0.5 \times 10^{-3}$ mol dm^{-3}	$[I] = 2.0 \times 10^{-3}$ mol dm^{-3}	$[I] = 5.0 \times 10^{-3}$ mol dm^{-3}	$[I] = 7.5 \times 10^{-3}$ mol dm^{-3}
	$a =$	1.23	5.17	8.03	10.37
60	$b =$	–	–	–	4.25
	$c =$	–	–	–	2.07
	$a =$	2.74	9.74	14.84	20.43
90	$b =$	–	–	7.2	6.75
	$c =$	–	–	2.70	2.62
	$a =$	4.98	16.22	20.94	26.39
120	$b =$	–	11.60	7.7	6.23
	$c =$	–	3.43	2.79	2.51
	$a =$	6.67	20.86	25.80	30.6
150	$b =$	–	11.09	7.4	5.65
	$c =$	–	3.37	2.74	2.39
	$a =$	9.38	–	–	33.95
160	$b =$	14.88	–	–	5.35
	$c =$	3.90	–	–	2.33

[a] a = percentage conversion, $b = \bar{M}_v \times 10^{-5}$, $c = [\eta] \times 10^{-2}\ \mathrm{ml\ g^{-1}}$

Table 4 Effect of monomer on molecular weights, when injected late in a run[a]: $[I] = 7.5 \times 10^{-3}\ \mathrm{mol\ dm^{-3}}$

Conversion (%)	Run A, $\bar{M}_v \times 10^{-5}$	Run B, $\bar{M}_v \times 10^{-5}$	Run C, $\bar{M}_v \times 10^{-5}$
7.5	0.8	–	–
10.0	0.95	4.2	4.2
15.0	0.80	6.1	6.35
20.0	–	6.7	7.45
25.0	–	6.65	7.65
30.0	–	5.8	6.50

[a] Runs A and B are control runs with initial monomer concentration $0.20\ \mathrm{mol\ dm^{-3}}$ and $0.30\ \mathrm{mol\ dm^{-3}}$ respectively. In run C, some extra monomer ($0.10\ \mathrm{mol\ dm^{-3}}$) was injected in the control run A, at about 5.0% conversion

Table 5 Effect of initiator on molecular weights of polymers when injected late in a run[a]: $[M] = 30 \times 10^{-2}\ \mathrm{mol\ dm^{-3}}$

Conversion (%)	Run A, $\bar{M}_v \times 10^{-5}$	Run B, $\bar{M}_v \times 10^{-5}$	Run C, $\bar{M}_v \times 10^{-5}$
10	5.60	4.20	–
15	7.25	5.80	–
20	7.70	6.70	8.05
25	7.50	6.75	7.80
27.5	7.20	6.45	7.55
30.0	–	5.81	6.39

[a] Runs A and B are control runs with initial initiator concentrations $5 \times 10^{-3}\ \mathrm{mol\ dm^{-3}}$ and $7.5 \times 10^{-3}\ \mathrm{mol\ dm^{-3}}$, respectively. In run C, extra initiator ($2.5 \times 10^{-3}\ \mathrm{mol\ dm^{-3}}$) was injected at 8.5% conversion of run A

$$(M_j^{\bullet})_w + S_2O_8^{2-} \xrightarrow{k_{10}} (M_j\text{–O–}SO_3^{-})_w + SO_4^{\bullet -} \quad (10)$$

in the water phase;

$$(M)_w \leftrightharpoons (M)_p \quad (11)$$

at the particle–water interface;

$$2(M_j^{\bullet})_w \xrightarrow{k_{tw}} \text{polymer} \quad (12)$$

in water; and

$$2(M_i^{\bullet})_p \xrightarrow{k_{tp}} \text{polymer} \quad (13)$$

in latex particles or between two active particles if they coagulate, for $i = 1$ to any value, say, 1000 or more.

In this reaction scheme, the following notation is used: $(M_j^{\bullet})_w$ are water-soluble oligomeric free radicals, $j = 1$ to 10, according to Dainton *et al.*[5]; $(M_i^{\bullet})_p$ are radicals present in the latex particles, which may be water-soluble or water-insoluble (if $i > 10$); if $i = j$, then $M_i^{\bullet}$ and $M_j^{\bullet}$ radicals are the same; it is assumed that $M_i^{\bullet}$ and $R^{\bullet}$ radicals are indistinguishable with respect to suggested chemical reactions; the radicals $M_i^{\bullet}$ having $i > 10$ would be found only in the polymer phase[14]; k_p and k_t are assumed to be independent of polymer chain lengths[11,15,16]. The reactions (i) between $SO_4^{\bullet -}$ and $(M_j^{\bullet})_w$ in the aqueous phase, (ii) between two non-geminate $SO_4^{\bullet -}$ radicals and (iii) between the $(M_i^{\bullet})_p$ and $SO_4^{\bullet -}$ radicals in the latex phase are believed to be not significant[8]. From the proposed reaction model[1,5,6,17–22], it is evident that the rate of initiation (R_i) in the aqueous phase is given by:

$$R_i = (2k_1 + 2k_5[M]_w + k_{10}[M_j^{\bullet}]_w)[S_2O_8^{2-}]V_w \quad (14)$$

Total rate of termination (R_t) in the aqueous and latex phases is given by:

$$R_t = 2k_{tp}[M_i^{\bullet}]_p^2 V_p + 2k_{tw}[M_j^{\bullet}]_w^2 V_w \quad (15)$$

where V_w and V_p are the volume fractions of the water phase and of the polymer phase, respectively, i.e. $V_w + V_p = 1.0$. We have estimated[3] $k_5 = 1.05 \times 10^{-5}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$, $k_{10} = 1.14 \times 10^3\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$, $k_1 = 1.7 \times 10^{-6}\ \mathrm{s^{-1}}$ and $[M_j^{\bullet}]_w = 10^{-9}\ \mathrm{mol\ dm^{-3}}$. It is seen that the initiation due to (10) is negligible compared to those due to (1) and (5) together at a given concentration of persulphate and of monomer. Hence neglecting reaction (10) in equation (14), we get in the steady state:

$$[M_j^{\bullet}]_w = \frac{(k_1 + k_5[M]_w)^{0.5}[S_2O_8^{2-}]^{0.5}V_w^{0.5}}{(k_{tp}\beta^2 V_p + k_{tw}V_w)^{0.5}} \quad (16)$$

where $\beta = [M_i^{\bullet}]_p/[M_j^{\bullet}]_w$ can have values as high as 1000 or more[21] and k_t would not alter significantly during the constant-rate period (believed to be the steady-state rate) from 10 to 30% conversion[20,21].

We assume[17–23] $[M_j^{\bullet}]_p/[M_j^{\bullet}]_w = [M]_p/[M]_w = \alpha$, where α is the distribution coefficient of the monomer between the polymer phase and aqueous phase under the experimental conditions. If $j = 1$, the above relation is not far from being true, because $M_1^{\bullet}$ and M have the same solubility in water. We get the steady-state rate of polymerization (R_p) as:

$$R_p = k_p[M]_w(V_w + \beta\alpha V_p) \times \frac{(k_1 + k_5[M]_w)^{0.5}[S_2O_8{}^{2-}]^{0.5}V_w{}^{0.5}}{(k_{tp}\beta^2 V_p + k_{tw}V_w)^{0.5}} \qquad (17)$$

α has been measured experimentally by the bromometric estimation of the monomer present in the aqueous phase containing a known amount of PMAN polymer (freshly prepared) and of monomer (MAN), initially at 50°C in an inert atmosphere of nitrogen for 24 h for equilibration, in the presence and absence of an added electrolyte (potassium sulphate) at various concentrations. The average value of α at 50°C was found to be about 1.8 ± 0.2 under our experimental conditions, viz. $V_w \gg V_p$ or $V_w \simeq 1.0$. We consider two cases to solve the equation (17).

Case 1. When aqueous phase polymerization and termination are more important than the corresponding reactions in the polymer phase, then at zero time or zero conversion, the locus of polymerization would be overwhelmingly in the aqueous phase. We assume that the rate at zero time or zero conversion would be the steady-state rate at zero time, $(R_p)_{t=0}$. Hence:

$$(R_p)_{t=0} = k_p k_{tw}^{-0.5}[M]_w V_w(k_1 + k_5[M]_w)^{0.5} \times [S_2O_8{}^{2-}]^{0.5} \qquad (18)$$

Taking $V_w = 1.0$ at zero conversion, and squaring (18), we get:

$$(R_p)^2_{t=0}/[M]^2_w = (k_p^2/k_{tw})(k_1 + k_5[M]_w)[S_2O_8{}^{2-}] \qquad (19)$$

The left-hand side of (19) has been plotted against $[S_2O_8{}^{2-}]$ at a given concentration of monomer in *Figure 8* and the line passed through the origin as required by equation (19). Taking k_p as 26 $dm^3\ mol^{-1}\ s^{-1}$ from the literature[12], k_1 as $1.7 \times 10^{-6}\ s^{-1}$ and k_5 as $1.05 \times 10^{-5}\ dm^3\ mol^{-1}\ s^{-1}$, the estimated value for k_{tw} from the slope ($=2.56 \times 10^{-8}\ dm^3\ mol^{-1}\ s^{-2}$, as obtained from *Figure 8*) was found to be $1.29 \times 10^5\ dm^3\ mol^{-1}\ s^{-1}$.

Case 2. If the polymerization occurs mainly in the monomer-adsorbed PMAN latex particles as postulated by the Smith–Ewart or Medvedev theory[11], and the aqueous phase termination is negligible, then:

$$R_p = k_p[M]_w(V_w + \alpha\beta V_p) \times \frac{(k_1 + k_5[M]_w)^{0.5}V_w^{0.5}[S_2O_8{}^{2-}]^{0.5}}{\beta(k_{tp}V_p)^{0.5}} \qquad (20)$$

Since $\beta = [M_i^{\bullet}]_p/[M_j^{\bullet}]_w = 1000$ or more, then $(\alpha\beta V_p) > V_w$ and so:

$$R_p = k_p[M]_w\alpha V_p^{0.5}k_{tp}^{-0.5}(k_1 + k_5[M]_w)^{0.5} \times V_w^{0.5}[S_2O_8{}^{2-}]^{0.5}$$

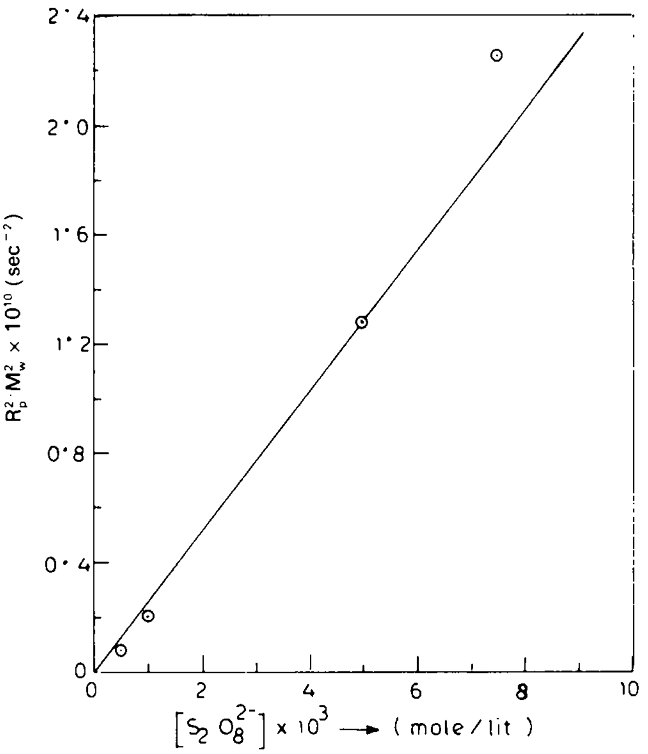

Figure 8 Plot of $R_p^2/[M]_w^2$ of equation (19) *versus* $[S_2O_8{}^{2-}]$. The line passes through the origin and has slope $2.56 \times 10^{-8}\ dm^3\ mol^{-1}\ s^{-1}$

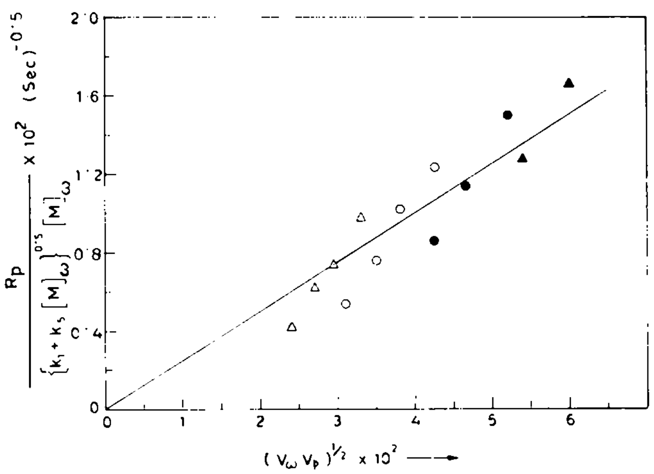

Figure 9 Left side of equation (21) *versus* $(V_pV_w)^{0.5}$. The line passes through the origin and has slope $0.24\ s^{-0.5}$: (△) 6% conversion, (○) 10% conversion, (●) 15% conversion, (▲) 20% conversion; data corresponding to 15% conversion are not shown in *Table 6*

or

$$R_p = k_p[M]_p V_p^{0.5}k_{tp}^{-0.5}(k_1 + k_5[M]_w)^{0.5} \times V_w^{0.5}[S_2O_8{}^{2-}]^{0.5}$$

Since $[M]_p = \alpha[M]_w$, rearranging the equation we get:

$$\frac{R_p}{(k_1 + k_5[M]_w)^{0.5}[M]_w} = k_p k_{tp}^{-0.5}\alpha[S_2O_8{}^{2-}]^{0.5}(V_pV_w)^{0.5} \qquad (21)$$

By plotting the left-hand side of (21) *versus* $(V_pV_w)^{0.5}$ at a given concentration of the initiator (5.0×10^{-3} mol dm^{-3}) and at various concentrations of the monomer (*Table 6*), we get a straight line (*Figure 9*) passing through the origin. From the slope of the line ($0.24\ s^{-0.5}$) we get $k_{tp} = 1.90 \times 10^2\ dm^3\ mol^{-1}\ s^{-1}$ at 50°C taking $\alpha = 1.8$ and k_p of MAN as 26 $dm^3\ mol^{-1}\ s^{-1}$.

Table 6 Estimation of $(V_pV_w)^{0.5}$ under various experimental conditions[a]: [persulphate] = 5.0×10^{-3} mol dm^{-3}; initial monomer, $[M]_1$, varies

$[M]_i$ (mol dm^{-3})	$[M]_w$ (mol dm^{-3})	Conversion (%)	$R_p \times 10^5$ (mol dm^{-3} s^{-1})	$(k_1 + k_5[M]_w)^{0.5} \times 10^3$ (s$^{-0.5}$)	$\frac{R_p \times 10^2}{(k_1 + k_5[M]_w)^{0.5}[M]_w}$ (s$^{-0.5}$)	$(V_pV_w)^{0.5} \times 10^2$
0.30	0.282	6.0	0.60	2.16	0.99	3.32
0.24	0.226	6.0	0.343	2.02	0.75	2.98
0.20	0.188	6.0	0.220	1.92	0.61	2.72
0.16	0.150	6.0	0.115	1.81	0.42	2.43
0.30	0.270	10.0	0.705	2.13	1.23	4.27
0.24	0.216	10.0	0.401	2.02	0.93	3.85
0.20	0.180	10.0	0.260	1.90	0.76	3.51
0.16	0.144	10.0	0.136	1.79	0.53	3.14
0.30	0.240	20.0	0.834	2.05	1.67	6.08
0.24	0.192	20.0	0.500	1.93	1.29	5.44
0.30	0.209	30.0	0.768	1.97	1.86	7.46

[a] $V_p + V_w = 1.0$; R_p = percentage conversion in time t/time t; i.e. rate at various conversions

The results presented suggest that the aqueous polymerization of MAN initially takes place entirely in the aqueous phase; but with the progress of the polymerization reactions, the loci of the polymerization would gradually shift into the monomer adsorbed PMAN latex particles, and the polymerization would continue in both phases.

From *Table 4* and *Figure 6* it is seen that, when monomer was injected late in a run, both the rate of polymerization and the $\bar{M}_v$ of polymers also increased. Since the kinetic chain length (γ) is equal to the rate of polymerization divided by the rate of initiation (R_p/R_i), therefore $\bar{M}_v$ would increase if R_p increases and R_i remains unaltered. Since it is a case of heterogeneous polymerization, and polymerization would mainly occur in the latex particles, it could be that the increased R_p was due to the increase of [M] at the reaction site when an additional quantity of monomer was injected into the system. However, increase of R_p and $\bar{M}_v$ would also be associated with the increase of the number of particles per millilitre (N), as given by the Smith–Ewart theory of emulsion polymerization[11], viz.:

$$R_p = Qk_p[M]\frac{N}{N_A} = \tfrac{1}{2}k_p[M]\frac{N}{N_A}$$

where $Q = 1/2$ according to Smith–Ewart, and N_A is the Avogadro number.

It is interesting to note that under identical experimental conditions (same molar concentration of monomer and initiator), the initial rate of polymerization of acrylonitrile (AN) is about two times faster than MAN (*Figure 10*). The literature value[12] of k_p of AN is 32.5×10^3 dm^3 mol^{-1} s^{-1} and that of MAN is 26 dm^3 mol^{-1} s^{-1} at 30°C. It seems that the presence of the methyl group in the 1-position of the molecule, $\overset{2}{C}H_2{=}\overset{1}{C}(CH_3)CN$, exhibits the steric barrier in the addition of $SO_4^{\cdot-}$ radical to the monomer molecule. It is also to be noted that the presence of methyl group in MAN decreases its solubility in water appreciably compared to that of AN. Similar observations were also recorded by Adhikari[24] in the polymerization of methyl acrylate (MA), methyl methacrylate (MMA) and ethyl methacrylate (EMA), where the initial rate of polymerization of MA was about two times faster than that of MMA and the initial rate of polymerization of ethyl acrylate (EA) was about three times faster than that of EMA.

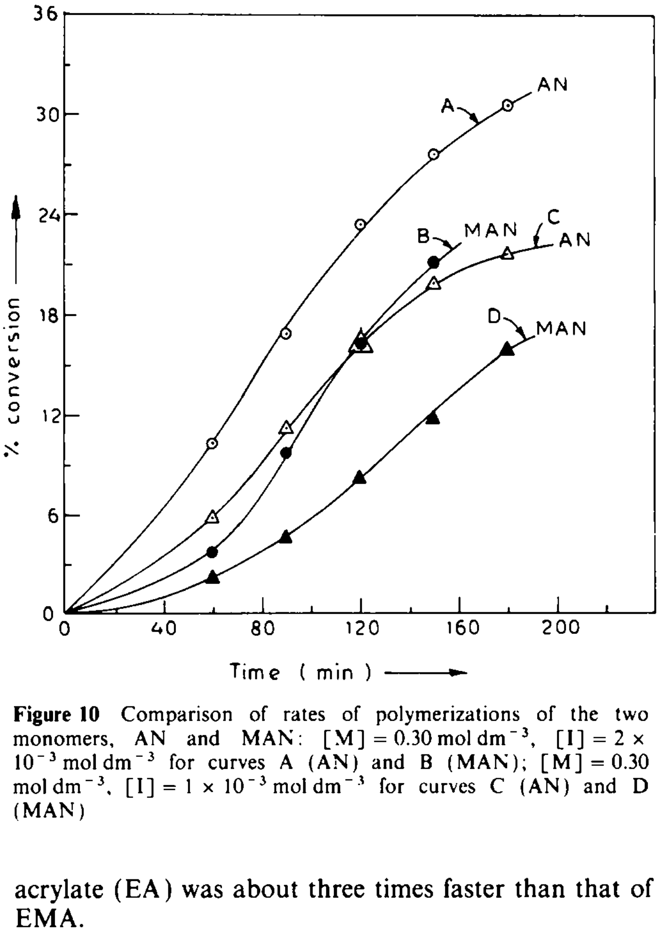

Figure 10 Comparison of rates of polymerizations of the two monomers, AN and MAN: [M] = 0.30 mol dm^{-3}, [I] = 2×10^{-3} mol dm^{-3} for curves A (AN) and B (MAN); [M] = 0.30 mol dm^{-3}, [I] = 1×10^{-3} mol dm^{-3} for curves C (AN) and D (MAN)

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