Persulfate Initiated Aqueous Polymerization of Acrylonitrile at 50°C in an Inert Atmosphere of Nitrogen Gas
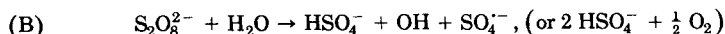
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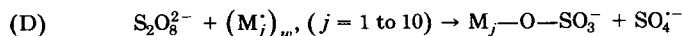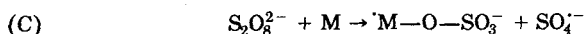
Synopsis

The rate of aqueous polymerization (R_p) of acrylonitrile (AN) initiated by potassium persulfate at 50°C, is given by:

$$R_p \propto \left(S_2O_8^{2-}\right)^{0.47 \pm 0.06} \times (M)^{1.40 \pm 0.059}$$

where (M) stands for monomer concentrations. It has been suggested that persulfate ions in aqueous solution (pH 4 to 7) decompose not only via the well established paths viz.: (A) and (B)

(A) $$S_2O_8^{2-} \rightarrow 2SO_4^{\cdot-}$$

(B) $$S_2O_8^{2-} + H_2O \rightarrow HSO_4^- + OH + SO_4^{\cdot-}, \left(\text{or } 2\,HSO_4^- + \tfrac{1}{2}\,O_2\right)$$

but also via (C) and (D) in the presence of AN monomer:

(C) $$S_2O_8^{2-} + M \rightarrow {}^{\cdot}M\!-\!O\!-\!SO_3^- + SO_4^{\cdot-}$$

(D) $$S_2O_8^{2-} + \left(M_j^{\cdot}\right)_w, (j = 1 \text{ to } 10) \rightarrow M_j\!-\!O\!-\!SO_3^- + SO_4^{\cdot-}$$

where $(M_j^{\cdot})_w$ is a water-soluble monomeric/oligomeric free radical. The separating polymer phase remains in aqueous solution as a stable colloid, or a precipitate, depending on the ionic strength of the medium. At high conversions in general, and even at low conversions at relatively higher monomer concentrations, (1.20 m/dm³), the colloidal latex polymer was found to have a tendency to form gel, and the viscosity of the medium was found to increase with conversions. The distribution coefficient of the monomer between the polymer and the aqueous phases was found to be (0.50 ± 0.10) at 50°C in the presence and absence of electrolytes (K_2SO_4 7.5×10^{-3} m/dm³). The termination rate constants in the aqueous phase (k_{tw}) and in the polymer phase (k_{tp}) have been estimated as given below:

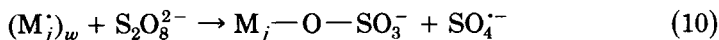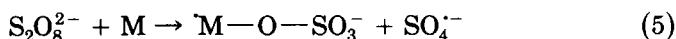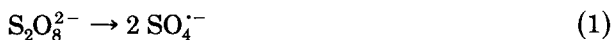$$k_{tw} = 5.95 \times 10^{10}; \text{ and } k_{tp} = 3.83 \times 10^7, \text{ in dm}^3/\text{m/s},$$

taking k_p of Dainton et al. as 6.22×10^4 (dm³/m/s) at 50°C.

INTRODUCTION

Recently, we have reported[1] the mode of persulfate decomposition in an aqueous unbuffered solution (pH 4 to 7) in the presence of nitrogen and acrylonitrile, and found that the following elementary reactions could explain

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the kinetic data quantitatively:

$$S_2O_8^{2-} \rightarrow 2\,SO_4^{\cdot-} \tag{1}$$

$$S_2O_8^{2-} + M \rightarrow {\cdot}M{-}O{-}SO_3^- + SO_4^{\cdot-} \tag{5}$$

$$(M_j^{\cdot})_w + S_2O_8^{2-} \rightarrow M_j{-}O{-}SO_3^- + SO_4^{\cdot-} \tag{10}$$

The thermal decomposition of persulfate in aqueous solutions at various pH in a given temperature, has been reviewed recently by Behrman and Edwards,[2a] and by Wilmarth et al.[2b] We have assumed that the Evans–Baxendale reaction (1) would be important at 50°C, and have ignored the reaction (1a), viz:

$$S_2O_8^{2-} + H_2O \rightarrow HSO_4^- + OH + SO_4^{\cdot-} \ \left(\text{or } 2\,HSO_4^- + \tfrac{1}{2}O_2\right), \tag{1a}$$
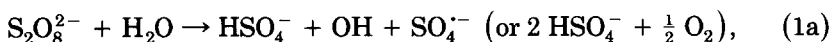
since the pH of the solution did not alter in the presence of monomer (AN), 1.20 m/dm³. It has been suggested that the reaction (1a) would be important at lower temperatures[2a] (below 30°C). From the kinetic data,[1] we have estimated k_5 as 1.70×10^{-5} (dm³/m/s) and k_{10} as 5.08×10^3 (dm³/m/s) at 50°C. In light of this finding, we have reinvestigated the persulfate-initiated aqueous polymerization of acrylonitrile (unbuffered and pH 4 to 7) at 50°C in the presence of nitrogen gas, and the results are reported here.

EXPERIMENTAL

The quality of chemicals used, their processing and purifications have been reported earlier.[1] The polymerization reactions were studied gravimetrically as well as dilatometrically.[3,4] The reaction was carried out in unbuffered solutions, in order to avoid the chain transfer reactions between the growing polymeric radicals and buffer reagents viz. HPO_4^{2-} and $H_2PO_4^-$ ions for pH 5 to 7. The pH of the medium was kept above 3, so that the H^+ ion catalyzed decomposition of persulfate ions would not be significant.[2,5] Further, we have found that K_2SO_4 (4.0×10^{-3} m/dm³) has no measurable effect on the rates of persulfate decompositions (1.0×10^{-3} m/dm³) under our experimental conditions. We did not use buffer solutions because the impurities (particularly traces of metal ions) present in the salts used for making buffer solutions would accelerate the decomposition of persulfate and also affect the polymerization reactions. Both the potassium persulfate (E. Merck GR grade) and the potassium sulfate (GR grade BDH) were recrystallized three times from the double-distilled water. Similar observations were made by Bovey et al.[6] who studied the effect of sodium perchlorate on persulfate decompositions in aqueous solutions of pH 7. Behrman and Edwards[2a] reported that the rates of persulfate decompositions would depend on the ionic strength of the medium in highly acidic and alkaline solutions. At a given temperature, the rate of persulfate decomposition would vary with the pH of the medium (in the pH range 3 to 14) and attain a maximum value at pH 7. Wilmarth et al.,[2b] on the other hand, have stated that the rate would be independent of pH (3 to 14) at a given temperature. We have found no measurable change in the rates of persulfate decompositions at 50°C in the pH range 4 to 7, provided all the reagents are thoroughly purified. During polymerizations, the ionic strength of the medium was kept constant by adding K_2SO_4.

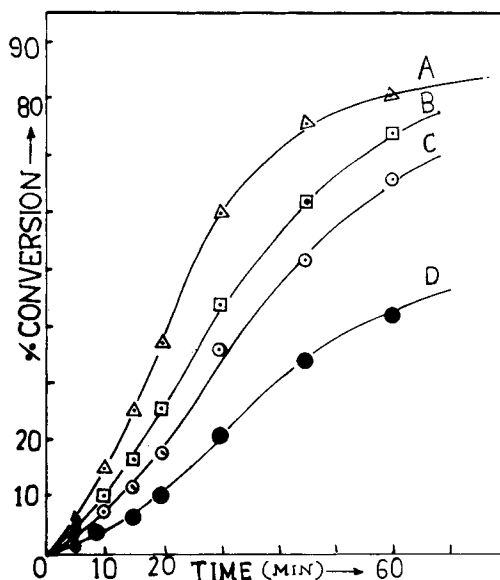Fig. 1.   The conversion-time (t) curves of acrylonitrile (AN) polymerization at 50°C in aqueous solution. Recipie: AN fixed, 1.20 (m/dm³); $K_2S_2O_8$ varies: (A) 1.82×10^{-2}; (B) 9.2×10^{-3}; (C) 4.6×10^{-3}; and (D) 1.82×10^{-3} (m/dm³). Ionic strength was kept constant by adding K_2SO_4.

RESULTS

The results of the aqueous polymerization of acrylonitrile initiated by $K_2S_2O_8$ are shown in Figures 1 to 4. Figure 1 shows the conversion-time curves at a given concentration of the monomer (1.20 m/dm³) and at various concentrations of the initiator, viz.: 1.8×10^{-2} to 1.8×10^{-3} (m/dm³). Figure 2 shows the determination of initial rate at zero time. Keeping the conversions within 10 to about 25%, the time average rates have been plotted against time and the resulting straight line has been extrapolated to zero time. It is assumed that[7,8] the intercept at zero time would be a measure of the initial rate at zero conversion or zero time at a given concentration of the initiator. Figure 3 shows the conversion-time curves at a given concentration of the initiator (1.80×10^{-2} m/dm³) and at various concentrations of the monomer, viz.: 1.20 to 0.30 (m/dm³).

The rates of polymerization were found to increase with the increase of monomer and initiator concentrations. Figure 4 displays the results obtained from the dilatometer. Figures 1, 2, and 4 show clearly that the shapes of the conversion-time curves were functions of both the monomer and the initiator concentrations. Figures 5 and 6 show the conventional order plots for the initiator and for the monomer, respectively. The order of monomer was found to be about 1.40 from the data of Figures 3 and 4, while the order of the initiator was found to be about 0.47 from the data of Figure 1. Figures 1 and 3 show that there were constant rate periods in a given run from about 10 to 30% conversions, and this implies that the constant rate in a given run is approximately independent of polymer volume (from 10 to 30% conversion), as required by the Smith-Ewart Theory (Case II) for the emulsion polymerization of sparingly water soluble styrene like monomers.
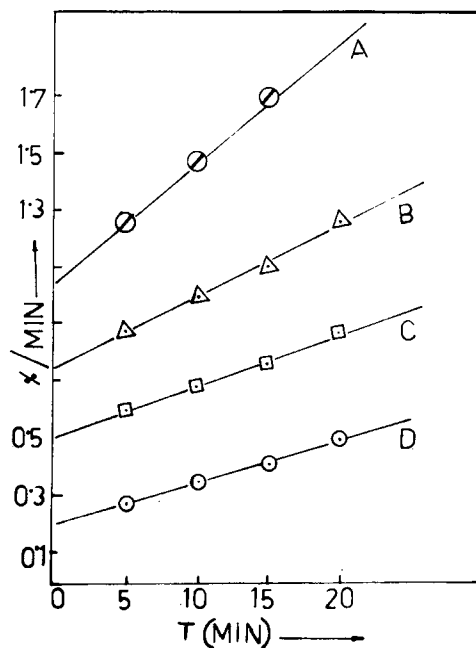
Fig. 2. Estimation of rate at zero time, $(R_p)_{t=0}$, or zero conversion from the intercept of the plot, time average rate (i.e., % conversion at time t/time t) versus time t at the early stages of the reaction. Recipe same as in Figure 1. (A) 1.82×10^{-2}; (B) 9.2×10^{-3}; (C) 4.6×10^{-3}; (D) 1.82×10^{-3} (m/dm^3) $K_2S_2O_8$.
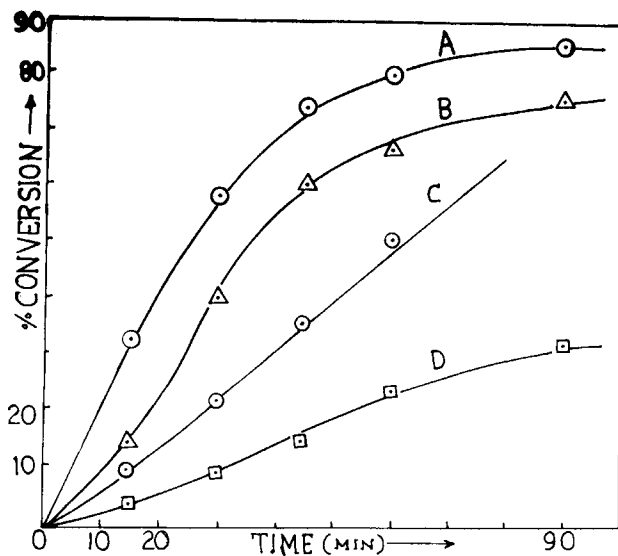

Fig. 3. Conversion-time (t) curves of AN polymerization at a given concentration of the initiator (1.80×10^{-2} m/dm^3), and at various concentrations of the monomer (AN): (A) 1.20; (B) 0.90; (C) 0.60; and (D) 0.30 (m/dm^3);
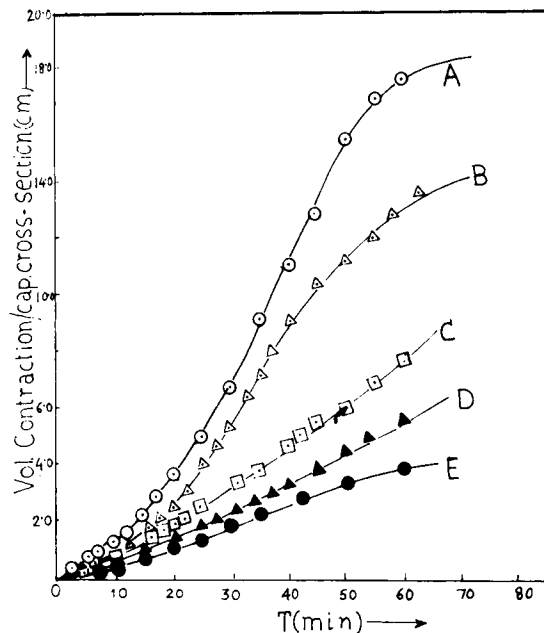
Fig. 4. Dilatometric results of polyacrylonitrile (PAN) formation at various AN concentra-
tions: here volume contraction/capillary cross section (0.0415 cm^2) versus time (t) has been
plotted. Persulfate fixed (1.0 × 10^{-3} m/dm^3) while AN varies: (A) 1.20; (B) 0.90; (C) 0.60; (D)
0.49; and (E) 0.30 (m/dm^3).

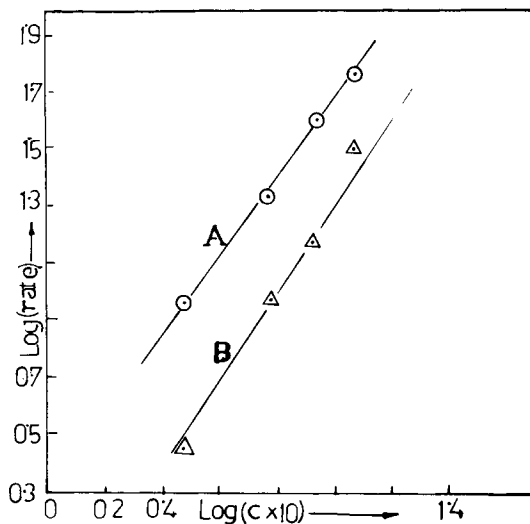Fig. 5. Order plot for the initiator from the rates of Polymerizations: (A) rate defined as %
polymerised in 30 min., (B) rate defined as (30% conversion/time) at various initiator concentra-
tions (C$_I$) for a given AN concentration, and the rates were estimated from the conversion-time
curves. The slope of the lines (A) or (B) was about 0.47 by the least square method. Data taken
from Fig. 1.

DISCUSSION

We have suggested the following mechanism for the thermal decomposition of persulfate in aqueous solutions in the presence of acrylonitrile monomer[1] (M):

(1)	$S_2O_8^{2-} \rightarrow 2\,SO_4^{\cdot-}$,	in the aqueous phase;
(2)	$SO_4^{\cdot-} + H_2O \rightarrow HSO_4^- + OH$,	in the aqueous phase,
(3)	$2\,OH \rightarrow H_2O + \frac{1}{2}\,O_2$,	in the aqueous phase;
(4)	$SO_4^{\cdot-} + M \rightarrow M_1^{\cdot}\,(= {}^{\cdot}M{-}O{-}SO_3^-)$,	in the aqueous phase;
(5)	$S_2O_8^{2-} + M \rightarrow M_1^{\cdot} + SO_4^{\cdot-}$,	in the aqueous phase;
(6)	$M_1^{\cdot} + M \xrightarrow{k_p} M_2^{\cdot}$,	in water, in the particle and also at the particle–water interface.
(7)	$\left(M_j^{\cdot}\right)_w \text{ or } \left(M_j^{\cdot}\right)_p + M \xrightarrow{k_p} M_{j+1}^{\cdot}$,	" " ";
(8)	$\left(M_j^{\cdot}\right)_w \text{ or } \left(M_j^{\cdot}\right)_p + M\,(= RH) \rightarrow k_{tr\cdot m}$ $\rightarrow M_j H + R^{\cdot}$	" " ";
(9)	$\left(M_j^{\cdot}\right)_w \rightleftharpoons \left(M_j^{\cdot}\right)_p$;	in the particle–water interface, and where $j = 1$ to 10.
(10)	$\left(M_j^{\cdot}\right)_w + S_2O_8^{2-} \rightarrow M_j{-}O{-}SO_3^-$ $+ SO_4^{\cdot-}$;	in water;
(11)	$(M)_w \rightleftharpoons (M)_p$,	at the particle–water interface.
(12)	$\left(M_j^{\cdot}\right)_w + P\,\text{(dead particle)}$ $\rightleftharpoons P^*\,\text{(active particle)}$;	at the particle–water interface.
(13)	$2\left(M_j^{\cdot}\right)_w \xrightarrow{k_{tw}} \text{polymer}$;	in water;
(14)	$2\left(M_i^{\cdot}\right)_p \xrightarrow{k_{tp}} \text{polymer}$;	in a latex particle, or between two active particles if they coagulate together; $i = 1$ to any value, say 1000 or more.

Here $\left(M_j^{\cdot}\right)_w$ are water-soluble monomeric or oligomeric free radicals ($j = 1$ to 10, according to Dainton et al.[9,10]). Radical reactivity is assumed to be independent of chain length in the propagation and the termination reactions[11] and also in reaction (10). It is assumed that $M_1^{\cdot}$ and $R^{\cdot}$ radicals are indistinguishable with respect to chemical reactions suggested here. Since the stationary concentration of primary radicals ($SO_4^{\cdot-}$) is believed to be very low[2a] and even lower in the presence of acrylonitrile, reactions between $SO_4^{\cdot-}$ and $\left(M_j^{\cdot}\right)_w$ in the aqueous phase, and between two nongeminate $SO_4^{\cdot-}$ radicals are assumed to be unimportant,[2a] while the negatively charged (due to sulfate end-groups) latex particles would possibly repel the $SO_4^{\cdot-}$ radicals, so that the interaction between the $\left(M_j^{\cdot}\right)_p$ and $SO_4^{\cdot-}$ radicals in the latex phase would not probably be significant. Further, since AN is not a solvent for its polymer (PAN), a fraction of PAN radicals may be buried in the polymer coils as found
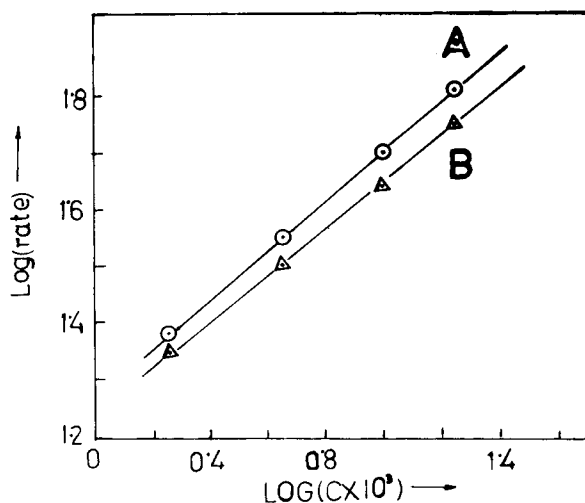
Fig. 6. Order plot for the monomer from the rate of polymer formation: (A) rate defined as % polymerized in 30 min., and (B) rate defined as % polymerized in 15 min. The slope of (A) or (B) was about 1.40 by the least-squares method. The monomer order was about 1.45 from the dilatometric results (Fig. 4).

by Bamford et al.[12] in the bulk polymerization of AN. No experimental evidence of radical burial was found in the aqueous polymerization of AN initiated by $Fe^{2+}-H_2O_2$ system,[9,10] or by $KMnO_4-H_2C_2O_4$ system.[31] Morris and Parts,[13] on the other hand, reported irreproducible rates of aqueous AN polymerization initiated by persulfate after 20% conversion, which might be due to the trapped radicals but in the present investigation we found the rates highly reproducible within ± 3 to 5%.

In our study, initiation took place in the aqueous phase, and particles were probably formed by the homogeneous nucleation mechanism of Fitch and Tsai[14] and of Dainton et al.[9,10] A $(M_j^{\cdot})_w$ radical, formed in water or coming out from an active latex particle into the aqueous phase, may propagate in water, may be absorbed by a dead or alive latex particle,[15,16] may interact with a water-soluble radical, and may be oxidized by the persulfate ions,[1,17,18,18a] in the aqueous phase. It is assumed that $(M_i^{\cdot})_p$ radicals, $i > 10$, being water insoluble, would be found only in the latex particles.[19] Reactions (9) and (11) are physical processes, and are believed to be occurring in the system during the reactions, although true equilibrium will never be established due to the polymerization reactions. The kinetic data are treated here in the light of the Equilbrium Theory of Harriott.[19] It is assumed that,[13–19] $(M_j^{\cdot})_p/(M_j^{\cdot})_w = (M)_p/(M)_w = \alpha$; where α is the distribution coefficient of the monomer between the polymer phase and the aqueous phase under the experimental conditions. α has been measured experimentally by the bromometric estimation of the monomer present in the aqueous phase containing a known amount of PAN polymer (freshly prepared, dried or wet) and of monomer AN initially at 50°C in an inert atmosphere of nitrogen after 8 h for equilibriation, in the presence and absence of added electrolyte, potassium sulfate, at various concentrations. The average value of α at 50°C was found to be 0.50 ± 0.10. If $j = 1.0$, then $(M_j^{\cdot})_p/(M_j^{\cdot})_w = \alpha$, otherwise the relation is

approximately correct as long as $(M_j^{\cdot})_w$ radicals are water soluble.[19] We also define a quantity, β, as $(M_i^{\cdot})_p/(M_j^{\cdot})_w$, where β can have values as high as 1000 or more.[19]

Rate of initiation (R_i) in the aqueous phase is given by

$$R_i = \left\{ 2k_1(S_2O_8^{2-}) + 2k_5(M)_w(S_2O_8^{2-}) + k_{10}(M_j^{\cdot})_w(S_2O_8^{2-}) \right\} V_w \quad (1)$$

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

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

Where V_w and V_p are the volume fractions of the water phase and of the polymer phase, respectively, that is, $V_w + V_p = 1.0$. We have estimated[1] $k_5 = 1.70 \times 10^{-5}$ (dm^3/m/s), $(M_j^{\cdot})_w = 10^{-9}$ (m/dm^3) and $k_{10} = 5.08 \times 10^3$ (dm^3/m/s) at 50°C. Taking $k_1 = 2.61 \times 10^{-6}$ s^{-1} at 50°C from Sarkar et al.[1] and Bawn and Margerison,[20] we see that the initiation due to (10) is negligble compared to those of (1) and (5) together at a given concentration of persulfate and of monomer. Hence, neglecting reaction (10) in Eq. (1), we get, in the steady state

$$(M_j^{\cdot})_w = \frac{\left[k_1 + k_5(M)_w \right]^{1/2}(S_2O_8^{2-})^{1/2} V_w^{1/2}}{\left[k_{tp}\beta^2 V_p + k_{tw}V_w \right]^{1/2}} \quad (3)$$

k_p and k_t are assumed to be independent of chain length,[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.[21,22]

Hence the steady-state rate of polymerization (R_p) is given by

$$R_p = k_p(M_j^{\cdot})_w(M)_w V_w + k_p(M_i^{\cdot})_p(M)_p V_p \quad (4)$$

or

$$R_p = k_p(M)_w \left[V_w + \beta \propto V_p \right] \frac{\left[k_1 + k_5(M)_w \right]^{0.5}(S_2O_8^{2-})^{0.5} V_w^{0.5}}{\left[k_{tp}\beta^2 V_p + k_{tw}V_w \right]^{0.5}} \quad (5)$$

If the monomer were taken 85.0 g/dm^3, volume of monomer would be $(85/0.8)/10^3 = 0.10625$ dm^3, and volume of water $= 0.89375$ dm^3, so that the total initial volume would be 1.0 dm^3. At 100% conversion, volume of polymer $85.0/1.17 = 72.65$ mL or 0.07265 dm^3. Hence volume fraction of polymer, $V_p = 0.075$ while $V_w = 0.925$. This shows that under our experimental conditions, $V_w > V_p$. Equation (5) may be simplified as follows:

Case I

If the aqueous phase polymerizations and terminations are more important than the corresponding reactions in the polymer phase, then at zero time or
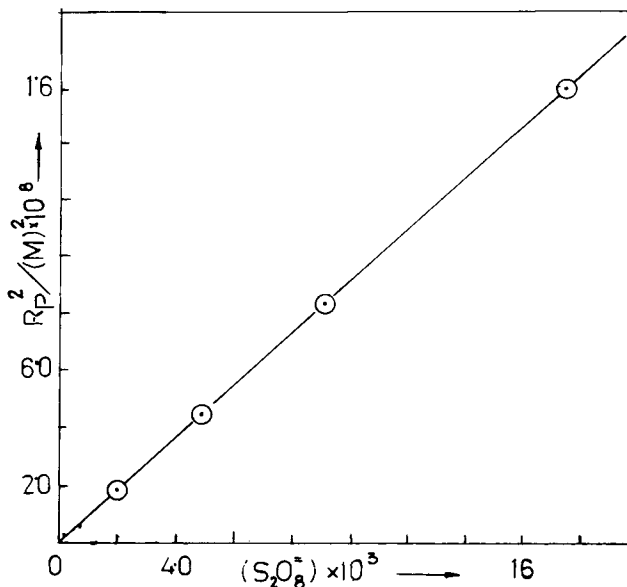
Fig. 7. $R_p^2/(M)^2$ of Eq. (7) versus $(S_2O_8^{2-})$ was plotted, and the line passed through the origin as required by Eq. (7).

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 $(R_p)_{t=0}$ (Fig. 2). Hence,

$$(R_p)_{t=0} = k_p k_{tw}^{-0.5}(M)_w V_w [k_1 + k_5(M)_w]^{0.5}(S_2O_8^{2-})^{0.5} \qquad (6)$$

Taking $V_w = 1.0$ at zero conversion, and squaring (6), we get

$$(R_p)_{t=0}^2/(M_w)^2 = (k_p^2/k_{tw})[k_1 + k_5(M_w)](S_2O_8^{2-}) \qquad (7)$$

At a given concentration of the monomer, here (M_w) was 1.20 (m/dm^3), plot of left-hand side of (7) versus $(S_2O_8^{2-})$ should give a straight line passing through the origin (Fig. 7). From the slope (= 1.50×10^{-6}, dm^3 m^{-1} s^{-2}) of Figure 7, k_{tw} can be estimated. Taking k_1 as 2.61×10^{-6} s^{-1} of Bawn and Margerison,[20] k_p as 6.22×10^4 (dm^3 m^{-1} s^{-1}) of Dainton et al.,[9,10,23,24] k_5 as 1.70×10^{-5} (dm^3 m^{-1} s^{-1}) of Sarkar et al.,[1] k_{tw} was found to be 5.95×10^{10} (dm^3 m^{-1} s^{-1}), which agrees with values of k_t in the aqueous phase estimated by Dainton et al., Thomas,[23] and Bamford.[24]

Case II

If the polymerization occurs mainly in the monomer adsorbed PAN-latex particles as postulated by the Smith-Ewart or Medvedev theory,[6,22] and

aqueous phase termination is negligible, then

$$R_p = k_p(M_w)\left[V_w + \alpha\beta V_p\right] \frac{\left[k_1 + k_5(M_w)\right]^{0.5}V_w^{0.5}(S_2O_8^{2-})^{0.5}}{\beta(k_{tp}V_p)^{0.5}} \qquad (8)$$

Since, $\beta = (M_i^{\cdot})_p/(M_j^{\cdot})_w = 1000$ or more,[19] then $(\alpha\beta V_p) > V_w$, and so,

$$R_p = k_p(M_w)\alpha V_p^{0.5}k_{tp}^{-0.5}\left[k_1 + k_5(M_w)\right]^{0.5}V_w^{0.5}(S_2O_8^{2-})^{0.5} \qquad (9)$$

or

$$R_p = k_p(M_p)V_p^{0.5}k_{tp}^{-0.5}\left[k_1 + k_5(M_w)\right]^{0.5}V_w^{0.5}(S_2O_8^{2-})^{0.5} \qquad (10)$$

since $(M_p) = \alpha(M_w)$. Equation (9) can be rearranged as

$$\frac{R_p}{\left[k_1 + k_5(M_w)\right]^{0.5}(M_w)} = k_p k_{tp}^{-0.5}\alpha(S_2O_8^{2-})^{0.5}(V_pV_w)^{0.5} \qquad (11)$$

By plotting LHS of (11) versus $(V_pV_w)^{0.5}$ at a given concentration of the initiator, and at various concentrations of the monomer, we get a straight line (Figure 8) passing through the origin. The slope of the line is 0.65 $s^{-0.5}$. Here $(S_2O_8^{2-}) = 1.8 \times 10^{-2}$ (m/dm³), and $\alpha = 0.5$, and we get $k_{tp} = 3.83 \times 10^7$ dm³ m⁻¹ s⁻¹) at 50°C.

Our results clearly show that in the aqueous polymerization of AN, the loci of polymerization would be almost entirely in the aqueous phase in a given run at zero conversion. With the progress of the polymerization reactions, the loci of polymerizations would gradually shift into the monomer adsorbed
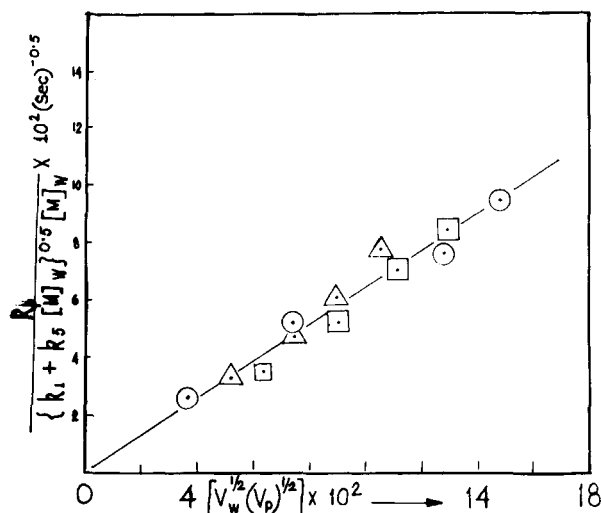

Fig. 8.   Left hand side of Eq. (11) versus $(V_p \cdot V_w)^{0.5}$ has been plotted. The line passed through the origin and had slope 0.65 (s)$^{-0.5}$. V_p = volume fraction of polymer and V_w = volume fraction of aqueous phase. (○) 40% conversion, (□) 30% conversion; and (△) 20% conversion.

PAN-latex particles, and polymerization would continue in both phases. This means that constant number of latex particles (N) would not be formed, but N would increase with conversion as found by Morris and Parts,[13] who estimated N by the light-scattering technique in the persulfate-initiated AN aqueous polymerization. Thomas et al.,[25] on the other hand, found N constant after about 10–15% conversion in the aquaous polymerization of AN initiated by the chlorate–bisulfite redox reaction, and N was measured by electron microscopy. It seems from the work of Thomas et al. and of Morris et al. that the characterization of latex particles in the aqueous polymerization of AN by the light scattering and electron microscopic methods, requires critical reinvestigation.

Order in monomer and in initiator seems to depend on the nature of the initiators.[9,10,13,14,23,24,26] In the persulfate-initiated aqueous polymerization of vinyl monomers, a fraction of the water-soluble oligomeric/polymeric radicals may undergo oxidation by the $S_2O_8^{2-}$ ions in the aqueous phase.[1,17,18] Dainton et al.[9,10] found that Fe^{3+} ions oxidized water-soluble PAN radicals in the aqueous phase. Incidentally, it may be pointed out that Dainton et al. studied Fe^{2+}–H_2O_2 redox initiated-aqueous polymerization of AN, and assumed steady-state hypothesis in the kinetic treatment of the data, although the Fenton's reaction has half-life of few seconds under the experimental conditions of Dainton et al. as stated by Bovey et al.,[5] and Baxendale et al.[27,28] In such cases, the steady-state hypothesis would not be applicable,[29] and so the interpretation of kinetic data of Dainton et al. must be accepted with reservation.

Very recently McCarthy et al.[30] have reported the seeded heterogeneous polymerization of acrylonitrile in aqueous solution initiated by $K_2S_2O_8$ and also by γ-rays. Some of their important findings are: (i) locus of polymerization is entirely on the surface of the latex particles, (ii) average number of radicals per particle was very high, about 250 (iii) radical capture efficiency by the particles was 100%, and (iv) no new particles were found to form in the absence of emulsified monomer oil droplets. They have suggested that the distribution coefficient of the monomer between the polymer phase and the aqueous phase at 50°C, would be between 0.5 to 2.0 (which agrees very well with our measured value 0.5 reported here). On this basis, they have estimated k_p as $12.0 \times 10^{+2}$ to 3.0×10^2 dm^3 m^{-1}s^{-1}) at 50°C, and have stated that the k_p and k_t values reported by Dainton et al. are very high. McCarthy et al.,[30] however, have assumed that there was no direct interaction between the persulfate ion and the monomer molecules, and no induced decomposition of persulfate ions in their system, which are not supported by our results.[1]

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