

# Thermal Decomposition of Potassium Persulfate in Aqueous Solution at 50°C in the Presence of Ethyl Acrylate

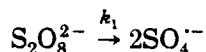
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## Synopsis

Potassium persulfate modes of thermal decomposition and reactions with ethyl acrylate in aqueous solution at 50°C in nitrogen atmosphere have been investigated. It has been found that the rate of persulfate decomposition may be expressed as  $-d(S_2O_8^{2-})/dt \propto (S_2O_8^{2-})^{1.00 \pm 0.06} \times (M)^{0.92 \pm 0.05}$  while the steady state rate of polymerization ( $R_p$ ) is given by  $R_p \propto (S_2O_8^{2-})^{0.50 \pm 0.05} \times (M)^{1.00 \pm 0.06}$  in the concentration ranges of the persulfate,  $10^{-3}$ – $10^{-2}$  (m/L), and monomer (M),  $4.62$ – $23.10 \times 10^{-2}$  (m/L), i.e., within its solubility range. In the absence of monomer, the rate of persulfate decomposition was slow and first order in persulfate at the early stages of the reaction when the pH of the solution was above 3.0. The separating polymer phase was a stable colloid at low electrolyte concentrations even in the absence of micelle generators. It has been shown that the oxidation of water soluble monomeric and oligomeric radicals by the  $S_2O_8^{2-}$  ions in the aqueous phase, viz.,  $M_j^{\cdot} + S_2O_8^{2-} \rightarrow M_j-O-SO_3^- + SO_4^{\cdot-}$ , is not kinetically significant in this system. It has been found that the reaction  $M + S_2O_8^{2-} \xrightarrow{k} M-O-SO_3^- + SO_4^{\cdot-}$  would also lead to chain initiation at the outset of the polymerization reaction.  $k$  has been estimated as  $5.41 \times 10^{-5}$  (L/m/s) at 50°C. Taking  $k_p$  as  $10^3$  (L/m/s),  $k_t$  has been estimated as  $0.168 \times 10^6$  (L/m/s). The partition coefficient ( $\beta$ ) of the monomer between the polymer phase and the aqueous phase was found to be  $16 \pm 2$ , at 50°C. The rate constant for persulfate ion dissociation has been found as  $1.40 \times 10^{-6} \text{ s}^{-1}$  at 50°C.

## INTRODUCTION

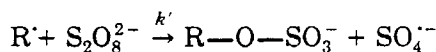
In the persulfate initiated aqueous or emulsion polymerization of vinyl monomers, it is generally assumed that the monomer, latex particles, detergents, or polymeric radicals, etc., would not bring about the induced decomposition of the persulfate ions.<sup>1-4</sup> Morris and Parts<sup>5</sup> found that the common vinyl monomers accelerated the decomposition of persulfate, and they assumed that the monomers influenced and increased the rate constant ( $k_1$ ) of the reaction



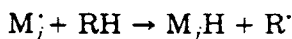
in order to account for the enhanced rate of persulfate decomposition. Dunn<sup>6</sup> reported that the analytical work of Morris and Parts could be in error, and suggested that the monomeric radicals ( $R^{\cdot}$ ) produced by the reaction, viz.,



would bring about the induced decomposition of persulfate by the reaction, viz.,



in the aqueous phase. Dunn<sup>6</sup> believes that  $k_1$  is not altered by the monomers as assumed by Morris and Parts, but he predicted through his model that the pH of the aqueous solution would decrease with the increase of monomer concentrations. Chang<sup>7</sup> postulated that  $R'$  would be produced in the latex particles in the emulsion polymerization of vinyl acetate due to the chain transfer reactions, viz.,



and these  $R'$  water-soluble radicals, when diffuse out into the aqueous phase, would be oxidized partly by the persulfate ions. In the vinyl acetate emulsion polymerization system, he estimated  $k'$  as  $2 \times 10^7$  (L/m/s) at 60°C. We have recently reported<sup>8</sup> a detailed analytical study of persulfate decomposition in aqueous solution at 50°C in the presence of acrylonitrile in nitrogen atmosphere, and found that the results would be consistent if a fraction of the monomeric water soluble radicals were oxidized by the persulfate ions in the aqueous phase, and  $k'$  in the acrylonitrile system was found to be about  $6.1 \times 10^3$  (L/m/s) at 50°C. There is no experimental evidence<sup>8</sup> in favor of Dunn's model of  $R'$  radical formation, and, if  $k'$  is as high as  $10^7$ – $10^8$  (L/m/s) in the vinyl acetate system of Chang, then persulfate ions would act as an inhibitor rather than an initiator at higher concentrations ( $10^{-2}$  m/L), which is not supported by the experimental data. In the persulfate–acrylonitrile system, it was found that the monomer interacted directly with the persulfate, and a fraction of the water soluble monomeric or oligomeric radicals were oxidized by the  $S_2O_8^{2-}$  ions in the aqueous phase and also probably at the particle–water interface. Here we are reporting the analytical results obtained in the ethyl acrylate–persulfate system at 50°C in an unbuffered aqueous solution in the presence of nitrogen.

## EXPERIMENTAL

The quality of chemicals used, and their purification and processing have been described elsewhere in detail.<sup>8,9</sup> Persulfate was estimated by the iodometric method of Kolthoff and Carr<sup>10</sup> in the presence and absence of monomer. The monomer was found not to influence the iodometric estimation of persulfate, but it did interfere in pH and in conductivity measurements of the aqueous solutions. It appeared that it probably got adsorbed at the glass–water interface of the glass electrode of the pH meter, and also at the electrodes of the conductivity cell. Measurement of pH and of conductance of aqueous solutions during polymerizations were thus not possible in this system.

The monomer (fluka/BDH grade) was first dehydrated over anhydrous calcium chloride, vacuum distilled, and the distillate was refluxed with 0.02% benzoyl peroxide in nitrogen atmosphere till the mixture got slightly viscous. It was then vacuum distilled; the middle fraction was used for polymerization reaction. Each experiment was carried out with freshly distilled monomer.

The monomer was found to form peroxide even when it was stored at 0–5°C overnight (tested by adding KI–dilute HCl to an aqueous solution of monomer and starch indicator) in a refrigerator. Polymerization reaction was followed dilatometrically as well as gravimetrically,<sup>9</sup> and the unreacted persulfate was estimated iodometrically<sup>8,10</sup> after the removal of the polymer from the aqueous solution.<sup>8</sup> Molecular weights of the polymers were determined viscometrically in thiophene free benzene solvent at 30°C. The value of the Huggin's constant ( $k_H$ ) in the equation

$$(\eta_{sp}/C) = (\eta) + k_H(\eta)^2 C$$

was found to be  $0.37 \pm 0.03$ , which agrees with the values of  $k_H$  for the polyacrylates–benzene system, viz., 0.35–0.45, as stated by Flory.<sup>11</sup> ( $\bar{M}_n$ ) was estimated from the relation<sup>12</sup>

$$(\eta) = 27.7 \times 10^{-3} (\text{mL/g}) \times (\bar{M}_n)^{0.67}$$

The colloid stability of the latex solution<sup>13,14</sup> was determined by titrating a known volume of the latex solution with a standard ( $N/20$ )  $\text{MgSO}_4$  solution. To avoid complications during polymerizations, no buffer solutions were used, nor any micelle generator. Ionic strength of the solution was kept constant by adding  $\text{K}_2\text{SO}_4$  wherever it was required.

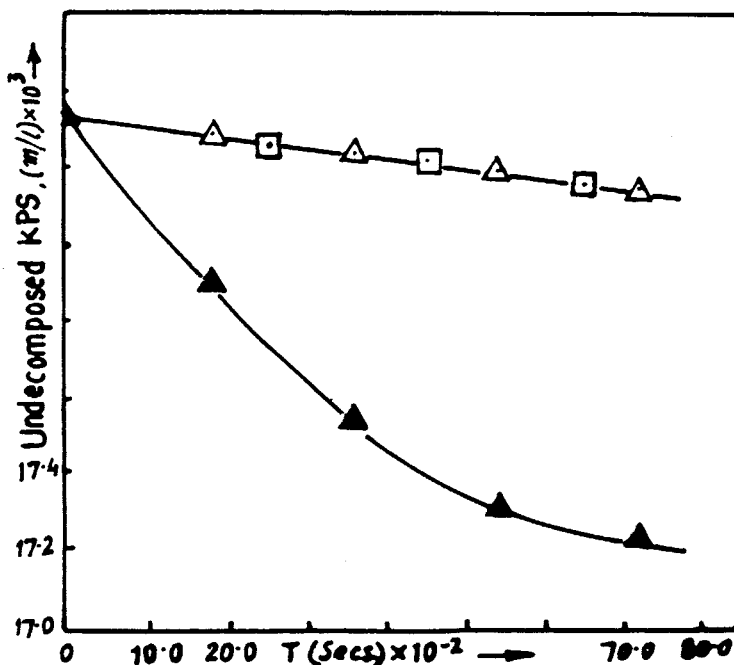


Fig. 1. Effect of monomer (ethyl acrylate) on the thermal decomposition of potassium persulfate ( $18.33 \times 10^{-3}$  m/L) in aqueous solution at 50°C in the presence of nitrogen: (▲) experimental in the absence of ethyl acrylate; (◻) estimated from the relation,  $C_t = C_0 \exp(-k_1 t)$ , where  $k_1 = 1.40 \times 10^{-6} \text{ s}^{-1}$  at 50°C (data of Bleckley<sup>2</sup>).  $C_t$  = concentration of persulfate at time  $t$  and  $C_0$  = initial concentration; (▲) in the presence of ethyl acrylate (0.2298 m/L).

## RESULTS

The decrease in persulfate concentrations as a function of time in the thermal decomposition of  $K_2S_2O_8$  in aqueous unbuffered solution at  $50^\circ C$  in nitrogen atmosphere in the presence and absence of ethyl acrylate is shown in Figure 1. It is evident that the monomer ethyl acrylate has accelerated the thermal decomposition of persulfate ions. Figure 2 shows the variations of time average rates of persulfate decomposition as a function of time at a given concentration of persulfate ( $18.10 \times 10^{-3}$  m/L) and at various concentrations of the monomer  $9.24$ – $23.10 \times 10^{-2}$  (m/L). From the intercepts of Figure 2, the time-average rates at zero time were taken as initial rates of persulfate decompositions at various concentrations of the monomer. In Figure 3, conventional order plot for the monomer, i.e.,  $\log$  (initial rate of persulfate decomposition) vs.  $\log$  (monomer concentration), at a given concentration of persulfate is shown, and the order of monomer is found to be  $0.92 \pm 0.05$ , i.e.,

$$-d(S_2O_8^{2-})/dt \propto (M)^{0.92 \pm 0.05}$$

Figure 4 shows the variations of the time average rates of persulfate decompositions at its various concentrations  $7.47$ – $20.0 \times 10^{-3}$  (m/L), and at a given concentrations of the monomer ( $23.10 \times 10^{-2}$  m/L). The intercepts of the straight line curves at zero time gave the initial rates of persulfate decomposition at its various concentrations. Figure 5 shows the order plot for the

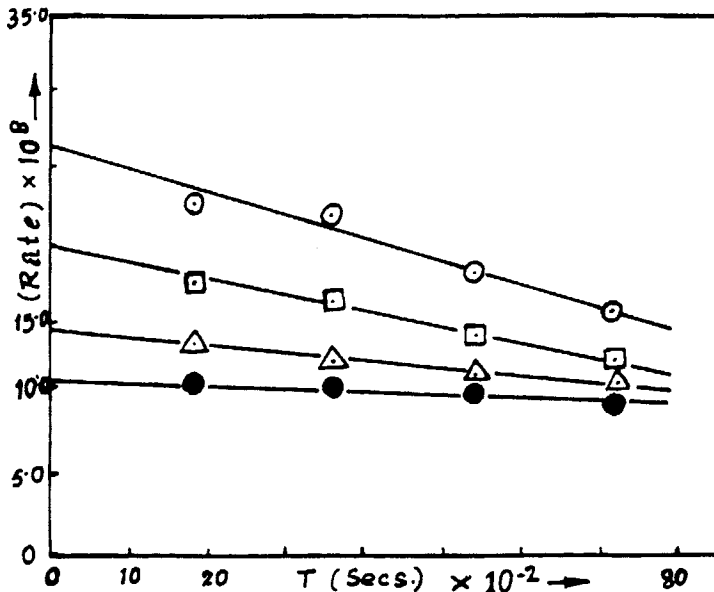


Fig. 2. Effect of monomer concentrations on the rates of persulfate decompositions. Time average rates (i.e., amount decomposed in time  $t$ /time  $t$ ) of persulfate decomposition in the presence of  $N_2$  gas and monomer have been plotted as a function of time. The linear curves have been extrapolated to zero time, and the intercept at zero time is assumed to give the initial rate of persulfate decomposition at various concentrations of the monomer: (●) monomer  $9.24 \times 10^{-2}$  (m/L); (Δ)  $13.86 \times 10^{-2}$  (m/L); (□)  $18.48 \times 10^{-2}$  (m/L); (○)  $23.10 \times 10^{-2}$  (m/L) at a given concentration of persulfate ( $18.10 \times 10^{-3}$  m/L).

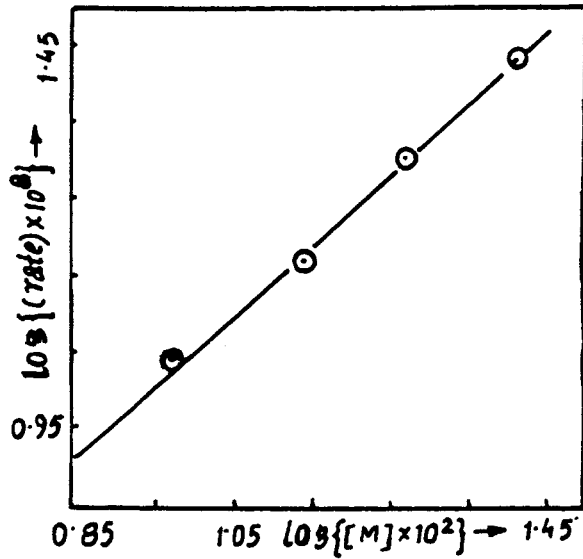


Fig. 3. Order plot of the monomer with respect to persulfate decomposition.  $\text{Log}_{10}$  (initial rate of persulfate decomposition in  $\text{m/L/s}$ ) has been plotted against  $\text{log}_{10}$  (monomer concentration in  $\text{m/L}$ ). The slope of the line is 0.92.

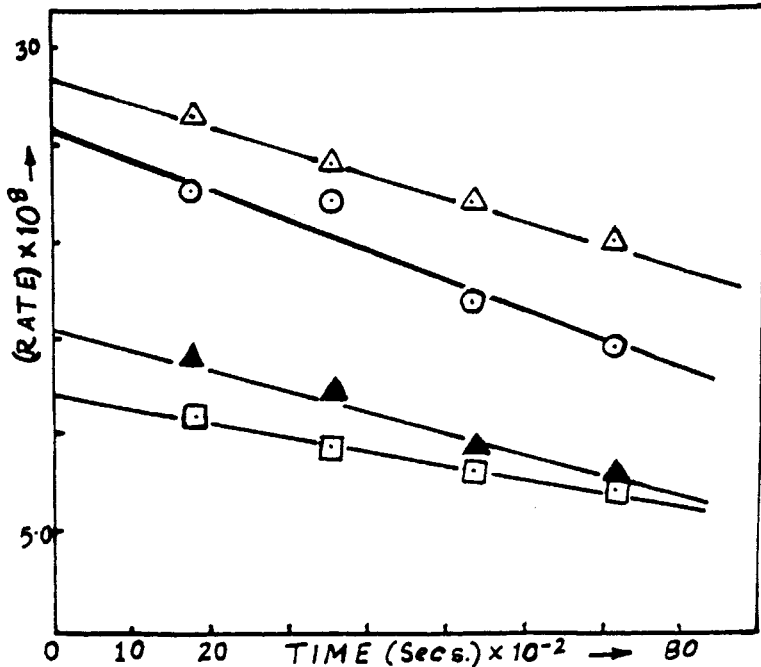


Fig. 4. Time average rates of persulfate decompositions at a given concentration of the monomer ( $23.10 \times 10^{-2} \text{ m/L}$ ) and at various concentrations of the persulfate have been plotted as a function of time: ( $\Delta$ )  $20.0 \times 10^{-3} \text{ (m/L)}$  persulfate ( $\odot$ )  $18.10 \times 10^{-3} \text{ (m/L)}$ ; ( $\blacktriangle$ )  $10.85 \times 10^{-3}$ ; ( $\square$ )  $7.474 \times 10^{-3} \text{ (m/L)}$  persulfate. The intercepts at zero time give the initial rates of persulfate decomposition at various concentrations of persulfate and at a given concentration of the monomer.

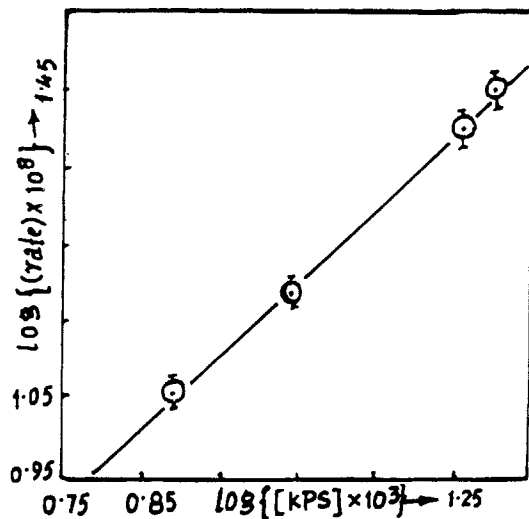


Fig. 5. Order plot of the persulfate with respect to persulfate decomposition in the presence of monomer.  $\log_{10}$  (initial rate of persulfate decomposition in m/L/s) vs.  $\log_{10}$  (concentration of persulfate in m/L) has been plotted. The slope of the line is unity.

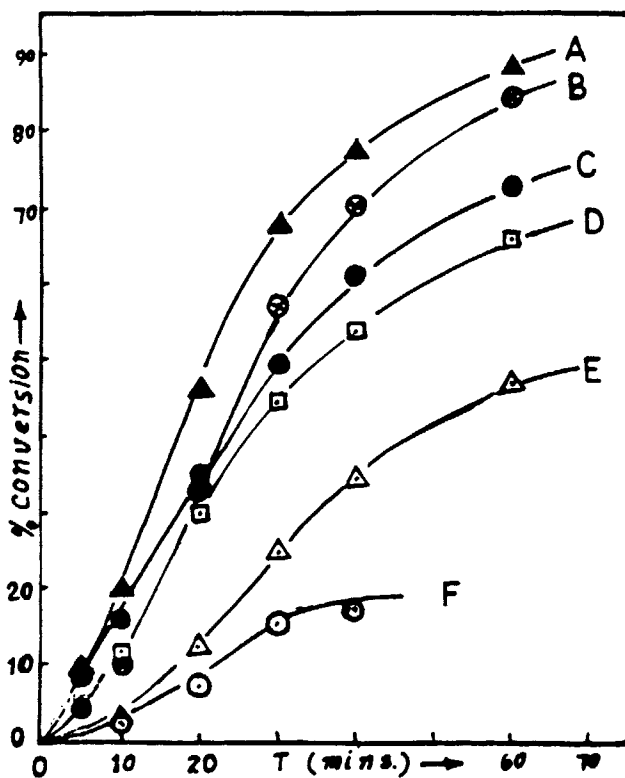


Fig. 6. Percent conversion of monomer to polymer. Recipe: persulfate ( $1.852 \times 10^{-3}$  m/L), and monomer varies: (A) 0.1622; (B) 0.138; (C) 0.1148; (D) 0.0944; (E) 0.06918; (F) 0.04624 (m/L). Monomer concentrations were kept below its solubility at  $50^{\circ}\text{C}$ .

persulfate, and it was found that

$$-d(S_2O_8^{2-})/dt \propto (S_2O_8^{2-})^{1.00 \pm 0.06}$$

Figure 6 shows the yield time curves for polyethyl acrylate formation at various concentrations of the monomer  $0.665-1.21 \times 10^{-2}$  (m/L) and at a given concentration of persulfate ( $1.852 \times 10^{-3}$  m/L). Figure 7 shows the order plot for the monomer in the polymerization reactions, and the steady state rate of polymerization ( $R_p$ ) was found to be

$$R_p \propto (M)^{1.02 \pm 0.08}$$

Figure 8 shows the order plot for the initiator in the polymerization reactions at various conversions of monomer to polymer. The average order of the initiator was,  $0.53 \pm 0.01$ , and hence

$$R_p \propto (S_2O_8^{2-})^{0.53 \pm 0.01}$$

Table I shows the formation of polymer, its molecular weight, and the

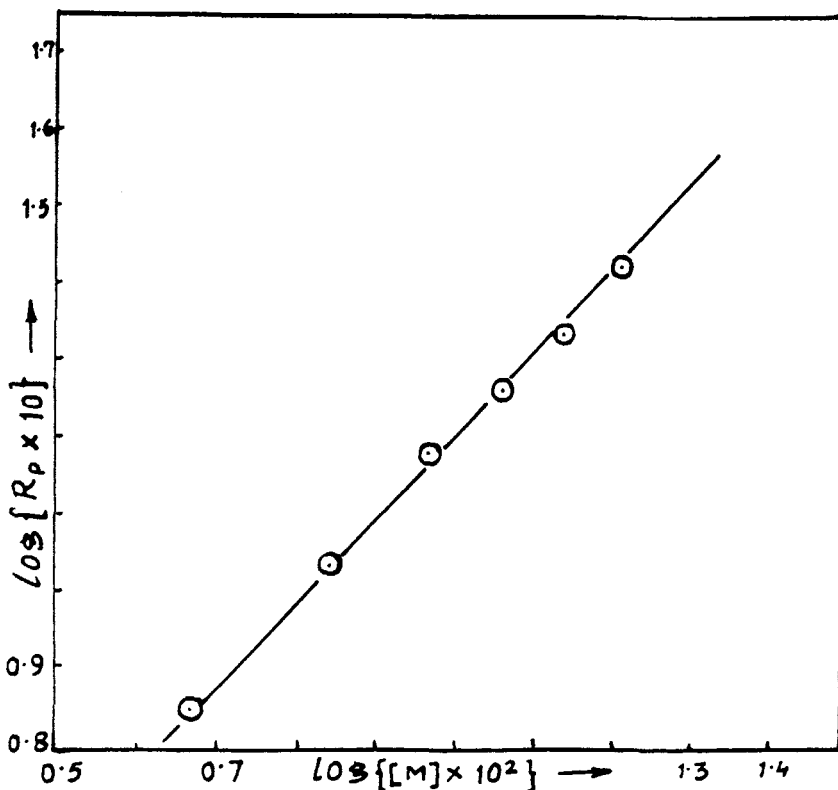


Fig. 7. Order plot of monomer with respect to polymerization reactions.  $\log_{10} (R_p, \text{ steady state rate, i.e., constant rate from 15 to 40\% conversion})$  vs.  $\log_{10} (\text{monomer concentration in m/L})$  has been plotted.  $R_p$  is in %/min. The slope of the line is about unity.

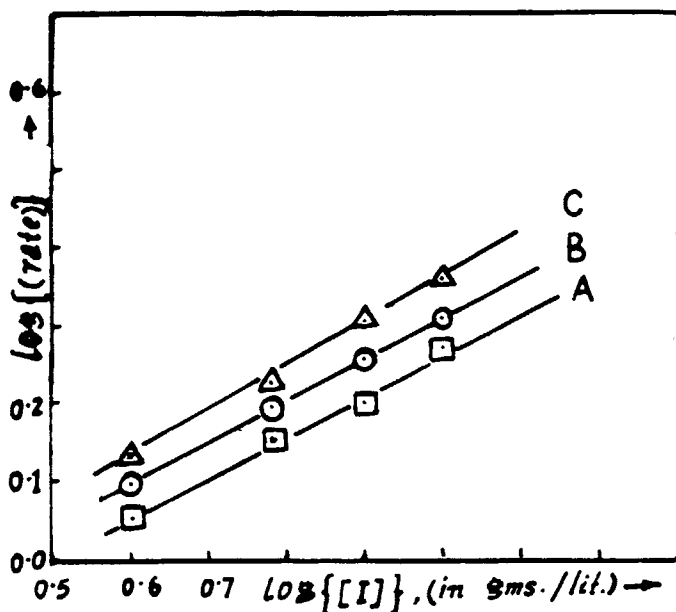


Fig. 8. The order plot of the initiator at various conversions of monomer to polymer: (A) rate from 10% conversion; (B) rate from 20% conversion; (C) rate from 30% conversion. Rates are in % conversion/min. The slope of A is 0.52, of B 0.53, and of C 0.54. Recipe of polymerization: monomer  $0.919 \times 10^{-1}$  (m/L) and persulfate varies from 0.60 to 1.0 g/L.

TABLE I  
Molecular Weights and Colloidal Stability of Polymers in the Latex Solution<sup>a</sup>

Time (min)	Conversion (%)	Colloid stability (mmol MgSO <sub>4</sub> /L)	Mol. wt ( $\bar{M}_n$ ) ( $\times 10^{-6}$ )
5.0	5.0	26.0	—
10.0	16.0	18.0	—
20.0	37.5	10.0	3.93
30.0	58.0	5.0	2.36
40.0	70.0	2.0	1.76
60.0	84.0	1.0	1.25

<sup>a</sup>Recipe: initiator  $1.48 \times 10^{-3}$  (m/L) and ethyl acrylate  $18.4 \times 10^{-2}$  (m/L) at 50°C. Ionic strength was  $1.11 \times 10^{-2}$  in (m/L) units, adjusted by adding K<sub>2</sub>SO<sub>4</sub>.

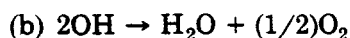
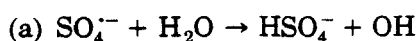
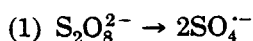
colloidal stability of the latex solution as a function of time in a given run. It has been found that in a polymerization experiment with KPS  $3.70 \times 10^{-2}$  (m/L), ethyl acrylate  $18.4 \times 10^{-2}$  (m/L) at 50°C, % conversion was 85.0 in 1 h, and 95.0 in 3 h, which indicates that after 80% conversion the rate of polymerization slows down. The latex was still in the colloidal state after 3 h.

## DISCUSSION

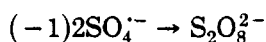
It is believed that persulfate ions decompose in aqueous solution in the presence of nitrogen in neutral or slightly alkaline (pH  $7.0 \pm 0.50$ ) solution by



a free radical mechanism,<sup>1,2,15,16</sup> viz.,



It is also assumed<sup>1,2,15,16</sup> that the recombination of  $\text{SO}_4^{\cdot-}$  ion radicals (geminate or nongeminate), viz.,



would not be significant inside and outside the solvent cage, because the stationary concentrations of  $\text{SO}_4^{\cdot-}$  ion radicals was believed to be trivial, because of reaction (a) and the thermal motions of ions and of solvent molecules at 50°C would disturb the orientation necessary for the geminate recombination of the ion radicals inside the solvent cage. If it is assumed that (-1) would also occur, then

$$\begin{aligned} d(\text{SO}_4^{\cdot-})/dt &= 2k_1(\text{S}_2\text{O}_8^{2-}) - 2k_{-1}(\text{SO}_4^{\cdot-})^2 - k_a(\text{SO}_4^{\cdot-})(\text{H}_2\text{O}) \\ &= 0 \text{ in the steady state (ss)} \end{aligned}$$

Reaction (a) being pseudo-unimolecular and first order. Hence,

$$(\text{SO}_4^{\cdot-})_{\text{ss}} = -(k_a/4k_{-1}) \pm [k_a^2 + 16k_1k_{-1}(\text{S}_2\text{O}_8^{2-})]^{1/2}/4k_{-1}$$

$k_a$  has been estimated<sup>17,18</sup> as  $10^3 \leq k_a \leq 10^4 \text{ s}^{-1}$  at 25°C, and if the reaction (-1) has zero activation energy, then  $k_{-1}$  at 50°C would be the same as  $k_{-1}$  at 25°C. The estimated values of  $k_{-1}$  are<sup>17,19</sup>  $3.7\text{--}8.8 \times 10^8 \text{ (L/m/s)}$  at 25°C. Taking  $k_a$  at 50°C as  $10^4 \text{ s}^{-1}$ ,  $k_{-1}$  as  $10^8 \times 8.8 \text{ (L/m/s)}$ , and  $(\text{S}_2\text{O}_8^{2-})$  as  $10^{-2} \text{ (m/L)}$ , it is found that

$$k_a^2 \gg \{16k_1k_{-1}(\text{S}_2\text{O}_8^{2-})\}$$

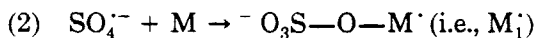
We have shown elsewhere<sup>8</sup> that  $k_a$  at 50°C may be as high as  $10^7 \text{ (L/m/s)}$ . Hence,

$$(\text{SO}_4^{\cdot-})_{\text{ss}} = -(k_a/4k_{-1}) \pm (k_a/4k_{-1})$$

which implies that either  $(\text{SO}_4^{\cdot-}) = 0$ , or negative, both of which are unacceptable. We conclude that (-1) does not occur to any significant extent under our experimental conditions.

Water-soluble vinyl monomer molecules will capture  $\text{SO}_4^{\cdot-}$  ion radicals and start initiation of polymerization in the aqueous medium. In that case,

reaction (a) has to compete with reactions (2) and (2a), viz.,



where R<sup>·</sup> is a monomeric water-soluble free radical, i.e., a monomer molecule without a H atom. It has been demonstrated experimentally, by measuring pH of the media<sup>8</sup> in the aqueous polymerization of acrylonitrile initiated by K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, that the reaction (2a) does not occur. It is assumed here that the reaction (2a) would not be significant in the ethylacrylate–persulfate system. In the presence of sufficient quantity of monomer in the aqueous phase, the reaction (a) would be suppressed, and all the primary SO<sub>4</sub><sup>·-</sup> ion radicals would disappear via (2). *k*<sub>2</sub> is not known, but the reported value of *k*<sub>2</sub> in the methylmethacrylate–persulfate system<sup>21</sup> at 20°C is 1.0 × 10<sup>9</sup> (L/m/s). Assuming this value for the ethylacrylate–persulfate system, we get

$$\begin{aligned} \text{rate of (2)/rate of (a)} &= 10^9 \times 18 \times 10^{-2}/10^4 \\ &= 18 \times 10^3, \text{ if } (\text{M}) = 18 \times 10^{-2} \text{ (m/L)} \end{aligned}$$

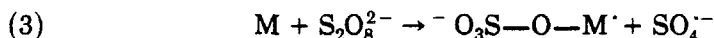
This shows clearly that almost all the primary radicals will disappear via (2). However, such a mechanism predicts that

$$-d(\text{S}_2\text{O}_8^{2-})/dt \propto (\text{M})^0 \times (\text{S}_2\text{O}_8^{2-})^{1.00}$$

but this equation is not supported by the experimental data of Figures 1 and 2, as the rate of persulfate decomposition is clearly a function of monomer concentration in the aqueous solution. The results presented here show that

$$-d(\text{S}_2\text{O}_8^{2-})/dt \propto (\text{M})^{0.92} \times (\text{S}_2\text{O}_8^{2-})^{1.00} \quad (1)$$

It seems that probably the monomer also reacts directly with the persulfate ions, viz.,



and there may be other elementary reactions through which the persulfate ions may undergo decomposition. The measured monomer order, viz. 0.92, indicates that persulfate decomposition takes place probably partly via (1) and partly via (3). Hence

$$-d(\text{S}_2\text{O}_8^{2-})/dt = k_1(\text{S}_2\text{O}_8^{2-})(\text{M})^0 + k_3(\text{M})^{1.0}(\text{S}_2\text{O}_8^{2-})^{1.0} \quad (2)$$

This hypothesis is supported by the fact that the rate of persulfate decomposition in a given run decreases with time or conversion of monomer to polymer (Table II). This suggests also that the reaction (3) in all probability will take place only in the aqueous phase, but not in the monomer swollen latex particles, nor at the particle–water interface.

TABLE II  
Decomposition of Persulfate ( $18.33 \times 10^{-3}$  m/L) at  $50^\circ\text{C}$  in the  
Presence of Ethylacrylate ( $22.975 \times 10^{-2}$  m/L)

Time ( $t$ ) (h)	Unreacted persulfate [(m/L) $\times 10^3$ ]	$-\Delta C$ [(m/L) $\times 10^3$ ]	$\Delta t$ (h)	$-\Delta C/\Delta t$ [(m/L/s) $\times 10^7$ ]	Conversion of monomer to polymer (%)
0.00	18.33	0.00	0.00	0.00	0.00
0.50	17.91	0.42	0.50	2.33	62.0
1.00	17.54	0.37	0.50	2.06	72.0
1.50	17.31	0.23	0.50	1.28	80.0
2.00	17.24	0.07	0.50	0.39	85.5

The results of Table II show clearly that as the conversion of monomer to polymer increases, the rate of persulfate decomposition decreases. This suggests that the polymer or the latex particles are not causing the induced decomposition of persulfate. After 1.5 h, the % monomer converted to polymer is about 80.0, and the unreacted persulfate is  $17.31 \times 10^{-3}$  (m/L). After another 0.5 h, the first-order reaction kinetics for persulfate decomposition gives

$$C_t = C_0 \times \exp(-k_1 t) = 17.31 \times 10^{-3} \times \exp(-1.4 \times 10^{-6} \times 1800),$$

$$= 17.27 \times 10^{-3} \text{ (m/L)}$$

while the measured value of  $C_t$  (undecomposed persulfate concentration at the end of 2 h) is  $17.24 \times 10^{-3}$  (m/L) (Table II). This supports strongly the hypothesis that the reaction (3) takes place mainly in the aqueous phase.

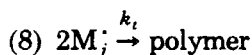
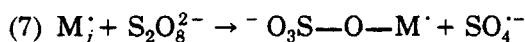
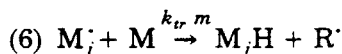
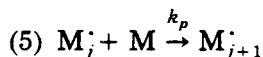
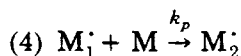
As the polymerization reaction starts, the concentration of monomer in the aqueous phase decreases with time, and the unreacted monomer will distribute itself between the latex particles (polymer phase) and the aqueous phase. The distribution coefficient of the monomer between the polymer and the aqueous phases, i.e.,  $(C_M)_{\text{poly}}/(C_M)_{\text{aqu}}$  at  $50^\circ\text{C}$  was found to be  $(16 \pm 2)$  by the bromometric estimation of the monomer in the aqueous phase. Because of these two factors, the concentration of monomer in the aqueous phase will fall sharply with time, and after 80% conversion there will be very little monomer in the aqueous phase, and thereafter the decomposition of persulfate will follow the 1st order kinetics through the reaction (1) only.

Now the steady state rate of polymerization ( $R_p$ ) is given by

$$R_p \propto (\text{S}_2\text{O}_8^{2-})^{0.53} \times (\text{M})^{1.00}$$

This result can be explained easily on the basis of homogeneous free radical initiated polymerization reaction mechanism, although the reactions under investigations were partly homogeneous and partly heterogeneous. Fitch et al.<sup>22</sup> observed that the heterogeneous aqueous polymerization of methylmethacrylate initiated by the persulfate-ferrous ion-bisulphite redox systems could be explained on the basis of homogeneous free radical initiated polymerization mechanism. We find here also that such a homogeneous mecha-

nism is capable of giving a quantitative description of the kinetic data.<sup>8</sup> Considering the following elementary reactions (1-8) occurring in the aqueous phase and also in the latex particles,



[reaction (7) may take place in the aqueous phase as well as at the particle-water interface], we can derive the rate equations, and test the mechanism with the analytical data. Since<sup>11,12</sup> ( $k_{tr} m/k_p$ ) is about  $10^{-5}$ , reaction (5) will predominate. Further ( $M_j^{\cdot}$ ) radical concentrations would be a function of monomer and of initiator concentrations, and if reaction (7) is kinetically significant then the order of monomer and of initiator in eq. (2) should be greater than unity for each reactant. Since the data do not support such a hypothesis, it seems that the reaction (7) may not be significant in this system. Ignoring reactions (6) and (7) for the moment, we get

$$\text{rate of initiation } (R_i) = 2k_1(S_2O_8^{2-}) + 2k_3(M)(S_2O_8^{2-})$$

$$\text{rate of termination } (R_t) = 2k_t(M_j^{\cdot})^2$$

Equating  $R_i = R_t$  in the steady state, we get

$$(M_j^{\cdot})_{ss} = k_t^{-1/2} \{k_1 + k_3(M)\}^{1/2} \times (S_2O_8^{2-})^{1/2}$$

and

$$R_p = k_p(M)(M_j^{\cdot})_{ss}$$

i.e.,

$$R_p = k_p k_t^{-1/2} \{k_1 + k_3(M)\}^{1/2} (M)(S_2O_8^{2-})^{1/2} \quad (3)$$

Experimentally,  $R_p$  has been estimated from the conversion-time curves during the constant rate period (i.e., from 10 to 40% monomer converted to polymer). As soon as polymerization starts in the aqueous phase, latex particles are formed due to the aggregation of insoluble hydrophobic polymer molecules.<sup>22</sup> The unreacted monomer will distribute itself between the latex

particles and the aqueous phase continuously during the reaction because of thermodynamic requirements. Since the distribution coefficient is about 16, it means that at a given conversion of monomer to polymer, about 96% of the unreacted monomer will be in the latex phase and the remaining 4% in the aqueous phase. So with time, the contribution of (3) will become less important in the absence of emulsified monomer droplets, and eventually become negligible compared to (1), followed by (2). Hence to a good approximation,  $R_p$  becomes

$$R_p = k_p k_t^{-1/2} k_1 (M) (S_2O_8^{2-})^{1/2} \tag{4}$$

which is consistent with the experimental results presented here. Squaring eq. (3), we get

$$R_p^2 / (M)^2 = (k_p^2 / k_t) \{k_1 + k_3 (M)\} (S_2O_8^{2-}) \tag{5}$$

and rearranging eq. (2), we get

$$\left[ \frac{1}{(S_2O_8^{2-})} \right] \left\{ -d(S_2O_8^{2-})/dt \right\} = k_1 + k_3 (M) \tag{6}$$

In Figure 9, the left-hand side of eq. (6) has been plotted against  $(M)$ , and it yields a straight line with an intercept, which gives  $k_1 = 1.40 \times 10^{-6} \text{ s}^{-1}$  at  $50^\circ\text{C}$  (which agrees very well with the value of  $k_1$  given by Bleckley<sup>2</sup>), while the slope gives  $k_3$  as  $5.41 \times 10^{-5} \text{ (L/m/s)}$  at  $50^\circ\text{C}$ .

At a given concentration of the monomer, a plot of  $R_p^2 / (M)^2$  vs.  $(S_2O_8^{2-})$  of eq. (5) has been shown in Figure 10, and the slope of the resulting straight line

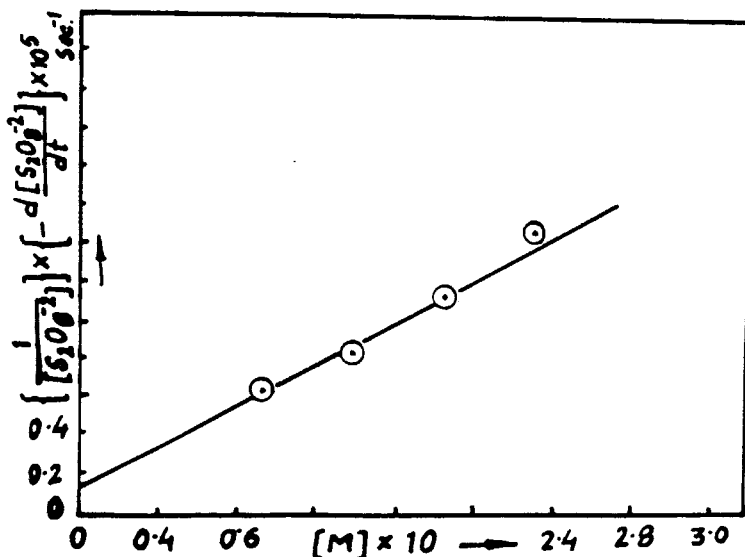


Fig. 9. Plot of  $\{1/(S_2O_8^{2-})\} \{-d(S_2O_8^{2-})/dt\}$  vs. monomer concentrations according to eq. (6) has been plotted. The intercept gives  $k_1$  as  $1.40 \times 10^{-6} \text{ s}^{-1}$  at  $50^\circ\text{C}$ , which is in excellent agreement with the value quoted by Bleckley.<sup>2</sup> The slope gives the value of  $k_3$  as  $5.41 \times 10^{-5} \text{ (L/m/s)}$ .

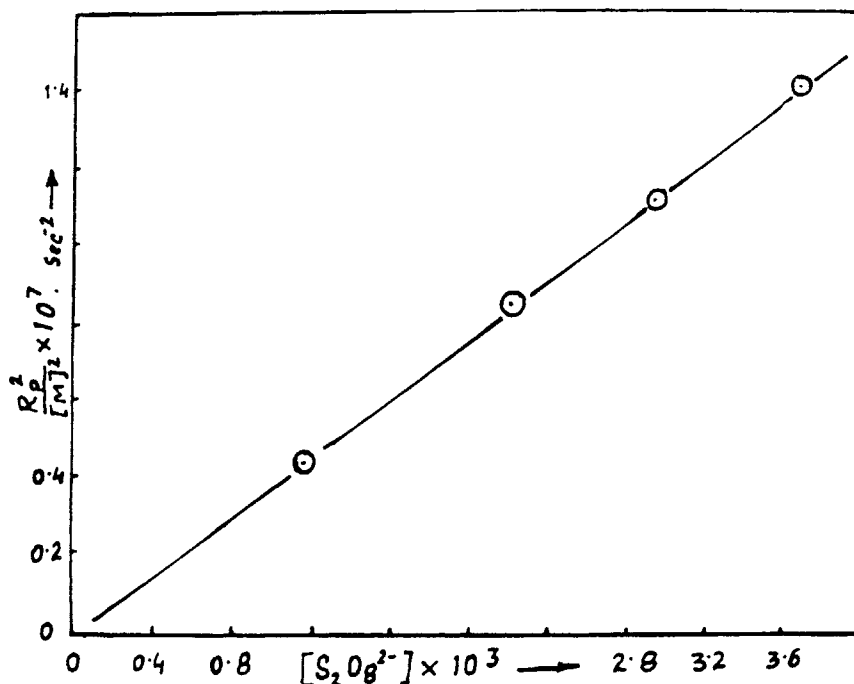


Fig. 10. Plot of  $R_p^2/(M)^2$  vs.  $(S_2O_8^{2-})^2$  according to eq. (5). The slope of the line gives  $k_t = 0.168 \times 10^6$  (L/m/s), taking  $k_p$  at  $50^\circ\text{C}$  as  $10^3$  (L/m/s) (which is the  $k_p$  for methyl acrylate polymerization<sup>12</sup>).  $R_p$  has been estimated from the experimental data corresponding to 20% conversion of monomer to polymer in order to avoid uncertainties in estimating the values of  $R_p$ .

gives  $k_t$  at  $50^\circ\text{C}$  as  $0.168 \times 10^6$  (L/m/s), if  $k_p = 10^3$  (L/m/s), (which is the  $k_p$  of methyl acrylate polymerization<sup>9,12</sup>),  $k_1 = 1.40 \times 10^{-6} \text{ s}^{-1}$ , and  $k_3 = 5.41 \times 10^{-5}$  (L/m/s).  $k_p$  of ethylacrylate polymerization is not known to us.

In Figure 11,  $\{-d(S_2O_8^{2-})/dt\}$  has been plotted as a function of  $(S_2O_8^{2-})$  at a given concentration of the monomer [eq. (2)]. Taking  $k_1 = 1.40 \times 10^{-6} \text{ s}^{-1}$  at  $50^\circ\text{C}$ ,  $k_3$  has been estimated from the slope of the straight line as  $5.45 \times 10^{-5}$  (L/m/s) which is in good agreement with the value of  $k_3$  from Figure 9.

If now we assume that the reaction (7) is also important, then

$$-d(S_2O_8^{2-})/dt = k_1(S_2O_8^{2-}) + k_3(M)(S_2O_8^{2-}) + k_7(M_j)_{\text{aqu}}(S_2O_8^{2-})$$

To a good approximation, we can estimate  $(M_j)_{\text{ss}}$  by equating  $R_i = R_t$ , ignoring reaction (7), because the experimental order of monomer and of initiator is not greater than unity in either case; i.e.,

$$(M_j)_{\text{ss}}^2 = \{[k_1 + k_3(M)]/k_t\}(S_2O_8^{2-})$$

By measuring  $\{-d(S_2O_8^{2-})/dt\}$  experimentally at various values of  $(M)$  and

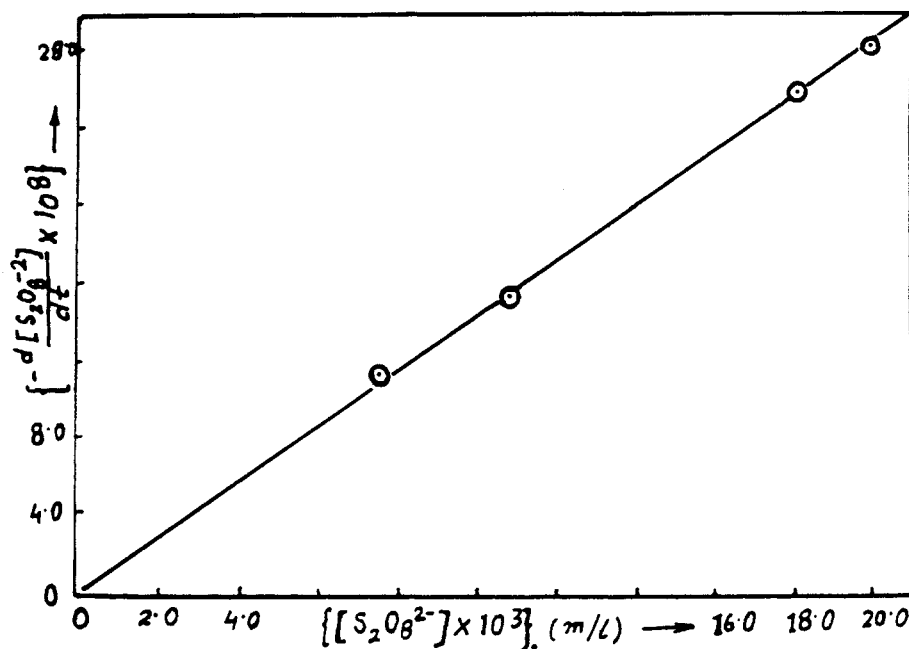


Fig. 11. Plot of  $-d(S_2O_8^{2-})/dt$  vs.  $(S_2O_8^{2-})$  concentrations at a given concentration of the monomer according to eq. (2). The slope of the line gives  $k_1 + k_3(M)$ . Taking  $k_1 = 1.40 \times 10^{-5} \text{ s}^{-1}$ ,  $(M) = 23.10 \times 10^{-2} \text{ (m/L)}$ ;  $k_3$  was found to be  $5.45 \times 10^{-5} \text{ (L/m/s)}$ , which is in excellent agreement with the values of  $k_3$  from Figure 9.

of  $(S_2O_8^{2-})$ ,  $k_7$  was estimated taking

$$(M_j)_{as} = (M_j)_{aq} + (M_j)_{polym}$$

and also

$$(M_j)_{polym}/(M_j)_{aq} = 16$$

for water-soluble polymeric radicals (possibly  $j = 1-4$ ). The values of  $k_7$  so obtained are shown in Table III. Since  $k_7$  comes out as a negative number in some cases (Table III), it implies that the reaction (7) probably does not occur to a significant extent, and this hypothesis will be consistent with the measured orders of the monomer and of the persulfate in eq. (2). Further,

$$k_7 = \frac{\{-d(S_2O_8^{2-})/dt\} - [k_1(S_2O_8^{2-}) + k_3(M)(S_2O_8^{2-})]}{(M_j)_{aq} \times (S_2O_8^{2-})}$$

The numerator is a difference of two rates, viz., experimental and theoretical, and is so small that it is not possible to estimate precisely with the analytical techniques used in this work. The root mean square average of  $k_7$  has been found to be  $7.65 \text{ (L/m/s)}$ .

TABLE III  
 Estimation of  $k_7$ 

(M) [(m/L) $\times 10^2$ ]	(S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> ) [(m/L) $\times 10^3$ ]	(M <sub>j</sub> ) <sub>ms</sub> <sup>2</sup> [(m/L) <sup>2</sup> $\times 10^{14}$ ]	(M <sub>j</sub> ) <sub>ms</sub> <sup>+</sup> [(m/L) $\times 10^7$ ]	(M <sub>j</sub> ) <sub>aq</sub> [(m/L) $\times 10^8$ ]	$k_7$ (L/m/s)	$[-\Sigma k_7^2/6]^{1/2}$ (L/m/s)
23.10	18.10	149.72	12.23	7.19	8.46	
18.48	18.10	122.80	11.08	6.52	(- )5.31	
13.86	18.10	95.87	9.79	5.76	(- )12.98	
9.24	18.10	68.94	8.30	4.88	(- )3.33	7.65
23.10	20.00	155.30	12.46	7.33	4.84	
23.10	10.85	89.75	9.47	5.57	6.98	

If reaction (7) were significant, then the product, M<sub>j</sub>-O-SO<sub>3</sub><sup>-</sup>, would be water-soluble (when  $j = 1-4$ ), and would escape gravimetric determination of yield in a given time. Under certain experimental conditions, we have gotten 95% conversion in 3 h, and the unconverted monomer (5%) would be present mainly in the latex particles where the polymerization would be very slow after 95% conversion since  $k_p$  would be diffusion controlled. Considering the loss of monomer during the polymerization reaction taking place in the reactor, and other experimental errors, we conclude that reaction (7) is not significant in the persulfate-ethyl acrylate system.<sup>20</sup>

Date of Table I show clearly that the polymer colloids are very unstable, and incipient coagulation of latex particles occur continuously during polymerization. Since colloidal stability of polymer colloids is directly proportional to the number of latex particles per mL,<sup>14</sup> it appears that the number of latex particles per mL did not remain constant during the reaction. The estimated molecular weights ( $\bar{M}_n$ ) of the order of  $10^6$  seem to be very high, and this implies errors in the values of the constants in the equation,  $(\eta) = K \times (\bar{M}_n)^a$ , given in the literature.<sup>12</sup>

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