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## **Aqueous Polymerization of Methyl Methacrylate Initiated by Potassium Pervanadate**

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### **ABSTRACT**

The aqueous polymerization of methyl methacrylate was kinetically studied using acidic ( $\text{H}_2\text{SO}_4$ ) potassium pervanadate as initiator. The initiator exponent was 0.3 and the monomer exponent was 1.0. Polymerization is considered to proceed by a radical mechanism, and termination takes place quite measurably by a degradative initiator transfer mechanism.

### **INTRODUCTION**

Oxidation reactions of organic systems by peroxy compounds and higher valent metallic compounds have been widely studied. Utilization of persalts as polymerization catalysts is well known, and potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ) has been extensively used as a free radical initiator in polymerization. Recently Nayak et al. [1-3] reported polymerization of vinyl monomers using peroxidiphosphate ( $\text{K}_2\text{P}_2\text{O}_8$ ), following a report of Hariharan and Meenakashi [4]. Oxidation of organic compounds by potassium pervanadate ( $\text{KVO}_4$ ) has rarely been studied. In the present investigation we used  $\text{KVO}_4$  as an initiator of polymerization of methyl methacrylate (MMA) in aqueous medium.

## EXPERIMENTAL

Materials

Monomer MMA was purified following standard procedures.  $KVO_4$  was prepared in the laboratory following the procedure of Henderson [5]. The  $H_2SO_4$  used was of analytical grade. Water distilled twice in all-glass (Corning brand borosilicate) apparatus was used as the polymerization medium.

Aqueous Polymerization of MMA

Aqueous polymerization was done in 150 mL stoppered conical flasks under nitrogen following the usual procedures [6, 7]. Usually, 1.5 mL of MMA was used in a total volume of 100 mL. The monomer was allowed to dissolve in the aqueous media under a blanket of nitrogen for about 20 h before the addition of the initiator. A dilute aqueous solution  $KVO_4$  was used as the initiator. Small amounts of  $H_2SO_4$  were added in the polymerization medium to effect polymerization. Most of the experiments were carried out at  $50^\circ C$ . Rate measurements were made following standard procedures [8].

Molecular Weight ( $\bar{M}_n$ )

Number-average molecular weights ( $\bar{M}_n$ ) of the polymethyl methacrylate (PMMA) samples, taken in benzene solution, were obtained viscometrically at  $30^\circ C$  using the following equation of Fox et al. [9] where  $[\eta]$ , the intrinsic viscosity, is expressed in dL/g:

$$[\eta] = 8.69 \times 10^{-5} \bar{M}_n^{0.76}$$

## RESULTS AND DISCUSSIONS

$KVO_4$  in aqueous medium did not initiate polymerization of MMA at  $50^\circ C$  without added acid ( $H_2SO_4$ ) in the medium in 3 h. However, in the presence of  $H_2SO_4$  ( $\leq 13.5 \times 10^{-3}$  mol/L) polymerization readily took place. In presence of  $H_2SO_4$  the initial polymerization medium containing  $KVO_4$  assumed a reddish-brown color. Inhibition periods at  $50^\circ C$  in the acid-aqueous system ranged between 10 and 15 min. Results are presented in Table 1 and Figs. 1-9. Percent conversion vs time plots (not showing the inhibition periods) are presented in Fig. 1. Rates of polymerization,  $R_p$ , were calculated from the slopes of the initial linear

TABLE 1. Aqueous Polymerization of MMA at 50°C Using KVO<sub>4</sub> as Initiator.  $[MMA] = 13.8 \times 10^{-2}$  mol/L and  $[H_2SO_4] = 13.5 \times 10^{-2}$  mol/L

Expt no.	$[KVO_4] \times 10^4$ mol/L	$R_p \times 10^4$ mol/L·s	$[\eta]$ (dL/g)	$1/\bar{P}_n \times 10^3$	Initiator exponent	$k_p^2/k_t$ (L/mol·s)
1	3.125	0.1910	1.85	0.2015		
2	6.250	0.2620	1.65	0.2345		
3	12.500	0.3060	1.55	0.2545		
4	18.750	0.3400	1.40	0.2910	0.3	12.78
5	25.000	0.3810	1.25	0.3380		
6	37.000	0.3530	0.90	0.5210		
7	50.000	0.3070	0.55	0.9960		

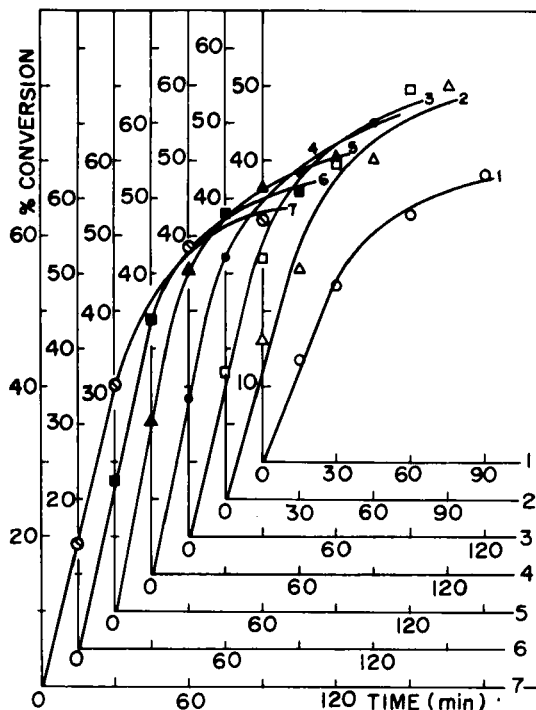


FIG. 1. Aqueous polymerization of MMA at 50°C using  $\text{KVO}_4$  as initiator in the presence of  $\text{H}_2\text{SO}_4$  ( $13.5 \times 10^{-2}$  mol/L). Plot of % conversion vs time (min). Data given for each curve is  $[\text{KVO}_4]$  mol/L. (1)  $3.125 \times 10^{-4}$ , (2)  $6.25 \times 10^{-4}$ , (3)  $12.5 \times 10^{-4}$ , (4)  $18.75 \times 10^{-4}$ , (5)  $25.00 \times 10^{-4}$ , (6)  $37.00 \times 10^{-4}$ , (7)  $50.00 \times 10^{-4}$ .

portion of these curves. Polymerization exhibited enhanced inhibition periods in the presence of air (or oxygen) and small amounts of hydroquinone. The polymer formed in the system gave a positive response to the dye partition test of Palit et al. [10] for anionic sulfate endgroups.

### Initiator Exponent

A plot of  $\log R_p$  vs  $\log [\text{KVO}_4]$  is shown in Fig. 2. The slope of this plot, which gives the initiator exponent (for  $[\text{KVO}_4] < 30 \times 10^{-4}$  mol/L) is 0.3. For  $[\text{KVO}_4] > 30 \times 10^{-4}$  mol/L,  $R_p$  follows a decreasing trend.

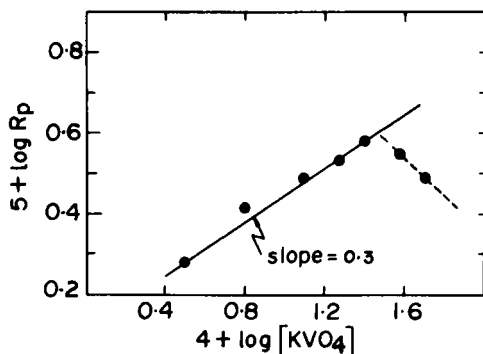


FIG. 2. Aqueous polymerization of MMA at 50°C using  $KVO_4$  as initiator in the presence of  $H_2SO_4$  ( $13.5 \times 10^{-2}$  mol/L). Plot of  $\log R_p$  vs  $\log (KVO_4)$ .

Monomer Exponent

$R_p$  values were also measured at several monomer concentrations using a fixed  $[KVO_4]$ . A linear plot of  $\log R_p$  vs  $\log [M]$  is shown in Fig. 3. The slope of this plot, which gives the monomer exponent, is 1.0.

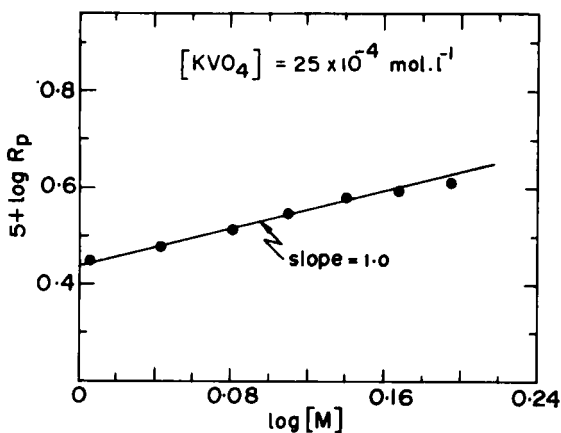


FIG. 3. Aqueous polymerization of MMA at 50°C, using  $KVO_4$  as initiator in the presence of  $H_2SO_4$  ( $13.5 \times 10^{-2}$  mol/L). Plot of  $\log R_p$  vs  $\log [M]$ .

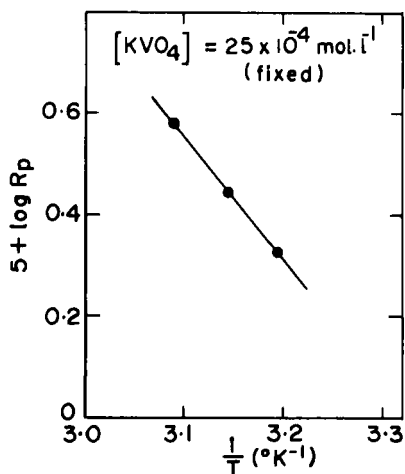


FIG. 4. Aqueous polymerization of MMA at 50°C using  $KVO_4$  as initiator in the presence of  $H_2SO_4$  ( $13.5 \times 10^{-3}$  mol/L). Plot of  $\log R_p$  vs  $1/T$

### Activation Energy

A plot of  $\log R_p$  vs  $1/T$ , where  $T$  is the absolute temperature in °K, is shown in Fig. 4. The activation energy calculated from the slope of this plot is 10.66 kcal/mol. This value is close to the reported activation energy value for the aqueous polymerization of MMA [11].

### Effect of Variation of $[H_2SO_4]$ on Rate

A plot of % conversion for 60 min of polymerization vs  $[H_2SO_4]$  is shown in Fig. 5. Percent conversion follows an increasing trend with increasing  $[H_2SO_4]$  initially, but tends to level off at high  $[H_2SO_4]$ . With no  $H_2SO_4$ , no polymerization was observed.

### Mechanism

The kinetic features (initiator exponent and monomer exponent) inhibitory effect of oxygen and hydroquinone and the results of end-group analysis indicate that the  $KVO_4$ -initiated polymerization of MMA in acid-aqueous medium takes place by a free radical mechanism. The exact mechanism of initiation or radical generation appears to be somewhat complex.

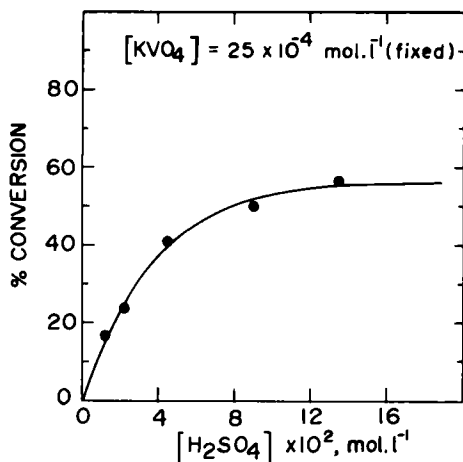


FIG. 5. Aqueous polymerization of MMA at 50°C using  $KVO_4$  as initiator in the presence of  $H_2SO_4$ . Plot of % conversion vs  $[H_2SO_4]$ .

$KVO_4$  as prepared is a reasonably stable yellow compound, particularly in the absence of moisture. In a dilute aqueous solution,  $KVO_4$  is reported to remain as a complex represented by the formula  $KVO_3 \cdot H_2O_2$  and is yellow in color. This compound is incapable of inducing polymerization of MMA in the dark but can do so in the presence of visible or ultraviolet light, a feature commonly exhibited by  $H_2O_2$  as well. In the presence of  $H_2SO_4$ , however, the compound changes into a more active species showing a reddish-brown color. The active species is considered [12] to be the peroxy vanadium sulfate,  $(VO_2)_2(SO_4)_3$ .

An acidic ( $H_2SO_4$ ) solution of  $KVO_4$  containing  $(VO_2)_2(SO_4)_3$  as the active species, the concentration of which is proportional to the concentration of initial  $KVO_4$  taken, readily induces polymerization of MMA in the dark in the temperature range of 40–50°C. Over the course of polymerization the reddish-brown color of the polymerization medium fades away and gradually, with the completion of polymerization, the color of the medium becomes pale yellow. As polymerization progresses, heptavalent vanadium in the form of  $(VO_2)_2(SO_4)_3$  is reduced to the pentavalent form, liberating sulfate ion radicals as shown in the following reaction. The final yellow color of the medium is due to the pentavalent vanadium.



The polymers produced would therefore bear anionic sulfate end-groups. This has been substantiated by the results of endgroup anal-



ysis as mentioned before. Incorporation [10] of some -OH endgroups is also very likely due to possible generation of OH radicals in the acid aqueous medium:



$$\frac{k_p^2}{k_t}$$

The value of the kinetic parameter  $k_p^2/k_t$  was obtained from the initial slope of the plot  $1/\bar{P}_n$  vs  $R_p$  at a fixed [MMA], Fig. 6, following the usual procedures and assumptions, with the help of the Mayo equation:

$$1/\bar{P}_n = 1.85(k_t/k_p^2)(R_p/[M]^2) + C_M + C_I \cdot [I]/[M] \quad (3)$$

where I stands for  $\text{KVO}_4$ , and  $C_M$  and  $C_I$  are the monomer and initiator transfer constants, respectively. Assuming that the initial slope would not change measurably due to transfer processes, the calcu-

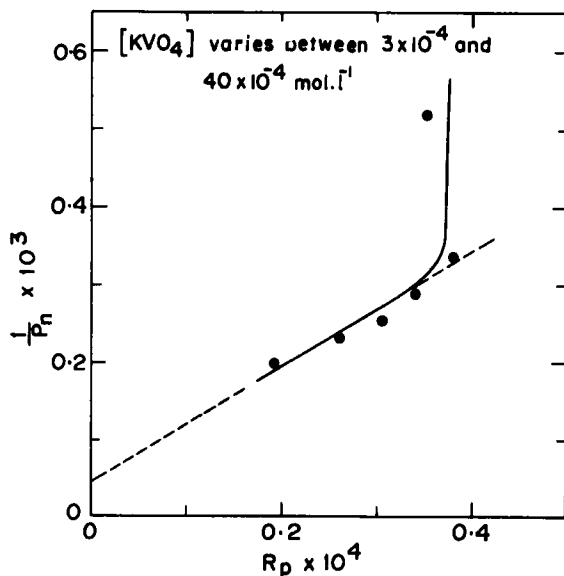


FIG. 6. Aqueous polymerization of MMA at 50°C using  $\text{KVO}_4$  as initiator in the presence of  $\text{H}_2\text{SO}_4$  ( $13.5 \times 10^{-2}$  mol/L). Plot of  $1/\bar{P}_n$  vs  $R_p$ .

lated value of  $k_p^2/k_t$  is 12.78 L/mol·s. This value is somewhat higher than those recently reported for the aqueous polymerization of MMA [13, 14].

### Initiator-Dependent Termination

Low initiator exponent, 0.3 ( $< 0.5$ ), is indicative of some initiator-dependent chain termination process in the present system. The decreasing trend in  $R_p$  with increasing  $[KVO_4]$  beyond  $[KVO_4] = 30 \times 10^{-4}$  mol/L (Fig. 2) can be understood on the basis of decreasing initiator efficiency, probably due to a pronounced or overwhelming initiator termination effect, direct or via primary radicals. Since the monomer order is unity, the kinetics appear to follow normal behavior with variation of monomer at a fixed concentration of the initiator.

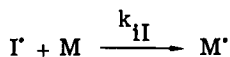
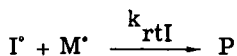
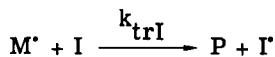
### Analysis of Primary Radical Termination and Degradative Initiator Transfer Process

The equation of Deb and Meyerhoff [15] developed to analyze the primary radical termination effect in the absence of any degradative chain transfer will assume the following form for the present polymerization:

$$\log \frac{R_p^2}{[KVO_4][M]^2} = \log \frac{fk_d k_p^2}{k_t} - 0.8684 \frac{k_{prt}}{k_1 k_p} \frac{R_p}{[M]^2} \quad (4)$$

where  $k_{prt}$  is the rate constant for the primary radical termination reaction and all other terms have their usual significance.

On the other hand, assuming a negligible primary radical termination effect, the following reactions may be considered to describe the overall degradative initiator transfer process:



The equation of Ghosh may be used for detecting the degradative initiator transfer effect. For the present system the equation will assume the following form:

$$\log \frac{R_p^2}{[KVO_4][M]^2} = \frac{fk_d k_p^2}{k_t} - 0.434 \frac{k_p^2}{k_t} \frac{k_{rtI}}{k_{tI} k_p} C_I \frac{[KVO_4]}{[M]} \quad (5)$$

Equations (4) and (5) permit separate plots of  $\log R_p^2/[KVO_4][M]^2$  against  $R_p/[M]^2$  and  $[KVO_4]/[M]$  for the analysis of the primary radical termination effect and the degradative initiator transfer effect, respectively, and such plots are shown in Figs. 7 and 8.

In each plot the experimental points fall more or less on a straight line with a negative slope (with a large scatter in Fig. 7, however), indicating that the nonideal termination effect envisaged is significant. Since the monomer exponent is unity, the initiator-dependent termination is largely due to the degradative process and the primary radical termination process appears to be of much less consequence.

### Initiator Transfer Effect

Equation (3) may be transformed into the following form to calculate the initiator transfer parameter ( $C_I$ ) in the aqueous system, taking the transfer constant of water to be zero [17]:

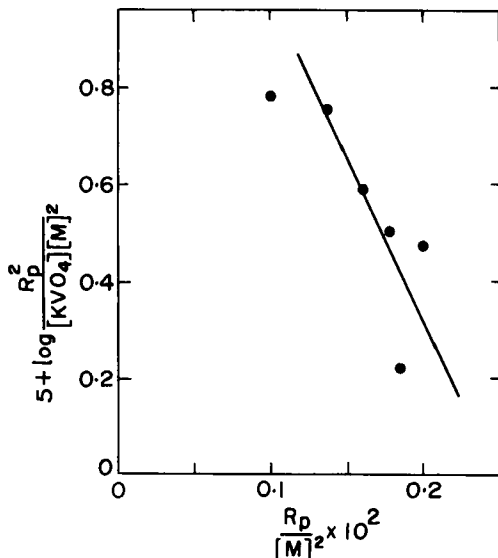


FIG. 7. Analysis of primary radical termination effect in aqueous polymerization of MMA at 50°C using  $KVO_4$  as initiator in the presence of  $H_2SO_4$  ( $13.5 \times 10^{-2}$  mol/L). Plot of  $\log R_p^2/[KVO_4][M]^2$  vs  $R_p/[M]^2$ .

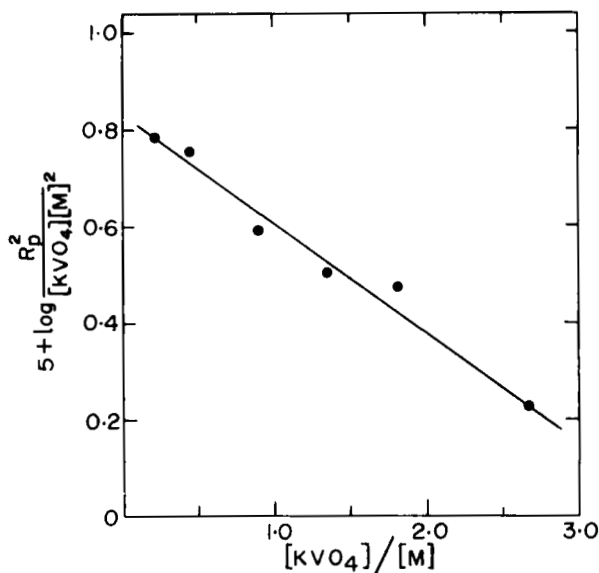


FIG. 8. Analysis of degradative initiator transfer effect in aqueous polymerization of MMA at 50°C using  $\text{KVO}_4$  as initiator in the presence of  $\text{H}_2\text{SO}_4$  ( $13.5 \times 10^{-2}$  mol/L). Plot of  $\log R_p^2 / [\text{KVO}_4][\text{M}]^2$  vs  $[\text{KVO}_4] / [\text{M}]$ .

$$\frac{1}{\bar{P}_n} - 1.85 \frac{k_t}{k_p^2} \frac{R_p}{[\text{M}]^2} = C_M + C_I \frac{[\text{KVO}_4]}{[\text{M}]} \quad (6)$$

A plot of the left-hand side of the Eq. (6) vs  $[\text{KVO}_4] / [\text{M}]$  at fixed MMA is shown in Fig. 9. The slope of the initial linear part of the plot is practically zero. The plot, however, shows a sharp rise in the values of the ordinate beyond a point indicated by an arrow in the plot. On consideration of  $\bar{P}_n$ , therefore, the degradative initiator transfer effect is detectable only in the higher range of  $[\text{KVO}_4]$ , but on consideration of kinetics, the same effect is detectable over the full range of  $[\text{KVO}_4]$  studied. The exact mechanism of the degradative process is not well understood. However, it is quite likely that in the present acid pervanadate initiator system, particularly at high concentrations of the initiator,  $\text{H}_2\text{O}_2$  concentration would be high enough to exhibit degradative chain transfer effects as represented by



Degradative effect arises due to the inactive nature of the  $\text{HO}_2$  radical [18, 19].

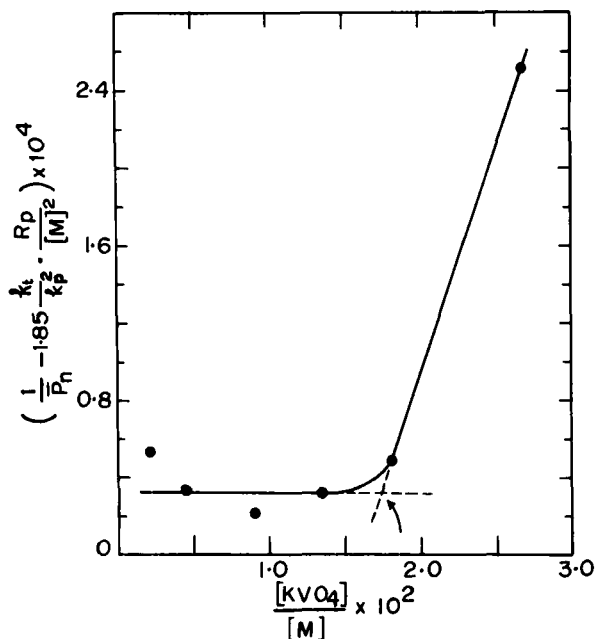


FIG. 9. Aqueous polymerization of MMA at 50 C using  $\text{KVO}_4$  as initiator in the presence of  $\text{H}_2\text{SO}_4$  ( $13.5 \times 10^{-2}$  mol/L). Plot of

$$\left[ \left( \frac{1}{\bar{P}_n} \right) - \left( 1.85 \frac{k_t}{k_p^2} \frac{R_p}{[M]^2} \right) \right] \text{ vs } \frac{[\text{KVO}_4]}{[M]}$$

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