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Acidic Peroxo Salts: A New Class of Initiators for Vinyl Polymerization. IV. Kinetics of Polymerization of Methyl Methacrylate Initiated by Potassium Monopersulfate Catalyzed by Ag(I)

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ABSTRACT

Kinetics of vinyl polymerization of methyl methacrylate (MMA) initiated by an acidic peroxo salt, such as potassium monopersulfate coupled with silver nitrate, have been investigated in aqueous medium over the temperature range from 35 to 50°C. The rates of polymerization (R_p) have been computed for various concentrations of the monomer and initiator. The effectiveness of various metal salts in catalyzing the polymerization reaction has been determined from the observed R_p values. The effects of the catalyst ($AgNO_3$), initiator, monomer, and various secondary aliphatic and aromatic amines on R_p and percentage conversion have been studied. The endgroups of the resultant polymers have been studied using standard methods. From the observed endgroups and kinetic results, a reaction scheme has been proposed involving initiation by $^{\cdot}OH$ or $SO_4^{-\cdot}$ radicals, generated by the interaction of the initiator with silver nitrate and termination by mutual combination.

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INTRODUCTION

The existence of peroxygen acids of sulfur and their salts was recognized nearly a century ago [1]. Although the oxidizing power of compounds such as $(NH_4)_2S_2O_8$ was noticed by Bayer et al. [2] as early as 1901, their ability to initiate radical polymerization was for the first time reported by Bacon [3] in 1946. Since then peroxydisulfate has been used widely as an initiator of vinyl polymerization [4-16] and graft copolymerization of vinyl monomers onto PVA [17], wool, and silk [18, 19].

The use of acidic peroxo salts such as $KHSO_5$ as oxidizing agents is of recent origin. Kennedy et al. [20] have given details of the use of $KHSO_5$ for oxidation of a multitude of organic compounds for preparative purpose. The higher oxidation potential (-1.44 V) of $KHSO_5$ than of peracetic acid, dichromate, H_2O_2, or perhydrates tempted us to explore its potentiality in connection with its use for kinetic studies of vinyl polymerization and graft copolymerization of vinyl monomers onto wool, silk, nylon, cellulose, PET, and PVA. We recently reported [21, 22] the use of $KHSO_5$ for kinetic studies of vinyl polymerization. Since $KHSO_5$ is very sensitive toward metallic salts, we have also been interested in evaluating the decomposition rate of it in the presence of a number of inorganic salts, with a view to use such salts as redox components for vinyl and graft copolymerization. The present report refers to the use of KHSO as an initiator for kinetic studies of vinyl polymerization of methyl methacrylate in the presence of $AgNO_3$ as the redox component and to an attempt to elucidate the mechanisms.

EXPERIMENTAL

Potassium monopersulfate ($KHSO_5$) was a gift from DuPont Co., U.S.A. Methyl methacrylate (Sisco Chemicals, Bombay, India) was first of all washed with 5% NaOH followed by deionized water to remove any trace of alkali, and was then dried over anhydrous calcium chloride. All other reagents were of BDH quality and were used as received.

Water used for the preparation of solution was distilled thrice over alkaline permanganate and deionized by passage through Biodeminrolit resin (Permutit Co., U.K.). Nitrogen for deaeration of the experimental system was purified by passage through Fieser's solution, saturated lead acetate solution, and finally through a wash bottle containing a little monomer.

A stock solution (0.1 $\underline{M}$) of the initiator was prepared by dissolving 6.145 g of $KHSO_5$ in deionized water in a 100-mL flask. The acidity of the stock solution was determined by titration against standard alkali using methyl orange as indicator. The percentage of active oxygen in the freshly prepared solution was estimated by iodometry to be 4.98 (theoretical value 5.2).

The polymerization of the monomer was carried out according to our previous method [22]. The precipitated polymer was filtered off, washed repeatedly with distilled water, and dried to constant weight at 70°C. the rates of polymerization were obtained gravimetrically; the rate of initiator consumption was determined iodometrically.

The molecular weights of the polymers were determined by viscometry using the appropriate Mark-Houwink relationship [23]:

$$[\eta] = 7.7 \times 10^{-3}\ \overline{M}_w^{0.7}\ \mathrm{dL/g}$$

The viscosities of the polymer solution in acetone (0.1%) were determined in an Ubbelohde-type suspended level dilution viscometer.

Endgroup Analysis

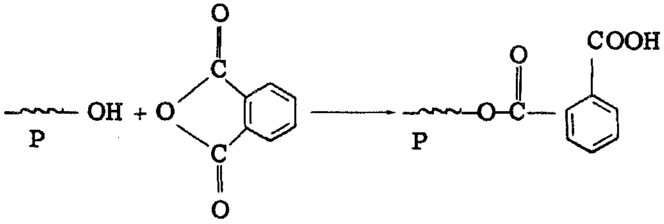
The endgroup analysis of the recovered polymers was carried out by the method of Palit [24] and Saha et al. [25] as follows.

Sulfate Endgroup

Polymethyl methacrylate (PMMA) was first precipitated from acetone. A 0.1% solution of PMMA was prepared in acetone. Methylene blue indicator was prepared by dissolving the crystals in 100 mL of N/100 HCl in benzene. A blank test was carried out by shaking the indicator solution, and no coloration was observed. Thereafter about 5 mL of the polymer solution in a test tube was shaken vigorously with about 3-4 mL of indicator solution and the contents were allowed to settle for about 1 h. A blue coloration of the benzene layer indicated the presence of strong acidic (sulfate) endgroups.

Hydroxyl Endgroup

Since the OH group is natural and itself does not respond to the dye partition test, an indirect method was adopted. A mixture of about 0.5 g of phthalic anhydride and PMMA was refluxed in 25 mL of benzene for 8-9 h, then washed with a solution of NaOH twice to remove the acidic impurities, and finally washed with distilled water to remove traces of alkali. The benzene solution was then directly tested for the –COOH group by the dye-partition test. A positive result was obtained. By this method the –COOH group is introduced to the polymer end by reacting with phthalic anhydride as shown on the following page:



RESULTS AND DISCUSSION

MMA was polymerized in aqueous medium at 35-50°C using $KHSO_5$ as initiator with $AgNO_3$ as the catalyst. Figure 1 includes a typical set of percentage conversion plots at various concentrations of $KHSO_5$ (0.0005-0.025 M) at a fixed concentration of $AgNO_3$ (0.002 M). MMA was also polymerized under identical conditions using $KHSO_5$ with a number of inorganic salts: $Na_2S_2O_3$, $NiSO_4$, $FeSO_4$, $AgNO_3$, $Cu(NO_3)_2$, $CuSO_4$, $CdSO_4$, $ZnSO_4$, $MnSO_4$, $MgSo_4$, $FeCl_3$, KCl, KBr, KI, Na_2SO_4, and Na_2SO_3. Under the reaction condition studied there is an induction period in all cases except for $Na_2S_2O_3$ and $AgNO_3$. With KI as the catalyst no polymers were formed, but there was immediate liberation of I_2 on addition of $KHSO_5$. The R_p values along with the induction period for each salt are presented in Table 1, which shows that under identical conditions the catalytic activities of the salts can be put in the order: $Na_2S_2O_3 > NiSO_4 > FeSO_4 > AgNO_3 > Cu(NO_3)_2 > CoSO_4 > CuSO_4 \geq CdSO_4 \geq ZnSO_4 > MnSO_4 \geq MgSO_4 > FeCl_3 > KCl > Na_2SO_4 > Na_2SO_3 > KBr$.

Rate of Polymerization

R_p was found to increase on increasing the monomer concentration (0.04694-0.3286 M). Plots of R_p vs [MMA] were linear and pass through the origin (Fig. 2). Further plots of log R_p vs log [MMA] were linear (Fig. 2) with a slope equal to unity. Both types of plots clearly indicate that the order with respect to monomer is unity. R_p also increased on increasing the initiator concentration from 0.005 to 0.02 M, after which the rate falls. Plots of R_p vs $[KHSO_5]^{1/2}$ within the concentration range mentioned are linear and pass through the origin (Fig. 3). Above 0.02 M of the initiator concentration there is a decreasing trend in the rate. Plots of log R_p vs log $[KHSO_5]$ within 0.005 to 0.02 M are linear (Fig. 3) with a slope equal to 0.495. This indicates that the rate with respect to initiator is one half The deviation in the rate at high initiator concentration may be attributed

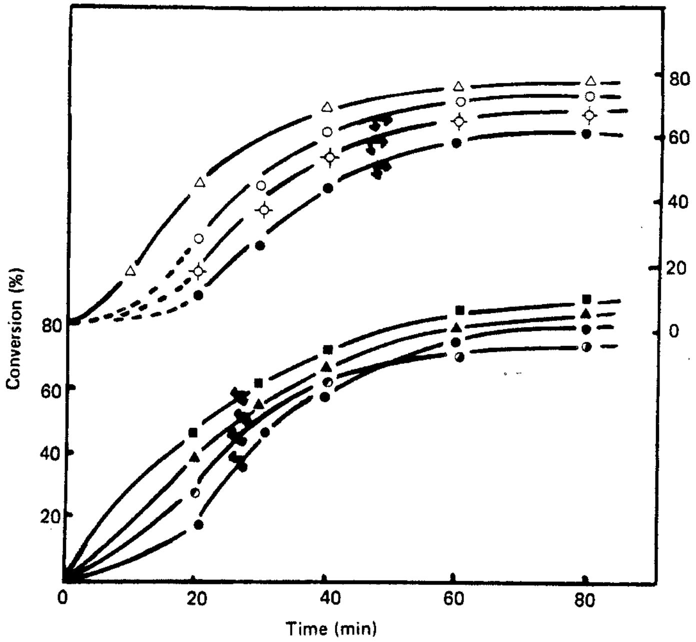


FIG. 1. The bottom curves show the variation of conversion % with time: effect of $KHSO_5$ concentration. [$AgNO_3$] = 0.002 M, [MMA] = 0.09388 M, 40°C. Plots: (●) [$KHSO_5$] = 0.005 M, (▲) [$KHSO_5$] = 0.01 M, (■) [$KHSO_5$] = 0.015 M, (◑) [$KHSO_5$] = 0.025 M. The top curves show the variation of conversion % with time: effect of N,N-diethylaniline concentration. [$KHSO_5$] = 0.02 M, [H^+] = 0.0136 M, [$AgNO_3$] = 0.002 M, [MMA] = 0.09388 M, 40°C. Plots: (△) Control, (○) [DEA] = 0.005 M, (-ϕ-) [DEA] = 0.01 M, (⊕) [DEA] = 0.02 M.

TABLE 1. Polymerization of Methyl Methacrylate (MMA) Initiated by $KHSO_5$ with Various Inorganic Salts. [$KHSO_5$] = 0.01 M, [salt] = 0.02 M, [MMA] = 0.09388 M, 50°C

Salt	Induction period (min)	$10^6 \times R_p$ (mol/L·s)
Control	61	0.03
$Na_2S_2O_3$	Nil	10.01
$NiSO_4$	8	9.965
$FeSO_4$	13	7.743

(continued)

TABLE 1 (continued)

Salt	Induction period (min)	$10^6 \times R_p$ (mol/L·s)
$AgNO_3$	Nil	6.44
$Cu(NO_3)_2$	40	6.132
$CoSO_4$	1	4.84
$CuSO_4$	55	3.927
$CdSO_4$	43	3.916
$ZnSO_4$	45	3.833
$MnSO_4$	2	3.486
$MgSO_4$	50	3.34
$FeCl_3$	35	2.72
KCl	45	1.89
Na_2SO_4	80	0.694
Na_2SO_3	50	0.542
KBr	100	0.403

to the fact that at high initiator concentration a large amount of Ag^{2+} is produced by the interaction of $KHSO_5$ with Ag(I), which causes a premature termination of polymer chains. A similar observation has been made by us in the $KHSO_5$/Co(II) initiated polymerization of methyl methacrylate [26]. Termination of polymer chains by higher valency metal ions above a certain concentration is well recognized [27].

The effect of temperature on the polymerization system is quite interesting. The R_p values increase on increasing the temperature from 35 to 50°C, beyond which the rate becomes sluggish. This might be due to the solubility of the polymer in its own monomer medium, which increases with temperature beyond 50°C.

Effect of Silver Nitrate

The effect of $AgNO_3$ of various concentrations has been computed in Fig. 4. It is seen that the initial rate of polymerization as well as the maximum conversion increase occurs on increasing the concentration of silver nitrate from 0.001 to 0.005 M, beyond which a decreasing trend is noticed. The rate enhancement within the concentration range studied might be due to two factors.

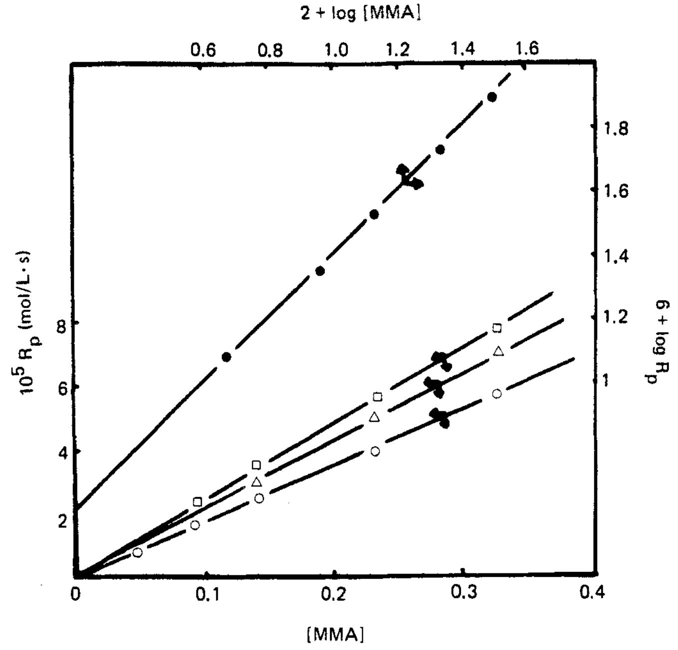


FIG. 2. The bottom curves show the variation of R_p with monomer at various temperatures. [$KHSO_5$] = 0.02 M, [H^+] = 0.0136 M, [$AgNO_3$] = 0.002 M. Plots: (○) 35°C, (△) 45°C, (□) 50°C. The top curve is a plot of 2 + log [MMA] vs 6 + log R_p at 50°C (●).

1. The increase in the concentration of $AgNO_3$ from 0.001 to 0.01 M results in the facile decomposition (induced activation) of $KHSO_5$ with easy production of the initiating free radicals.
2. The oxidation of Ag^+ to unstable Ag^{2+}, which might also act as an initiator. The ability of higher unstable valency metal ions to initiate vinyl polymerization is well recognized [28, 29].

The decrease in the trend at high $AgNO_3$ concentration (above 0.01 M) might be due to premature termination of the polymer chain by an excess of Ag^{2+} produced by the oxidation of Ag^+. The termination of polymer chain by metal ions has been observed by Bamford et al. [30] in the AIBN-initiated polymerization of vinyl monomers in the presence of $FeCl_3$.

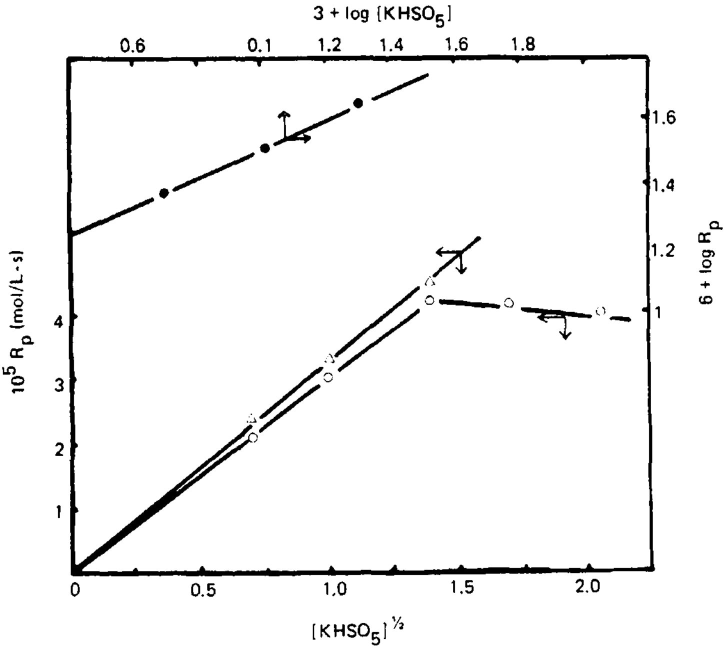


FIG. 3. The bottom curves show the variation of R_p with initiator concentration at various temperatures. [$AgNO_3$] = 0.002 M, [MMA] = 0.14082 M. Plots: (○) 35°C, (△) 50°C. The top curve is a plot of 6 + log R_p vs 3 + log [$KHSO_5$] at 50°C (●).

Effect of Added Amines

In order to find the effect of amines on free radical initiated vinyl polymerization, various amines have been tried. It is observed that the addition of aliphatic secondary amines like N,N-diethyl amines (0.0005-0.015 M) has no effect on the free radical polymerization of vinyl monomers. The presence of N,N-diethylaniline in the reaction mixture in a concentration range from 0.005 to 0.01 causes a remarkable induction period and simultaneously the initial rate of polymerization and maximum conversion are depressed (Fig. 1). The depression in the rate might be due to the retarding effect of the N-oxide produced by the oxidation of the additive by the initiator. N-oxides are well known as retarders of vinyl polymerization [31]. With aniline the polymerization reaction was completely inhibited, and on the addition of $KHSO_5$ a yellow coloration developed which persisted.

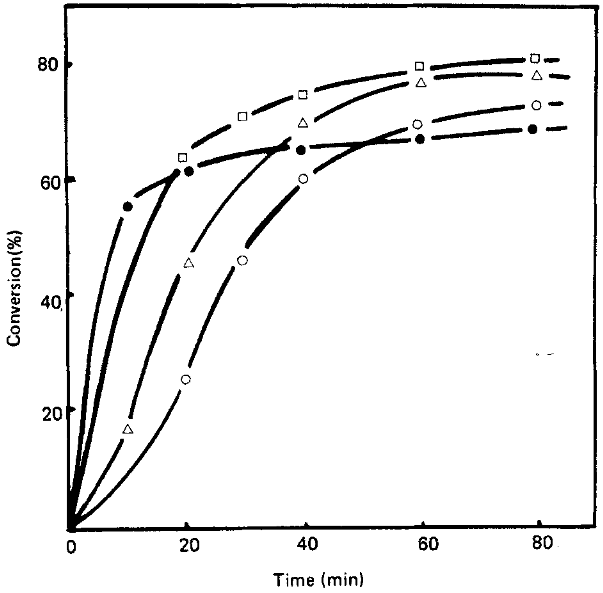


FIG. 4. Variation of conversion % with time: effect of $AgNO_3$ concentration. [$KHSO_5$] = 0.02 M, [H^+] = 0.0136 M, [MMA] = 0.09388 M, 40°C. Plots: (○) [$AgNO_3$] = 0.001 M, (△) [$AgNO_3$] = 0.002 M, (□) [$AgNO_3$] = 0.005 M, (●) [$AgNO_3$] = 0.015 M.

This behavior of aromatic amine might be due to its facile oxidation to quinones [32] which are strong inhibitors. A similar observation has been made by Saha et al. [25] for the polymerization of AN by Ce(IV) in the presence of N,N-dimethylaniline.

REACTION MECHANISM AND RATE LAW

The polymerization of methyl methacrylate in aqueous media initiated by $KHSO_5$ in the presence of $AgNO_3$ shows features characteristic of heterogeneous polymerization. The reaction mixture becomes heterogeneous as soon as polymerization starts due to the insolubility of the polymer (PMMA) in the aqueous phase.

From the relationship between measurable parameters and variables, a reaction scheme has been proposed involving initiation by free radicals ($SO_4^{-\cdot}$ or $OH^\cdot$) produced by the interaction of the initiator ($KHSO_5$) with $AgNO_3$ and termination by mutual combination.

$$HSO_5^- + Ag^+ \xrightarrow{k_d} OH^{\bullet} + SO_4^{-2} + Ag^{2+} \qquad (1a)$$

$$HSO_5^- + Ag^+ \xrightarrow{k_d} SO_4^{-\bullet} + OH^- + Ag^{2+}$$

$$(R^{\bullet} = SO_4^{-\bullet} \text{ or } OH^{\bullet}) \qquad (1b)$$

Initiation:

$$R^{\bullet} + M \xrightarrow{k_i} R\text{–}M^{\bullet} \qquad (2)$$

Propagation:

$$\begin{array}{l} R\text{—}M^{\bullet} + M \xrightarrow{k_p} R\text{–}M_2^{\bullet} \\ \vdots \\ R\text{—}M^{\bullet}_{n-1} + M \longrightarrow R\text{–}M_n^{\bullet} \end{array} \qquad (3)$$

Termination:

$$R\text{–}M_n^{\bullet} + R\text{–}M_m^{\bullet} \xrightarrow{k_t} \text{polymer} \qquad (4)$$

Applying the steady-state principle to the primary radical $R^{\bullet}$ as well as to the growing polymer radical $R\text{–}M_n^{\bullet}$, and taking the radical reactivity as independent of radical size, we obtain

$$-d[M]/dt = R_p = k_p[R\text{–}M_n^{\bullet}][M] \qquad (5)$$

$$R_p = (k_d/k_t)^{1/2}k_p[M][I]^{1/2} \qquad (6)$$

Where M = monomer and I = initiator.

Equation (6) requires that R_p is directly proportional to [M] and $[I]^{1/2}$. These orders of the rate have been observed in the present case (see Figs. 2 and 3).

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