

Peroxydiphosphate/Bisulfite-Initiated Polymerization of Acrylamide and Its Retardation Kinetics

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SYNOPSIS

The kinetics of aqueous polymerization of acrylamide with peroxydiphosphate/bisulfite redox pair was studied at $35 \pm 0.2^\circ\text{C}$ under atmospheric oxygen. The rate of polymerization was found to be of first power to monomer, half-power to catalyst, and 0.75 power to activator concentration. The overall energy of activation was calculated to be 11.0 kcal/deg mol between 25 and 45°C . The effect of addition of organic solvents and dinitrobenzenes as retarders on the rate of polymerization were studied kinetically and retardation constants for nitro compounds were evaluated by a newly proposed method (intercept method), when two retarders act simultaneously.

INTRODUCTION

Introduced by Hariharan and Meenakshy¹ peroxydiphosphate forms an efficient redox couple with various reducing agents such as acids,² sodium thiosulfate,³ metal ions,⁴ etc. In the present work this oxidant has been coupled with sodium metabisulfite for polymerization of acrylamide, under atmospheric oxygen. The role of oxygen like an inhibitor or retarder in free radical polymerization has been well recognized, but its catalytic activity in vinyl polymerization is less studied. In the present work the oxygen acts as a catalyst for the polymerization which is supported by the fact that in the absence of oxygen considerably low yield of polymer is obtained in a quite long period. The resulting polyacrylamide finds a wide number of applications in various industries such as a flocculent, sizing agent, flooding agent for petroleum recovery, etc. Besides the usual kinetic treatment, the course of polymerization has been studied under retardation by two different retarders simultaneously, and a different kinetic scheme has been framed for the determination of retardation constants for each retarder. This part of the work, of course, makes it different

from traditional kinetic treatment of retarded polymerization.

EXPERIMENTAL

Preparation of Materials

Acrylamide (E. Merck) was recrystallized twice from methanol (analytical reagent grade) and dried in vacuum. Potassium peroxydiphosphate used was given by E. Merck (India) and sodium metabisulfite was from the British Drug House (analytical reagent grade). Benzene alcohols, dimethyl formamide, and the three dinitrobenzenes were also from E. Merck (analytical reagent grade). Other chemicals used were also of guaranteed reagent (GR) grade. Fresh solutions were prepared for each run and bidistilled water was used for the purpose.

Technique

The apparatus employed was the same as adopted in our earlier communications.^{5,6} The course of polymerization was followed by estimation of double bonds of unpolymerized acrylamide as described by Wallace and Young⁷ and percentage conversion was calculated by the formula given by Misra et al.⁸ The reaction mixture containing calculated amount of acrylamide, metabisulfite, and requisite amount of

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conductivity water was taken in a Pyrex reaction flask and was placed in a thermostat set at $35 \pm 0.2^\circ\text{C}$ for 1 h to attain the thermal equilibrium. The polymerization was then initiated by introducing a calculated amount of potassium peroxydiphosphate into the reaction flask with constant stirring. The initial concentration of monomer was determined by withdrawing and introducing a definite aliquot of reaction mixture into an iodine flask containing a known quantity of ice-cold brominating reagent, as soon as the polymerization is initiated. Several aliquots were then withdrawn at desired time intervals and introduced into iodine flasks containing a known amount of ice-cold brominating reagent, followed by addition of 1 M H_2SO_4 , were stoppered immediately, shaken well, and kept in the dark to allow bromination to take place completely. The excess bromine was then back titrated against sodium thiosulphate solution using excess KI and starch as indicator.

The percentage conversion was calculated by using the following formula:

$$\% \text{ conversion} = \frac{C(V_t - V_0) \cdot M}{20w}$$

where C = concentration of thiosulphate solution with respect to reaction with KIO_3 (in normality), V_0 = volume of $\text{Na}_2\text{S}_2\text{O}_3$ required at zero time, V_t = volume of $\text{Na}_2\text{S}_2\text{O}_3$ required at different time intervals, M = molecular weight of acrylamide, and w = weight of the acrylamide present in aliquot withdrawn for the estimation of unchanged monomer.

Every precaution was taken to bring the reproducibility of the results within 5%. For studying the course of polymerization retarded by organic solvents and nitro compounds, 5 mL of each organic solvent and solutions of the three dinitrobenzenes (*o*-, *m*-, and *p*-) prepared in 0.05 mL benzene were added to the aqueous reaction medium, respectively. The total volume of reaction mixture was always maintained to 100 mL.

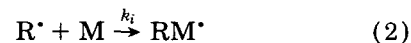
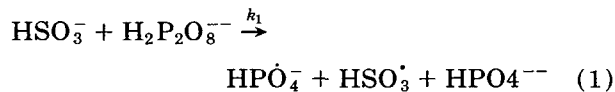
RESULTS AND DISCUSSION

Mechanism

A plausible free radical mechanism has been proposed for unretarded polymerization of monomer (M) as follows:

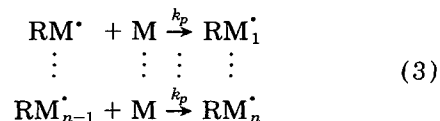
(a) *Initiation*: Bisulfite in aqueous solution reacts with water molecules to give HSO_3^- ions⁹ which fur-

ther reacts with peroxydiphosphate ion to generate free radicals as below:

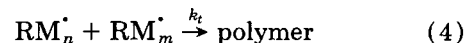


where either of the radicals produced in eq. (1) may be taken as R^\cdot .

(b) *Propagation*:



(c) *Termination*:



The 0.5 power of rate of polymerization with respect to catalyst (peroxydiphosphate) supports the bimolecular mode of termination.

Rate Expression

Based on steady state kinetic assumptions, the following rate expression has been derived:

$$R_p = k_p \left(\frac{k_1}{2k_t} \right)^{0.5} [\text{M}] [\text{HSO}_3^-]^{0.5} [\text{H}_2\text{P}_2\text{O}_8]^{0.5} \quad (5)$$

Equation (5) is in agreement with our experimental outcome.

Monomer Dependence

The initial rate of polymerization and percentage conversion were found to increase with increase in the concentration of monomer in the range $3.0\text{--}20.0 \times 10^{-2}$ mol/L [Fig. 1(a)]. It is quite clear that, on increasing the concentrations of monomer, the availability of monomer molecules in the propagation step increases which therefore brings about an increase in the initial rate and percentage conversion. The initial rate of polymerization was taken as % polymerization/6 min and a double logarithmic plot between monomer concentration and R_p was a straight line [Fig. 1(b)]. The slope of which gave the value of monomer exponent. It was 0.87 in the present case, which is slightly lower than the normal value of unity.^{10,11}

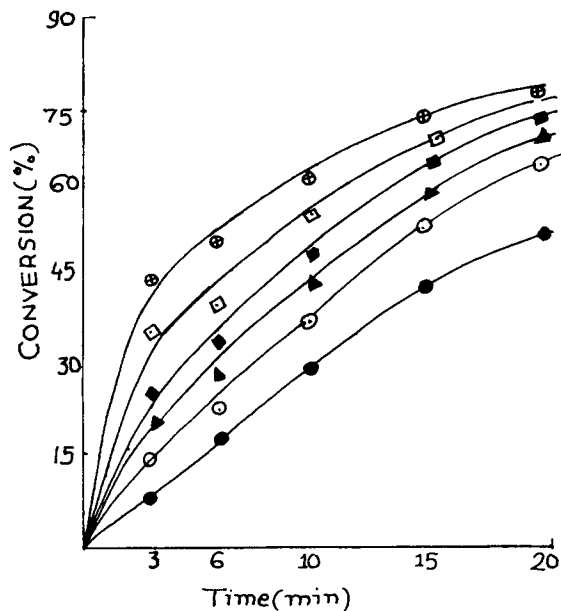


Figure 1(a) Time vs. conversion curve for the polymerization of acrylamide with varying initial monomer concentration (mol/L) at fixed [peroxydiphosphate] = 4.0×10^{-3} mol/L; [bisulfite] = 3.4×10^{-3} mol/L, $35 + 0.2^\circ\text{C}$; (●) 3.0×10^{-2} ; (○) 5.0×10^{-2} ; (▲) 7.5×10^{-2} ; (■) 10×10^{-2} ; (□) 15.0×10^{-2} ; (⊕) 20×10^{-2} .

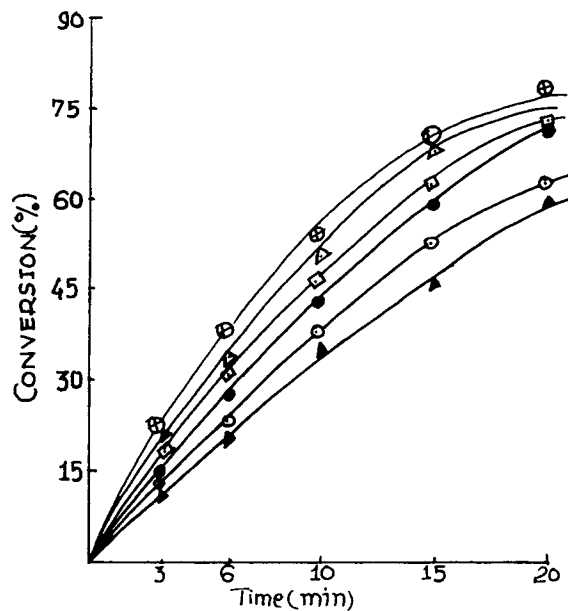


Figure 2 Time vs. conversion curve for the polymerization of acrylamide with varying initial catalyst (peroxydiphosphate) concentration (mol/L) at fixed [monomer] = 5.0×10^{-2} mol/L, [bisulfite] = 3.4×10^{-3} mol/L, $35 + 0.2^\circ\text{C}$: (▲) 2.5×10^{-3} ; (○) 4.0×10^{-3} ; (●) 6.0×10^{-3} ; (□) 8.0×10^{-3} ; (△) 4.5×10^{-3} ; (⊕) 12.0×10^{-3} .

Catalyst and Activator Dependence

Both the initial rate and percentage conversion increase on increasing the concentration of catalyst (peroxydiphosphate) and activator (bisulfite) in the studied range of $2.5\text{--}12.0 \times 10^{-3}$ mol/L and $2.5\text{--}7.0 \times 10^{-3}$, respectively (Figs. 2 and 3). On increasing the concentrations of redox components in the sys-

tem, the number of initiating species (free radicals $R\cdot$) increases which, in turn, increases the rate of polymerization and percentage conversion. From double log plot (Fig. 4) the exponent values to the

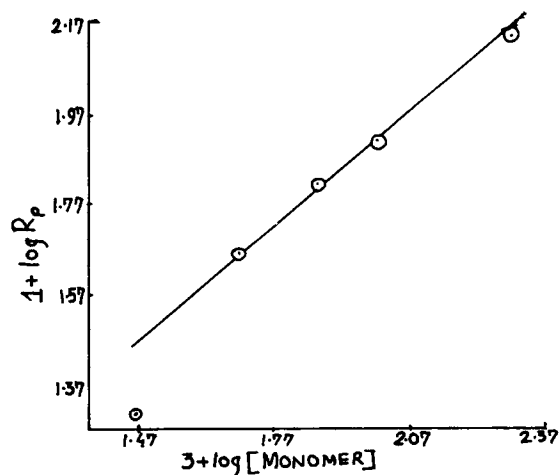


Figure 1(b) Double logarithmic plot of the initial rate of polymerization (R_p in % conversion per minute) vs. the initial concentration of monomer slope = 0.87.

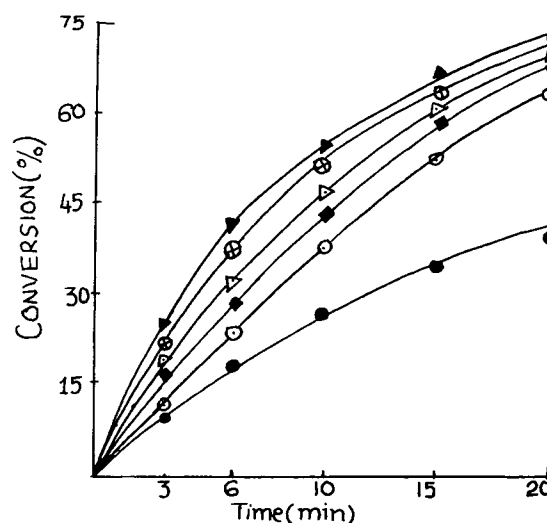


Figure 3 Time vs. conversion curve for the polymerization of acrylamide with varying initial activator (metabisulfite) concentrations (mol/L) at fixed [monomer] = 5.0×10^{-2} mol/L, [peroxydiphosphate] = 4.0×10^{-3} mol/L, $35 + 0.2^\circ\text{C}$: (●) 2.5×10^{-3} ; (○) 3.4×10^{-3} ; (■) 4.2×10^{-3} ; (△) 5.0×10^{-3} ; (⊕) 5.8×10^{-3} ; (▲) 7.0×10^{-3} .

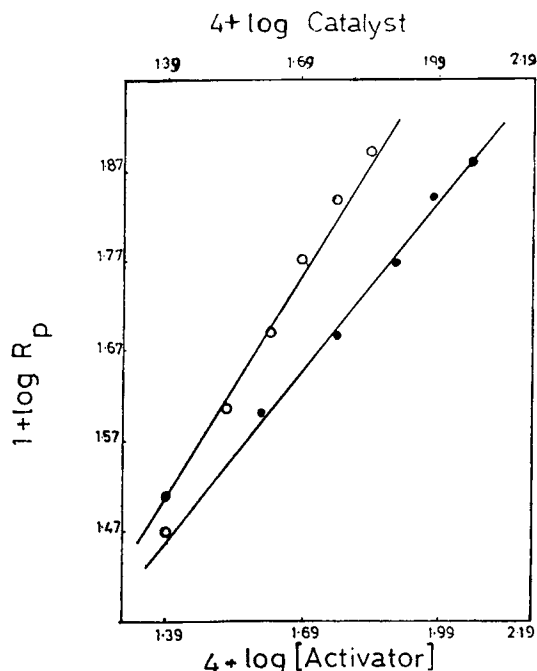


Figure 4 Double logarithmic plot of the initial rate of polymerization (R_p in % conversion per minute) vs. the initial concentrations of catalyst (●) and activator (○), with slopes 0.60 and 0.75, respectively.

catalyst and activator have been found to be 0.60 and 0.75, respectively. The deviation of the observed exponent of 0.75 for the activator from the theoretical value of 0.50 may be attributed to the oxidation of bisulfite by atmospheric oxygen.⁹ The 0.5 exponent for catalyst is supported by many other similar systems.¹²

Temperature Effect

When the temperature of the reaction medium is increased in the range of 25–45°C, the rate of polymerization and percentage conversion increases (Fig. 5). The observed increase is probably due to the rise in the rate of radical generation and propagation steps. The overall energy of activation has been found to be 11.0 kcal/deg mol (Fig. 6) from the Arrhenius plot, which is of the same order as found in other redox systems.¹³

Effect of Retarders

Organic Solvents

It has been found that the use of water-miscible organic solvents reveals the influence of the medium on the polymerization and the properties of resulting

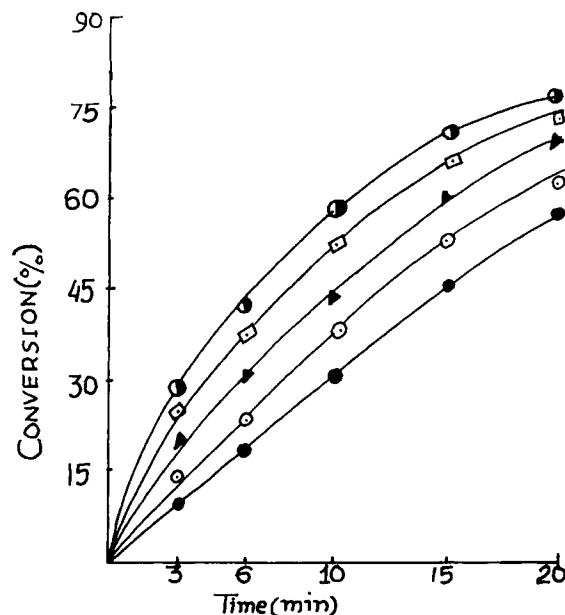


Figure 5 Time vs. conversion curve for the polymerization of acrylamide at varying temperatures (°C) at fixed [monomer] = 5.0×10^{-2} mol/L, [peroxydiphosphate] = 4.0×10^{-3} mol/L, [bisulfite] = 3.4×10^{-3} mol/L: (●) 25; (○) 30; (▲) 35; (□) 40; (⊙) 45.

polymer.¹⁴ Keeping this in mind, various organic solvents (such as methanol, ethanol, isopropanol, etc.) were added to the reaction medium and were found to retard the polymerization (Fig. 7). The retarding effect of these solvents, when added in

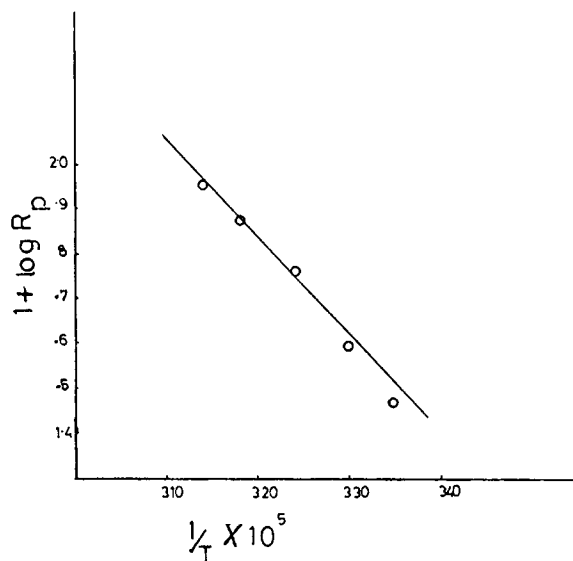


Figure 6 Arrhenius plot of the initial rate of polymerization vs. reciprocal of absolute temperature (T) of polymerization.

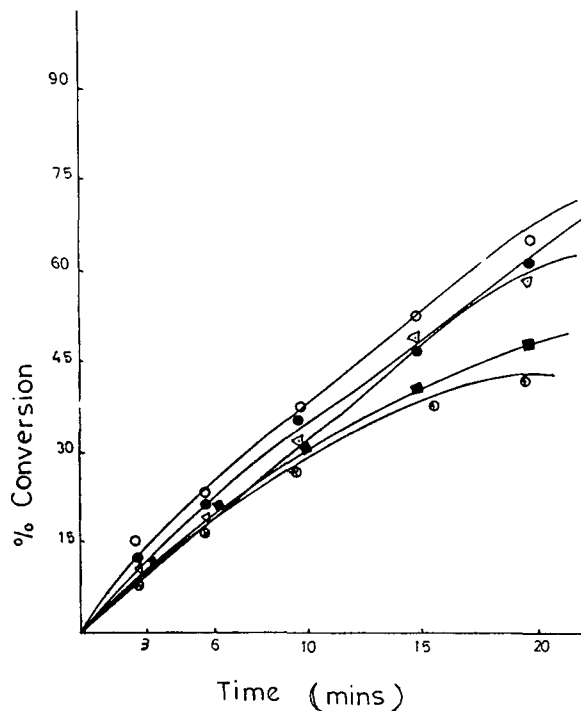
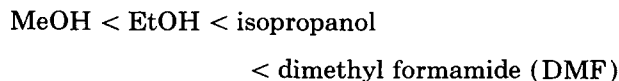
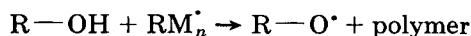


Figure 7 Effect of addition of water miscible organic solvents on the polymerization rate of acrylamide at fixed [monomer] = 5×10^{-2} mol/L, [peroxydiphosphate] = 4.0×10^{-3} mol/L, [bisulfite] = 3.4×10^{-3} mol/L, $35 \pm 0.2^\circ\text{C}$: (○) control; solvents (all 5% v/v): (●) methanol, (▼) ethenol; (■) isopropanol; (⊙) DMF.

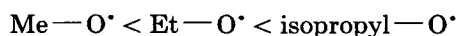
equal quantity (5% v/v) was found in the following increasing order:



The mechanism of retardation by these solvents may be explained by the abstraction of a hydrogen atom by propagating macroradical, resulting in the formation of an alkoxy radical as given below:



The stability of resulting alkoxy radical decides the efficiency of a particular solvent. Since the stabilities of alkoxy radical are in the following order,



the order of retarding efficiencies of these solvents, as observed here, is thus explained. Besides the hydrogen abstraction mechanism, other causes of retardation may be mentioned as below:

1. The addition of organic solvents to the reaction medium decreases the area of shielding of a strong hydration layer in aqueous medium, resulting in the termination of the radical end of the growing chain.
2. Some amount of catalyst may be consumed in the oxidation of these solvents which reduces the concentration of catalyst and thus suppresses the rate of polymerization. Similar types of results have been obtained elsewhere.¹⁵

Dinitrobenzenes

Aromatic nitro compounds are the second most important class of polymerization inhibitors (and retarders) after quinones. Although these compounds completely inhibit the polymerization of vinyl acetate,¹⁶ they only retard that of styrene¹⁷ and have little effect on methyl methacrylate.¹⁸

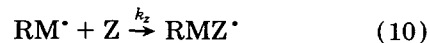
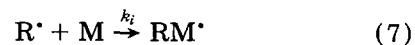
In order to study the polymerization kinetics under retardation, retarders such as *o*-, *m*-, and *p*-dinitrobenzenes were added at very low concentration (1×10^{-4} mol/L) to the reaction medium (Fig. 8) in the form of a solution prepared in benzene, which also acts as the second retarder in the system. The following kinetic scheme has been proposed for the evaluation of retardation constants.

Mechanism

For redox-initiated polymerization retarded by two retarders simultaneously, the following equations may be given:



where "redox" stands for the present peroxydiphosphate/bisulfite system and R for the free radicals produced in eq. (1):



(here W and Z are two different retarders such as benzene and the dinitrobenzene isomers, respectively).

Now,

$$\frac{-d[\text{M}]/dt}{(-d[\text{M}]_{\text{retd.}}/dt)} = \frac{k_p[\text{M}][\text{RM}^*]}{k_p[\text{M}][\text{RM}^*]_{\text{retd.}}} = \frac{[\text{RM}^*]}{[\text{RM}^*]_{\text{retd.}}}$$

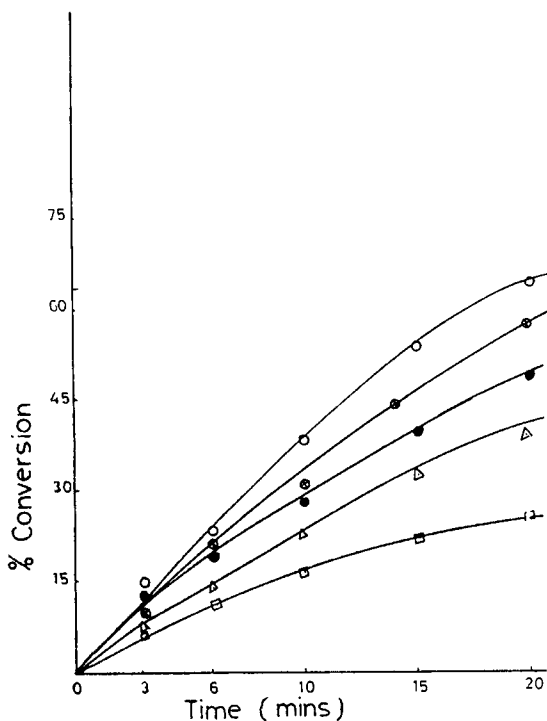


Figure 8 Effect of addition of retarders on the rate of polymerization of acrylamide at fixed [monomer] = 5.0×10^{-2} mol/L, [Peroxydiphosphate] = 4.0×10^{-3} mol/L, [bisulfite] = 3.4×10^{-3} mol/L, $35 \pm 0.2^\circ\text{C}$: (O) control set; (⊕) [benzene] = 5.89×10^{-2} mol/L; (●) [o-dinitrobenzene] = 1×10^{-4} mol/L; (Δ) [m-dinitrobenzene] = 1×10^{-4} mol/L; (□) [p-dinitrobenzene] = 1×10^{-4} mol/L.

Also,

$$\frac{[\text{RM}^*]}{[\text{RM}^*]_{\text{retd.}}} = \frac{k_p[\text{M}] + k_w[\text{W}] + k_z[\text{Z}]}{k_p[\text{M}]} \quad (11)$$

Here $-d[\text{M}]/dt$ and $-d[\text{M}]_{\text{retd.}}/dt$ are the rate of disappearance of monomer under normal and retarded conditions, respectively. Similarly $[\text{RM}^*]$ and $[\text{RM}^*]_{\text{retd.}}$ being also the concentrations of secondary free radicals under above-stated conditions, respectively.

For simplicity, let $-d[\text{M}]/dt = X$ and $-d[\text{M}]_{\text{retd.}}/dt = X'$

We have, from eq. (11),

$$\frac{X}{X'} = 1 + \frac{k_w}{k_p} \frac{[\text{W}]}{[\text{M}]} + \frac{k_z}{k_p} \frac{[\text{Z}]}{[\text{M}]}$$

or

$$\frac{X}{X'} = 1 + I \frac{[\text{W}]}{[\text{M}]} + J \frac{[\text{Z}]}{[\text{M}]} \quad (12)$$

or

$$\frac{X - X'}{X'} = I \frac{[\text{W}]}{[\text{M}]} + J \frac{[\text{Z}]}{[\text{M}]} \quad (13)$$

Here I and J are respective retardation constants for w and Z retarders.

Now,

$$\frac{-d[\text{W}]}{dt} = k_w[\text{W}][\text{RM}^*] \quad (14)$$

$$\frac{-d[\text{Z}]}{dt} = k_z[\text{Z}][\text{RM}^*] \quad (15)$$

Now, upon integration of eqs. (14) and (15), we get

$$[\text{W}] = [\text{W}_0] - kt \quad (16)$$

and

$$[\text{Z}] = [\text{Z}_0] - k't \quad (17)$$

where $[\text{W}_0]$ and $[\text{Z}_0]$ being the initial concentrations of the two retarders and K and K' are two constants. For the linear portion of the percentage conversion vs. t curve, X and X' will also be constant and, therefore, on combining eqs. (13), (16), and (17), we get

$$[\text{M}] = \frac{1}{(X - X')/X'} \cdot \{I[\text{W}_0] + J[\text{Z}_0]\} - \frac{(IK + JK')}{(X - X')/X'} t \quad (18)$$

It is also clear that for a single retarder W , eq. (18) reduces to

$$[\text{M}] = \frac{I[\text{W}_0]}{(X - X')/X'} - \frac{IK}{(X - X')/X'} t \quad (19)$$

From eqs. (18) and (19), it is quite obvious that a plot drawn between $[\text{M}]$ vs. t would be a straight line from intercept of which I and J may easily be calculated. Hence the method has been named the "intercept method."

RESULTS

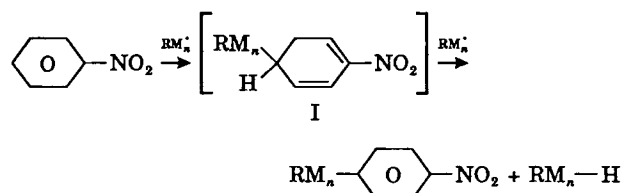
On the basis of eqs. (18) and (19), the retardation constants for benzene and the three dinitrobenzenes have been calculated and summarized in Table I and Figure 9.

Table I Benzene and Dinitrobenzenes as Retarders in Acrylamide Polymerization at $35 \pm 0.2^\circ\text{C}$

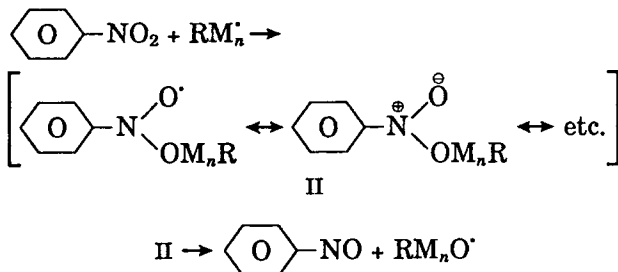
Retarder	$\{[W_0] \text{ or } [Z_0]\} \times 10^4$	k_z/k_p
Benzene	589	0.11
<i>o</i> -Dinitrobenzene	1.0	33
<i>m</i> -Dinitrobenzene	1.0	205
<i>p</i> -Dinitrobenzene	1.0	345

DISCUSSION

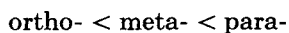
According to a mechanism proposed by Price,¹⁹ the growing macroradical (RM_n^\cdot) attacks on the aromatic ring, yielding a resonance-stabilized intermediate radical (I) which may further react with another propagating radical as follows:



According to another mechanism, proposed by Hammond and Bartlett,²⁰ the growing macroradical attacks the oxygen atom of nitro-group forming a radical II, which is also resonance stabilized and may further break as follows:



In the case of dinitro compounds, according to the mechanism proposed by Price, the meta isomer would be a more effective retarder than the para isomer. In the case of vinylacetate polymerization, the opposite has been reported.²¹ In the present work we found the following order:



We may account for our results by the following

reasons: The macroradical formed may attack oxygen as per the reaction given above and then the comparative reactivities of three isomers may be explained on the basis of resonance stabilization of intermediate radical species. It is quite clear that the contribution from resonance structures involving the two nitro groups will play an important role in stabilizing the radical intermediate in the three dinitrobenzenes. In the case of the para isomer, since the free nitro group can readily assume the required coplaner configuration²² with respect to benzene ring and other nitro group, this isomer would be the most effective towards macroradical attack. In the case of the meta isomer, the two nitro groups are inclined about 11° to the plane of benzene ring with a result that its contribution will be less than the para isomer,²³ which makes this retarder weaker than the para one. In the ortho isomer, due to large steric hindrance, the two nitro groups will be nonplaner with the benzene ring and its contribution towards resonance structures will be the least.

To conclude, we may say that the new redox initiating system potassium peroxydiphosphate-so-

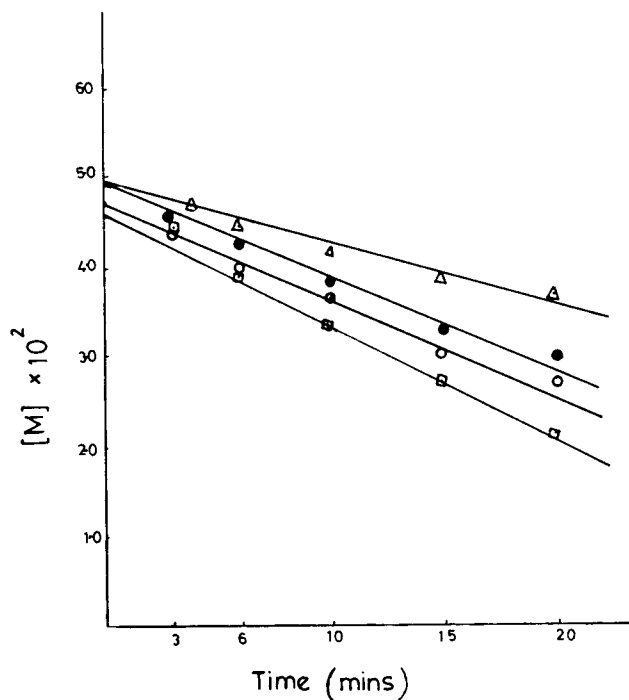


Figure 9 $[M]$ vs. time curve for the polymerization of acrylamide at fixed $[\text{monomer}] = 5.0 \times 10^{-2} \text{ mol/L}$, $[\text{peroxydiphosphate}] = 4.0 \times 10^{-3} \text{ mol/L}$, $[\text{bisulfite}] = 3.4 \times 10^{-3} \text{ mol/L}$, $35 \pm 0.2^\circ\text{C}$: (O) $[o\text{-dinitrobenzene}] = 1 \times 10^{-4} \text{ mol/L}$; (●) $[m\text{-dinitrobenzene}] = 1 \times 10^{-4} \text{ mol/L}$; (Δ) $[p\text{-dinitrobenzene}] = 1 \times 10^{-4} \text{ mol/L}$; (□) $[\text{benzene}] = 5.89 \times 10^{-2} \text{ mol/L}$.

dium metabisulfite works well for the polymerization of acrylamide, and retardation constants may also be calculated by the method called the "intercept method" by us in the present work.

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