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# Retardation of Permanganate-Initiated Polymerization of Acrylonitrile by Phenol

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## ABSTRACT

The mechanism and kinetics of the retardation of the permanganate-initiated polymerization of acrylonitrile by phenol have been studied in the temperature range of 30 to 45°C. The effect of monomer, metal ion, phenol, sulfuric acid, organic solvents, and some inorganic salts on the polymerization has been studied. The most remarkable observation in the present investigation was the negative intercept obtained from a plot of $[M]/R_p$ versus $1/[M]$ of the rate mechanism. This observation appears to be a general phenomenon for all inhibiting substrates. A reaction mechanism has been suggested and a suitable rate law has been proposed.

## INTRODUCTION

Very few workers have studied the retardation kinetics of polymerization of vinyl monomers. Rout et al. [1] have reported the retardation of the Ce(IV)-initiated polymerization of acrylonitrile by chalcone.

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Pospisil et al. [2] have reported the stabilization of paraffin wax at 163°C and an oil solution of carotene at 75°C by methylene bisphenols. Stabilizers and antioxidants have been well recognized for their commercial importance. Waters et al. [3] have reported the inhibiting action of monohydric phenols on the autoxidation of olefinic oils. The retardation or inhibition of polymerization is very much related to the above investigations. Bird and Russell [4], and Tüdős, Pospisil, and Foldes-Berezhnykh [5, 6] have contributed significantly to this field of inhibited or retarded polymerization kinetics. In this communication we present a kinetic study of the retardation of the permanganate-initiated polymerization of acrylonitrile by phenol in acid medium.

## EXPERIMENTAL

Acrylonitrile (American Cyanamid) was washed with 5% sodium hydroxide and 3% orthophosphoric acid followed by repeated washing with conductivity water in order to remove the hydroquinone (2%) inhibitor from the monomer. Then the monomer was dried over anhydrous calcium chloride. Such reagents as potassium permanganate, phenol, and sulfuric acid were either BDH AnalaR or E. Merck GR grade. Conductivity water was prepared by redistilling distilled water over alkaline permanganate in an all-glass Pyrex unit, and was used for the preparation of reagents and solutions. The polymerization was studied under atmospheric conditions.

The required amounts of monomer, sulfuric acid, and the solution of phenol in water were placed in the reaction vessel (Pyrex tube fitted with a $B_{24\text{-}29}$ socket carrying a $B_{24\text{-}29}$ cone with inlet and outlet tube) and thermostatted at the desired temperature. An appropriate amount of permanganate solution (freshly prepared in 1 $\underline{M}$ $H_2SO_4$) was then added and the polymerization was arrested after a specified time interval by the addition of a known excess of ferrous ammonium sulfate solution. The polymer was filtered off, washed well with conductivity water, and dried to constant weight. The rate of polymerization was calculated from the slope of a plot of time vs yield.

## DISCUSSION

### Relation between Percentage Conversion and Time

The time conversion was studied at different retarder (phenol) concentrations (Fig. 1). It was found that the percentage of conversion increases with time, and a limiting conversion is attained within 30 min. The percentage conversion was found to decrease with an increase of phenol concentration. This is attributed to the retarding

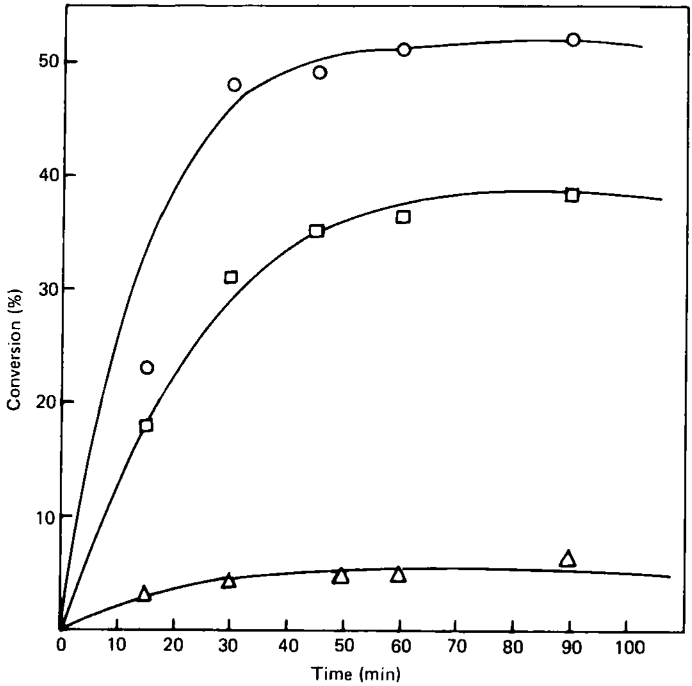


FIG. 1. Time-conversion plot. $[H_2SO_4]$ = 0.5 mol/L, [M] = 0.7513 mol/L, $[KMnO_4]$ = 0.005 mol/L. (○) [Phenol] = Nil, (□) [phenol] = 0.00025 mol/L, (△) [phenol] = 0.001 mol/L.

action of phenol on the rate of polymerization. Beyond 0.001 mol/L of phenol, the polymerization is practically inhibited.

## Reaction Mechanism and Kinetic Scheme

Permanganate can alone initiate the polymerization of acrylonitrile in aqueous sulfuric acid medium. Since phenol inhibits the polymerization of acrylonitrile by permanganate, it is proposed that the radical produced from phenol by interaction with permanganate may not be taking part in the initiation but is involved in the termination step (primary radical termination). The IR spectrum of the polymer (polyacrylonitrile obtained using phenol as the substrate) does not show the presence of a phenolic –OH group absorption between 3650-3590 $cm^{-1}$, but shows an aryl etherial absorption at 1100-1200 $cm^{-1}$, indicating the absence of the phenolic –OH group in the radical. The common feature in both the uninhibited and inhibited polymerization is the formation of the Mn(III) species from permanganate via Mn(IV) (as $MnO_2$). This Mn(III) initiates polymerization.

## Uninhibited Polymerization

Initiation:

$$\mathrm{Mn(III)} + \mathrm{M} \xrightarrow{k_i} \mathrm{M}^\bullet + \mathrm{Mn(II)} + \mathrm{H}^+ \qquad (1)$$

Propagation:

$$\mathrm{M}^\bullet + \mathrm{M} \xrightarrow{k_p} \mathrm{M}_2^\bullet \qquad (2)$$

$$\mathrm{M}^\bullet_{n-1} + \mathrm{M} \xrightarrow{k_p} \mathrm{M}_n^\bullet \qquad (3)$$

Termination:

$$\text{Linear: } \mathrm{M}_n^\bullet + \mathrm{Mn(III)} \xrightarrow{k_t} \text{polymer} \qquad (4)$$

$$\text{Mutual: } \mathrm{M}_n^\bullet + \mathrm{M}_n^\bullet \xrightarrow{k_t} \text{polymer} \qquad (5)$$

## Inhibited Polymerization

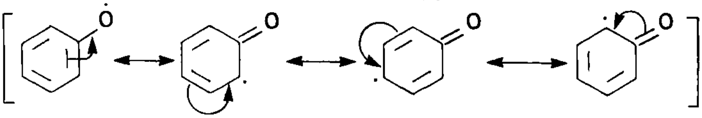
In the presence of phenol (AH) as inhibitor:

Initiation:

$$\mathrm{AH} + \mathrm{Mn(III)} \overset{K}{\rightleftharpoons} \text{complex} \xrightarrow{k} \mathrm{A}^\bullet + \mathrm{Mn(II)} + \mathrm{H}^+ \qquad (6)$$

where $A^\bullet$ is the resonance stabilized radical.

$A^\bullet =$



(7)

Termination:

$$\mathrm{A}^\bullet + \mathrm{M}_n^\bullet \xrightarrow{k_t} \mathrm{MnA} \qquad (8)$$

$$\mathrm{AH} + \mathrm{M}_n^\bullet \xrightarrow{k_t} \mathrm{M_nH} + \mathrm{A}^\bullet \qquad (9)$$

Oxidation:

$$A^{\cdot} + \mathrm{Mn(III)} \xrightarrow{k_o} \text{oxidation product} \tag{10}$$

At higher concentrations of the inhibitor, Reactions (4) and (5) are neglected.

By applying steady-state kinetics, the following expression for the rate of polymerization has been derived:

$$R_p = \frac{k_p k_o k_i [M]^2 [\mathrm{KMnO_4}]}{Kk k_t[\mathrm{AH}] - k_i k_t [M]} \tag{11}$$

The termination step is assumed to be exclusively by the radical formed by the interaction of Mn(III) with phenol. The proposed rate expression satisfactorily explains all the kinetic results obtained.

## Effect of Monomer on Rate

The rate of polymerization increases with an increase of monomer concentration (0.45 to 1.05 mol/L). Excellent linear plots were obtained when $R_p$ was plotted against $[M]^2$ at three different temperatures (Fig. 2), which indicates a second-order dependence with respect to [M]. By rearranging Eq. (11) we have

$$\frac{[M]}{R_p} = \frac{Kk k_t[\mathrm{AH}]}{k_p k_o k_i [M][\mathrm{KMnO_4}]} - \frac{k_t}{k_p k_o [\mathrm{KMnO_4}]} \tag{12}$$

By plotting $[M]/R_p$ versus $1/[M]$ (Fig. 3), the composite rate constants were calculated and a negative intercept was observed which was highly remarkable. This is quite in agreement with the generalization made by Rout et al. [1] that all inhibiting substrates give a negative intercept in a plot of $[M]/R_p$ versus $1/[M]$.

## Effect of Permanganate on Rate

The rate of polymerization increases with an increase of the concentration of permanganate up to a certain value ($6.25 \times 10^{-3}$ mol/L). Beyond this, the rate decreases steadily (Fig. 4). The maxima in the curves obviously reflect a sudden change in the reaction mechanism

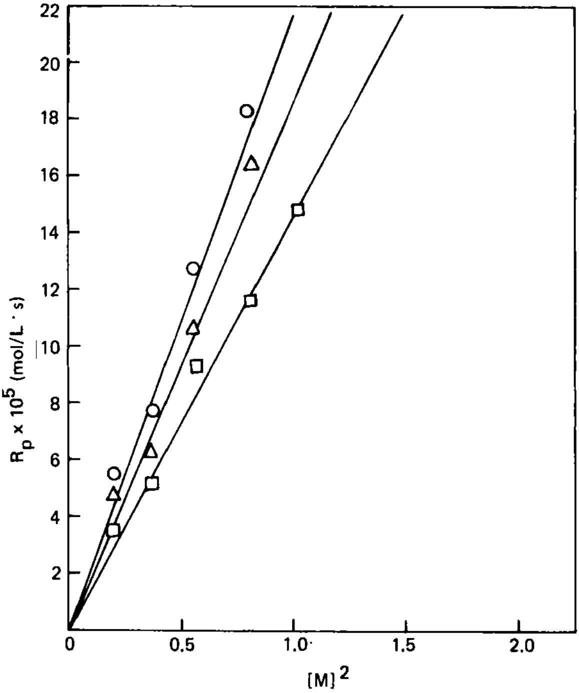


FIG. 2. Plot of $R_p$ vs $[M]^2$. $[H_2SO_4] = 0.5$ mol/L, $[KMnO_4] = 0.005$ mol/L, [phenol] = 0.00025 mol/L. (○) = 35°C, (△) = 40°C, (□) = 45°C.

beyond a particular limit, and this can be attributed to the predominance of primary radical termination over mutual termination.

## Effect of Phenol on Rate

The rate of polymerization $R_p$ decreases with an increasing concentration of phenol (Fig. 5). Similar observations have been reported by Simonye et al. [6] and Bird et al. [4] in their studies of the effect of phenols on the polymerization of vinyl acetates. The retarding action of phenol can be accounted for in a manner similar to that proposed by Barlett et al. [7] for the polymerization of allyl acetates. The propagating polymer chain undergoes termination by the resonance stabilized free radical produced from phenol by interaction with Mn(III). The formation of a Mn(III)-phenol complex was distinctly observed at a

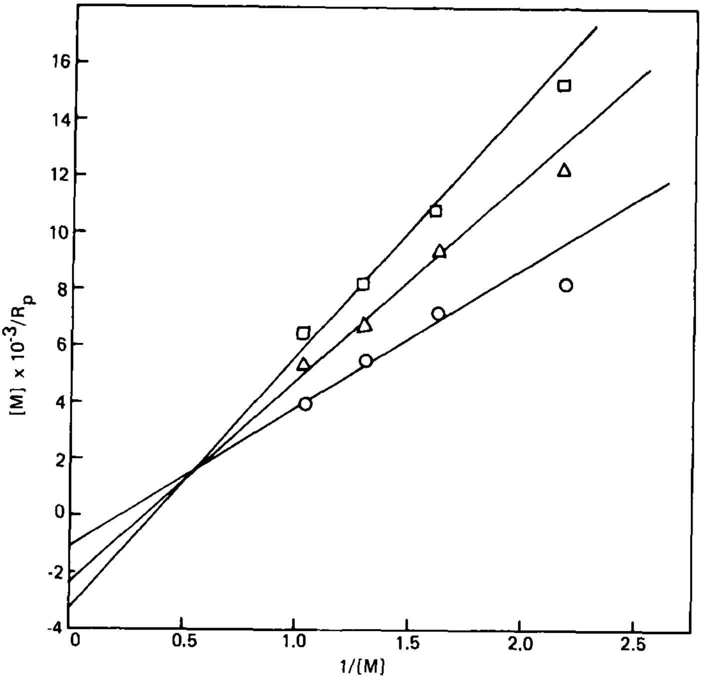


FIG. 3. $[M]/R_p$ vs $1/[M]$ plot. $[H_2SO_4]$ = 0.5 mol/L, $[KMnO_4]$ = 0.005 mol/L, [phenol] = 0.00025 mol/L. (○) = 35°C, (△) = 40°C, (□) = 45°C.

higher concentration of phenol ($7.5 \times 10^{-4}$ mol/L) from the red coloration of the reaction mixture.

## Effect of Sulfuric Acid

The rate of polymerization increases with an increase of acid concentration up to a certain value (0.3 mol/L) and thereafter decreases slowly.

## Effect of Organic Solvents

The polymerization experiments were carried out in aqueous sulfuric acid medium. The effects of some organic solvents when added

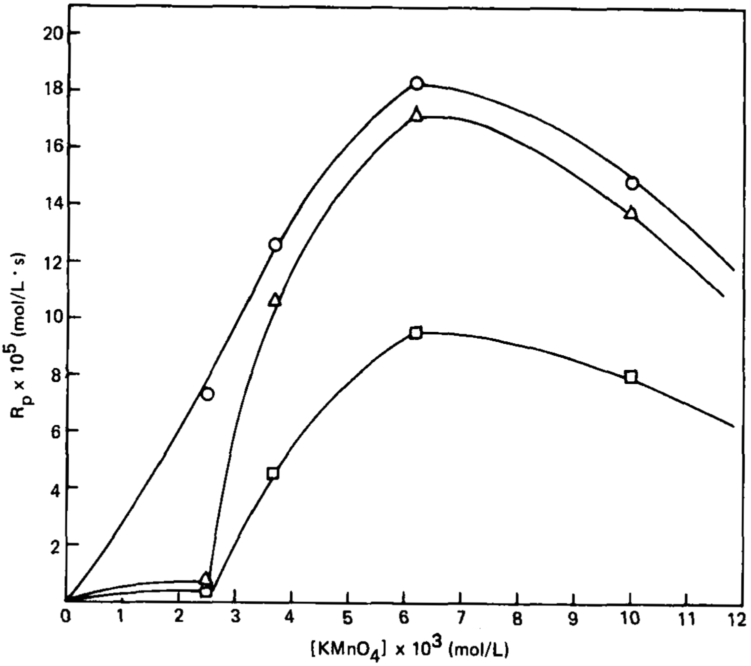


FIG. 4. $R_p$ vs $[KMnO_4]$ plot. $[H_2SO_4]$ = 0.4 mol/L, [M] = 0.7513 mol/L, [phenol] = 0.00025 mol/L. (○) 30°C, (△) = 35°C, (□) = 40°C.

in equal proportions (5% v/v) have been studied and the rate of polymerization was found to increase in the following order: DMF > MeOH > EtOH > control > dioxane.

## Effect of Salts

The effect of some salts such as $MnSO_4$, $K_2SO_4$, NaCl, and $CuSO_4$ on polymerization was studied. All the salts except $CuSO_4$ enhance the rate of polymerization considerably. This behavior is contrary to that observed in the polymerization of acrylonitrile by the permanganate-glucose redox system [10]. This seems to be a general feature of all retarding substrates. This may be attributed to the ionic dissociation of the added electrolyte which decreases the primary

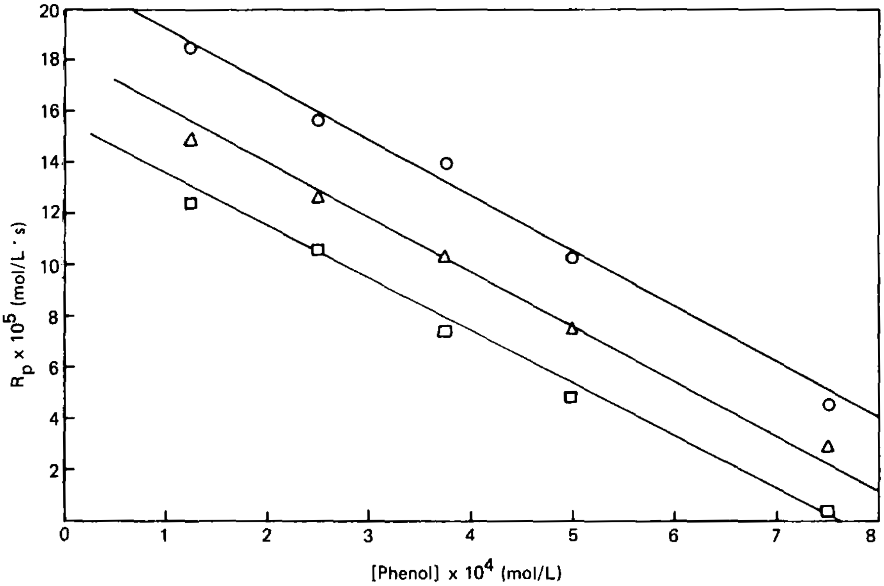


FIG. 5. $R_p$ vs [phenol] plot. [$H_2SO_4$] = 0.5 mol/L, [M] = 0.7513 mol/L, [$KMnO_4$] = 0.005 mol/L. (○) = 30°C, (△) = 35°C, (□) = 40°C.

radical termination to a considerable extent, thereby increasing the rate of polymerization.

## Effect of Temperature

The polymerization was studied in the temperature range of 30 to 40°C. A very interesting observation was noticed of the effect of temperature on $R_p$. The rate of polymerization decreases as the temperature increases from 30 to 45°C. Similar observations have also been reported in certain redox systems [10]. The overall energy of activation as calculated from Arrhenius plot (Fig. 6) was found to be -18.18 kcal/mol.

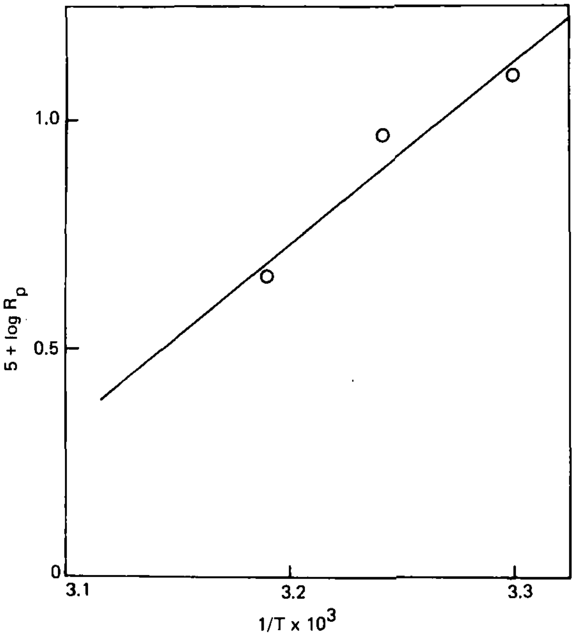


FIG. 6. Arrhenius plot.

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