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Rajani K. Samal[a]; Prafulla K. Sahoo[a]; Sakti P. Bhattacharjee[a]; Himanwj S. Samantaray[a]
[a] Macromolecular Research Laboratory Department of Chemistry, Ravenshaw College, Cuttack, Orissa, India

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Kinetics of Inhibition and Retardation of Methyl Methacrylate Polymerization by Phenols

RAJANI K. SAMAL,* PRAFULLA K. SAHOO,
SAKTI P. BHATTACHARJEE, and HIMANWJ S. SAMANTARAY

Macromolecular Research Laboratory
Department of Chemistry
Ravenshaw College
Cuttack 753003, Orissa, India

ABSTRACT

A systematic investigation has been conducted of the effect of various phenols (mono- and bicyclic) on the potassium monopersulfate-initiated polymerization of methyl methacrylate catalyzed by $Na_2S_2O_3$ in aqueous medium at 45°C. It is found that all the phenols, irrespective of their low or high transfer constants, behave as weak retarders within a certain concentration range (0.0005-0.0025 M), above which they behave both as inhibitors and retarders. The rate of this process is dependent upon the substituents in the phenols and often on their positions. For comparison, the reaction has also been studied in the absence of phenols, and the effect of monomer, initiator, and temperature on the rate has been noted. The mechanism of inhibition and retardation has been proposed and various rate parameters have been evaluated.

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*To whom correspondence should be addressed.

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INTRODUCTION

In common with more familiar chain reactions, addition polyreactions are susceptible to catalysis and inhibition. The existence of an induction period was noted in many of the early investigations of vinyl polymerization [1]. The length of this induction period was somewhat ill defined, and it was suggested by researchers [2] that it is produced by impurities in the monomer. Extensive investigation in this field was carried out by Foord [3] during his study of the inhibition effect of organic compounds on the free-radical polymerization of styrene. From some 130 organic compounds tested as inhibitors, he found that quinones were the most effective. Since, then, a number of workers [4-15] have studies the kinetics of vinyl polymerization in the presence of a multitude of quinones to elucidate the mechanism of inhibition and retardation of polymerization. Caldwell et al. [7] reported the mechanism of the reaction between hydroquinone and poly(methyl methacrylate) free radicals by kinetic methods. Russell et al. [16], Breitenbach [17], and Edwards et al. [18] studied the effect of phenols on the AIBN-initiated polymerization of styrene. Kice [19] studied the inhibition effect of hydroquinone and other compounds on AIBN-initiated polymerization of methyl methacrylate and suggested inhibition or retardation mechanisms.

Review of the literature reveals that little attention has been paid to the kinetic investigation of the effect of phenols on vinyl polymerization involving an acidic peroxo oxidizer as initiator. Since phenols are susceptible to oxidation in a reaction medium containing an oxidizing agent, they might exhibit interesting effect on radical polymerization of vinyl monomers. We have, therefore, been led to study the effect of various phenols on radical polymerization, using a new class of acidic peroxo salt, $KHSO_5$ (a powerful oxidizer), as initiator. In previous work [20] we determined the effect of phenols on the acidified permanganate/thioglycerol-initiated polymerization of methyl acrylate. We now report the inhibition and retardation effects of various phenols on the potassium monopersulfate-initiated polymerization of methyl methacrylate, in the presence of $Na_2S_2O_3$ as the catalyst. The mechanisms of inhibition and retardation are suggested and various rate parameters are evaluated.

EXPERIMENTAL

Potassium monopersulfate was a gift sample and was used without further purification. A stock solution (0.013 M) of the initiator was used throughout the investigation. The strength of the stock solution was reexamined from time to time by estimation of the active oxygen in the solution.

Methyl methacrylate was purified by washing with 5% sodium hydroxide, followed by triple distilled water, and finally dried over anhydrous calcium chloride. Salts used as catalyst were of BDH quality. Phenols used were commercial products and were used after purification by standard methods.

The polymerization reactions were carried out as reported earlier [20]. After the desired time, the reactions were arrested and then kept in a freezing mixture to eliminate the possibility of further reaction. The precipitated polymers were filtered out and dried to constant weight at 70°C. The conversion percentage and rate of polymerization were calculated from the weights.

The molecular weights ($\overline{M}_v$) of the purified polymers were determined viscometrically by the appropriate Mark-Houwink relationship. The viscosities of the polymer solutions (1%) were determined in an Ubbelohde-type suspended-level dilution viscometer in acetone at 30°C, using the relationship [21]

$$[\eta] = 7.7 \times 10^{-3}\ \overline{M}_v^{\ 0.7}.$$

RESULTS AND DISCUSSION

Results of Preinhibition-Retardation Studies

In the present investigation, it was found that, under our experimental conditions, $KHSO_5$ alone initiates the polymerization of methyl methacrylate with moderate efficiency, and the net reaction leads to a low conversion after an appreciable induction period. In order to study the effect of phenols on the polymerization process, it was thought worth while to find conditions where the polymerization would be initiated instantaneously without any induction period. We found that with all other conditions constant, addition of a trace of inorganic salts enhanced the conversion of the monomer to polymer considerably and decreased the induction period. Salts like $AgNO_3$ and $Na_2S_2O_3$, and to some extent $CoSO_4$ and $MnSO_4$, gave no or negligible induction periods.

The polymerization rates (R_p) for various salts along with the respective induction period are noted in Table 1. From the results, it was clear that the $KHSO_5/Na_2S_2O_3$, $KHSO_5/AgNO_3$, and to some extent the $KHSO_5/CoSO_4$ and $KHSO_5/MnSO_4$, couples are suitable for the study of the effect of phenols on the polymerization of methyl methacrylate.

Further, in order to find the maximum conversion condition, the

TABLE 1. Polymerization of Methyl Methacrylate by Potassium Monopersulfate, Coupled with Various Inorganic Salts. $[KHSO_5] = 0.013$ M, $[H^+] = 3.4 \times 10^{-3}$ M, [Salt] = 0.02 M, [MMA] = 0.09388 M, 50°C

Salt	Induction period, min	10^6 R_p mol/(L·s)
Control	61	0.03
$Na_2S_2O_3$	Nil	10.01
$NiSO_4$	8	9.86
$FeSO_4$	13	7.74
$AgNO_3$	Nil	6.44
$Cu(NO_3)_2$	40	6.13
$CoSO_4$	1	4.84
$CuSO_4$	55	3.93
$CdSO_4$	43	3.92
$ZnSO_4$	45	3.83
$MnSO_4$	2	3.49
$MgSO_4$	50	3.34
$FeCl_3$	35	2.72
KCl	45	1.89
Na_2SO_3	50	0.54

polymerization was carried out at various concentrations of the initiator, $Na_2S_2O_3$, and at various temperatures, and from the results the most versatile condition was chosen to study the effect of phenols.

Effect of Initiator Concentration

The initial rate of polymerization and the maximum conversion were found to increase with an increase in the concentration of $KHSO_5$

(0.0025-0.01 M) while the concentrations of the other reagents and the temperature were kept constant ($[Na_2S_2O_3]$ = 0.01 M, [MMA] = 0.09388 M, 45°C). Beyond 0.01 M initiator concentrations, the rate decreases. This might be due to exhaustive oxidation of $Na_2S_2O_3$, which interferes with the initiation process.

Effect of $Na_2S_2O_3$ Concentration

Methyl methacrylate was polymerized by the $KHSO_5/Na_2S_2O_3$ couple at various concentrations of $Na_2S_2O_3$ (0.005-0.03 M) and at fixed concentrations of other reagents and constant temperature ($[KHSO_5]$ = 0.013 M, [MMA] = 0.09388 M; 45°C). It was found that the initial rate of polymerization and the maximum conversion increase with increasing $[Na_2S_2O_3]$ (0.005-0.01 M) and then decrease even though a small induction period is noticed at 0.02 M. The existence of this small induction period may be due to lowering the temperature to 45°C (as compared to the results in Table 1). Interestingly, at still higher concentrations of $Na_2S_2O_3$, (above 0.02 M), the induction periods were considerable, with simultaneous retardation of the rate. The plausible explanation of this behavior is that raising the concentration of $Na_2S_2O_3$ decreases the concentration of the initiating radical at the initiation site due to major consumption of $KHSO_5$ through an oxidation process. The high oxidation potential of $KHSO_5$ (-1.44 V) and greater reducing ability of $Na_2S_2O_3$ might lead to a facile oxidation-reduction reaction to form $Na_2S_4O_6$. The oxidation of $Na_2S_2O_3$ to $Na_2S_4O_6$, even by weak oxidizers like $FeCl_3$ and I_2, is well known [22].

Rate of Polymerization ($R_p{}^0$)

The rate of polymerization ($R_p{}^0$) increased regularly on increasing the concentration of the monomer (0.04694-0.3285 M). R_p also increased with increased temperature from 35 to 45°C, above which the increase was not significant. Plots of R_p versus [MMA] are linear, passing through the origin and plots of log R_p versus log [MMA] are linear with an intercept on the rate axis (Fig. 1) and a slope of unity. This indicates a first-order dependence of the rate on monomer concentration.

Further, R_p increased on raising the concentration of the initiator

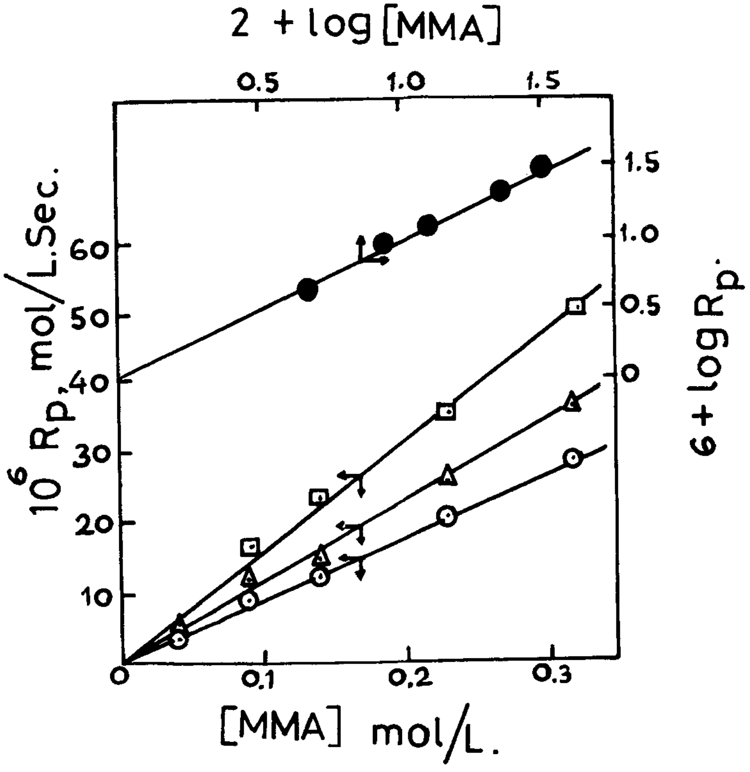

FIG. 1. Variation of rate of polymerization (R_p) with monomer at various temperatures: $[Na_2S_2O_3] = 0.01$ M, $[KHSO_5] = 0.013$ M. Temperatures for R_p vs [MMA]: (⊙) 35°C, (▲) 40°C, (▣) 45°C. Temperature for ($6 + \log R_p$) vs ($2 + \log$ [MMA]): (●) 35°C.

($KHSO_5$) to 0.013 M. Plots of R_p versus $[KHSO_5]^{1/2}$ were linear, passing through the origin, and plots of log R_p versus log $[KHSO_5]$ were linear with an intercept on the rate axis (Fig. 2) and a slope of 0.5. These plots show the order with respect to the initiator to be one half.

Results of Retardation and Inhibition Studies

The polymerization reaction was carried out at 45°C in the presence of a number of phenols and naphthols, like phenol, hydroquinone, resorcinol, o-cresol, m-cresol, p-cresol, o-nitrophenol, p-nitro-

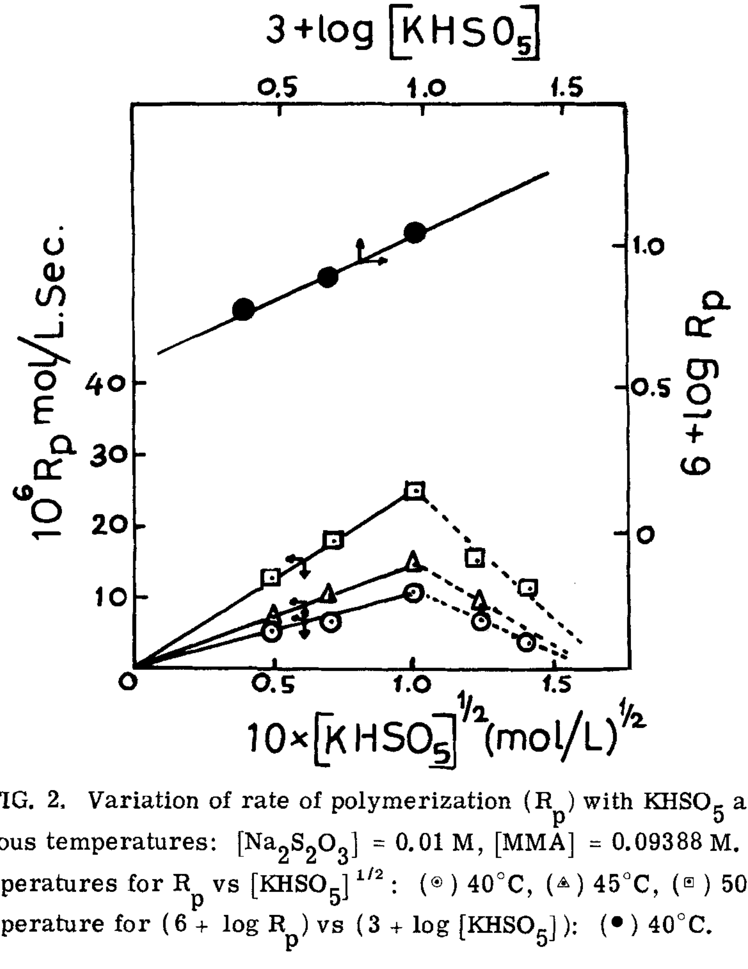

FIG. 2. Variation of rate of polymerization (R_p) with $KHSO_5$ at various temperatures: $[Na_2S_2O_3] = 0.01$ M, [MMA] = 0.09388 M. Temperatures for R_p vs $[KHSO_5]^{1/2}$: (⊙) 40°C, (▲) 45°C, (▣) 50°C. Temperature for ($6 + \log R_p$) vs ($3 + \log [KHSO_5]$): (●) 40°C.

phenol, α-naphthol, and β-naphthol at various concentrations. The results show that, with all the additives at 0.001 M, the initial rate of polymerization and the maximum conversion are more or less retarded. Further, when the concentration of the phenolics was raised beyond 0.0025 M, all of them exhibited a definite inhibition period, accompanied by further retardation of the rate. The phenomena of inhibition and retardation become significant as the phenol concentration increases further. It is surprising that with o- and p-nitrophenol, the polymerization is completely inhibited at 0.005 M, and no polymer was detected even after 2 h. A summary of the experimental results obtained is given in Table 2, which also includes the relative rate of polymerization (Φ), a quantity defined by Kice [19] as $\Phi = R_p/R_p{}^0$,

TABLE 2. Polymerization of Methyl Methacrylate in the Presence of Various Phenols and Naphthols. $[KHSO_5] = 0.013$ M, $[Na_2S_2O_3] = 0.01$ M, [MMA] = 0.09388 M, 45°C, $R_p{}^0 = 17.36 \times 10^{-6}$ mol/(L·s)

Retarder	[Retarder], mol/L	$10^6 R_p$, mol/(L·s)	Φ
Phenol	0.001	10.27	0.592
	0.0025	5.92	0.341
	0.005	5.42	0.312
	0.01	4.31	0.248
	0.02	4.47	0.200
Hydroquinone	0.001	12.49	0.719
	0.0025	8.33	0.479
	0.005	6.25	0.360
	0.01	4.86	0.280
	0.02	2.91	0.167
Resorcinol	0.001	13.19	0.760
	0.0025	8.61	0.496
	0.005	6.39	0.368
	0.01	4.44	0.256
	0.02	3.19	0.184
o-Cresol	0.001	12.36	0.712
	0.0025	11.13	0.641
	0.005	9.72	0.560
	0.01	7.22	0.416
	0.02	6.25	0.360
m-Cresol	0.001	11.80	0.679
	0.0025	11.24	0.645
	0.005	10.13	0.583
	0.01	7.08	0.408
	0.02	6.60	0.380

(continued)

TABLE 2 (continued)

Retarder	[Retarder], mol/L	$10^6 R_p$, mol/(L·s)	Φ
p-Cresol	0.001	11.80	0.679
	0.0025	11.10	0.639
	0.005	10.41	0.599
	0.01	8.05	0.494
	0.02	6.60	0.380
o-Nitrophenol	0.001	9.72	0.560
	0.002	9.01	0.519
	0.0025	8.611	0.496
	0.005	-	-
	0.01	-	-
	0.02	-	-
p-Nitrophenol	0.001	9.86	0.568
	0.002	9.39	0.541
	0.0025	9.03	0.519
	0.005	-	-
	0.01	-	-
	0.02	-	-
α-Naphthol	0.001	13.14	0.756
	0.0025	10.42	0.600
	0.005	9.83	0.566
	0.01	3.05	0.176
	0.02	2.08	0.119
β-Naphthol	0.001	13.19	0.760
	0.0025	11.10	0.639
	0.005	7.50	0.432
	0.01	3.75	0.216
	0.02	2.50	0.144

where R_p and $R_p^{\,0}$ denote the rates of retarded and unretarded polymerization, respectively.

Reaction Mechanism and Kinetic Expressions

It is generally accepted that any chemical moiety which arrests or retards the polymerization of vinyl monomers does so by reaction with either initiator or polymer free radicals to yield a new free radical. The newly generated free radical, being relatively unreactive toward monomer, is chiefly consumed by reaction with other free radicals, resulting in chain termination. Apart from this, there exists the possibility that a fraction of the newly generated radical is instead consumed by reaction with monomer as in true copolymerization or chain transfer.

Considering the cited possibilities, the following reaction mechanism is suggested which is similar to those reported by other workers [7, 19].

1. Initiation: Rate

$$HSO_5^- \xrightarrow[\text{catalyst}]{k_d} SO_4^{-\bullet} + OH^-$$

$$2k_d f\,[HSO_5^-]$$

$$HSO_5^- \xrightarrow[\text{catalyst}]{k_d} OH^\bullet + SO_4^{2-}$$

($R^\bullet = SO_4^{-\bullet}$ and $OH^\bullet$)

2. Propagation:

$$R^\bullet + M \xrightarrow{k_p} R^\bullet \qquad k_p[R^\bullet][M]$$

(where $R^\bullet$ = growing polymer radical)

3. Trapping:

$$R^\bullet + I \xrightarrow{k_r} x^\bullet \qquad k_r[R^\bullet][I]$$

4. Copolymerization:

$$X^\bullet + M \xrightarrow{k_o} R^\bullet \qquad K_o[X^\bullet][M]$$

5. Termination:

(a) $X^\cdot + R^\cdot \xrightarrow[2k]{k_{t_1}}$ dead product $\qquad k_{t_1}[X^\cdot][R^\cdot]$

(b) $X^\cdot + X^\cdot \xrightarrow{k_{t_2}}$ dead product $\qquad 2k_{t_2}[X^\cdot]^2$

(c) $R^\cdot + R^\cdot \xrightarrow{2k_{t_3}}$ dead product $\qquad 2k_{t_3}[R^\cdot]^2$

In this scheme, $R^\cdot$ is a chain-carrying radical, I is the added inhibitor or retarder, and $X^\cdot$ is the newly generated radical formed by the interaction of $R^\cdot$ with r. $X^\cdot$ may be generated either by the trapping of $R^\cdot$ by I or by transfer of an atom or group to $R^\cdot$ from I.

Applying the usual steady-state principle to the primary initiating radical, as well as to the growing polymer radicals, and taking radical reactivity as independent of radical size, we obtain

6. $$d[R^\cdot]/dt = 2k_d f[HSO_5^-] + k_o[X^\cdot][M] - k_r[R^\cdot][I] - 2k_{t_3}[R^\cdot]^2 - k_{t_1}[R^\cdot][X^\cdot] = 0$$

7. $$d[X^\cdot]/dt = k_r[R^\cdot][I] - k_o[X^\cdot][M] - k_{t_1}[R^\cdot][X^\cdot] - 2k_{t_2}[X^\cdot] = 0$$

Further, the rate of inhibited or retarded polymerization is given by

8. $$R_p = \frac{-d \ln [M]}{dt} = k_p[R^\cdot]$$

which gives $R_p/k_p = [R^\cdot]$.

Similarly, the rate of uninhibited reaction will be given by

9. $$R_p^{\,0} = \left(\frac{-d \ln [M]}{dt}\right)_{\text{uninhibited}} = k_p[R_o^\cdot]$$

where $[R_o^\cdot]$ is the concentration of the radicals in the absence of the inhibitor or retarder. Equation (9) gives $R_p^{\,0}/k_p = [R_o^\cdot]$.

With the help of these equations and by considering the various fraction of the inhibitor or retarder consumed in different steps, we obtain the following kinetic expression:

$$10.\quad \frac{\Phi 2[I]}{(1-\Phi^2)}\left[1+\sqrt{1+\frac{C(1-\Phi^2)}{\Phi^2}}\right]=\frac{2k_{t_3}R_p}{k_pk_r}\sqrt{1+\frac{C(1-\Phi^2)}{\Phi^2}}+\left(\frac{k_o}{k_{t_1}}\,\frac{2k_{t_3}[M]}{k_r}\right)$$

where Φ = relative rate of polymerization and $C = 4k_{t_3}k_{t_2}/k_{t_1}^{\,2}$.

Equation (10) requires that plots of

$$\frac{\Phi^2[I]}{1-\Phi^2}\left[1+\sqrt{1+\frac{C(1-\Phi^2)}{\Phi^2}}\right]\ \text{vs}\ R_p\sqrt{1+\frac{C(1-\Phi^2)}{\Phi^2}}$$

at various concentration for a given inhibitor or retarder should be linear with the slope and intercept equal to $2k_{t_3}/k_pk_r$ and $2k_ok_{t_3}[M]/k_rk_{t_1}$, respectively. Knowledge of the value of $2k_{t_3}/k_p$ and $2k_{t_3}$ from the literature at the experimental temperature will help in the evaluation of the kinetic parameters k_r and k_o/k_{t_1}. Values of these parameters determine which paths of the reaction scheme are predominant.

Evaluation of k_r, k_o/k_{t_1} and Interpretations

Equation (10) was found to hold for the data of the present investigation, and straight-line plots were obtained in almost all cases (Figs. 3-7) for $C = 10^{-4}$. Values of k_r and k_o/k_{t_1} have been calculated from the slopes and intercept of these plots, using the values of $2k_{t_3}/k_p$, k_p, and $2k_{t_3}$ calculated for the present experimental temperature, from the work of Matheson et al. [23] and Bevington et al. [24]. The resulting rate parameters are shown in Table 3.

Further, the plots indicate that, with the phenols and naphthols, no wastage of X˙ through Reaction (4) seems to have taken place, i.e., no reinitiation or copolymerization is favored. From the first column of Table 3 it is evident that all the phenols and naphthols are, indeed, extremely reactive toward free radicals. The difference in reactivity

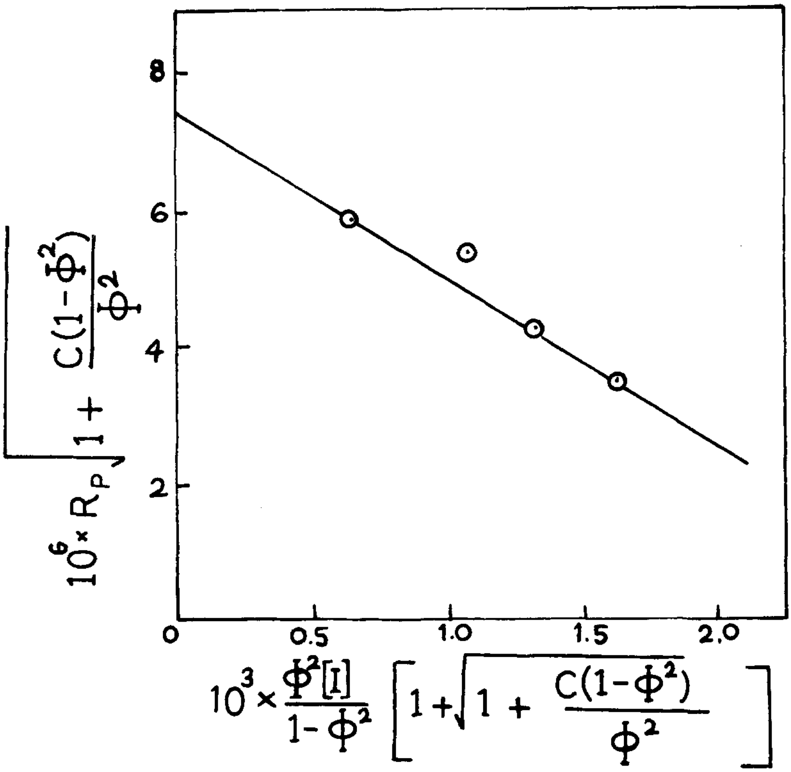

FIG. 3. Plot of $\frac{\Phi^2[I]}{1-\Phi^2}\left[1+\sqrt{1+\frac{C(1-\Phi^2)}{\Phi^2}}\right]$ vs $R\sqrt{1+\frac{C(1-\Phi^2)}{\Phi^2}}$ for $C = 10^{-4}$. (○) = phenol.

between them may be due to the relative position of the phenolic OH group with respect to the other substituents. This indicates that Reaction (3) is significant, and that the growing radicals are being effectively captured by the phenols and naphthols.

The second column of Table 3 includes k_o/k_{t_1}, which is a measure of the stability of the radical X$^\cdot$; the larger the value of k_o/k_{t_1}, the less stable the radical. The k_o/k_{t_1} values obtained in our case indicate that the radical X$^\cdot$ generated by interaction of the radical R$^\cdot$ with the phenols and naphthols (I) is unstable and disappears through Reaction (5a) and, to some extent perhaps, through Reaction (5b).

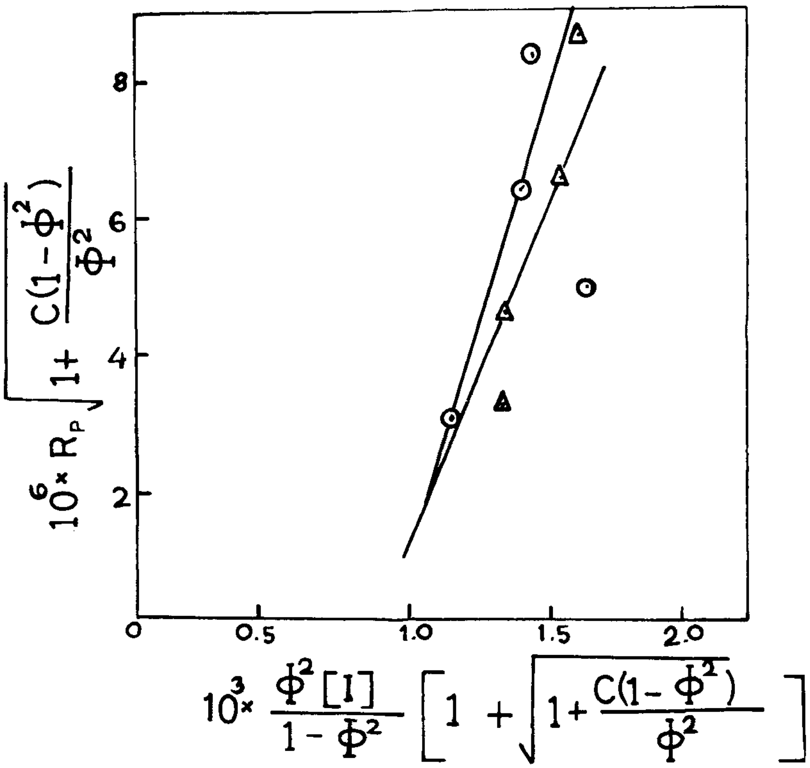

FIG. 4. Same as Fig. 3 but for (⊙) hydroquinone and (△) resorcinol.

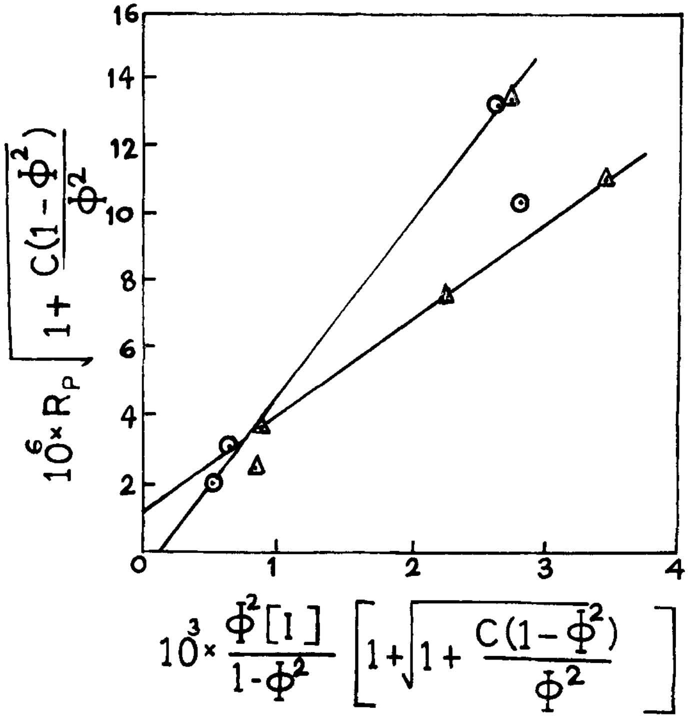

FIG. 5. Same as Fig. 3 but for (⊙) α-naphthol and (△) β-naphthol.

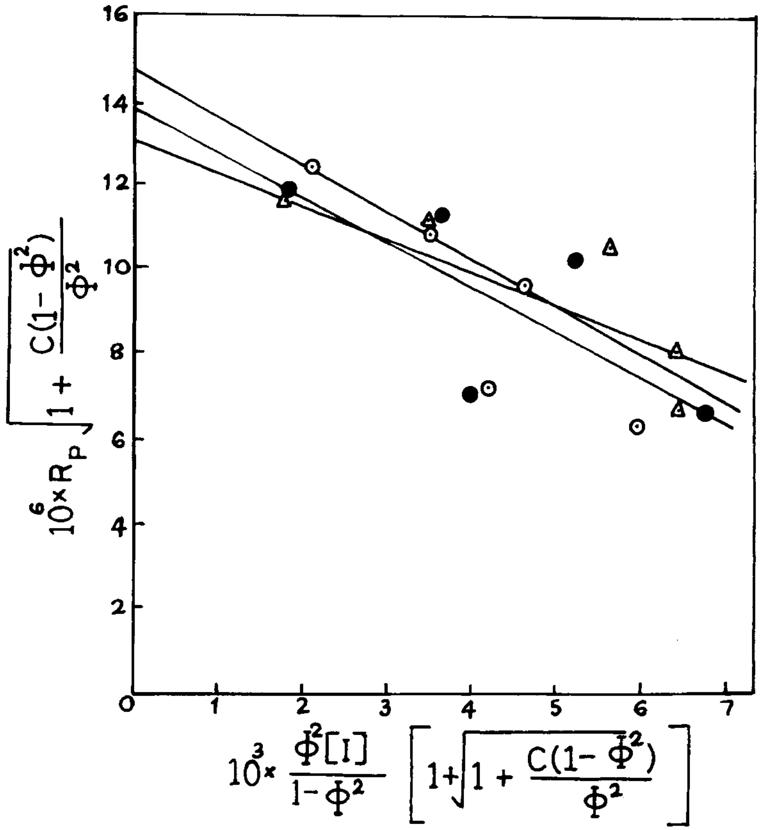

FIG. 6. Same as Fig. 3 but for (⊙) o-cresol, (●) m-cresol, and (△) p-cresol.

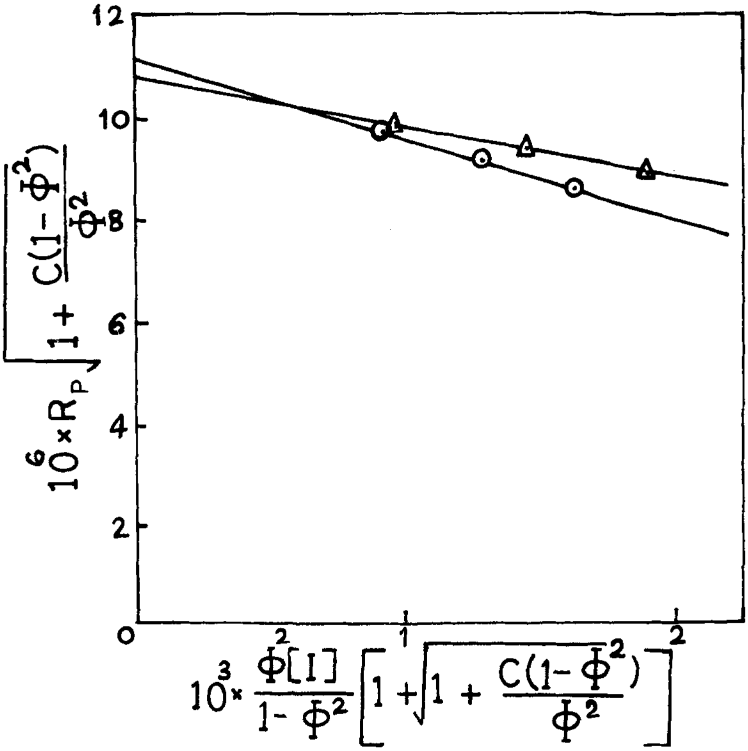

FIG. 7. Same as Fig. 3 but for (⊙) o-nitrophenol and (△) p-nitrophenol.

TABLE 3. Rate Parameters for Inhibitors or Retarders in the Polymerization of Methyl Methacrylate

Compounds	$k_r \times 10^{-7}$, L/(mol·s)	$k_o/k_{t_1} \times 10^6$
Phenol	2.73	140
Hydroquinone	5.4	-
Resorcinol	0.71	-
o-Cresol	5.84	588
m-Cresol	6.48	611
p-Cresol	8.69	776
o-Nitrophenol	4.24	326
p-Nitrophenol	5.78	428
α-Naphthol	1.32	-
β-Naphthol	2.34	19

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