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Kinetics of Polymerization of Methyl Methacrylate Initiated by AIBN in the Presence of Acetophenone

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ABSTRACT

The present investigation aims at estimating the retarding effect of acetophenone in the polymerization of methyl methacrylate initiated by α,α'-azobisisobutyronitrile in the temperature range of 50 to 60°C. The results are interpreted in terms of Tüdős kinetic parameter (β). The effects of varying concentrations of substrate, monomer, initiator, and salts have been investigated. A suitable reaction scheme and rate expression have been suggested on the basis of the experimental findings, and another kinetic parameter (K) to represent the reactivity of acetophenones toward the polymer radical has been obtained graphically.

INTRODUCTION

Kinetic studies of the retarding influence of various organic substrates with different monomers like acrylonitrile and methyl methacrylate were reported earlier [1, 2]. In continuation of this work,

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we report in this article the effect of acetophenone on the rate of polymerization of methyl methacrylate (MMA) initiated by azobisisobutyronitrile (AIBN).

Tüdős [3] has suggested a kinetic parameter β which is proportional to the reactivity of a substrate for the growing polymer radical (i.e., k_3) of

$$\beta = \mu k_3 x^{1/2}/2(R_i k_4)^{1/2} \tag{1}$$

where R_i = rate of initiation
k_4 = mutual termination rate
μ = stoichiometry of the inhibition process

It has also been shown that the numerical value of β can be calculated from

$$\beta = \phi x^{1/2}/[ZH] \tag{2}$$

where $\phi = \frac{1}{2}[(R_{p(rel)})^{-1} - (R_{p(rel)})]$, $R_{p(rel)} = R_p{}^0$

where R_p = rate of polymerization in the presence of acetophenone
$R_p{}^0$ = rate of polymerization in the absence of acetophenone
x = initial concentration of initiator
[ZH] = initial concentration of retardor (acetophenone)

EXPERIMENTAL

Azobisisobutyronitrile, methyl methacrylate, and acetic acid were all BDH Analar or E. Merck (G.R.) products and were purified by standard methods. Acetophenone was distilled twice before use. The experimental procedure followed has been described earlier [1], and all the kinetic results were described in terms of the Tüdős parameter β.

RESULTS AND DISCUSSION

Effect of Substrate Concentration

Azobisisobutyronitrile brings about the polymerization of methyl methacrylate, and the rate has been found to decrease in the presence of acetophenone. The proposed reaction scheme for the given reaction explains the role of acetophenone in the given polymerization process.

It is observed that acetophenone participates in the process of termination by reacting with the growing PMMA radical in the following way:

$$ZH + M_n^{\bullet} \longrightarrow M_n\text{—}H + Z^{\bullet}$$

This process of hydrogen abstraction is considered to be solely responsible for the retarding influence of acetophenone (Table 1, Fig. 1).

Effect of Temperature

With an increase of temperature, the values of β gradually decrease. This is to be expected as there is greater initiation at a higher temperature, resulting in less retardation (Table 1, Fig. 1).

Effect of Initiator Concentration

The value of β has been found to be independent of the AIBN concentration in a particular monomer and substrate concentration (Table 2).

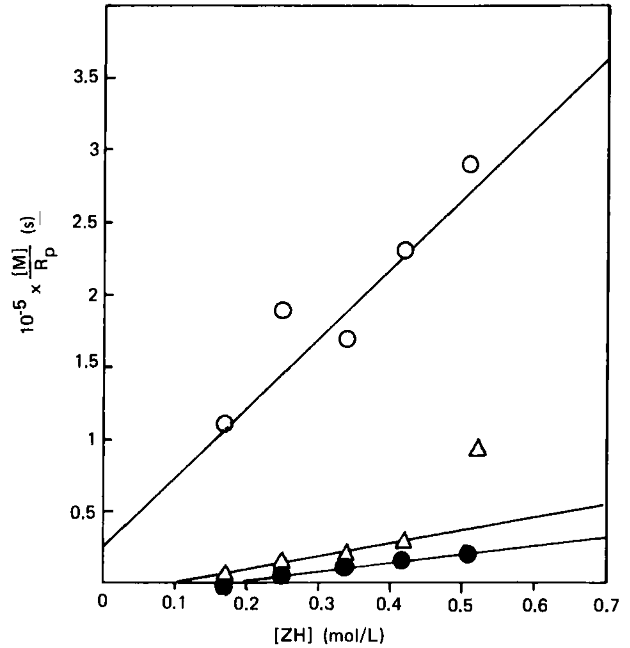

FIG. 1. Effect of substrate concentration: [MMA] = 0.9349 mol/L, [AIBN] = 0.01 mol/L, acetic acid = 35% (v/v), (○) at 50°C, (△) at 55°C, (●) at 60°C.

TABLE 1. Effect of [Acetophenone] on Values of β at Different Temperatures. [MMA] = 0.9349 mol/L, [AIBN] = 0.01 mol/L, Acetic Acid = 35% (v/v)

Temperature (°C)	Initial molar concentration of acetophenone	Rate of polymerization in the presence of acetophenone, $10^5 \times R_p$ mol/L·s	$(R_p)_{rel}$	β values		
				Calculated	Average	Graphical
50	0.1708	0.7068	0.1350	2.1288		
	0.2562	0.5058	0.0966	2.0011		
	0.3416	0.4859	0.0928	1.5635	1.7744	1.5860
	0.4270	0.3838	0.0733	1.5878		
	0.5124	0.3199	0.0611	1.5907		
55	0.1708	2.8348	0.4898	0.4438		
	0.2562	2.2347	0.3861	0.4297		
	0.3416	1.7446	0.3014	0.4414	0.4755	1.33
	0.4270	1.3835	0.2390	0.4618		
	0.5124	0.9164	0.1583	0.6009		
60	0.1708	4.5207	0.5669	0.3501		
	0.2562	3.4994	0.4388	0.3590		
	0.3416	3.0984	0.3885	0.3196	0.3475	1.0011
	0.4270	2.7364	0.3431	0.3009		
	0.5124	1.8089	0.2268	0.4080		

TABLE 2. Effect of [AIBN] on values of β at 55°C. [MMA] = 0.9349 mol/L, [Acetophenone] = 0.4270 mol/L, Acetic Acid = 35% (v/v)

[AIBN] (mol/L)	$10^5 \times R_p$ mol/L·s	$(R_p)_{rel}$	$\beta_{calculated}$
0.005	0.1256	0.1588	0.254
0.01	1.0681	0.1926	0.2926
0.015	1.5781	0.2516	0.2666
0.02	2.1293	0.3036	0.2474
0.025	2.2088	0.2902	0.2920

Similar observations have also been made by Tüdös et al. [3] in connection with the retarding effect of phenol on the polymerization of vinyl acetate and also by Rout et al. [1] in connection with the kinetics of retardation by phenol of the polymerization of acrylonitrile.

Effect of Monomer Concentration

With an increase of monomer concentration, β has been found to decrease (Table 3, Fig. 2). A plot of R_p versus [M] has been found to be linear, thus supporting the validity of our scheme. The decrease in the value of β is perhaps due to a relatively higher increase in the rate of polymerization with increasing monomer concentration.

Effect of Salts

Bamford et al. [4] have studied the effects of salts on some vinyl polymerizations. The addition of such salts as $MnSO_4$, $FeCl_3$, KCl,

TABLE 3. Effect of [MMA] on Values of β at 55°C. [Acetophenone] = 0.4270 mol/L, [AIBN] = 0.01 mol/L, Acetic Acid = 35% (v/v)

[MMA] (mol/L)	$R_p \times 10^5$ mol/L·s	$(R_p)_{rel}$	$\beta_{calculated}$
0.7012	0.9248	0.1515	0.7550
0.7947	1.3164	0.2071	0.5412
0.8882	1.4186	0.2166	0.5152
0.9817	1.596	0.2245	0.4952
1.0752	1.8556	0.2345	0.4718
1.1687	1.7571	0.245	0.4492

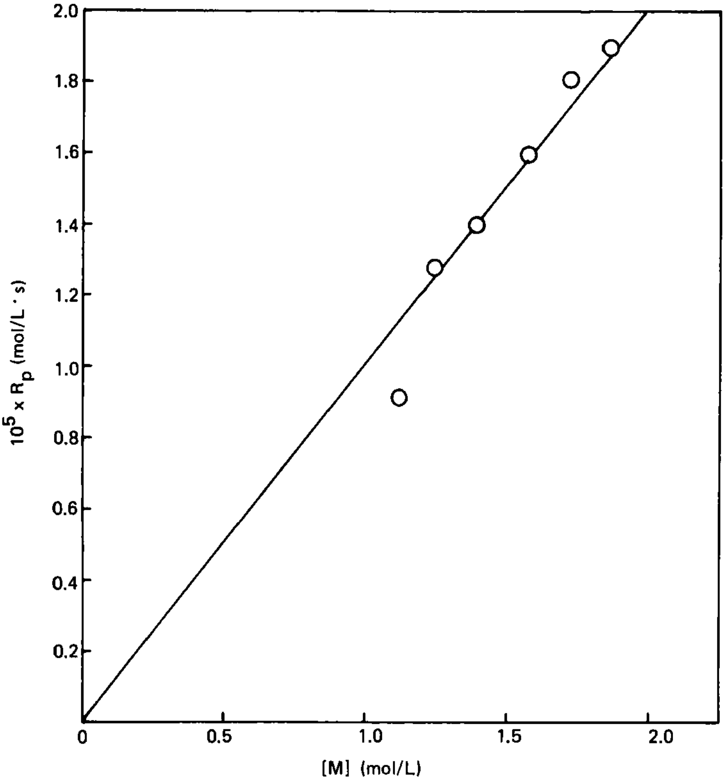

FIG. 2. Effect of monomer concentration: [acetophenone] = 0.427 mol/L, [AIBN] = 0.01 mol/L, acetic acid = 35% (v/v), (○) at 55°C.

and K_2SO_4 facilitates retardation, resulting in an increase in the value of β (Table 4). The increased retardation is perhaps a consequence of stabilization of a polar transition state of the hydrogen abstraction process between the growing PMMA radical and acetophenone. The complexing ability of the salt may be a contributing factor in the retardation process [5].

PROPOSED KINETIC SCHEME AND RATE EXPRESSION

The following reaction scheme has been proposed. Based on it, a kinetic expression has been derived making the usual assumptions of steady-state concentration of the radicals.

TABLE 4. Effect of Salts on Values of β at 55°C. [Acetophenone] = 0.4270 mol/L, [MMA] = 0.9349 mol/L, [AIBN] = 0.01 mol/L, Acetic Acid = 35% (v/v)

Salt	[Salt] (mol/L)	$\beta_{\text{calculated}}$
$MnSO_4$	0.0125	1.1475
	0.0625	1.9352
$Co(NO_3)_2$	0.0125	0.0742
	0.0625	0.0994
$FeCl_3$	0.0125	0.3053
	0.0625	0.3662
K_2SO_4	0.0125	0.4735
	0.0625	3.1604
KCl	0.0125	0.1590
	0.0625	0.1771

Initiation:

$$M + I \longrightarrow M^{\bullet} \qquad (K_1)$$

Propagation:

$$M^{\bullet} + M \rightsquigarrow M_n^{\bullet} + M \longrightarrow P \qquad (K_2)$$

Termination:

$$ZH + M_n^{\bullet} \longrightarrow M_n\text{—}H + Z^{\bullet} \qquad (K_3)$$

$$M_n^{\bullet} + M_n^{\bullet} \longrightarrow M_n\text{—}M_n \qquad (K_4)$$

$$M_n^{\bullet} + Z^{\bullet} \longrightarrow M_n\text{—}Z \qquad (K_5)$$

where M, ZH, I_2, and P represent the monomer, retarder (acetophenone), initiator, and chain carrier, respectively.

At steady state:

$$\frac{d[Z^\bullet]}{dt} = K_3[ZH][M_n^\bullet] - K_5[Z^\bullet][M_n^\bullet] = 0$$

or

$$[Z^\bullet] = \frac{K_3}{K_5}[ZH] \tag{3}$$

Also

$$\frac{d[M_n^\bullet]}{dt} = R_i - K_3[ZH][M_n^\bullet] - K_4[M_n^\bullet]^2 - K_5[Z^\bullet][M_n^\bullet] = 0 \tag{4}$$

R_i, the rate of initiation, is assumed to be constant. Substituting the value of $[Z^\bullet]$ from Eq. (3) in Eq. (4), and taking the positive value of $[M_n^\bullet]$:

$$[M_n^\bullet] = \frac{-K_3[ZH] + (K_3^2[ZH]^2 + K_4R_i)^{1/2}}{K_4} \tag{5}$$

which on rearrangement gives

$$[M_n^\bullet] = \frac{-K_3}{K_4}[ZH] + \left(\frac{K_3^2}{K_4^2}[ZH]^2 + \frac{R_i}{K_4}\right)^{1/2} \tag{6}$$

The rate of polymerization is given by

$$R_p = K_2[M_n^\bullet][M] \tag{7}$$

On rearrangement:

$$\frac{[M]}{R_p} = \frac{K_3[ZH]}{K_2R_i} + \frac{1}{K_2}\left(\frac{K_4}{R_i}\right)^{1/2} \tag{8}$$

Equation (8) requires a linear dependence of $[M]/R_p$ on [ZH] (Fig. 1). The slope $K = K_3/K_2R_i$ of Eq. (8), which is proportional to the reactivity of the substrate with the growing polymer radical (K_3), can also be directly used as another kinetic parameter for expressing the retarding influence of acetophenone.

GRAPHICAL DETERMINATION OF β

By correlating the values of the slope and the intercept in the plot of $[M]/R_p$ vs $[ZH]$, we get the relationship

$$\beta = \frac{\text{slope} \times [\text{initiator}]^{1/2}}{\text{intercept}}$$

if the stoichiometry μ is assumed to be 2.

β values have been found graphically by using the above relationship. The graphical values of β, so determined, have been found to agree closely with the calculated β values derived from Tüdős' relationship (Table 1).

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