Kinetic Investigation on the Photopolymerization of Methyl Methacrylate Using Iodine Trichloride as Initiator

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ABSTRACT

The photopolymerization of MMA in visible light was studied at 45°C using ICl_3 as the photoinitiator. The initiator exponent was found to be 0.16 and the monomer exponent varied between 1.0 to 1.50, depending on the nature of the solvent. Analysis of the data revealed that the polymerization was induced by a free radical mechanism. Nonideality of the kinetics was explained on the basis of 1) Monomer-dependent chain initiation and 2) Initiator-dependent chain termination via degradative initiator transfer.

INTRODUCTION

Reports of the effectiveness of iodine [1], bromine [2], chlorine [3], iodine monobromide [4], and iodine monochloride [5] as initiators in the polymerization of methyl methacrylate (MMA) are available. Iodine trichloride is also expected to initiate the polymerization of MMA. In the present studies we have examined the suitability of ICl_3 as the photoinitiator of polymerization of MMA. Related results

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and the kinetics of polymerization under photoactivation are re-
ported.

EXPERIMENTAL

Materials

Monomer methyl methacrylate (MMA) was purified by the usual
procedures. ICl_3, obtained from E. Merck, Germany, was used as
the photoinitiator without further purification. All solvents used were
reagent grade and were purified by the usual procedures and were
distilled once before use in the polymerization reaction.

Polymerization

The polymerization of MMA was studied dilatometrically at $45 \pm$
$0.05°C$ following a procedure described elsewhere [6]. Polymers
formed at low conversion ($< 10\%$) were removed and isolated by pre-
cipitation with petroleum ether and drying under vacuum at $80°C$.

Intrinsic Viscosity

Intrinsic viscosities $[\eta]$ in dL/g of polymers taken in benzene
solution were obtained from measurements of solution viscosity at
$30 \pm 0.05°C$ using an Ubbelohde viscometer. Molecular weights
($\overline{M}_n$) of polymethyl methacrylate (PMMA) were calculated according
to the equation [7]

$$[\eta] = 8.69 \times 10^{-5} \overline{M}_n^{0.76} \qquad ([\eta] \text{ in dL/g}) \qquad (1)$$

RESULTS AND DISCUSSION

Absorption spectra in the visible and near ultraviolet region for
iodine trichloride in carbon tetrachloride and in MMA solutions are
given in Fig. A.

No polymerization of MMA occurred with ICl_3 at $45°C$ within a
period of about 200 min in the dark. In the presence of light, however,
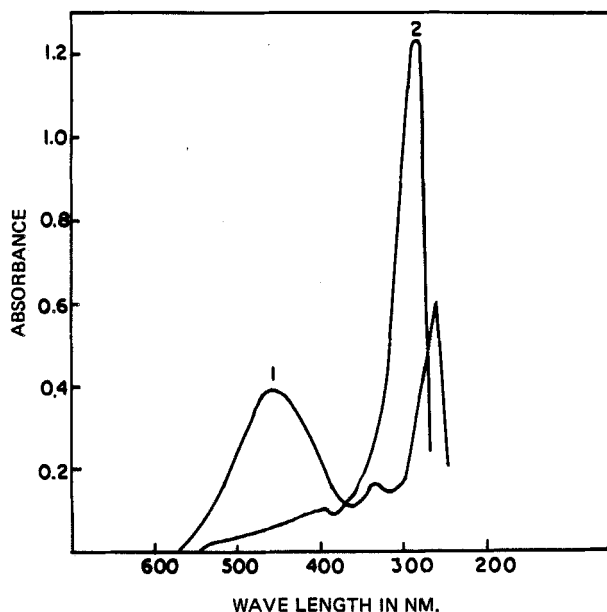polymerization started after an inhibition period (10 to 80 min).

FIG. A. Visible and near ultraviolet absorption spectra of (1) Iodine trichloride (0.001 mol/L) in CCl$_4$ and (2) iodine trichloride (0.001 mol/L) in MMA.

Initiator Exponent

Data on bulk photopolymerization of MMA at 45°C using different ICl$_3$ concentrations (6.6755 × 10^{-4} to 5.1172 × 10^{-6} mol/L) are presented in Table 1. Rates of polymerization, R$_p$, were calculated from the initial zones of % conversion vs time plots (Fig. 1). The initiator exponent determined from the slope of the plot of log R$_p$ vs log [ICl$_3$] was found to be 0.16 (Fig. 2). Photopolymerization in contact with air produced slightly enhanced inhibition, but in the presence of dissolved hydroquinone (0.001 mol/L) there was much pronounced inhibition of polymerization. The polymers gave a positive response to the dye partition test [8] for a halogen endgroup.

k_p^2/k_t Value

The kinetic parameter k_p^2/k_t at 45°C was evaluated from the slope of the plot of $1/\overline{P}_n$ vs $R_p/[M]^2$ (Fig. 3) in accordance with the Mayo equation [9]:

TABLE 1. Photopolymerization of MMA at 45°C Using ICl_3 as the Photoinitiator

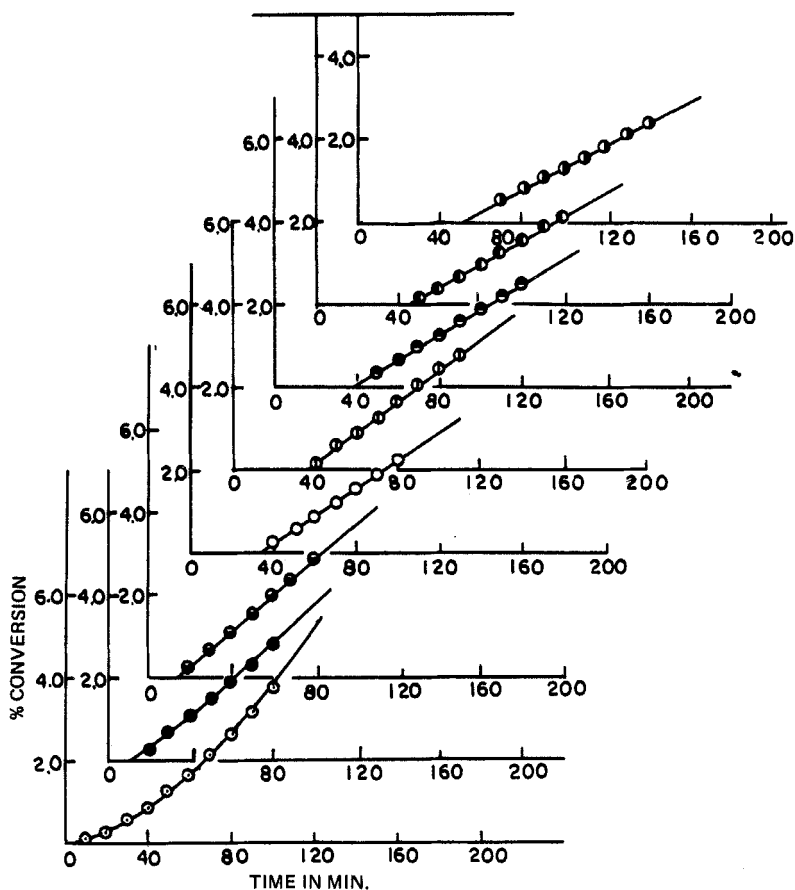| $[ICl_3] \times 10^4$ (mol/L)	$R_p \times 10^5$ (mol/L·s)	$[\eta]$ (dL/g)	$1/\overline{P}_n \times 10^4$	$R_p/[M]^2 \times 10^8$	Initiator exponent	$k_p^2/k_t \times 10^2$
6.6755	8.0	0.21	35.36	0.9551		
5.1172	7.5	0.3525	17.889	0.8954		
2.5586	7.0	0.60	8.968	0.8353		
2.1112	6.866	1.045	4.280	0.8197		
1.0163	5.633	2.205	1.6021	0.6725		
0.6617	6.0	1.565	2.515	0.7163	0.16	0.6521
0.5117	5.05	2.899	1.116	0.6029		
0.2558	4.816	3.046	1.047	0.5749		
0.1952	4.5	3.365	0.918	0.5372		
0.1383	4.616	3.410	0.904	0.5511		
0.1023	3.916	4.108	0.703	0.4675		
0.05117	3.966	4.082	0.712	0.4735		

% CONVERSION

TIME IN MIN.

FIG. 1. Photopolymerization of MMA in bulk at 45°C using iodine
trichloride as the photoinitiator. Plot of % conversion vs time in
minutes. Data given for each curve is [ICl₃] in mol/L: (⊚) 6.675 ×
10⁻⁴, (●) 5.1172 × 10⁻⁴, (◒) 2.5586 × 10⁻⁴, (○) 1.0163 × 10⁻⁴,
(⊙) 6.6175 × 10⁻⁵, (◓) 5.117 × 10⁻⁵, (◐) 2.5586 × 10⁻⁵, (◑) 1.952
× 10⁻⁵.

$$\frac{1}{\overline{P}_n} = 1.85 \; \frac{k_t}{k_p^{\,2}} \; \frac{R_p}{[M]^2} + \sum \frac{R_{tr}}{R_p} \tag{2}$$

where the last term on the right-hand side was included to account
for chain transfer effects, assuming this would not affect the slope
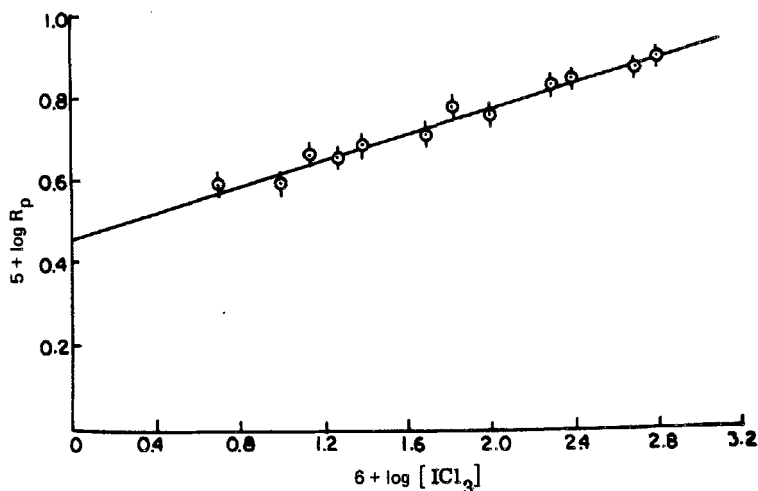of the plot over a low range of initiator concentration. The apparent

FIG. 2. Photopolymerization of MMA in bulk at 45°C using iodine trichloride as the photoinitiator. Plot of log R_p vs log $[ICl_3]$.

k_p^2/k_t value calculated from the slope of the initial zone of the plot is 0.6521×10^{-2} L/mol·s. It was assumed in the calculation that any perturbation of the termination from the usual bimolecular mechanism [10] (85% disproportionation, 15% combination) will not measurably affect the initial slope of the plot in Fig. 3.

Monomer Exponent

The photopolymerization of MMA was further studied in the presence of different concentrations of several solvents such as benzene, carbon tetrachloride, dioxane, methanol, and chloroform. Monomer exponent calculated from the slope of the respective plots of log R_p vs log $[M]$ (Fig. 4) ranges between 1.0 to 1.50, depending on the nature of the solvents used.

Activation Energy

The apparent activation energy E_a $(= E_p - E_t/2)$ for the photopolymerization of MMA using ICl_3 as the photoinitiator is found to be 4.88 kcal/mol.
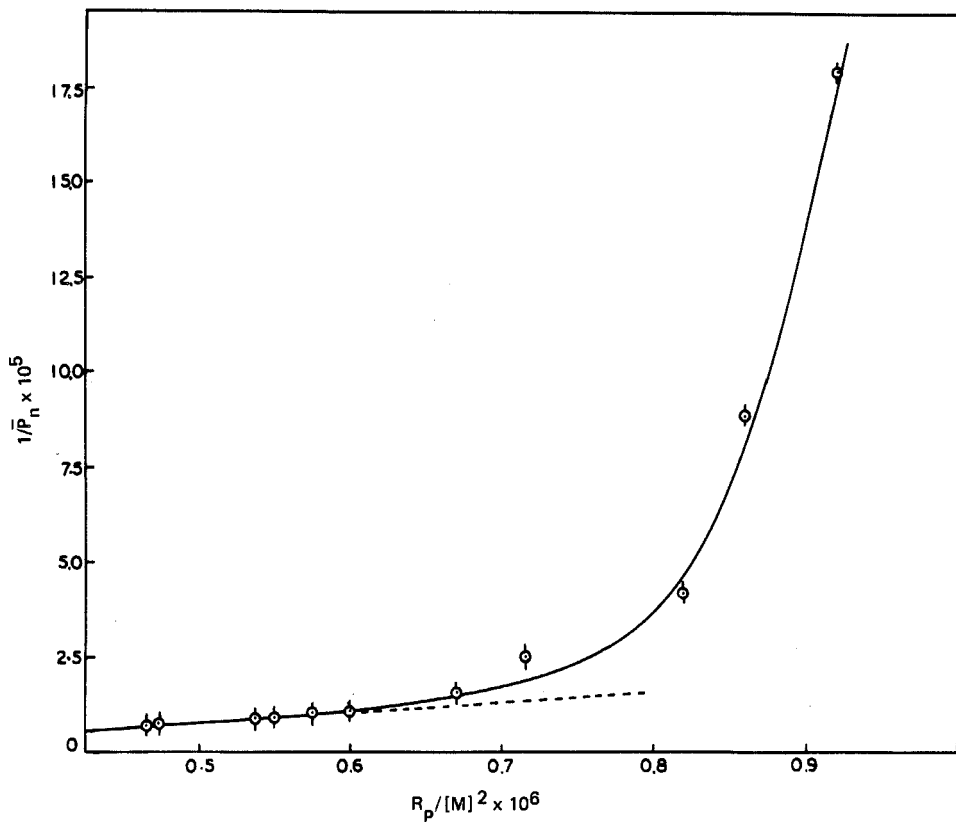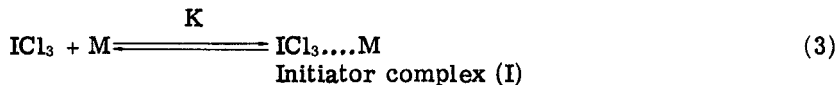
FIG. 3. Photopolymerization of MMA in bulk at 45°C using iodine trichloride as the photoinitiator. Plot of $1/\overline{P}_n$ vs $R_p/[M]^2$.

Mechanism

Kinetic data, the inhibitory effect of hydroquinone, and the results of endgroup analysis indicate a radical mechanism. The radical generation process may be considered to follow an initial complexation reaction between monomer and initiator molecules, as indicated by the UV spectra of ICl_3 in CCl_4 and in MMA.

$$ICl_3 + M \overset{K}{\rlap{\rule{2cm}{0.4pt}}} ICl_3\ldots.M \qquad\qquad (3)$$

$$\text{Initiator complex (I)}$$

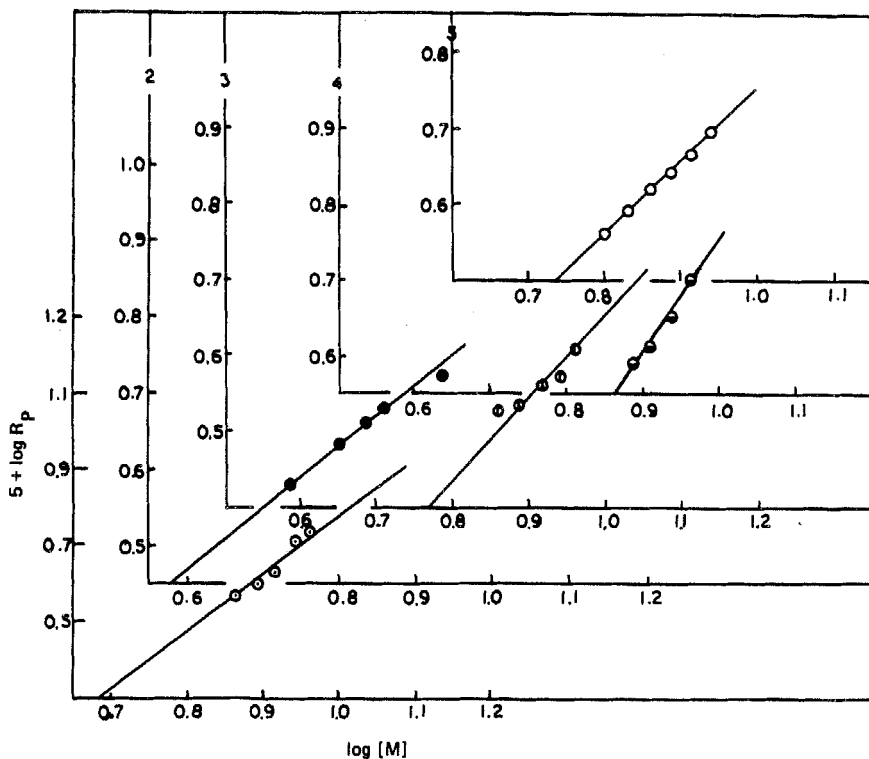$$I \overset{h\nu}{\relbar\joinrel\longrightarrow} \text{pair of radicals} \qquad\qquad (4)$$

FIG. 4. Photopolymerization of MMA (solution) at 45°C using iodine trichloride as the photoinitiator. Plot of log R_p vs log $[M]$.

Data given for each curve are solvent, $[ICl_3]$, and slope (monomer exponent): (⊙) C_6H_6, 5.287 × 10^{-5} mol/L, 1.5; (●) Dioxane, 4.163 × 10^{-5} mol/L, 1.0; (⊙) MeOH, 3.027 × 10^{-5} mol/L, 1.1; (◕) CCl₄, 6.308 × 10^{-5} mol/L, 1.5; (○) CHCl₃, 5.073 × 10^{-5} mol/L, 1.0.

Initial concentration of the initiating complex (I) is then equal to $K[ICl_3][M]$ where K is the equilibrium constant of the initiator monomer complexation reaction.

Initiator Transfer

Equation (2) may be used in the form

$$\frac{1}{\overline{P}_n} - 1.85 \frac{k_t}{k_p^2} \frac{R_p}{[M]^2} = C_M + C_I K [ICl_3] \qquad (5)$$
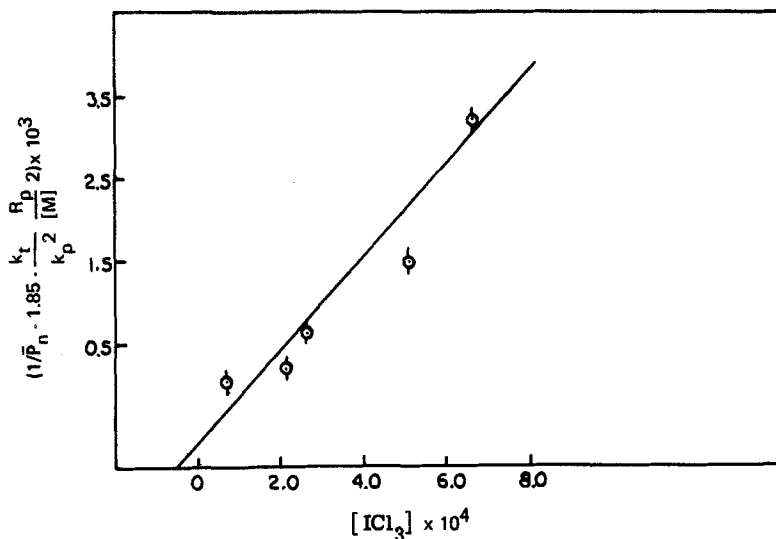
FIG. 5. Photopolymerization of MMA in bulk at 45°C using iodine trichloride as the photoinitiator. Plot of

$$\left(\frac{1}{\overline{P}_n} - 1.85 \frac{k_t R_p}{k_p^{\,2}[M]^2} \right) \text{ vs } [ICl_3].$$

to determine the initiation transfer parameter $(C_I K)$ where C_I is the initiator transfer constant in the polymerization of MMA in bulk. Here $[ICl_3]$ is the initial concentration of ICl_3 and C_M is the monomer transfer constant. A plot of the left-hand side of Eq. (5) vs $[ICl_3]$ is given in Fig. 5, and the slope of the plot giving the value of $C_I K$ is 6.0344 L/mol.
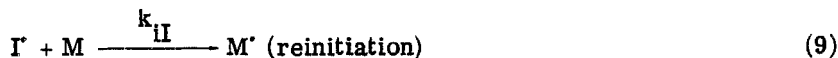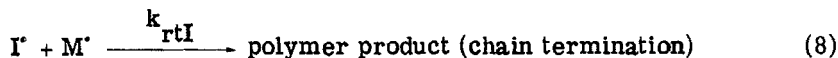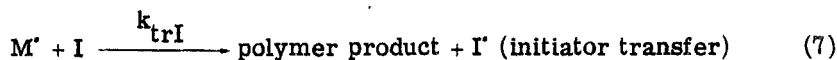
Termination

The observed initiator exponent of 0.16 clearly indicates that some initiator-dependent termination process is significant along with the usual mode of bimolecular termination.

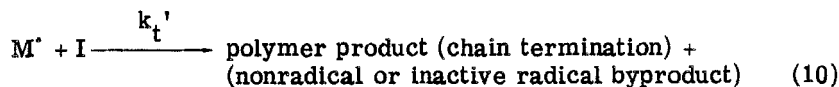The initiator-dependent termination process may be of two kinds:

1) Primary radical termination:

$$M^\bullet + R^\bullet \xrightarrow{\ \ k_{prt}\ \ } \text{polymer product} \tag{6}$$
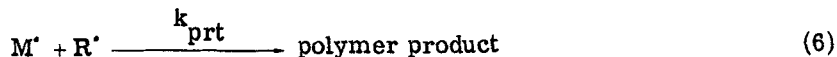
2) Termination via degradative initiator transfer, either (a) with re-initiation, such as

$$M^{\cdot} + I \xrightarrow{\quad k_{trI} \quad} \text{polymer product} + I^{\cdot} \text{ (initiator transfer)} \qquad (7)$$

$$I^{\cdot} + M^{\cdot} \xrightarrow{\quad k_{rtI} \quad} \text{polymer product (chain termination)} \qquad (8)$$

$$I^{\cdot} + M \xrightarrow{\quad k_{iI} \quad} M^{\cdot} \text{ (reinitiation)} \qquad (9)$$

or, (b) with little reinitiation, such as

$$M^{\cdot} + I \xrightarrow{\quad k_{t}' \quad} \begin{array}{l} \text{polymer product (chain termination)} + \\ \text{(nonradical or inactive radical byproduct)} \end{array} \qquad (10)$$

Analysis of Primary Radical Termination Effect

The equation of Deb and Meyerhoff [11], which would assume the following form for the present polymerization, may be used to detect primary radical termination (in the absence of degradative initiator transfer process):

$$\log \frac{R_p^{\,2}}{[ICl_3][M]^3} = \log \frac{Kfk_d k_p^{\,2}}{k_t} - 0.8684 \frac{k_{prt}}{k_i k_p} \frac{R_p}{[M]^2} \qquad (11)$$

Here the factor Kfk_d may be replaced by an equivalent factor $K\phi\epsilon I_0$, where ϕ is the quantum yield for chain initiation, ϵ is the molar absorptivity for the active radiation, and I_0 is the incident light intensity. A negative slope for the plot of the left-hand side of Eq. (11) against $R_p/[M]^2$ (Fig. 6), indicating measurable primary radical termination, was obtained for the photopolymerization of MMA in bulk at 45°C. The value of $k_{prt}/k_i k_p$ calculated from the slope of this plot is 3.083×10^6 mol·s/L. The value of Kfk_d, or more precisely of $K\phi\epsilon I_0$, obtained from the intercept of this plot is 48.489×10^{-5} L/ mol·s.
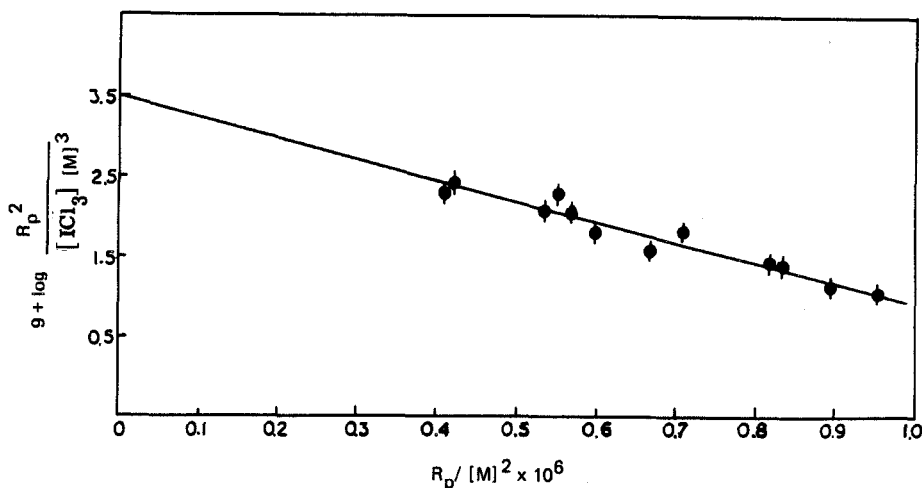
FIG. 6. Photopolymerization of MMA in bulk at 45°C using iodine trichloride as the photoinitiator. Analysis of primary radical termination. Plot of log $\dfrac{R_p^2}{[ICl_3][M]^3}$ vs $R_p/[M]^2$.

Analysis of Degradative Chain Transfer Effect

Degradative Initiator Transfer with Reinitiation Effect

An equation derived by Deb [12] to analyze degradative chain (initiator) transfer with reinitiation was simplified by Ghosh et al. [13] to the following form:

$$\ln \frac{R_p^2}{[I][M]^2} = \ln \frac{fk_d k_p^2}{k_t} - \frac{k_p^2}{k_t} \frac{k_{rtI}}{k_{iI}k_p} C_I \frac{[I]}{[M]} \tag{12}$$

In the present case $[I] = K[ICl_3][M]$ and hence we have

$$\log \frac{R_p^2}{[ICl_3][M]^3} = \log \frac{fKk_d k_p^2}{k_t} - 0.434 \frac{k_p^2}{k_t} \frac{k_{rtI}}{k_{iI}k_p} C_I K[ICl_3] \tag{13}$$

Here C_I is the initiator transfer constant. A plot of the left-hand side of Eq. (13) against $[ICl_3]$ is shown in Fig. 7. The experimental points
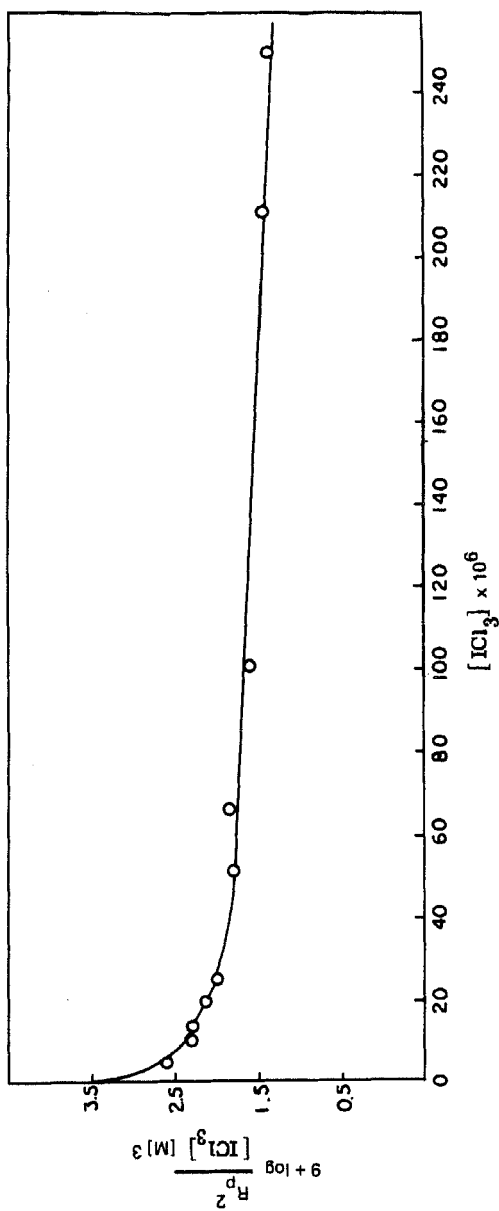
FIG. 7. Photopolymerization of MMA in bulk at 45°C using iodine trichloride as the photoinitiator. Analysis of degradative initiator transfer with reinitiation. Plot of log $(R_p{}^2/[ICl_3][M]^3)$ vs $[ICl_3]$.
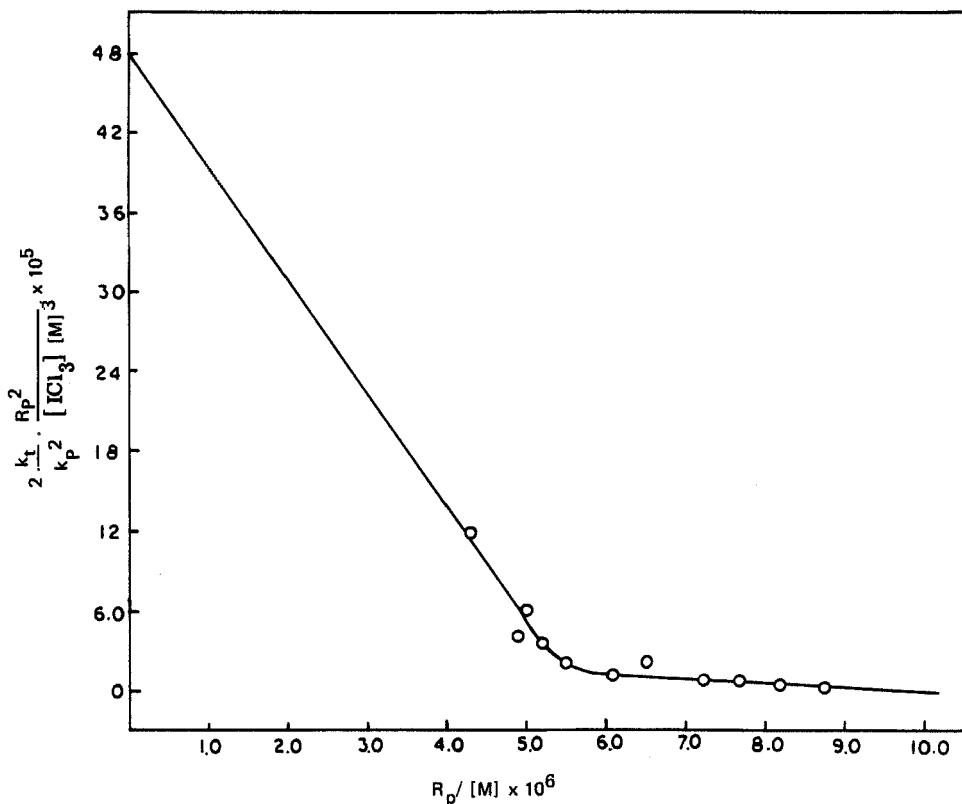
FIG. 8. Photopolymerization of MMA in bulk at $45°C$ using iodine trichloride as the photoinitiator. Analysis of degradative initiator transfer (no reinitiation). Plot of

$$\frac{2k_t}{k_p^2} \frac{R_p^2}{[\,ICl_3\,][\,M\,]^3} \text{ vs } R_p/[\,M\,].$$

fall on two straight lines, each with a negative slope, the one at very low initiator concentrations giving a much higher slope than the other at a relatively high initiator concentration range. Degradative initiator transfer is thus clearly indicated and the effect is very much more predominant at low than at high initiator concentrations. From the intercept of the plot (Fig. 7), the value of the kinetic parameter Kfk_d, i.e., $K\phi\epsilon I_0$, is 48.4×10^{-5} L/mol·s.

Degradative Initiator Transfer with Little Reinitiation

This aspect may be analyzed according to the following approach. Under steady-state conditions we have

$$\frac{R_i}{R_p} = \frac{R_t}{R_p} = \frac{2k_t[M^\cdot]^2 + k_t'[I][M^\cdot]}{R_p}$$

$$= \frac{2k_t[M^\cdot]^2 + k_t'K[ICl_3][M][M^\cdot]}{R_p} \tag{14}$$

or

$$R_i = \frac{2k_t}{k_p^2}\frac{R_p^2}{[M]^2} + \frac{k_t'K}{k_p}R_p[ICl_3]$$

$$= 2\phi\epsilon I_0 K[ICl_3][M] \tag{15}$$

or

$$\frac{2k_t}{k_p^2}\frac{R_p^2}{[M]^3[ICl_3]} = 2\phi\epsilon I_0 K - \frac{k_t'K}{k_p}\frac{R_p}{[M]} \tag{16}$$

A plot of the left-hand side of Eq. (16) against $R_p/[M]$, which gives a straight line with negative slope (Fig. 8), is obtained for the present polymerization of MMA. The nature of the plot is similar to that shown in Fig. 7, and the values of the parameter $\phi\epsilon I_0 K$ obtained from both plots are very close. Thus, degradative initiator transfer of either kind can easily account for the nonideal kinetics in the present photopolymerization.

Although we have reasonable indication for primary radical termination as a possible cause for nonideality, consideration of the dependence of R_p on monomer concentration predicts it to be of much less consequence. For ideal or normal kinetics (bimolecular termination) in the present photopolymerization, the monomer exponent should be 1.5 on the basis of the initiation mechanism envisaged; for significant primary radical termination, the expected monomer exponent would be > 1.5, the limiting value being 2.0, while for some kind of degradative initiator transfer the expected value of monomer

exponent would be < 1.5, the limiting value being 1.0. With the observed monomer exponent in the range of 1 to 1.5, the nonideality in the present photopolymerization appears to be largely due to degradative initiator transfer.

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