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Photopolymerization of Methyl Methacrylate with the Use of Phenyliododichloride as Photoinitiator

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ABSTRACT

Phenyliododichloride, $C_6H_5ICl_2$, can induce photopolymerization of methyl methacrylate almost instantaneously at 40° C under visible light. The initiator order and monomer order were 0.3 and close to 1.5, respectively, for $[C_6H_5ICl_2] < 5.0 \times 10^{-4}$ mol/L while the corresponding values were 0 and 1.0, respectively, for $[C_6H_5ICl_2] > 5.0 \times 10^{-4}$ mol/L. Kinetic and other data indicate a radical polymerization mechanism that involves complexation of a monomer molecule with $C_6H_5ICl_2$ prior to the radical generation step. Termination appears to take place both by a bimolecular mechanism and by a degradative initiator transfer mechanism at low $[C_6H_5ICl_2]$, but it appears to take place almost exclusively by the latter mechanism when $[C_6H_5ICl_2]$ is high.

INTRODUCTION

It has been reported from our laboratory that iodine monobromide, IBr, can easily induce polymerization of methyl methacrylate (MMA) on photoactivation [1]. This interhalogen finds extensive use in the determination of olefinic unsaturation in a wide range of organic materials including fats and oils, resins, plastics, and rubber.

Phenyliododichloride, $C_6H_5ICl_2$, finds some use as a chlorinating agent in organic systems [2], and we have examined its suitability as a radical initiator for vinyl polymerization, particularly under photoactivated condition. Related results are reported in the present paper.

EXPERIMENTAL

Materials

Commercial monomer, MMA, was purified following the usual procedures [3].

Phenyliododichloride, $C_6H_5ICl_2$, was prepared according to the method of Garvey et al. [2]. A stock solution of $C_6H_5ICl_2$ in MMA was used in polymerization experiments.

All solvents used were of reagent grade and were purified by distillation.

Polymerization of MMA

Photopolymerization of MMA in bulk and in dilute systems with $C_6H_5ICl_2$ as photoinitiator was carried out dilatometrically under nitrogen atmosphere according to a procedure given before [3]. Polymers formed at low conversion (< 10%) were isolated by precipitation with petroleum ether and subsequent drying under vacuum at 30°C.

Intrinsic Viscosity

The intrinsic viscosity $[\eta]$ of the polymers were measured in benzene solution at 30 ± 0.05°C in a Ubbelohde viscometer. Molecular weights ($\overline{M}_n$) were calculated using [4]

$$[\eta] = 8.69 \times 10^{-5} \overline{M}_n^{0.76} \tag{1}$$

RESULTS

Absorption spectra of $C_6H_5ICl_2$ in benzene and in MMA solutions are given in Fig. 1.

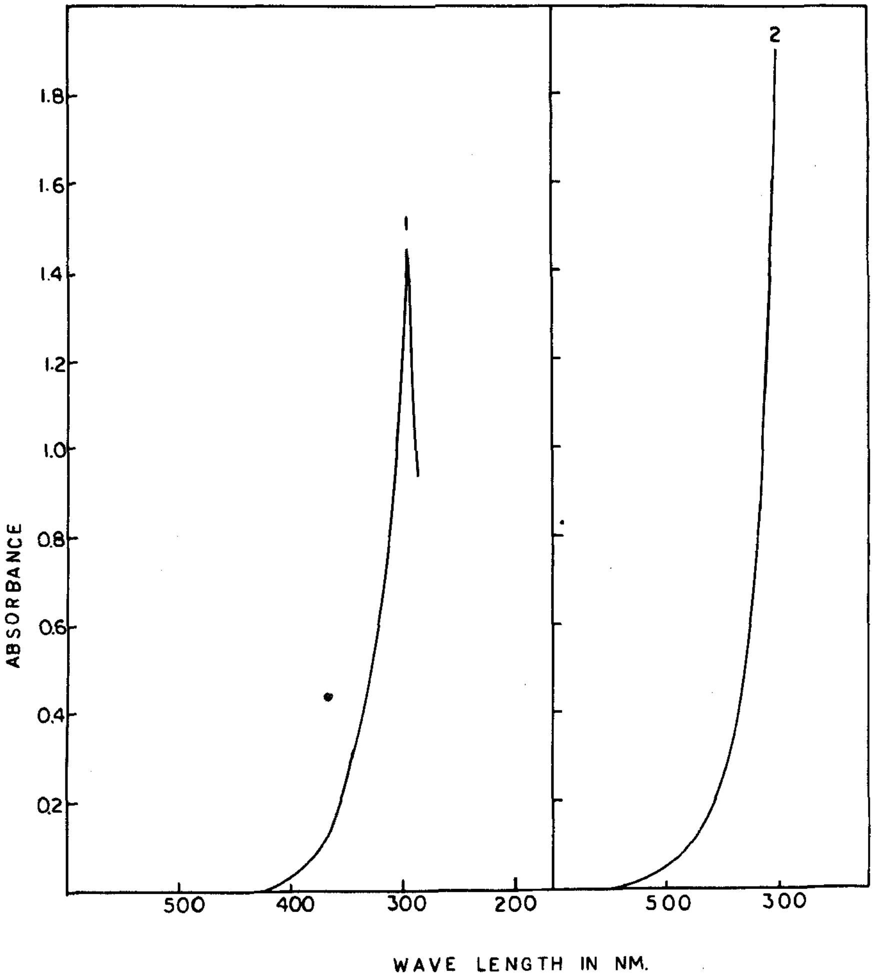

FIG. 1. Visible and near ultraviolet absorption spectra of (1) $C_6H_5ICl_2$ (0.001 M) in MMA and (2) $C_6H_5ICl_2$ (0.001 M) in C_6H_6.

Bulk Polymerization

Results of bulk polymerization of MMA at 40°C at different concentrations of $C_6H_5ICl_2$ are given in Table 1.

The rates of polymerization were calculated from the % conversion-time curves given in Fig. 2. The plots have got some special features: an initial linear zone of short duration (15-25 min) is followed by a

TABLE 1. Photopolymerization of MMA in Bulk at 40°C with Phenyliododichloride as the Photoinitiator

$[C_6H_5ICl_2]$ $\times 10^4$ mol/L	$R_p \times 10^5$ (mol/L·s)	$(R_p)_i \times 10^5$ (mol/L·s)	$[\eta]$ (dL/g)	$1/P_n \times 10^3$	$R_p/[M]^2 \times 10^5$ $(mol^{-1} \cdot L \cdot s^{-1})$	$(R_p)_i/[M]^2 \times 10^5$ $(mol^{-1} \cdot L \cdot s^{-1})$
0.34	2.68	3.76	3.03	0.1054	0.0317	0.0445
0.74	3.04	6.54	2.90	0.1117	0.0360	0.0774
1.20	4.54	7.18	2.46	0.1387	0.0537	0.0850
1.70	4.70	9.16	1.50	0.2661	0.0556	0.1084
2.50	4.96	10.41	1.465	0.2743	0.0587	0.1232
3.70	5.51	11.66	1.370	0.2998	0.0652	0.1380
5.00	5.31	11.90	1.294	0.3232	0.0628	0.1409
7.40	3.20	15.90	0.677	0.7581	0.0378	0.1882
9.30	3.26	18.22	0.505	1.1147	0.0385	0.2157
14.80	3.39	23.15	0.455	1.2802	0.0401	0.2741
32.80	3.57	24.40	0.445	1.3163	0.0422	0.2889
65.60	3.40	25.46	0.332	1.9357	0.0402	0.3014
98.60	3.73	35.11	0.305	2.1767	0.0441	0.4157
842.80	2.08	44.64	-	-	-	-

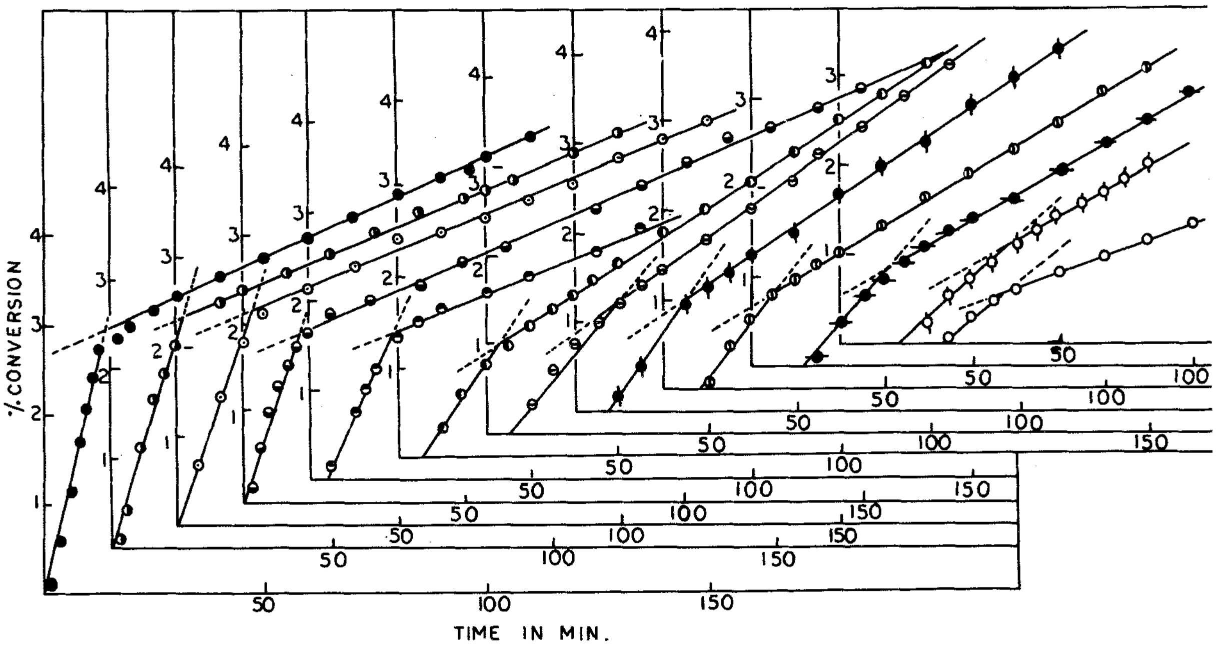

FIG. 2. Photopolymerization of MMA in bulk at 40° C with $C_6H_5ICl_2$ initiator. $C_6H_5ICl_2$ concentrations are: (●) 98.6×10^{-4} M, (◑) 65.6×10^{-4} M, (⊙) 14.8×10^{-4} M, (⊖) 32.8×10^{-4} M, (○) 9.3×10^{-4} M, (●) 5.4×10^{-4} M, (⊖) 4.2×10^{-4} M, (⧫) 3.7×10^{-4} M, (⦶) 2.5×10^{-4} M, (●) 1.7×10^{-4} M, (○) 1.2×10^{-4} M, (○) 0.74×10^{-4} M.

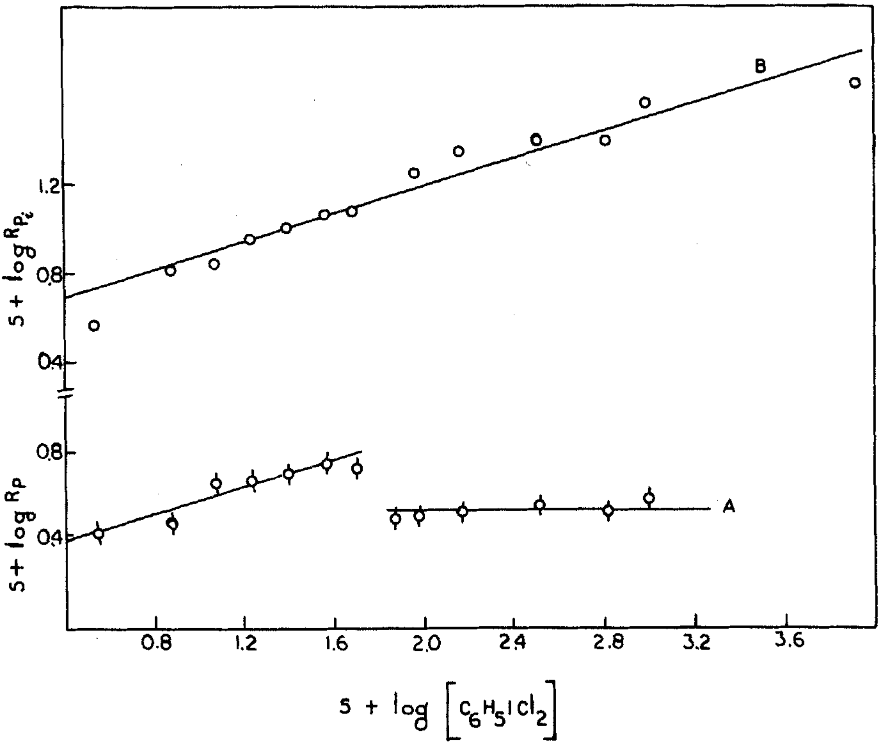

FIG. 3. Plot of (A) log R_p vs log$[C_6H_5ICl_2]$ and (B) log $(R_p)_i$ vs log $[C_6H_5ICl_2]$ for the photopolymerization of MMA in bulk at 40° C.

final linear (steady) zone over a much longer period. The final linear zone was characterized by a smaller slope compared to the initial slope. The photopolymerization is almost instantaneous when the initiator concentration was $\geq 1.5 \times 10^{-3}$ mol/L and inhibition periods of 10-25 min were observed with lower initiator concentrations. For kinetic analysis, steady rates of polymerization (R_p) were considered. The initiator exponent determined from the slope of log R_p vs log $[C_6H_5ICl_2]$ plot (Fig. 3, Plot A) is 0.3 up to about an initiator concentration of 5.0×10^{-4} mol/L; R_p, however, becomes independent of $[C_6H_5ICl_2]$ for $[C_6H_5ICl_2] > 5.0 \times 10^{-4}$ mol/L. Interestingly, the initiator exponent determined from a similar plot, log $(R_p)_i$ vs log $[C_6H_5ICl_2]$ (Fig. 3, Plot B) is close to 0.3 over the full range of

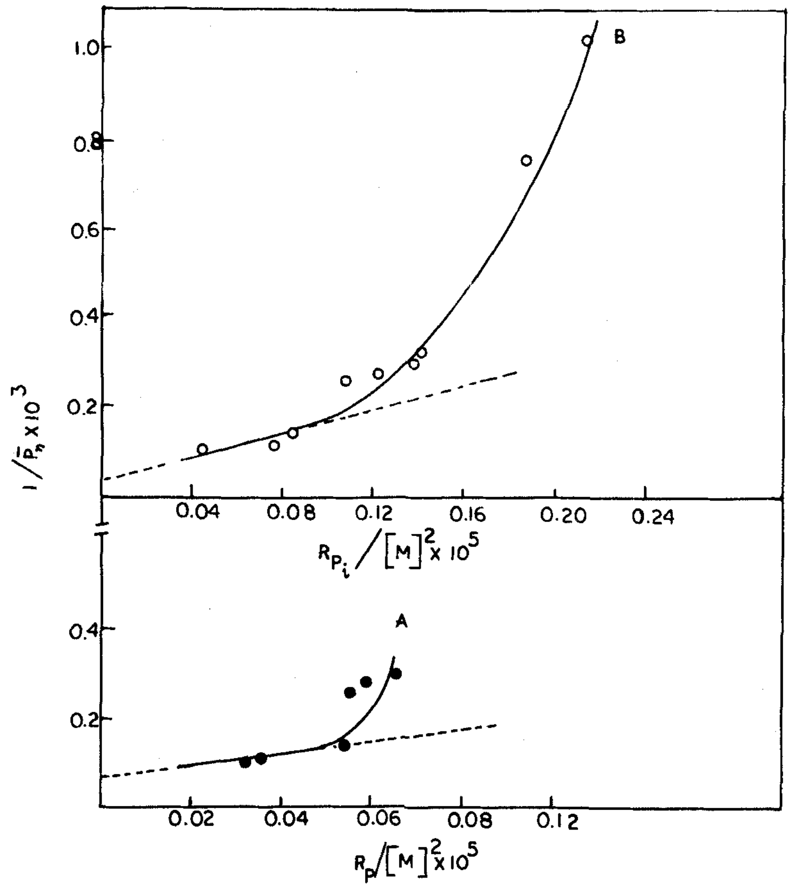

FIG. 4. Plot of (A) $1/\bar{P}_n$ vs $R_p/[M]^2$ and (B) $1/\bar{P}_n$ vs $(R_p)_i/[M]^2$ *for the photopolymerization of MMA in bulk at 40° C.*

initiator concentration examined; $(R_p)_i$ being the initial rate of polymerization.

A plot of $1/\bar{P}_n$ vs $R_p/[M]^2$ (Fig. 4, Plot A) indicates that the k_p^2/k_t value for $C_6H_5ICl_2$-induced photopolymerization of MMA is 1.40×10^{-2} L/mol·s. Considering $(R_p)_i$ and $\bar{P}_n$ data (Fig. 4, Plot B), k_p^2/k_t value equals 1.41×10^{-2} L/mol·s. This value is in good agreement with some reported values [3, 5] of k_p^2/k_t for MMA photopolymerization at 40° C.

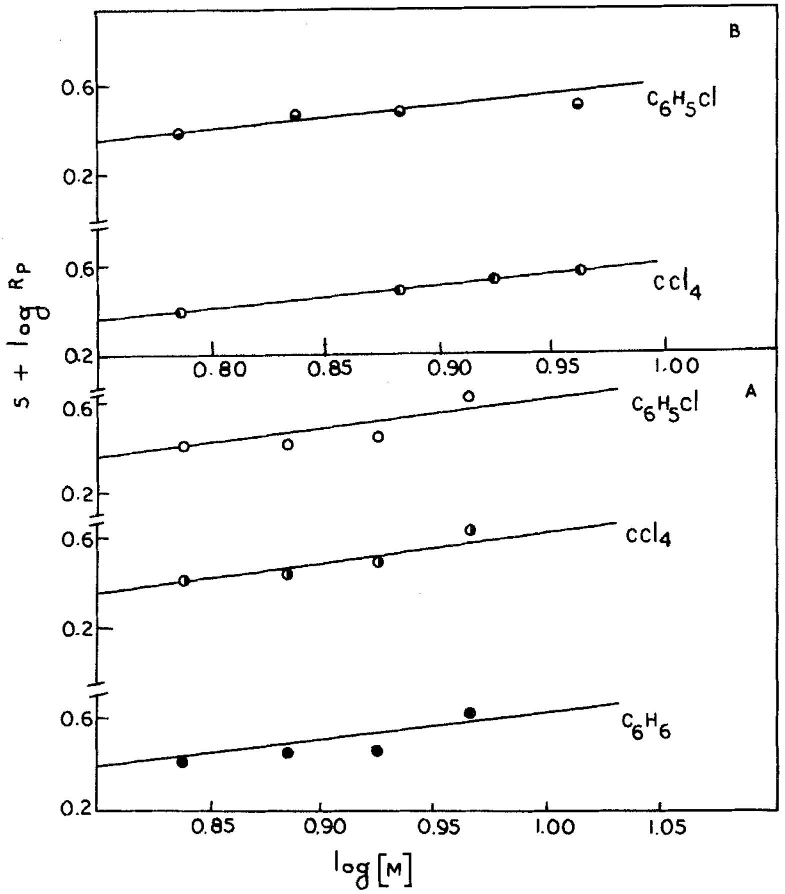

FIG. 5. Plot of log R_p vs log [M] for the photopolymerization of MMA in diluted systems. For each curve the data given are [$C_6H_5ICl_2$] in mol/L, solvent, and slope. A: (●) 1.2×10^{-4}, C_6H_6, 1.3; (◑) 1.2×10^{-4}, CCl_4, 1.4; (○) 1.2×10^{-4}, C_6H_5Cl, 1.3. B: (◐) 31.9×10^{-4}, CCl_4, 1.0; (⊖) 222.7×10^{-4}, C_6H_5Cl, 1.0,

The apparent activation energy E_a ($E_a = E_p - E_t/2$) of this photopolymerization is 4.4 kcal/mol (close to some reported values).

Polymerization in Solution

$C_6H_5ICl_2$-induced photopolymerization of MMA at 40°C in dilute systems indicates that the monomer exponents given by the slope of log R_p vs log [M] plots (Fig. 5A) using benzene, carbon tetrachloride, and chlorobenzene as the diluents are within the range 1.3 to 1.4 which is close to but less than 1.5 for $[C_6H_5ICl_2] < 5.0 \times 10^{-4}$ mol/L. However, for much higher $[C_6H_5ICl_2]$ (30×10^{-4} to 220×10^{-4} mol/L), the monomer exponent values in each solvent system is unity (Fig. 5B).

DISCUSSION

Mechanism

From a knowledge of the dependence of the rate (R_p) on the initiator and monomer concentrations, the following mechanism is proposed to describe the $C_6H_5ICl_2$-induced photopolymerization of MMA.

Radical generation step:

$$C_6H_5ICl_2 + M \overset{K}{\rightleftharpoons} [C_6H_5ICl_2 \ldots M]$$

Initiating complex (I)

$$I \xrightarrow[h\nu]{k_d} \text{Pair of radicals} \tag{2}$$

Propagation:

$$M^{\bullet} + M \xrightarrow{k_p} M^{\bullet} \tag{3}$$

Termination:

I. Bimolecular termination:

$$M^{\bullet} + M^{\bullet} \xrightarrow{k_t} \text{Polymer product} \tag{4a}$$

II. Initiator dependent termination via degradative initiator transfer:

$$M^{\bullet} + I \xrightarrow{k_t'} \text{polymer} + I^{\bullet} \text{ (inactive radical or no reinitiation)} \tag{4b}$$

Here I is the $C_6H_5ICl_2$-monomer complex (1:1), called the initiating complex, and K is the equilibrium constant of the complexation reaction.

Rate of initiation R_i is then expressed as:

$$R_i = 2fk_d[I] = 2fk_dK[C_6H_5ICl_2][M] \tag{5}$$

Rate of termination R_t and chain radical concentrations $[M^\cdot]$ may be expressed as follows.

Case I:

$$R_t = 2k_t[M^\cdot]^2 \text{ (bimolecular termination)}$$

Then,

$$2k_t[M^\cdot]^2 = 2fk_dK[C_6H_5ICl_2][M]$$

Therefore,

$$[M^\cdot] = \left(\frac{fk_dK}{k_t}\right)^{0.5} [C_6H_5ICl_2]^{0.5} [M]^{0.5} \tag{6a}$$

Case II:

$$R_t = k_t'[M^\cdot][I] = k_t'[M^\cdot]K[C_6H_5ICl_2][M] \quad \text{(termination via degradative initiator transfer)}$$

Then,

$$k_t'K[M^\cdot][C_6H_5ICl_2][M] = 2fk_dK[C_6H_5ICl_2][M]$$

Therefore,

$$[M^\cdot] = 2fk_d/k_t' \tag{6b}$$

The rate of propagation R_p is then expressed as follows.

Case I:

$$R_p = k_p[M][M^\cdot]$$

$$= k_p \left(\frac{fk_dK}{k_t}\right)^{0.5} [C_6H_5ICl_2]^{0.5} [M]^{1.5} \tag{7}$$

Case II:

$$R_p = k_p \left(\frac{2fk_d}{k_t'}\right) [M] \tag{8}$$

The observed kinetic data for the present photopolymerization at low [$C_6H_5ICl_2$] can be explained by considering significant degradative initiator transfer along with the usual bimolecular termination, the initiator exponent being 0.3 (intermediate between zero and 0.5) and the monomer exponent being 1.3-1.4 (somewhat less than 1.5 but greater than 1). However, rate Eq. (8), based on termination being exclusively due to degradative initiator transfer, clearly explains our experimental observations (monomer exponent of 1.0 and zero initiator exponent) for high [$C_6H_5ICl_2$]. Thus the degradative initiator transfer process takes place over the entire initiator concentration range, and this unusual process pushes the normal bimolecular termination effect practically to insignificance when [$C_6H_5ICl_2$] is high.

Degradative Initiator Transfer

The nonideality of the present photopolymerization over the whole range of [$C_6H_5ICl_2$] can thus be understood on the basis of degradative initiator transfer, and to further analyse the initiator-dependent termination process, the following simplified equation of a general nature used by Ghosh et al. [5] may be used:

$$\ln \frac{R_p^2}{[I][M]^2} = \ln \frac{fk_d k_p^2}{k_t} - \frac{k_p^2}{k_t} \frac{k_{rtI}}{k_{iI} k_p} C_I \frac{[I]}{[M]} \tag{9}$$

For the present system, $[I] = K[C_6H_5ICl_2][M]$, and hence the above equation, may be written

$$\log \frac{R_p^2}{[C_6H_5ICl_2][M]^3} = \log \frac{fk_d k_p^2 K}{k_t} - 0.434 \frac{k_p^2}{k_t} \frac{k_{rtI}}{k_{iI} k_p} C_I K[C_6H_5ICl_2] \tag{10}$$

The kinetic constants on the right-hand side have their usual significance [5, 6]. From a plot of the left-hand side of Eq. (10) against

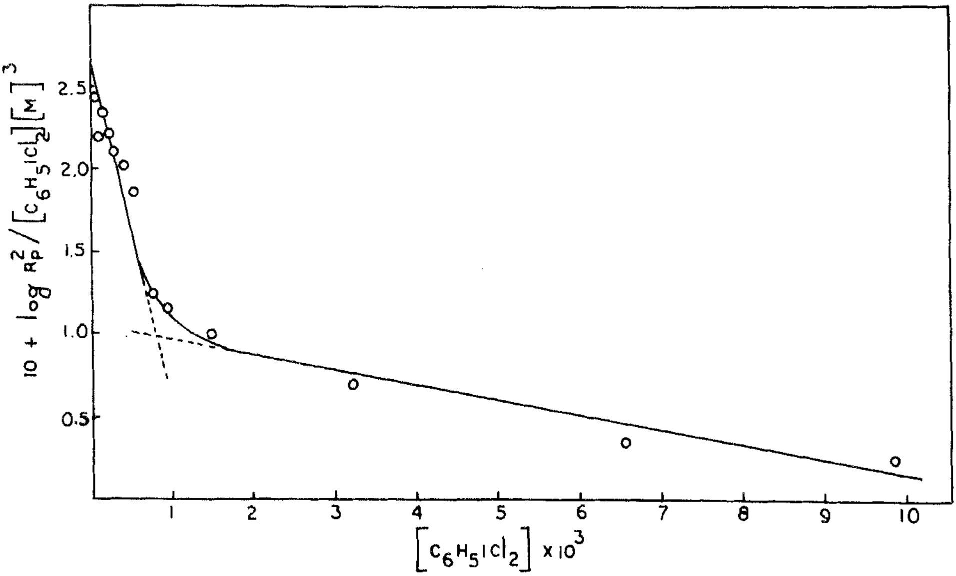

FIG. 6. Plot of log $R_p^2/[C_6H_5ICl_2][M]^3$ vs $[C_6H_5ICl_2]$ for the photopolymerization of MMA in bulk at 40°C for analysis of degradative transfer.

$[C_6H_5ICl_2]$, with data for bulk polymerization (Fig. 6), it is seen that there are two linear zones with negative slopes–one with much higher (negative) slope in the low range of $[C_6H_5ICl_2]$ and the other with a much lower (negative) slope in the higher range of $[C_6H_5ICl_2]$. A significant changeover in the overall termination mechanism around 0.75×10^{-3} mol/L $[C_6H_5ICl_2]$ is clearly evidenced. The nature of this plot (Fig. 6) also indicates the significance of the degradative initiator transfer in the present photopolymerization over the whole range of $[C_6H_5ICl_2]$. From the intercept of the plot and with knowledge of k_p^2/k_t, the value of fk_dK at 40°C is found to be 2.84×10^{-6} $L^2/mol^2 \cdot s$.

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