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## Photopolymerization of Methyl Methacrylate Using Iodine Monochloride as the Photoinitiator

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### ABSTRACT

Iodine monochloride,  $\text{ICl}_2$ , can easily induce photopolymerization of MMA at  $40^\circ\text{C}$  under visible light. Initiator order and monomer order are 0.5 and 2, respectively, at low  $[\text{ICl}_2]$ , while the corresponding values at high  $[\text{ICl}_2]$  are 0 and 3. Kinetic and other data indicate a radical polymerization mechanism that involves complexation of monomer molecules with  $\text{ICl}_2$ , which is second order in  $[\text{M}]$ , prior to radical generation. Termination of polymerization proceeds bimolecularly at low  $[\text{ICl}_2]$ , and unimolecularly, involving reaction with the initiator at high  $[\text{ICl}_2]$  (initiator termination).

### INTRODUCTION

It has been recently reported from our laboratory that iodine monobromide can easily induce polymerization of methyl methacrylate on photoactivation [1] by a radical mechanism. The present paper reports the results of studies on the kinetics of photopolymerization of methyl methacrylate (MMA) employing iodine monochloride as the photoinitiator.

## EXPERIMENTAL

### Materials

A commercial monomer, MMA, was purified following the usual procedures [2].

A stock solution of iodine monochloride (ICl) for use in polymerization experiments was prepared by mixing equal volumes of equimolar solutions of freshly prepared chlorine and analytical grade iodine, both in carbon tetrachloride.

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

### Polymerization of MMA

Photopolymerization of MMA in bulk and in solution systems with ICl as photoinitiator was carried out dilatometrically under nitrogen atmosphere according to a procedure given before [2]. In each polymerization experiment the volume percentage of carbon tetrachloride was kept fixed at 4.2%. Polymers formed at low conversions (< 10%) were isolated by precipitation with petroleum ether and subsequent drying under vacuum at 80°C.

### Intrinsic Viscosity

The intrinsic viscosities  $[\eta]$  of the polymers were measured in benzene solution at  $30 \pm 0.05^\circ\text{C}$  in a Ubbelohde viscometer. Molecular weights ( $\bar{M}_n$ ) were calculated using the following equation [3]:

$$[\eta] = 8.69 \times 10^{-5} \bar{M}_n^{0.76} \quad (1)$$

## RESULTS

Absorption spectra in the visible and near ultraviolet regions for iodine, chlorine, and iodine monochloride in carbon tetrachloride and in MMA solutions are given in Fig. 1.

### Bulk Polymerization

Results of bulk photopolymerization of MMA at 40°C at different  $[\text{ICl}]$  are given in Table 1.

The rates of polymerization,  $R_p$ , were calculated from initial linear

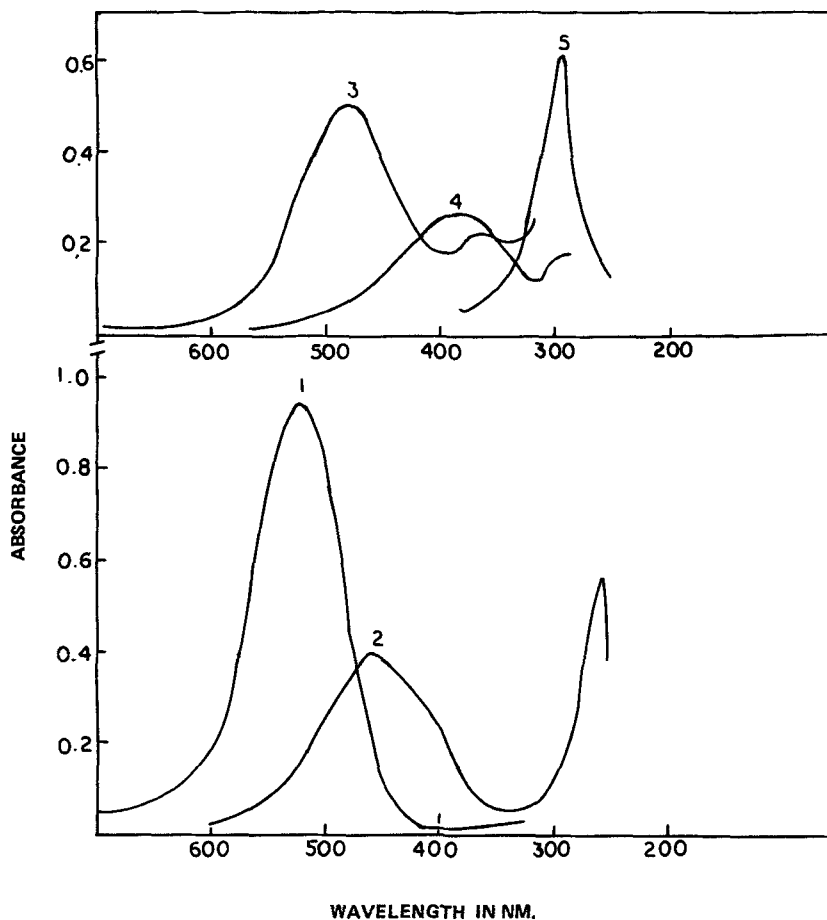


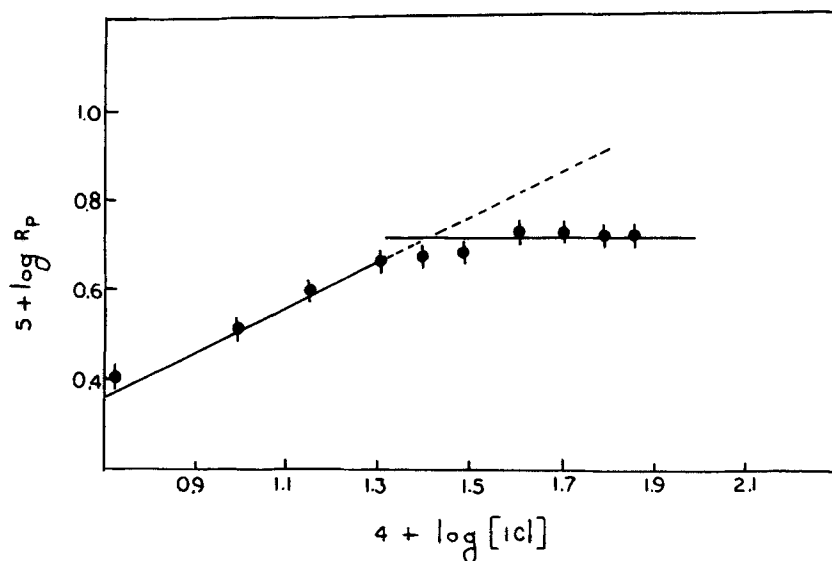
FIG. 1. Visible and near ultraviolet absorption spectra of (1) iodine (0.001 mol/L), (2) iodine monochloride (0.001 mol/L), each in  $\text{CCl}_4$ ; (3) iodine (0.001 mol/L), (4) iodine monochloride (0.001 mol/L), and (5) chlorine (0.0006 mol/L), each in MMA.

zones of the conversion-time curves. The initiator exponent obtained from the slope of  $\log R_p$  vs  $\log [\text{ICl}]$  plot (Fig. 2) is 0.5 in the low range of  $[\text{ICl}]$  ( $< 2.5 \times 10^{-3}$  mol/L). However,  $R_p$  becomes independent of  $[\text{ICl}]$  for  $[\text{ICl}] > 2.5 \times 10^{-3}$  mol/L.

A plot of  $1/\bar{P}_n$  vs  $R_p/[M]^2$  (Fig. 3) indicates that determination of the  $k_p^2/k_t$  parameter from the usual graphical analysis of  $\bar{P}_n$  and  $R_p$

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

$[\text{ICl}] \times 10^4$ mol/L	$R_p \times 10^5$ mol/L·s	$[\eta]$ (dL/g)	$1/\bar{P}_n \times 10^2$	$R_p/[\text{M}]^2 \times 10^5$
5.32	2.54	0.667	0.0773	0.0327
10.20	3.24	0.490	0.1161	0.0418
14.40	4.01	0.430	0.1380	0.0517
20.60	4.55	0.303	0.2187	0.0587
24.74	4.66	0.244	0.2912	0.0601
30.92	4.80	0.200	0.3773	0.0619
41.20	5.20	0.147	0.5659	0.0670
51.54	5.32	0.145	0.5793	0.0686
61.80	5.00	0.118	0.7610	0.0645
73.40	5.30	-	-	-

FIG. 2. Plot of  $\log R_p$  vs  $\log [\text{ICl}]$  for photopolymerization of MMA in bulk at 40°C.

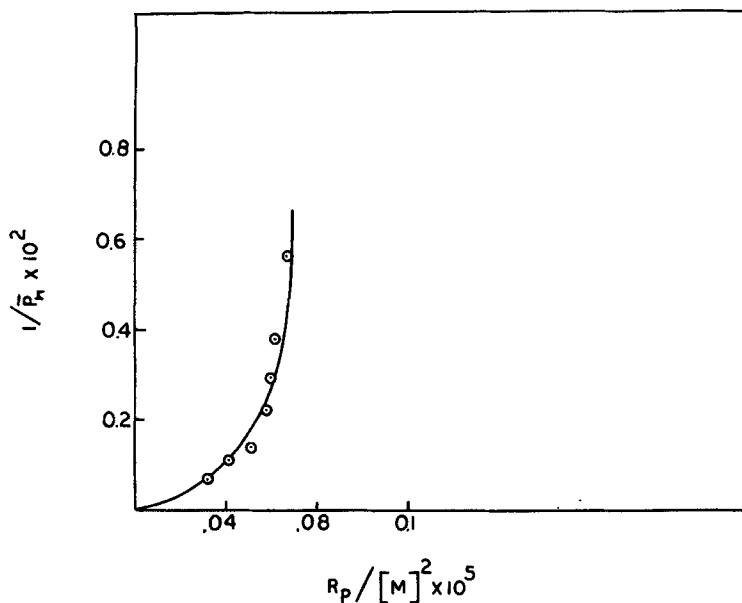


FIG. 3. Plot of  $1/\bar{P}_n$  vs  $R_p/[M]^2$  for photopolymerization of MMA in bulk at 40°C.

data for the present photopolymerization system is difficult and uncertain due to a sharp upward deviation from linearity right from the beginning. The nature of the plot is also indicative of a prominent initiator transfer effect which appears to become degradative in nature at high  $[ICl]$ . For calculations, the  $k_p^2/k_t$  value at 40°C is taken [4] as  $1.4 \times 10^{-2}$  L/mol·s.

The apparent activation energy  $E_a$  ( $E_a = E_p - E_t/2$ ) of this photopolymerization is 5.2 kcal/mol.

### Polymerization in Solution

Photopolymerization of MMA at 40°C, with the use of ICl photo-initiator, revealed an interesting phenomenon in diluted system using benzene, carbon tetrachloride, chloroform, and chlorobenzene as solvents. For  $[ICl] < 2.5 \times 10^{-3}$  mol/L, the monomer exponent in each solvent system, i.e., the slope of  $\log R_p$  vs  $\log [M]$  plot (Fig. 4) is close to 2.0, while it is close to 3.0 for  $[ICl] > 2.5 \times 10^{-3}$  mol/L.

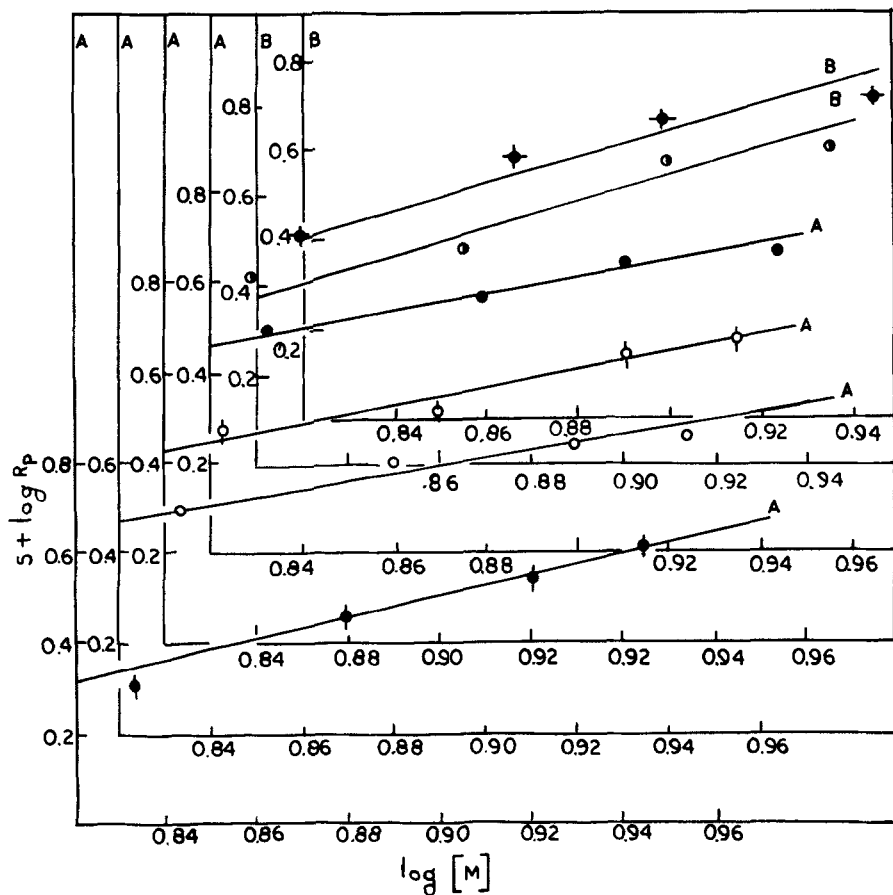


FIG. 4. Plot of  $\log R_p$  vs  $\log [M]$  for photopolymerization of MMA in diluted systems. For each curve, data given are  $[ICl]$  in mol/L. Solvent and slope: (A):  $\blacklozenge 14.4 \times 10^{-4}$ ,  $CHCl_3$ , 2.2;  $\bullet 24.74 \times 10^{-4}$ ,  $CCl_4$ , 1.92;  $\bullet 20.6 \times 10^{-4}$ ,  $C_6H_6$ , 1.85;  $\circ 20.6 \times 10^{-4}$ ,  $C_6H_5Cl$ , 2.1. (B):  $\bullet 61.8 \times 10^{-4}$ ,  $CCl_4$ , 2.9;  $\blacklozenge 61.8 \times 10^{-4}$ ,  $CHCl_3$ , 2.9.

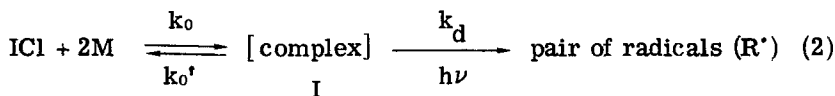
## DISCUSSION

### Mechanism

$ICl$ -initiated photopolymerization of MMA was found to be strongly inhibited in the presence of hydroquinone. Polymers prepared gave a positive response to the dye partition test of Palit et al. [5] for the

presence of halogen atom end groups in them. These observations indicate a radical mechanism, and the following steps may be considered for the mechanism of ICl-induced photopolymerization of MMA.

Radical generation process:

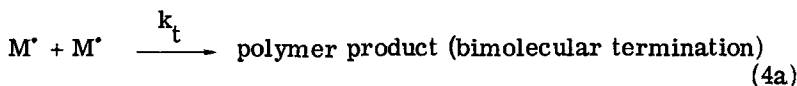


Propagation:

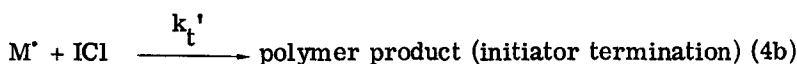


Termination:

Route I (at low [ICl]):



Route II (at high [ICl]):



The rate of (propagation) polymerization  $R_p$  can then be expressed as:

Case I (for [ICl],  $< 2.5 \times 10^{-3}$  mol/L):

$$R_p = k_p (fk_d K_o / k_t)^{0.5} [\text{ICl}]^{0.5} [\text{M}]^2 \quad (5)$$

Case II (at high [ICl],  $> 2.5 \times 10^{-3}$  mol/L):

$$R_p = k_p (2fk_d K_o / k_t') [\text{M}]^3 \quad (6)$$

Here I is the initiating complex formed in situ between an iodine monochloride molecule and two monomer molecules, R' is the initiating radical, M and M' are the monomer molecules and growing chains respectively and  $K_o$  is given by  $k_o/k_{o'}$ . The overall mechanism is much like that considered for the IBr-induced photopolymerization of MMA [1].



The two rate Eqs. (5) and (6) clearly explain our experimental observations, i.e., a monomer exponent of 2.0 and an initiator exponent of 0.5 for low  $[ICl]$  ( $< 2.5 \times 10^{-3}$  mol/L) and a monomer exponent of 3.0 and an initiator exponent of 0 for high  $[ICl]$  ( $> 2.5 \times 10^{-3}$  mol/L).

### Degradative Initiator Transfer

The pronounced nonideality in the present photopolymerization at high  $[ICl]$  arises due to degradative initiator transfer. To analyze this possibility, we assume that the primary radical termination effect is negligible in the higher initiator concentration range where  $R_p$  is practically independent of  $[ICl]$ .

For analysis of the effect of degradative initiator transfer in vinyl polymerization radically initiated by the decomposition of a lone initiator, I, Deb and Mayerhoff [6] deduced a suitable expression which was further simplified by Ghosh et al. [4]:

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

For the present system,  $[I] \approx K_0 [ICl][M]^2$ , and hence the above equation will take the form

$$\ln \frac{R_p^2}{[ICl][M]^4} = \ln \frac{fk_d K_0 k_p^2}{k_t} - \frac{k_p^2}{k_t} \frac{k_{rtI}}{k_{iI} k_p} K_0 C_I [ICl][M]$$

or

$$\log \frac{R_p^2}{[ICl][M]^4} = \log fk_d K_0 \frac{k_p^2}{k_t} - 0.434 \frac{k_p^2}{k_t} \frac{k_{rtI}}{k_{iI} k_p} K_0 C_I [ICl][M] \quad (7)$$

From a graphical plot of the left-hand side of Eq. (7) against  $[ICl][M]$ , with data for bulk polymerization (Fig. 5), it is seen that up to  $[ICl] = 2.5 \times 10^{-3}$  mol/L the experimental points fall on a straight line parallel to the abscissa, indicating thereby a negligible initiator-dependent termination, the significant termination mechanism being bimolecular in nature. But for  $[ICl] > 2.5 \times 10^{-3}$  mol/L, the experimental points fall on a straight line with a negative slope, indicating significant initiator-dependent termination (degradative initiator transfer). The value of the parameter  $fk_d K_0$  at 40°C, evaluated from the intercept, is found to be  $0.125 \times 10^{-7}$  L<sup>2</sup>/mol<sup>2</sup>·s. Likewise, the value of

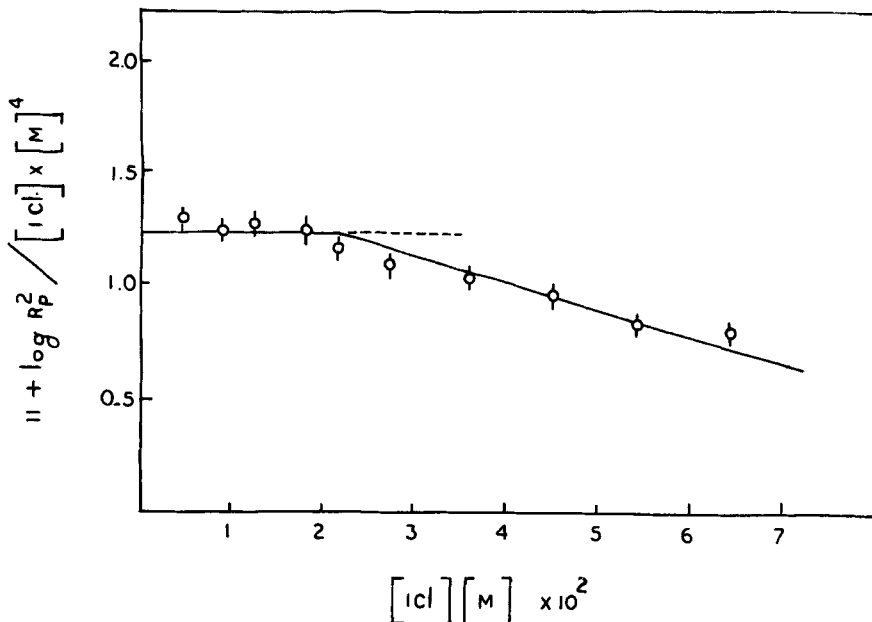


FIG. 5. Plot of  $\log R_p^2 / ([ICl][M]^4)$  vs  $[ICl][M]$  for photopolymerization of MMA in bulk at 40°C for analysis of degradative initiator transfer (with reinitiation effect).

$(k_{rtI}/k_{il}k_p)K_0C_P$  determined from the slope, is  $0.192 \times 10^4$  Ls/mol. The value of the important initiator termination parameter  $k_{rtI}/k_{il}k_p$  can then be evaluated from the knowledge of the initiator transfer parameter  $K_0C_P$  where  $C_I$  is the initiator transfer constant.

Initiator Transfer Parameter,  $K_0C_I$

Determination of  $K_0C_I$  is done with the help of the Mayo equation which assumes the following form to describe the present photopolymerization in bulk:

$$\frac{1}{P_n} - 1.85 \frac{k_t}{k_p^2} \frac{R_p}{[M]^2} = C_M + K_0C_I [ICl][M] \tag{8}$$

The value of  $K_0C_P$  computed from the slope of the plot of the left-hand

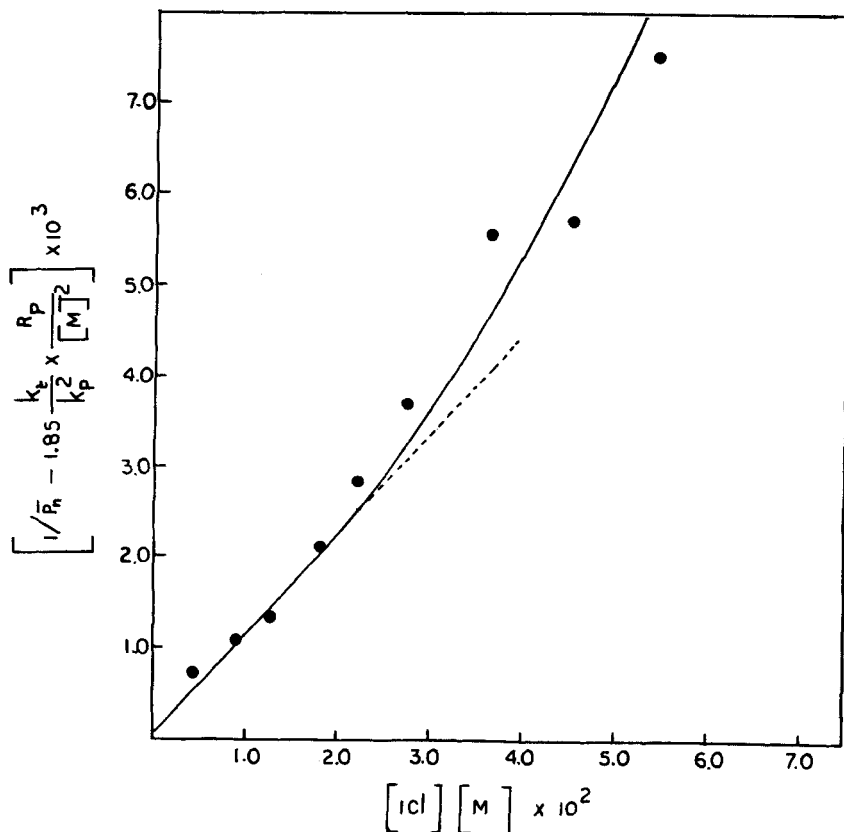
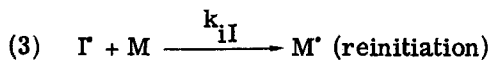
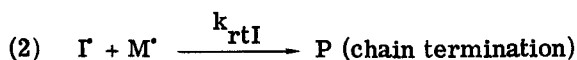
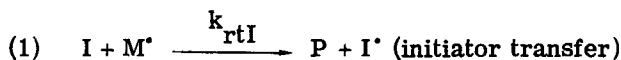


FIG. 6. Plot of  $1/\bar{P}_n - (1.85k_t R_p/k_p^2 [M]^2)$  vs  $[ICl][M]$  for photopolymerization of MMA in bulk at  $40^\circ\text{C}$  for determination of initiator transfer constant.

side of Eq. (8) vs  $[ICl][M]$  (Fig. 6), is  $0.112 \text{ L}^2/\text{mol}^2$ . At a high initiator concentration ( $[ICl] > 2.5 \times 10^{-3} \text{ mol/L}$ ), the plot is seen to deviate from the initial linearity,  $\bar{P}_n$  values becoming unusually low, primarily because the initiator transfer process under this condition becomes degradative in nature. The calculated value of the initiator termination parameter  $k_{rti}/k_{il}k_p$  is  $1.71 \times 10^4 \text{ mol}\cdot\text{s/L}$ .

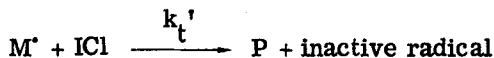
#### Reaction Scheme to Describe Nonideality

Following the initiator transfer reaction, we may consider two more reaction steps to account for the degradative effect:



Having observed normal kinetics at low [ICl] and with a good indication for a near-normal chain transfer effect under this condition, Reaction Step (2) appears to be inconsequential at low [ICl], and the values of  $k_{iI}$  and  $k_p$  seem to be comparable. At high [ICl], the concentration of radical  $I^*$  derived in Step (1) becoming relatively high, Step (2) assumes significance, leading to the degradative effect observed. Mutual annihilation of radicals  $I^*$  under this condition, however remote otherwise, cannot possibly be completely ruled out.

We may, however, consider a more simplified reaction to describe the initiator-dependent termination, intrinsically different from that considered above:



Here, chain termination by the free iodine monochloride is considered to take place by direct reaction without a reinitiation effect. Evidently the derived radical intermediate is considered to be inherently inactive or it becomes inactive by some uncertain mechanism.

Under Steady Condition

$$\frac{R_i}{R_p} = \frac{\text{Overall rate of termination}}{R_p} = \frac{2k_t[M^*]^2 + k'_t[M^*][ICl]}{R_p}$$

or

$$R_i = \frac{2k_t R_p^2}{k_p^2 [M]^2} + \frac{k'_t [ICl]}{k_p [M]} R_p = 2fk_d K_0 [ICl] [M]^2$$

or

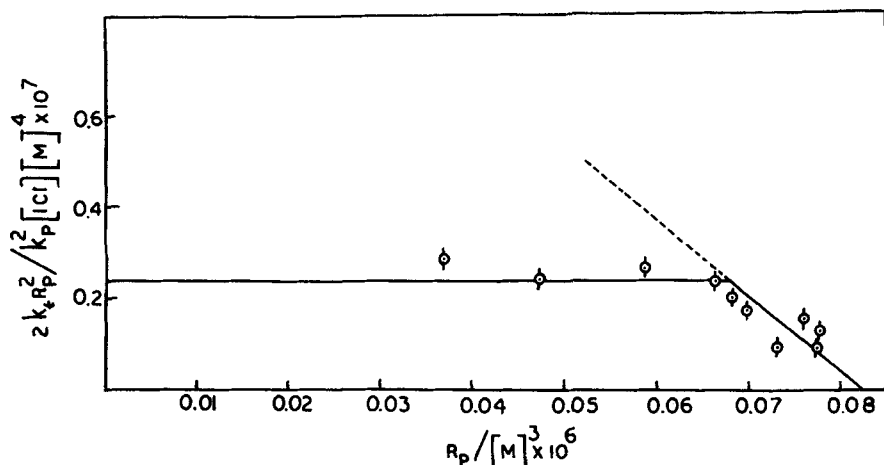


FIG. 7. Plot of  $(2k_t R_p^2 / k_p^2 [ICl][M]^4)$  vs  $R_p / [M]^3$  for photopolymerization of MMA in bulk at  $40^\circ\text{C}$  for analysis of initiator termination via degradative chain transfer with no reinitiation effect.

$$\frac{2k_t R_p^2}{k_p^2 [ICl][M]^4} = 2fk_d K_0 - \frac{k_t'}{k_p} \frac{R_p}{[M]^3} \quad (9)$$

For significant initiator-dependent termination via degradative initiator transfer with little reinitiation effect, a plot of  $2k_t R_p^2 / k_p^2 [ICl][M]^4$  vs  $R_p / [M]^3$  should give a straight line with a negative slope. This is actually observed with data at a high range of  $[ICl]$ , while in a low  $[ICl]$  range the slope is practically zero, indicating termination to be exclusively bimolecular in nature. The calculated values of  $(k_t'/k_p)$  and  $(fk_d K_0)$  computed from the slope and intercept of the plot (Fig. 7) are 1.66 and  $0.12 \times 10^{-7} \text{ L}^2/\text{mol}^2 \cdot \text{s}$ , respectively. It is interesting to note that the calculated values of  $fk_d K_0$  on the basis of Eqs. (7) and (9) are in good agreement.

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