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Polymerization of Methyl Methacrylate Using Acridone-Bromine Combination as the Photoinitiator

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ABSTRACT

The photopolymerization of methyl methacrylate (MMA) in visible light was studied at 40°C using the acridone-bromine (acridone-Br_2) combination as the photoinitiator. The polymerization was found to proceed via a free radical mechanism, and the radical generation process was considered to follow an initial complexation reaction between monomer and each initiator component (acridone and Br_2), followed by further interaction between these two initiator-monomer complexes. Kinetic data indicated a lower-order dependence of R_p on initiator concentrations (initiator exponent < 0.5). Initiator-dependent chain termination was significant along with the usual bimolecular mode of chain termination. The monomer exponent varied from about 1.00 to 2.00, depending on the nature of solvents used. The nonidealities in this system were also analyzed.

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INTRODUCTION

A nitrogen-bearing heterocyclic compound, acridone [1], is known to induce polymerization of methyl methacrylate (MMA) under photoactive condition, but the inhibition period is high and the rate of polymerization (R_p) is moderate. When bromine (Br_2) is used in combination with acridone, the polymerization system is characterized by a negligible inhibition period and a high rate of polymerization. It is also reported [2] that bromine forms charge-transfer complexes with some heterocyclic (nitrogen-bearing) compounds which also act as photoinitiators in vinyl polymerization. Studies of the effect of a photoactive compound, such as bromine, on the kinetics and related features of acridone-induced photopolymerization were therefore considered to be of immediate interest and relevance in this context. The present paper reports the results of our kinetic investigations of MMA polymerization using a combination of acridone and bromine as the photoinitiator.

EXPERIMENTAL

Materials

Monomer (MMA) and solvents were purified by standard techniques as described in earlier papers [2, 3]. Acridone was prepared and purified in this laboratory by standard procedures [4]. Merck analytical grade bromine was used without further purification.

Polymerization

The photopolymerization of MMA was studied dilatometrically under nitrogen atmosphere at $40 \pm 0.05°C$ in the presence of a 125-W high-pressure mercury vapor lamp using a combination of acridone and bromine as the photoinitiator. Polymers formed at low conversions (< 10%) were removed from the dilatometer, then precipitated, washed with petroleum ether, and finally dried in vacuo.

Intrinsic Viscosity

Intrinsic viscosities $[\eta]$ of the polymers taken in benzene solution were measured at $30 \pm 0.05°C$ according to the usual procedure. Molecular weights ($\overline{M}_n$) and hence degrees of polymerization ($\overline{P}_n$) of polymers were determined by using the relationship [5]

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

RESULTS

The photopolymerization of MMA in visible light was readily induced by the acridone-Br_2 combination as the initiator; no polymerization was, however, observed within 150 min at 40°C in the dark using the same initiator combination. The inhibition periods for the photopolymerization of MMA with the acridone-Br_2 combination as the initiator were found to be almost negligible compared to those observed for the photopolymerization of MMA with acridone used alone as the initiator. The rates of acridone-induced photopolymerization are significantly enhanced when Br_2 is used in combination with acridone as the initiator in the same system. Bromine alone, however, fails to initiate polymerization of MMA at 40°C within 25 min under the same experimental conditions (Table 1). It is therefore apparent that the acridone-Br_2 combination is an adequate system for MMA polymerization. Hydroquinone produced strong inhibitory effects on the photopolymerization of MMA initiated by the acridone-Br_2 combination. The prepared polymers gave a positive response to the dye partition test, indicating a halogen endgroup [6].

Spectroscopic Studies of the Acridone-Br_2-MMA System

Formation of complexes between acridone and MMA and between Br_2 and MMA have been reported from our laboratory [1, 3] as evidenced by visible and UV absorption studies.

In the present studies, visible and UV absorption spectra of dilute solutions of acridone (1×10^{-4} mol/L), Br_2 (1×10^{-3} mol/L), and a mixture of acridone (1×10^{-4} mol/L) and Br_2 (1×10^{-3} mol/L) in CCl_4 are given in Fig. 1a. From this figure it is clear that the spectrum of the mixture (acridone and Br_2) is just the summation of the spectra of acridone (λ_{max} 392, 373, 305, and 262 nm) and Br_2 (λ_{max} 400-420 nm), thereby indicating that no interaction takes place between acridone and Br_2 in CCl_4.

Spectral studies of dilute solutions of acridone, Br_2, and their mixture in MMA were also carried out, and the relevant data are given in

TABLE 1. Photopolymerization of MMA at 40°C Using Acridone, Bromine, and Acridone-Br_2 Combination as Initiator

[Acridone] $\times 10^4$ mol/L	[Bromine] $\times 10^3$ mol/L	Inhibition period (min)	$R_p \times 10^5$ mol/L
2.0286	-	45	11.1111
-	9.645	25	5.2083
2.0286	9.645	0	45.454

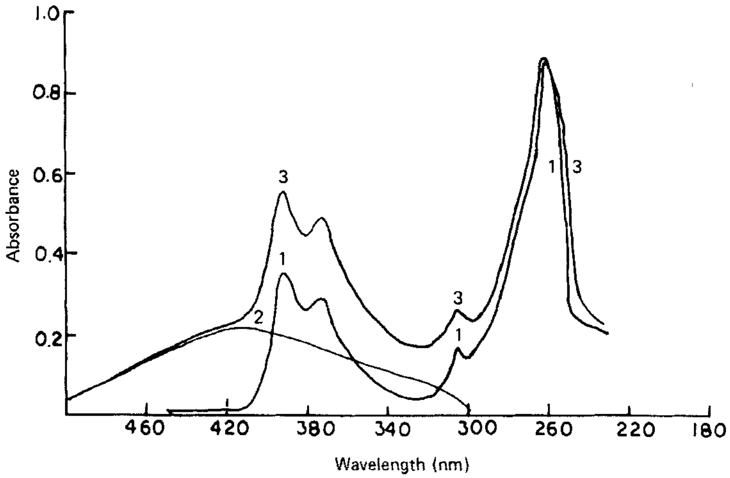


FIG. 1a. Visible and near-ultraviolet absorption spectra of (1) acridone (1×10^{-4} mol/L) in CCl_4, (2) bromine (1×10^{-3} mol/L) in CCl_4, and (3) mixture of bromine (1×10^{-3} mol/L) and acridone (1×10^{-4} mol/L) in CCl_4.

Fig. 1b. From this figure it is seen that the absorbance values of a given mixture of acridone and Br_2 in MMA are the same as the addition of the absorbance of the corresponding solutions of acridone-MMA (λ_{max} 383 and 260 nm) and Br_2-MMA (λ_{max} 410-415 and 256 nm). Therefore, no complexation or related interaction between acridone or acridone-MMA complex on the one hand, and Br_2 or Br_2-MMA complex on the other, is indicated from our spectral studies.

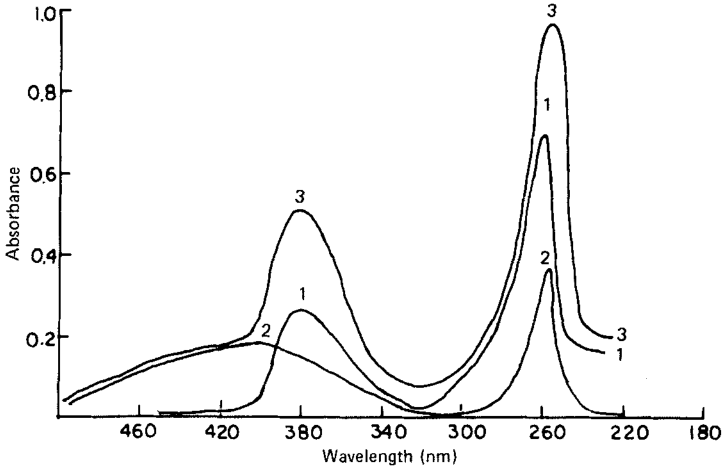


FIG. 1b. Visible and near-ultraviolet absorption spectra of (1) acridone (1×10^{-4} mol/L) in MMA, (2) Br_2 (1×10^{-3} mol/L) in MMA, and (3) mixture of acridone (1×10^{-4} mol/L) in Br_2 (1×10^{-3} mol/L) in MMA.

Kinetics of Photopolymerization of MMA Using Acridone-Br_2 Combination as Initiator

Initiator Exponent

Results of two sets of experiments (bulk polymerization of MMA at 40°C), one with fixed [acridone] and varying [Br_2] and the other with fixed [Br_2] and varying [acridone] are presented in Table 2. Slopes of the corresponding logarithmic plots, Figs. 2a and 2b, give the value of the bromine exponent as 0.354 and of the acridone exponent as 0.263, respectively. The initiator exponents observed are less than expected from the usual square-root dependence for free radical polymerization [3]. Thus the low initiator exponents indicate some initiator-dependent termination along with the usual bimolecular mode of termination.

k_p^2/k_t Value

The kinetic parameter k_p^2/k_t at 40°C was evaluated from $\bar{P}_n$ and R_p data; that is, from the slope of the plot of $1/\bar{P}_n$ vs $R_p/[M]^2$ shown in Fig. 3 and Table 2, in accordance with the Mayo equation [7] written in the following form for the present system:

TABLE 2. Photopolymerization of MMA at 40°C Using Acridone-Br_2 Combination as Initiator

[Acridone] × 10^4 mol/L	[Bromine] × 10^3 mol/L	$R_p \times 10^4$ mol/L·s	$\frac{R_p}{[M]^2} \times 10^5$	[η] (dL/g)	$\frac{1}{\bar{P}_n} \times 10^3$	Initiator exponent	$\frac{k_p^2}{k_t} \times 10^2$
2.0286	0.1929	1.1366	0.1370	0.798	0.61		
"	0.3858	1.2820	0.1545	0.788	0.62		
"	0.7395	1.7730	0.2137	0.704	0.72		
"	0.9645	2.1276	0.2564	0.637	0.82	0.3546	
"	1.4468	2.2222	0.2678	0.614	0.862		
"	1.9291	2.3809	0.2870	0.593	0.902		
"	3.8583	3.1250	0.3767	0.540	1.02		
"	9.6458	4.5454	0.5479	0.431	1.367		
							1.123
0.1521	9.984	2.439	0.2940	0.604	0.821		
0.2028	"	2.631	0.3171	0.609	0.897		
0.2537	"	2.857	0.3444	0.584	0.92		
0.4057	"	3.125	0.3767	0.557	0.98	0.263	
0.6085	"	3.333	0.4017	0.53	1.045		
0.8114	"	3.5714	0.4303	0.503	1.12		
1.0143	"	4.0000	0.4821	0.468	1.23		
2.0286	"	4.5600	0.5497	0.432	1.37		
4.0572	"	4.347	0.5240	0.434	1.381		

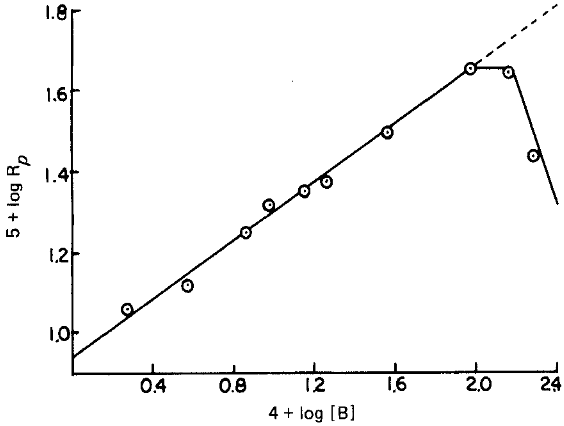


FIG. 2a. Photopolymerization of MMA in bulk at 40°C using acridone-Br_2 combination as photoinitiator. Plot of log R_p vs log [B] at fixed acridone concentration [A] and varying bromine concentration [B].

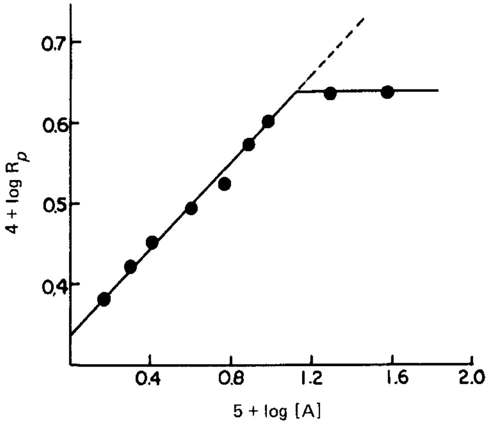


FIG. 2b. Photopolymerization of MMA in bulk at 40°C using acridone Br_2 combination as photoinitiator. Plot of log R_p vs log [A] at fixed bromine concentration [B] and varying acridone concentration [A].

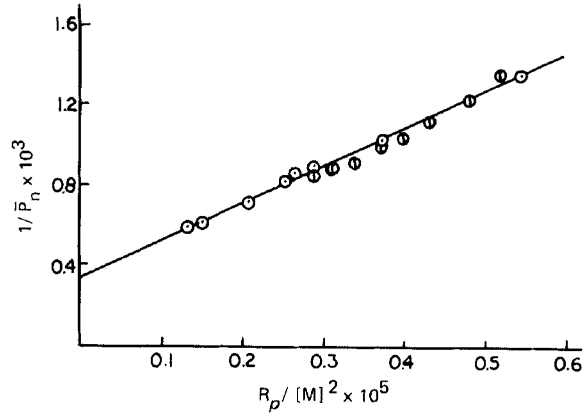


FIG. 3. Photopolymerization of MMA in bulk at 40°C using acridone-Br_2 combination as photoinitiator. Plot of $1/\bar{P}_n$ vs $R_p/[M]^2$. (⊙) Fixed [A]; (⦶) fixed [B].

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

where the last term in the right-hand side is included to account for chain transfer effects, assuming that this would not affect the slope of the plot over the low range of initiator concentration. The apparent k_p^2/k_t value calculated from the slope of the initial linear zone of the plot is 1.123×10^{-2} L/mol·s. It was assumed in the calculation that perturbation of the termination process from the usual bimolecular mechanism [8] (85% disproportionation, 15% combination) will not measurably affect the initial slope of the plot in Fig. 3.

Monomer Exponent

The photopolymerization of MMA was also studied at 40°C using fixed concentrations of acridone (1.0143×10^{-4} mol/L) and bromine (9.666×10^{-3} mol/L) in the presence of different concentrations of several solvents such as benzene, acetone, chloroform, dimethylformamide, and carbon tetrachloride. Monomer exponents, calculated from the slope of the respective plots of log R_p vs log [M] in the unusual dilution range shown in Fig. 4, are 2.0 in C_6H_6, 1.00 in acetone, 1.00 in $CHCl_3$, 1.034 in DMF, and 1.05 in CCl_4.

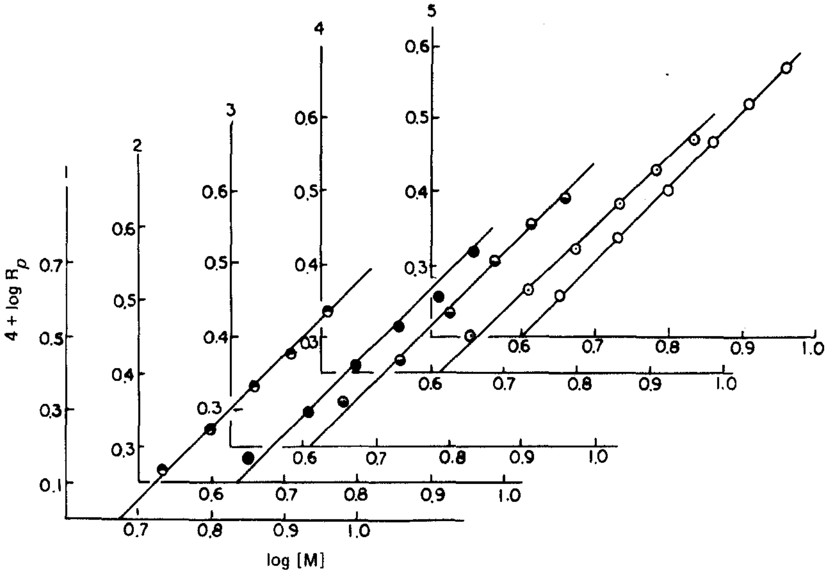


FIG. 4. Photopolymerization of MMA in solution at 40°C using acridone-Br_2 combination as photoinitiator. Plot of log R_p vs log [M]. Concentration of acridone (1.0143×10^{-4} mol/L) and bromine (9.666×10^{-3} mol/L) are fixed for each case. Data given for each curve are solvent and monomer exponent:

(1)	◓	C_6H_6;	2.00
(2)	●	CCl_4;	1.05
(3)	◒	Acetone;	1.00
(4)	◉	$CHCl_3$;	1.00
(5)	○	DMF;	1.03

Activation Energy

The photopolymerization of MMA in bulk was also carried out at four different temperatures (40, 45, 50, and 55°C) using fixed concentrations of acridone (8.114×10^{-5} mol/L) and bromine (9.984×10^{-3} mol/L). From the slope of the Arrhenius plot (log R_p vs 1/T) shown in Fig. 5, the apparent activation energy, E_a, for the present system was calculated to be 4.18 kcal/mol, and this value is close to some of the reported values of activation energy for the photopolymerization of MMA [9].

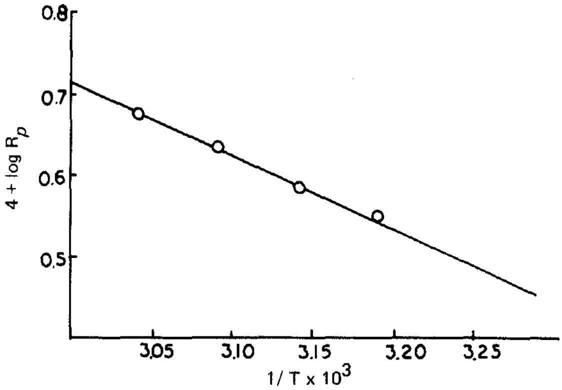
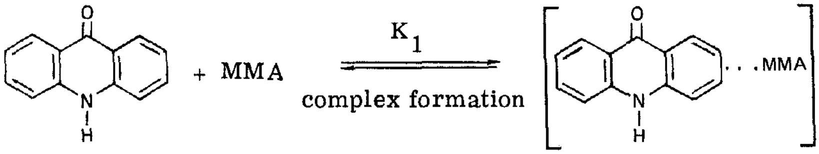


FIG. 5. Effect of temperature on the photopolymerization of MMA using acridone-Br_2 combination as photoinitiator. Plot of log R_p vs 1/T.

MECHANISM

Kinetic data, the inhibitory effect of hydroquinone, and endgroup analysis indicate a radical mechanism for this polymerization system. The radical generation process may be considered to follow an initial complexation reaction between monomer and each initiator component (acridone and Br_2) as evidenced by spectral analysis.



Acridone (A) (M) Complex I_1

$K_1[A][M]$ (3)

$$\underset{(B)}{Br_2} + \underset{(M)}{MMA} \underset{\text{complex formation}}{\overset{K_2}{\rightleftharpoons}} \underset{\text{Complex } I_2}{[Br\text{–}Br. . .MMA]} \qquad K_2[B][M] \tag{4}$$

$$I_1 + I_2 \xrightarrow[\text{production of primary radical}]{k_d} 2R^{\bullet} \text{ (pair of radicals)}$$

$$2fk_dK_1K_2 \times [A][B][M]^2 \tag{5}$$

$$R^{\bullet} + M \xrightarrow[\text{initiation of polymer chain}]{k_i} M^{\bullet} \qquad k_i[R^{\bullet}][M] \tag{6}$$

$$M^{\bullet} + M \xrightarrow[\text{propagation}]{k_p} M_1^{\bullet} \qquad k_p[M^{\bullet}][M] = R_p \tag{6a}$$

$$M_1^{\bullet} + M \longrightarrow M_2^{\bullet} \tag{6b}$$

$$\vdots \quad \vdots$$

$$M^{\circ} + M^{\bullet} \xrightarrow[\text{termination of growing chains by mutual deactivation}]{k_t} \text{polymer} \qquad k_t[M^{\bullet}]^2 \tag{7}$$

Concentration of the actual initiating species, I_1 and I_2, can be taken to be equal to $K_1[A][M]$ and $K_2[B][M]$, respectively, where K_1 and K_2 are the equilibrium constants for the acridone-monomer and bromine-monomer complexation reactions, respectively. The factor f represents total efficiency of the initiator, and the k_d, k_i, k_p, and k_t have the usual significance.

Termination

The observed low initiator exponent values (< 0.5) indicate that some initiator-dependent termination process is significant along with the usual mode of bimolecular termination. The initiator-dependent termination may arise due to primary radical termination and/or degradative initiator transfer:

(i) Primary radical termination:

$$M^{\bullet} + R^{\bullet} \xrightarrow{k_{prt}} \text{polymer product} \qquad k_{prt}[M^{\bullet}][R^{\bullet}] \tag{8}$$

(ii) Termination via degradative initiator transfer with little reinitiation:

$$I_1 + I_2 + M^{\bullet} \xrightarrow{k_t'} \begin{array}{l}\text{polymer product} \\ \text{nonradical} \\ \text{or inactive} \\ \text{radical byproduct}\end{array} + k_t'[I_1][I_2][M^{\bullet}] \qquad (9)$$

Analysis of Primary Radical Termination Effect

The primary radical termination effect in the absence of any degradative initiator transfer process may be evaluated by using the equation derived by Deb-Meyerhoff [10] in the following form:

$$\log \frac{R_p^2}{[A][B][M]^4} = \log \frac{fk_dK_1K_2kp^2}{k_t} - 0.8684 \frac{k_{prt}}{k_ik_p} \frac{R_p}{[M]^2} \qquad (10)$$

The left-hand side of Eq. (10) was plotted against $R_p/[M]^2$ and the plot gave a straight line with negative slope, shown in Fig. 6, thereby indicating a measurable primary radical termination effect. The value of the parameter k_{prt}/k_ik_p as obtained from the slope is 1.178×10^5.

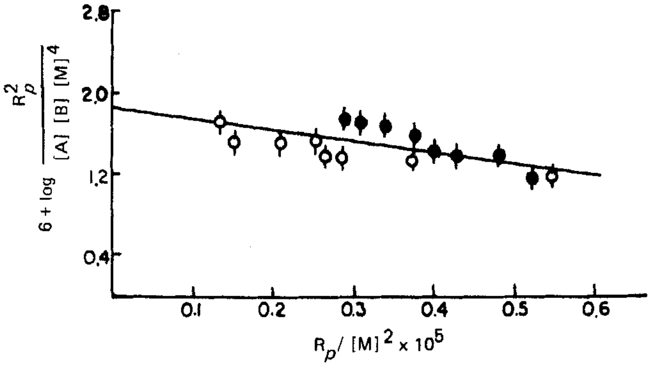


FIG. 6. Analysis of primary radical termination effect on the photopolymerization of MMA at 40°C using acridone-Br_2 combination as photoinitiator. Plot of $\log R_p^2/[A][B][M]^4$ vs $R_p/[M]^2$. (○) Fixed [A]; (●) fixed [B].

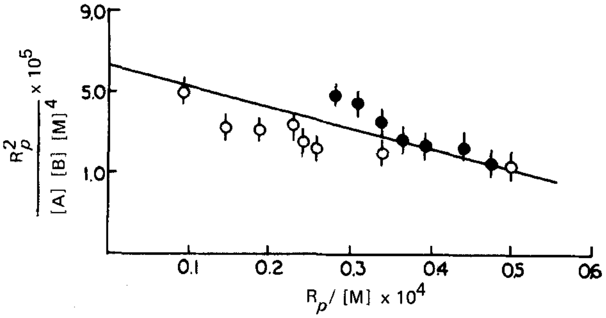


FIG. 7. Analysis of degradative initiator transfer effect (with little reinitiation) on the photopolymerization of MMA at 40°C using acridone-Br_2 combination as photoinitiator. Plot of $R_p^2/[A][B][M]^4$ vs $R_p/[M]$. (○) Fixed [A]; (●) fixed [B].

Analysis of Degradative Initiator Transfer with Little Reinitiation Effect

In the absence of primary radical termination and assuming steady-state condition, a simple kinetic analysis leads to

$$2k_t[M^\cdot]^2 = 2fk_dK_1K_2[A][B][M]^{2-} - k_t'[I_1][I_2][M^\cdot] \tag{11}$$

or

$$2\frac{k_t}{k_p^2}\,\frac{R_p^2}{[M]^2} = 2fk_dK_1K_2[A][B][M]^2 - \frac{k_t'K_1K_2[A][B][M]R_p}{k_p} \tag{12}$$

or

$$\frac{R_p^2}{[A][B][M]^4} = \frac{fk_dK_1K_2k_p^2}{k_t} - \frac{k_t'K_1K_2k_p}{2k_t}\,\frac{R_p}{[M]} \tag{13}$$

A plot of the left-hand side of Eq. (13) against $R_p/[M]$, which gives a straight line with negative slope (Fig. 7), is obtained for the present polymerization of MMA. The nature of the plot is similar to that shown in Fig. 6, and the values of $fk_dK_1K_2k_p^2/k_t$ obtained from both plots (Figs. 6 and 7) are very close. The value of $K_t'K_1K_2/k_p$ as calculated from the slope of the plot (Fig. 7) is 1.92 × 10^2, and gives clear evidence for the degradative initiator transfer.

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