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

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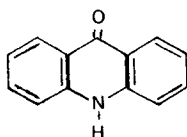
ABSTRACT

The photopolymerization of methyl methacrylate (MMA) in visible light was kinetically studied at 40°C using the acridone-chlorine (acridone-Cl₂) 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 (MMA) and each initiator component (acridone and Cl₂). Kinetic data indicated a lower order dependence of R_p on initiator concentration (initiator exponent < 0.5), and the monomer exponent varied from about 1.00 to 1.25, depending on the nature of the solvents used. Initiator-dependent chain termination was significant along with the usual bimolecular mode of chain termination. The nonidealities in this system are analyzed.

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INTRODUCTION

It has been recently reported from our laboratory that acridone [1]



can easily initiate vinyl polymerization under photoactive condition, and it has been also observed that the polymerization system was highly improved in the acridone-bromine [2] combination than that of acridone alone. Studies of the effect of photoactive compound, such as chlorine, on the kinetic and related features of acridone-induced photopolymerization was therefore considered to be of immediate interest and relevance in this context. The present paper reports the results of our kinetic investigation of methyl methacrylate (MMA) polymerization using the acridone-Cl₂ combination as the photoinitiator.

EXPERIMENTAL

Materials

Monomer (MMA) and solvents were purified by standard techniques as described in earlier papers [3, 4]. Acridone was prepared and purified in this laboratory by the standard procedures [5]. Chlorine was prepared in this laboratory by oxidation of hydrochloric acid (A.R. grade) with pure potassium permanganate. The liberated chlorine gas was bubbled through a scrubber of distilled water and then through another scrubber of concentrated sulfuric acid (A.R. grade). The purified Cl₂ gas was finally dissolved in purified carbon tetrachloride at low temperature (<5°C) to the desired range of concentration, and the concentration was determined iodometrically.

Polymerization

The photopolymerization of MMA in bulk and in solution was carried out dilatometrically under a nitrogen atmosphere at $40 \pm 0.01^\circ\text{C}$, and illuminated by a 125-W high-pressure mercury vapor lamp using a combination of acridone and chlorine as the photoinitiator. Polymers formed at low conversions (<10%) were removed from the dilatometer, precipitated, washed, and finally dried in vacuo.

Intrinsic Viscosity

The intrinsic viscosities $[\eta]$ of the polymers were measured in benzene solution at $30 \pm 0.01^\circ\text{C}$ according to the usual procedure. Molecular weights (\bar{M}_n) and hence degrees of polymerization, \bar{P}_n , of polymers were determined using the relationship [6]

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

RESULTS

The photopolymerization of MMA in visible light was readily induced by the acridone- Cl_2 combination as the initiator; no polymerization was observed, however, within 120 min at 40°C in the dark using the same initiator combination. The inhibition periods for the photopolymerization with the acridone- Cl_2 combination as initiator were only 0-5 min, which are significantly lower than those observed for the photopolymerization of MMA with either acridone [1] (IP 40-100 min) or chlorine (IP 20-100 min) alone as initiator are presented in Table 1. The rates of acridone-induced photopolymerization were also significantly enhanced by the presence of chlorine in the system shown in Table 1. From the experimental results it is seen that the presence of chlorine brings about an overall improvement in the acridone-induced photopolymerization of MMA. Hydroquinone produced a strong inhibitory effect on the photopolymerization of MMA initiated by the acridone- Cl_2 combination. The prepared polymers gave a positive response to the dye partition test, indicating a halogen endgroup [7].

TABLE 1. Photopolymerization of MMA at 40°C Using Acridone, Chlorine, and the Acridone- Cl_2 Combination as Initiators

[Acridone] $\times 10^4$ mol/L	[Chlorine] $\times 10^3$ mol/L	Inhibition period (min)	$R_p \times 10^5$ mol/L·s
2.0286	-	45	11.111
-	5.523	20	4.016
2.0286	5.523	5	16.129

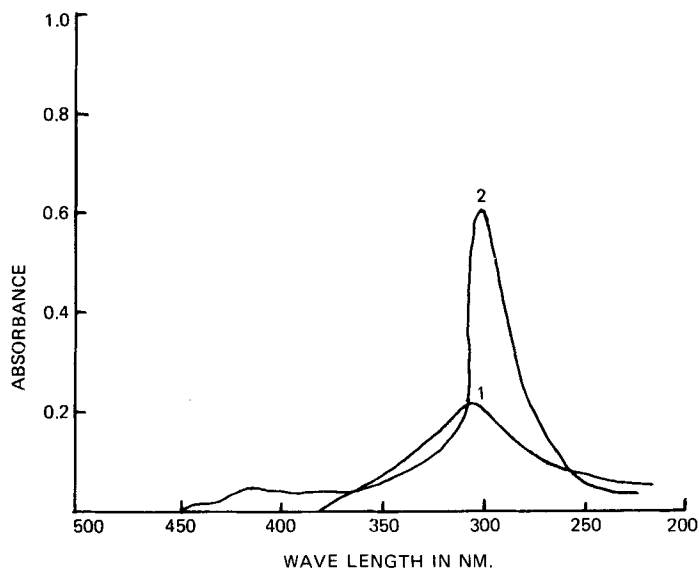


FIG. 1a. Visible and near-ultraviolet absorption spectra of (1) chlorine (1×10^{-4} mol/L) in CCl_4 and (2) chlorine (1×10^{-4} mol/L) in MMA.

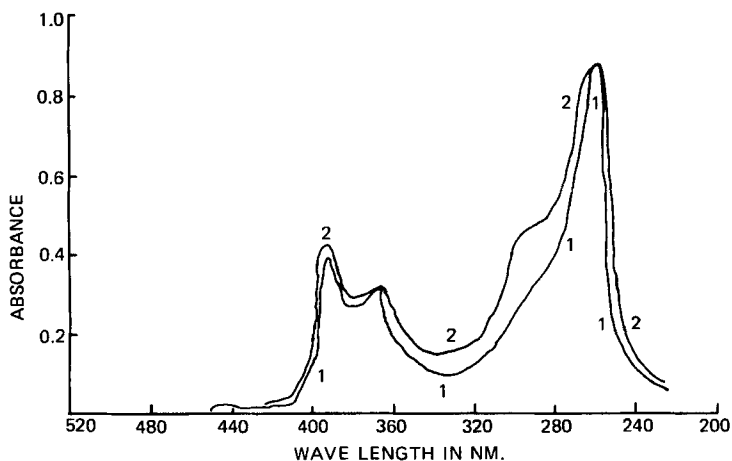


FIG. 1b. Visible and near-ultraviolet absorption spectra of (1) mixture of acridone (1×10^{-4} mol/L) and chlorine (1×10^{-4} mol/L) in CCl_4 , and (2) mixture of acridone (1×10^{-4} mol/L) and chlorine (1×10^{-4} mol/L) in MMA.

Spectroscopic Studies

It has been recently reported that acridone forms a complex with MMA [1]. Absorption spectra in the visible and near-ultraviolet region for chlorine in CCl_4 and in MMA solution clearly indicate the formation of a complex between chlorine and MMA as shown in Fig. 1a. UV and visible absorption spectra of a mixture of acridone and chlorine in a 1:1 molar proportion in CCl_4 and in MMA are given in Fig. 1b. From Fig. 1b it is also clear that there is no complexation or related interaction between acridone or the acridone-MMA complex on the one hand and Cl_2 or the Cl_2 -MMA complex on the other hand.

Kinetics of Photopolymerization of MMA Using the Acridone- Cl_2 Combination

Results of two sets of experiments (bulk polymerization of MMA at 40°C), one with fixed [acridone] and varying [Cl_2] and the other with fixed [Cl_2] and varying [acridone], are presented in Table 2.

The slope of the corresponding logarithmic plots (Fig. 2) give a chlorine exponent of 0.036 and an acridone exponent of 0.277. When acridone is used alone, the initiator exponent was found to be 0.32 [1], which is slightly higher than that obtained for the acridone exponent by using the acridone- Cl_2 combination as the initiator in bulk. A similar trend was observed when Cl_2 was used alone as a photoinitiator; the Cl_2 exponent is 0.11 (Fig. 3), and it was significantly higher than the Cl_2 exponent of 0.036 obtained from the present system.

The contribution to the rate of polymerization in the combined system (acridone- Cl_2) due to chlorine is calculated from

$$R_{P_C} = \sqrt{R_{P_{A-C}}^2 - R_{P_A}'^2} \quad (2)$$

Similarly the contribution for R_{P_A} due to acridone is calculated from the formula

$$R_{P_A} = \sqrt{R_{P_{A-C}}^2 - R_{P_C}'^2} \quad (3)$$

TABLE 2. Photopolymerization of MMA at 40°C using the Acridone-Cl₂ Combination as Initiator

[Acridone] × 10 ⁴ mol/L	[Chlorine] × 10 ³ mol/L	R _P ^{A-C} × 10 ⁵ mol/L·s	$\frac{R_P^{A-C}}{[M]^2} \times 10^5$	[η] (dL/g)	1/ $\bar{P}_n \times 10^3$	Initiator exponent	k _P ² /k _t × 10 ²
4.0572	0.2523	12.500	0.1506	0.927	0.501		
"	0.3784	12.658	0.1525	0.887	0.530		
"	0.5047	12.820	0.1545	0.880	0.534		
"	0.6309	12.987	0.1565	0.870	0.545	0.036	
"	1.2618	13.157	0.1586	0.846	0.565		
"	2.5232	13.513	0.1629	0.830	0.578		
"	3.7844	13.698	0.1651	0.820	0.590		
"	5.0472	13.888	0.1674	0.824	0.585		
"	6.3090	13.888	-	-	-		0.573
0.1521	5.5231	7.936	0.0956	1.315	0.316		
0.2028	"	8.474	0.1021	1.260	0.334		
0.2537	"	9.259	0.1116	1.170	0.368		
0.4057	"	10.101	0.1217	1.02	0.463	0.277	
0.6085	"	11.764	0.1418	0.940	0.492		
0.8114	"	12.345	0.1488	0.930	0.499		
1.0143	"	13.513	0.1629	0.840	0.570		
2.0286	"	16.129	0.1944	0.775	0.634		
4.0572	"	13.888	-	-	-		

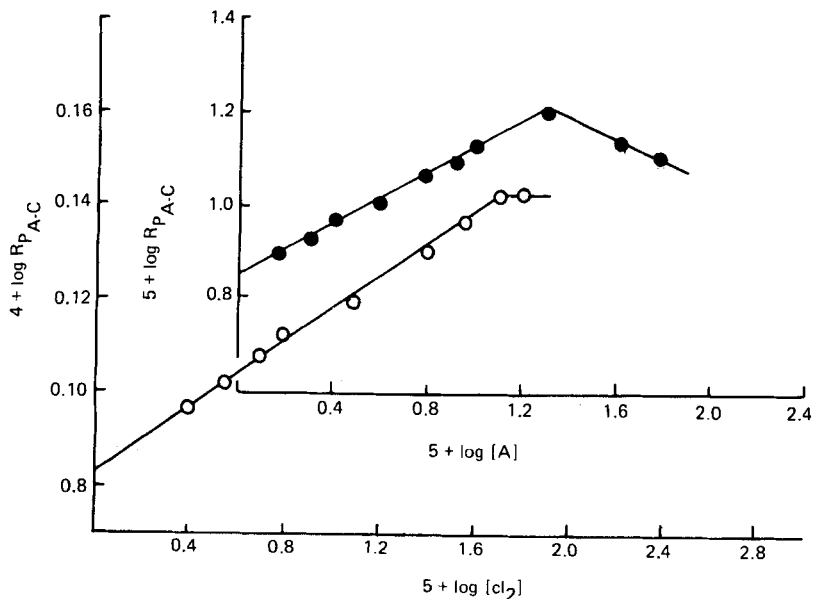


FIG. 2. Photopolymerization of MMA in bulk at 40°C using acridone- Cl_2 combination as photoinitiator Plot of $\log R_{P_{A-C}}$ vs $\log [\text{Cl}_2]$ at fixed acridone concentration $[\text{A}]$ and varying chlorine concentration $[\text{Cl}_2]$ (○). Plot of $\log R_{P_{A-C}}$ vs $\log [\text{A}]$ at fixed chlorine concentration $[\text{Cl}_2]$ and varying acridone concentration $[\text{A}]$ (●).

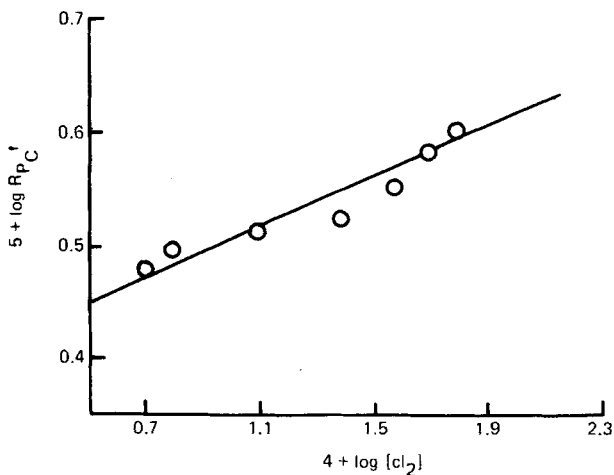


FIG. 3. Photopolymerization of MMA in bulk at 40°C using chlorine as photoinitiator. Plot of $\log R_{P_C}$ vs $\log [\text{Cl}_2]$.

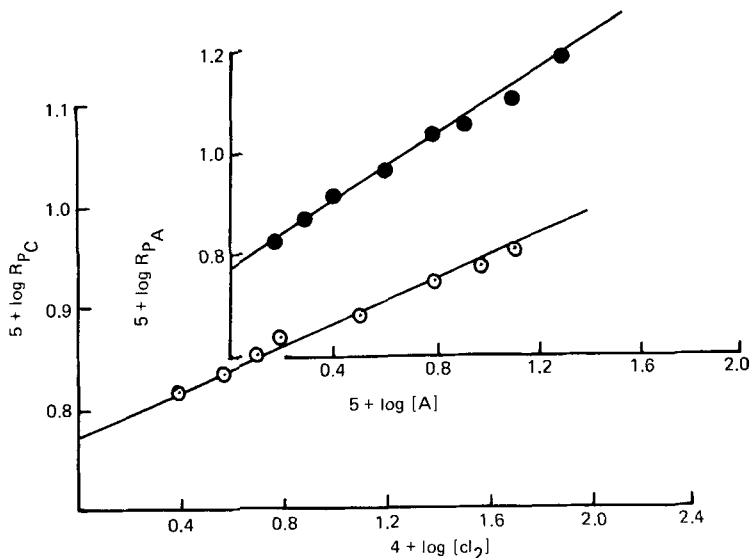


FIG. 4. Photopolymerization of MMA in bulk at 40°C using acridone-Cl₂ combination as photoinitiator. Plot of log R_{P_C} vs log [Cl₂] (⊙).

Plot of log R_{P_A} vs log [A] (●).

where R_{P_{A-C}} is the rate of polymerization using the acridone-Cl₂ combination as the initiator and R_{P_A} and R_{P_C} are the rates of polymerization using acridone and chlorine independently as the initiators in the polymerization of MMA.

Slopes of the plots of log R_{P_C} vs log [Cl₂] and log R_{P_A} vs log [acridone] (Fig. 4) give the value of the initiator exponent of chlorine as 0.11 and of the initiator exponent for acridone as 0.32, and these values are exactly equal to the acridone exponent and Cl₂ exponent when they are used separately as the photoinitiator (Tables 3A and 3B).

k_P²/k_t Value

The kinetic parameter k_P²/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_{A-C}}/[M]²,

TABLE 3A. Photopolymerization of MMA at 40°C Using the Acridone-Cl₂ Combination as Initiator

[Acridone] × 10 ⁴ mol/L	[Chlorine] × 10 ³ mol/L	R _{P A-C} × 10 ⁵ mol/L·s	R _{P A} × 10 ⁵ mol/L·s	R _{P C} × 10 ⁵ mol/L·s
4.0572	0.2523	12.500	10.638	6.564
"	0.3784	12.658	"	6.860
"	0.5047	12.820	"	7.154
"	0.6309	12.987	"	7.449
"	1.2618	13.157	"	7.742
"	2.5232	13.513	"	8.333
"	3.7844	13.698	"	8.629
"	5.0472	13.888	"	8.928

TABLE 3B. Photopolymerization of MMA at 40° C Using the Acridone-Cl₂ Combination as Initiator

[Acridone] × 10 ⁴ mol/L	[Chlorine] × 10 ³ mol/L	R _P _{A-C} × 10 ⁵ mol/L·s	R _P _C × 10 ⁵ mol/L·s	R _P _A × 10 ⁵ mol/L·s
0.1521	5.5231	7.936	4.016	6.818
0.2028	"	8.474	"	7.438
0.2537	"	9.259	"	8.321
0.4057	"	10.101	"	9.248
0.6085	"	11.764	"	11.041
0.8114	"	12.345	"	11.658
1.0143	"	13.513	"	12.888
2.0286	"	16.129	"	15.609

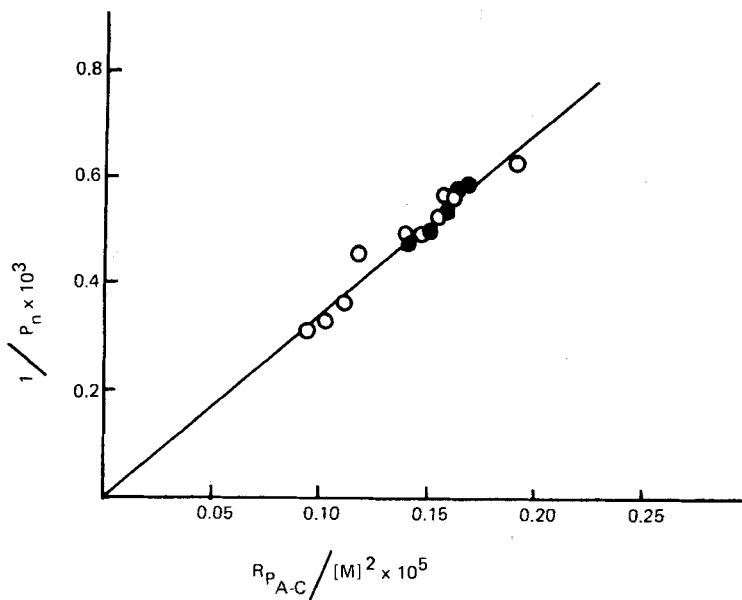


FIG. 5. Photopolymerization of MMA in bulk at 40°C using acridone-Cl₂ combination as photoinitiator. Plot of $1/\bar{P}_n$ vs $R_{P_{A-C}}/[M]^2$. (•) Varying [Cl₂] and fixed [A]. (○) Fixed [Cl₂] and varying [A].

shown in Fig. 5 and Table 2, in accordance with the Mayo equation [8] written in the following form for the present system:

$$\frac{1}{\bar{P}_n} = 1.85 \frac{k_t}{k_p^2} \frac{R_{P_{A-C}}}{[M]^2} + \sum \frac{R_{tr}}{R_{P_{A-C}}} \quad (4)$$

where the last term on the right-hand side was included to account for chain transfer effects (normally, this would not affect the slope of the plot over the low range of initiator concentration). The value of k_p^2/k_t computed from the slope of this linear plot (Fig. 5) is 0.57×10^{-2}

L/mol's. It was assumed in the calculation that perturbation of the termination process by the usual bimolecular mechanism [9] (85% disproportionation, 15% combination) will not measurably affect the initial

slope of the plot in Fig. 5. This value is lower than some of the reported values [3, 4].

Monomer Exponent

The photopolymerization of MMA was also studied at 40°C using the acridone-Cl₂ combination as initiator at fixed concentrations (acridone 1.0143×10^{-4} mol/L and chlorine 6.55×10^{-3} mol/L) in the presence of varying concentrations of such solvents as benzene (C₆H₆), acetone, and chloroform (CHCl₃). The monomer exponents calculated from the slope of the respective plots of $\log R_{P_{A-C}}$ vs $\log [M]$ in the usual

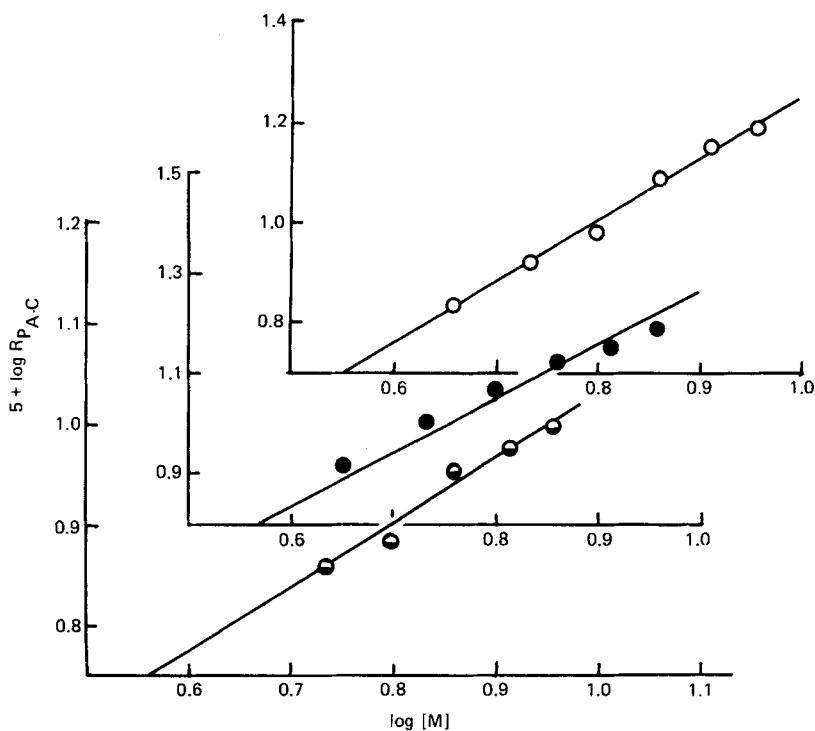


FIG. 6. Photopolymerization of MMA in solution at 40°C using acridone-Cl₂ combination as photoinitiator. Plot of $\log R_{P_{A-C}}$ vs $\log [M]$. Data given for each curve are solvent and monomer exponent. (●) C₆H₆, 1.25; (●) CHCl₃, 1.0; (○) acetone, 1.21.

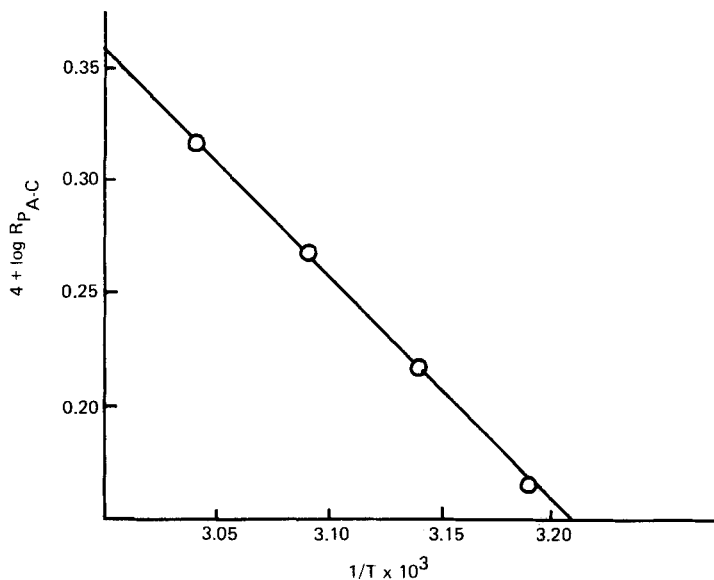


FIG. 7. Effect of temperature on the photopolymerization of MMA using acridone- Cl_2 combination as photoinitiator. Plot of $\log R_{P_{A-C}}$ vs $1/T$.

dilution range shown in Fig. 6 are 1.25 in C_6H_6 , 1.21 in acetone, and 1.0 in CHCl_3 .

Activation Energy

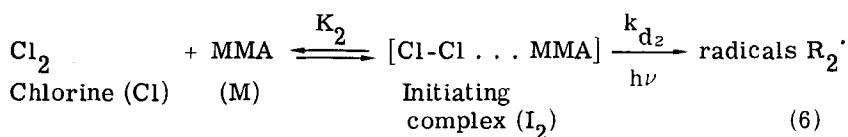
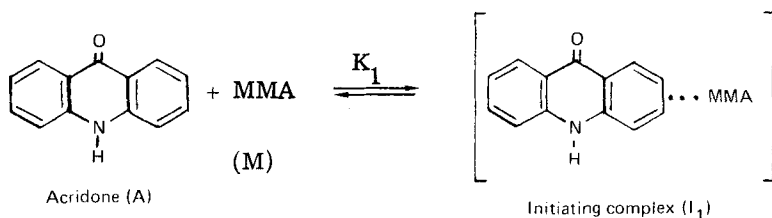
The photopolymerization of MMA was also carried out at different temperatures in the range 40-55°C, using fixed concentrations of acridone (1.0143×10^{-4} mol/L) and chlorine (5.523×10^{-3} mol/L). From the slope of the Arrhenius plot ($\log R_{P_{A-C}}$ vs $1/T$) shown in

Fig. 7, the apparent activation energy, E_a , for the present system was calculated to be 4.493 kcal/mol, and this value is close to some of the reported activation energy values for the photopolymerization of MMA [4, 10].

DISCUSSION

Mechanism

The photopolymerization of MMA initiated by the acridone- Cl_2 combination was found to be strongly inhibited in the presence of hydroquinone. The polymers prepared gave a positive response to the dye partition test for the presence of a halogen atom. The observations and kinetic data indicate a radical mechanism, and the radical generation process may be considered to follow an initial complexation reaction between monomer and each initiator component (acridone and Cl_2) as evidenced by spectral analysis:



The initial concentrations of the initiating complexes I_1 and I_2 are then equal to $K_1[\text{A}][\text{M}]$ and $K_2[\text{Cl}_2][\text{M}]$, respectively, where K_1 and K_2 are the equilibrium constants for the acridone-monomer and chlorine-monomer complexation reactions, respectively.

In the light of our experimental observations, we propose that the primary radicals $R_1 \cdot$ and $R_2 \cdot$ are the key radicals for initiation of MMA polymerization in the present system. The observed low initiator exponents and k_p^2/k_t values indicate a significant initiator-dependent termination process along with the usual bimolecular termination.

Analysis of Initiator-Dependent Termination in Bulk Photopolymerization with the Acridone-Cl₂ Combination

The initiator-dependent termination may arise due to primary radical termination and/or degradative initiator transfer.

(a) Primary Radical Termination

The primary radical termination effect in the absence of any degradative initiator transfer process may be analyzed by using the equation derived by Deb and Meyerhoff [11], which assumes the following forms for the present photopolymerization system, where the participation of acridone and chlorine has been considered independently:

$$\log \frac{R_P^2}{[A][M]^3} = \log \frac{K_1 f_1 k_{d_1} k_P^2}{k_t} - 0.8684 \frac{k_{Prt}}{k_i k_P} \frac{R_{PA}}{[M]^2} \quad (7)$$

and

$$\log \frac{R_P^2}{[Cl_2][M]^3} = \log \frac{k_2 f_2 k_{d_2} k_P^2}{k_t} - 0.8684 \frac{k_{Prt}}{k_i k_P} \frac{R_{PC}}{[M]^2} \quad (8)$$

The left-hand sides of Eqs. (7) and (8) were plotted against the corresponding $R_P/[M]^2$ value (Fig. 8), and the plots gave a straight line with a negative slope for each curve, thereby clearly indicating a measurable primary radical termination effect. The value of $k_{Prt}/k_i k_P$, calculated from the slope of the plots (Fig. 8), are 0.5443×10^6 for acridone and 2.055×10^6 for chlorine when they are used in combination with each other. When acridone and chlorine are used alone as initiators, the value of $k_{Prt}/k_i k_P$ is 0.619×10^6 for acridone [1] and 3.0×10^6 for chlorine (Fig. 9), respectively. The values of $f_1 k_{d_1} K_1$ and $f_2 k_{d_2} K_2$ are found to be 12.93×10^{-5} for acridone and 5.77×10^{-5} for chlorine (Fig. 8) for the present photopolymerization system. The calculated values of $f k_d K$ for acridone (3.33×10^{-5}) [1] and chlorine (2.82×10^{-5} , Fig. 9), when they are used separately as photoinitiators, are much lower than that of the present initiator system (acridone-Cl₂).

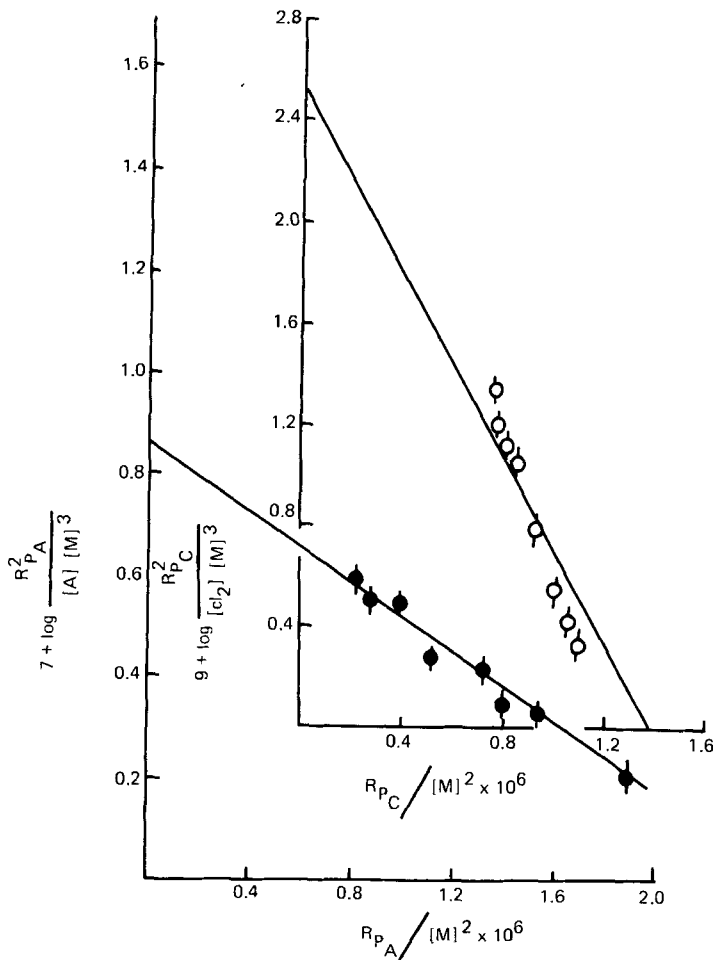


FIG. 8. Analysis of primary radical termination effect on the photopolymerization of MMA at 40°C using acridone-Cl₂ combination as photoinitiator. Plot of $\log R_{P_A}^2/[A][M]^3$ vs $R_{P_A}/[M]^2$, (●). Plot of $\log R_{P_C}^2/[Cl_2][M]^3$ vs $R_{P_C}/[M]^2$, (○).

From the above experimental results it is evident that the rate of initiation for the photopolymerization of MMA with the use of the acridone-Cl₂ combination as the initiator is much higher than that of the respective rates of initiation when acridone and Cl₂ are used independently in the same monomer system.

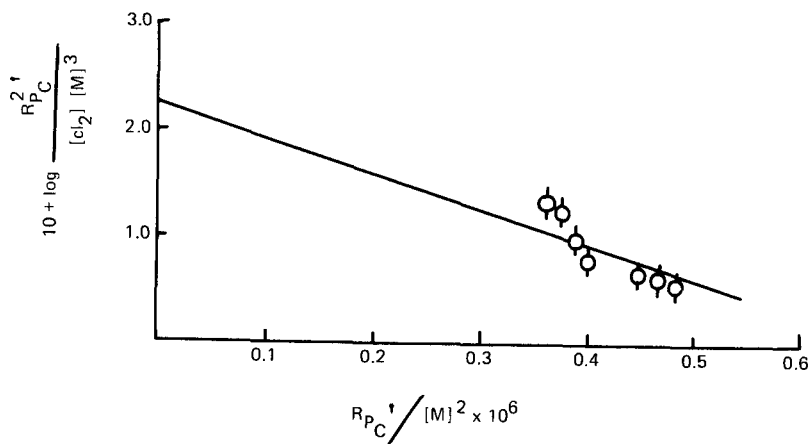


FIG. 9. Primary radical termination effect on the photopolymerization of MMA at 40°C using chlorine as photoinitiator. Plot of $\log R_{P_C}{}^2 / [Cl_2][M]^3$ vs $R_{P_C}' / [M]^2$.

b. Degradative Initiator Transfer with Little Reinitiation Effect

In the absence of any primary radical termination process and under steady-state conditions, the following relationships may be used to analyze termination via degradative initiator transfer for the present photopolymerization system:

$$2 \frac{k_t}{k_P^2} \frac{R_{P_A}^2}{[A][M]^3} = 2f_1 k_{d_1} K_1 - \frac{k_t' K_1}{k_P} \frac{R_{P_A}}{[M]} \quad (9)$$

and

$$2 \frac{k_t}{k_P^2} \frac{R_{P_C}^2}{[Cl_2][M]^3} = 2f_2 k_{d_2} K_2 - \frac{k_t' K_2}{k_P} \frac{R_{P_C}}{[M]} \quad (10)$$

Plots of the left-hand sides of Eqs. (9) and (10) against the corresponding value of $R_P/[M]$ give straight lines with negative slopes (Fig. 10), for the present polymerization of MMA. The values of $k_t' K_1/k_P$ and $k_t' K_2/k_P$ for acridone and chlorine are 12.7 and 2.72, respectively, and give clear evidence of the degradative initiator transfer for the present system.

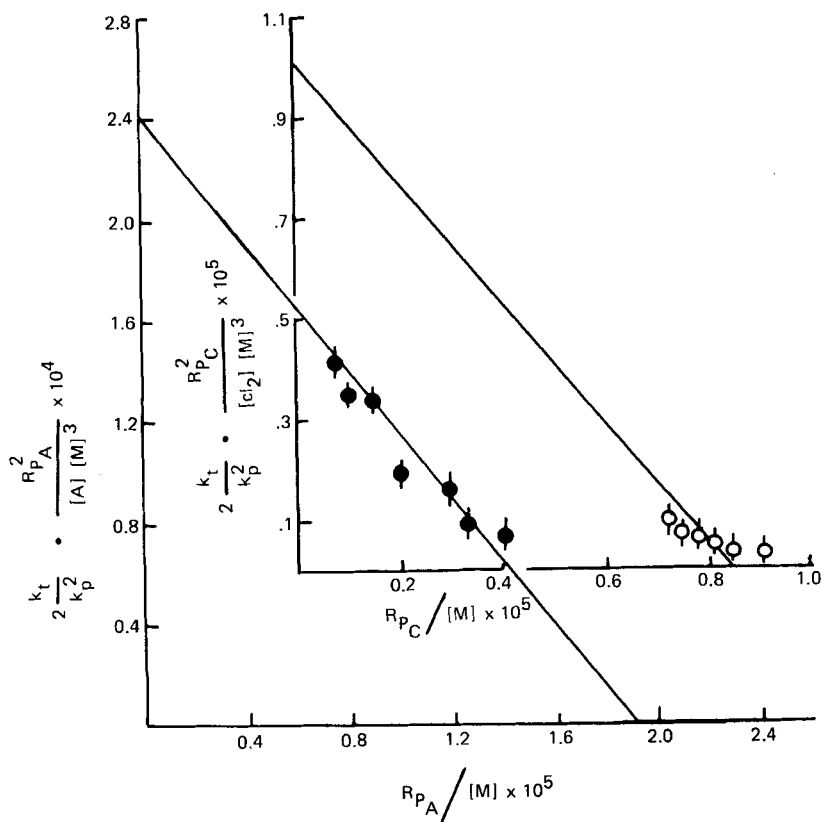


FIG. 10. Analysis of degradative initiator transfer effect (with little reinitiation) on the photopolymerization of MMA at 40°C using acridone-Cl₂ combination as photoinitiator. Plot of $2k_t/k_p^2 \cdot R_{pA}^2 / [A][M]^3$ vs $R_{pA} / [M]$ (•). Plot of $2k_t/k_p^2 \cdot R_{pC}^2 / [Cl_2][M]^3$ vs $R_{pC} / [M]$ (○).

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