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Use of an Internal Keto-Imino Compound as the Photoinitiator in the Polymerization of Methyl Methacrylate

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ABSTRACT

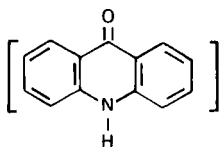
Photopolymerization of MMA in visible light was studied at 40°C using acridone as the photoinitiator. The polymerization was found to proceed via a free radical mechanism and the radical generation process was considered to follow an initial complexation reaction between monomer and acridone. Kinetic data indicated a lower order dependence of R_p on the initiator concentration (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 1.0 to 1.5, depending on the nature of the solvent used. The nonidealities in this case were also analyzed.

INTRODUCTION

It has been reported that certain ketones [1, 2], amines, [3, 4], and a mixture of ketones and amines [5, 6] induce the photopolymerization of vinyl monomers under photoactivation. Studies of the effect of a

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typical heterocyclic compound which has internal keto and imino groups, such as acridone



on the kinetics and related feature of MMA photopolymerization were therefore considered relevant and interesting. Results of related studies are reported in this paper.

EXPERIMENTAL

Materials

Monomer (MMA) and different solvents were purified following standard procedures. Preparation of acridone was by the procedure described elsewhere [7].

Photopolymerization was studied dilatometrically under nitrogen atmosphere at $40 \pm 0.05^\circ\text{C}$ and the various kinetic parameters were determined according to the usual procedures [8]. Polymers formed at low conversions ($< 10\%$) were removed from the dilatometers and isolated by precipitation with petroleum ether and subsequent drying under vacuum at 50°C . Molecular weights (\bar{M}_n) or degree of polymerization (\bar{P}_n) of the polymers were determined viscometrically.

Intrinsic Viscosity

Intrinsic viscosities $[\eta]$ of polymers taken in benzene solution were measured at $30 \pm 0.05^\circ\text{C}$ in a Ubbelohde viscometer according to the usual procedure. Molecular weights (\bar{M}_n) and hence degree of polymerization (\bar{P}_n) of polymers were determined using the relationship [9]

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

RESULTS

Absorption spectra in the visible and near-ultraviolet regions for acridone and a mixture of acridone and MMA in DMF solvent are given in Fig. 1.

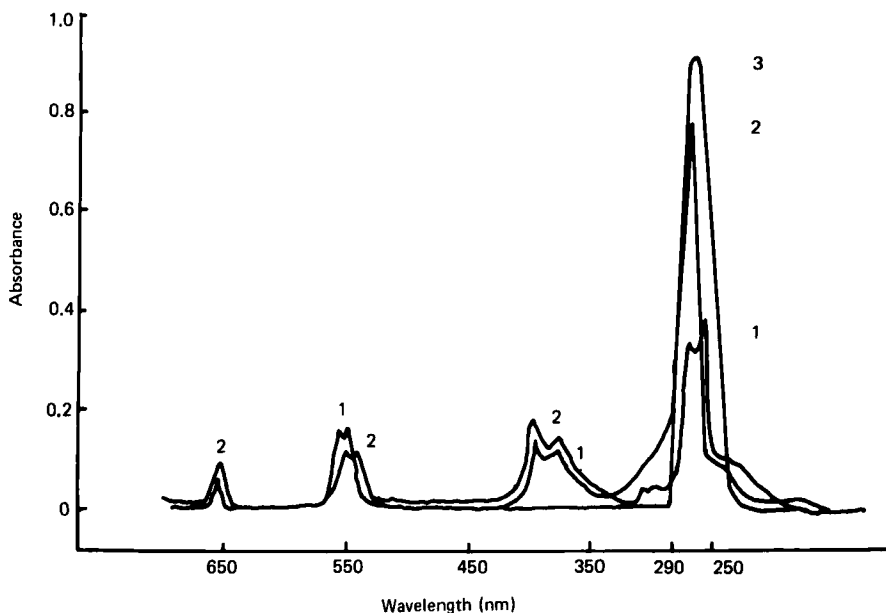


FIG. 1. Visible and near-ultraviolet absorption spectra of (1) acridone (0.0001 mol/L), (2) mixture of acridone and MMA (both 0.0001 mol/L), and (3) MMA (0.0001 mol/L), each in DMF solvent.

In the presence of acridone no polymerization of MMA was observed within 3 h at 40°C in the dark. Polymerization was, however, induced in the presence of light after an inhibition period (IP) of the order of 40 to 100 min, with lower [acridone] giving a higher IP in general. IP is considered to arise due to adventitious impurities (such as traces of oxygen) in the polymerization system.

Initiator Exponent

Data on the bulk photopolymerization of MMA at 40°C using different [acridone] (1.0143×10^{-3} to 1.0143×10^{-5} mol/L) are given in Table 1. Rates of polymerization, R_p , were calculated from the initial linear zones of % conversion vs time plots (Fig. 2). The initiator exponent as determined from the slope of a $\log R_p$ vs \log [acridone] plot (Fig. 3) is 0.33 in the low range [acridone] ($< 2.0286 \times 10^{-4}$ mol/L). However, R_p becomes independent of [acridone] for [acridone] $> 2.0286 \times 10^{-4}$ mol/L. Photopolymerization in contact with air produced slightly enhanced inhibition, but in the presence of dissolved

TABLE 1. Photopolymerization of MMA at 40°C Using Acridone as the Photoinitiator

[Acridone] × 10 ⁴ mol/L	R _p × 10 ⁵ mol/L.s	[η] (dL/g)	$\frac{1}{\bar{P}_n} \times 10^3$	$\frac{R_p}{[M]^2} \times 10^5$	Initiator exponent	$\frac{k_p^2}{k_t} \times 10^2$
0.1014	4.166	2.70	0.1227	0.5023		
0.1521	4.761	2.35	0.1473	0.574		
0.2537	5.872	1.88	0.1976	0.7079		
0.4057	6.592	1.668	0.2312	0.7947		
0.6085	7.246	1.462	0.275	0.8735	0.329	0.958
0.8114	8.620	1.205	0.3559	1.039		
1.014	8.928	1.132	0.385	1.076		
2.0286	11.111	0.849	0.5624	1.339		
4.057	10.638	-	-	-		
6.085	10.635	-	-	-		

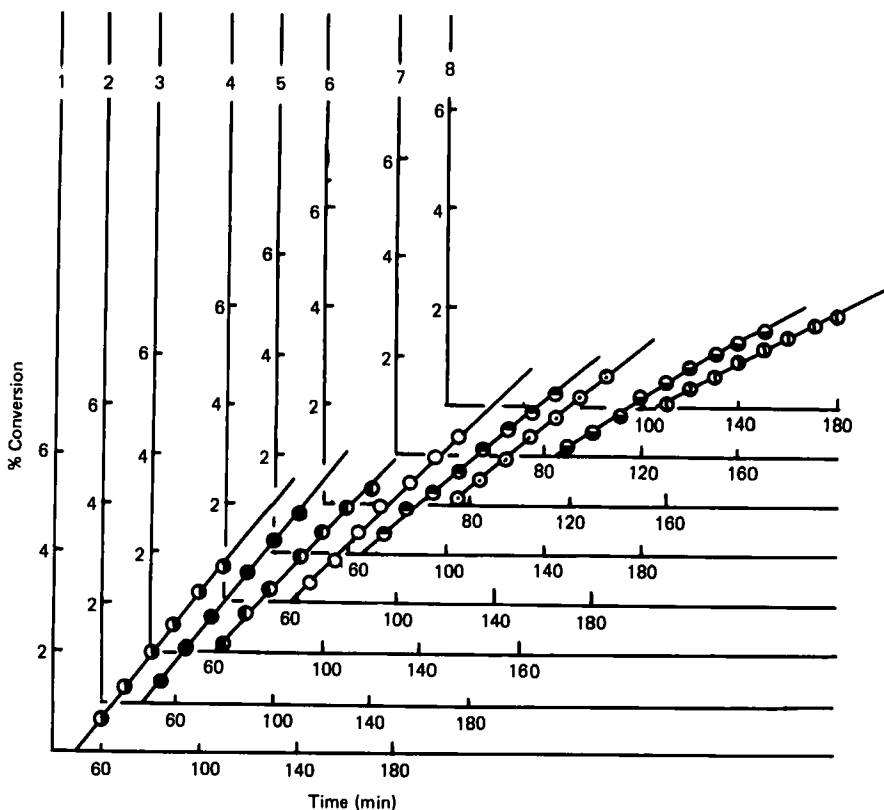


FIG. 2. Photopolymerization of MMA in bulk at 40°C using acridone as photoinitiator. Data given for each curve is [acridone] in mol/L: (1) (◐) 4.057×10^{-4} , (2) (●) 2.028×10^{-4} , (3) (◑) 1.0143×10^{-4} , (4) (◒) 8.114×10^{-5} , (5) (◓) 6.085×10^{-5} , (6) (◔) 4.0572×10^{-5} , (7) (◕) 2.537×10^{-5} , (8) (◖) 1.5214×10^{-5} .

hydroquinone (0.001 mol/L) there was a pronounced inhibition of polymerization.

k_p^2/k_t Value

The kinetic parameter k_p^2/k_t at 40°C was evaluated from the slope of a plot of $1/\bar{P}_n$ vs $R_p/[M]^2$ (Fig. 4) in accordance with the Mayo equation [10]:

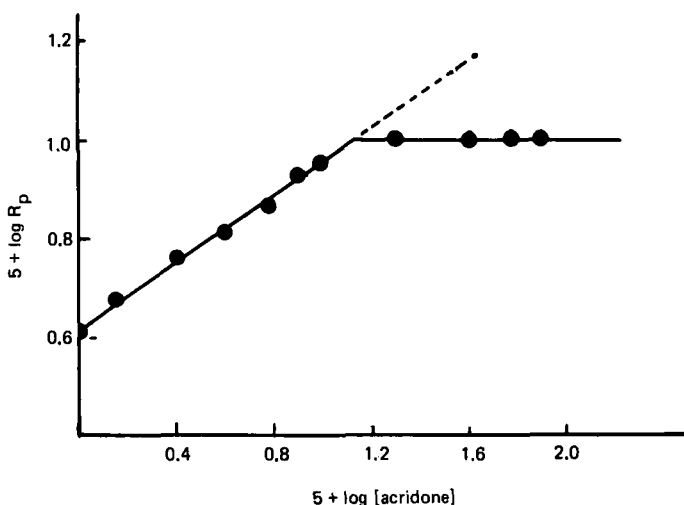


FIG. 3. Photopolymerization of MMA in bulk at 40°C using acridone as photoinitiator.

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

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 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 0.958×10^{-2} L/mol·s. It was assumed in the calculation that perturbation of the termination process from the usual bimolecular mechanism [11] (85% disproportionation, 15% combination) would not measurably affect the initial slope of the plot in Fig. 4.

Monomer Exponent

With a fixed [acridone] for each solvent, photopolymerization of MMA was further studied in the presence of different concentrations of several solvents: benzene, acetone, chloroform, DMF, and carbon tetrachloride. The monomer exponent calculated from the slope of the respective plots of $\log R_p$ vs $\log [M]$ (Fig. 5) ranges between 1.0 to 1.50, depending on the nature of the solvent used.

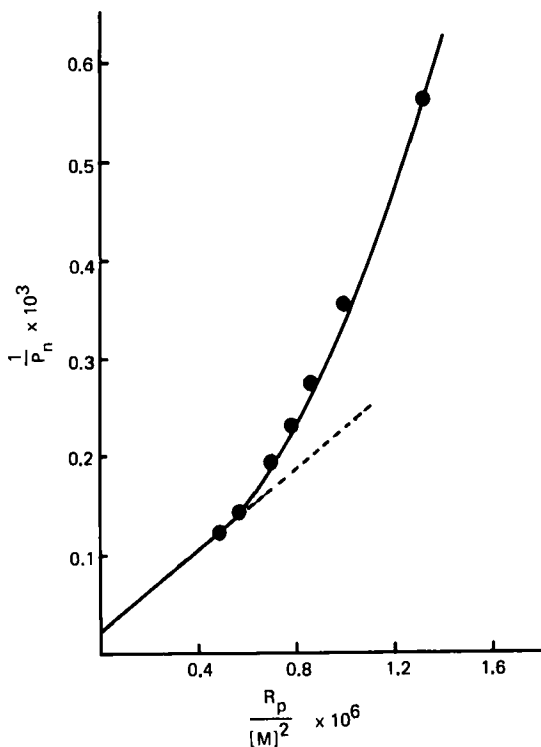


FIG. 4. Photopolymerization of MMA in bulk at 40°C using acridone as photoinitiator.

Activation Energy

The apparent activation energy E_a ($E_a = E_p - E_{t/2}$) for the present photopolymerization was calculated from the Arrhenius plot of $\log R_p$ vs $1/T$ (Fig. 6), where T is the absolute temperature and the value of E_a is found to be 4.83 kcal/mol. This value is slightly higher than some of reported values of activation energy for the photopolymerization of MMA [12].

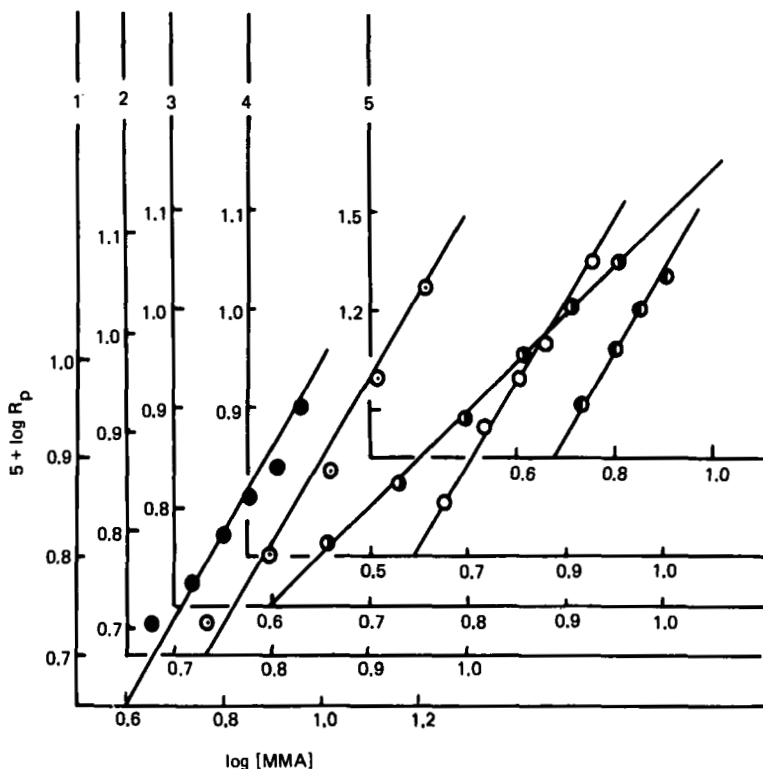


FIG. 5. Photopolymerization of MMA in solution at 40°C using acridone as photoinitiator. Data given for each curve are solvent [acridone] and slope (monomer exponent). (●) C_6H_6 , 1.014×10^{-4} , 1.01; (○) acetone, 2.026×10^{-4} mol/L, 1.5; (◐) $CHCl_3$, 2.026×10^{-4} mol/L, 1.0; (◑) DMF, 2.026×10^{-4} mol/L, 1.0; (◒) CCl_4 , 2.026×10^{-4} mol/L, 1.0.

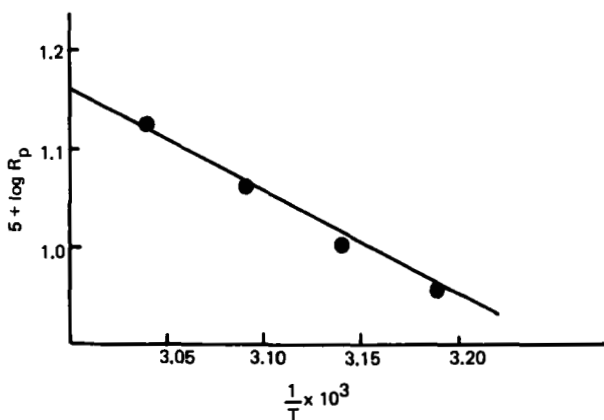
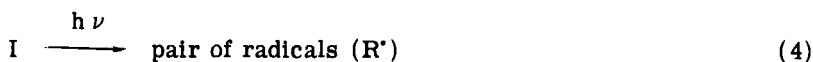
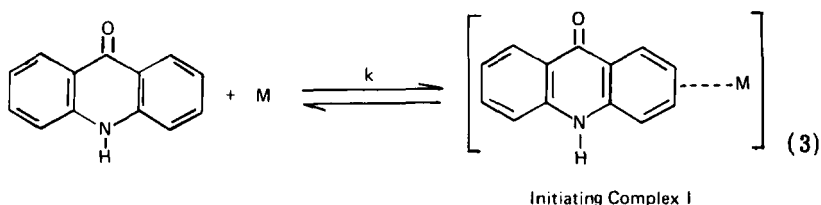


FIG. 6. Photopolymerization of MMA in bulk at 40°C using acridone as photoinitiator.

DISCUSSION

Mechanism

Kinetic data on the inhibitory effect of hydroquinone indicate a radical mechanism for this polymerization system. The radical generation process is considered to follow an initial complexation reaction between monomer and initiator molecules. Evidence of monomer-acridone complexation is shown by the UV absorption spectra in Fig. 1.



The initial concentration of Initiating Complex I is then equal to k [acridone][M], where k is the equilibrium constant for the initiator-monomer complexation reaction.

For bulk photopolymerization, a low acridone exponent (0.33) indicates a significant initiator-dependent termination process along with the usual bimolecular termination.

Initiator Transfer

Equation (2) may be used in the following form to determine the initiator transfer parameter ($C_I K$) where C_I is the initiator transfer constant in the photopolymerization of MMA in bulk:

$$\frac{1}{\bar{P}_n} - 1.85 \frac{k_t}{k_p^2} \frac{R_p}{[M]^2} = C_M + C_I K [\text{acridone}] \quad (5)$$

where [acridone] is the initial concentration of acridone and C_M is the monomer transfer constant. A plot of the left-hand side of Eq. (5) vs [acridone] is given in (Fig. 7), and initial slope of the plot, giving the value of $C_I K$, is 1.724 L/mol.

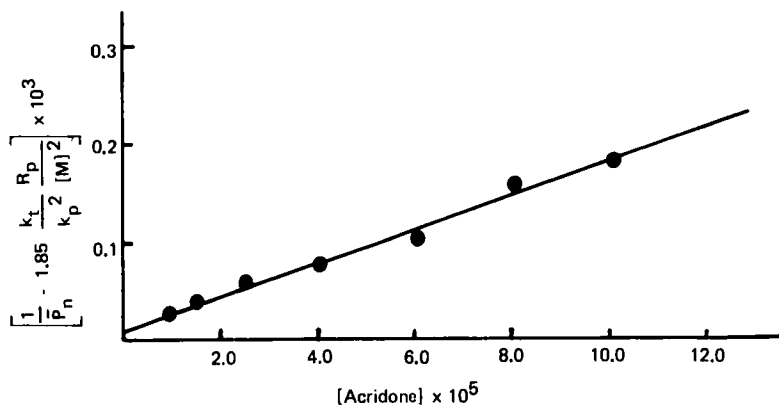


FIG. 7. Photopolymerization of MMA in bulk at 40°C using acridone as photoinitiator.

Solvent Transfer

In the presence of different solvents, Eq. (5) can be written as

$$\frac{1}{\bar{P}_n} - 1.85 \frac{k_t}{k_p^2} \frac{R_p}{[M]^2} = C_M + C_I K[\text{acridone}] + C_S \frac{[S]}{[M]} \quad (6)$$

where C_S is the solvent transfer parameter or chain transfer constant and $[S]$ is the solvent concentration. A plot of the left-hand side of Eq. (6) vs $[S]/[M]$ is given in Fig. 8. From the slope of the corresponding linear plots, the chain transfer constants for dimethylformamide, acetone, chloroform, and benzene in the present photopolymerization at 40°C are 0.84×10^{-4} , 0.55×10^{-3} , 0.163×10^{-3} , and 0.288×10^{-3} , respectively.

Analysis of Initiator-Dependent Termination in Bulk Photopolymerization with Acridone

Initiator-dependent termination may arise due to primary radical termination and/or degradative initiator transfer. The kinetic data collected may be used to analyze these initiator-dependent termination effects [13-16] with the help of the following equations.

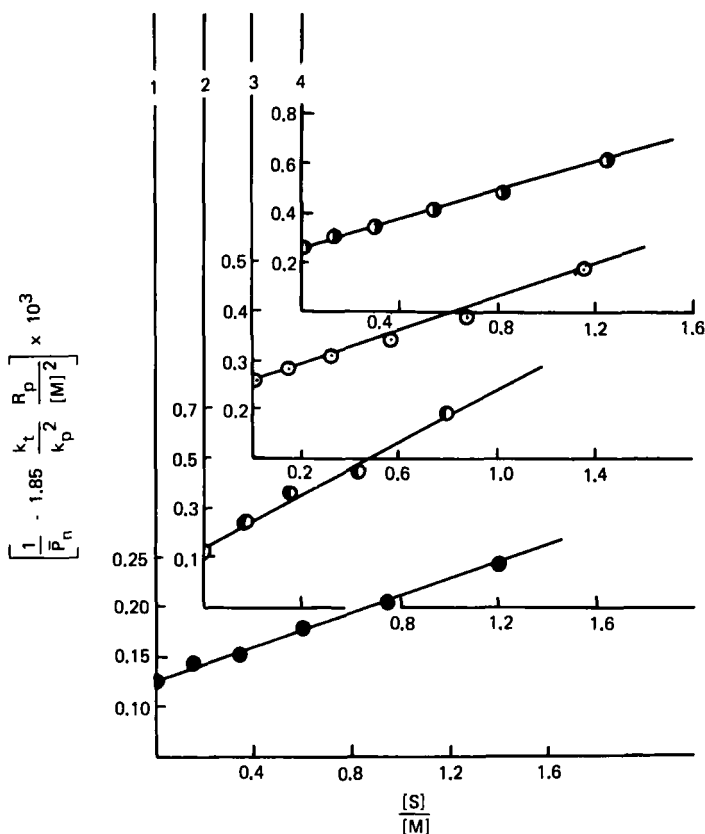


FIG. 8. Photopolymerization of MMA in solution at 40°C using acridone as photoinitiator. (1) DMF, (2) acetone, (3) CHCl₃, (4) C₆H₆.

For primary radical termination characterized by the rate constant k_{prt} :

$$\log \frac{R_p^2}{[\text{acridone}][M]^3} = \log \frac{fk_d K k_p^2}{k_t} - 0.8684 \frac{k_{prt}}{k_i k_p} \frac{R_p}{[M]^2} \quad (7)$$

For degradative initiator transfer:

With the reinitiation effect characterized by the rate constant k_{rtI}/k_{iI} :

$$\log \frac{R_p^2}{[\text{acridone}] [M]^3} = \log K_f k_d \frac{k_p^2}{k_t} - 0.434 \frac{k_p^2}{k_t} \frac{k_{rt} I}{k_{tI} k_p} C_I K [\text{acridone}] \quad (8)$$

With little reinitiation effect characterized by the rate constant k_t' :

$$\frac{2k_t}{k_p^2} \frac{R_p^2}{[\text{acridone}] [M]^3} = 2fk_d K - \frac{k_t' K}{k_p} \frac{R_p}{[M]} \quad (9)$$

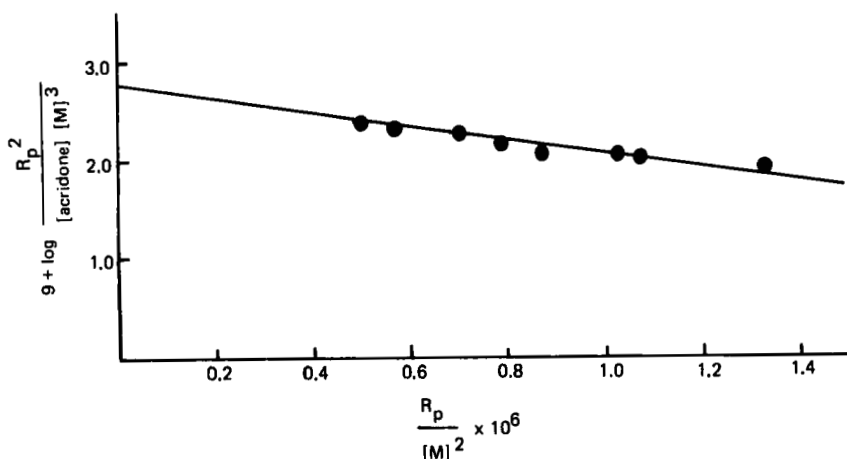


FIG. 9. Photopolymerization of MMA in bulk at 40°C using acridone as photoinitiator. Analysis of primary radical termination.

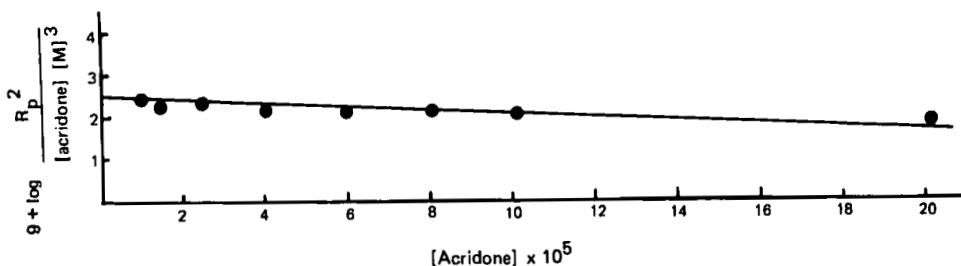


FIG. 10. Photopolymerization of MMA in bulk at 40°C using acridone as photoinitiator. Analysis of degradative initiator transfer with reinitiation.

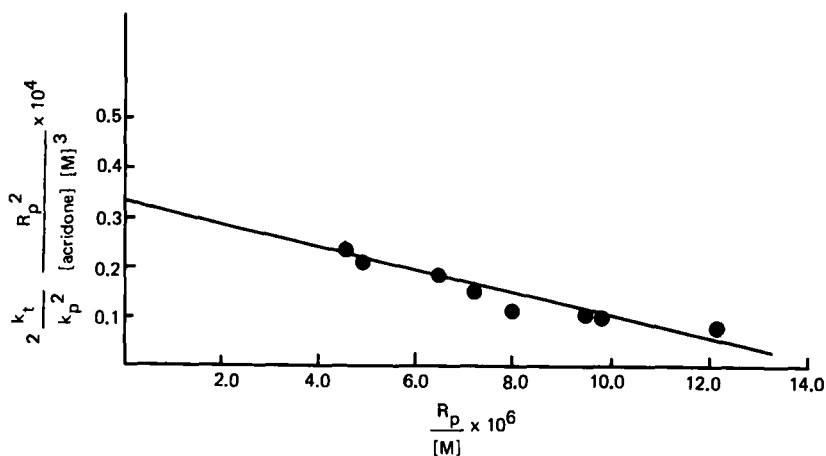


FIG. 11. Photopolymerization of MMA in bulk at 40°C using acridone as photoinitiator.

Graphical plots of Eqs. (7), (8), and (9) as shown in Figs. 9, 10, and 11 give evidence for primary radical termination and/or degradative initiator transfer processes in the present photopolymerization, the slope of each plot being negative. The values of $k_{prt}/k_i k_p$, $k_{rtI}/k_i k_p$ and $k_t'K/k_p$ obtained from the slope of the plots are $6.19 \times 10^5 \text{ mol}\cdot\text{s/L}$, $8.257 \times 10^5 \text{ mol}\cdot\text{s/L}$, and 2.272 L/mol , respectively.

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