

## LIST OF PUBLICATIONS

1. Photopolymerization of methyl methacrylate using Rhodamine 6G and benzoyl peroxide combination as photoinitiator in non-aqueous media. J. Pol. Sci. Part A : Polymer Chemistry, 24, 1053-1063 (1986)
2. Photopolymerization of methyl methacrylate using a combination of Auramine-O and benzoyl peroxide as photoinitiator in non-aqueous media J. Polym. Mater. 5, 265-271 (1988)
3. Photopolymerization of methyl methacrylate using a combination of Michler's ketone and benzoyl peroxide as photoinitiator. Accepted by European Polymer Journal
4. Redox polymerization of methyl methacrylate using Crystal Violet Lactone in combination benzoyl peroxide as initiator. Ready for communication

# Photopolymerization of Methyl Methacrylate Using a Combination of Rhodamine 6G and Benzoyl Peroxide as Photoinitiator in Nonaqueous Media

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## Synopsis

Photopolymerization of methyl methacrylate (MMA) in visible light was studied at 40°C using Rhodamine 6G–Benzoyl peroxide combination as photoinitiator. The photopolymerization proceeds by a free radical mechanism and the radical generation process occurs by an initial complexation reaction between the initiator components. 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 bimolecular mode of chain termination.

## INTRODUCTION

Certain dyes<sup>1-6</sup> are known to induce photopolymerization of some vinyl monomers when used as a lone initiator or in combination with other compounds. Benzoyl peroxide and tertiary amines of both aromatic and aliphatic kinds have been studied as radical-initiator systems in vinyl polymerization by different workers<sup>7-9</sup> and in most of these reported studies initiation of polymerization was indicated to take place by radical mechanism through thermal or photodecomposition of an initial complex formed between the redox components in each case. The dye Rhodamine 6G was chosen as the reducing component of the redox initiator in combination with benzoyl peroxide ( $Bz_2O_2$ ) in the present studies in view of the presence of aromatic amine moieties in its structure and polymerization of methyl methacrylate monomer was studied kinetically in bulk or in nonaqueous solutions under photocondition.

The dye rhodamine 6G suitably taken into benzene solution failed to initiate polymerization of MMA both in the dark and under photoactive condition at 40°C but in the presence of benzoyl peroxide, photopolymerization readily took place at 40°C at rates substantially higher than those obtained using  $Bz_2O_2$  as the lone initiator. Results of kinetic and related studies on photopolymerization of methyl methacrylate induced by rhodamine 6G– $Bz_2O_2$  combination as the photoinitiator in nonaqueous media are reported in the present paper.

## EXPERIMENTAL

MMA was purified by usual procedures.<sup>10,11</sup> All the solvents used were of reagent grade and were distilled once before use in polymerization experiments. The cationic dye rhodamine 6G (in the chloride salt form) is

insoluble in benzene and very sparingly soluble in MMA. To make it organosoluble, the dye was dissolved in water in a stoppered test tube and then made strongly alkaline with sodium hydroxide, whereby the hydroxide base was formed. The dye was then easily extracted in benzene on thorough shaking. The deep orange-yellow benzene extract is quite stable if kept over sodium hydroxide pellets and it remains in the anhydrobase form (simply denoted as Rh) in the benzene solution thus prepared.<sup>12,13</sup> Benzoyl peroxide ( $Bz_2O_2$ ) obtained from BDH was recrystallized from chloroform and dried in vacuum before use. Concentration of dye in benzene was determined gravimetrically by evaporating the solvent from a known volume of the benzene extract.

### Photopolymerization

Photopolymerization of MMA was studied dilatometrically under nitrogen atmosphere at 40°C in the presence of a 125 W Mercury vapor lamp using known quantities of Rhodamine 6G (Rh) in benzene solution and of  $Bz_2O_2$  as the initiator combination. Polymers formed at low conversion (<10%) were removed from the dilatometer, precipitated with petroleum ether, washed, and finally dried in vacuum. Molecular weights,  $\bar{M}_n$  and hence the degree of polymerization,  $\bar{P}_n$  of the polymers were determined viscometrically in benzene solution following a procedure described before.<sup>10,11</sup>

### RESULTS

Photopolymerization of MMA in visible light was readily induced by rhodamine 6G- $Bz_2O_2$  combination as initiator, though little polymerization was observed within 2 h at 40°C in the dark with the same initiator system. The inhibition period (5-15 min) for the photopolymerization of MMA with the initiator combination was appreciably lower and the corresponding rates of polymerization were higher than those observed for polymerization with  $Bz_2O_2$  alone as the photoinitiator. The Hydroquinone produced strong inhibiting effect on the present photopolymerization.

#### Spectrophotometric studies of the Rhodamine 6G(anhydrobase)- $Bz_2O_2$ system

Dilute solutions of  $Bz_2O_2$  in benzene has no absorbance in the visible region. Visible absorption spectra of dilute benzene solutions of the dye anhydrobase (Rh) ( $2.0 \times 10^{-5}$  mol.  $l^{-1}$ ) and a mixture of the anhydrobase (Rh) ( $2.0 \times 10^{-5}$  mol.  $l^{-1}$ ) and  $Bz_2O_2$  ( $2.0 \times 10^{-5}$  mol.  $l^{-1}$ ) in benzene are given in Fig. 1, each showing an absorption peak at about 525 nm, the Rh/ $Bz_2O_2$  mixture showing a much higher absorbance at 525 nm than the anhydrobase, Rh. It is clearly indicated, therefore that  $Bz_2O_2$  forms a complex with rhodamine 6G anhydrobase and the complex acts as the actual initiating species(I).

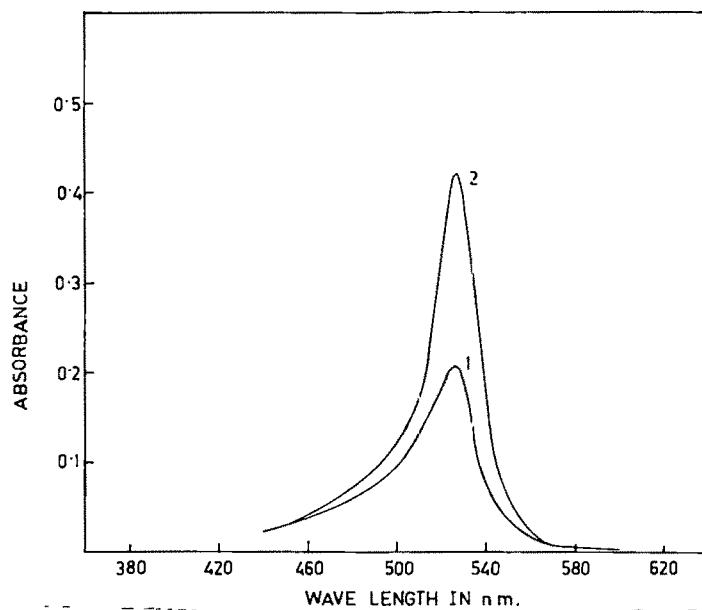


Fig. 1. Visible absorption spectra of rhodamine 6G and mixture of rhodamine 6G and benzoyl peroxide in benzene solution (1)  $[Rh] = 2.0 \times 10^{-6} \text{ mol L}^{-1}$  and (2)  $[Rh] = 2.0 \times 10^{-6} \text{ mol L}^{-1}$  and  $[Bz_2O_2] = 2.0 \times 10^{-6} \text{ mol L}^{-1}$ .

#### Kinetics of Photopolymerization of MMA using Rhodamine 6G- $Bz_2O_2$ combination as initiator

Rates of photopolymerization ( $R_p$ ) using different concentration of the initiator components at  $40^\circ\text{C}$  are shown in Table - 1.  $R_p$  was determined from the slope of the linear plots of % conversion vs. time (not shown).

Initiator exponents given by the slope of the plot of  $\log R_p$  vs  $\log [Rh][Bz_2O_2]$  is 0.37, (Fig. 2). The initiator exponent is less than that expected from the usual square-root dependence for free radical polymerization.

TABLE I  
Photopolymerization of Methyl Methacrylate using Rhodamine 6G and Benzoyl peroxide Combination as Photoinitiator

$[Rh] \times 10^4$ (mol L <sup>-1</sup> )	$[Bz_2O_2] \times 10^2$ (mol L <sup>-1</sup> )	$R_p \times 10^5$ (mol L <sup>-1</sup> s <sup>-1</sup> )	$[\eta]$ (dL g <sup>-1</sup> )	$(1/\bar{P}_n \times 10^4)$	$k_p^2/k_t \times 10^2$ (l mol <sup>-1</sup> s <sup>-1</sup> )
25.69	3.10	18.6	0.70	7.25	1.07
17.13	3.10	16.7	0.90	5.21	
12.85	3.10	15.2	1.13	3.86	
8.56	3.10	13.9	1.22	3.49	
6.42	3.10	12.8	1.30	3.21	
4.28	3.10	9.8	1.57	2.50	
2.14	3.10	8.3	1.73	2.20	
8.56	6.31	19.6	0.60	8.88	
8.56	4.18	16.7	0.90	5.21	
8.56	3.10	13.9	1.22	3.41	
8.56	2.14	11.9	1.37	2.99	
8.56	1.55	10.8	1.48	21.71	
8.56	0.70	7.9	1.79	2.11	

**$k_p^2/k_t$  Value and Activation Energy**

The kinetic parameter  $k_p^2/k_t$  at 40°C was evaluated from  $\bar{P}_n$  and  $R_p$  data using the following equation:<sup>14,15</sup>

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

where  $C_I$  and  $C_M$  are initiator transfer constant and monomer transfer constant, respectively.

A plot of  $1/\bar{P}_n$  vs  $R_p/[M]^2$  is shown in Figure 3.

The plot is linear over low  $[I]$  indicating that the effect of transfer reactions on  $\bar{P}_n$  is negligible over low  $[I]$ . At higher range of  $[I]$ , however, the plot shows a large deviation from linearity, indicating that the effect of the transfer reactions, particularly the initiator transfer reaction, which is negligible at low range of  $[I]$ , becomes significant at higher range of  $[I]$ . The value of the kinetic parameters  $k_p^2/k_t$  obtained from the initial linear zone of the plot as in Figure 3 is  $1.07 \times 10^{-2} \text{ L} \cdot \text{mol}^{-1} \text{ s}^{-1}$ . This value is in good agreement with the literature.<sup>10,11,16,17</sup> The apparent activation energy  $E_a$ , ( $E_a = E_p - E_t/2$ ) of the bulk photopolymerization was found to be 3.05 Kcal/mol which is close to some of the reported values for free radical polymerization of MMA.<sup>18,19</sup>

**End-Group Analysis**

Spectral data (Fig. 1) reveal that the anhydrobase form of Rhodamine 6G dye (Rh) in benzene solution shows absorbances over the visible region 460–580 nm, giving a peak absorbance at 525 nm. Purified polymers prepared by using  $\text{Bz}_2\text{O}_2$ -Rh combination as the photoinitiator system were brown in color and when studied in acetonitrile solution they showed appreciable absorbances over the 360–540 nm region, Figure 4, much in contrast to the absence of color and absorbance in the visible region when examined similarly for a polymer prepared thermally (60°C) using only  $\text{Bz}_2\text{O}_2$  as the initiator. Thus, the color and the absorbance in the visible region of the ( $\text{Bz}_2\text{O}_2$ -Rh) initiated polymers indicate the presence of rhodamine moieties in them as endgroups which were incorporated in the

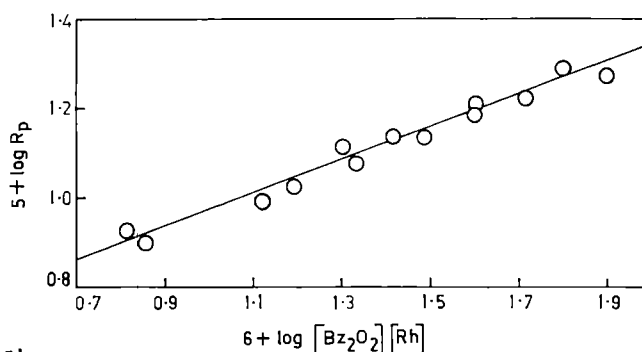


Fig. 2. Photopolymerization of MMA at 40°C using rhodamine 6G- $\text{Bz}_2\text{O}_2$  complex as initiator, Plot of  $\log R_p$  vs  $\log [\text{Bz}_2\text{O}_2][\text{Rh}]$ .

PHOTOPOLYMERIZATION OF METHYL METHACRYLATE 1057

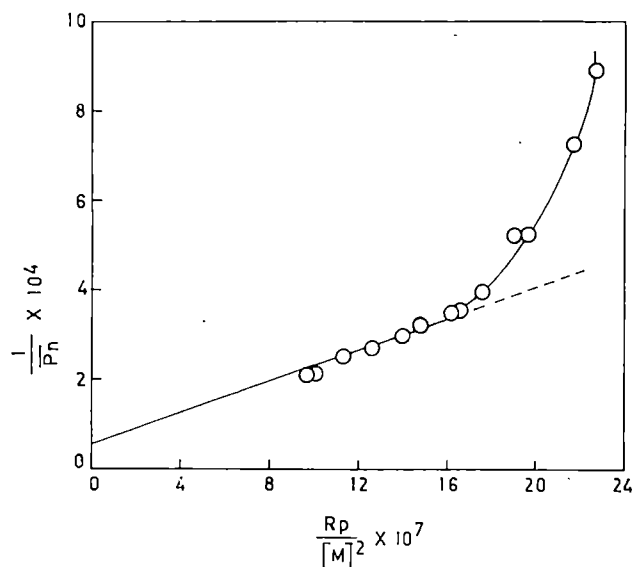


Fig. 3. Photopolymerization of MMA at 40°C using rhodamine 6G-Bz<sub>2</sub>O<sub>2</sub> complex as initiator, Plot of 1/P<sub>n</sub> vs R<sub>p</sub>/[M]<sup>2</sup>.

polymers at the initiation step involving radicals derived from the dye (Rh) molecule.

**Initiator Transfer**

Equation (1) may be rearranged in the following form to determine the initiator-transfer parameter (C<sub>I</sub>K);

$$\frac{1}{P_n} - 1.85 \frac{k_t}{k_p^2} \frac{R_p}{[M]^2} = C_M + C_I K \frac{[Rh] [Bz_2O_2]}{[M]} \quad (2)$$

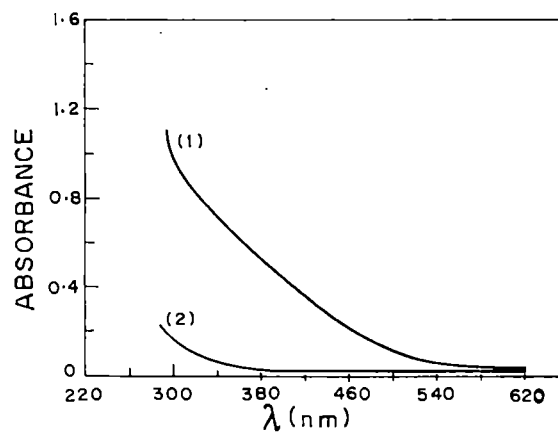


Fig. 4. Visible absorption spectra of PMMA in acetonitrile solution (1.4%). Plot of absorbance vs wave length (λ) for (1) PMMA initiated by rhodamine 6G-Bz<sub>2</sub>O<sub>2</sub> in light at 40°C and (2) PMMA initiated by Bz<sub>2</sub>O<sub>2</sub> in the dark at 60°C.

where  $[I] = K[\text{Rh}][\text{Bz}_2\text{O}_2]$  and  $K$  is the equilibrium constant of the complexation reaction between Rh and  $\text{Bz}_2\text{O}_2$ .

The left-hand side of eq. (2) was plotted against  $([\text{Rh}][\text{Bz}_2\text{O}_2])/[\text{M}]$  (Fig. 5) and from the slope of the initial linear zone of the plot, the value of  $C_I K$  was found to be  $15 \text{ L mol}^{-1}$ .

### Monomer Exponent

Photopolymerization of MMA was also studied at  $40^\circ\text{C}$  using fixed  $[\text{Rh}]$  ( $1.23 \times 10^{-3} \text{ mol L}^{-1}$ ) and  $[\text{Bz}_2\text{O}_2]$  ( $3.1 \times 10^{-2} \text{ mol L}^{-1}$ ) in the presence of several solvents such as benzene, acetone, and chloroform, taking different concentrations of the solvent in each case. From the slope of the respective plots of  $\log R_p$  vs  $\log [\text{M}]$ , (Fig. 6) the monomer exponent value was found to be unity in each case.

### Mechanism

Kinetic data, endgroup analysis and inhibitory effect of hydroquinone indicate a radical mechanism. The radical generation process is believed to follow an initial complex formation between rhodamine 6G, (Rh) and benzoyl peroxide, ( $\text{Bz}_2\text{O}_2$ ) as is evidenced by spectral analysis, Figure 1.

The optimum concentration range for the two initiating components for photopolymerization of MMA at measurable rates were found to be  $10^{-4}$ – $10^{-3} \text{ mol L}^{-1}$  for  $[\text{Rh}]$  and  $10^{-3}$ – $10^{-2} \text{ mol L}^{-1}$  for  $[\text{Bz}_2\text{O}_2]$ . Formation of anhydrobase, and the complexation and radical generation reactions may be represented as follows:

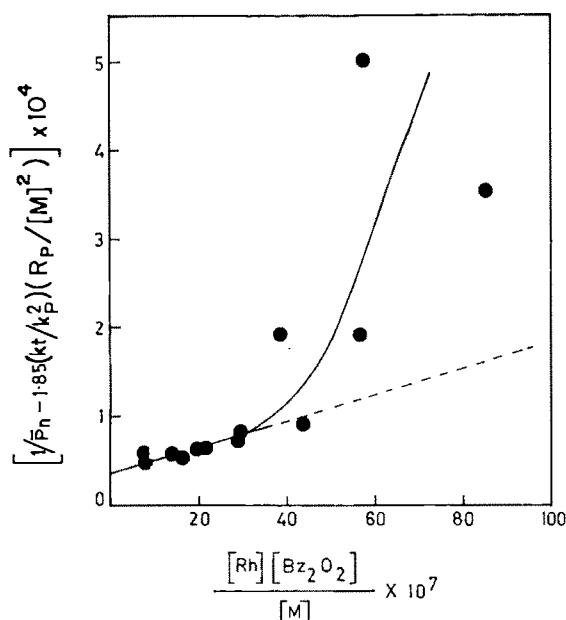
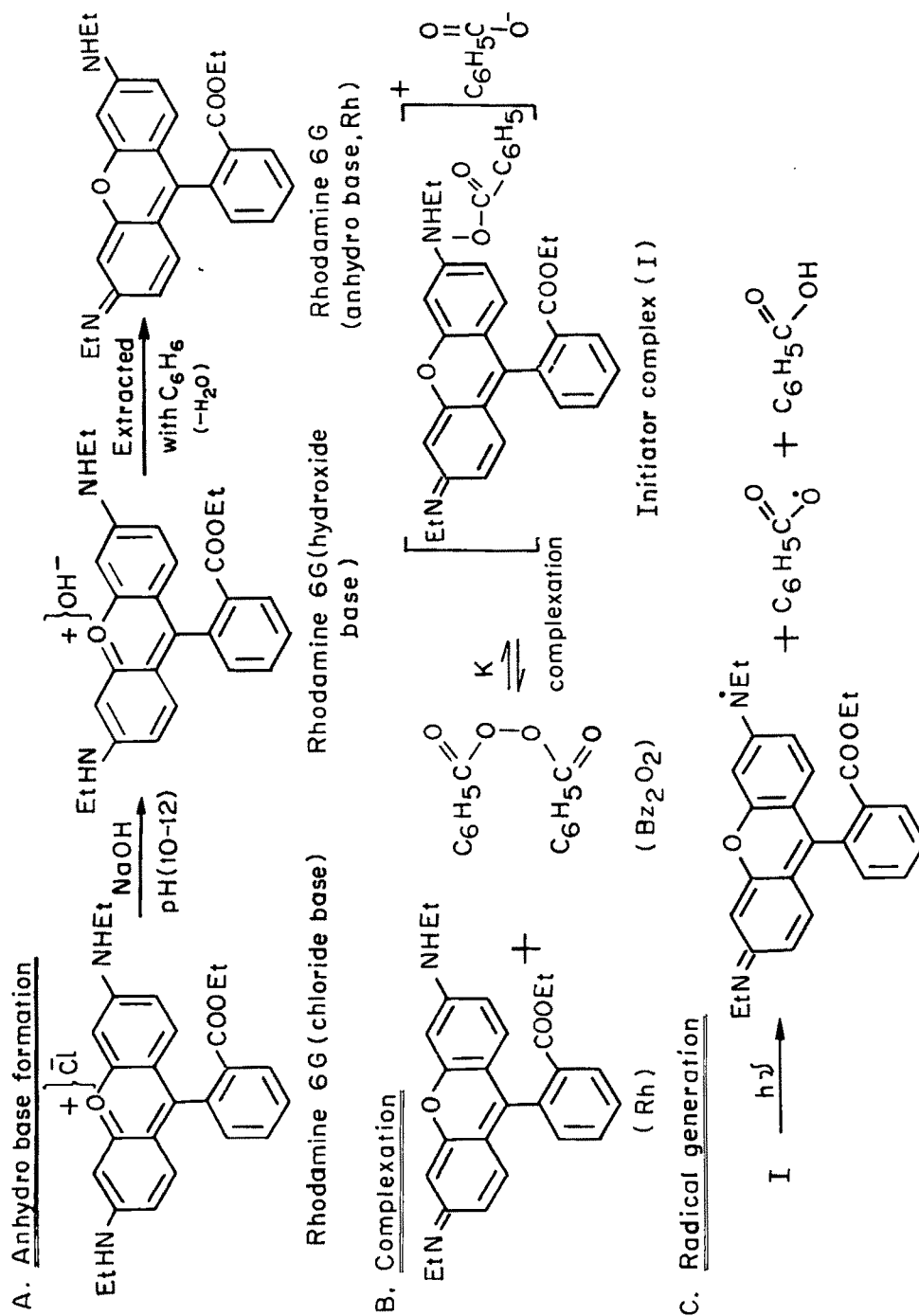


Fig. 5. Photopolymerization of MMA at  $40^\circ\text{C}$  using rhodamine 6G– $\text{Bz}_2\text{O}_2$  complex as initiator, Plot of  $(1/P_n - 1.85 k_t/k_p^2 R_p/[M]^2)$  vs  $[\text{Rh}][\text{Bz}_2\text{O}_2]/[\text{M}]$ .





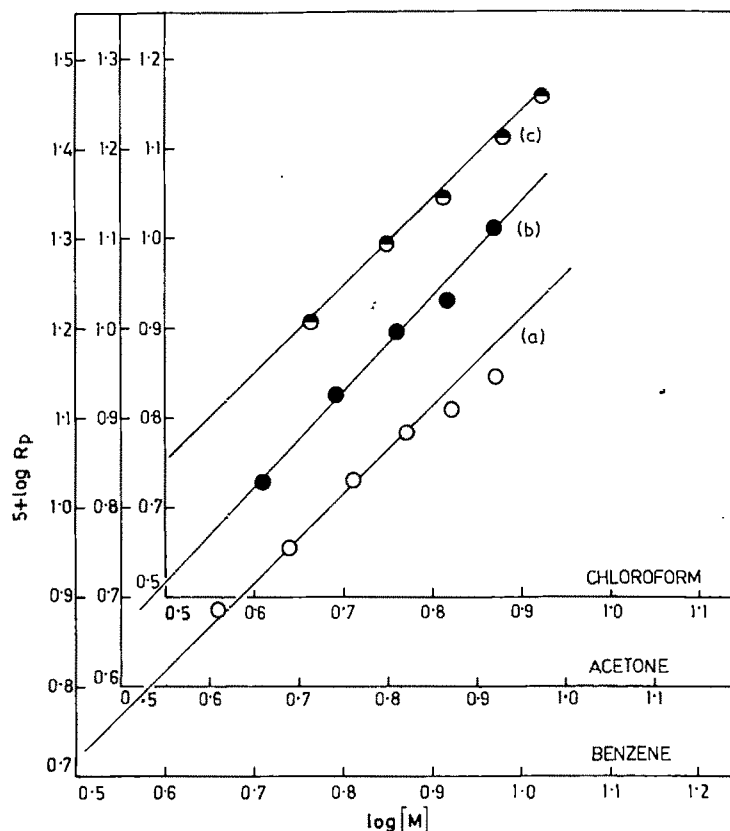


Fig. 6. Photopolymerization of MMA at 40°C using rhodamine 6G-Bz<sub>2</sub>O<sub>2</sub> complex as initiator, Plot of log R<sub>p</sub> vs log [M]. Data given for each curve are solvent and slope (monomer exponent). (a) ○, benzene, 1.00; (b) ●, Acetone, 1.04; (c) ○, Chloroform, 1.00.

The concentration of the initiating complex (*I*) formed as above may be represented as:

$$[I] = K [\text{Rh}][\text{Bz}_2\text{O}_2]$$

where *K* is the equilibrium constant of the complex formation reaction.

#### Termination

The deviation from the usual square-root dependence of *R<sub>p</sub>* on initiator concentration (initiator exponent value < 0.5) indicates the occurrence of some initiator-dependent termination processes along with the usual bimolecular mode of termination. Two different kinds of initiator dependent termination processes may be considered for further analysis of the kinetic data: (A) Primary radical termination, and (B) Termination via degradative initiator transfer.

##### (A) Analysis of Primary Radical Termination Effect

Primary radical-termination effect may be analyzed by using the equation derived by Deb and Meyerhoff<sup>20</sup> which assumes the following form for the

present photopolymerization:

$$\log \frac{R_p^2}{[M]^2[Rh][Bz_2O_2]} = \log \frac{fk_d K k_p^2}{k_t} - 0.8684 \frac{k_{prt}}{k_i k_p} \frac{R_p}{[M]^2} \quad (3)$$

A plot of the left-hand side of the above equation against  $R_p/[M]^2$ , using the data for bulk polymerization, gave a straight line with a negative slope, Figure 7, which is clearly indicative of a measurable primary radical-termination effect. The value of  $k_{prt}/k_i k_p$  calculated from the slope of the plot is  $1.53 \times 10^6 \text{ mol s L}^{-1}$ . From the intercept of the plot and using the value of  $k_p^2/k_t$  the value of  $fk_d K$  was found to be  $1.30 \times 10^{-3} \text{ L mol s}^{-1}$ .

(B) Analysis of Degradative Initiator Transfer Effect

Two modes of degradative initiator transfer may be considered: (i) with reinitiation effect and (ii) with little reinitiation effect.

The following equation [eq. (4)] derived according to the approach of Deb<sup>21</sup> and simplified by Ghosh and Mitra<sup>22</sup> may be used to analyze the degradative effect as in case (i),

$$\log \frac{R_p^2}{[Bz_2O_2][Rh][M]^2} = \log \frac{fk_d K k_p^2}{k_t} - 0.434 \frac{k_p^2}{k_t} \cdot \frac{k_{rt}}{k_{it} k_p} C_I K \frac{[Bz_2O_2][Rh]}{[M]} \quad (4)$$

(where  $C_I$  is the initiator transfer constant) and equation (5) derived according to the approach described earlier,<sup>23</sup> may be used to analyze the degradative effect as in case (ii);

$$\frac{2k_t}{k_p^2} \frac{R_p^2}{[M]^2[Rh][Bz_2O_2]} = 2fk_d K - \frac{k_t' K}{k_p} \cdot \frac{R_p}{[M]} \quad (5)$$

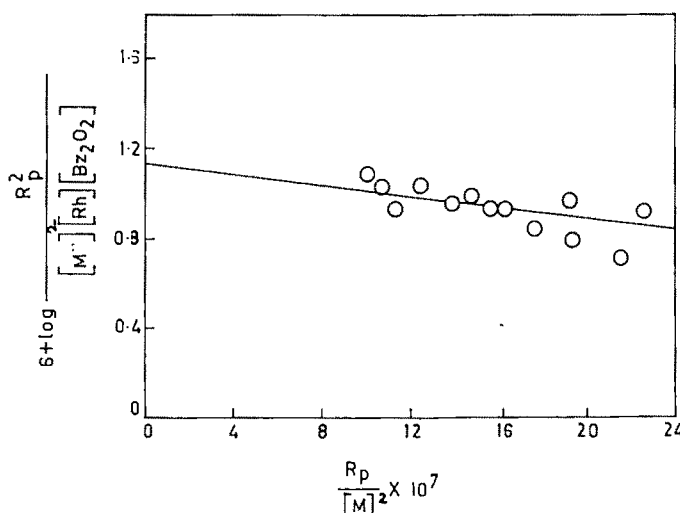


Fig. 7. Photopolymerization of MMA at 40°C using rhodamine 6G-Bz<sub>2</sub>O<sub>2</sub> complex as initiator; plot of  $\log R_p^2/[M]^2[Rh][Bz_2O_2]$  vs  $R_p/[M]^2$ .

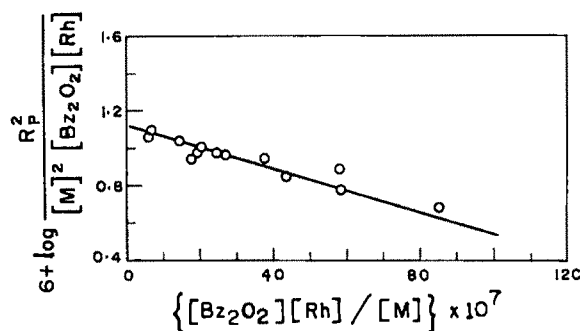


Fig. 8. Photopolymerization of MMA at 40°C using rhodamine 6G-Bz<sub>2</sub>O<sub>2</sub> complex as initiator; plot of  $\log R_p^2/[M]^2[Rh][Bz_2O_2]$  vs  $[Bz_2O_2][Rh]/[M]$ .

Plots of the left-hand side of eq. (4) vs  $[Bz_2O_2][Rh]/[M]$  and of the left-hand side of eq. (5) vs  $R_p/[M]$  given in Figure 8 and 9, respectively, show a negative slope each, thereby indicating the existence of the degradative initiator transfer effects in question. Using the value of  $C_1K$ , the value of the kinetic parameter  $k_{tr}/k_{it}k_p$  was calculated at  $7.9 \times 10^5$  mol s L<sup>-1</sup> from the slope of the plot in Figure 8. The value of  $\frac{K k'_t}{k_p}$  obtained from the slope of the plot in Figure 9, is 52.3 L mol<sup>-1</sup>. From the intercepts of the plots, Figure 8 and 9, values of  $f k_d K$  are found as  $1.30 \times 10^{-3}$  L mol s<sup>-1</sup> and  $1.32 \times 10^{-3}$  L mol s<sup>-1</sup>, respectively.

The values of  $f k_d K$ , equivalent to  $K \phi \epsilon I_0$  for photopolymerization<sup>24</sup> (where  $I_0$  is the incident light intensity in moles of light quanta per liter second,  $\epsilon$  is the molar absorptivity of the initiator  $I$  for the wave length of radiation absorbed in  $\phi$  is the quantum yield for radical production in photopolymerization) obtained on the basis of different considerations from plots as in Figures 7-9, are in very close agreement.

It is interesting to note that photopolymerization of MMA with Rhodamine 6G-Bz<sub>2</sub>O<sub>2</sub> combination as initiator as detailed here follows nonideal kinetics, the termination process being significantly initiator dependent. Monomer exponent values in different solvent systems being nearly unity, it may be further concluded that primary radical termination is by and

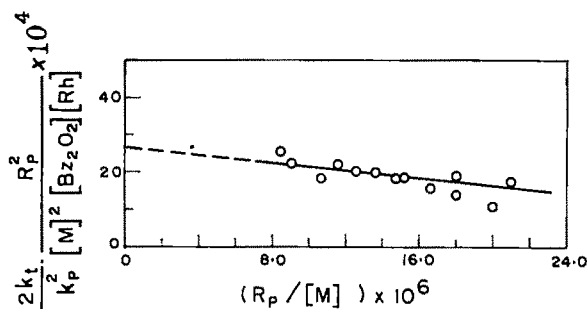


Fig. 9. Photopolymerization of MMA at 40°C using rhodamine 6G-Bz<sub>2</sub>O<sub>2</sub> complex as initiator; plot of  $2 k_t/k_p^2 R_p^2/[M]^2[Rh][Bz_2O_2]$  vs  $R_p/[M]$ .

large inconsequential and the kinetic nonideality is primarily due to the degradative initiator-transfer reactions.

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# Photopolymerization of Methyl Methacrylate Using a Combination of AuramineO and Benzoyl Peroxide as Photoinitiator in Nonaqueous Media

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## SYNOPSIS

*Photopolymerization of methyl methacrylate (MMA) was studied at 40°C in visible light using auramineO-benzoyl peroxide combination as photoinitiator. The photopolymerization occurs by a free radical mechanism. A complex formed between the initiator components prior to radical generation is considered to be the actual initiating species. Initiator exponent observed was 0.25 and the monomer exponent in different solvents is nearly unity. The kinetic non-ideality in terms of relatively low initiator exponent interpreted on the basis of significant chain termination at least in part via gradative initiator transfer along with the usual bimolecular mode of termination. A mechanism of polymerization has been suggested.*

## INTRODUCTION

Reports<sup>1-6</sup> on vinyl polymerization using selected dyes as sensitizers or initiators, particularly under photoirradiation in aqueous medium are available. Reports<sup>7-9</sup> on vinyl polymerization using selected amines, particularly tertiary amines in redox combination with benzoyl peroxide via radical mechanisms are also available. Dye sensitized polymerization in nonaqueous media is, however, scantily reported.

Results of kinetics of photopolymerizations of methyl methacrylate in non-aqueous system using AuramineO dye in redox combination with benzoyl peroxide are the subject matter of this paper.

## EXPERIMENTAL

Monomer methyl methacrylate (MMA) was purified following usual procedures.<sup>10, 11</sup> All the solvents used in the experiments were of reagent grade and were distilled before use. Benzoyl peroxide (Bz<sub>2</sub>O<sub>2</sub>) obtained from BDH was recrystallized from chloroform and dried in vacuum before use. Aqueous solution of AuramineO dye is colored yellow. Benzene solution of the dye was prepared by extracting the aqueous alkaline solution (pH 10) of the dye hydrochloride with benzene at room temperature. The aqueous hydroxide base readily got transformed into the anhydrobase form when the benzene extract is preserved over NaOH pellets. The anhydrobase

solution in benzene is colored very pale yellow. The dye in the hydrochloride form is, however, insoluble in benzene. The benzene extract is stable when kept over sodium hydroxide pellets.<sup>12, 14</sup> Concentration of the dye in benzene was determined gravimetrically by evaporating the solvent from a known volume of benzene extract under vacuum.

### Photopolymerization

Photopolymerization of MMA was carried out dilatometrically under nitrogen atmosphere at  $40 \pm 0.05^\circ\text{C}$  under the exposure of a 125 W mercury vapour lamp using a combination of known quantities of AuramineO (Au) and benzoyl peroxide ( $\text{Bz}_2\text{O}_2$ ) in benzene solution. Polymers formed at low conversions ( $< 10\%$ ) were removed from the dilatometers, precipitated and washed with petroleum ether and dried in vacuum. Molecular weight ( $\bar{M}_n$ ) and hence the degree of polymerization,  $\bar{P}_n$  of Selected polymers was determined viscometrically in benzene solution at  $30 \pm 0.05^\circ\text{C}$  using the following relationship,<sup>10, 11</sup>

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

### RESULTS

Photopolymerization of MMA in visible light was readily induced at  $40^\circ\text{C}$  using AuramineO/ $\text{Bz}_2\text{O}_2$  initiator combination. However, no polymerization was observed within 2 hrs at  $40^\circ\text{C}$  using the same initiator system in the dark. The inhibition period (10-25 mins) for the photopolymerization of MMA with the initiator combination was much lower and the corresponding rates of polymerization were higher than those observed for polymerization with  $\text{Bz}_2\text{O}_2$  alone as the photoinitiator. Benzoquinone produced strong inhibitory effect in the present photopolymerization.

#### Spectrophotometry of AuramineO/ $\text{Bz}_2\text{O}_2$ System

Dilute solutions of  $\text{Bz}_2\text{O}_2$  in benzene has no

absorbance in the visible region. Visible absorption spectra of dilute benzene solutions of the dye anhydrobase, (Au) ( $2 \times 10^{-5}$  mol.  $\text{L}^{-1}$ ) and of a mixture of Au ( $2 \times 10^{-5}$  mol.  $\text{L}^{-1}$ ) and  $\text{Bz}_2\text{O}_2$  ( $2 \times 10^{-5}$  mol.  $\text{L}^{-1}$ ) in benzene show a absorption peak at about 442 nm, the Au/ $\text{Bz}_2\text{O}_2$  combination showing a much higher absorbance at 442 nm than the anhydrobase, Au. This is clearly indicative of the formation of a complex between  $\text{Bz}_2\text{O}_2$  and the AuramineO anhydrobase (Au) and the complex acts as the actual initiating species (I).

### Kinetic Data

Kinetic data on the photopolymerization of MMA at  $40^\circ\text{C}$  using varying concentrations of the initiator components are shown in Table I. Rates of photopolymerization,  $R_p$ , were calculated from the slope of the initial linear zones of % conversion vs. time plots (not shown).

Initiator exponent as determined from the slope of the plot of  $\log R_p$  vs.  $\log [\text{Au}] [\text{Bz}_2\text{O}_2]$  is 0.25 which is less than that expected from the usual square-root dependence of free radical polymerization (Fig. 1).

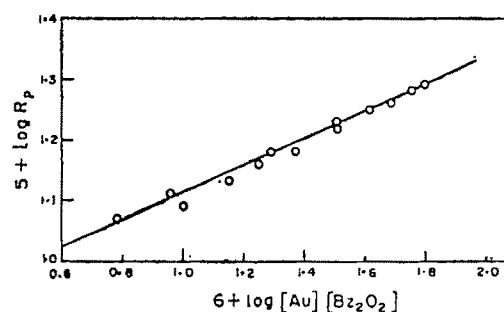


Fig. 1. Photopolymerization of MMA at  $40^\circ\text{C}$  using AuramineO- $\text{Bz}_2\text{O}_2$  complex as initiator: Plot of  $\log R_p$  vs.  $\log [\text{Au}][\text{Bz}_2\text{O}_2]$ .

#### $k_p^2/k_t$ Value and Activation Energy

The kinetic parameter  $k_p^2/k_t$  at  $40^\circ\text{C}$  was determined from the slope of  $1/\bar{P}_n$  vs.  $R_p/[M$

TABLE 1. Photopolymerization of MMA (Bulk) and 40°C using AuramineO and Benzoyl Peroxide Combination as Photoinitiator

$[Au] \times 10^4$ (mol. L <sup>-1</sup> )	$[Bz_2O_2] \times 10^3$ (mol. L <sup>-1</sup> )	$R_p \times 10^4$ (mol. L <sup>-1</sup> s <sup>-1</sup> )	$[\eta]$ (dL g <sup>-1</sup> )	$\frac{1}{\bar{P}_n} \times 10^4$	$\frac{k_p^2}{k_t} \times 10^2$ (L mol <sup>-1</sup> s <sup>-1</sup> )
26.61	2.29	1.91	0.66	7.83	
21.38	2.29	1.81	0.74	6.74	
14.12	2.29	1.69	0.88	5.36	
8.51	2.29	1.51	1.13	3.86	
3.98	2.29	1.28	1.30	3.21	
2.66	2.29	1.18	1.40	2.91	
					0.97
8.51	7.38	1.93	0.64	8.16	
8.51	4.90	1.78	0.76	6.51	
8.51	3.77	1.66	0.93	4.99	
8.51	2.77	1.53	1.10	4.00	
8.51	2.12	1.45	1.17	3.69	
8.51	1.65	1.35	1.24	3.42	
8.51	1.19	1.23	1.33	3.12	

lot, Fig. 2, using the Mayo equation, written in the following form for the present system,

$$\frac{1}{\bar{P}_n} = 1.85 \frac{k_t}{k_p^2} \cdot \frac{R_p}{[M]^2} + C_M + C_I \frac{[I]}{[M]} \quad (1)$$

here  $[I]$  and  $[M]$  are initiator and monomer concentration respectively and  $C_I$  and  $C_M$  are the initiator and monomer transfer constants.

The negligible effect of transfer reactions on  $\bar{P}_n$  over low  $[I]$  is reflected in the linearity of the plot over low  $[M]$ . The large deviation from linearity at higher range of  $[I]$  indicates that the effect of chain transfer, particularly of the initiator transfer reaction is significant at higher range of  $[I]$  though it is practically negligible at low range of  $[I]$ . The value of kinetic parameter  $k_p^2/k_t$  obtained from the initial linear zone of the plot as in Fig. 2 is  $0.97 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$  which is close to or of the same order as those reported in the literature<sup>10,11,14-16</sup>.

The apparent activation energy  $E_a$ ,  $\left(E_a = E_p - \frac{E_t}{2}\right)$  for the bulk photopolymerization was found to be 2.80 k. cal/mol which is somewhat on the lower side than some of the reported values on free radical polymerization of MMA<sup>17,18</sup>.

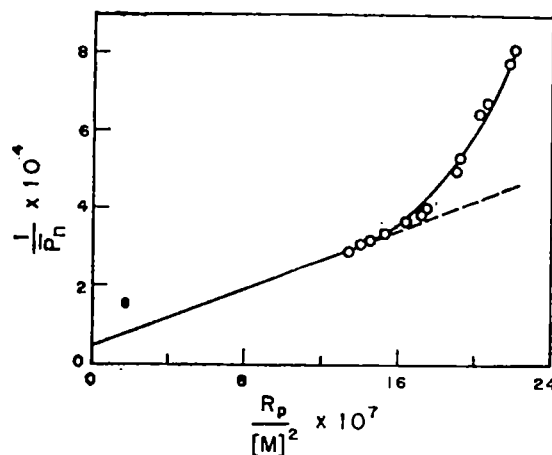


Fig. 2. Photopolymerization of MMA at 40°C using AuramineO-Bz<sub>2</sub>O<sub>2</sub> complex as initiator: Plot of  $1/\bar{P}_n$  vs.  $R_p/[M]^2$ .

#### End-Group Analysis

Spectral data reveals that the anhydrobase (Au) form of AuramineO dye in benzene solution shows absorbances over the visible region 380-480 nm giving a maximum peak absorbance at 442 nm. Purified polymers (PMMA) prepared by using Au/Bz<sub>2</sub>O<sub>2</sub> combinations are not perfectly white (as the thermal PMMA) and they

give very pale yellowish solutions in benzene or acetonitrile. The test polymers in dilute acetonitrile solutions show measurable absorbances over the 360-480 nm region when measured spectrophotometrically, in contrast to near absence of absorbance in the visible region for purified PMMA prepared at 60°C using only Bz<sub>2</sub>O<sub>2</sub> as the initiator. Thus, the color and the absorbance in the visible region of purified PMMA photoinitiated by Au/Bz<sub>2</sub>O<sub>2</sub> initiator combination indicate the presence of AuramineO dye moieties as end groups which were incorporated in the polymers at the initiation step involving radicals derived from the dye (Au) molecule.

#### Initiator Transfer

To determine the initiator transfer parameter (C<sub>1</sub>K) eq. (1) may be written in the following form:

$$\frac{1}{P_n} - 1.85 \frac{k_t}{k_p^2} \frac{R_p}{[M]^2} = C_M + C_1 K \frac{[Au][Bz_2O_2]}{[M]} \quad (2)$$

where (1) = K[Au][Bz<sub>2</sub>O<sub>2</sub>] and K is the equilibrium constant of the complexation reaction between Au and Bz<sub>2</sub>O<sub>2</sub>.

The left hand side of eq. (2) was plotted against [Au][Bz<sub>2</sub>O<sub>2</sub>]/[M], (Fig. 3) and from the slope of the initial linear zone of the plot, the value of C<sub>1</sub>K and found to be 17.8 L mol<sup>-1</sup>.

#### Monomer Exponent

Photopolymerization of MMA was also studied at 40°C using fixed [Au] (1.412 × 10<sup>-3</sup> mol L<sup>-1</sup>) and [Bz<sub>2</sub>O<sub>2</sub>] (2.29 × 10<sup>-2</sup> mol L<sup>-1</sup>) in the presence of several solvents such as benzene, dimethyl formamide, acetone and chloroform. From the slope of the respective plots of log R<sub>p</sub> vs log [M], the monomer exponent values were found to be unity in each case.

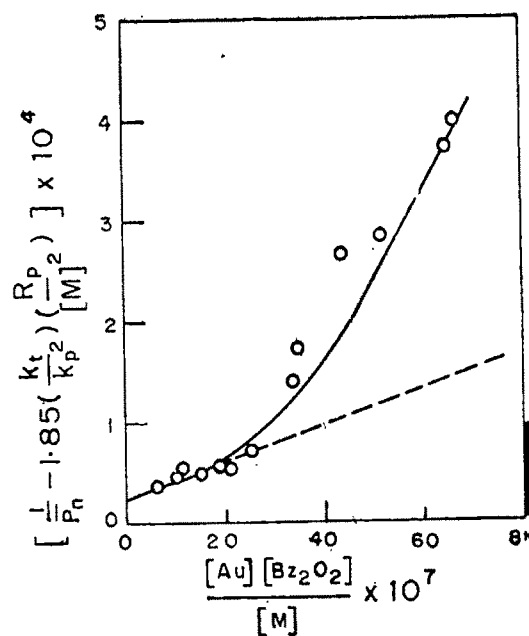


Fig. 3. Photopolymerization of MMA at 40°C using AuramineO-Bz<sub>2</sub>O<sub>2</sub> complex as initiator: Plot of  $\left(\frac{1}{P_n} - 1.85 \frac{k_t}{k_p^2} \frac{R_p}{[M]^2}\right)$  vs.  $\frac{[Au][Bz_2O_2]}{[M]}$ .

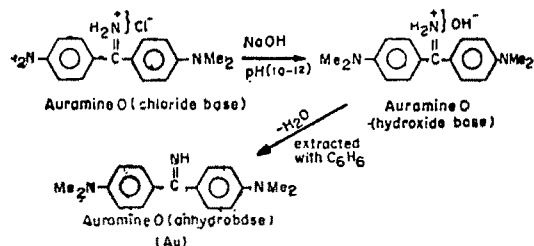
#### Mechanism

A radical mechanism is indicated by kinetic data, end group analysis and inhibitory effect of benzoquinone. The radical generation process follows an initial complex formation between AuramineO anhydrobase (Au) and benzoyl peroxide (Bz<sub>2</sub>O<sub>2</sub>) which is evidenced by spectral data.

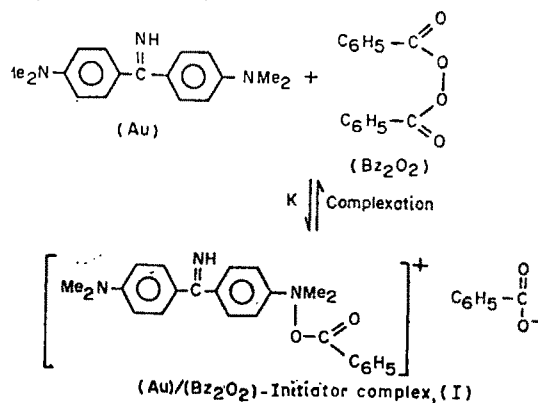
The optimum concentration range for the two initiating components for photopolymerization of MMA at measurable rates was found to be 10<sup>-4</sup> – 10<sup>-3</sup> mol. L<sup>-1</sup> for [Au] and 10<sup>-3</sup> – 10 mol. L<sup>-1</sup> for [Bz<sub>2</sub>O<sub>2</sub>]. Formation of the dye anhydrobase, complexation between the initiating components and the radical generation reaction may be represented as follows:



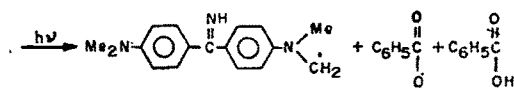
**Formation of Anhydrobase of AuramineO**



**Complexation between the Dye Anhydrobase (Au) and Benzoyl Peroxide (Bz<sub>2</sub>O<sub>2</sub>)**



**Radical Generation**



The concentration of the initiating complex (I) formed as above may be represented as  $[I] = K[Au][Bz_2O_2]$  where K is the equilibrium constant of the complexation reaction.

**Termination**

The observed initiator exponent value of 0.5 is viewed as a deviation from the usual square root dependence of R<sub>p</sub> on initiator concentration, occurrence of some initiator-dependent termination process along with the normal bimolecular mode of termination is therefore indicated. The initiator-dependent terminations may proceed by two different mechanisms,

- (a) Primary radical termination, and
- (b) Termination via degradative initiator transfer.

**Primary Radical Termination Effect:** To analyze this effect, the kinetic expression developed by Deb and Meyerhoff<sup>19</sup> may be used and the expression assumes the following form for the present photo-polymerization:

$$\log \frac{R_p^2}{[M]^2[Au][Bz_2O_2]} = \log \frac{fk_d k_p^2}{k_t} - 0.8684 \frac{k_{prt}}{k_i k_p} \frac{R_p}{[M]^2} \quad (3)$$

A plot of the left hand side of the above equation against R<sub>p</sub>/[M]<sup>2</sup>, Fig. 4, using the data for bulk polymerization gave a straight line with a negative slope, indicating a measurable primary radical termination effect. The value of k<sub>prt</sub>/k<sub>i</sub>k<sub>p</sub> calculated from the slope of the plot is 6.103 × 10<sup>5</sup> mol.s.L<sup>-1</sup>. From the intercept of the plot and using the value of k<sub>p</sub><sup>2</sup>/k<sub>t</sub>, the value of fkdK was found to be 1.03 × 10<sup>-2</sup> L mol<sup>-1</sup> s<sup>-1</sup>.

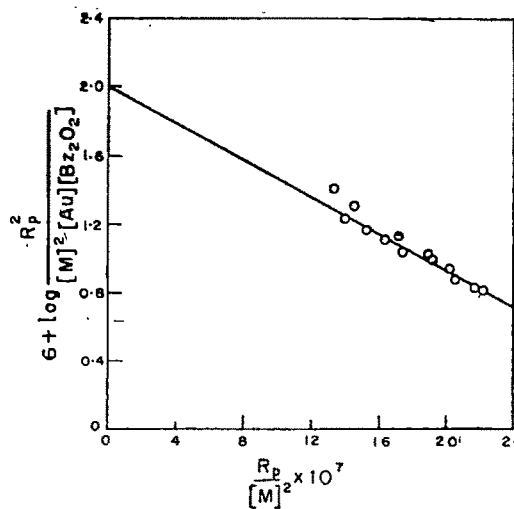


Fig. 4. Photopolymerization of MMA at 40°C using AuramineOBz<sub>2</sub>O<sub>2</sub> complex as initiator: Plot of

$$\log \frac{R_p^2}{[M]^2 [Au] [Bz_2O_2]} \text{ vs. } \frac{R_p}{[M]^2}$$

**Analysis of Degradative Initiator Transfer Effect:** Two modes of degradative initiator transfer may be considered: (i) with reinitiation effect, and (ii) with little reinitiation effect.

The following equation (eq. 4) derived according to the approach of Deb<sup>20</sup> and simplified by Ghosh and Mitra<sup>21</sup> can be used to analyze the degradative effect as in case (i).

$$\log \frac{R_p^2}{[M]^2[Au][Bz_2O_2]} = \log \frac{fk_d K k_p^2}{k_t} - 0.434 \frac{k_p^2}{k_t} \frac{k_{rti}}{k_{it} k_p} \cdot C_1 K \frac{[Au][Bz_2O_2]}{[M]} \quad (4)$$

where  $C_1$  is the initiator transfer constant.

Equation (5) derived according to the approach described earlier<sup>7</sup> may be used to analyse the degradative effect with little reinitiation, as in case (ii),

$$2 \frac{k_t}{k_p^2} \cdot \frac{R_p^2}{[M]^2[Au][Bz_2O_2]} = 2fk_d K - \frac{k_t'}{k_p} \cdot K \frac{R_p}{[M]} \quad (5)$$

Plots of the left side of Eq. (4) vs.  $\frac{[Au][Bz_2O_2]}{[M]}$

and of the left hand side of Eq. (5) vs.  $R_p/[M]$  given in Figs. 5 and 6 respectively, show a negative slope in each case thus giving evidence to degradative initiator transfer effects of either kind considered above.

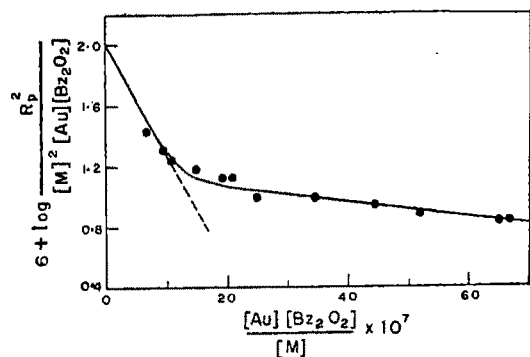


Fig. 5. Photopolymerization of MMA at 40°C using AuramineO— $Bz_2O_2$  complex as initiator: Plot of

$$\log \frac{R_p^2}{[M]^2[Au][Bz_2O_2]} \text{ vs. } \frac{[Au][Bz_2O_2]}{[M]}$$

Using the value of  $C_1 K$ , the value of kinetic parameter  $k_{rti}/k_{it} k_p$  was calculated  $9.75 \times 10^{-6} \text{ mol. s. L}^{-1}$  from the slope of plot in Fig. 5. The value of  $\frac{k_t'}{k_p} \cdot K$  obtained from the slope of the plot in Fig. 6, is  $12.3 \times 10^2 \text{ mol}^{-1}$ .

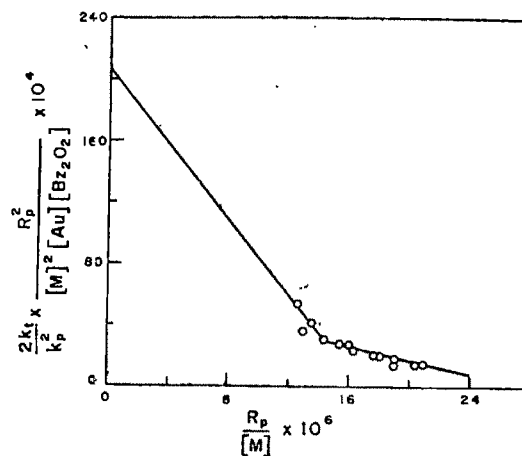


Fig. 6. Photopolymerization of MMA at 40°C using AuramineO— $Bz_2O_2$  complex as initiator: Plot of

$$\frac{2 k_t}{k_p^2} \cdot \frac{R_p^2}{[M]^2[Au][Bz_2O_2]} \text{ vs. } \frac{R_p}{[M]}$$

Interestingly, the values of  $fk_d K$ , calculated separately from the intercepts of Fig. 5 and Fig. 6 are very close and the average value of the parameter is  $1.03 \times 10^{-3} \text{ L. mol}^{-1} \cdot \text{s}^{-1}$  which is in excellent agreement with the value obtained from Fig. 4 based on a different consideration.

Thus, it is seen that the photopolymerization of MMA with AuramineO/ $Bz_2O_2$  combination as initiator follows non-ideal kinetics, the termination process being significantly initiator dependent.

Since the monomer exponents in different solvent systems were unity, it may be concluded that the primary radical termination mechanism is not of much relevance to the present polymerization, and degradative initiator transfer reactions are considered to be the consequent factors that give rise to prominent kinetic non-idealities.

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