

SUMMARY

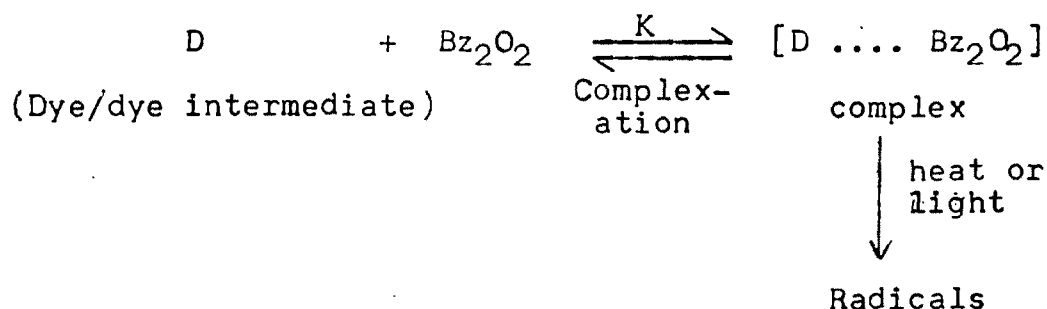
In the present thesis results on the kinetic and related investigations on the polymerization of methyl methacrylate (MMA), a vinyl monomer at a low temperature (40°C) using four selected initiator systems containing redox combinations of benzoyl peroxide and certain dyes and dye intermediates bearing secondary or tertiary amine moieties in their molecules in non-aqueous medium in separate sets of experiments under photo or thermal conditions have been presented. The four systems selected were, i) Rhodamine 6G anhydrobase (Rh) - benzoyl peroxide (Bz_2O_2) combination, ii) Auramine O anhydrobase (Au) - benzoyl peroxide (Bz_2O_2) combination, iii) Michler's ketone (MK) benzoyl peroxide (Bz_2O_2) combination and iv) Crystal Violet Lactone (CVL) - benzoyl peroxide (Bz_2O_2) combination. The water soluble cationic dyes Rhodamine-6G and Auramine O were converted to their respective organosoluble anhydrobase forms for use in the non-aqueous polymerization of MMA, whereas Michler's ketone and Crystal Violet Lactone being soluble in MMA were used as such. Preliminary experiments were conducted for the evaluation of the suitability and relative ease of thermal or photopolymerization of MMA using the four dye intermediates as such or in combination with benzoyl peroxide.

The general features of the polymerization of MMA using different initiator combinations in various concentrations in influencing the rates were studied. Subsequent studies made relate to the kinetics of the polymerizations of MMA using the above initiator combinations in bulk and under diluted conditions and detailed studies have also been made for the evaluation of various kinetic parameters for the polymerization of MMA using the above initiator systems.

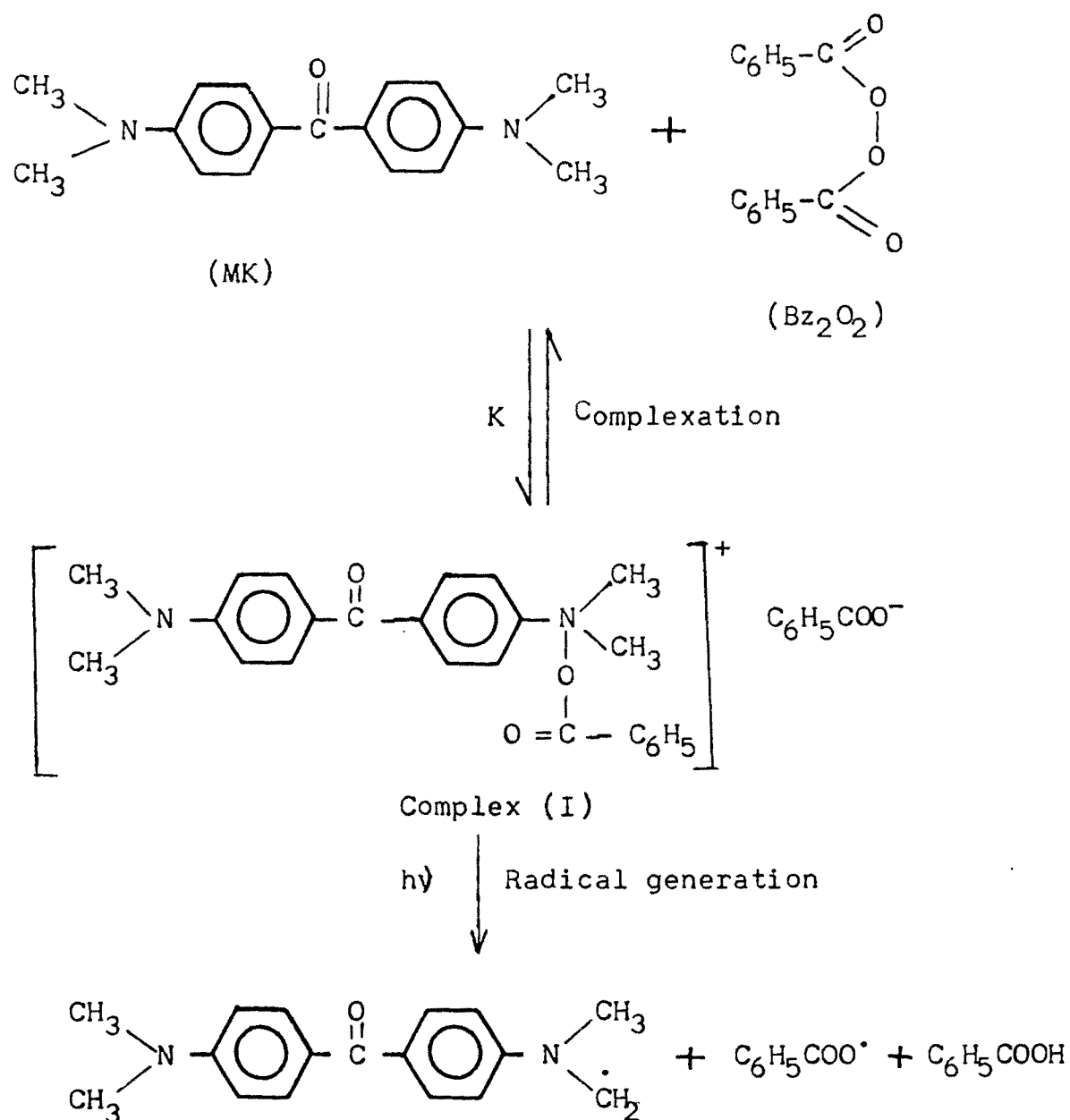
In the absence of benzoyl peroxide all of Rhodamine 6G anhydrobase (Rh), Auramine O anhydrobase (Au), Michler's ketone (MK) and Crystal Violet Lactone (CVL) failed to initiate polymerization at 40°C underphotoconditions when studied upto 3 hours. In combination with benzoyl peroxide, only CVL was found to initiate appreciable polymerization in the dark at 40°C whereas very little polymerization in the dark was observed in case of MK-Bz₂O₂ (IP-150 min) system; both Rh-Bz₂O₂ and Au-Bz₂O₂ failed to initiate polymerization of MMA in the dark at 40°C when studied upto 2 hours. However, all of Rh, Au and MK in combination with Bz₂O₂ readily induced polymerization of MMA at 40°C under photoactive conditions.

Spectrophotometric studies of the various dye or dye intermediate - benzoyl peroxide (Bz_2O_2) system and of the polymer end groups

Separate spectral analyses of the different dyes or dye intermediates (Rh, Au, CVL and MK), of Bz_2O_2 and those of Rh- Bz_2O_2 , Au- Bz_2O_2 , MK- Bz_2O_2 and CVL- Bz_2O_2 combinations in the UV-VIS region in appropriate solution (using benzene or acetonitrile as solvent) were made and it was indicated that when mixed together, the dye or dye intermediate and Bz_2O_2 formed 1:1 equilibrium complex. This complex is considered to be the actual initiating species which readily decomposes photolytically (in case of Rh, Au and MK - Bz_2O_2 combinations) or thermally (in case of CVL- Bz_2O_2) to generate radicals.



Considering any one of the four initiator systems used in our studies of polymerization of MMA viz. Michler's ketone (MK) - benzoyl peroxide (Bz_2O_2) system, the complexation and radical generation process can be written as :



Here, a donor-acceptor complex (I) formed between Michler's ketone (MK) and benzoyl peroxide (Bz₂O₂) is considered to be the actual initiating species. The concentration of this intermediate complex is denoted by $[I] = K[MK][Bz_2O_2]$, where K is the equilibrium constant of the complexation reaction. This complex decomposes into a benzoyloxy and α -amino radical.

Evidences of the generation of radicals from the complex, thermally or photochemically, were obtained from the results of the end-group analysis of the polymers formed using each initiator system. End-group analysis indicated the incorporation of dye/dye intermediate moieties in the polymer initiated by the different initiator combinations as end groups presumably during chain initiation involving radicals derived from the dye molecule.

Photopolymerization kinetics

Detailed studies of the polymerization at 40°C using Rh-Bz₂O₂, Au-Bz₂O₂ and MK-Bz₂O₂ systems under photoconditions and using CVL-Bz₂O₂ combination in dark in separate sets of experiments with varying concentration of Bz₂O₂ at a fixed concentration of the dye/dye intermediate and vice-versa have been done. It was observed that the polymerizations were associated with appreciable reaction rates and low inhibition periods (0.5-25 min) at the studied concentration ranges of the initiator components. An increase in the concentration of the initiator components caused enhancement in the rate of polymerization (R_p) and lowering of inhibition period. Table-I gives a gist of the data of the range of inhibition periods and rates at the concentration range of each initiator system used in the polymerization of MMA.

Table I : Polymerization of MMA at 40°C using initiator systems comprising of a dye or dye-intermediate and Bz₂O₂

Condition of Polymerization	Initiator system	Concentration range		Range of Inhibition period, min.	Range of rate R _p × 10 ⁴ mol.L ⁻¹ s ⁻¹
		[Dye] × 10 ³ mol.L ⁻¹	[Bz ₂ O ₂] × 10 ³ mol.L ⁻¹		
Photo	Rh-Bz ₂ O ₂	0.2-3	0.7-6	5-15	0.8 - 2
Photo	Au-Bz ₂ O ₂	0.2 - 3	1 - 7	8-25	1 - 2
Photo	MK-Bz ₂ O ₂	0.05 - 1	0.05 - 5	0.5 - 22	2-5
Thermal	CLV-Bz ₂ O ₂	3 - 50	1 - 5	1 - 30	2-8

Specific data on the effect of concentrations of the initiator components of each initiator system on the rate of polymerization of MMA is tabulated in Table II. It is apparent from Table II that comparable [Au], [Rh] and [CVL] resulted in comparable rates of polymerization of MMA although in case of CVL-Bz₂O₂ system, polymerization was carried out in dark with less [Bz₂O₂]. MK-Bz₂O₂ is the best among the four initiator systems studied showing relatively high rates of polymerization for comparable concentrations of initiator components.

Table II : Polymerization of MMA at 40°C using initiator systems comprising of a dye or dye-intermediate and Bz_2O_2

Condition of polymerization	Initiator system	[Dye] $\times 10^3$ mol.L ⁻¹	[Bz_2O_2] $\times 10^3$ mol.L ⁻¹	[Dye][Bz_2O_2] $\times 10^5$	$R_p \times 10^6$ mol.L ⁻¹ s ⁻¹
Photo	Rh- Bz_2O_2	2.57	3.00	7.7	1.86
Photo	Au- Bz_2O_2	2.66	2.29	6.1	1.91
Photo	MK- Bz_2O	1.00	1.00	1.0	4.39
Thermal	CVL- Bz_2O_2	3.00	1.00	3.0	2.27

The polymerization of MMA with the different initiator systems were characterized by the following kinetic features :

a) Low initiator exponent value (< 0.5)

The initiator exponent was 0.37 for Rh- Bz_2O_2 initiated system, 0.25 for Au- Bz_2O_2 initiated system, 0.21 for MK- Bz_2O_2 initiated system and 0.40 for CVL- Bz_2O_2 initiated system.

b) k_p^2/k_t values

The value of k_p^2/k_t was 1.07×10^{-2} L.mol⁻¹s⁻¹ for Rh- Bz_2O_2 initiated system, 0.97×10^{-2} L.mol⁻¹s⁻¹ for Au- Bz_2O_2 initiated system, 1.39×10^{-2} L.mol⁻¹.s⁻¹ for MK- Bz_2O_2 initiated system and 1.41×10^{-2} L.mol⁻¹.s⁻¹ for CVL- Bz_2O_2 initiated system.

c) Variable monomer exponent values in presence of different solvents in each case

Monomer exponents of the different initiator systems in various solvents are summarized in Table III.

Table III : Polymerization of MMA at 40°C in diluted systems using initiator combinations comprising of a dye or dye-intermediate and Bz₂O₂

Solvent Initiator combination	Monomer Exponent			
	Rh-Bz ₂ O ₂	Au-Bz ₂ O ₂	MK-Bz ₂ O ₂	CVL-Bz ₂ O ₂
Benzene	1.00	1.00	1.35	0.90
Acetone	1.04	1.00	1.86	0.94
Chloroform	1.00	1.00	1.28	0.65
Methanol	-	-	1.68	-
Dimethyl formamide	-	1.00	-	-
Acetonitrile	-	-	-	0.75
Condition of polymerization	Photo	Photo	Photo	Thermal

Both Rh-Bz₂O₂ and Au-Bz₂O₂ systems produced data of monomer exponent equal to unity thereby indicating practically normal kinetics with respect to solvent effect. Monomer exponent values < 1 for CVL-Bz₂O₂ system and > 1 for MK-Bz₂O₂ system indicate that with CVL-Bz₂O₂ system rate enhancement

takes place which arises presumably as a consequence of solvent modification of the initiation step leading to faster generation of primary radicals whereas in case of MK-Bz₂O₂ system, solvent-induced retardation of rate is much in prominence.

d) Attachment of dye moieties as end groups in the polymer

End-group analysis of the polymers formed initiated by the different initiator systems studied indicate that dye/dye intermediate moieties are incorporated as end groups in each case presumably during the chain initiation involving radicals derived from the dye/dye intermediate molecule.

e) Interpretation of the kinetic non-idealities

Initiator dependent termination processes of the following kinds are considered in addition to the usual bimolecular mechanism of the termination :

- i) Primary radical termination
- ii) Degradative initiator transfer - a) with reinitiation effect and b) with little reinitiation effect.

The above termination processes were analyzed by using the following equations :

- i) Deb and Meyerhoff³⁵ equation for the analysis of primary radical termination effect :

$$\log \frac{R_p^2}{[M]^2[D][Bz_2O_2]} = \log \frac{fk_d K k_p^2}{k_t} - 0.8684 \frac{k_{prt}}{k_i k_p} \frac{R_p}{[M]^2} \quad (1)$$

ii) Two equations were used to analyze the degradative initiator transfer effect

a) Ghosh-Mitra¹⁴ equation for the analysis of degradative initiator transfer effect with reinitiation :

$$\log \frac{R_p^2}{[M]^2[D][Bz_2O_2]} = \log \frac{fk_d K k_p^2}{k_t} - 0.434 \frac{k_p^2}{k_t} \frac{k_{rtI}}{k_i I k_p} C_I K \frac{[D][Bz_2O_2]}{[M]} \quad (2)$$

b) Equation derived by Ghosh²¹⁸ for the analysis of degradative initiator effect with little reinitiation :

$$\frac{2 k_t}{k_p^2} \frac{R_p^2}{[M]^2[D][Bz_2O_2]} = 2 f k_d K - \frac{k_t' K}{k_p} \frac{R_p}{[M]} \quad (3)$$

With the help of equations (1), (2) and (3), evidence for the above additional termination processes were obtained by graphical treatment of kinetic data for bulk polymerization as 40°C.

f) Kinetic parameter ($fk_d K$) relating to initiator decomposition or radical generation

From the treatment of kinetic data based on equation (1) to equation (3) given above, the kinetic parameter

f $k_d K$ was evaluated for each initiator combination system and its values in mol.L s^{-1} for Rh-Bz₂O₂, Au-Bz₂O₂, MK-Bz₂O₂ and CVL-Bz₂O₂ are 1.3×10^{-3} , 10.3×10^{-3} , 640×10^{-3} and 1.63×10^{-3} respectively.

A much high value for the MK-Bz₂O₂ system in particular, presumably indicates a high K value for the complexation reaction between the initiator components for this system or a very high k_d value. On consideration of comparable range of rates of polymerization for the different systems it may be concluded that the MK-Bz₂O₂ system is characterized by a high equilibrium constant (K value) for the complexation reaction between the initiator components.

The f $k_d K$ values at 40°C are in the order (MK-Bz₂O₂) >> (Au-Bz₂O₂) > (CVL-Bz₂O₂), (Rh-Bz₂O₂).

The various kinetic parameters obtained from the studies of the polymerization of MMA at 40°C using different initiator combinations are summarized in Table IV.

From the kinetic treatments it is revealed that in the case of MK-Bz₂O₂ initiated polymerization of MMA, kinetic non idealities arise more as a consequence of primary radical termination and the role of degradative initiator transfers reactions appear to be of much less significance whereas the termination processes are significantly initiator dependent in case of Rh-Bz₂O₂, Au-Bz₂O₂ and CVL-Bz₂O₂ initiated polymerization of MMA.

Table IV : Polymerization of MMA at 40°C using initiator systems comprising of a dye or dye intermediate and Bz₂O₂. Summary of kinetic and other parameters

Parameters	Initiator system			
	Rh-Bz ₂ O ₂	Au-Bz ₂ O ₂	MK-Bz ₂ O ₂	CVL-Bz ₂ O ₂
1. Condition of Polymerization	Photo	Photo	Photo	Thermal
2. Initiator exponent	0.37	0.25	0.21	0.40
3. Monomer exponent	1.00	1.00	1.28-1.86	0.65-0.94
4. $(k_p^2/k_t) \times 10^2$ (L.mol ⁻¹ s ⁻¹)	1.07	0.97	1.39	1.41
5. Apparent Activation Energy (K cal.mol ⁻¹)	3.05	2.80	2.68	11.50
6. Initiator Transfer parameter C _I K (L mol ⁻¹)	15	14.5	-	9.6
7. Monomer Transfer constant C _M x10 ⁻⁵	3.0	2.0	-	1.0
8. $fk_dK \times 10^3$ (L mol.s ⁻¹)	1.3	10.3	640	1.62
9. $(k_{prt}/k_i k_p) \times 10^{-5}$ (mol.s.L ⁻¹)	1.53	6.10	3.0	0.37
10. Kk_t'/k_p (L mol ⁻¹)	70.0	12.3x10 ²	4.0x10 ⁴	18.3
11. $(K_{rtI}/k_{iI} k_p) \times 10^{-5}$ (mol.s L ⁻¹)	7.9	97.5	-	2.9
12. Polymerization Mode	Radical	Radical	Radical	Radical