PHOTOPOLYMERIZATION OF METHYL METHACRYLATE USING MERCAPTOBENZTHIAZOLES AS PHOTOINITIATOR

**THESIS SUBMITTED FOR THE DEGREE OF
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PREFACE

The present thesis contains the results of kinetic and related studies on the photopolymerization of methylmetharcylate, a vinyl monomer in presence of mercaptobenzothiazoles as initiator. The work was carried out in the laboratories of Plastics and Rubber Technology Department, University of Calcutta

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CHAPTER –I

GENERAL INTRODUCTION

1.1: Introduction:

Polymer science has achieved a new dimension both from its fundamental aspect and technological development since the inception of its macromelecular concept about half a century ago. During this period many new monomer has been synthesized and evaluated particularly to meet the different industrial applications. Parallel to these developmental work fundamental research has also been tuned to understand the mechanism of polymerization processes.

Vinyl and related monomers are known to undergo polymerization through a typical chain reaction process which may be activated thermally in presence of a catalyst or initiator or by various other means. The chain process starts from an active centre which may be of the free radical type or of the ionic (cationic or anionic) type. Free radical chain mechanism for polymerization of vinyl and related monomers are primarily due to **Taylor** and **Bates**[1] and **Staudinger**[2]. Chain mechanism for polymerization involving ionic intermediates was proposed by **Whitmore**[3] and **others**[4].

In any case the activation of a vinyl monomer ($CH_2 = CHX$) molecule results in opening up of the double bond and the activated molecule then reacts with successive monomer molecules to form a long chain polymer.

1.2 Kinetics of Free Radical Vinyl Polymerization:

The polymerization of a vinyl monomer M, induced by a free radical initiator I may be schematically represented as follows:

i) Initiator decomposition followed by chain initiation

$$I \xrightarrow{K_d} 2R^{\bullet} \text{ ------------------------ } (1)$$

$$R^{\bullet} + M \xrightarrow{K_i} RM^{\bullet}_1 \text{ ----------------------- } (2)$$

ii) Chain propagation

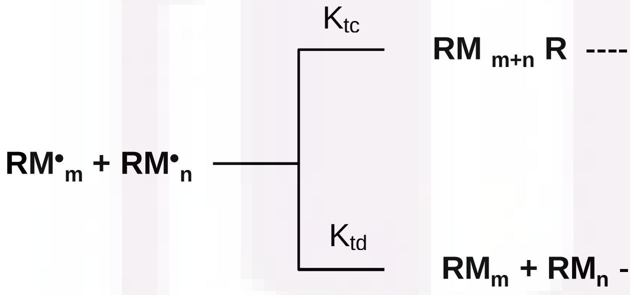
$$\mathbf{RM^{\bullet}_1} + \mathbf{M} \xrightarrow{K_p} \mathbf{RM^{\bullet}_2} \text{ ---------------------- } (3)$$

$$\mathbf{RM^{\bullet}_2} + \mathbf{M} \xrightarrow{K_p} \mathbf{RM^{\bullet}_3}$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\mathbf{RM^{\bullet}_n} + \mathbf{M} \longrightarrow \mathbf{RM^{\bullet}_{n+1}}$$

iii) Chain termination:



$$\mathbf{RM^{\bullet}_m} + \mathbf{RM^{\bullet}_n} \xrightarrow{K_{tc}} \mathbf{RM_{m+n}R} \text{ ---------------------- -------- } (4)$$

$$\mathbf{RM^{\bullet}_m} + \mathbf{RM^{\bullet}_n} \xrightarrow{K_{td}} \mathbf{RM_m} + \mathbf{RM_n} \text{ -------------------------- } (5)$$

Where $\mathbf{R^{\bullet}}$ is the free radical generated from the initiator I and $\mathbf{RM^{\bullet}_1}$, $\mathbf{RM^{\bullet}_2}$, $\mathbf{RM^{\bullet}_3}$ etc are the growing polymer chains, each bearing a radical centre at the growing chain and $\mathbf{RM_m}$, $\mathbf{RM_n}$, $\mathbf{RM_{m+n}}$R are the terminated final polymer molecules.

It is clear from the above scheme that the initiator fragments (R) from the "end groups" by sealing one or both ends of the polymer chains.

According to the scheme presented above the initiator I, first decomposes into a pair of primary radicals $\mathbf{R^{\bullet}}$ as in equation (1) and then each primary radical $\mathbf{R^{\bullet}}$ interacts with the monomer molecule **M** to yield a monomer radical $\mathbf{RM^{\bullet}_1}$ as in equation (2). These two steps are characterised by $\mathbf{K_d}$, the rate of decomposition of initiator and $\mathbf{K_i}$, the rate constant for the initiation of polymerization respectively. The growth of the polymer molecule by the addition of monomer to $\mathbf{RM^{\bullet}_1}$ and the successive radicals, as presented in equation (3) is characterized by $\mathbf{K_p}$, the rate constant for propogation reaction, where the radical activity is assumed to be independent of the chain length and extent of reaction.

The growth of the radicals are generally stopped through a bimolecular reaction involving in each case a pair of chain radicals and this may take place by two different mechanisms, viz., termination by combination, equation (4) and termination by disproportionation, equation (5) respectively. For most kinetic purposes the bimolecular nature of termination process is important irrespective of whether coupling/disproportionation assumes dominance. The overall mechanism of termination reaction may be expressed as:

$$\mathbf{2RM^{\bullet}_{m}} \xrightarrow{K_t} \text{Dead polymer} \text{ ------------------ } (6)$$

and the overall rate constant of termination, $\mathbf{K_t}$ may be expressed as:

$$\mathbf{K_t} = \mathbf{K_{tc}} + \mathbf{K_{td}} \text{ ---------------------------------- } (7)$$

It follows from the above scheme that dead polymer formed by combination would contain two initiator fragments (R) per polymer molecule as chain ends, whereas disproportionation would lead to polymers having only one initiator fragment (R) per molecule and fifty percent of polymer molecules would contain one unsaturation at one of their chain ends.

According to equation (1) and (2) the rate of initiation ($\mathbf{R_i}$) of chain radicals may be expressed as:

$$R_i = \left(\frac{d[M^{\bullet}]}{dt}\right)_i = 2\, f\, K_d\, [I] \text{ ------------------- } (8)$$

where **[M•]** represents the total concentration of all radicals irrespective of their size, **[I]** is the concentration of initiator and **‘f’** is the initiator efficiency.

The rate of chain termination (R_t) from equation (4) or (5) may be written as:

$$R_t = - \left(\frac{d[M^{\bullet}]}{dt} \right)_t = 2\, K_t\, [M^{\bullet}]^2 \text{ -------------------- } (9)$$

The factor ‘2’ enters as a result of disappearance of two radicals at each incidence of termination reaction.

Assuming a steady state condition for the chain process and bimolecular termination of growing polymer chains, the rate of propagation, $\mathbf{R_p}$ which in effect may be taken as the overall rate of polymerization, is given by the following **expression**[5].

$$R_p \quad = \quad K_{\mathbf{p}} \left(\frac{f\, K_d}{K_t} \right)^{1/2} [\,I\,]^{1/2}\ [\,M\,] \text{ ------------------------- } (10)$$

1.3 Chain transfer:

In the vinyl polymerization kinetics, the molecular weight or the degree of polymerization is inversely related to the rate of polymerization. To explain the disagreement of many practical polymerization processes with this relationship **Flory**[6] proposed the occurrence of certain reactions limiting the growth of polymer molecule without reducing the number of active centres and termed these reactions as chain transfer reactions. These reactions can be depicted as:

$$\sim\!\sim\!\sim\!\sim M^{\bullet} \;+\; XA \;\xrightarrow{K_{\mathbf{tr}}}\; M - X \;+\; A^{\bullet} \text{ ---------------- } (11)$$

Where $\boldsymbol{\sim\!\sim\!\sim\!\sim M^{\bullet}}$ is the growing polymer chain and **XA** may be monomer, initiator or any other substances and **X** is the atom or species transferred.

The rate of chain transfer reaction is given by:

$$R_{tr} \quad = \quad K_{tr} \ [M^{\bullet}] \ [XA] \qquad \text{---------------------------} \ (12)$$

where K_{tr} is the rate constant for the chain transfer reaction. Chain transfer yields a new radical $\mathbf{A^{\bullet}}$ which then adds to monomer molecule to initiate a new chain.

$$A^{\bullet} \quad + \quad M \xrightarrow{K_a} M^{\bullet} \quad \text{--------------------------} \ (13)$$

Chain transfer usually lowers the $\overline{\mathbf{P}}_{\mathbf{n}}$ value. The effect of chain transfer on $\mathbf{R_p}$ depends on the fact that whether the rate of reaction (13) is comparable to that of ordinary propagation reaction or not. The kinetic possibilities encountered in vinyl polymerization is listed in

Table – 1.1

Case	Condition of polymerization	Description of the observed effect	Effect on R_p	Effect on $\overline{P}_n$
1	$K_p >> K_{tr}, K_a \approx K_p$	Normal chain transfer	None	Decrease
2	$K_p << K_{tr}, K_a \approx K_p$	Telomerization	None	Large decrease
3	$K_p >> K_{tr}, K_a < K_p$	Retardation	Decrease	Decrease
4	$K_p << K_{tr}, K_a < K_p$	Degradative chain transfer	Large decrease	Large decrease

The number average degree of polymerization $\overline{\mathbf{P}}_{\mathbf{n}}$ is no longer given by ν or 2ν for termination by disproportionation and combination respectively. In the polymerization process, the molecular weight of the polymer formed may be controlled at a specified level using controlled chain transfer process.

The degree of polymerization can now be redefined as the rate of polymerization divided by the sum of all rates of chain terminating process (i.e., the normal termination mode plus all chain transfer reactions). For the general case of polymerization initiated by thermal homolysis of a catalyst, involving termination by coupling and chain transfer (to monomer, initiator and solvents), the number average degree of polymerization is given by:

$$\overline{P_n} = \frac{R_p}{R_{t/2} + K_{tr,M}[M][M^\bullet] + K_{tr,S}[S][M^\bullet] + K_{tr,I}[I][M^\bullet]} \quad \text{----- (14)}$$

The first term in the denominator denotes the rate of formation of chain ends through termination by combination and other three terms denote the rate of formation of pairs chain ends through chain transfer to monomer solvent and initiator respectively. A chain transfer constant **C** for a substance is defined as the ratio of the rate constant **K_{tr}** for the chain transfer reaction to the rate constant **K_p** for the propagation reaction. The chain transfer constants for monomer **C_M**, solvents **C_S** and initiator **C_I** may be given by:

$$C_M = \frac{K_{tr,M}}{K_p}, \quad C_S = \frac{K_{tr,S}}{K_p}, \quad C_I = \frac{K_{tr,I}}{K_p} \quad \text{-------------------- (15)}$$

Thus combining the equations (8), (10), (14), and (15) we obtain:

$$\frac{1}{\overline{P_n}} = \frac{K_t}{K_p^2} \bullet \frac{R_p}{[M]^2} + C_M + C_S\frac{[S]}{[M]} + C_I\frac{[I]}{[M]} \quad \text{-------------------- (16)}$$

The above equation is commonly known as Mayo equation.

1.3a Transfer to Monomer and Initiator:

In absence of solvents or any other additives equation (16) changes to:

$$\frac{1}{\overline{P_n}} = \frac{K_t}{K_p^2} \bullet \frac{R_p}{[M]^2} + C_M + C_I\frac{[I]}{[M]} \quad \text{-------------------------------- (17)}$$

In absence of any transfer to initiator or at low $\mathbf{R_p}$ a plot of $\mathbf{1/\overline{P}_n}$ against $\mathbf{R_p/[M]^2}$ would give a straight line. But at higher $\mathbf{R_p}$**,** i.e., at higher initiator concentration**s**, the plot may deviate from linearity due to large contribution of initiator transfer. The slope of initial linear zone is used to determine the $\mathbf{K_p^2/K_t}$ value and intercept on the $\mathbf{1/\overline{P}_n}$ will give the value of $\mathbf{C_M}$, i.e., monomer transfer constant.

Now rearranging the equation (17) we obtain:

$$\frac{1}{\overline{P}_n} - \frac{K_t}{K_p^2} \bullet \frac{R_p}{[M]^2} = C_M + C_I \frac{[I]}{[M]} \qquad \text{------------------------------------} \ (17a)$$

A plot of left hand side of equation **(17a)** vs **[I]/[M]** would give a straight line, the slope of which is $\mathbf{C_I}$, the intercept being $\mathbf{C_M}$.

Most of the vinyl monomers are of very low transfer value (of the order of 10^{-5} to 10^{-4}). Different initiators have different range of transfer constants depending on the nature of the initiator used.

1.3b Transfer to Solvents or Other Additives:

In presence of solvents or any other additives with which the radical centre is transferred, the term $\mathbf{C_S}$([**S**]/[**M**]) of equation (16) makes a major contribution to the degree of polymerization. At low initiator concentration the last term is negligible, the first term may be kept constant by so adjusting the initiator concentration as to keep $\mathbf{R_p}$/[**M**]^2 constant while [**S**] is varied. Under these conditions equation (16) becomes:

$$\frac{1}{\overline{P}_n} = \frac{1}{\left(\overline{P}_n\right)_0} + C_s \frac{[S]}{[M]} \qquad \text{--------------------------------------} \ (17b)$$

Where $(\overline{P}_n)_0$ is the average degree of polymerization in absence of solvents. $\mathbf{C_S}$ can be obtained from the plot of ($\mathbf{1/\overline{P}_n}$) vs [**S**]/[**M**].

1.4 Non-ideality in Kinetics of Vinyl Polymerization:

The kinetic relationship developed in the previous section (equation 10) predicts that the rate of free radical vinyl polymerization should be proportional to the first power of monomer concentration and to the square root of initiator concentration. This is found to be the general behaviour of free radical chain polymerization. A number of side effects, not considered in the normal polymerization scheme have been put forward in order to explain the observed kinetic deviations from the general relationship and they are:

a) Primary radical termination,
b) Cage effect,
c) Retardation by solvents,
d) Enhancement in rate of initiation,
e) Dependence of propagation rate constant on the nature of solvent,
f) Effect of viscosity of polymerization on termination rate.

1.4a Primary radical termination:

If the primary radical $\mathbf{R^\bullet}$ terminate a growing polymer chain, a reaction order in [M] greater than unity, and in [I] less than 0.5 are expected. The fact that the rate constant for the reaction $\mathbf{M^\bullet + R^\bullet}$ is about 60 times greater than $\mathbf{R^\bullet + R^\bullet}$ in AIBN initiated polymerization of Styrene in DMF was observed by various **workers**[7,8]. A number of **workers**[7-10] attempted to arrive at some kinetic expression considering the primary radical termination effect in free radical vinyl polymerization. Recently **Deb** and **Meyerhoff**[11,12] have developed the following equation for analysis and detection of primary radical termination effect in a polymerization system.

$$l_n \frac{R_p^2}{[M]^2\,[I]} = l_n \frac{2fK_dK_p^2}{Kt} - 2\,\frac{K_{prt}}{K_iK_p} \bullet \frac{R_p}{[M]^2} \qquad \text{------------------ (18)}$$

where $\mathbf{K_{prt}}$ is the rate constant for the primary radical termination reaction. In presence of primary radical termination effect a negative slope is obtained in the plot of left hand side of the above equation (18) vs $\mathbf{R_p/[M]^2}$. The slope and intercept are used to determine the important parameter like $\mathbf{K_{prt}/\ K_iK_p}$ and $\mathbf{fK_d}$. For the concept that $\mathbf{R_t = 2K_t\ [M^\bullet]^2}$ (instead of $\mathbf{R_t} = \mathbf{K_t}\ [\mathbf{M^\bullet}]^2$, considered by Deb and Meyerhoff) the factor 2 in the first term of the right hand side of the equation (18) will vanish.

1.4b Cage Effect:

Matheson[13] proposed a mechanism in order to explain the deviation of monomer order from the general equation–10. He assumed that the concept of **Frank and Rabinowitch**[14] for photolysis in solution is also applicable to free radical vinyl polymerization. According to him, when an initiator decomposes into two radicals, the latter is confined by surrounding solvents or monomer molecules so that they could suffer many collisions which may lead to their mutual deactivation before being finally separated or reacting individually with monomer. **Jenkins**[15] proposed the following scheme of reactions to develop the kinetic relationship, neglecting chain transfer.

			Rate Constant	
I	$\longrightarrow$	$2R^\bullet$	K_d	.... (19a)
$(2R^\bullet)$	$\longrightarrow$	Q	K_r	.... (19b)
$(R^\bullet)+M$	$\longrightarrow$	$M^\bullet$	K_x	.... (19c)
$(R^\bullet)$	$\longrightarrow$	$R^\bullet$	K_d	.... (19d)
$R^\bullet + R^\bullet$	$\longrightarrow$	$Q^{/}$	$K_r^{/}$	.... (19e)
$R^\bullet + M$	$\longrightarrow$	$M^\bullet$	$K_x^{/}$	.... (19f)
$M^\bullet + M$	$\longrightarrow$	$M^\bullet$	K_p	.... (19g)
$M^\bullet + M$	$\longrightarrow$	P	K_t	.... (19h)

where

$M^\bullet$ stands for radical containing at least one monomer unit,

$R^\bullet$ for primary radicals derived from decomposition of initiator,

Q for products formed between two primary radicals within the cage,

$Q^/$ for product of reaction between radicals diffused from cage, and

P for dead polymer molecule.

Brackets indicate species confined in cages of solvents or monomer molecule. Reaction (19e) and (19f) are analogous to (19b) and (19c), but the difference is that they occur only after the reaction (19d). The rate of (19e) is second order with respect to **$R^\bullet$** but the rate of (19b) is first order with respect to **$(R^\bullet)$**, since the primary radicals are necessarily formed in pairs in the independent cages. It is evidently shown that for all practical values of [**M**], reaction (19e) is negligible. By application of steady state assumption, the rate of polymerization may be expressed as:

$$R_p = K_{\mathbf{p}}\left(\frac{K_d}{K_t}\right)^{1/2}[\,I\,]^{1/2}\left(\frac{K_{\mathbf{d}} + K_{\mathbf{x}}[M]}{K_{\mathbf{R}} + K_{\mathbf{D}} + K_{\mathbf{X}}[M]}\right)^{1/2}[\,M\,] \text{ ---------- } (20)$$

Now, there exist two cases in which one of the two processes via (19c) and (19d) may predominate.

Case - I

when $K_{\mathbf{D}} >> K_{\mathbf{X}}[M]$

$$R_p = K_{\mathbf{p}}\left(\frac{K_d}{K_t}\right)^{1/2}[\,I\,]^{1/2}\left(\frac{K_{\mathbf{d}}}{K_{\mathbf{R}} + K_{\mathbf{D}}}\right)^{1/2}[\,M\,] \text{ ------------------------- } (21)$$

where the order of reaction with respect to the monomer is unity.

Case - II

when $K_{\mathbf{D}} << K_{\mathbf{X}}[M]$

$$R_p = K_{\mathbf{p}}\left(\frac{K_d}{K_t}\right)^{1/2}[\,I\,]^{1/2}\left(\frac{K_{\mathbf{x}}}{K_{\mathbf{R}} + K_{\mathbf{x}}[M]}\right)^{1/2}[M]^{3/2} \text{ ----------------} (22)$$

If the nature of **Q** is uncertain, it is very difficult to discuss the efficiency of initiation **'f'** in light of cage effect. The common initiators **BZ_2O_2** and **AIBN** eliminate small unreactive molecules in the course of their decomposition and these reactions may occur within the cage. **Q**, therefore, be the products of combination and disproportionation reaction between the pairs of phenyl or cyanoisopropyl radicals according to the catalyst employed. In such case '**f'** is less than unity.

It follows that there exists four cases as given in the following table.

Table – 1.2

Case	f	Order of R_p with respect to [M]	$-\frac{D[I]}{Dt}$
I	$Q \equiv I$, 1, independent of [M]	1.0	Independent of [M]
	$Q \equiv \cancel{I}$, 1, independent of [M]	1.0	Independent of [M]
II	$Q \equiv I$, 1, independent of [M]	1.5 – 1.0	dependent on [M]
	$Q \equiv \cancel{I}$, 1, dependent on [M]	1.5 – 1.0	Independent of [M]

There is only one case when **'f'** is a function of [**M**]. This case is originally treated by **Matheson**[13]. But **Flory**[16] criticised it. According to **Jenkins**[15], unless the diffusion coefficient is very much less than 10^{-5} cm^{-2} sec^{-1} for primary radicals, it appears that the monomer is unlikely to exert any appreciable influence on the events that occur within the cage but it may affect the physical aspects of the diffusion process, as pointed out by **Flory**[16].

1.4c Retardation by Solvents:

A large number of workers[12-23] analysed the problem solvent-retarded free radical vinyl polymerization, to have a look into the kinetic features for such cases. According to **Burnett** and **Loan**[16,19] the radicals of low reactivity produced by transfer of active centre to solvent molecule could either react with the monomer molecule to re-initiate a chain or get involved in termination reactions. **George** and **Onyon**[17] postulated that **CCl_4** might facilitate the germinate recombination of primary radicals for **AIBN** initiated **Styrene** polymerization in **CCl_4**.

In his treatment of non-ideal polymerization Deb[12] arrived at the following kinetic expression where Degradative chain transfer effect is the sole cause of retardation.

$$\frac{[I]\,[M]^2}{R_p^2} = \frac{1}{A} + \frac{1}{A}\,\frac{2K_p^2}{K_t} \sum C_X \,\frac{[X]}{[M]}\,\frac{K_{rtx}}{K_{ix}\,K_p}\left(1+\frac{K_{rtx}\,R_p}{K_{ix}\,K_p\,[M]^2}\right)^{-1} \text{-------} \ (23)$$

where A = 2f K_d K_p^2/K_t, C_X is the chain transfer constant for additive **X**, **K_{ix}** is the rate constant for the re-initiation involving **$X^\bullet$** derived from the transfer reaction and K_{rtx} is the rate constant of the cross termination reaction involving **$X^\bullet$** and the macro-radical.

At low Rp a negative slope of a plot of left hand side of equation (23) against $Rp/[M]^2$ would indicate the occurrence of degradative chain transfer in a polymerization system.

Recently **Ghosh** and **Mitra**[23] have shown, during the treatment of their data on photopolymerization of **MMA** initiated by quinolone-bromine charge transfer complex in various solvents, that degradative chain transfer to solvent modified initiating complex is probably the cause of the observed retardation in some solvents.

1.4d Enhancement in Rate of Initiation:

The increase in rate of initiation **R_i** depends on the increase in initiator efficiency **'f'** or increase in decomposition rate constant **'K_d'**. The rate enhancing effect of various halobenzenes and naphthalene in **AIBN** initiated polymerization of **MMA** was explained by **Burnett et al**[16,24] on the basis of enhancement in rate of initiation, **R_i** due to the solvent-induced increase in efficiency of initiation. Latter study of **Brunett et al**[27] showed that although the initiator efficiency is a positive factor for increase in **R_i**, the contribution of variation of **K_d** should also be taken into account.

Tobolosky and **Matlack**[25] observed that in the **Cumene** hydroperoxide initiated polymerization of **Styrene** and **MMA** in various solvents, the rate of initiation **R_i**, was enhanced by reaction of **Cumene** hydroperoxide and solvent, and according to them.

$$R_i = K_1 [I] [M] + K_2 [S] [I] \quad \text{---------------------------} (24)$$

where K_1 and K_2 are rate constants of initiation depending on monomer and solvent respectively. Assuming bimolecular termination, the following relationship was obtained:

$$\frac{2k_t R_p^2}{K_p^2 [M]^3 [I]} = K_1 + K_2 \frac{[S]}{[M]} \quad \text{---------------------} (25)$$

as $R_i = \dfrac{2k_t R_p^2}{K_p^2 [M]^2}$, equation (25) can be written as:

$$\frac{R_i}{[M] [I]} = K_1 + K_2 \frac{[S]}{[M]} \quad \text{---------------------} (26)$$

A plot of left hand side of equation (25) and (26) against [S]/[M] should give a straight line, the intercept and slope of which give the value of K_1 and K_2 respectively.

More recently Ghosh et al[26] reported rate enhancing effects of a large number of solvents in the bromine-induced photopolymerization of MMA at 40°C. They postulated the formation of charge transfer complexes of bromine with the respective solvents, causing an increase in rate of generation of radicals with ultimate enhancement in rate of initiation.

1.4e Dependence of propagation rate constant on the nature of the solvent:

According to **Bamford** and **Brumby**[28] and **Bonta et al**[29] the rate of propagation constant $\mathbf{K_p}$ is independent on the nature of the solvent. **Bamford** and **Brumby**[28] suggested that there were three possibilities for dependence of $\mathbf{K_p}$ on the solvent:

a) The reactivity of the monomer might be influenced by interaction with solvent and such deviation is normally revealed by negative deviation from **Raoult's law**[30]. However observations on mixtures of **MMA** and bromobenzene did not show any such deviation.

b) The concentration of monomer in the immediate environment of a growing radical may differ from that of bulk liquid phase. This could arise, for example, from conformational differences in the polymer chains in different media. Measurement of intrinsic viscosity of a sample of polymer at 25^{o}C in a range of solvents indicated that the solvent used did not produce significant effect of this kind, this was consistent with the observed variation in K_t which seems to arise purely from viscosity changes.

c) The reactivity of the radicals may be influenced by the solvents. This possibility was consistent with the mechanism advanced by **Henrici-Olive** and **Olive**[31-34], and offered the most acceptable interpretation of **Bamford** and **Brumby's** results. Latter **Burnett et al**[27] showed from their experimental results that although complex formation between macromolecule and solvent could never be excluded, the variation in K_p seems rather small to be explained on the basis of such a strong interaction. They proposed that the effect might be simply due to variation in solvation of the radical end.

1.4f Effect of viscosity of polymerization on termination rate:

It has been found that the termination rate constant and molecular weight of vinyl polymer are dependent on viscosity of the polymerization medium. A number of workers[8,27,35-48] have shown that for **MMA** polymerization K_t is inversely proportional to the medium viscosity. **Yokota** and **Itoh**[36] have confirmed that in absence of any other interference $R_p \alpha \eta 1/2$ for MMA polymerization at 30^{0}C. The inverse relationship of K_t and η for MMA polymerization in a number of solvents has been satisfactorily utilized[27,28], to explain the observed kinetic deviations.

1.5 Photopolymerization:

Photochemical reactions[49,50] can also lead to initiation of polymerization and may be divided into three broad categories viz, uncatalysed, catalysed and sensitized photo initiation.

Uncatalysed photopolymerization:

Monomer **M** may generate excited species **M*** by absorbing light quanta on irradiation, which subsequently undergoes homolytic fission to produce radicals.

$$M \quad + \quad h\nu \quad \longrightarrow \quad M^* \quad \text{------------------ (27)}$$

$$M^* \quad \longrightarrow \quad R^{\bullet} + R^{/\bullet} \quad \text{------------- (28)}$$

These radicals are capable of initiating polymerization.

Sensitized photopolymerization:

Another method of photochemical initiation involves photosensitization. Photo-sensitizer **(Z)** used in the system absorbs light energy and transfers it to a monomer or initiator, which does not undergo sufficient excitation at that frequency of light causing homolytic fission of the monomer or initiator **(C)**

$$Z \quad + \quad h\nu \quad \longrightarrow \quad Z^* \qquad \text{-------------- (29)}$$

$$Z^* \quad + \quad C \quad \longrightarrow \quad Z \quad + \quad C^* \quad \text{-------------- (30)}$$

Radicals are subsequently produced from the excited compound **C***, which initiates the polymerization.

$$C^* \quad \longrightarrow \quad R^{\bullet} + R^{/\bullet} \qquad \text{--------------------- (31)}$$

The state **C*** cannot be produced directly by the compound **C** with the light of frequency ν. The absorption of energy by **C** is due to **Z*** which is able to transfer energy at an appropriate frequency suitable for excitation of **C**.

Benzophenone (BP) is the one of the most widely used sensitizers for radical reactions.

Catalysed photopolymerization:

In case of catalysed photo initiation initiators undergo fragmentation and generate radicals which initiate polymerization.

1.6 Kinetics of photopolymerization:

Photopolymerization of vinyl monomers involve the kinetics of linear chain reactions and may be considered to consist of four distinct steps, namely, (i) the production of the primary radicals, (ii) the initiation of the chain radicals, (iii) the propagation of the chain radicals and (iv) the removal of the radicals, by combination, for example. There may also be chain transfer with various species (e,g., with solvents) in the system.

One of the various methods for the generation of primary radicals by the use of light is photolytic decomposition of a substance called the initiator. The initiator absorbs light to raise the molecule to a higher electronic state. The excited species then decomposes to give radicals. The rate of formation of photolytically produced primary free radicals $\mathbf{R}^{\bullet}$ from the initiator, I, is the product of the quantum yield ϕ and the intensity of absorbed light **Ia**. Assuming the validity of Beer’s law, the rate of radical production through decomposition is:

$$R_d = \phi I_a = \phi I_0 (1 - e^{-\varepsilon l [I]}) \quad \text{------------------------} (32)$$

where I_0 is the incident light intensity, l, the path length in the system and [I] is the concentration of the initiator of extinction coefficient ε. For low values of the exponent equation 32 becomes:

$$R_d = I_0 \phi l \varepsilon [I] \quad \text{--------------------------} (33)$$

If there are no competitive processes in the photolytic reaction, the quantum yield ϕ should equal **2** when one quantum absorbed results in two free radicals. More usually, however, ϕ is less than this ideal because of competitive processes. Photolytic reactions in solution often have low quantum yields due to recombination of radicals in the “cage”[51,52]. The two radicals have a high probability of escaping from each other if they posse’s high kinetic energy. Thus it might be expected that the more the energy of the absorbed quantum exceeds the bond energy of the photolyzable linkage, the higher will be the value of **ϕ.** The viscous drag on the radicals opposes their separation in the cage, and hence ϕ should decrease when the microscopic (or local) viscosity is increased. This diffusion-controlled process is particularly important for radical recombination since the activation energy is very low. The principal effect of raising the temperature will be to decrease the viscosity and hence to increase the quantum yield. It has been observed the microscopic viscosity is practically that of the pure solvent for a polymer solution[53] with polymer concentration upto about 10%.

Once the primary radicals escape from the cage they can attack a monomer molecule to form **$RM^\bullet$**, the start of the chain reaction:

$$R^\bullet \quad + \quad M \xrightarrow{K_i} RM^\bullet \qquad \text{--------------------} \ (34)$$

The rate of initiation is given by:

$$R_i \quad = \quad K_i\,[R^\bullet]\,[M] \qquad \text{--------------------} \ (35)$$

The first chain radical **$RM^\bullet$** , thus produced, reacts with monomer to produce **$RM^\bullet_2$** and so on. A typical step in the propagation is:

$$RM^\bullet_n \quad + \quad M \xrightarrow{K_p} R^\bullet_{n+1} \qquad \text{-------------------} \ (36)$$

It is generally assumed that the propagation rate constant, **K_p**, is the same for all the propagation steps independent of the size[54] of **$RM^\bullet_n$.** The rate of the propagation is:

$$R_p \quad = \quad K_p\,[P^\bullet]\,[M] \qquad \text{---------------------} \ (37)$$

where [**$P^\bullet$**] is the sum of the concentrations of the growing chain radicals. The propagation reaction is not diffusion controlled because the activation energy of the propagation steps is about **7 K.Cal.mole^{-1}**.

The propagation of the chains continue until one or another termination takes place. One type of termination occurs when the growing chain radical reacts with another. The rate of this reaction is:

$$R_t \quad = \quad K_t\,[P^{\bullet}]^2 \qquad \text{--------------------} \ (38)$$

The termination could be by combination and/or by disproportionation. Termination by disproportionation has a much higher activation energy. Like most radical reactions, the combination of chain radicals has a low activation energy and hence is diffusion controlled. In low viscosity liquids, ordinary radical–radical reaction rates are of the order of **10^{11} *l* .mole^{-1}. Sec^{-1}** whereas for chain radical terminations K_t is of the order of **10^{7} *l* .mole^{-1}. Sec^{-1}** or lower. Obviously the enormous discrepancy in values for small and large radicals arises from segmental diffusion as being the rate-determining step for chain–radical combination[55,56]. This termination rate constant is generally considered to be independent of molecular weight.

Applying the steady–state condition for the primary radicals, one obtains, using equation–33.

$$I_0\,\phi\,/\,\varepsilon\,[I] \quad = \quad K_i\,[R^{\bullet}]\,[M] \qquad \text{--------------------} \ (39)$$

where [R$^{\bullet}$] refers to the steady–state concentration of primary radicals. Also the steady–state concentration of chain radicals is:

$$[P\bullet] \quad = \quad \left\{\frac{I_0\,\phi\,/\,\varepsilon\,[I]}{K_t}\right\}^{1/2} \qquad \text{-------------------} \ (40)$$

The rate of consumption of monomer, i.e., the rate of polymerization is

$$-\,\frac{d[M]}{dt} \quad = \quad R_p \quad = \quad K_p\,[P^{\bullet}]\,[M] \ \text{-------------} \ (41)$$

Substituting the value of [P•] from equation 40 into equation 41 we have:

$$Rp = K_p \left\{ \frac{I_0 \, \phi \, / \, \varepsilon \, [I]}{K_t} \right\}^{1/2} [M] \quad \text{--------------------- (42)}$$

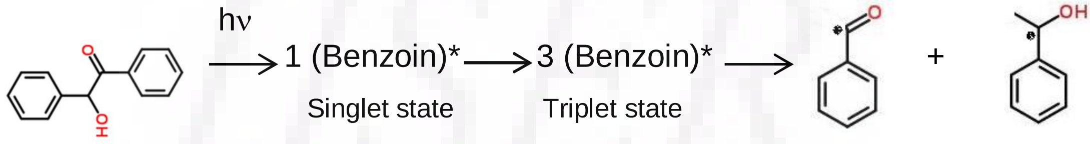
OR

$$R_p = \frac{K_p}{[K_t]^{1/2}} [R_i]^{1/2} \; [M] \quad \text{--------------------- (43)}$$

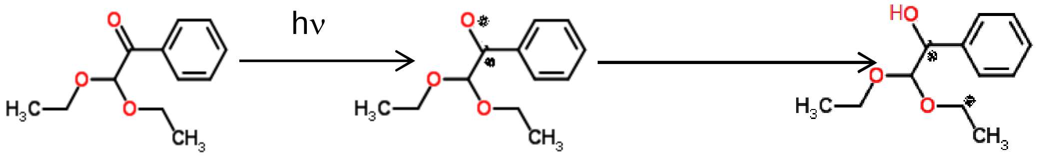
1.7 Photoinitiating systems:

Among the various systems studied so far the most important are the following from their industrial applications.

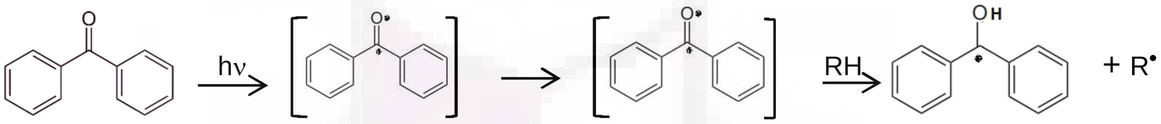
Benzoin and it's derivatives. The dissociation of Benzoin probably occurs via dissociation of the excited triplet state to form free radicals (Norrish type I cleavage)[57-59]



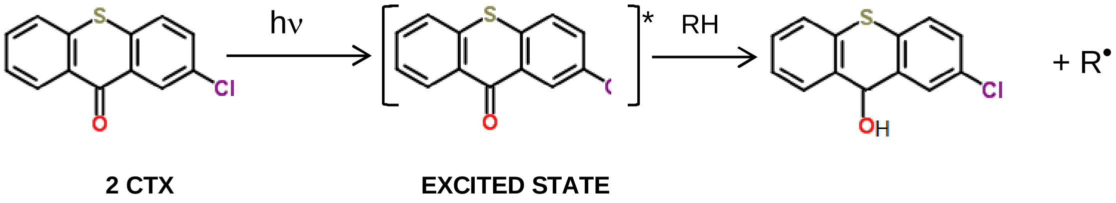
Acetophenone derivatives. The most important of them are dialkoxyacetophenone (e.g., diethoxyacetophenone) and chlorinated Acetophenone derivatives. Diethoxy-Acetophenone undergoes a Norrish type II cleavage yielding a biradical as the chain initiating species[60-62]:



Aromatic ketone/amine combinations. In this system the most important one is Benzophenone which reacts by hydrogen abstraction and is photo–reduced to benzopinacol in the presence of hydrogen donars[57,63–65]. Benzophenone undergoes a photo–induced excitation predominantly at 340 nm and reaches to its triplet state through intersystem crossing and then reacts with the hydrogen donar to yield radicals.

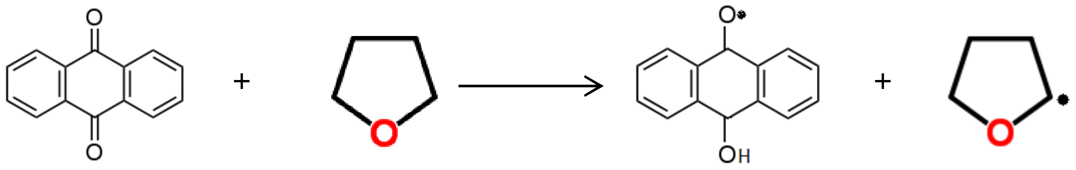


Thioxanthone and derivatives[66,67]. Among them the most important are, 2-Chlorothioxanthone and 2-Isopropylthioxanthone. The latter has good solubility (as it is a liquid) in many solvents. 2-Chlorothioxanthone (2CTX) is, however, a solid. 2-Chlorothioxanthone probably reacts by a hydrogen abstraction method.



2CTX has absorption bands at 260 nm and 385 nm.

Quinines are another class of photoinitiator. The reaction mechanism of these compounds are very similar to benzophenones[68–70]. A typical reaction scheme for anthraquinone in MMA and Tetrahydrofuran is shown below[57,71,72].



(AQH) (THF) $(AQH^\bullet)$ $(THF^\bullet)$

$$THF^\bullet + MMA \longrightarrow \text{Polymer radical } P^\bullet$$

Organic peroxides can also be used as photoinitiator but they need strong light to decompose into radicals, because the peroxy group absorbs strongly at 254 nm but does not respond to radiation above 320 nm. It is therefore transparent to the 365 nm wavelength emitted from the medium pressure UV mercury lamp. Inorganic peroxides such as hydrogen peroxide, H_2O_2, and peroxydisulphates have application for photopolymerization reactions[73].

Among the metal compounds and ions which can be used as photoinitiator / sensitizer, the most important are, Uranyl salts, Cobalt salts, Metal Carbonyl compounds.

Uranyl salts are photo–sensitizers. The Uranyl ion is a true sensitizer as it is not reduced or oxidized. UO^{2+} readily sensitizes monomers such as acrylamide[74], methacrylamide[75] and hydroxylalkyl acrylates[76].

Azidoamine Cobalt III salts photopolymerize acrylamide, methacrylamide, methyl methacrylate, acrylonitrile and N–vinyl–pyrrolidone[77–80]. The mode of action is probably a one–electron transfer from azide to Cobalt III, and homolytic cleavage of the cobalt–azide bond to produce azide radicals and the Cobalt II amine complex[81]. Strong cage effects give low quantum yields (<0.2) and polymerization occurs via a free radical mechanism.

Metal Carbonyl compounds such as Rhenium Carbonyl $Re_2(CO)_{10}$ and manganese carbonyl, $Mn_2(CO)_{10}$, cause photopolymerization at 365 nm and 436 nm respectively[82]. Irradiation in the presence of monomer results in polymerization slowly with $Re_2(CO)_{10}$ possibly by hydrogen abstraction. $Mn_2(CO)_{10}$ is ineffective under similar conditions. When specific chlorinated or brominated compounds are present both carbonyl complexes initiate with high efficiency ($\phi \sim 1$). The primary radicals are probably produced by:

$$Me_2(CO)_{10} \longrightarrow Me(CO)_4 + Me(CO)_6$$

$$Me(CO)_4 + CCl_4 \longrightarrow Me(CO)_4Cl + {}^{\bullet}CCl_3$$

CHAPTER – II

LITERATURE REVIEW

2.1 Literature Review:

Numerous sulphur compounds have been used as photo–initiators/ sensitizers. Some of these include[83]

Alkyl disulphides such as di-n-butyl disulphide
Aralkyl disulphides such as dibenzyl disulphide
Aryl disulphides such as diphenyl disulphide
Aroyl disulphides such as dibenzoyl disulphides
Acyl disulphides such as diacetyl disulphide
Cyclo alkyl disulphides such as dibornyl disulphide

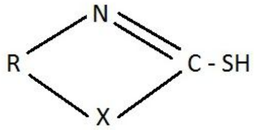
Simple disulphides, like dimethyl disulphide, posses relatively strong **S–S** bond, needing **72 K.Cal** per mole to undergo dissociation[84]. Those with more of a complicated nature such as diaryl disulphides have less stability and generate free radicals when irradiated with actinic radiation in the wave length range 280–400 nm[85].

Aliphatic disulphides absorb maximally in the neighbourhood of 254 nm with molar extinction coefficients from about 200 to 600[86]. Loss of the maximum at high pH is associated with alkali cleavage via the hydrogen α to the **S–S** linkage. The disulphide bond is also cleaved by ultraviolet light to yield free radicals and the **S–S** bond cleavage often follows the pattern[87].

$$C_4H_9S \quad — \quad SC_4H_9 \xrightarrow{h\nu} 2C_4H_9S^{\bullet}$$

The type of fission in the disulphide linkage can be of paramount importance. Asymmetric rupture of the **C–S** linkage may provide the inhibiting radical $\mathbf{C_6H_5SS^{\bullet}}$ for diphenyl disulphide, resulting in a retarding effect on the system in contrast to the formation of a faster reacting $\mathbf{C_6H_5S^{\bullet}}$ free radicals.

Mercaptans[88] and Thiols[89] are the other class of photoinitiators containing sulphur, e.g.,



Such as 2–Mercaptobenzothiazole

where R = Ortho-arylene radical
X = S, O or NH
R — SH Such as thiophenol

where R = aryl or substituted aryl.

Photoinitiators possessing the **S–H** linkage create via photoinduced bond rupture the radicals **RS$^\bullet$** and **H$^\bullet$** which initiate the subsequent chain reaction.

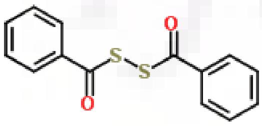
There are many monosulphides, disulphides and polysulphides that have shown notable photoactivity. Some examples of these are shown below[90–92]

$C_6H_5 - S_n - C_6H_5$ where n = 2 – 4

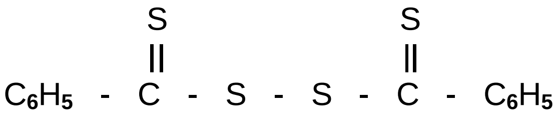
Diphenyl polysulphide

$C_6H_5 - CH_2 - S_n - CH_2 - C_6H_5$ where n = 2 – 4

Dibenzyl polysulphide

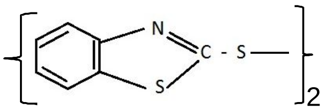


Dibenzoyl disulphide

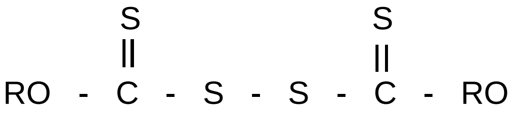


$$C_6H_5 - \overset{\overset{\displaystyle S}{\|}}{C} - S - S - \overset{\overset{\displaystyle S}{\|}}{C} - C_6H_5$$

Dithiobenzoyl disulphide



Dibenzothiazoyl disulphide

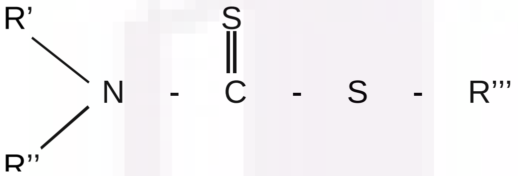


$$RO-\overset{\overset{S}{\|}}{C}-S-S-\overset{\overset{S}{\|}}{C}-RO$$

where R = CH_3, C_2H_5, C_4H_9

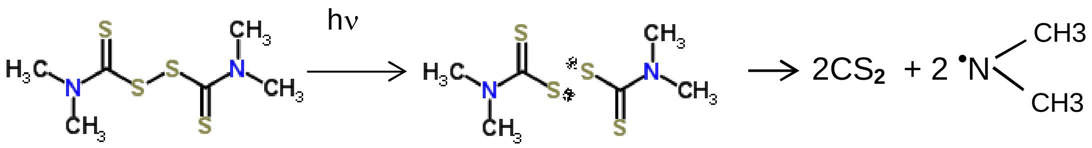
Dialkyl xanthogen disulphide

Dithiocarbamates[93] which have the general formula and their several



S-aryldithiocarbamate derivatives have been studied as photoinitiators for methyl methacrylate[94]. The order of effectiveness was found to be $CH_3O > CH_3 > Cl$ where the groups refer to the para–substituted carbamate derivatives. The chain transfer constant at room temperature for benzodithiocarbamate is 5.5 so that it's concentration should be very low in order to obtain reasonably high molecular weight polymer.

Several thiuram derivatives[95–98] have also been studied as photoinitiators. Among them tetramethyl thiuram monosulfide is an excellent sensitizer for photopolymerization[99]. This sensitizer is particularly attractive in that it has an absorption maxima at 400 nm, and its absorption extends considerably into the visible region. The photodissociation of tetramethyl thiuram disulphide may be depicted as[100]



Sulphur compounds have also found use in photografting and in the photochemical production of block copolymers. Polystyrene prepared by tetramethyl thiuram disulphide used as a thermal initiator has an end group, the diethyldithio-carbamate group[92].

Mercaptan olefin copolymerization has been investigated in depth by W. R. Grace and Co. Ltd[101,102] for the preparation of photopolymer relief printing plates. The overall reaction is a free radical addition of the thiol to an olefinic or allylic double bond.

$$RSH + CH_2 = CHR \xrightarrow{h\nu} RS{-}CH_2{-}CH_2{-}R$$

2.2 Main Theme of the present thesis:

Organic sulphur compounds are widely used in rubber industries as accelerator as well as curing agents. Not only do they influence the course of these reactions, but the presence of accelerator fragments in the finished product is important for its ultimate properties and in particular, the weathering property of the material.

In vinyl polymerization organic sulphur compounds are well known chain transfer agents and are often used for controlling mol. Wt. of the polymers. However their participation in polymerization reactions as initiators especially under irradiation has also been reported in the literature, though the detailed mechanism is not well understood in many cases.

Some of the important sulphur–containing photoinitiators includes alkyl and aryl disulphides, thiocarbamates, thiurams, mercaptans and thiols, sulfenates, chloro-sulfonamodes, etc. Of all these compounds, thiurams and disulphides have got relatively wider attention as photoinitiators in vinyl polymerization.

The lower electron affinity of the sulphur atom should lead to a higher energy, loose–bond, non–bonding electron pair in the sulphur atom. As a consequence transitions involving these electrons $n \rightarrow \pi^*$, $n \rightarrow \sigma^*$ etc. occur at higher wavelength than with oxygen containing analogs. It is thus possible to generate free radicals when irradiated with actinic radiation in the wavelength range 280–400 nm.

The prime objective of the present work is concerned with the photoinitiation of vinyl monomers using organic sulphur compounds containing mercaptobenzothiozole moiety. We have observed that these compounds are not only effective photoinitiators but they also incorporate the benzothiazole moieties in the polymer chains as end groups. In an attempt to explore this possibility of attaching end group in the polymer chain, to increase their antioxidant activity, a detailed kinetic and mechanistic study has been undertaken and selecting 2–mercaptobenzothiazole as photoinitiator. Experiments have also been carried out in presence of some additives such as benzoyl peroxide and solvents. The effect of some substitution has also been investigated using dicyclohexyl benzothiazole sulfenamide as photoinitiator.

CHAPTER – III

EXPERIMENTAL

3.1 Purification of monomer:

The monomer was purified from its inhibitors by repeated washing with 4% aqueous sodium hydroxide solution followed by washing with distilled water, the inhibitor free monomer was dried over fused calcium chloride by keeping it overnight. The dried monomer was then distilled under reduced pressure and the middle fraction was collected and used for polymerization.

3.2 Purification of solvents:

All the solvents used in the polymerization were of reagent grade. The solvents were dried before distillation by the following procedures.

Benzene was dried over metallic sodium, carbon tetrachloride (CCl_4), chloroform and cyclohexane over molecular sieve. The dried solvents were finally purified by distillation prior to use in the polymerization.

3.3 Purification of initiators and inhibitors:

Mercaptobenzothiazole: It was purified by recrystallization twice from benzene. The melting point of the purified material was observed to be 178°C.

Benzoyl peroxide: It was recrystallized twice from absolute alcohol to get the pure material.

Dicyclohexyl benzothiazole sulphonamide: This was also purified by recrystallization twice from benzene and the melting point was observed to be 105°C.

Hydroquinone: This material was recrystallized twice from absolute alcohol to get the pure material and the melting point was noted to be 171°C.

3.4 Purification of Nitrogen Gas:

This gas, as obtained from Indian Oxygen in pressure cylinder was purified by passing it through a pair of alkaline pyrogallol scrubber to remove any trace amount of oxygen, if any, and then dried by passing it through concentrated sulphuric acid scrubber, one potassium hydroxide packed scrubber and finally a silica gel packed scrubber.

3.5 Dilatometric technique:

The course of polymerization was followed by dilatometric technique[103], which is based on the change of density / volume (contraction) during conversion of monomer to polymer in a polymerization process.

With the dilatometric technique conversion of less than 1% can be accurately determined by proper experimental set up. Another great advantage is that the density is not dependent on small difference in structure, or to any noteworthy extent on degree of polymerization.

3.6 Equipments and their description for the dilatometric process:

3.6a Dilatometer: The dilatometer was made of a cylindrical borosilicate glass ampoule of about 10 ml capacity fitted with a capillary of about 20 cm length. This was calibrated by the usual method[104] and the average cross–section was found to be 0.048 sq.cm.

3.6b Thermostatic bath:

To carry out polymerization at a particular temperature the dilatometer was placed in a thermostatic bath. The thermostated bath consisted of a 10 litre boro-silicate glass vessel filled with distilled water and fitted with a stirrer, a temperature controlling unit with a 125 watt immersion heater. The controlling of temperature was effected with an electromagnetic relay and contact thermometer system which control the temperature of the bath within $\pm$ 0.05°C. The bath was covered with black paper and there was a small (2 cm wide) window (uncovered vertical section) in front of the bath through which light entered from the light source to irradiate the liquid within the dilatometer immersed in the bath. The bath was covered from the top with a suitable aluminium cover to avoid heat loss and also evaporation.

3.6c Light source:

For photopolymerization experiments high pressure 125 watt mercury vapour lamp (Philips India Ltd.), was used as the light source.

It is known from the literature that the intensity of the lamp does not decrease appreciably in the first 100 hrs and therefore the use of the lamp was restricted within 90 hrs.

3.7 Experimental procedure to follow the course of Polymerization in Dilatometer:

3.7a Procedure: The dilatometer was filled with requisite amount of monomer, initiator and other additives (when used), flushed with purified Nitrogen gas, stoppered and placed in the thermostated bath. After allowing some time for the dilatometer to attain the temperature of the bath, the light source was placed in front of the window of the bath to illuminate the dilatometer. The volume contraction during polymerization was measured by a cathetometer.

3.7b Isolation and purification of polymer:

After the requisite amount of contraction, the dilatometer was taken out from the thermostated bath and the polymer solution taken out quantitatively from the dilatometer. The polymer was isolated from the solution by precipitation with large excess of nonsolvent, Methanol. The polymer was then purified by reprecipitation and finally collected by filtration and dried under vacuum.

3.7c Calculation:

After the polymer was collected through the procedure mentioned in the last section, its quantity was measured by weighing to a constant weight in an electronic balance (Mettler).

The total percent conversion was then calculated from the initial weight of the monomer taken and the weight of the polymer thus obtained. This total percent conversion was then distributed into the corresponding total contraction observed in the dilatometer.

If **'V_M'** is the initial volume of the monomer taken, **'W_P'** is corresponding weight of the polymer and **'X'** is the contraction

$$\text{Percent conversion} = \frac{W_P}{V_M\,\rho_M} \times 100 = \text{P. C.}$$

The factor for the dilatometer to convert each contraction into percent conversion (P.C) can then be obtained in the following way:

$$\text{Factor} = \frac{\text{Total percent conversion}}{\text{Total contraction, 'X' in mm}}$$

The overall rate of polymerization, R_p, can then be obtained from the following equation:

$$R_p = \frac{\text{P. C}}{t} \times \frac{1000}{100 \times 100 \times 60} \text{ ------------------ (44)}$$

where 't' is the time of polymerization in minute.

3.8 Molecular weight:

The molecular weight of the polymer sample is related to its intrinsic viscosity $[\eta]$ for its solution in a given solvent by Mark Houwink equation:

$$[\eta] \quad = \quad K\,\overline{M}^{\alpha}$$

where K and α are constants for a particular polymer solvent system at a given temperature.

For determining the viscosity of the polymer solution we have used an Ubbelohode Viscometer with a flow time 124.4 seconds for Benzene at 30°C. The experiment was carried out in a thermostated bath maintained at 30 ± 0.05°C. After determination of the intrinsic viscosity, the molecular weight of the polymer was calculated from the following equation[105]

$$[\eta] \quad = \quad 8.69 \times 10^{-5}\ \overline{M}_n^{\,0.76} \quad \text{-----------------} \ (45)$$

3.9 Rate of initiation (R_i):

The rate of initiation was determined from the length of inhibition period due to the use of an inhibitor, hydroquinone (HQ), and the inhibitor concentration:

$$\text{Rate of initiation} \quad = \quad \frac{\text{Concentration of inhibitor (mol. lit}^{-1}\text{)}}{\text{Inhibition period (secs)}}$$

The inhibition period was measured from the percent conversion vs time plot and the actual inhibition period was obtained after deducting the usual inhibition period associated with the system.

3.10 End group determination:

For determining the end group we have done a comparative experiment with pure polymer (thermally polymerized) and the polymer obtained by using the photoinitiator and the experiment was done with the help of spectroscopy. For this experiment the polymer containing the initiators was purified by reprecipitation from benzene solution (three times) and the instrument used for recording the UV–spectra Is a Perkin Elmer 5508 Spectro–photometer. We also recorded the spectra of the initiators.

CHAPTER – IV

RESULTS AND DISCUSSION

4.1 Photopolymerization of MMA using Mercaptobenzothiazole as Photoinitiator

4.1.1 Introduction:

Organic sulphur compounds have long been used both as an accelerator as well as vulcanizing agent for rubber. It has been established that in many cases the mode of action of these compounds towards rubber is through free radicals. Vulcanization can also be carried out photochemically when dibenzodithiozyl disulphide and hydrogen sulphide are present[106]. The vulcanizing effect was assumed to involve benzothiazoyl disulphide radicals.

Tetramethylthiuram monosulphides is an excellent sensitizer for photo-polymerization[107]. Several S–aryldithiocarbamate derivatives have been studied as photoinitiators for methyl methacrylate[108]. Diphenyl, dibenzoyl and dibenzothiazole disulphides also act as sensitizers[109] for the photopolymerization of vinyl monomers.

It has been mentioned in the literature[88,89] that 2–mercaptobenzothiazole can be used as photoinitiator but no detail kinetic study has been done so far. In this section we have presented the kinetics of photopolymerization of MMA using MBT as photoinitiator.

4.1.2 Photopolymerization of MMA in bulk:

Results based on the kinetic and related studies on the photopolymerization of MMA with MBT system as the photoinitiator at 40^{o}C, are presented in the present section. No polymerization was observed in the dark at 40^{o}C. The polymerization was associated with some inhibition period ranging from 30 to 75 minutes, depending on the concentration of initiator used. Typical free radical scavengers like hydroquinone inhibited the photopolymerization indicating a radical nature of the process.

4.1.3 Results:

4.3.1a Initiator order:

The results of the photopolymerization of MMA in bulk initiated by MBT at 40^{o}C are presented in Table – 4.1. The overall rates of polymerization (Rp) were

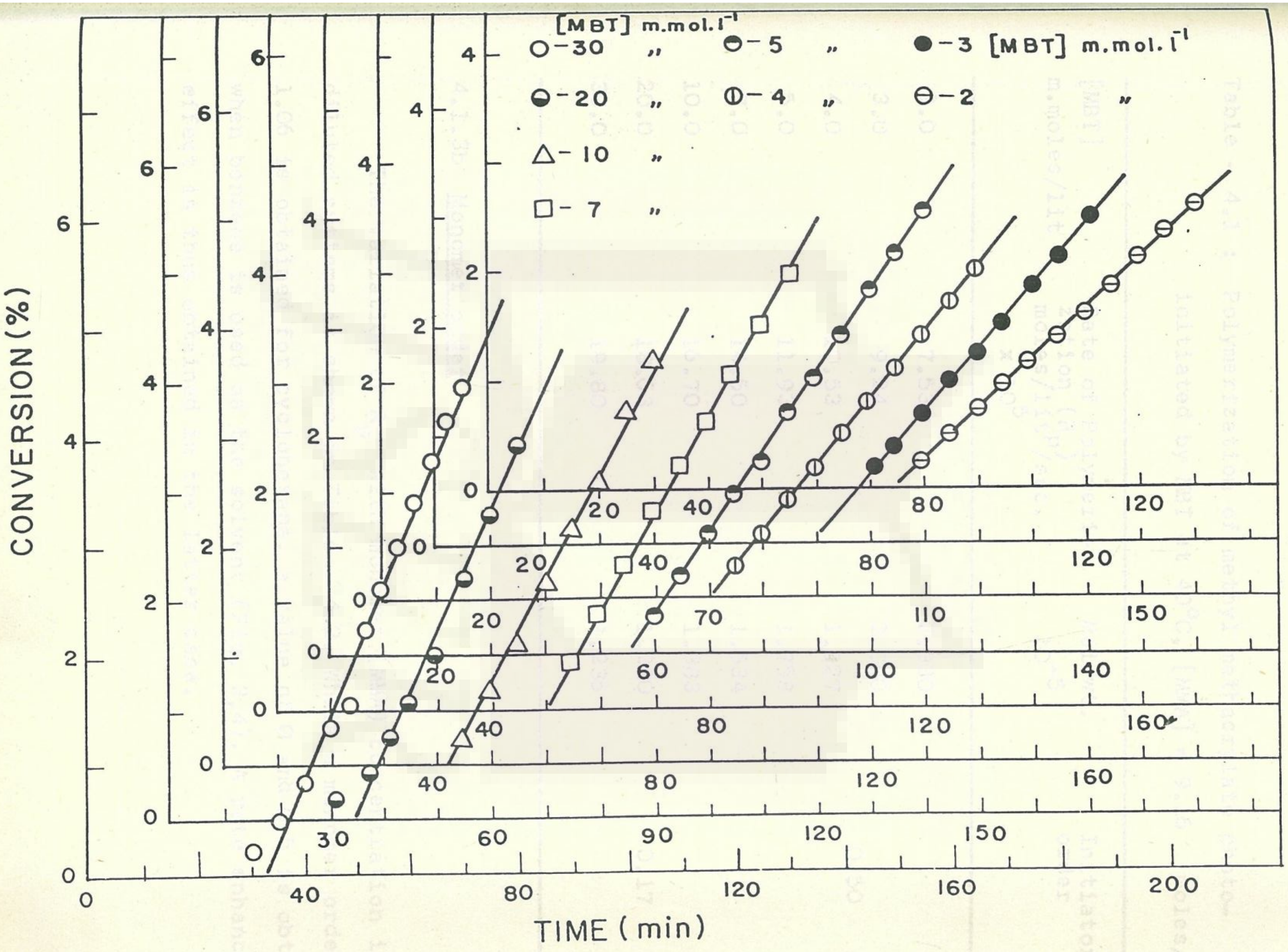


Fig - 1 : Effect of [MBT] on the photopolymerization of MMA at 40°C using MBT as initiator.

obtained from the initial slopes of the linear plots of % conversion vs time (Fig.–1). The order of reaction with respect to the initiator as obtained from the plot of **log R_p** vs **log [I]** (Fig.–2) is 0.5 for the concentration region 2 x 10^{-3} to 1 x 10^{-2} M/L while the order is 0.17 for the region 2 x 10^{-2} to 6 x 10^{-2} M/L. This low initiator order at the higher initiator concentrations may be due to some non–ideality of the system related to the termination and / or transfer effect as discussed latter.

Table–4.1

Polymerization of methyl methacrylate photoinitiated by MBT at 40°C, [MMA] = 9.16 moles/lit.

[MBT] m.moles/lit	Rate of polymerization (R_p) moles/lit/sec x 10^5	Mol. wt 10^{-5}	Initiator order
2.0	7.53	2.330	0.50
3.0	9.24	2.080	
4.0	10.53	1.927	
5.0	11.93	1.758	
7.0	14.50	1.534	
10.0	16.70	1.383	0.17
20.0	18.63	1.280	
30.0	19.80	1.236	

4.1.3b Monomer order:

The variation of R_p with monomer (MMA) concentration in diluted systems is shown in Table–4.2. While a monomer order of 1.06 is obtained for cyclohexane, a value of 0.0 and 0.5 is obtained when benzene is used as the solvent (Fig.–3,4). A rate enhancement effect is thus obtained in the latter case.

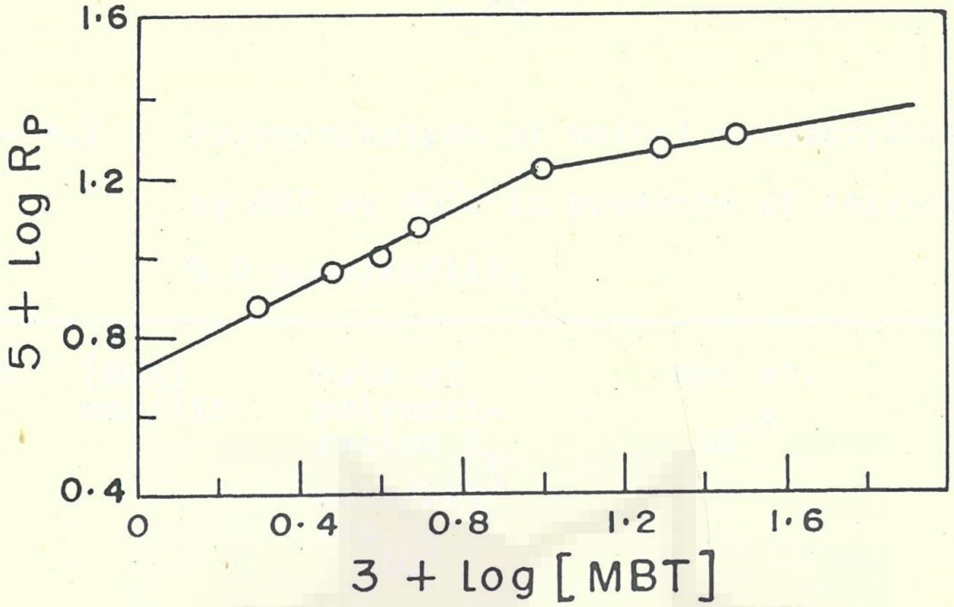


Fig.-2 : Photopolymerization of MMA at 40°C using MBT as initiator.

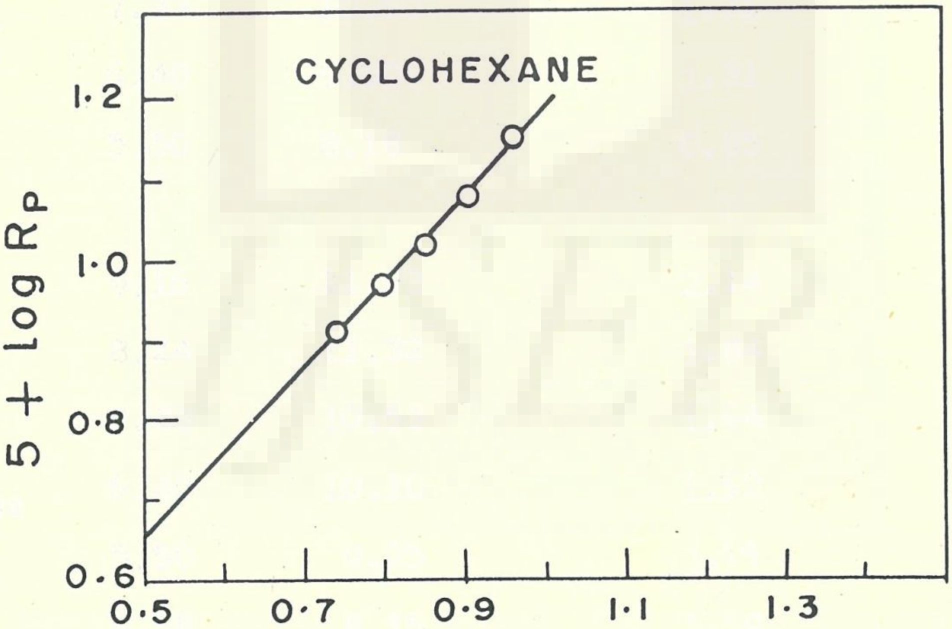


Fig.-3: Photopolymerization of MMA in presence of cyclohexane at 40°C using MBT as initiator.

Table–4.2

Polymerization of methyl methacrylate photoinitiated by MBT at 40°C in presence of solvents, [MBT] = 5.0 m.moles/lit.

Solvent	[MMA] mol/lit	Rate of polymerization (R_p) moles/lit/sec x 10^5	Mol wt 10^{-5}	Monomer order
Cyclohexane	9.16	14.12	2.14	1.06
	8.24	12.06	1.90	
	7.33	10.60	1.71	
	6.40	9.50	1.31	
	5.50	8.18	0.85	
Benzene	9.16	11.93	2.14	0.0 and 0.5
	8.24	11.32	1.84	
	7.33	10.53	1.64	
	6.40	10.10	1.52	
	5.50	9.25	1.44	
	4.58	8.15	1.39	
	3.66	7.53	1.26	
	2.75	6.30	1.02	

4.1.3c Rate of initiation:

The rate of initiation, $\mathbf{R_i}$, was experimentally determined from inhibition period measurements using hydroquinone as the inhibitor (Table–4.3, Fig. 5). The rate constant for the decomposition of the initiator ($\mathbf{K_d}$) was obtained from the spectrophotometric studies of the initiator (MBT) solution in monomer (MMA) under irradiation (Table–4.4)

Table–4.3

Polymerization of methyl methacrylate photoinitiated by MBT in presence of hydroquinone (HQ) as inhibitor at 40°C,

[MBT] = 5.0 m.moles/lit, [MMA] = 9.16 moles/lit.

Rate of Polymerization (R_p), moles. lit^{-1}. Sec^{-1} x 10^5	[HQ] moles. lit^{-1} x 10^5	Inhibition period (t) min	Rate of Initiation (R_i), moles. lit^{-1}. Sec^{-1} x 10^8	Average R_i x 10^8	$\frac{K_p}{K_t^{1/2}}$
11.93	4.0	28	2.38	2.37	0.084
	3.0	20	2.50		
	2.0	15	2.22		

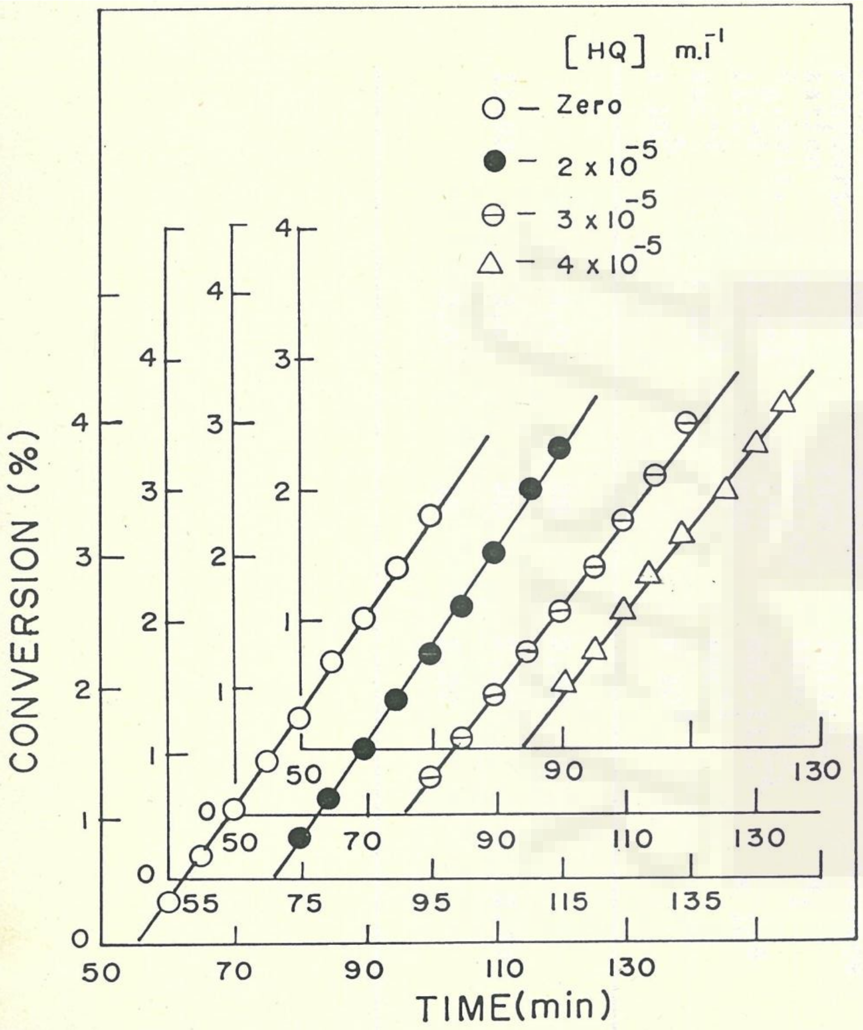


Fig.-5: Photopolymerization of MMA at 40°C in presence of Hydroquinone using MBT as initiator.

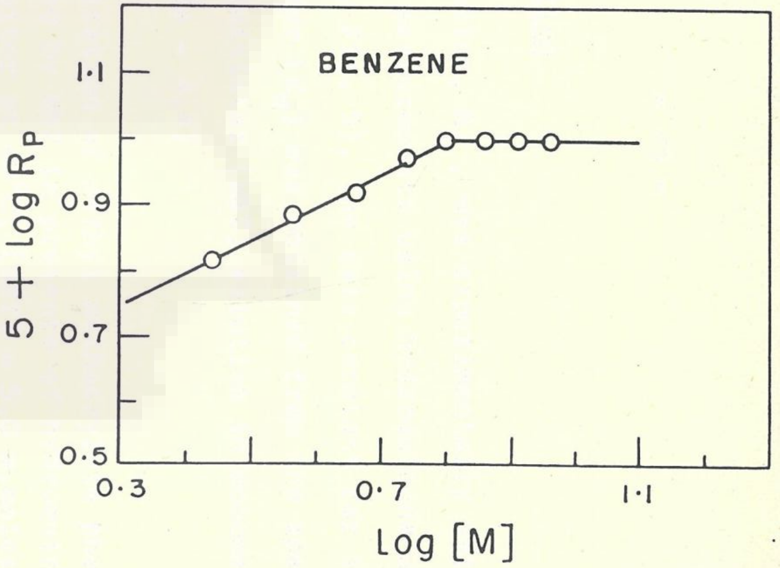


Fig.-4 : Photopolymerization of MMA in presence of benzene at 40°C using MBT as initiator.

4.1.3d: $K_p/K_t^{1/2}$ value:

This kinetic parameter was calculated from the experimental results of $\mathbf{R_i}$ and $\mathbf{R_p}$ data for the undiluted system (MBT = 5 x 10^{-3} M/L) and is presented in Table–4.3 Using this value of $K_p/K_t^{1/2}$ the mode of termination was obtained from the slope of the plot of $1/\overline{P_n}$ vs $R_p/[M]^2$ (Fig. 6, Table–4.5)

The initiator transfer constants were calculated using the Mayo Equation (Table–4.6, Fig.7)

Table – 4.4

Spectrophotometric study on the photodecomposition of MBT in presence of methyl methacrylate

Irradiation time min	K_d sec^{-1} x 10^6	Average K_d sec^{-1} x 10^6	R_i x 10^8 $m.l^{-1}.s^{-1}$	[a] x 10^3 $m.l^{-1}$	Equilibrium constant * K
15	6.02	6.07	2.37	5	0.64
30	6.17				
45	6.04				

✷ The equilibrium constant K was calculated from the relation:

Ri = 2f Kd K[a]/1 + K (Page–57) and assuming f = 1.

Table – 4.5

Data for the analysis of mode of termination

[MMA] = 9.16 moles.lit^{-1}, $K_p/K_t^{1/2}$ = 0.084

[MBT] m.moles.lit^{-1}	Rate of Polymerization (R_p), moles. lit^{-1}. sec^{-1} x 10^5	Average degree of polymerization $\overline{P_n}$	Mode of termination $\frac{Y + 2}{Y + 1}$
2.0	7.53	2330	1.85
3.0	9.24	2080	
4.0	10.53	1927	
5.0	11.93	1758	
7.0	14.50	1534	
10.0	16.70	1383	
20.0	18.63	1280	
30.0	19.80	1236	

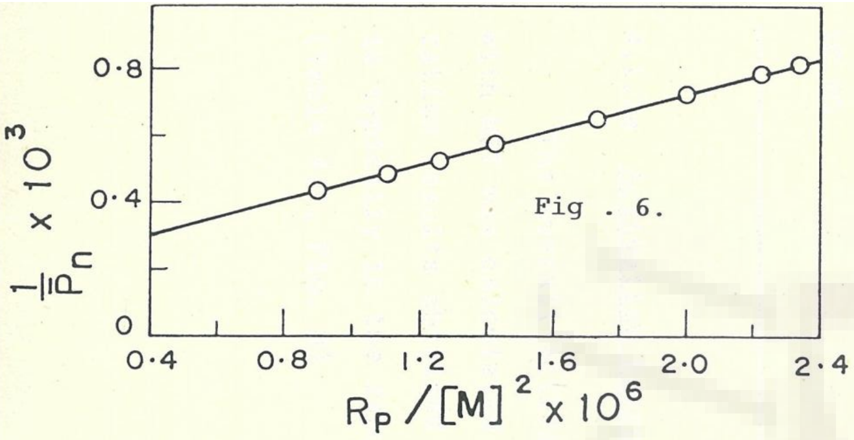


Fig . 6.

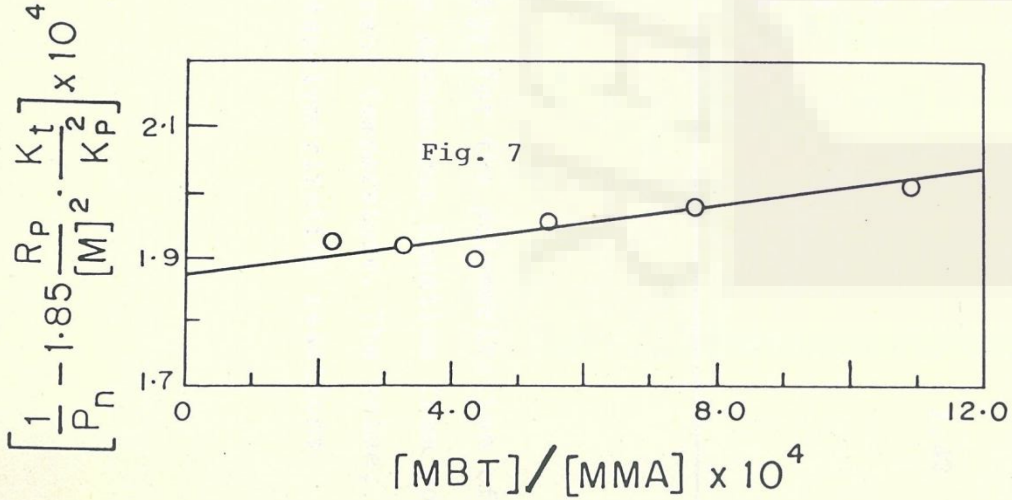


Fig. 7

Photopolymerization of MMA at 40°C using MBT as initiator.

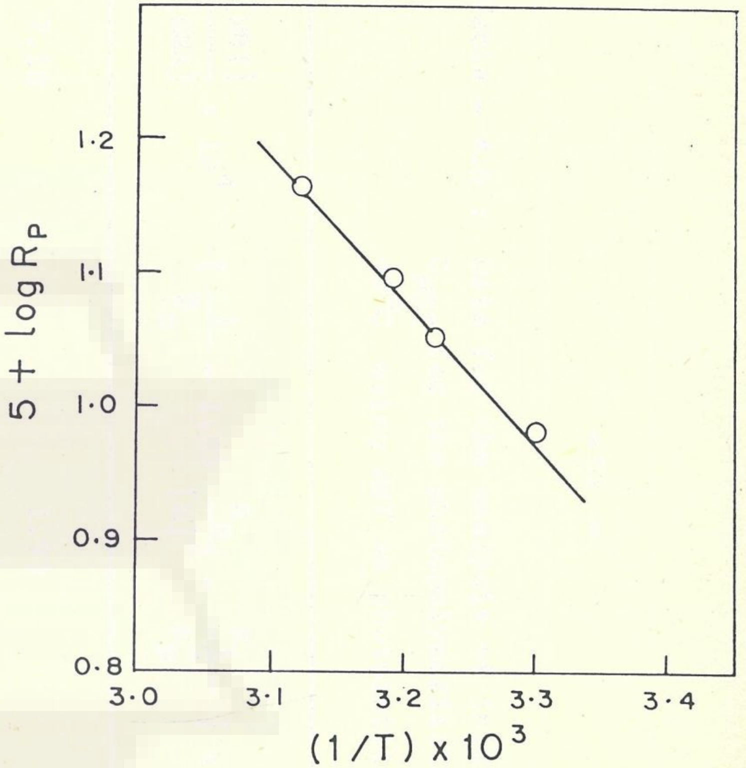


Fig. 8 : Effect of temperature on the photopolymerization of MMA using MBT as initiator.

Table – 4.6

Data for the analysis of initiator transfer constant C_{MBT} for the photopolymerization of MMA (bulk) at 40°C using MBT as photoinitiator

$\frac{[MBT]}{[MMA]} \times 10^4$	$\left\{ \frac{1}{Pn} - 1.85 \frac{R_p}{[M]^2} \bullet \frac{K_t}{K_p^2} \right\} \times 10^4$	$C_{MBT} \times 10^{-2}$
2.18	1.93	1.42
3.27	1.92	
4.36	1.90	
5.46	1.96	
7.64	1.98	
10.90	2.01	

4.1.3e Activation energy:

The overall activation energy for the polymerization of MMA with MBT was calculated using the Arrhenius Equation from polymerization results obtained at different temperature. The value, 4.80, is typically in the range of photopolymerization reactions (Table–4.7, Fig.8)

Table – 4.7

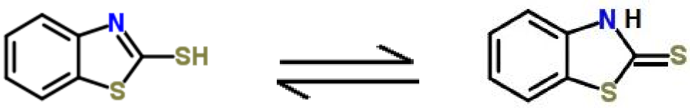
Effect of temperature on the photopolymerization of MMA using MBT as photoinitiator

$[MBT] = 5 \times 10^{-3}$ m.l^{-1}

Temperature °C	Temperature °A	$\frac{1}{T} \times 10^{-3}$	$R_p \times 10^5$ m. l^{-1}. S^{-1}	5 + log R_p	E_a K. Cal. m^{-1}
30	303	3.30	9.55	0.980	4.80
35	308	3.24	11.22	1.050	
40	313	3.19	12.50	1.097	
45	318	3.14	14.62	1.165	

4.1.3f Absorption spectra:

2-Mercaptobenzothiazole may exist in two tautomeric forms[110], namely thione (I) and thiol (II) forms. The thione form is, however, present both in the solid and solution state as obtained from the UV-spectral analysis (Fig.9). The corresponding spectra of mercaptobenzothiazole disulphide is also included in the Fig. for reference



(II) (I)

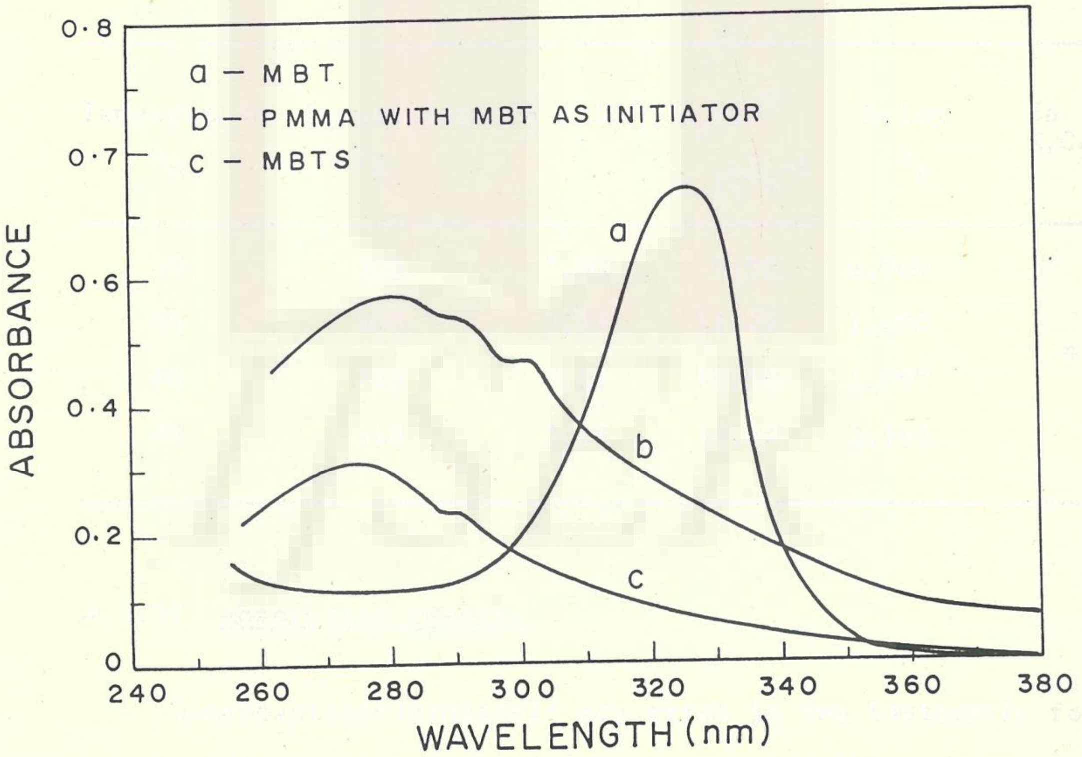


Fig. 9 : UV-Absorption spectra of MBT, MBT-PMMA and MBTS in acctonitrile.

Analysing the above spectral Fig. it can be said that the absorption maxima at 324 nm is characteristic of >c=s form. The conversion of thione form to thiol form takes place when the temperature is raised to 40^{o}C or higher of the solution of MBT in benzene[110]. This is in accordance with our spectral analysis, when a decrease in the absorbance at 324 nm occurs with the change in temperature as shown in Fig.10.

It is interesting to record the spectra of the polymer photoinitiated by MBT, which shows the incorporation of end groups with the same chromophor having absorption maxima at 275 nm.

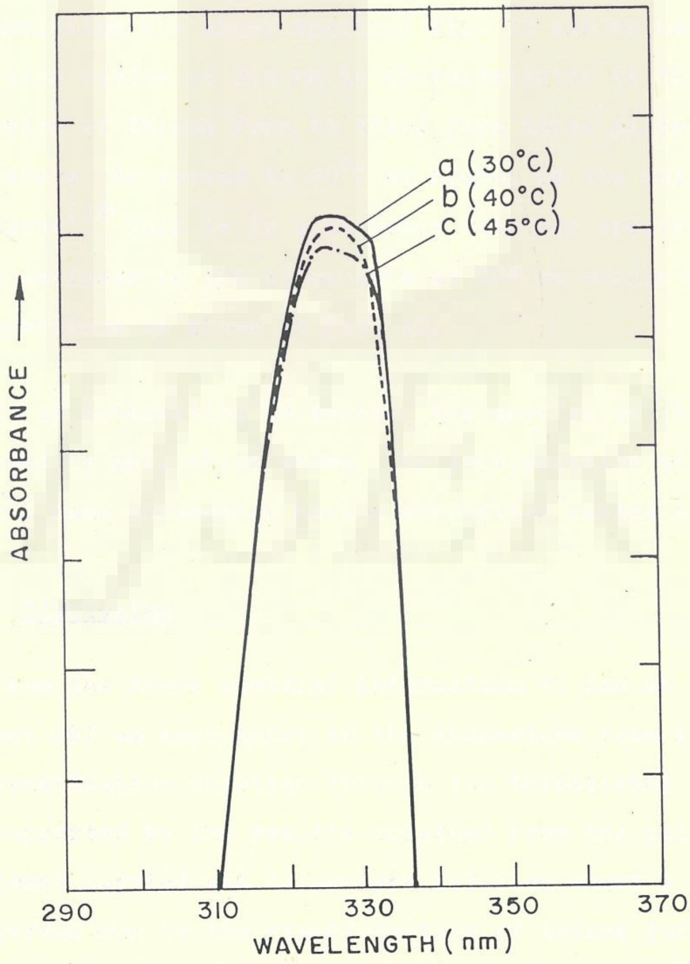


Fig. 10 : UV-Absorption spectra of MBT in benzene at different temperatures.

4.1.4 Discussion:

From the above spectral information it can be concluded that although MBT as such exist in the thioketone form it takes part in polymerization reaction through its thioalcohol form. This is also supported by the results obtained from the polymerization experiment carried out in benzene solution where a rate enhancement is observed due to the transformation of thione form to the thiol form of MBT (Table – 4.8, Fig.10).

The value of $\mathbf{K_p/K_t^{1/2}}$ (viz. 0.084) as calculated from measurements is in good agreement with the literature value. The mode of termination shows that about 15% termination occurs by disproportionation which is quite similar to that of polymerization of MMA using thermal radical initiator at 60^{o}C. The low value of initiator transfer constant suggests that no appreciable initiator transfer occurs during the process.

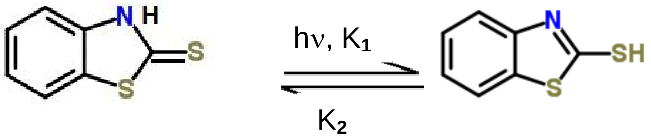
Table – 4.8

Photopolymerization of MMA in presence of benzene at a fixed MMA concentration at 40^{o}C using [MBT] as photoinitiator.

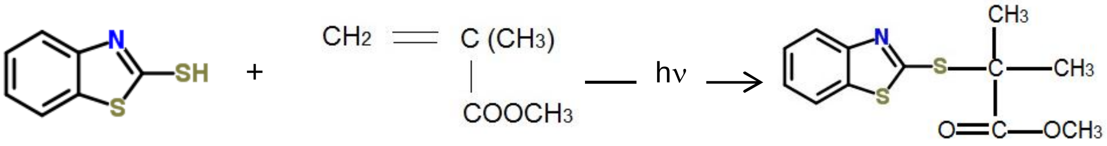
[MBT] = 5.0 m.mole.lit^{-1}, [MMA] = 5.5 moles.lit^{-1}

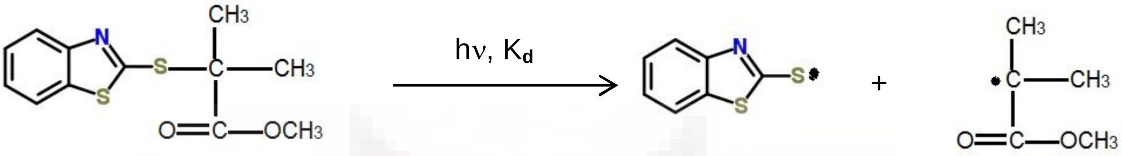
Benzene [S] moles.lit^{-1}	Rate of polymerization R_p x 10^5 m. l^{-1}. s^{-1}	[S]/R_p^2 x 10^{-8}	Mol. wt x 10^{-5}	K' Calculated from Equ.(x) on page 55
1.11	8.69	1.47	1.77	0.9
1.66	9.04	2.03	1.51	
2.22	9.18	2.63	1.43	
2.77	9.98	2.78	1.38	
3.33	10.20	3.20	1.32	

It is well known that thiols add to the olefinic double bond[111] and this process is accelerated in presence of light. It is therefore suggested that an addition complex is formed between MMA and MBT which then decomposes photochemically into radicals to initiate polymerization, as shown below:



(X)





[I] [$R_1^\bullet$] [$R_2^\bullet$]

$$R_1^\bullet + \text{MMA (M)} \xrightarrow{K_i} \text{MMA}^\bullet\ (M^\bullet)$$

$$R_2^\bullet + \text{MMA (M)} \xrightarrow{K_i} \text{MMA}^\bullet\ (M^\bullet)$$

$$M^\bullet + M \xrightarrow{K_p} P^\bullet \text{ (polymer radical)}$$

$$P^\bullet + P^\bullet \xrightarrow{K_t} \text{terminated polymer}$$

The active form of MBT, i.e. thiol–MBT, thus produced photochemically has a low effective concentration in the reaction medium and this is probably the reason for a relatively longer induction period associated with the polymerization process.

To obtain a rate expression a steady state with respect to the thiol–MBT is assumed. Let **'a'** be the initial concentration of thione–MBT and **'x'** is the concentration of thiol–MBT at time **'t'** in presence of light.

At equilibrium

$$K_1 ([a] - [x]) = K_2 [x], \text{ or } [x] = \frac{K [a]}{1 + K}$$

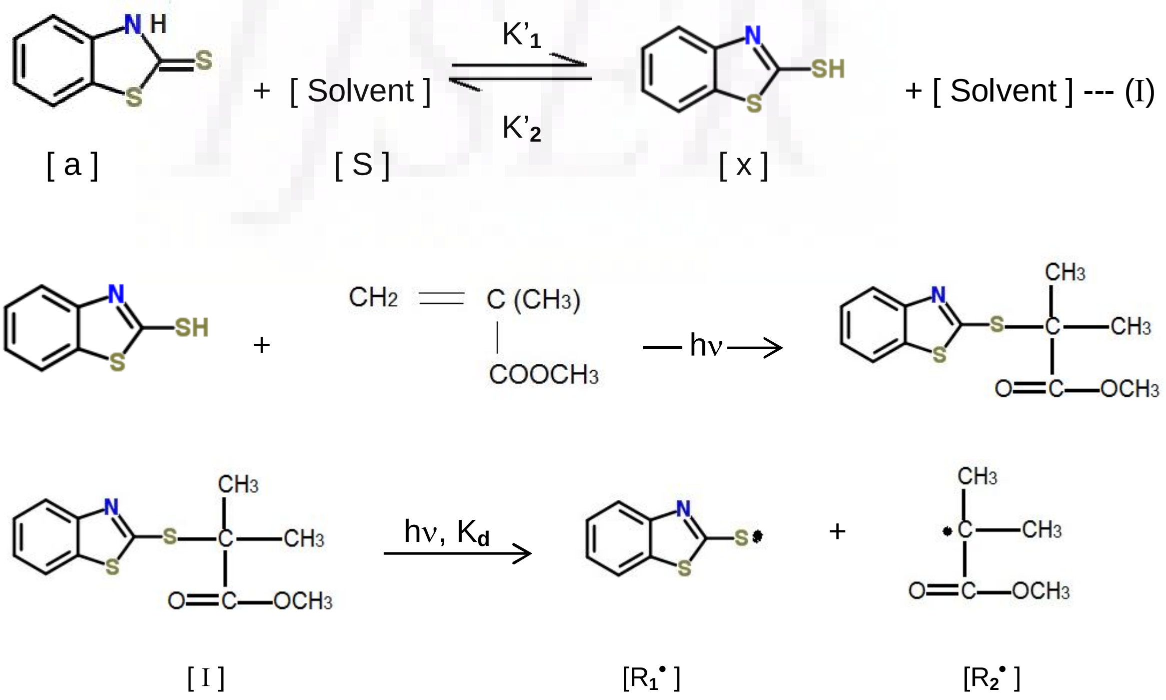
where K is equilibrium constant

Assuming [I] $\cong$ [x] and with usual steady state concept we get,

$$Rp = \frac{K_p}{K_t^{1/2}} \left\{ \frac{f\, K_d\, [\, a\,]\; K}{1 + K} \right\}^{1/2} [\, M\,]$$

The above rate expression indicates that the reaction order with respect to monomer is unity and that for initiator is 0.5 which is in accordance with our experimental results (Fig.2 and 3). It is also observed that the initiator order is 0.5 for the lower concentrations of initiator while it is only 0.17 for the higher concentrations (2×10^{-2} to 6×10^{-2} M/L). This is due to the primary radical termination effect as observed by the negative slope (Fig.11) when the data is processed following the equation of Deb and Myerhoff. The equilibrium constant was calculated from the experimentally determined values of $\mathbf{R_i}$ and $\mathbf{K_d}$ of the initiator and the value is presented in Table – 4.4.

However for diluted systems, particularly with active solvent like benzene, the situation is different. In solution the keto–enol tautomerism exist and the solvents which can form hydrogen bonding stabilizes the keto form while the enol form is stabilized in other solvents by forming an intramolecular bond. The following reaction scheme is, therefore, proposed for solvents which stabilize the thio–alcohol form of MBT.



$$R_1^{\bullet} + \text{MMA (M)} \xrightarrow{K_i} \text{MMA}^{\bullet}\ (M^{\bullet})$$

$$R_2^{\bullet} + \text{MMA (M)} \xrightarrow{K_i} \text{MMA}^{\bullet}\ (M^{\bullet})$$

$$M^{\bullet} + M \xrightarrow{K_p} P^{\bullet}\ \text{(polymer radical)}$$

$$P^{\bullet} + P^{\bullet} \xrightarrow{K_t} \text{terminated polymer}$$

From Scheme I

$$K'_1\ [a - x]\ [S] = K'_2\ [x], \text{ or } [x] = \frac{K'\ [a]\ [S]}{1 + K'\ [S]}$$

where [a] is the initial concentration of thione–MBT, [x] is the concentration of thiol–MBT at time **'t'**, K' is the tautomeric equilibrium constant for diluted system and [S] is the concentration of solvent.

Accordingly we can get:

$$R_p = \frac{K_p}{K_t^{1/2}} \left\{ \frac{f\,K_d\,K'\ [a]\ [S]}{1 + K'\ [S]} \right\}^{1/2} [M]$$

By rearranging

$$\frac{[S]}{R_p^2} = \frac{K_t}{K_p^2}\ \frac{1}{f\,K_d\ [a]\ [M]^2} \bullet \frac{1}{K'} + \frac{K_t}{K_p^2}\ \frac{1}{f\,K_d\ [a]\ [M]^2}\ [S] \quad \text{------ (x)}$$

Thus for an active solvent a plot of $[S] / R_p^2$ vs [S] at constant monomer concentration should be linear and yield the value of K'. The experimental results agree well with the proposed mechanism (Fig.12) and the value of K' is found to be 0.9 (Table – 4.8). The value of K (0.64) is less compared to K' (0.9) and the accelerating effect of benzene on the rate of polymerization of MMA is thus quite apparent.

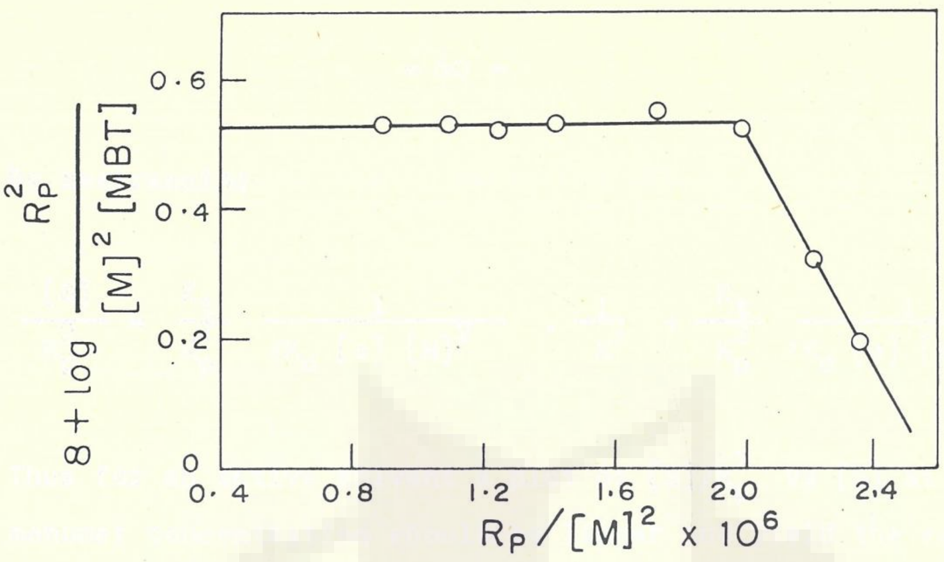


Fig. 11 : Analysis of primary radical termination in the photopolymerization of MMA at 40°C using MBT as initiator.

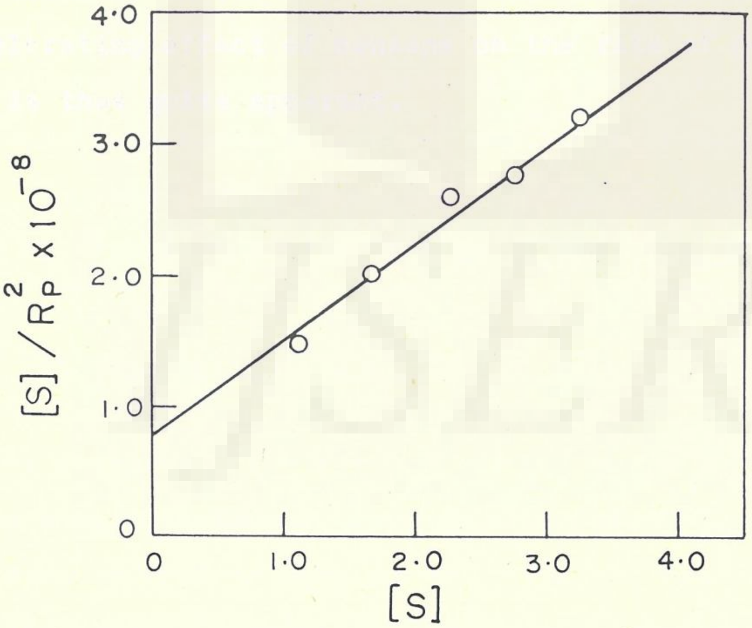


Fig. 12 : Photopolymerization of MMA in presence of benzene at 40°C using MBT as initiator.

4.2 Photopolymerization of MMA using MBT–BZ_2O_2 Combination as photoinitiator:

4.2.1 Introduction:

It has already been mentioned in the earlier chapter that thiols can form addition product with vinyl compounds and the process of addition can be catalysed by peroxide[111]. Based on this information we have taken the present MBT–BZ_2O_2 system for the photopolymerization of MMA to understand the mechanism of MBT initiation in a better way. Benzoyl peroxide was selected particularly because it does not participate in initiation of MMA under the present experimental set up, particularly with the irradiation system. In this system the effect of BZ_2O_2 have been studied in detail for the photopolymerization of MMA using MBT as photoinitiator.

4.2.2 Photopolymerization of MMA in Bulk:

The polymerization was carried out using MBT–BZ_2O_2 combination as photoinitiator in a dilatometer at 40°C. However no polymerization occurred in dark at 40°C. Typical free radical scavenger like hydroquinone inhibited the photopolymerization indicating a radical nature of the process.

4.2.3 Results:

4.2.3a Initiator order:

The rate of photopolymerization, R_p, of MMA initiated by MBT–BZ_2O_2 system at 40°C are presented in Table–4.9. The overall rates of polymerization, R_p, were obtained from the slopes of the linear plots of % conversion vs time (Fig.13a and 13b). Two sets of experiments were carried out, in one set, concentration of MBT was varied (2.5×10^{-4}m.l^{-1} to 50.0×10^{-4}m.l^{-1}) keeping concentration of BZ_2O_2 fixed (5.0×10^{-4}m.l^{-1}), while in other set the concentration of BZ_2O_2 was varied (2.5×10^{-4}m.l^{-1} to 50.0×10^{-4}m.l^{-1}) when the concentration of MBT was kept constant at 10.0×10^{-4}m.l^{-1}. In both cases, R_p, reaches a maxima with increasing concentration of either [MBT] or [BZ_2O_2] and then becomes more or less constant as obtained from the plot of log R_p vs log [MBT] (Fig.14a) and log R_p vs log [BZ_2O_2] (Fig.14b) respectively. The order of reaction with respect to the initiator [MBT] is 0.52 for the concentrations 2.5×10^{-4} m.l^{-1} to 10.0×10^{-4} m.l^{-1} while it is 0.1 for the concentration 10.0×10^{-4}m.l^{-1} to 50.0×10^{-4}m.l^{-1} and for [BZ_2O_2] the same is 0.5 for concentrations 2.5 x 10^{-4} m.l^{-1} to 5.0 x 10^{-4} m.l^{-1} and 0.08 for the concentration 5.0 x 10^{-4} m.l^{-1} to 50.0 x 10^{-4} m.l^{-1}. In both the cases initiator order is very close to 0.5 upto certain initiator concentration range while it is nearly zero above this range. The reason for this very low value of initiator order is discussed latter.

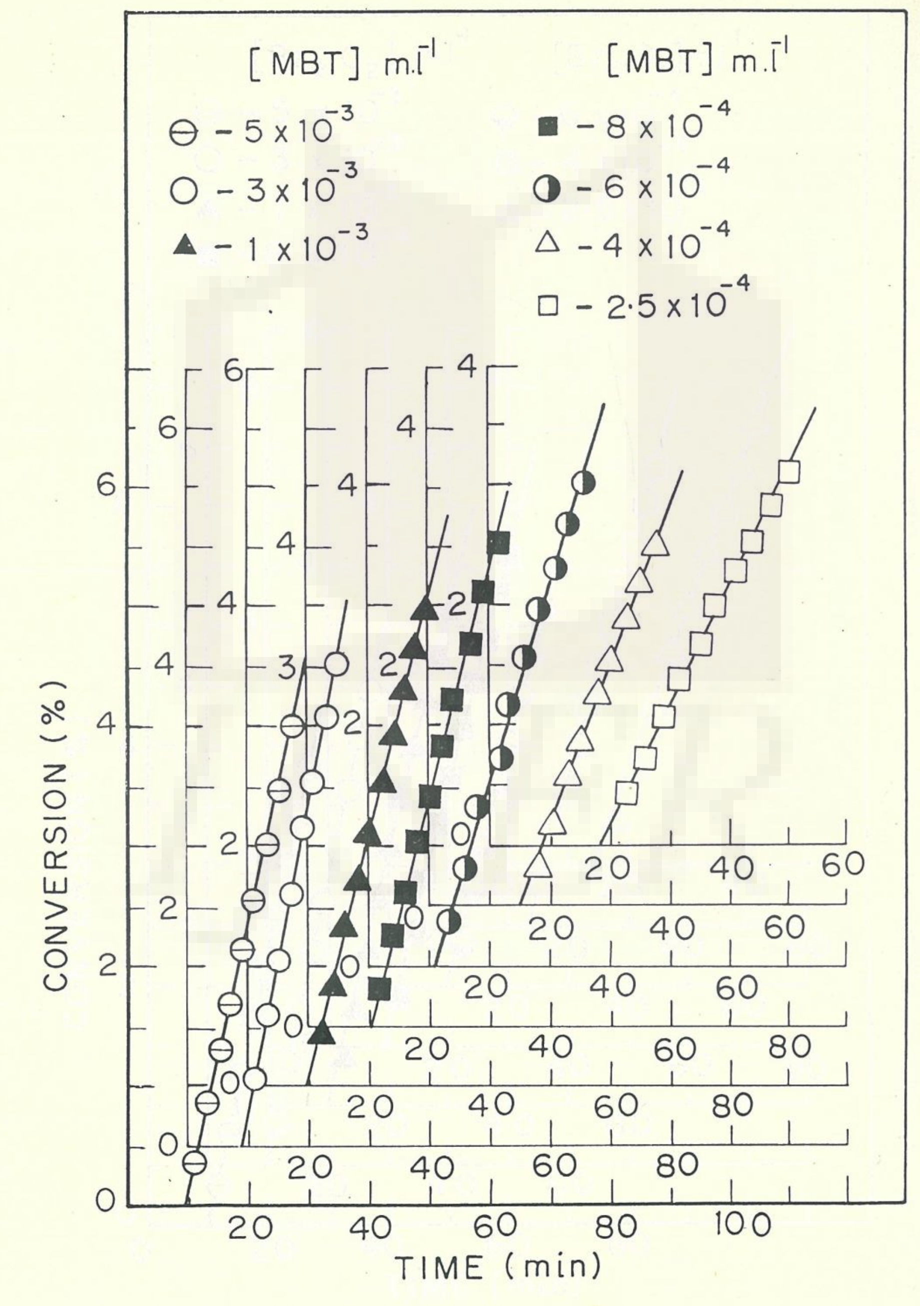


Fig. 13a : Effect of [MBT]on the photopolymerization of MMA at 40°C using MBT - BZ_2O_2 combination as initiator. [BZ_2O_2] = 5 x 10^{-4} m.l^{-1} (fixed).

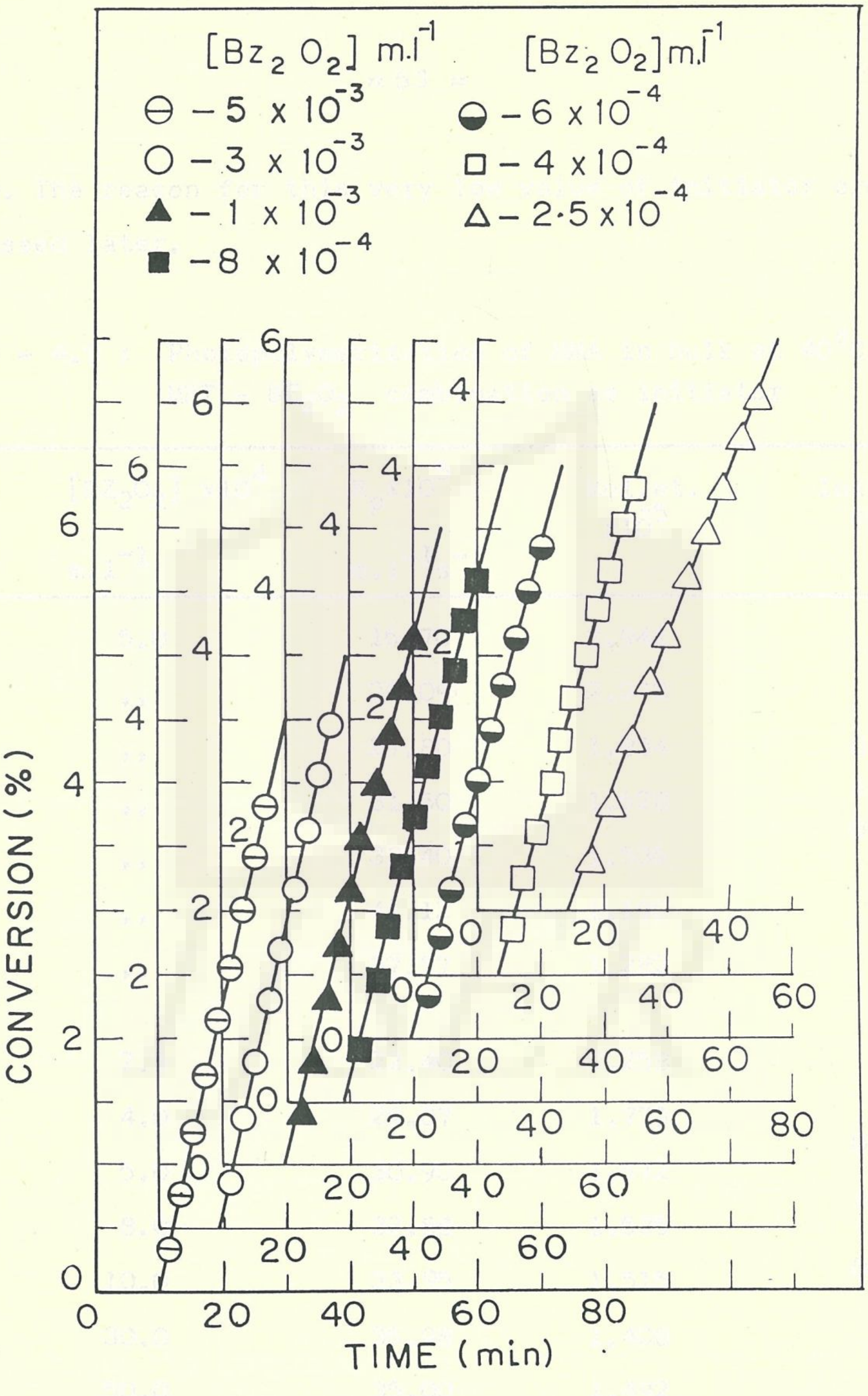


Fig. 13b : Effect of [BZ_2O_2] on the photopolymerization of MMA at 40°C using MBT - BZ_2O_2 combination as initiator. [MBT] = 1 x 10^{-3}m.l.$^{-1}$ (fixed).

Table – 4.9

Photopolymerization of MMA in bulk at 40^{o}C using MBT–BZ_2O_2 combination as initiator

[MBT] x 10^4 m. l^{-1}	[BZ_2O_2] x 10^4 m. l^{-1}	R_p x 10^5 m. l^{-1}. s^{-1}	Mol. wt x 10^{-5}	Initiator order
2.5	5.0	16.70	2.941	0.52 and 0.10
4.0	"	22.09	2.272	
6.0	"	27.80	1.834	
8.0	"	31.50	1.628	
10.0	"	33.40	1.536	
30.0	"	41.12	1.190	
50.0	"	37.57	1.282	
10.0	2.5	22.40	2.258	0.50 and 0.08
"	4.0	29.07	1.779	
"	5.0	30.90	1.672	
"	8.0	32.88	1.535	
"	10.0	33.95	1.515	
"	30.0	36.98	1.408	
"	50.0	35.00	1.492	

4.2.3b Monomer order:

The variation of R_p with monomer (MMA) concentration in diluted systems is shown in Table–4.10. The solvents used were benzene, carbon tetrachloride (CCl_4) and tetrahydrofuran (THF). The polymerization was carried out at 40^{o}C using the initiator concentrations [MBT] = 1 x 10^{-3} m.l^{-1} (fixed) and [BZ_2O_2] = 0.5 x 10^{-3} m.l^{-1} (fixed). For each of the diluents, R_p, was measured at different dilutions. Monomer order as obtained from the plot of log R_p vs log [MMA] is nearly 1.0 in each case, Table – 4.10 (Fig.15).

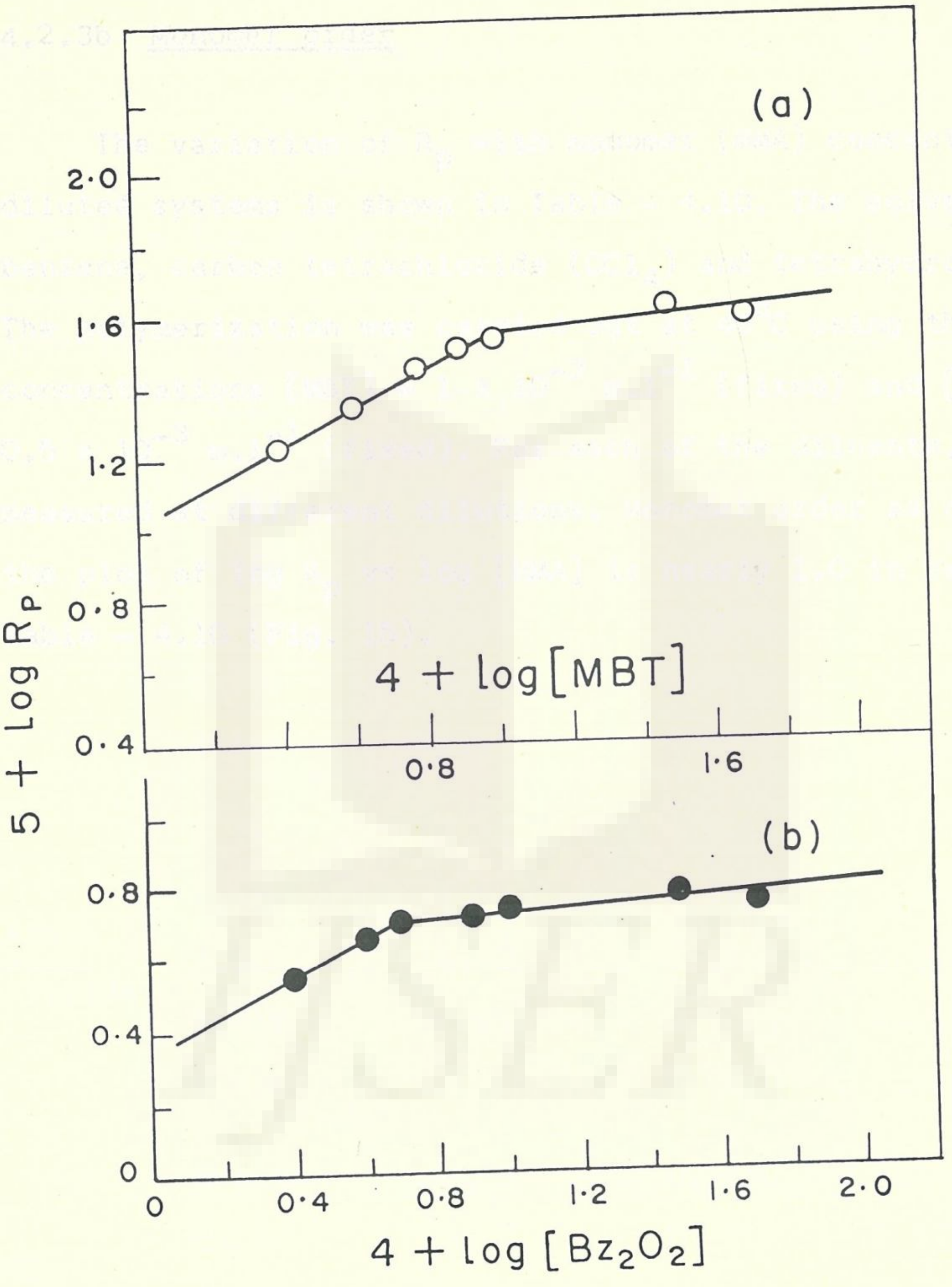


Fig. 14 : Photopolymerization of MMA at 40°C using MBT - BZ_2O_2 combination as initiator.

Table – 4.10

Photopolymerization of MMA at 40°C using MBT–BZ_2O_2 combination as initiator in presence of various solvents.

[MBT] = 1 x 10^{-3} m.l^{-1}, [BZ_2O_2] = 0.5 x 10^{-3} m.l^{-1}

Solvents	[M] m. l^{-1}	R_p x 10^5 m. l^{-1}. s^{-1}	log [M]	5 + log R_p	Monomer order
Benzene	8.244	30.26	0.9160	1.4808	1.06
	7.328	26.72	0.8649	1.4268	
	6.412	23.66	0.8069	1.3740	
	5.496	19.74	0.7400	1.2953	
	4.580	16.18	0.6608	1.2089	
Carbon tetra chloride	9.160	34.19	0.9618	1.5338	1.08
	8.244	31.73	0.9160	1.5014	
	7.328	26.60	0.8649	1.4248	
	6.412	22.82	0.8069	1.3583	
	5.496	19.48	0.7400	1.2895	
THF	9.160	34.19	0.9618	1.5338	1.00
	8.244	29.92	0.9160	1.4759	
	7.328	27.05	0.8649	1.4321	
	6.412	22.82	0.8069	1.3583	
	5.496	18.55	0.7400	1.2683	

4.2.3c Rate of initiation:

The rate of initiation, R_i, was experimentally determined from the inhibition period measurements and hydroquinone (HQ) was used as the inhibitor. The polymerization experiments were carried out at 40°C using the optimum initiator concentration, [MBT] = 1 x 10^{-3} m.l^{-1} (fixed), [BZ_2O_2] = 0.5 x 10^{-3} m.l^{-1} (fixed) while changing the hydroquinone (HQ) concentration from 4 x 10^{-5} m.l^{-1} to 8 x 10^{-5} m.l^{-1}. The rate of initiation was calculated from the inhibition period and the concentration of hydroquinone, the results are shown in Table – 4.11 (Fig.16)

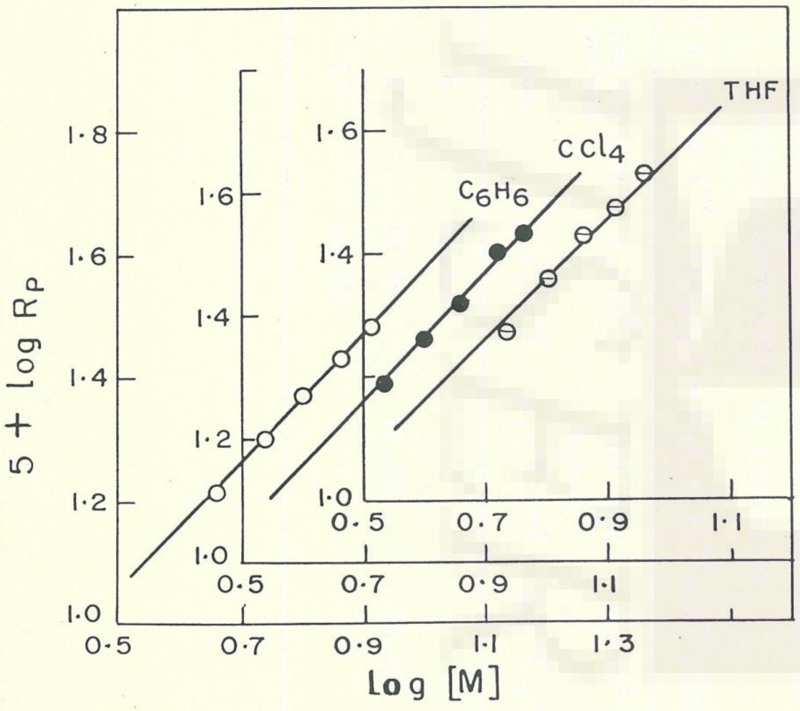


Fig. 15 : Photopolymerization of MMA in presence of solvents at 40°C using MBT-BZ_2O_2 combination as initiator.

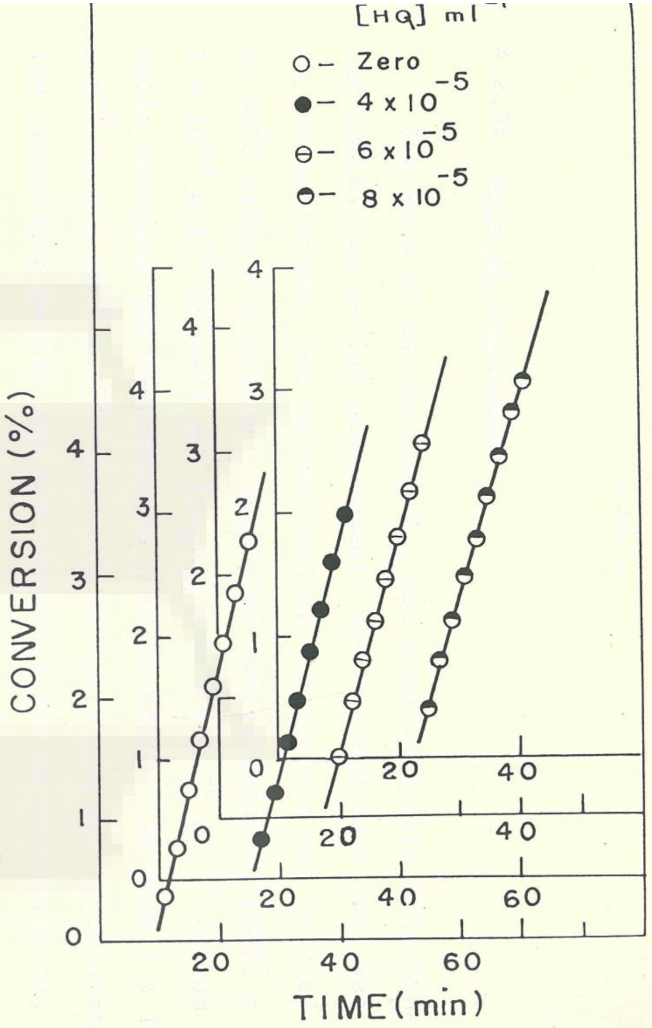


Fig. 16 : Photopolymerization of MMA at 40°C in presence of Hydroquinone using MBT-BZ_2O_2 combination as initiator.

Table – 4.11

Photopolymerization of MMA in bulk at 40°C using MBT–BZ_2O_2 combination as initiator in presence of hydroquinone (HQ) as inhibitor.

[MBT] = 1×10^{-3} m.l^{-1}, [BZ_2O_2] = 0.5×10^{-3} m.l^{-1}, [MMA] = 9.16 m.l^{-1}

[HQ] x 10^5 m. l^{-1}	Inhibition period, min	$R_i \times 10^8$ m. l^{-1}. s^{-1}	Average $R_i \times 10^8$ m. l^{-1}. s^{-1}	$R_p \times 10^5$ m. l^{-1}. s^{-1}	$K_p/K_t^{1/2}$
4.0	6	11.11	11.28	33.30	0.108
6.0	8	12.50			
8.0	13	10.25			

4.2.3d $K_p/K_t^{1/2}$ value:

This important kinetic parameter was calculated from the experimentally obtained R_i and R_p data for the undiluted system, and the result is shown in Table – 4.11. The observed value (0.108) is in the typical range for the photopolymerization of MMA. The modes of termination have been calculated using this $K_p/K_t^{1/2}$ value and the slope of the plot $1/\overline{P}n$ vs $Rp/[M]^2$ for both the cases, i.e. at fixed [MBT] and at fixed [BZ_2O_2] and the corresponding results are shown in Table – 4.12 (Fig.17a and 17b). The results 1.78 for MBT and 1.82 for BZ_2O_2 are very close to the well-established value of 1.85.

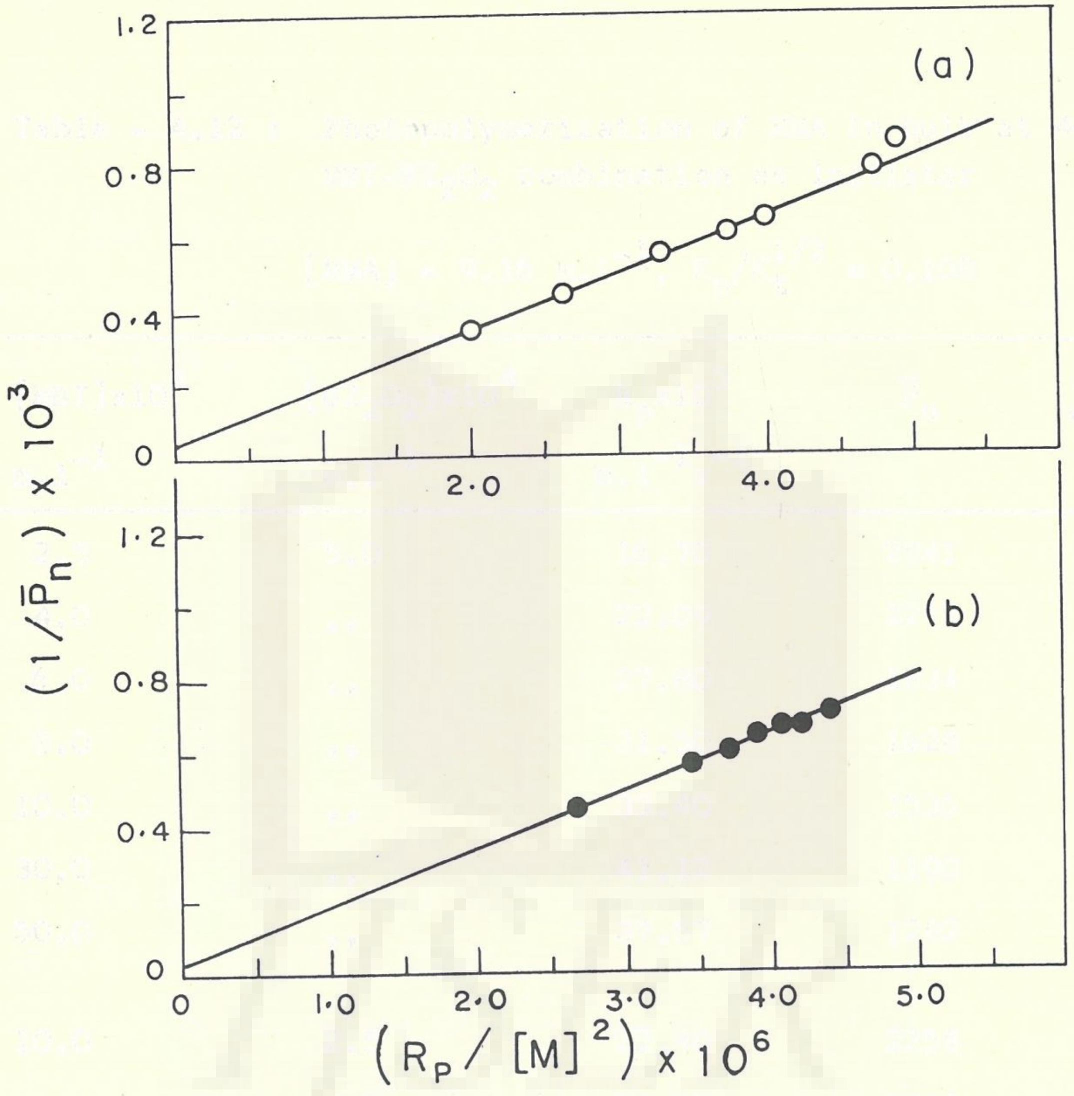


Fig. 17 : Photopolymerization of MMA at 40°C using $MBT-BZ_2O_2$ combination as initiator.

Table – 4.12

Photopolymerization of MMA in bulk at 40°C using MBT–BZ_2O_2 combination as initiator

[MMA] = 9.16 m.l^{-1}, $K_p/K_t^{1/2}$ = 0.108

[MBT] x 10^4 m. l^{-1}	[BZ_2O_2] x 10^4 m. l^{-1}	R_p x 10^5 m. l^{-1}. s^{-1}	$\overline{P}_n$	$\frac{Y+2}{Y+1}$
2.5	5.0	16.70	2941	1.78
4.0	"	22.09	2272	
6.0	"	27.80	1834	
8.0	"	31.50	1628	
10.0	"	33.40	1536	
30.0	"	41.12	1190	
50.0	"	37.57	1282	
10.0	2.5	22.40	2258	1.82
"	4.0	29.07	1779	
"	5.0	30.90	1672	
"	8.0	32.88	1535	
"	10.0	33.95	1515	
"	30.0	36.98	1408	
"	50.0	35.00	1492	

4.2.3e Initiator transfer:

The initiator transfer constants C_{MBT} and C_{BZ2O2} may be determined by using the Mayo equation which in the present case may be written as:

$$\frac{1}{\overline{P}_n} - 1.78 \frac{K_t}{K_p^2} \bullet \frac{R_p}{[M]^2} = C_M + C_{MBT} \frac{[MBT]}{[MMA]}$$

and

$$\frac{1}{\overline{P}_n} - 1.82 \frac{K_t}{K_p^2} \bullet \frac{R_p}{[M]^2} = C_M + C_{BZ2O2} \frac{[BZ_2O_2]}{[MMA]}$$

The left hand side of the above equations were plotted against [MBT] / [MMA] at fixed [BZ_2O_2] and [BZ_2O_2] / [MMA] at fixed [MBT] and the slope of the plots yielded the value of 0.04 for C_{MBT} and 0.033 for C_{BZ2O2} respectively, Table–4.13 (Fig.18a and 18b). These values are typically within the order normally observed with typical free radical initiators.

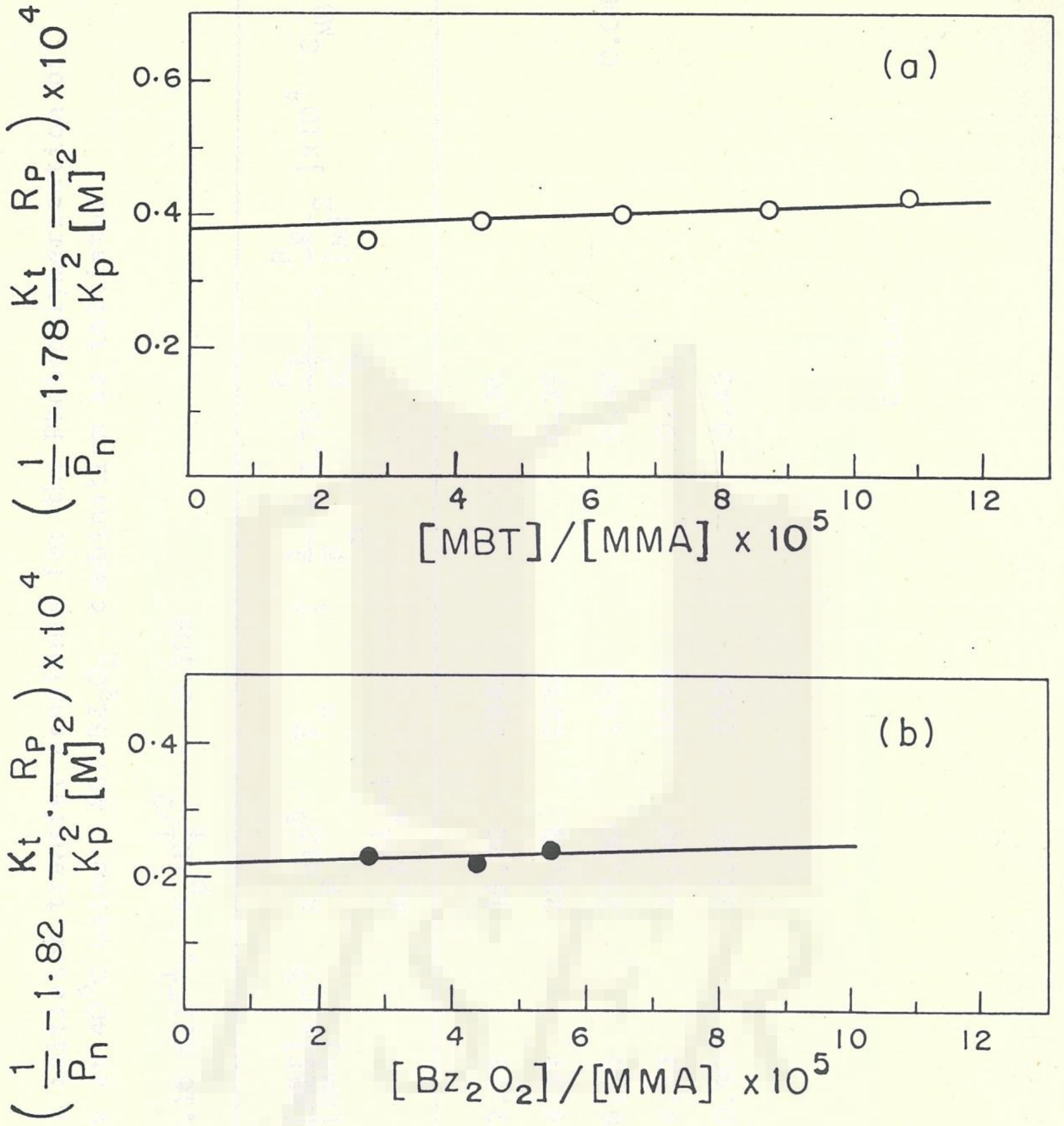


Fig. 18 : Photopolymerization of MMA at 40°C using MBT - BZ_2O_2 combination as initiator.

Table – 4.13

Analysis of initiator transfer constants for the photopolymerization of MMA in bulk at 40°C using MBT–BZ_2O_2 combination as initiator

$[MMA] = 9.16$ m. l^{-1}, $K_p/K_t^{1/2} = 0.108$

[MBT] x10^4 m. l^{-1}	[BZ_2O_2] x10^4 m. l^{-1}	$\frac{[MBT]}{[MMA]} \times 10^5$	R_px10^5 m. l^{-1}. s^{-1}	$\bar{P}_n$	$\left\{\frac{1}{\bar{P}_n} - 1.78 \frac{Kt}{K_p^2} \frac{R_p}{[M]^2}\right\} \times 10^4$	C_{MBT}
2.5	5.0	2.73	16.70	2941	0.36	0.04
4.0	“	4.37	22.09	2272	0.39	
6.0	“	6.55	27.80	1834	0.40	
8.0	“	8.73	31.50	1628	0.42	
10.0	“	10.90	33.40	1536	0.43	
[BZ_2O_2] x10^4 m. l^{-1}	[MBT] x10^4 m. l^{-1}	$\frac{[BZ_2O_2]}{[MMA]} \times 10^5$	R_p x 10^5 m. l^{-1}. s^{-1}	P_n	$\left\{\frac{1}{\bar{P}_n} - 1.82 \frac{Kt}{K_p^2} \frac{R_p}{[M]^2}\right\} \times 10^4$	C_{BZ2O2}
2.5	10.0	2.73	22.40	2258	0.23	0.033
4.0	“	4.37	29.07	1779	0.22	
5.0	“	5.46	30.90	1672	0.24	

4.2.3f Activation energy:

A set of bulk polymerization of MMA using the optimum initiator concentrations, viz. $[MBT] = 1 \times 10^{-3}$ m. l^{-1} and $[BZ_2O_2] = 0.5 \times 10^{-3}$ m. l^{-1} was carried out at four different temperatures, 25°C, 30°C, 35°C and 40°C. From the slope of the Arrhenius plot, log R_p vs 1/T, where T is in absolute temperature, the apparent activation energy E_a ($E_a = E_p - E_{t/2}$) is found to be 3.55 K.Cal.m^{-1}, Table – 4.14 (Fig.19). The observed value is in good order for typical photopolymerization systems involving an initiation step which is independent of temperature.

Table – 4.14

Effect of temperature on the photopolymerization of MMA at 40°C using MBT–BZ_2O_2 combination as initiator

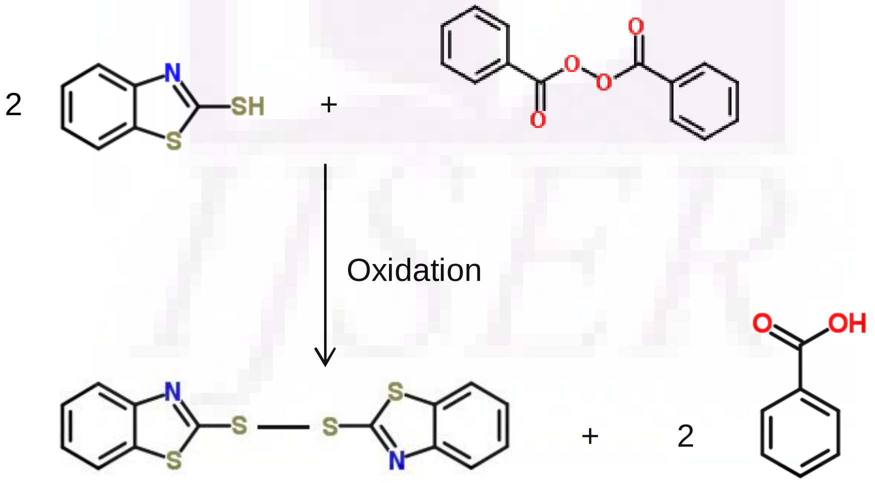
$[MBT] = 1 \times 10^{-3}$ m.l^{-1}, $[BZ_2O_2] = 0.5 \times 10^{-3}$ m.l^{-1}

Temperature °C	Temperature °A	$\frac{1}{T} \times 10^3$	R_p x 10^5 m. l^{-1}. s^{-1}	5 + log Rp	E_a K.Cal.m^{-1}
25	298	3.35	18.09	1.2574	3.55
30	303	3.30	22.63	1.3546	
35	308	3.24	28.45	1.4540	
40	313	3.20	33.95	1.5308	

4.2.4 Discussion:

The photopolymerization of MMA with MBT–BZ_2O_2 combination was found to be strongly inhibited in presence of low concentration of hydroquinone. The polymerization thus appears to take place by a radical mechanism.

During the study on the effect of initiator concentration on the rate of polymerization it is observed that the rate increased upto optimum value while changing [MBT] and keeping [BZ_2O_2] fixed and vice-versa. Further to this optimum value there was no significant change in rate at the corresponding changing initiator concentrations. It is also observed that the break points in the initiator order curves (Fig.14a and 14b) corresponding to an initiator concentrations of [MBT] = 10 x 10^{-4} m.l^{-1}, [BZ_2O_2] = 5 x 10^{-4} m.l^{-1}. The concentration of [BZ_2O_2] thus corresponds to exactly half the concentration of [MBT]. If BZ_2O_2 acts as an oxidizing agent then one mole of BZ_2O_2 will oxidize two moles of MBT as shown below.



The above reaction is also supported by the spectrophotometric study on the combination MBT–BZ_2O_2 in acetonitrile medium. The UV–Spectra of the combination before and after reaction for 60 minutes at room temperature (Fig.20) has been recorded. It can be seen from these spectra that the absorption maxima at 324 nm (corresponding to the >C=S form of MBT) is present when MBT and BZ_2O_2 was just mixed but the maxima shifted to 270 nm after the same mixture was allowed to react for 60 minutes. Thus the intensity of maxima at 270 nm increased with time. This shows that MBT is oxidized by BZ_2O_2 under the present reaction condition.

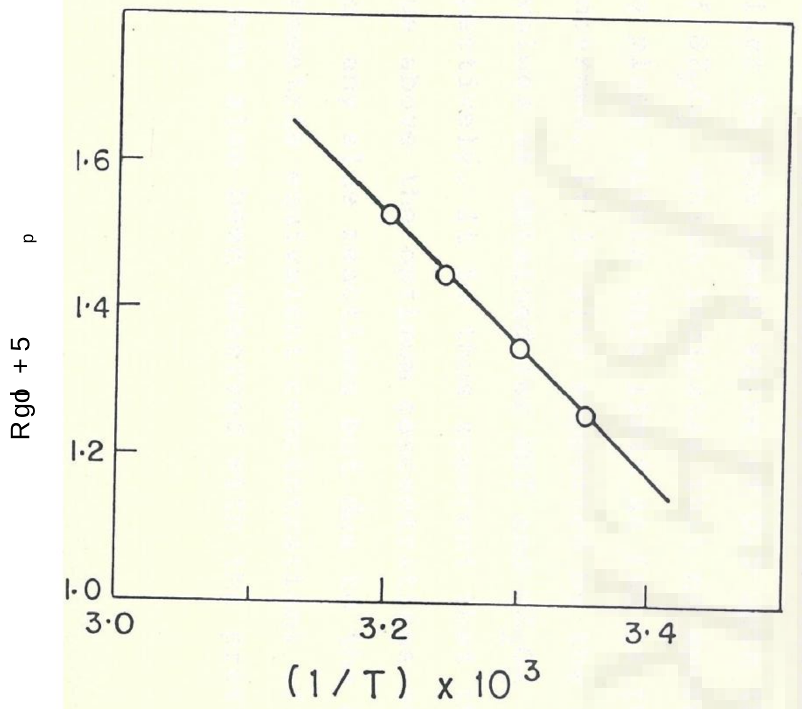


Fig. 19 : Effect of temperature on the photopolymerization of MMA using MBT-BZ_2O_2 combination as initiator.

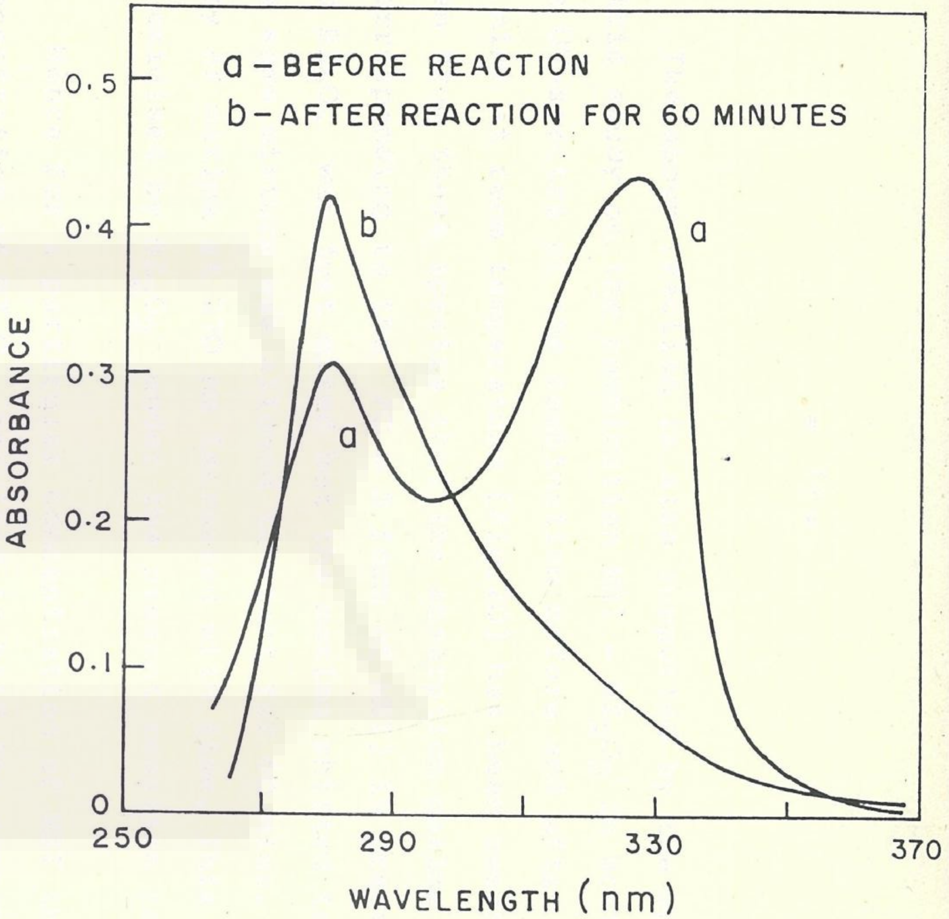
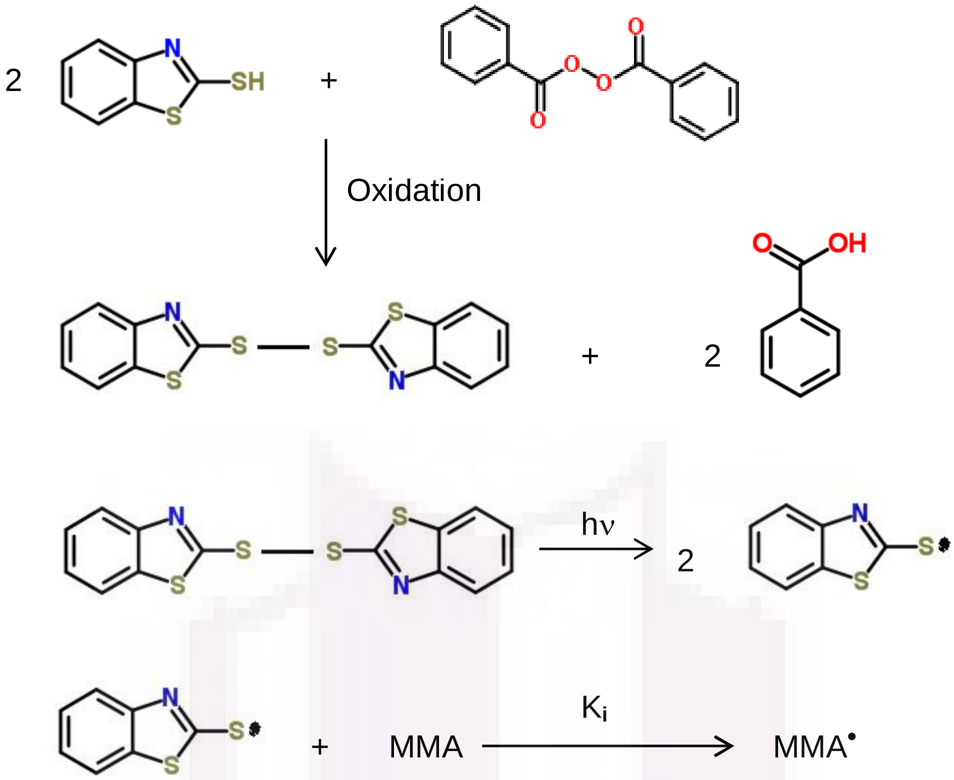


Fig. 20 : UV-Absorption spectra of MBT-BZ_2O_2 mixture in acetonitrile recorded at room-temperature.

Hence for a particular concentration of MBT the effective concentration of BZ_2O_2 required is half the concentration of MBT which is practically observed in the two sets of polymerization (Fig.14a and 14b). The value of the initiator order was observed to be similar to the ideal value of 0.5 upto this effective concentration of BZ_2O_2 which indicates that no appreciable side reactions are taking place within this limit as far as the effect of initiator is concerned. It is also supported by the low initiator transfer constant values as obtained for MBT and BZ_2O_2 viz. 0.04 and 0.033 respectively. It is thus apparent that the very low initiator order value above the optimum concentrations of MBT and BZ_2O_2 is not due to any side reactions but due to the non-availability of the stoichiometric equivalent concentrations of either MBT or BZ_2O_2. It has also been observed with the present experimental system that BZ_2O_2 does not initiate photopolymerization of MMA at 40^{o}C upto 60 minutes with [BZ_2O_2] of $2x10^{-3}$ and $5x10^{-3}$ m.l^{-1} and this is the reason why the rate is not increasing when the [BZ_2O_2] is increased above the optimum concentration $5x10^{-4}$ m.l^{-1} upto $50x10^{-4}$ m.l^{-1} (Fig.14b). Further in the previous study with MBT–MMA system a rate of polymerization value of $9.24x10^{-5}$ m.l^{-1}.s^{-1} and $11.93x10^{-5}$ m.l^{-1}.s^{-1} for $30x10^{-4}$ m.l^{-1} and $50x10^{-4}$ m.l^{-1} concentrations of MBT have been obtained. These values of R_p are much less compared to the optimum value of $33.40x10^{-5}$ m.l^{-1}.s^{-1} in the present [MBT] changing system and these values themselves indicate that [MBT] as such will not have appreciable effect on the initiator order above $10x10^{-4}$ m.l^{-1} as has been experimentally observed (Fig.14a).

During the analysis of the modes of termination in the present system we have obtained values of 1.78 and 1.82 for MBT and BZ_2O_2 respectively which are very close to the reported value of 1.85 for the thermal polymerization of MMA at 60^{o}C.

Based on the above discussions and the experimental results the following simple scheme of reaction may be outlined.



$$MMA^{\bullet} + MMA \xrightarrow{K_p} P^{\bullet}$$

$$P^{\bullet} + P^{\bullet} \xrightarrow{K_t} P \text{ (terminated polymer)}$$

The above reaction scheme would correspond to the normal rate equation, viz.

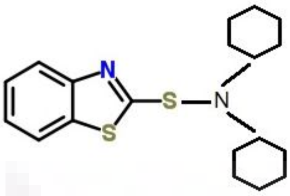
$$R_p = \frac{K_p}{K_t^{1/2}} [R_i]^{1/2} [MMA]$$

and our experimental results agree well with the above rate expression.

4.3 Photopolymerization of MMA using Dicyclohexyl Benzothiazole Sulphenamide (DCS) as initiator:

4.3.1 Introduction:

In the previous two systems detailed kinetic studies have been made for the Photopolymerization of MMA using MBT and MBT–BZ_2O_2 combination as photoinitiator. In the present case a substituted MBT, viz. dicyclohexyl benzothiazole sulphenamide (DCS) has been selected as the photoinitiator. The molecular structure of DCS is similar to MBT except the H–atom of the 2–Mercapto group which has been replaced by a dicyclohexyl amine group as shown below:



This system is interesting from the point of view that there will be no tautomeric form as it exists in case of MBT and also how efficiently DCS would act as photoinitiator compared to MBT. A detailed kinetic study on the photopolymerization of MMA using DCS as the photoinitiator is presented in this section.

4.3.2 Photopolymerization of MMA in bulk:

The polymerization of MMA using DCS as photoinitiator is associated with some small inhibition period ranging from 8 to 16 minutes, which is within the limitation of our experimental set up. However no polymerization occurred in the dark at 40^{o}C. The polymerization was also inhibited by typical free radical scavengers, viz. hydroquinone indicating a free radical mechanism for the polymerization.

4.3.3 Results:

4.3.3a Initiator order:

The results of the photopolymerization of MMA in bulk initiated by DCS at 40^{o}C are presented in Table–4.15 and the corresponding rate curves are presented in Fig.21. The order of reaction with respect to the initiator as obtained from the plot of log R_p vs log [DCS] is 0.44, Fig.22 which is little less than the usual value of 0.5. The reason for this low value is discussed latter.

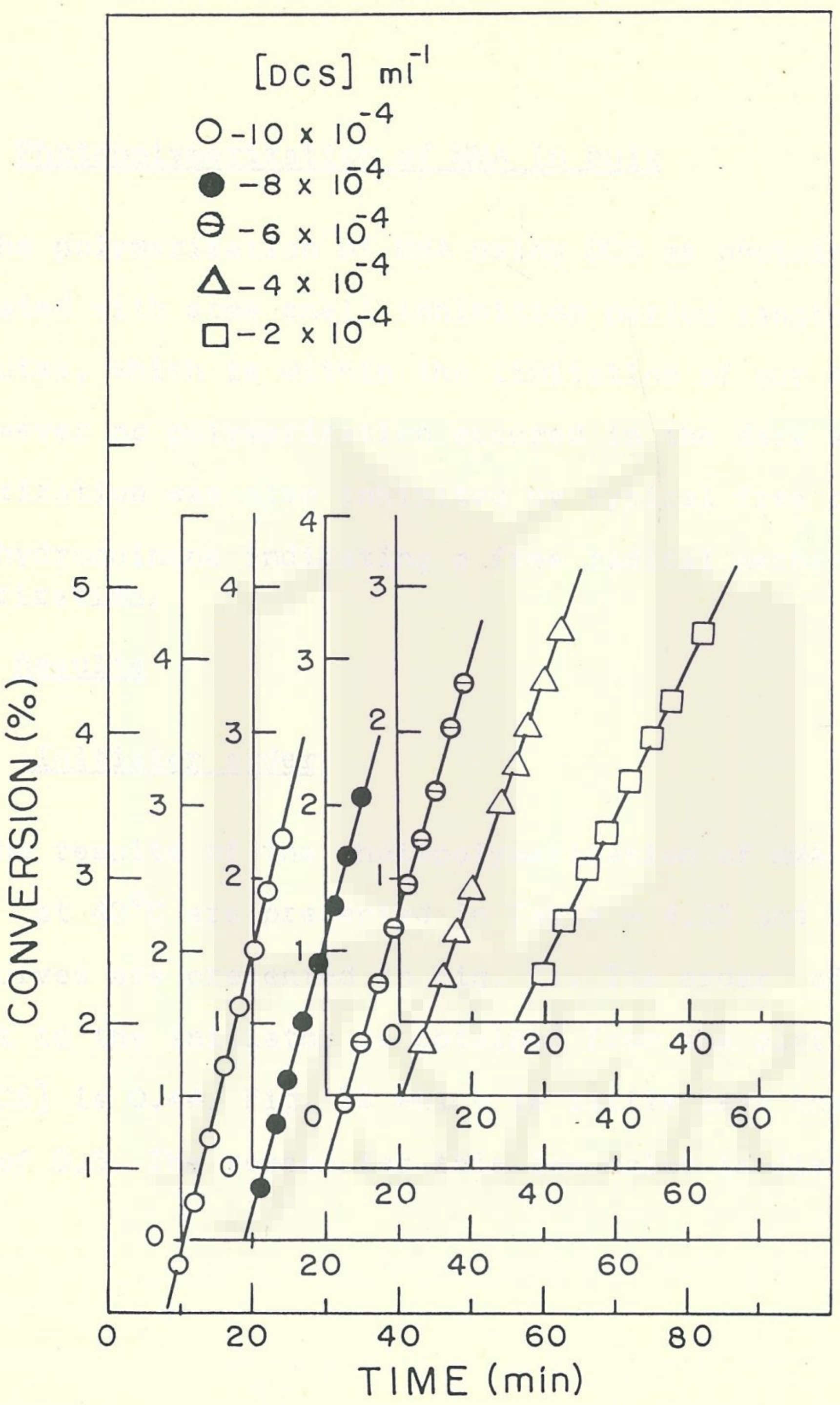


Fig. 21 : Effect of [DCS] on the photopolymerization of MMA at 40°C using DCS as initiator.

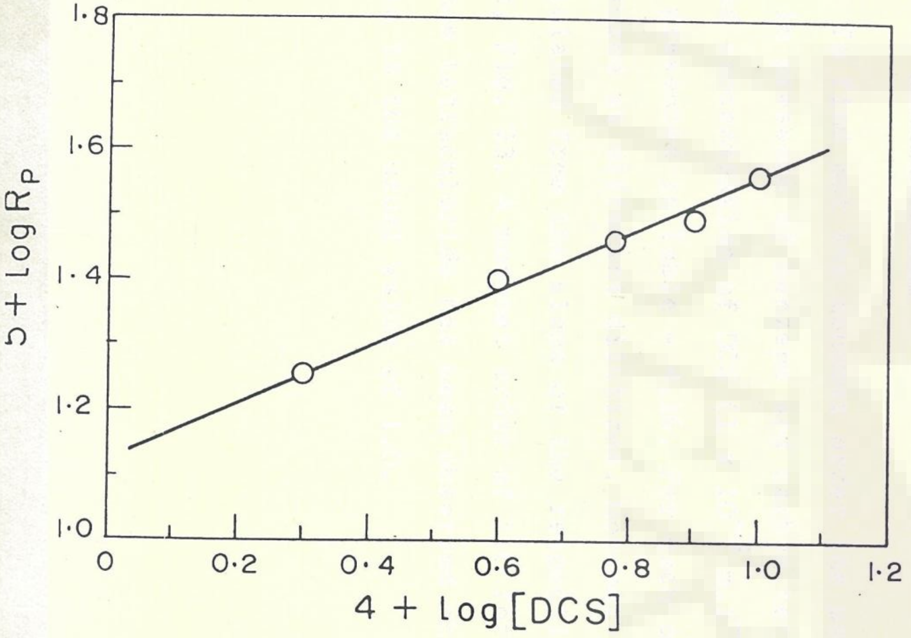


Fig. 22 : Photopolymerization of MMA at 40°C using DCS as initiator.

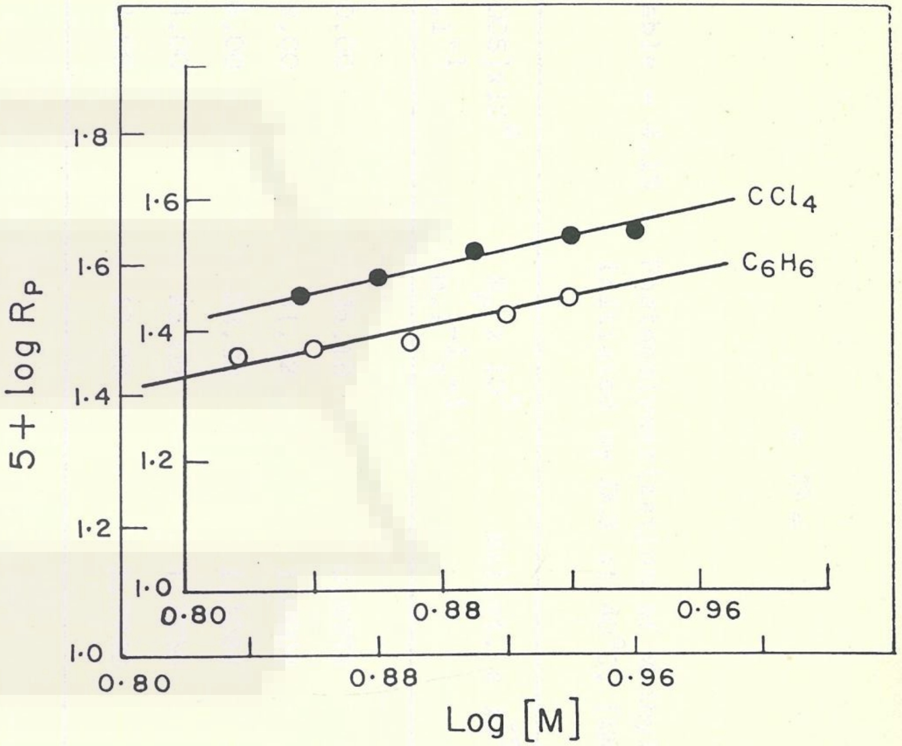


Fig. 23 : Photopolymerization of MMA in presence of solvents at 40°C using DCS as initiator.

Table – 4.15

Photopolymerization of Methyl Methacrylate
Photoinitiated by DCS at 40^oC, [MMA] = 9.16 moles / lit.

[DCS] x 10^4 m.l^{-1}	R_p x 10^5 m.l^{-1}.s^{-1}	Mol. wt. x 10^{-5}	Initiator order
10.0	36.18	0.8772	0.44
8.0	31.12	1.0204	
6.0	28.80	1.1084	
4.0	25.05	1.2750	
2.0	17.90	1.7740	

4.3.3b Monomer order:

To find out the monomer order the polymerization was carried out in presence of benzene and carbon tetrachloride as solvent at a fixed concentration of DCS (1 x 10 $^{-3}$ m.l^{-1}) at 40^oC and the results are presented in Table – 4.16. For each of the diluents, R_p, was measured at different dilutions. Monomer order in each case was calculated from the slope of the respective log R_p vs log [MMA] plot, Fig.23. A monomer order of 1.0 for benzene and 1.04 for carbon tetrachloride has been observed which are similar / very close to the value of 1.0.

Table – 4.16

Photopolymerization of Methyl Methacrylate Photoinitiated by DCS at 40^oC
In presence of diluents, [DCS] = 1.0 m. moles / lit.

Diluents	[MMA] m.l^{-1}	R_p x 10^5 m.l^{-1}.s^{-1}	log [MMA]	5 + log R_p	Monomer order
Benzene	8.70	35.78	0.94	1.55	1.0
	8.24	33.40	0.92	1.52	
	7.78	30.15	0.89	1.48	
	7.33	29.98	0.86	1.47	
	6.87	28.84	0.836	1.46	
CCl_4	8.70	35.25	0.94	1.55	1.04
	8.24	34.79	0.92	1.54	
	7.78	32.93	0.89	1.517	
	7.33	30.22	0.86	1.480	
	6.87	28.46	0.836	1.454	

4.3.3c Rate of initiation:

In order to find out the rate of initiation for the polymerization of MMA using DCS as the photoinitiator, the polymerization reaction was carried out in presence of hydroquinone (HQ), used as an inhibitor, at a fixed concentration of DCS (1.0 x 10^{-3} m.l^{-1}) and the temperature was kept at 40^oC in all the cases. The rate of initiation was calculated from the observed extended inhibition period and the inhibitor concentration used. The inhibition periods were extended due to the addition of hydroquinone (HQ). The results are presented in Table – 4.17 and Fig.24.

Table – 4.17

Photopolymerization of MMA using DCS as photoinitiator in presence of hydroquinone (HQ) as inhibitor at 40^oC.

[DCS] = 1 x 10^{-3} m.l^{-1}, [MMA] = 9.16 m.l^{-1}

[HQ] x 10^5 m. l^{-1}	Inhibition period, min	R_i x 10^8 m. l^{-1}. s^{-1}	Average R_i x 10^8 m. l^{-1}. s^{-1}	R_p x 10^5 m. l^{-1}. s^{-1}	$K_p/K_t^{1/2}$
4.0	3	22.22	21.48	36.18	0.085
6.0	5	20.00			
8.0	6	22.22			

4.3.3d $K_p/K_t^{1/2}$ value:

This kinetic parameter has been calculated from the experimental results of R_i and R_p data from the undiluted system (DCS = 1 x 10^{-3} m.l^{-1}) and the value is presented in Table–4.17.

The mode of termination was obtained from the slope of the plot of $1/\overline{P}n$ vs $R_p/[M]^2$ using the experimentally determined $K_p/K_t^{1/2}$ and the results are presented in Table–4.18, Fig.25.

Table – 4.18

Photopolymerization of MMA using DCS as photoinitiator at 40^oC.

[MMA] = 9.16 m.l^{-1}, $K_p/K_t^{1/2}$ = 0.085

[DCS]x10^4 m.l^{-1}	R_p x 10^5 m.l^{-1}.s^{-1}	$\frac{R_p}{[M]^2}$ x10^6	$\overline{P}n$	$\frac{1}{\overline{P}n}$ x 10^3	$\frac{Y+2}{Y+1}$
10.0	36.18	4.31	877.2	1.14	1.838
8.0	31.12	3.71	1020	0.98	
6.0	28.80	3.43	1108	0.90	
4.0	25.05	2.98	1275	0.78	
2.0	17.90	2.13	1744	0.57	

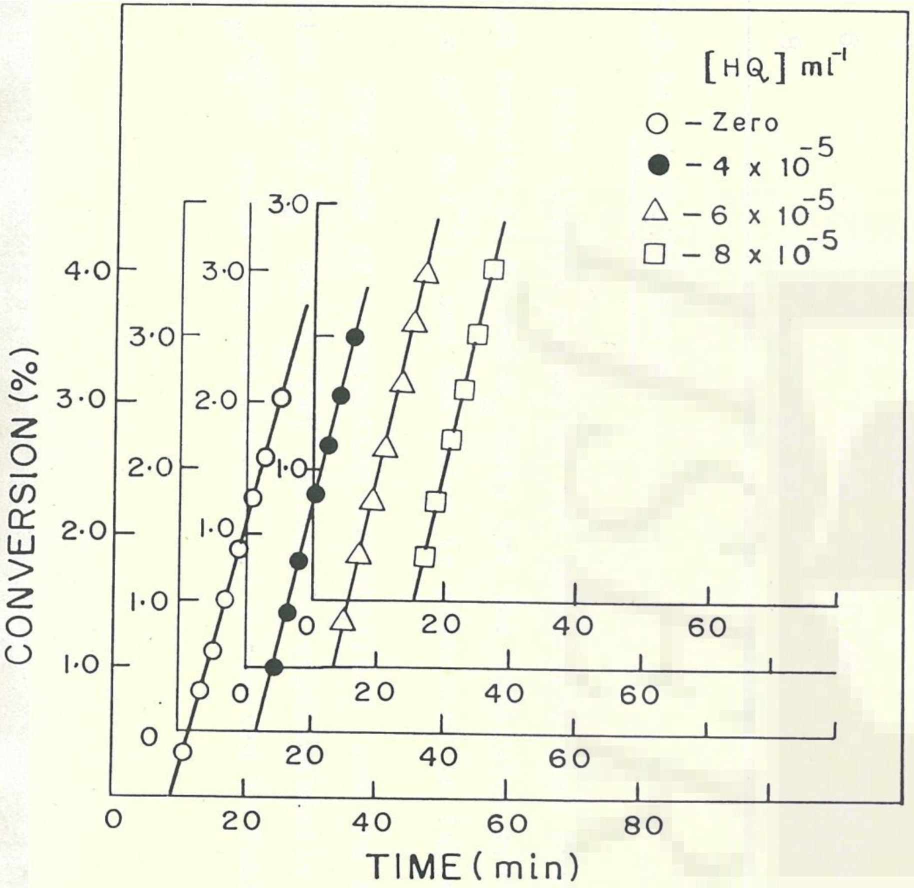


Fig. 24 : Photopolymerization of MMA at 40°C in presence of Hydroquinone using DCS as initiator.

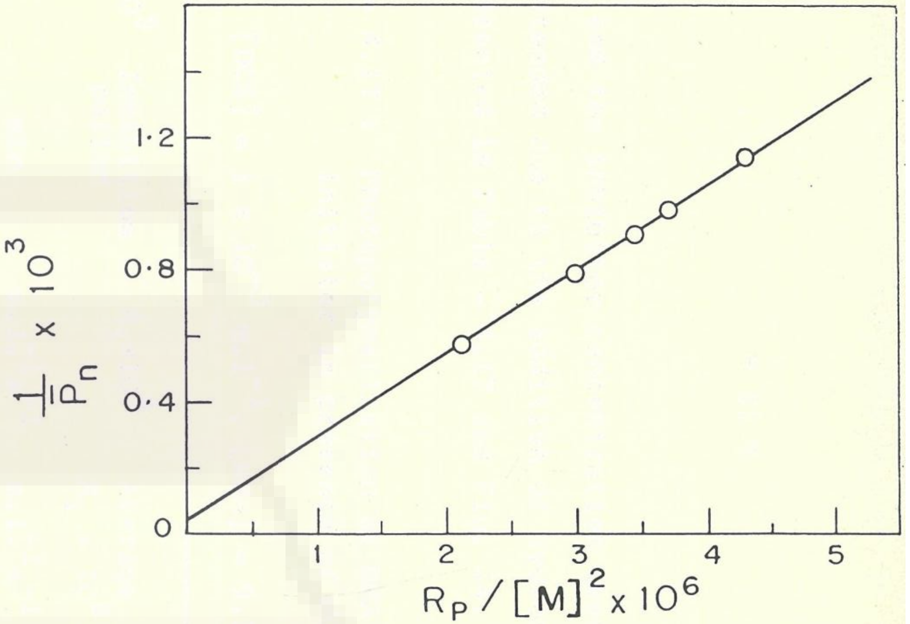


Fig. 25 : Photopolymerization of MMA at 40°C using DCS as initiator.

4.3.3e Initiator transfer:

The initiator transfer constant C_{DCS} was calculated from the Mayo equation using the experimentally obtained values of $K_p/K_t^{1/2}$ and Y+2/Y+1 which in this case may be written as:

$$\frac{1}{\overline{P}_n} - 1.838 \frac{Kt}{K_p^2} \bullet \frac{R_p}{[M]^2} = C_M + C_{DCS} \frac{[DCS]}{[MMA]}$$

The corresponding results are presented in Table–4.19, Fig.26.

Table – 4.19

Data for the analysis of initiator transfer constant C_{DCS} for the photopolymerization of MMA using DCS as initiator at 40°C

$[MMA] = 9.16\ m.l^{-1}$, $Y+2/Y+1 = 1.838$, $K_p/K_t^{1/2} = 0.085$

[DCS] x10^4 m. l^{-1}	$\frac{[DCS]}{[MMA]}$ X 10^4	R_px10^5 m. l^{-1}. s^{-1}	$\overline{P}_n$	$\left\{\frac{1}{\overline{P}_n} - 1.838 \frac{Kt}{K_p^2} \frac{R_p}{[M]^2}\right\}$ x10^4	C_{DCS}
10.0	1.09	36.18	877.2	0.43	0.25
8.0	0.87	31.12	1020	0.37	
6.0	0.65	28.80	1108	0.29	
4.0	0.44	25.05	1275	0.25	
2.0	0.22	17.90	1774	0.21	

4.3.3f Activation energy:

The activation energy for the polymerization of MMA with DCS was calculated from the plot of log R_p vs 1/T according to Arrhenius equation after the polymerization was carried out at 32°C, 36°C, 40°C and 45°C at a fixed DCS concentration ($1x10^{-3}\ m.l^{-1}$) and the results are presented in Table–4.20, Fig.27. The value for the apparent activation energy E_a was found to be 2.9 K.Cal.m^{-1} which is in good order for typical photopolymerization systems.

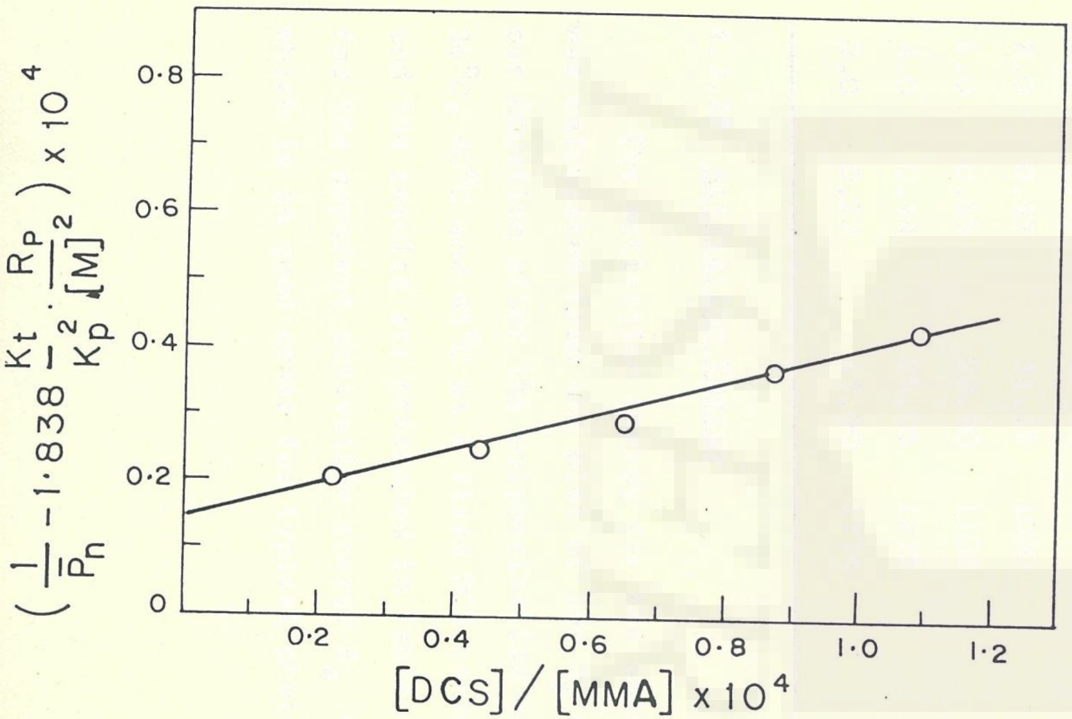


Fig. 26 : Photopolymerization of MMA at 40°C using DCS as initiator.

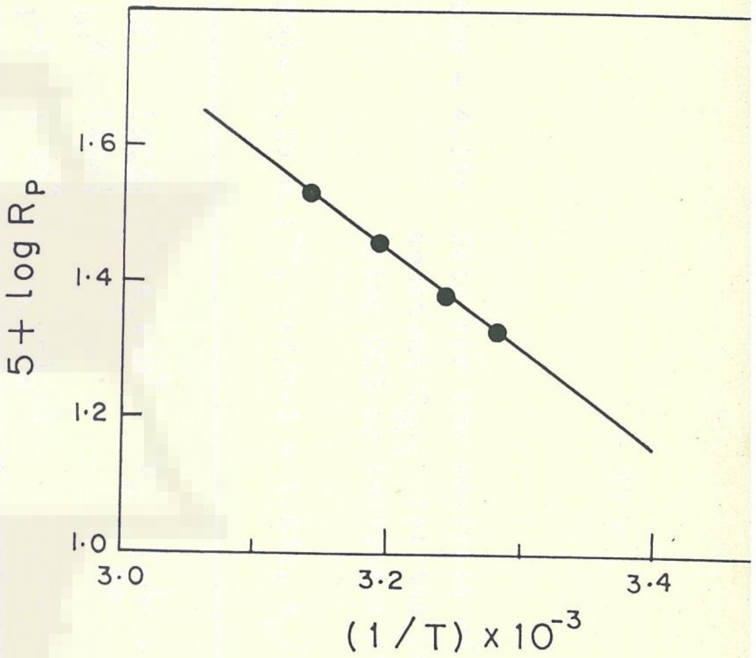


Fig.: 27 : Effect of temperature on the photopolymerization of MMA using DCS as initiator.

Table – 4.20

Photopolymerization of MMA in bulk using DCS as initiator at different temperatures

[DCS] = 1 x 10^{-3} m.l^{-1}

Temperature °C	Temperature °A	$\frac{1}{T} \times 10^3$	$R_p \times 10^5$ m. l^{-1}. s^{-1}	5 + log Rp	E_a K.Cal.m^{-1}
32	305	3.280	21.57	1.330	2.9
36	309	3.236	23.91	1.378	
40	313	3.190	29.22	1.460	
45	318	3.140	34.38	1.536	

4.3.4 Discussion:

From the above results it is clear that DCS is an efficient photoinitiator like MBT–BZ_2O_2 combination system. The initiator exponent value was found to be 0.44 which is somewhat lower compared to the usual value of 0.5. This low value along with a lower value of $K_p/K_t^{1/2}$ compared to MBT–BZ_2O_2 combination system point out some deviations from the normal kinetic behaviour. This non-ideality may be due to degradative initiator transfer and / or primary radical termination effect.

Analysis of primary radical termination effect:

This was analysed by using the kinetic and related data with the help of the following modified form of Deb and Myerhoff[11] equation for detection as well as overall evaluation of primary radical termination effect:

$$\log \frac{R_p^2}{[DCS]\,[M]^2} = \log \frac{f\,K_d\,K_p^2}{K_t} - 0.8684\,\frac{K_{prt}}{K_i\,K_p} \bullet \frac{R_p}{[M]^2}$$

Here, K_{prt} is the rate constant for primary radical termination reaction. A plot of left hand side of the above equation against $R_p/[M]^2$ would give a straight line with negative slope indicating the occurrence of primary radical termination during polymerization and the results are presented in Table–4.21, Fig.28. The value of the parameter $K_{prt} / K_i\,K_p$ was found to be 4×10^4 m.s.l^{-1} from the slope of the above plot.

Table – 4.21

Data for the analysis of primary radical termination in photopolymerization of MMA using DCS as initiator at 40^{o}C

[MMA] = 9.16 m.l^{-1}

[DCS]x10^4 m.l^{-1}	R_p x 10^5 m.l^{-1}.s^{-1}	$\frac{R_p}{[MMA]^2} \times 10^6$	$6 + \log \frac{R_p^2}{[MMA]^2 [DCS]}$	$\frac{K_{prt}}{K_i K_p}$
10.0	36.18	4.31	0.193	4 x 10^4
8.0	31.12	3.70	0.159	
6.0	28.80	3.43	0.217	
4.0	25.05	2.98	0.272	
2.0	17.90	2.13	0.280	

Analysis of degradative initiator transfer effect:

This aspect may be analysed according to the following approach. Under steady state condition we may write:

$$R_i = R_t = 2K_t [M^\bullet]^2 + K'_t [I] [M] = 2K_t [M^\bullet]^2 + K'_t [DCS] [M^\bullet]$$

or $$R_i = 2 \frac{K_t}{K_p^2} \bullet \frac{R_p^2}{[M]^2} + K'_t [DCS] \frac{R_p}{K_p [M]} = 2 f Kd [DCS]$$

or $$2 \frac{K_t}{K_p^2} \bullet \frac{R_p^2}{[M]^2 [DCS]} = 2 f Kd - \frac{K'_t}{K_p} \bullet \frac{R_p}{[M]}$$

The plot of left hand side of the above equation against R_p / [M] should give a straight line with negative slope in case of degradative initiator transfer. The results of the analysis are presented in Table – 4.22, Fig.29 and the value of K'_t / K_p was found to be 5.0 from the slope of the above plot:

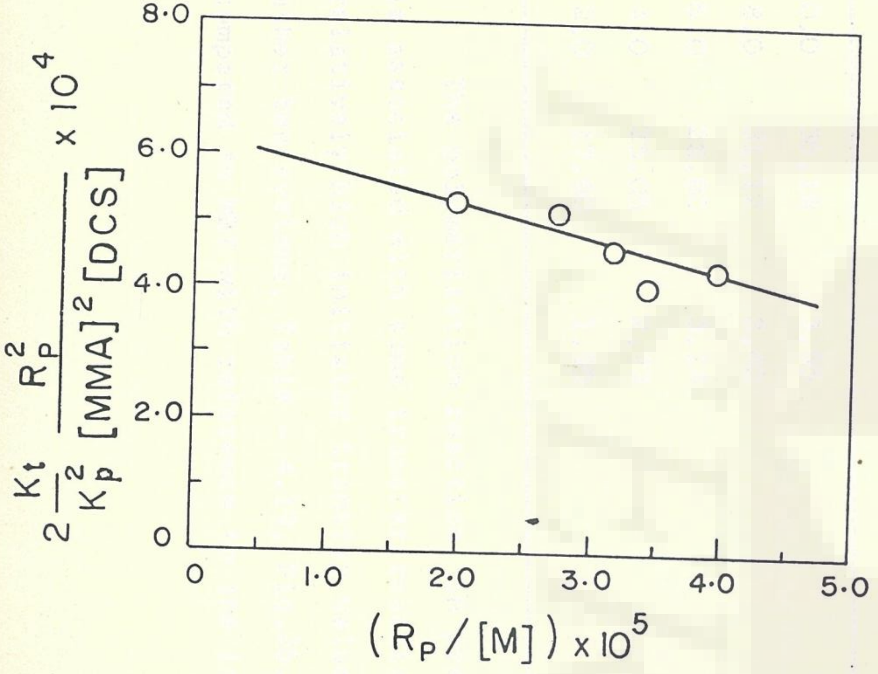


Fig. 29 : Analysis of degradative initiator transfer in the photopolymerization of MMA at 40°C using DCS as initiator.

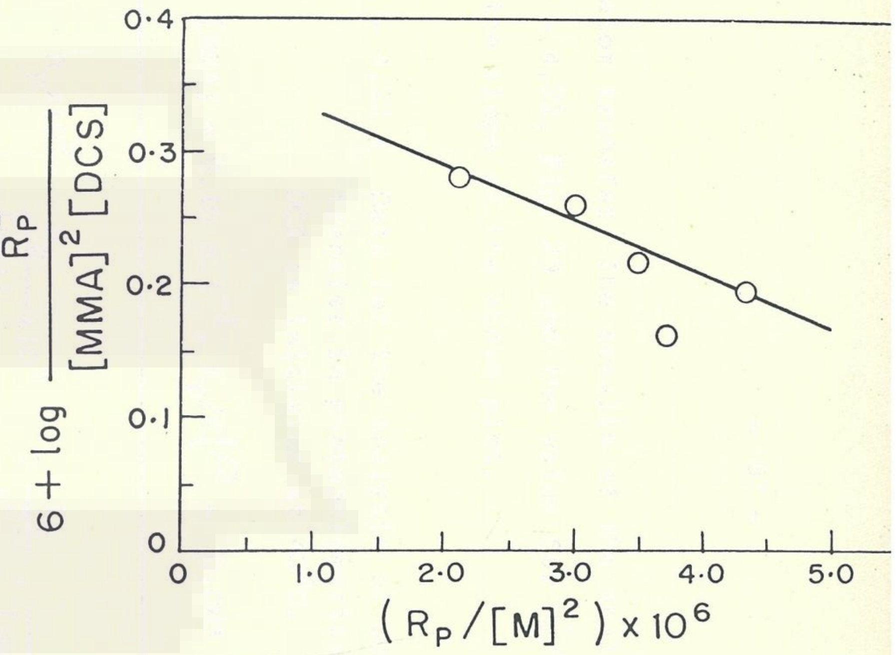


Fig. 28 : Analysis of primary radical termination in the photopolymerization of MMA at40°C using DCS as initiator.

Table – 4.22

Data for the analysis of degradative initiator transfer in photopolymerization of MMA using DCS as initiator at 40^{o}C

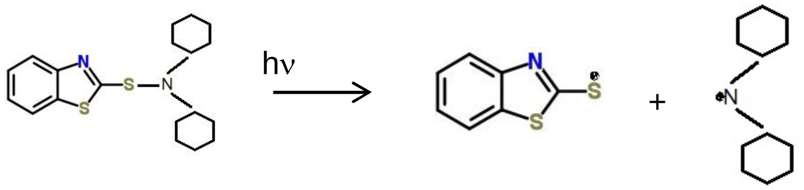
[MMA] = 9.16 m.l^{-1}, $K_p/K_t^{1/2}$ = 0.085

[DCS]x10^{4} m.l^{-1}	R_p x 10^{5} m.l^{-1}.s^{-1}	$\frac{R_p}{[MMA]}$ X10^{5}	$2\,\frac{K_t}{K_p^2} \bullet \frac{R_p^2}{[MMA]^2\,[DCS]}$ x 10^{4}	$\frac{K'_t}{K_p}$
10.0	36.18	3.95	4.32	5.0
8.0	31.12	3.40	3.99	
6.0	28.80	3.14	4.56	
4.0	25.05	2.73	5.17	
2.0	17.90	1.95	5.28	

The polymerization reaction, in presence of DCS as initiator is associated with some transfer reactions is also supported by the relatively high initiator transfer value (0.25) compared to the other two systems, Table – 4.19, Fig.26. DCS system is more efficient compared to MBT with reference to the low activation energy value, 2.9 compared to 4.8. This is expected because of easier photochemical decomposition of S–(substituted)N bond.

When the UV absorption spectra of DCS and the corresponding polymer (Fig.30) are analysed it is observed that the DCS fragment is present in the polymer as an end group and it has similar absorption like DCS. There is no absorption maxima in the region 324 nm characteristic of MBT due to its thione form in the tautomeric structure,

Based on the above discussion and experimental results the following simple scheme of reaction may be proposed:



(R$_2^{\bullet}$)

(R$_1^{\bullet}$)

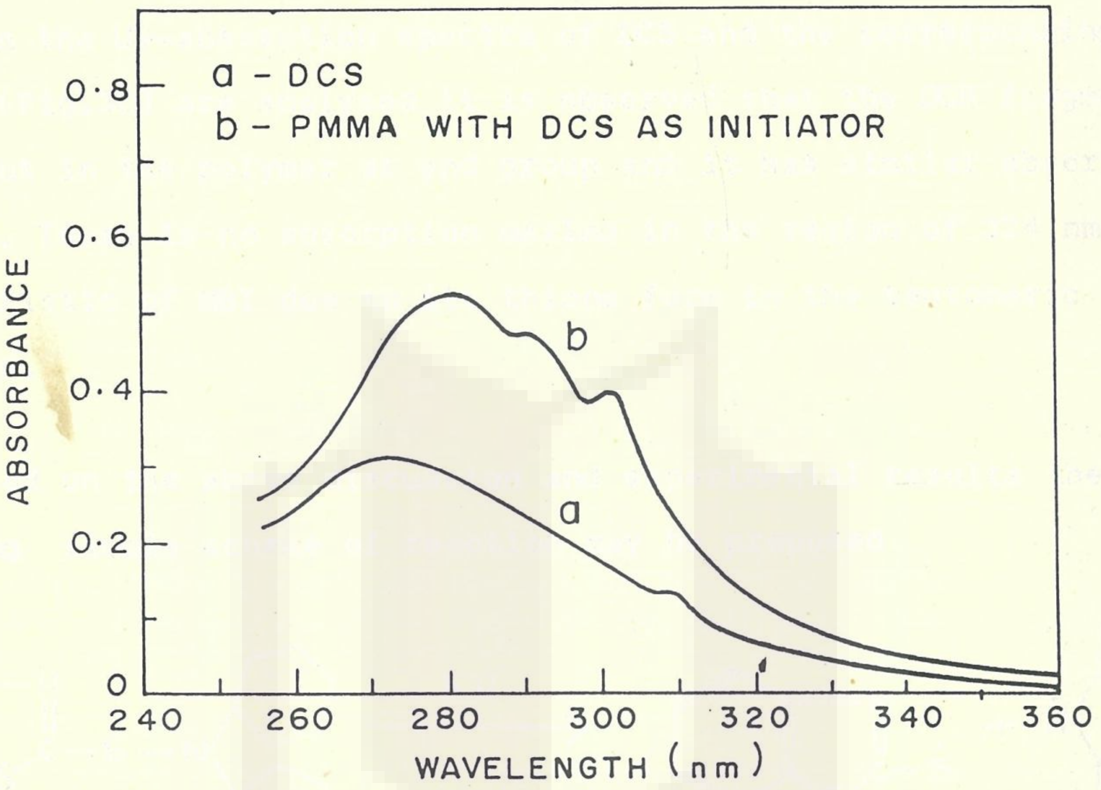


Fig. 30 :UV-Absorption spectra of DCS and DCS-PMMA in acetonitrile.

$$R_1^{\bullet} \quad + \quad MMA\ (M) \xrightarrow{K_i} MMA^{\bullet}\ (M^{\bullet})$$

$$R_2^{\bullet} \quad + \quad MMA\ (M) \xrightarrow{K_i} MMA^{\bullet}\ (M^{\bullet})$$

$$M^{\bullet} \quad + \quad M \xrightarrow{K_p} P^{\bullet}$$

$$P^{\bullet} \quad + \quad P^{\bullet} \xrightarrow{K_t} \text{terminated polymer}$$

COMPARATIVE STUDIES
ON THE THREE SYSTEMS

Comparative studies on the three systems:

The results of the photopolymerization experiments using MMA as the monomer and MBT, MBT–BZ_2O_2 combination and DCS as initiators are summarised in Table–4.23. It is apparent from the table that among the three systems DCS is the most efficient one as indicated by high rate of initiation (R_i) viz., $21.48\text{x}10^{-8}$ $m.l^{-1}.s^{-1}$ and low activation energy (E_a) viz., 2.9 $K.Cal.m^{-1}$. The next efficient system is MBT–BZ_2O_2 combination where benzoyl peroxide is oxidizing MBT to form mercaptobenzo-thiazole disulphide (MBTS), a supporting reaction before MBT forms an addition product with the monomer. This is also supported by the control experiments using MBT and BZ_2O_2 in absence of monomer and isolating the resultant MBTS as precipitate. Here also the energy of activation (E_a) is low, i.e., 3.55 $K.Cal.m^{-1}$ and rate of initiation (R_i) is high, i.e., $11.28\text{x}10^{-8}$ $m.l^{-1}.s^{-1}$ compared to MBT but the two parameters are lower than the DCS system. When MBT is used as the photoinitiator the rate of initiation (R_i) is somewhat low, $2.37\text{x}10^{-8}$ $m.l^{-1}.s^{-1}$ and the activation energy (E_a) is a little bit high 4.8 $K.Cal.m^{-1}$ compared to two other systems indicating that MBT forms the least efficient system. It is also evident from Table – 4.23 that benzene has some pronounced effect when MBT alone is used as photoinitiator compared to the other two systems and this phenomena has been explained on the basis of participation of MBT in tautomeric form. Also it has been observed that a high induction period is associated with the system using MBT alone compared to the other two systems and this has also been ascribed to the tautomeric effect through which the active form (thiol) of MBT is first generated and subsequently participates in the initiation reaction.

The monomer order with respect to benzene is 1.06 and 1.0 for MBT–BZ_2O_2 combination and DCS systems respectively while it is 0.0 and 0.5 for two concentration ranges of monomer in case of MBT. These low values in case of MBT system has been explained on the basis of participation of benzene in the tautomeric structure of MBT.

The initiator order is 0.5 and 0.17 for two concentration ranges of MBT. The lower value indicates some non-ideal kinetic behaviour and on analysing this has been found to be due to primary radical termination effect. The kinetic parameter K_{prt} / K_iK_p, obtained from the respective plot is $9.0\text{x}10^5$. For MBT–BZ_2O_2 combination

Table – 4.23

System	Induction period range, min	Initiator order	Monomer order w.r.t benzene	Ri x 10^8 m.l^{-1}.s^{-1}	E_a K.Cal.m^{-1}	C_I	K_{prt} / K_i K_p	Mol. wt range X 10^{-5}
MBT	30 – 75	0.50 and 0.17	0.0 and 0.5	2.37	4.8	1.42x10^{-2}	9.0x10^{5}	2.33 to 1.236
MBT–BZ_2O_2 at fixed MBT	9 – 14	0.50 and 0.08	1.06*	11.28*	3.55*	3.3x10^{-2}	------	2.258 to 1.492
MBT–BZ_2O_2 at fixed BZ_2O_2	9 – 18	0.52 and 0.10	1.06*	11.28*	3.55*	4.0x10^{-2}	------	2.941 to 1.282
DCS	8 – 16	0.44	1.0	21.48	2.9	2.5x 10^{-1}	4x10^{4}	0.8772 to 1.7740

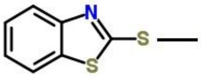
✸ The results were obtained when both the initiators were kept constant at the optimum value viz.,

[MBT] = 1 x 10^{-3} m.l^{-1}, [BZ_2O_2] = 0.5 x 10^{-3} m.l^{-1}

System the initiator order has been observed to be 0.52 and 0.08 when [MBT] was varied keeping [BZ_2O_2] constant while it is 0.5 and 0.08 when [BZ_2O_2] was varied and [MBT] was kept constant. The low value at the higher concentration region of either MBT or BZ_2O_2 has been explained to be due to non-availability of stoichiometric amount of the initiators. In case of DCS system the initiator order was found to be 0.44. This low value has been explained on the basis of primary radical termination and/or degradative initiator transfer effect (Fig.28, 29). The value of K_{prt} / K_iK_p was found to be 4.0 x 10^4. This is a lower value compared to that obtained from MBT system which is evident when we compare the respective initiator concentrations in two cases. For MBT system the primary radical termination effect was observed in the concentration region of 1 x 10^{-2} to 3 x 10^{-2} m.l^{-1} for [MBT] while the same effect for DCS has been observed in the concentration region of 2.0 x 10^{-4} to 10.0 x 10^{-4} m.l^{-1} for [DCS]. The initiator transfer constant C_{MBT}, was found to be 1.42 x 10^{-2} for the lower initiator concentration. However in MBT–BZ_2O_2 system the values are 4.0 x 10^{-2} and 3.3 x 10^{-2} for C_{MBT} and C_{BZ2O2} respectively. For DCS system a relatively higher value of 2.5 x 10^{-1} for C_{DCS} was obtained indicating considerable initiator transfer in the form of degradative initiator transfer and / or primary radical termination (Fig.28, 29) compared to two other systems.

The molecular weights for MBT system were found to vary from 2.33 x 10^5 to 1.236 x 10^5 for the initiator concentrations 2 x 10^{-3} to 30 x 10^{-3} m.l^{-1}, while for MBT–BZ_2O_2 system it varied from 2.941 x 10^5 to 1.282 x 10^5 for concentrations of MBT from 0.25 x 10^{-3} to 5 x 10^{-3} m.l^{-1} at a fixed BZ_2O_2 concentration (0.5 x 10^{-3} m.l^{-1}). However for DCS system the corresponding values were somewhat lower viz., 0.8772 x 10^5 to 1.774 x 10^5 for the concentrations from 1 x 10^{-3} to 0.2 x 10^{-3} m.l^{-1}.

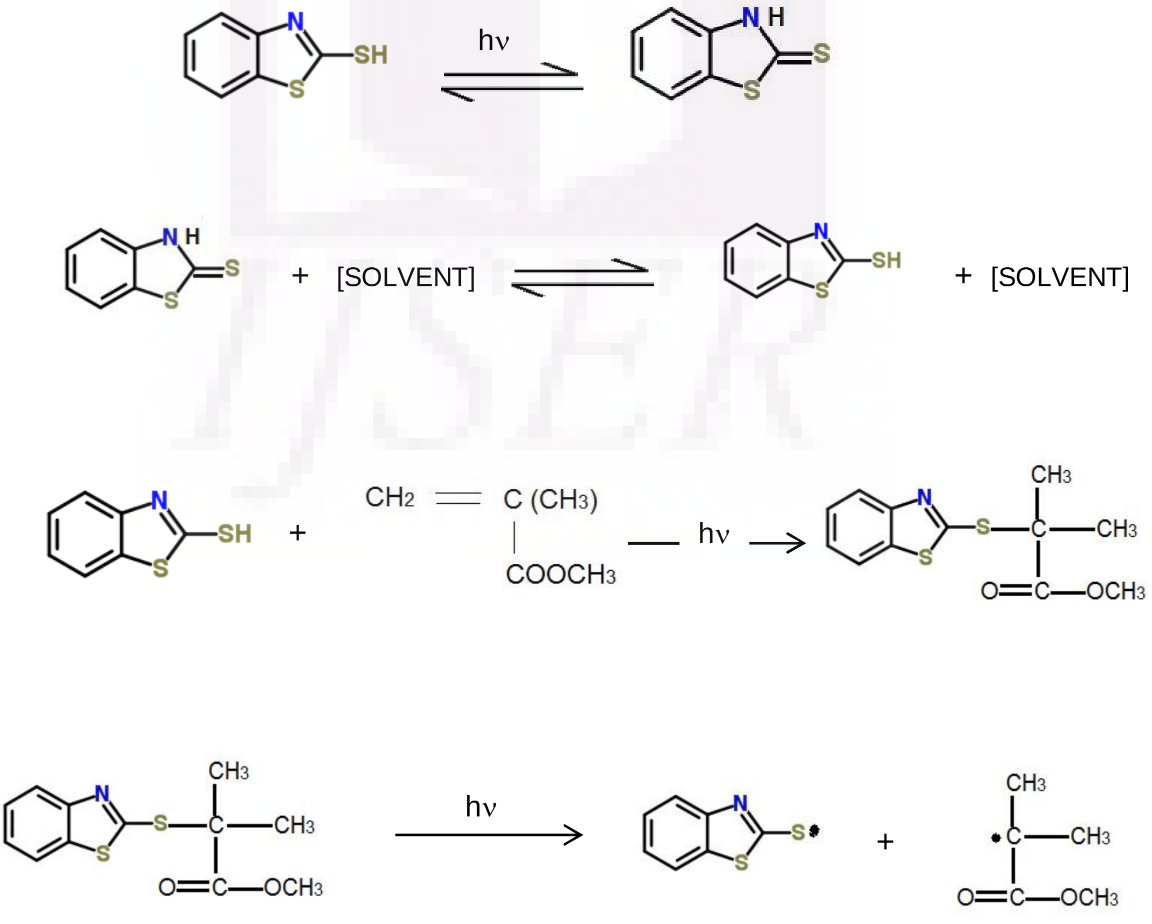
It is interesting to analyse the UV–absorption spectra of the three initiators and resulting polymers. There exists an absorption maxima in the region of 324 nm for MBT but the same is not present in the corresponding polymer where it is present in the region of 275 nm. The former maxima is due to >C=S structure while the latter corresponds to –C–S–C– structure. When BZ_2O_2 is mixed with MBT in acetonitrile and allowed to stand at room temperature, the absorption maxima at 324 nm gradually shifts to 275 nm (Fig.20) due to the formation of mercaptobenzothiazole disulphide having –C–S–S–C– structure. For DCS the absorption maxima was found to be in the region of 275 nm both for the initiator as well as for the corresponding polymer. Thus in all the three cases the benzothiazole moiety i.e.,



fragment is entering into the polymer as end group.

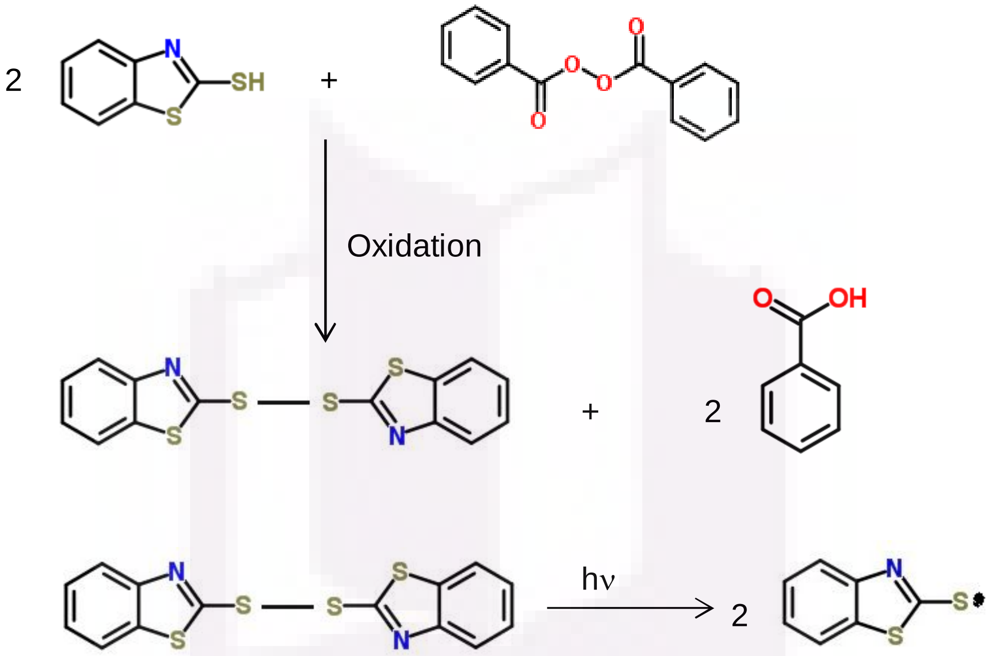
Based on the above informations the following reaction schemes have been proposed in three different systems:

MBT – system:



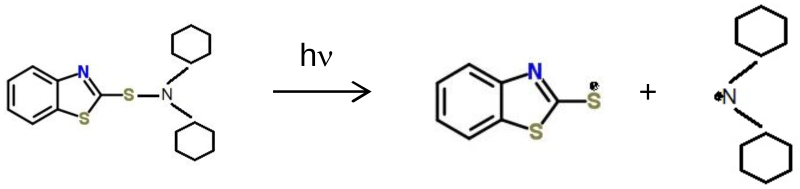
The primary reaction in this case is the formation of an adduct with the monomer which then decomposes into radicals in presence of light to initiate polymerization reaction.

MBT – BZ_2O_2 combination system:



Here primary reaction is the oxidation of MBT to the corresponding disulphide (MBTS) which then decomposes photochemically into the primary radicals to initiate the polymerization.

DCS – system:



No supporting reactions are required here for the generation of the actual initiator. It decomposes readily into the corresponding radicals in presence of light to initiate polymerization.

SUMMARY

Summary:

Organic sulphur compounds have notable photoactivity and some of them have also been used as photoinitiator for the polymerization of vinyl monomers, the most important among them are tetra-alkyl thiuram monosulphide and disulphide, S–aryl-dithiocarbamates, diaryl, dibenzoyl and dibenzothiazolyl disulphide, alkyl and aryl sulfonyl chlorides, chlorosulfonamides, mercaptans and thiols. However in most of the above systems no detailed kinetic studies have been reported in the literature for the photopolymerization of vinyl monomers. We have, therefore, undertaken a detailed kinetic and mechanistic studies using a few of the above systems and in particular mercaptobenzothiazole system (2–Mercaptobenzothiazole), an organic sulphur compound of the above class, has been chosen for the present study. The effect of peroxide on this compound and the effect of 2–substitution in the MBT molecule have also been studied in detail. The present thesis comprises of the photopolymerization of MMA using (a) MBT, (b) MBT–BZ_2O_2, and (c) DCS as photoinitiators and the results are summarised below.

a) Photopolymerization of MMA with the use of MBT as initiator:

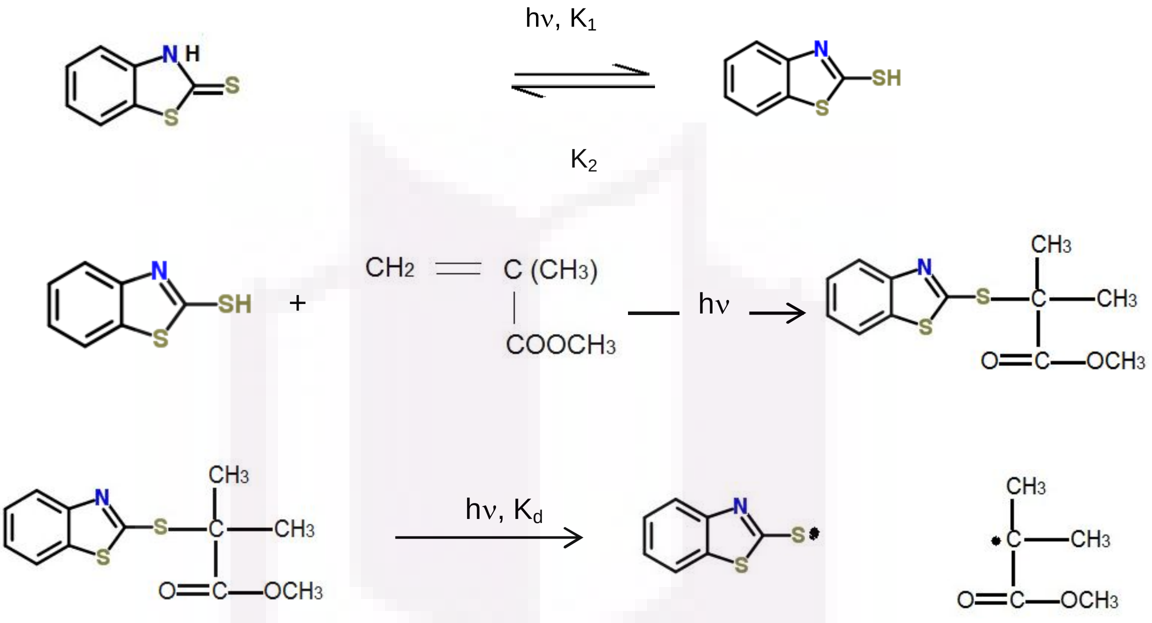
The polymerization was associated with a relatively high induction period ranging from 30 to 75 minutes depending on the concentration of initiator used. While studying the polymerization the following kinetic features were observed.

Initiator exponent value is 0.5 and 0.17 and the low value is due to primary radical termination in the higher concentration region (2 x 10^{-2} to 6 x 10^{-2} $m.l^{-1}$). The rate of initiation (R_i) was observed to be 2.37 x 10^{-8} $m.l^{-1}.s^{-1}$ and the corresponding $K_p/K_t^{1/2}$ value is 0.084. The mode of termination was also calculated and it was observed that 85% termination occurs by combination and 15% by disproportionation These values are same as reported for thermal polymerization of MMA at 60°C. The rate constant for the decomposition of the initiator (K_d) as obtained by spectrophotometric study from the decay in absorbance at 325 nm was found to be 6.07 x 10^{-6} sec^{-1}. The overall activation energy obtained by carrying out polymerization experiments at different temperatures and then following an Arrhenius type of plot was 4.8 $K.Cal.m^{-1}$. This value is in good order for typical photopolymerization systems. Monomer exponent values were found to be 1.06

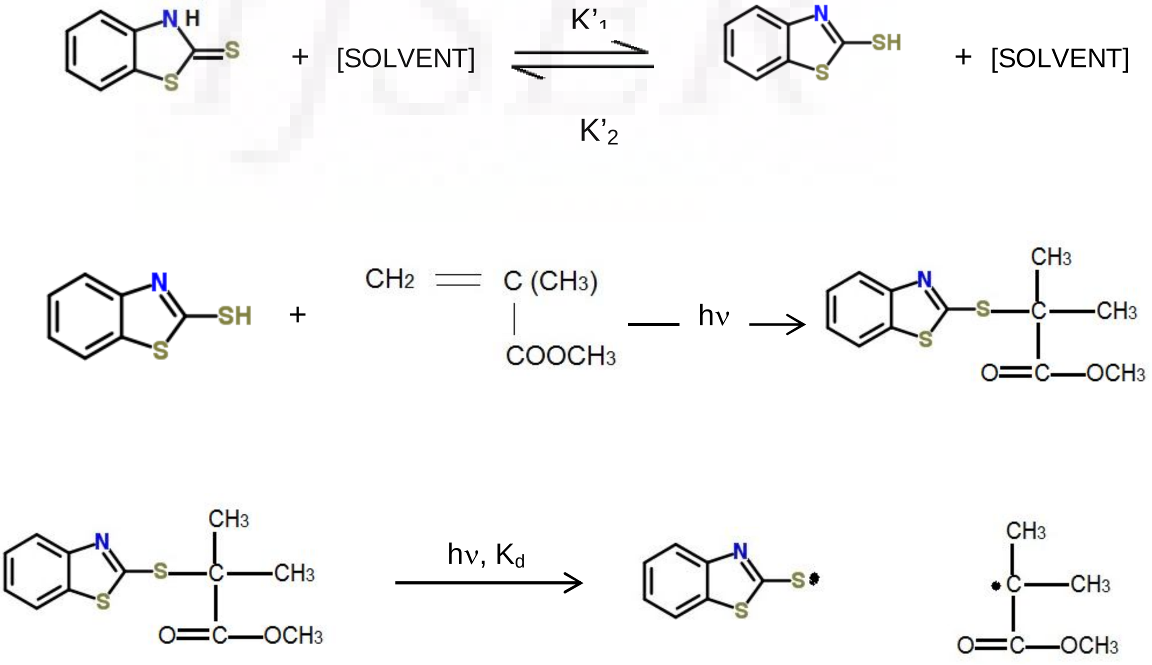
(Cyclohexane) and 0.0 and 0.5 (Benzene). It is thus apparent that cyclohexane behaves as in inert solvent while benzene has a rate enhancing effect.

Based on the above results the following scheme of reaction has been outlined for the generation of radicals.

Undiluted systems:



Diluted system with active solvents:



Based on the above scheme of reactions the following rate equations were deduced which agree well with the experimental results.

For undiluted systems:

$$R_p = \frac{K_p}{K_t^{1/2}} \left\{ \frac{f\, K_d\, K\, [a]}{1 + K} \right\}^{1/2} [M]$$

For diluted systems with active solvents:

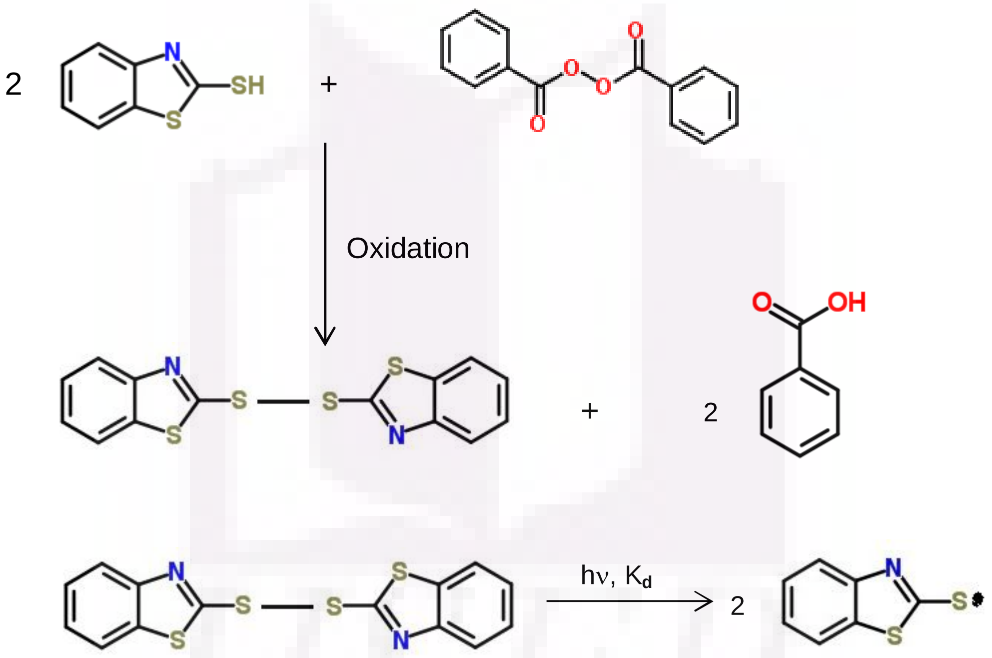
$$R_p = \frac{K_p}{K_t^{1/2}} \left\{ \frac{f\, K_d\, K'\, [a]\, [S]}{1 + K'\, [S]} \right\}^{1/2} [M]$$

b) Photopolymerization of MMA with the use of MBT–BZ_2O_2 combination as initiator

The polymerization of MMA started readily with MBT–BZ_2O_2 combination as photoinitiator. Much shorter inhibition periods were obtained with this system compared to MBT system. These short induction periods are within the limitation of our experimental set up. However no polymerization of MMA occurred under the present experimental condition using only BZ_2O_2 in the system. The polymerization reactions were characterised by the following kinetic features.

Initiator exponent values were found to be 0.52 and 0.1 with respect to MBT and 0.5 and 0.08 with respect to BZ_2O_2. The very low initiator exponent values were observed for a concentration region above critical concentration of the combination MBT–BZ_2O_2 while varying MBT and BZ_2O_2 respectively. The system behaved ideally upto the critical concentration but the very low value above the critical concentration was due to the non-availability of stoichiometric proportions of the two initiator components. The rate of initiation (Ri) was found to be 11.28 x 10^{-8} m.l^{-1}.s^{-1} and the value of $K_p/K_t^{1/2}$ was calculated to be 0.108. The value for mode of termination was 1.78 with respect to MBT and 1.82 with respect to BZ_2O_2. A value of 3.55 K.Cal.m^{-1} was obtained for the overall activation energy which corresponded to efficient photopolymerization reaction. Values for the monomer order were found to be 1.06 (Benzene), 1.08 (CCl4) and 1.0 (THF) which are very close / similar to the usual value of 1.0

Based on these experimental results the reactions for the generation of radicals have been outlined as follows:



The kinetic features also indicate that the normal rate equation for the polymerization reaction would be valid in this case.

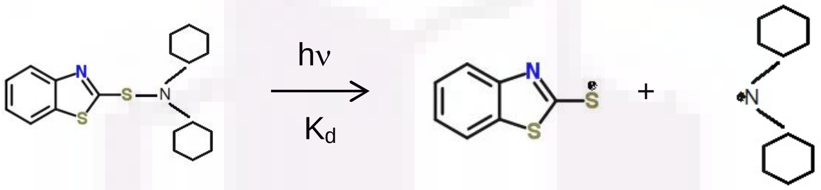
c) Photopolymerization of MMA using DCS as initiator:

In this case also the polymerization was induced readily and the following kinetic features were observed.

The initiator exponent value was found to be 0.44 which is somewhat lower than the normal value of 0.5. A high value for the rate of initiation (R_i) viz., $21.48\text{x}10^{-8}$ $\text{m.l}^{-1}.\text{s}^{-1}$ was obtained indicating that this is the most efficient system. This is also supported by the fact that a low value of the overall activation energy, 2.9 K.Cal.m^{-1}

is required for the present system. The value of $K_p/K_t^{1/2}$ and the mode of termination was calculated to be 0.085 and 1.838 respectively. The monomer exponent values were found to be 1.0 (Benzene) and 1.04 (CCl_4). Here both the solvents behaved as an inert solvent.

Following the above experimental results the scheme of reaction for the generation of radicals may be outlined as below:



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