Kinetics and mechanism of polymerization of methyl methacrylate initiated by stibonium ylide

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Abstract. Homopolymerization of methyl methacrylate (MMA) was carried out in the presence of triphenylstibonium 1,2,3,4-tetraphenyl-cyclopentadienylide as an initiator in dioxane at $65°C \pm 0.1°C$. The system follows non-ideal radical kinetics ($R_p \propto [M]^{1.4}\ [I]^{0.44}$) due to primary radical termination as well as degradative chain-transfer reaction. The overall activation energy and average value of k_p^2/k_t were 64 kJ mol^{-1} and 0.173×10^{-3} l mol^{-1} s^{-1} respectively.

Keywords. Triphenylstiboniumylide; methyl methacrylate; non-ideal radical kinetics; mechanism.

1. Introduction

The stereospecific polymerization of various acrylates and methacrylate has been studied by using a variety of initiators such as triphenyl phosphine and iron(III) complex,[1] thiol,[2] the D-glucose-ceric ion redox system,[3] benzyol peroxide,[4] tert-hexyl peroxy pivalate[5] and fullerene.[6] Recently, some ylides containing non-metals like nitrogen,[7–10] sulphur[11] and phosphorus[12] have been used for the polymerization of methyl methacrylate MMA.

Recently use of *p*-acetylenzylidene triphenyl arsonium ylide [*p*-ABTAY] as radical initiator for the homopolymerization of methyl methacrylate,[13] vinyl acetate[14] and copolymerization of styrene with vinyl acetate[15] has been reported.

The properties of ylides are very much dependent on the identity of the heteroatom. The dipolar and nucleophilic character of the ylides appear to increase their stability. However, the triphenylstibonium 1,2,3,4-tetraphenylcyclopentadienylide, because of its synthetic problems, has not been examined earlier in the polymer science.

2. Experimental

Monomer and solvents were purified according to procedures reported in literature.[16,17] The ylide was prepared by the method of Lloyd.[18] Briefly it is as follows.

A solution of 2.19×10^{-4} moles of 1,2,3,4-tetraphenylcyclopentadiene (Aldrich), 7.46×10^{-4} moles of *p*-toluene sulphonylhydrazide (Fluka AG) in 6.3 ml diethyl amine was kept at 0°C for 10 days. It was then followed by addition of 3.5 ml water, 5 ml ether and dried over anhydrous silica gel, when yellow crystals of diazo compound were obtained. It was washed with methanol.

A solution containing 2.64×10^{-4} moles of diazo-compound, 7.35×10^{-5} moles of Cu(II) bishexafluoroacetylacetonato (Merck) as catalyst and 4.95×10^{-5} moles of triphenylstibonium (Merck) in 10 ml benzene were refluxed for 2 h. The evaporation of the solvent in vacuum produced stibonium ylide in 14.5% yield.

3. Polymerization procedure

The polymerization was carried out in a dioxane at $65 \pm 0.1°C$ under an inert atmosphere of nitrogen for 5 h. The rate of polymerization (R_p) was determined dilatometry from the slope of linear portion of conversion vs time plots. The intrinsic viscosity [h] of polymer(s) was determined in benzene at $30 \pm 0.1°C$ using an ubbelohde viscometer. The average degree of polymerization ($\bar{P}_n$) was calculated.[19]

4. Results and discussion

The ylide initiated polymerization at 65°C have been summarized in (tables 1–3) and (figures 1–8)

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because it failed to initiate the polymerization below 60°C.

4.1 *Effect of [ylide]*

The effect of stibonium ylide on the rate of polymerization was studied by varying the [ylide] from 1.16×10^{-5} to 5.78×10^{-5} mol l^{-1}, while keeping [MMA] constant as 3.0 mol l^{-1} (figure 1 and table 1). The polymerization was associated with an induction period of about 50–60 min. The extended induction period is often seen feature in the case of ylide initiated polymerization of various vinyl monomers.[20] The ylide initiated the radical polymerization of methyl methacrylate and the R_p increased when ylide concentration increased from 1.16×10^{-5} to 5.78×10^{-5} mol l^{-1}. The value is less than expected for ideal radical kinetics. The initiator exponent, calculated from the slope of the plot log R_p versus log [ylide], is 0.44 ± 0.01 (Figure 2). The average degree of polymerization ($\bar{P}_n$) decreases with the increase in [ylide] (table 1). The value of k_p^2/k_t, determined from the slope of a plot (figure 3) of $(1/\bar{P}_n)$ vs $R_p/[M]^2$, is 0.173×10^{-3} l mol^{-1} s^{-1}.

4.2 *Effect of [MMA]*

The effect of [MMA] on the R_p has been studied by varying [MMA] from 0.75 to 3.0 mol l^{-1}, whereas [ylide] has been kept constant 2.31×10^{-5} mol l^{-1} (table 2). It is clear that the R_p is a direct function of [MMA]. The monomer exponent, calculated from the slope of the linear plot of log R_p against log [MMA], is 1.4 ± 0.02 (figure 4). This confirms that the system follows non-ideal kinetics. The average degree of polymerization increases with increase of monomer concentration (table 2).[21–22]
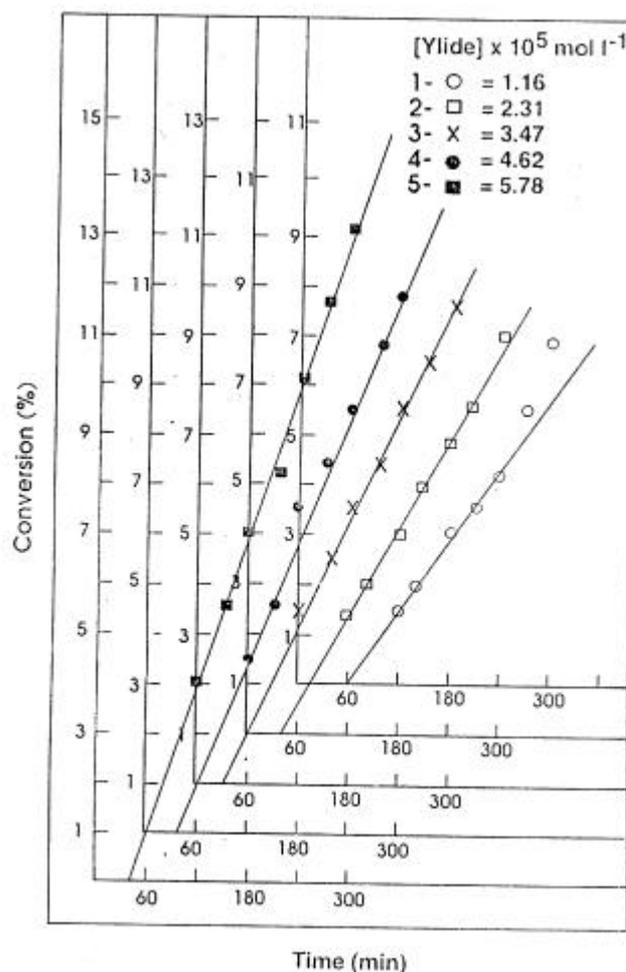
4.3 *Effect of temperature*

The polymerization runs were also carried out at 70 and 75°C in order to evaluate energy of activation of the system. The value, calculated from the linear
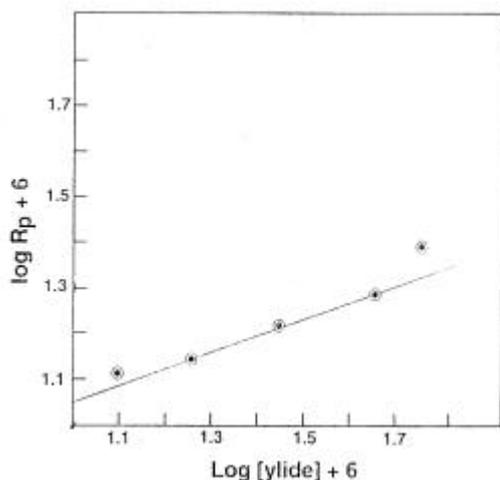
Table 2. Effect of methyl methacrylate concentration on the polymerization of methyl methacrylate [MMA].

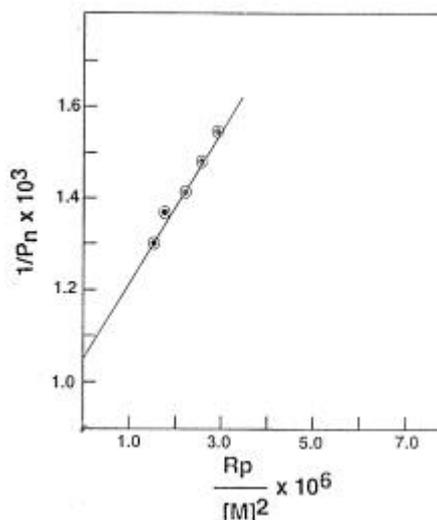[Ylide] = 2.31×10^{-5} mol l^{-1}; temperature = $65 \pm 0.1°C$; solvent = dioxane; time = 300 min

Run No.	[MMA] × 10^5 (mol l^{-1})	Percentage conversion	$R_p \times 10^5$ mol l^{-1} s^{-1}	$\bar{P}_n$
1	0.75	3.6	0.21	458
2	1.50	4.6	0.50	521
3	2.25	6.1	0.91	649
4	3.00	7.9	1.40	736

Figure 1. Percentage conversion vs time plots for homopolymerization of methyl methacrylate: [ylide] = 1.16 to 5.78×10^{-5} mol l^{-1}; [MMA] = 3.0 mol l^{-1}; temp. = $65 \pm 0.1°C$; solvent = dioxene; time = 300 min; [(1) = 1.16×10^{-5} mol l^{-1}; (2) = 2.31×10^{-5} mol l^{-1}; (3) = 3.47×10^{-5} mol l^{-1}; (4) = 4.67×10^{-5} mol l^{-1}; (5) = 5.78×10^{-5} mol l^{-1}].

Table 1. Effect of [ylide] on the polymerization of methyl methacrylate [MMA].

[MMA] = 3.0 mol l^{-1}; temperature = $65 \pm 0.1°C$; solvent = dioxane; time = 300 min

Run No.	[ylide] × 10^5 (mol l^{-1})	Percentage conversion	$R_p \times 10^5$ mol l^{-1} s^{-1}	$\bar{P}_n$
1	1.16	6.8	1.20	780
2	2.31	7.9	1.40	736
3	3.47	9.6	1.66	711
4	4.62	10.7	1.94	672
5	5.78	13.1	2.50	749

Figure 2. Relationship $\log R_p$ and log [ylide] for the homopolymerzation of methyl methacrylate: [ylide] = 1·16 to 5·78 × 10^{-5} mol l^{-1}; [MMA] = 3·0 mol l^{-1}; temp. = 65 ± 0·1°C; time = 300 min; solvent = dioxene.

Figure 3. Relationship between $1/\bar{P}_n$ and $R_p/[M]^2$ for the homopolymerzation of methyl methacrylate: [ylide] = 1·16 to 5·78 × 10^{-5} mol l^{-1}; [MMA] = 3·0 mol l^{-1}; temp. = 65 ± 0·1°C; time = 300 min; solvent = dioxene.

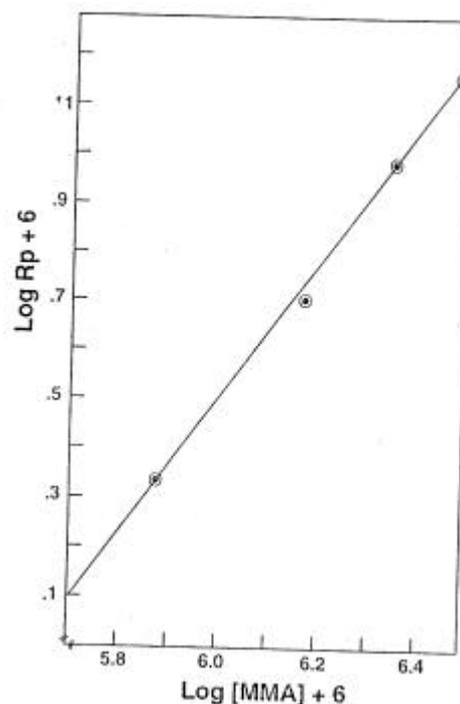**Table 3.** Effect of inhibitor on the rate of polymerization of [MMA]

[Ylide] = 2·31 × 10^5 mol l^{-1}; [MMA] = 3·0 mol l^{-1}; temp. = 65 ± 0·1°C; time = 300 min; solvent = dioxene

Run No.	[Inhibitor] (mol^{-1})	Percentaqge conversion	$R_p \times 10^5$ (mol l^{-1} s^{-1})
1	–	7·9	1·4
2	*Hydroquinone*		
	1·5 × 10^{-3}	3·9	0·95
	4·5 × 10^{-3}	1·1	0·1
	7·5 × 10^{-1}	No polymer	No polymer
3	*Nitrobenzene*		
	0·81	4·4	1·0
	1·62	2·1	0·5
	2·43	No polymer	No polymer
4	*Aniline*		
	0·89	5·1	1·2
	1·78	3·8	1·1
	2·67	No polymer	No polymer

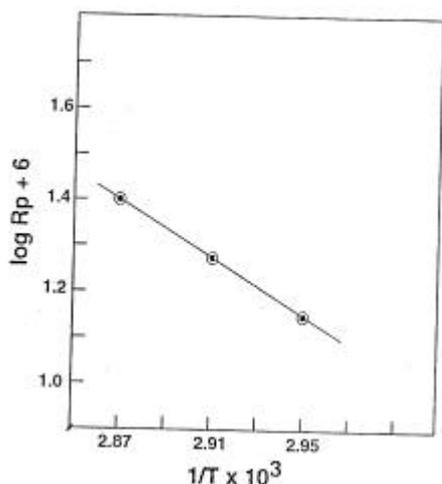plot of $\log R_p$ vs polymerization temperature, is 64 kJ mol^{-1} (figure 5).

4.4 *Causes of non-ideality*

The value of initiator exponent suggests that the system follows non-ideal kinetics. The kinetic non-ideality can be explained by analyzing the role of triphenyl stibonium 1,2,3,4-tetraphenyl-cyclopendiene as primary radical termination and degradative chain transfer agent. To analyze the effect of primary


Figure 4. Relationship log [MMA] and $\log R_p$ for the homopolymerzation of methyl methacrylate: [ylide] = 2·31 × 10^{-5} mol l^{-1}; [MMA] = 0·75 to 3·0 mol l^{-1}; temp. = 65 ± 0·1°C; time = 300 min; solvent = dioxene.

radical termination a suitable modified expression given by Deb and Meherhoff[23] in the following form is used:

Figure 5. Plot of $\log R_p$ vs polymerization temperature (Arrhenius plot): [ylide] $= 2\cdot31 \times 10^{-5}$ mol l^{-1}; [MMA] $= 3\cdot0$ mol l^{-1}; temp. $= 65$, 70, $75 \pm 0\cdot1°$C; time $= 300$ min; solvent $=$ dioxene.
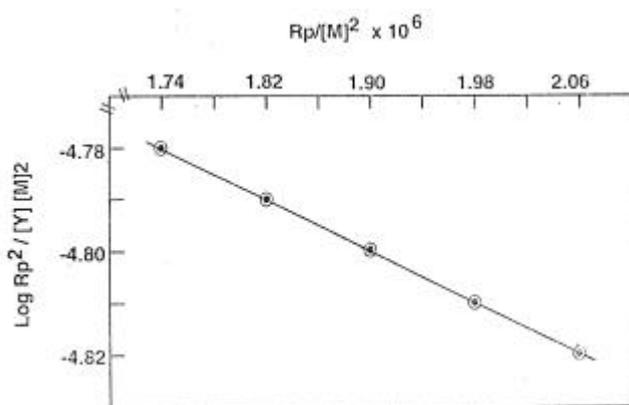
Figure 6. Plot of $\log R_p^2/[Y][M]^2$ and $R_p/[M]^2$: [ylide] $= 1\cdot16$ to $5\cdot78 \times 10^{-5}$ mol l^{-1}; [MMA] $= 2\cdot53$ mol l^{-1}; temp. $= 65 \pm 0\cdot1°$C; time $= 300$ min; solvent $=$ dioxene.
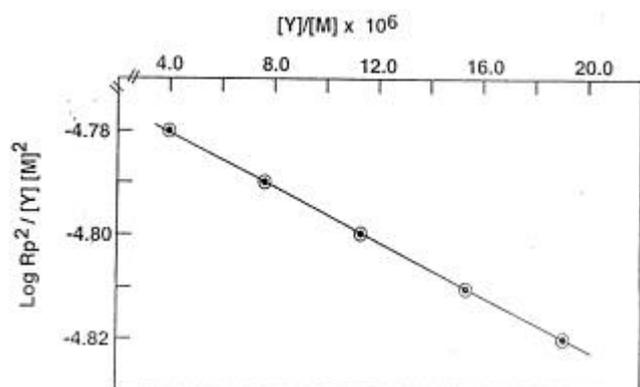
Figure 7. Plot of $\log R_p^2/[Y][M]^2$ and [Y]/[M]: [ylide] $= 1\cdot16$ to $5\cdot78 \times 10^{-5}$ mol l^{-1}; [MMA] $= 2\cdot53$ mol l^{-1}; temp. $= 65 \pm 0\cdot1°$C; time $= 300$ min; solvent $=$ dioxene.

$$\log \frac{R_p^2}{[Y][M]^2}$$

$$= \log \frac{2 f_k k_d k_p^2}{k_t} - 0.8684 \frac{k_{prt}}{k_y \times k_p} \times \frac{R_p}{[M]^2},$$

where Y and M represent ylide and monomer respectively. A plot of the above equation vs $R_p/[M]^2$ gave a negative slope (figure 6) indicating primary radical termination due to ylide for the present system. The following equation, derived by Deb[24] and further simplified by Ghosh and Mitra[25] was used to examine the role of ylide as degradative chain transfer agent:

$$\log \frac{R_p^2}{[Y][M]^2}$$

$$= \frac{\log 2 f_k k_d k_p^2}{k_t} - 0.434 \frac{k_p^2}{k_t} \times \frac{k_{rt} Y}{k_{il} k_p} \times C_1 \frac{[Y]}{[M]},$$

where C_1 is the ylide transfer constant. The plot of the above equation vs $[Y]/[M]$ also gave a negative slope (figure 7), thereby suggesting chain transfer reaction due to ylide.

The non-ideal kinetics in the arsonium ylide initiated polymerization of vinyl monomers like vinyl acetate[14] MMA[13,26] has been attributed to primary
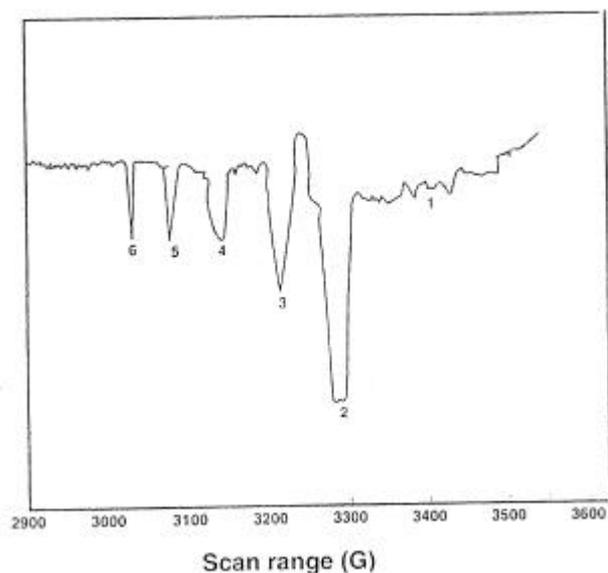

Figure 8. ESR spectrum of polymethyl methacrylate mixture.

radical termination and degradative chain transfer reaction. Further the polymerization of few vinyl monomer initiated by N[8,9,27] and P[28] ylide also follows non-ideal kinetics due to primary radical termination and degradative chain transfer.

5. Mechanism

The effect of free radical inhibitors like hydroquinone, aniline and nitrobenzene on the polymerizaiton under the same reaction conditions (table 3) has also been studied to conform free radical mode of polymerization. Triphenylstibonium 1,2,3,4-tetraphenylcyclopentadienylide undergoes bond fission between the heteroatom and the phenyl group to yield phenyl radical[29] which initiates polymerization reaction. This is confirmed by ESR spectrum (the ESR spectrum was recorded on X-band EPR 109 E-line century series spectrometer at room temperature) of living system at 2 h which show six hyperfine lines due to the phenyl radical (figure 8).

5.1 *Generation of initiator radical*
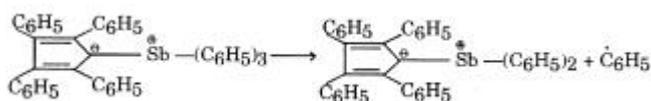
The initiation step is as follows:
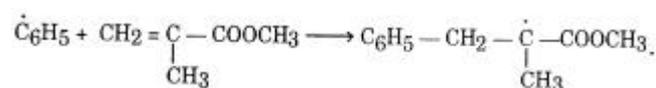
6. Conclusions

On the basis of the above evidences it may be concluded that the polymerization of methyl methcrylate initiated by triphenyl stibonium 1,2,3,4-tetraphenycyclopentadienylide, follows non-ideal radical kinetics due to primary radical termination as well as degradative chain transfer reaction.

Acknowledgement

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