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# PHENACYL DIMETHYL SULFONIUM YLIDE-MERCURIC CHLORIDE COMPLEX INITIATED RADICAL POLYMERIZATION OF STYRENE

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## ABSTRACT

The metal-ylide initiated radical polymerization of styrene (sty) at 85 ± 0.1°C using dioxane as inert solvent was examined. The kinetic parameters average rate of polymerization (Rp) and reaction orders with respect to initiator and monomer have been determined and found to be 0.3 and 1.11 respectively. The polymerization was retarded by hydroquinone and non-polar solvent. However polar solvent favoured the polymerization. The activation energy ($\Delta E$) and $k_p^2/k_t$ values were 72.0 kJ $mol^{-1}$ and $1.87 \times 10^{-3}$ l $mol^{-1}s^{-1}$ respectively. A suitable mechanism consistent, with the observed kinetic data is proposed.

## INTRODUCTION

For the last twenty five years, ylides have been known to be versatile ligands for transition metal (1,2). The chemistry of sulfur ylide complexes have been reviewed by Weber (3).

A literature search reveals that although research publications have documented on the effect of various ylides like sulphur ylide (4), nitrogen ylide(5), arsonium ylide (6) on the polymerization of styrene, the effect of metal-ylide complexes has hardly been exploited , we therefore felt it worthwhile to study the poly

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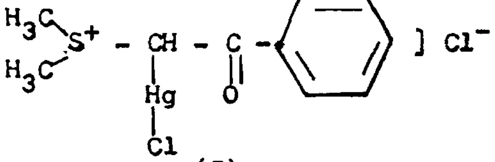
merization of styrene using the phenacyldimethyl sulfonium ylide-mercuric chloride (PDSY-$HgCl_2$) as an initiator. We report our investigations on polystyrene obtained by radical polymerization of styrene with this complex.

## MATERIALS

Styrene and solvents were purified according to established procedures (7,8). Bromine(E.Merck) and dimethyl sulfide (Merck 6230316) were used as received. Phenacyl dimethyl sulfonium ylide was prepared as described by Ratts et al.(9) and its mercuric chloride complex (I), was prepared by the method of Singhal et al.(10). It was insoluble in non-polar solvents such as benzene, carbon tetrachloride but soluble in polar solvents like dimethyl formamide, dimethylsulfoxide and dioxane IR$\nu$ (C = O) = 1620 - 1650 $cm^{-1}$. Analysis found : C,26.9 H, 2.7, Cl 16.0% calculated : C, 26.8, H 2.8 Cl, 16.0%.



(I)

## METHODS

Polymerization runs were carried out at 85 ± 0.1°C using dilatometric apparatus under an inert atmosphere of nitrogen for 120 minutes. The polymer, precipitated with acidified methanol was dried in vacuum to constant weight. The polymerization rate (Rp) was calculated from the slopes of linear percentage (%) conversion time plots.

The average degree of polymerization for various polystyrene samples, was determined with a Ubbelohde viscometer in benzene at 30 ± 0.1°C using the relation (11)

$$\bar{P}_n = 1770 [\eta]^{1.4}$$

## RESULTS

Phenacyldimethyl sulfonium ylide and a mercuric chloride solution in dioxane failed to initiate the polymerization of styrene whereas the complex initiated it. Therefore, the polymerization of styrene in dioxane at

85 ± 0.1°C was carried out during 90 minutes. The polymerization conditions and results are summarized in Table 1 to 3 and illustrated in Fig. 1-7. The polymerization was associated with 2-12 minutes induction period.

## DISCUSSION

### Effect of [PDSY - $HgCl_2$]

The rate of polymerization (Rp) increases consistently with increase in [PDSY - $HgCl_2$] from 3.7 to 51.8x$10^{-4}$ mol $l^{-1}$ for fixed monomer concentration (Table 1).

The initiator exponent value, calculated from the slope of the plot log Rp against log[PDSY + $HgCl_2$] is 0.3 (Fig.2), considerably lower than 0.50 expected for simple radical polymerization. The average degree of polymerization ($\bar{P}_n$) decreases with the increase in [PDSY-$HgCl_2$]. The intercept on the $1/\bar{P}_n$ axis in the plot of $1/\bar{P}_n$ vs $[I]^{0.5}$ (Fig.3) indicates that the system follows non-ideal kinetics.

The ratio of the squared propagation rate constant to termination rate constant, $kp^2/kt$ calculated from the slope of the plot of $1/\bar{P}_n$ versus $Rp/[M]^2$ is 1.87x$10^{-3}$ l $mol^{-1}s^{-1}$.

### Effect of [Styrene]

Table 2 illustrates the influence of the monomer on Rp upon varying monomer concentration from 1.15 to 2.88 mol $l^{-1}$ with constant [PDSY - $HgCl_2$]. It is noteworthy that Rp is a direct function of [Sty]. A plot of log Rp versus log[Sty] is linear with 1.11 order, which is higher than the value of unity expected for ideal radical polymerization (Fig.4). Various explanations[12-15] for non-ideality in vinyl polymerization have been proposed but with limited success. It is now accepted that primary radical termination and degradative chain transfer are the most important causes of non-ideality.

### Causes of non-ideality

In order to detect degradative chain transfer, Deb equation [16] in the following form was used :

$$\ln Rp^2/[I][M]^2 = \ln f_{kd}\, kp^2/kt - kp^2/krt\ I/$$

$$ki\ kir\ I\ C_I[I]/[M]$$

where $C_I$ is the initiator transfer constant. The plot of the left hand side of this equation versus [I]/[M]

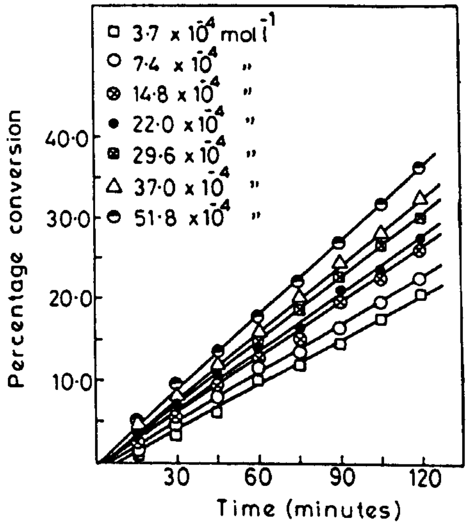


Fig.1 [Sty] = 1.73 mol $l^{-1}$, Time = 2 hours, Temperature = 85 ± 0.1°C.

## TABLE 1

Effect of PDSY-$HgCl_2$ complex on the rate of polymerization of styrene initiated by phenacyldimethyl sulfonium ylide complex of mercuric chloride

| [PDSY-$HgCl_2$] mol $l^{-1}$x$10^4$ | Percentage conversion (%) | Rp x $10^5$ mol $l^{-1}s^{-1}$ | $\bar{P}_n$ |
|---|---|---|---|
| 3.7 | 18.8 | 4.75 | 270 |
| 7.4 | 23.5 | 5.94 | 202 |
| 14.8 | 27.5 | 6.66 | 181 |
| 22.0 | 28.5 | 7.14 | 121 |
| 29.6 | 30.1 | 7.61 | 103 |
| 37.0 | 32.4 | 8.65 | 97 |
| 51.8 | 36.6 | 9.31 | 92 |

[Sty] = 1.73 mol $l^{-1}$, Time = 2 hours,
Temperature = 85 ± 0.1°C.

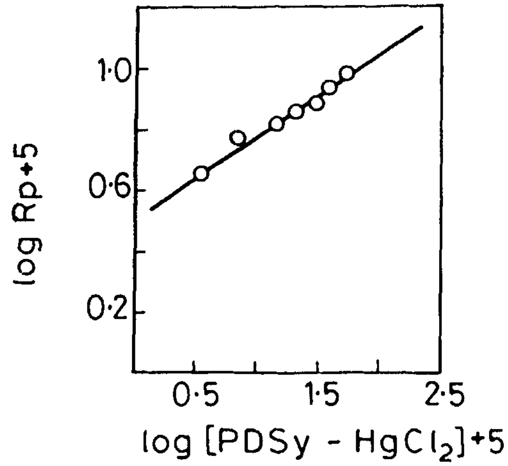


Fig.2 Relationship between log[PDSY-HgCl$_2$] versus log Rp for the polymerization of styrene

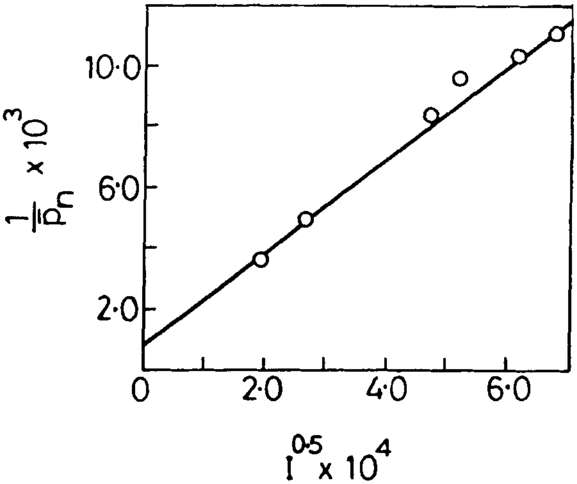


Fig.3 Relationship between 1/$\bar{P}_n$ versus square root concentration of initiator for the polymerization of styrene

TABLE 2

Effect of [Styrene] on the rate of polymerization of styrene initiated by phenacyl dimethyl solfonium ylide complex of mercuric chloride.

| [Styrene] mol $l^{-1}$ | Percentage conversion (%) | Rp x $10^5$ mol $l^{-1}s^{-1}$ |
|---|---|---|
| 1.15 | 19.55 | 3.82 |
| 1.73 | 23.50 | 5.94 |
| 2.30 | 31.05 | 8.27 |
| 2.88 | 35.65 | 10.63 |

$[PDSY + HgCl_2] = 1.4 \times 10^{-4}$ mol $l^{-1}$, Time = 2 hours
Temperature = 85 ± 0.1°C.

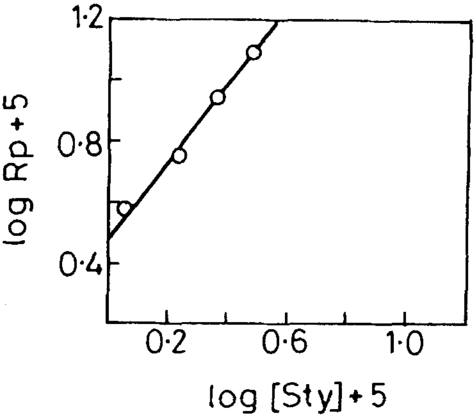


Fig.4 Relationship between log[Sty] versus log Rp for the polymerization of styrene.

has a negative slope but degradative chain transfer does not seem most effective in our system because according to the literature, it is apparent that such transfer is most effective at very low polymerization rates and the initiator exponent must be higher than 0.5 [16].

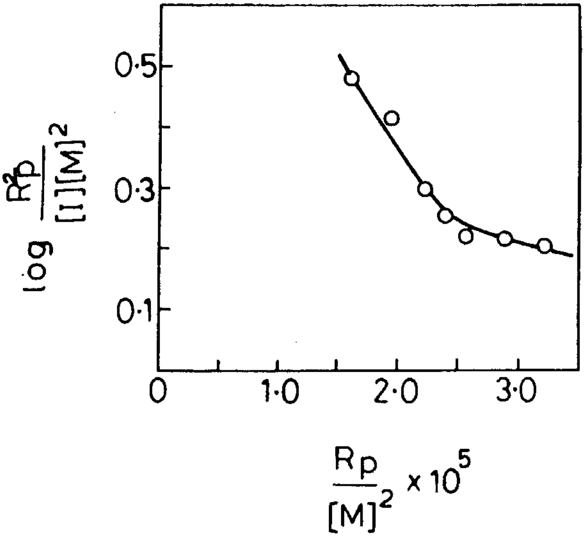


Fig.5 Relationship between log $Rp^2/[I][M]^2$ versus $Rp/[M]^2$

In order to detect primary radical termination, the equation developed by Deb and Meyerhoff [17] was used to analyze the possibility of termination in the following manner :

$$\log Rp^2/[I][M]^2 = kt\ kd\ Rp^2/kt - 0.8684\ k_{prt}/ki\ kp\ Rp/[M]^2$$

The plot of log $Rp^2/[I][M]^2$ versus $Rp/[M]^2$ (Fig.5) has a negative slope, indicating primary radical in the present system. Such termination was further confirmed by the low initiator and high monomer exponent, which match with literature value [15].

## Effect of additives

The effects of a polar solvent viz. dimethyl sulfoxide (DMSO) and a non-polar solvent, viz. benzene, have also been studied. The results are given in Table 3. Apparently DMSO, being a polar solvent, facilitates the dissociation of metal-ylide complex thereby increasing the polymerization rate, whereas the non-polar benzene supresses the initiator dissociation. The effect of hydroquinone confirms the radical mode of polymerization.

TABLE 3

Effect of[additives] on the rate of polymerization of styrene initiated by phenacyl dimethyl sulfonium ylide complex of mercuric chloride

| Additive | [Additive] mol $l^{-1}$ | Percentage conversion (%) | Rp x $10^5$ mol $l^{-1}s^{-1}$ |
|---|---|---|---|
| DMSO | 0 | 23.5 | 5.94 |
| | 2.35 | 26.3 | 7.24 |
| | 4.69 | 29.5 | 8.75 |
| Benzene | 1.88 | 20.48 | 5.27 |
| | 3.75 | 16.67 | 3.98 |
| Hydroquinone | $3.0\times10^{-2}$ | 19.24 | 4.26 |
| | $9.0\times10^{-2}$ | 14.85 | 3.57 |

[PDSY - $HgCl_2$] = $7.4\times10^{-4}$ mol $l^{-1}$, [Styrene] = 1.73 mol $l^{-1}$, Time = 2 hours, Temperature = 85 ± 0.1°C.

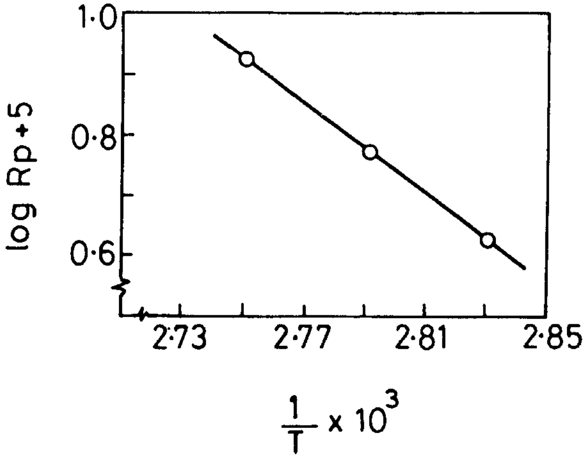


Fig.6 Relationship between 1/T versus log Rp for the polymerization of styrene

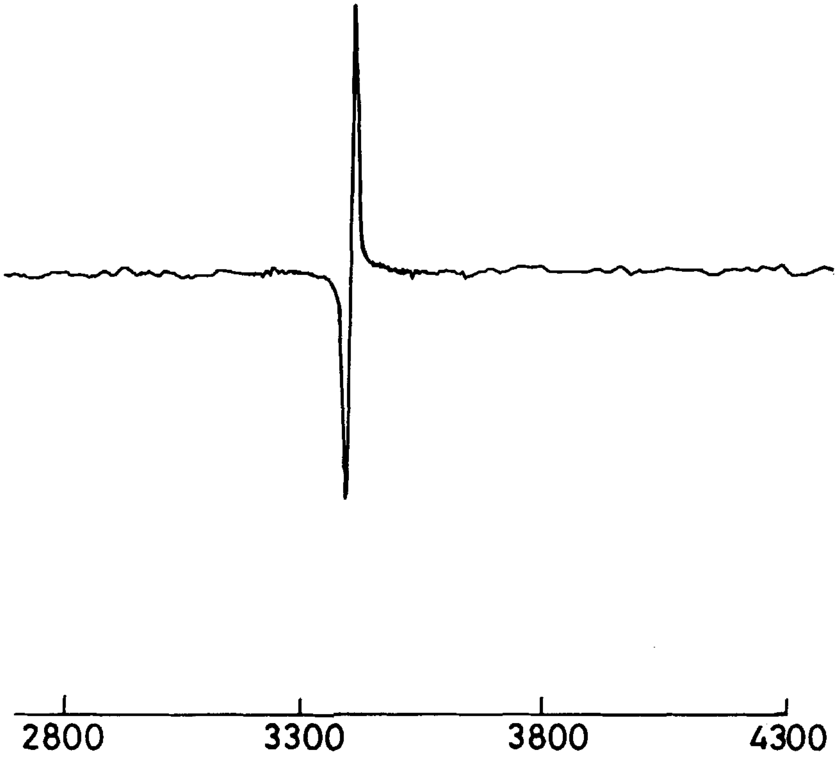


Fig.7 esr spectrum of reaction mixture

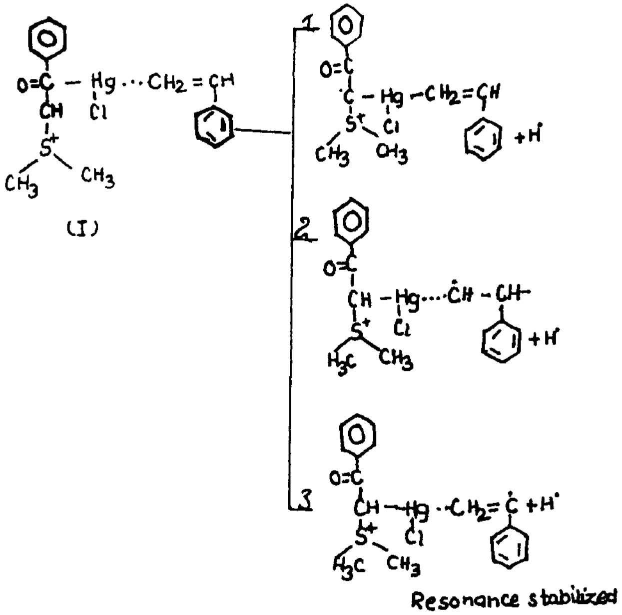
## Effect of temperature

The rate of polymerization increases with temperature and the overall Arrhenius activation energy ($\Delta E$) for styrene, calculated from the corresponding slope of Arrhenium plot of log Rp versus 1/T (Fig.6) is 72.0 kJ mol$^{-1}$.

## Mechanism

All results illustrated in figure 1-7 summarized in Table 1-3 confirm that PDSY - $HgCl_2$ complex initiates radical polymerization of styrene. The mechanism of the system was confirmed by esr spectrum of polymer content The gyromagnetic ratio (g), calculated from fig.7 as 1.979 is close to the value given for H atom ($g = 2.0036 \pm 0.03$).

There are 3 possible ways by which the metal-ylide complex can dissociate to yield free radical. Route 1 is not possible because the formation of $CH_3$ is rejected by esr spectra of polymer content.



It will therefore give an additional band in esr spectra. Therefore, Route 3 seems to be most probable because other radical is highly resonance stabilized (b).

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