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Kinetics and Mechanism of Polymerization of Methyl Methacrylate using Selenonium Ylide as a Novel Initiator

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Polymerization of Methyl methacrylate (MMA) was carried out in dioxan at 60 ± 1°C for 90 min in dilatometer under nitrogenous atmosphere using diphenylselenonium 2,3,4,5-tetraphenylcyclopentadienylide (selenonium ylide) as a novel initiator. The exponent values for initiator and monomer were computed as 0.32 and 1.59, respectively. The overall activation energy and k_p^2/k_t were found 42.1 k J mol^{-1} and 0.819 l mol^{-1}s^{-1}, respectively. The free radical mode of polymerization was confirmed by ESR spectroscopy. The FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopic techniques were used for its characterization.

Keywords: Methyl methacrylate, selenonium ylide, kinetics, mechanism.

1 Introduction

In the synthesis of polymers, initiators play an important role; they not only initiate the polymerization, but also affect the properties of forming polymers. Among several initiators, ylides, in particular, comprise a significant fraction of the organic chemical literature but their applications in the domain of polymer science are of recent history of 25 years.

A literature search reveals, frequent occurrence of reports regarding the used ylides containing N (1,2), P (3,4), S (5,6), As (7,8), Sb (9,10) and Bi (11,12) heteroatoms as initiator. However, literature is still scarce of even single publication regarding the use of selenonium ylide in the realm of polymer science. It may be attributed to difficulties associated with the synthesis and stability of selenonium ylide.

Therefore, we have studied the kinetics and mechanism of polymerization of MMA using diphenylselenonium 2, 3, 4, 5-tetraphenylcyclopentadienylide as a novel initiator.

2 Experimental

Methyl methacrylate (Merck) was purified by the standard method (13). Tetraphenylcyclopentadiene (Acros), p-toluenesulphonylhydrazide (Aldrich), diphenyl selenide (Lancaster) and solvents (Merck) were used as received. Selenonium ylide was prepared by the Lloyd (14) method.

2.1 Polymerization Procedure

The polymerization reactions were carried out in a dilatometer under the inert atmosphere of nitrogen for 90 min at 60 ± 1°C in dioxan using selenonium ylide as an initiator. The polymer(s) formed were precipitated with acidified methanol and dried to constant weight. The rate of polymerization (R_p) was calculated from the slopes of the linear plot of percent conversion vs. time (Figs. 1, 2). The intrinsic viscosity (η_{int}) of polymer(s) was determined in benzene at 30 ± 1°C using an Ubbelohde viscometer. The following Mark-Houwink equation was used to calculate viscosity average molecular weight [$\bar{M}_v$]:

$$[\eta_{int}] = K\,[\bar{M}_v]^{\alpha}$$

Where, K and α are constants.

3 Results and Discussion

The kinetics of polymerization of MMA was studied by varying the concentrations of MMA and initiator. The polymerization reactions were associated with an induction period of 2–8 min. The results of kinetic investigations of the polymerization of MMA are shown in (Table 1) and (Figs. 1–7).

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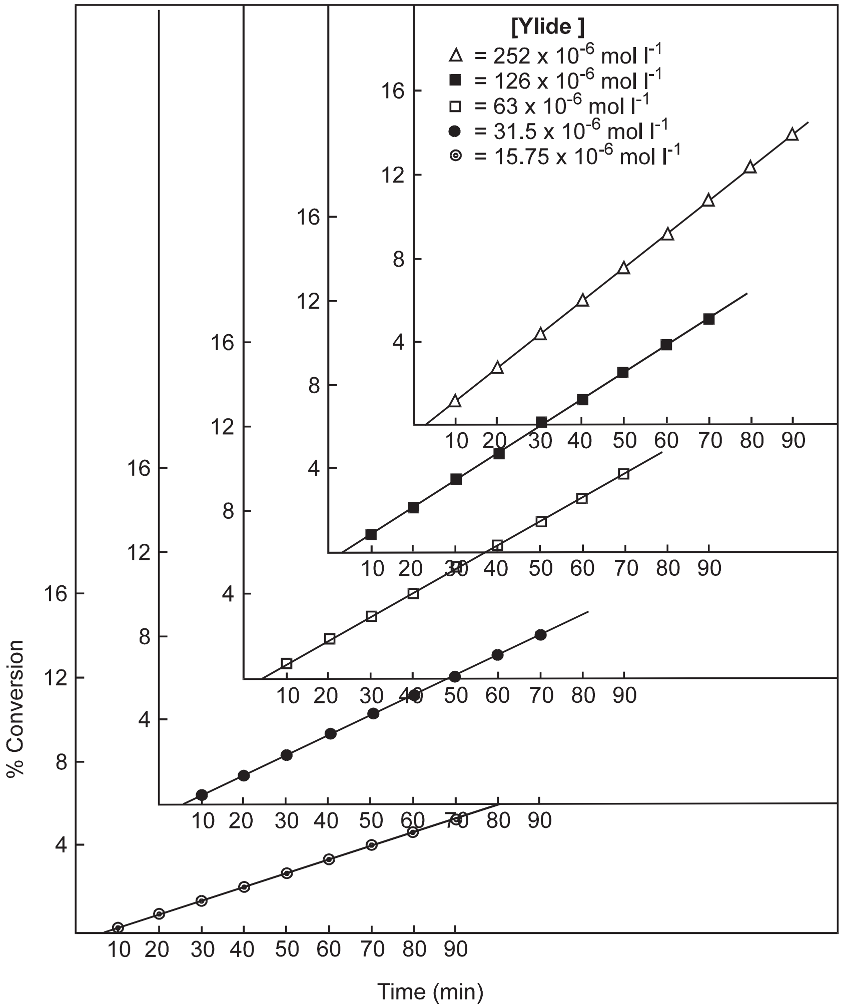


Fig. 1. Percentage conversion vs. time plots of radical polymerization of MMA using selenonium ylide. [MMA] = 1.43 mol l^{-1}, Time = 90 min, Temperature = 60 ± 1°C.

3.1 Effect of Initiator

The concentration of ylide was varied from 15.75×10^{-6} to 252×10^{-6} mol l^{-1}. The R_p increases with the increase in the concentration of initiator. The exponent value for this is calculated as 0.32 from the slope of linear plot of log R_p vs. log [ylide] (Fig. 3), which is less than the value expected (0.5) for ideal kinetics. The value of k_p^2/k_t determined from the slope of the plot of $1/[\bar{M}_v]$ Vs $R_p/[M]^2$ (Fig. 4) is 0.819 l $mol^{-1}s^{-1}$.

Table 1. Effect of concentrations of initiator and monomer on the rate of polymerization

S. No.	*[Ylide] × 10^6 mol l^{-1}*	*[MMA] mol l^{-1}*	*Percent conversion*	*$R_p \times 10^6$ mol l^{-1} s^{-1}*	*$[\bar{M}_v]$*
1	15.75	1.43	5.3	16.88	59840
2	31.5	1.43	7.85	22.51	50050
3	63	1.43	9.5	29.12	40790
4	126	1.43	10.8	33.29	36390
5	252	1.43	13.4	41.04	32140
6	15.75	0.572	1.6	2.118	—
7	15.75	2.28	6.4	33.86	—
8	15.75	3.12	8.8	57.77	—
9	15.75	4.00	10.95	85.18	—

Temperature = 60 ± 1°C, Time = 90 min.

3.2 Effect of Monomer

The effect of monomer concentration on the rate of polymerization was studied by varying its concentration from 0.572 to 4.0 mol l^{-1}. The exponent value for this is 1.59 calculated from the linear plot of log R_p vs. log [MMA] (Fig. 5), which is higher than the value expected (1.0) for ideal kinetics.

The deviation in the values of initiator and monomer exponent suggests that the present system follows non-ideal kinetics. The non-ideality can be explained on the basis of

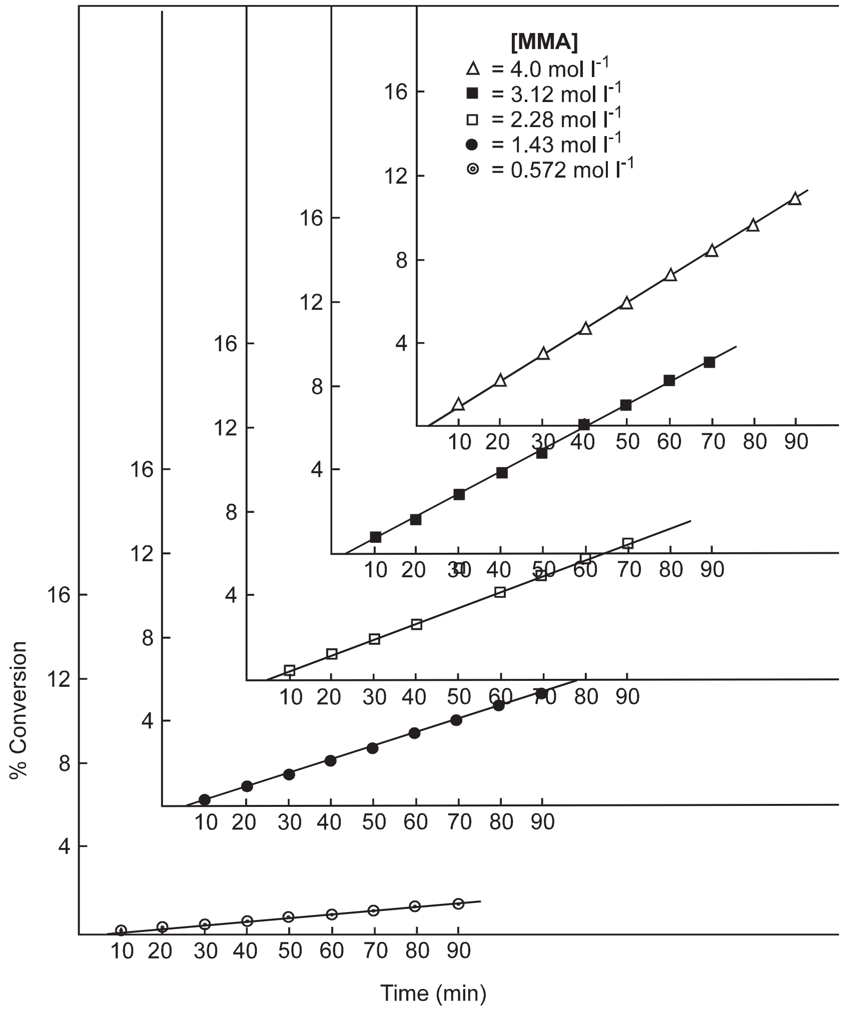


Fig. 2. Percentage conversion vs. time plots of radical polymerization of MMA using selenonium ylide. [Ylide] = 15.75×10^{-6} mol l^{-1}, Time = 90 min, Temperature = 60 ± 1°C.

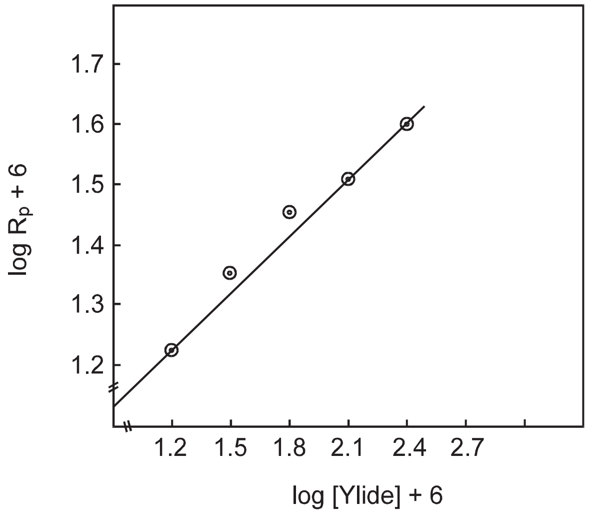


Fig. 3. Plot of log R_p vs. log [Ylide]. [MMA] = 1.43 mol l^{-1}, Time = 90 min, Temperature = 60 ± 1°C.

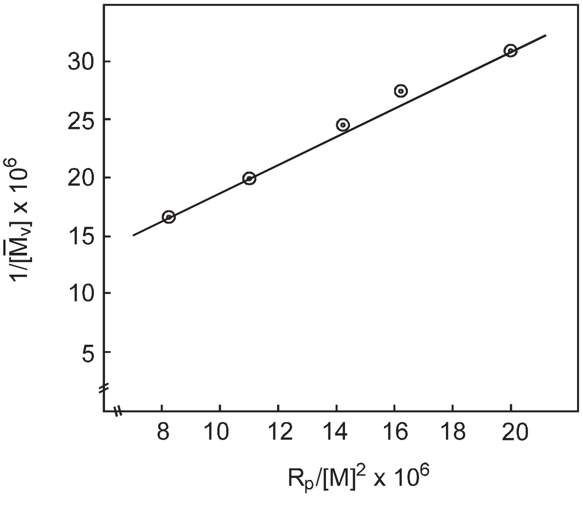


Fig. 4. Plot of $1/[\bar{M}_v]$ vs. $R_p/[M]^2$. [MMA] = 1.43 mol l^{-1}, Time = 90 min, Temperature = 60 ± 1°C.

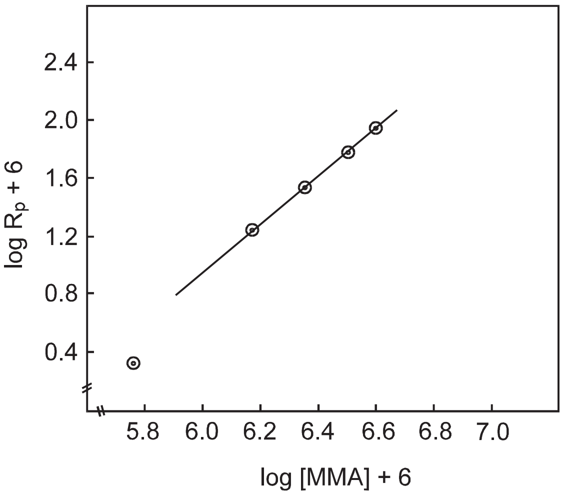


Fig. 5. Plot of log $R_p$vs. log [MMA]. [Ylide] = 15.75 × 10^{-6}mol l^{-1}, Time = 90 min, Temperature = 60 ± 1°C.

termination through primary radicals or via degradative chain transfer to initiator.

The effect of primary radical termination is analyzed by the expression given by Deb and Meyerhoff (15) in the following form:

$$\log\frac{R_p^2}{[I][M]^2}=\log\frac{2f_k\,k_d\,k_p^2}{k_t}-0.8684\frac{k_{prt}}{k_ik_p}\frac{R_p}{[M]^2} \qquad (1)$$

Where, $[I]$ and $[M]$ are the concentrations of initiator and monomer, respectively. A plot of the log $R_p^2/[I][M]^2$ vs. $R_p/[M]^2$gives a negative slope (Fig. 6) indicating significant primary radical termination for the present system.

The equation derived by Deb (16) was further simplified by Ghosh and Mitra (17) and used to examine the degradative chain transfer to initiator.

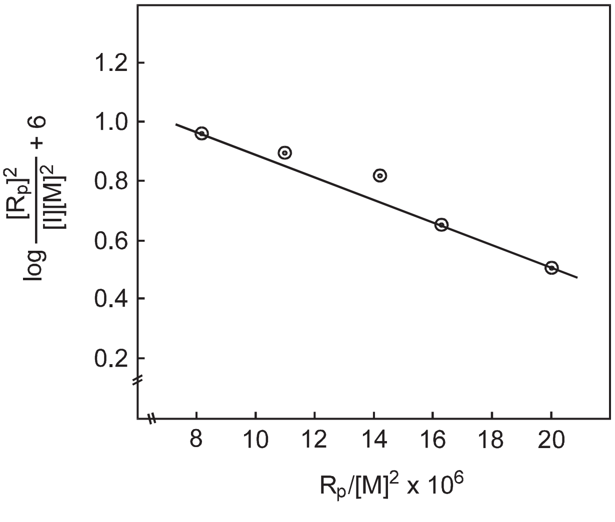


Fig. 6. Plot of log $R_p^2/[I][M]^2$vs. $R_p/[M]^2$. [MMA] = 1.43 mol l^{-1}, Time = 90 min, Temperature = 60 ± 1°C.

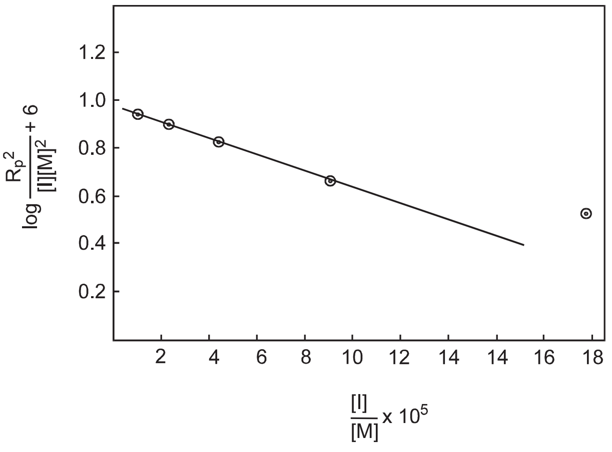


Fig. 7. Plot of log $R_p^2/$ $[I][M]^2$ vs. $[I]/[M]$. [MMA] = 1.43 mol l^{-1}, Time = 90 min, Temperature = 60 ± 1°C.

$$\log\frac{R_p^2}{[I][M]^2}=\log\frac{2f_k\,k_d\,k_p^2}{k_t}-0.434\frac{k_p^2k_{rtI}}{k_ik_{iI}k_p}C_I\frac{[I]}{[M]} \qquad (2)$$

Where, C_I is the initiator transfer constant.

The plot of the log $R_p^2/[I][M]^2$ vs. $[I]/[M]$ (Fig. 7) was linear with negative slope showing degradative chain transfer.

3.3 Effect of Temperature

The polymerization reactions were also carried out at different temperatures (60°–90°C) for 90 min at a fixed concentration of monomer [1.43 mol l^{-1}] and initiator [15.75 × 10^{-6}mol l^{-1}]. The rate of polymerization increases with an

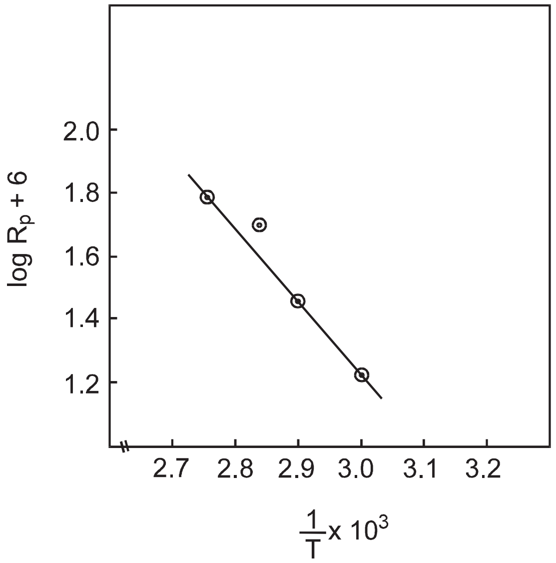


Fig. 8. Plot of log $R_p$vs. 1/T. [Ylide] = 15.75 × 10^{-6} mol l^{-1}, [MMA] = 1.43 mol l^{-1}, Time = 90 min.

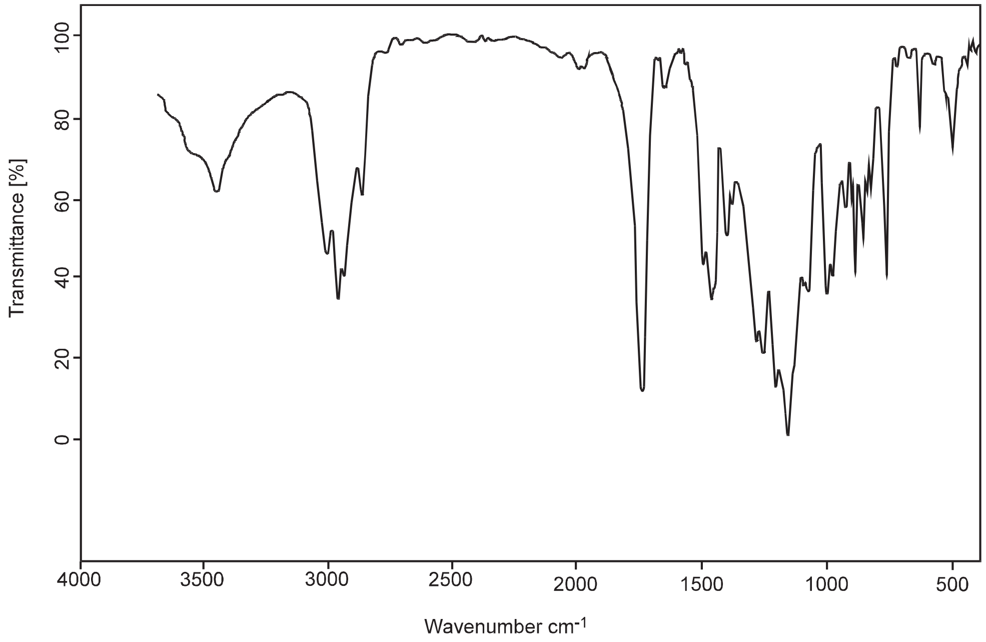


Fig. 9. FT-IR spectrum of PMMA of sample no. 1.

increase in temperature. The energy of activation is calculated as 42.1 k J mol^{-1} by the linear plot of log R_p vs. $1/T$ (Fig. 8).

3.4 Characterization of Polymer

Different spectroscopic techniques are used to characterize and determine the stereochemistry of the formed polymers. The FT-IR spectrum (Fig. 9) of poly methyl methacrylate (PMMA) shows a band at 1729.51 cm^{-1} for carbonyl group and a band at 1063 cm^{-1} indicating the syndiotactic nature of the polymer (18). ^{1}H-NMR (Fig. 10) shows peaks at 0.83 ppm (for α methyl protons), 1.24–2.0 ppm for protons in the backbone of polymer, 3.6 ppm (for methoxy protons) and confirms the syndiotactic nature of polymer (19, 20).

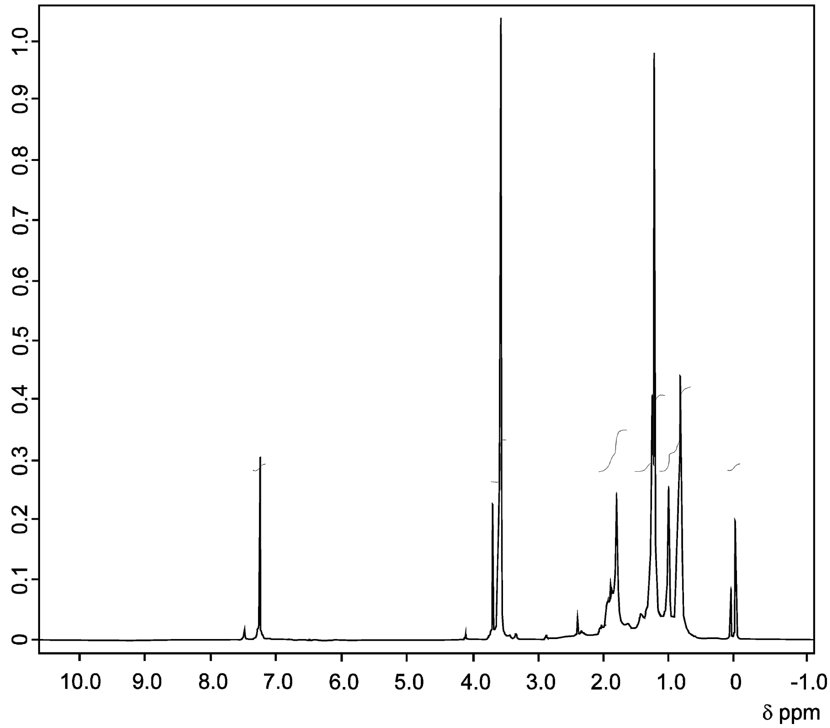


Fig. 10. ^{1}H-NMR spectrum of PMMA of sample no. 1.

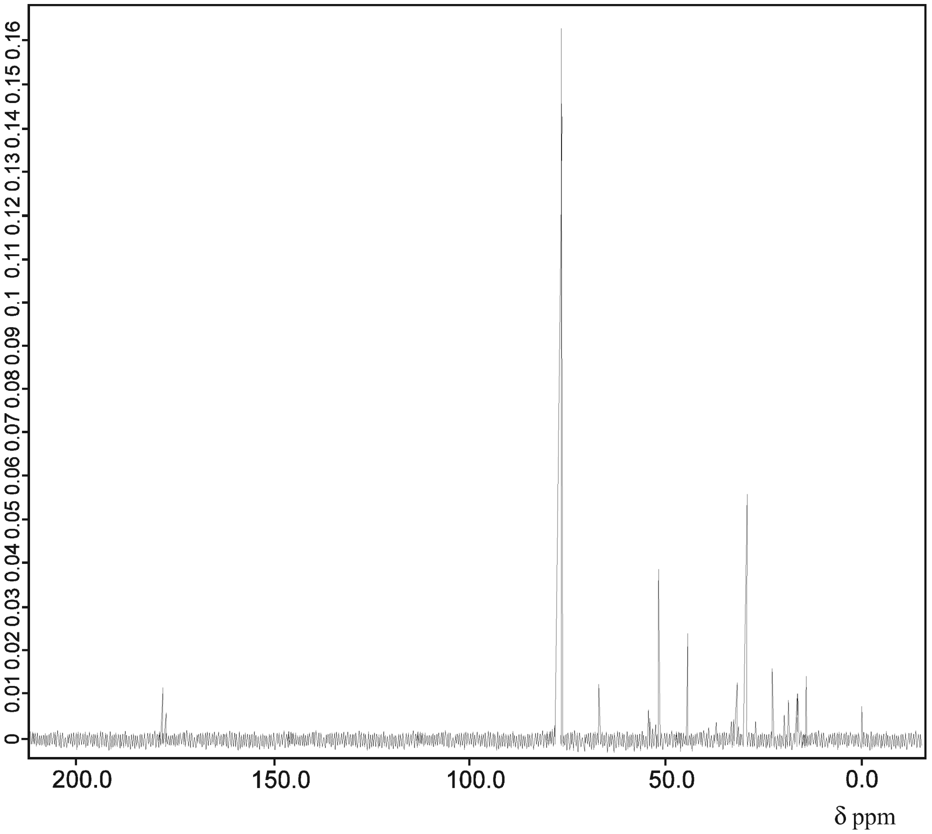


Fig. 11. ^{13}C-NMR spectrum of PMMA of sample no. 1.

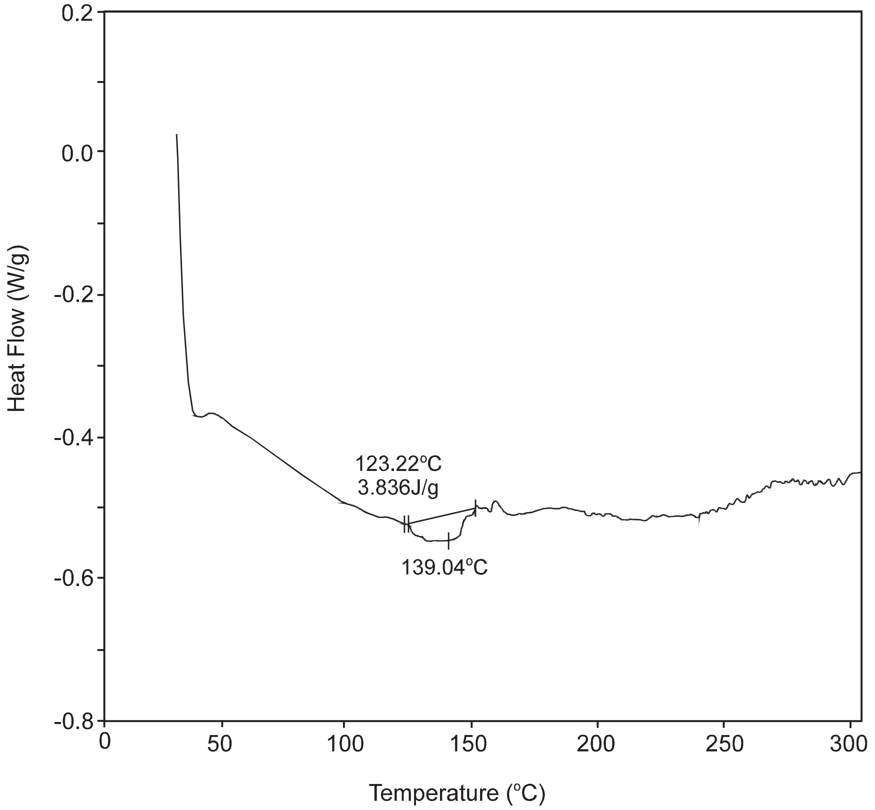


Fig. 12. DSC of PMMA of sample no. 1.

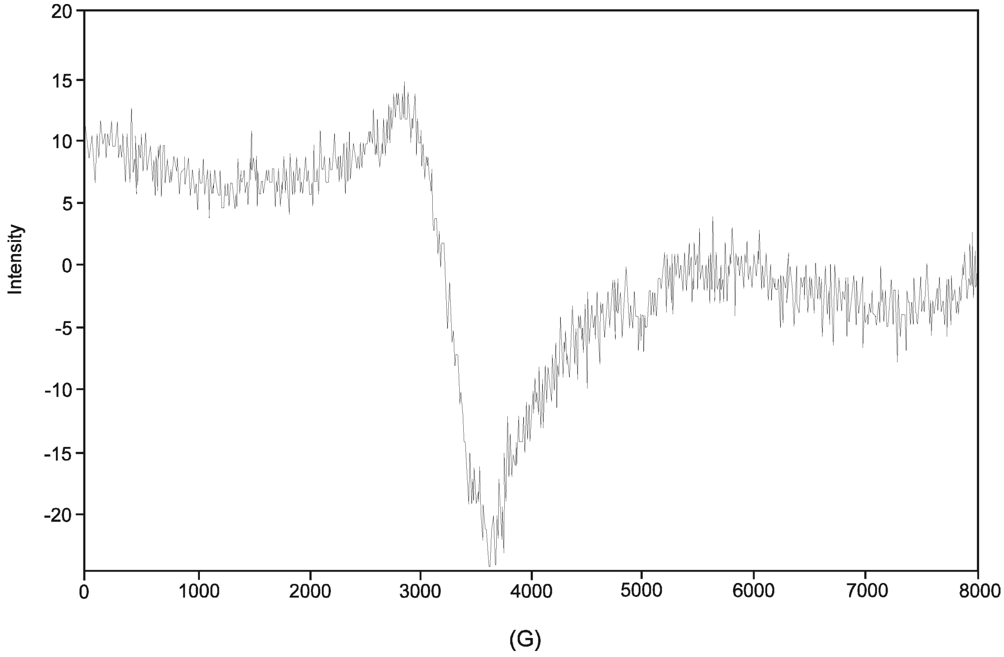
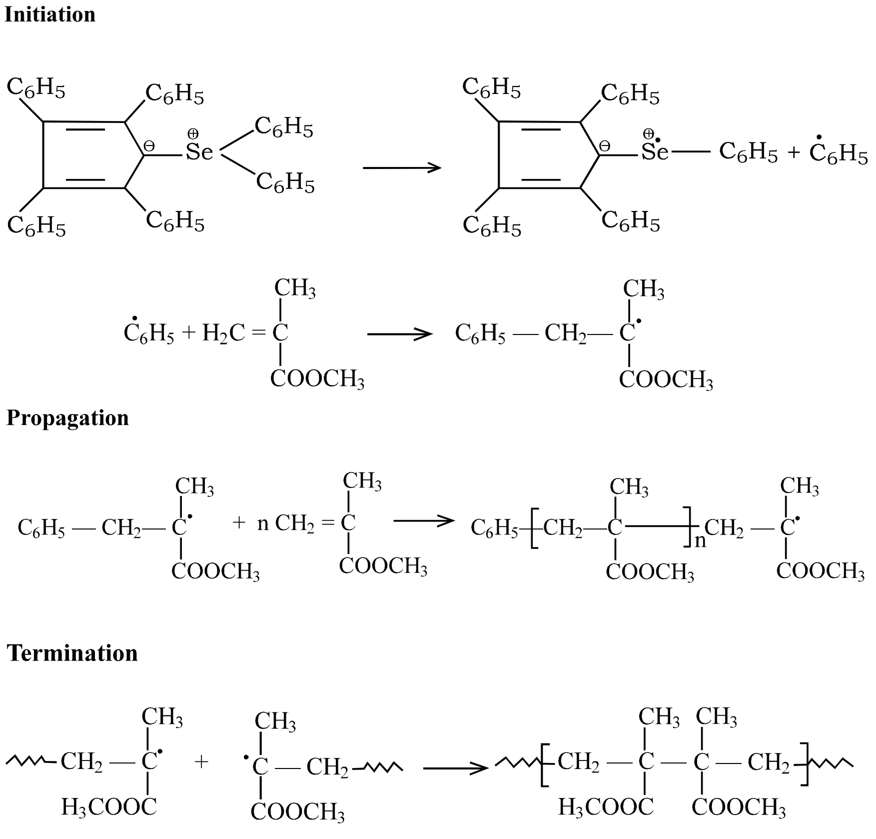


Fig. 13. ESR spectrum of PMMA of sample no. 1.

^{13}C-NMR (Fig. 11) shows peaks at 14.2 ppm for (for carbon of α methyl protons), at 22.78 ppm for carbon in the backbone (—CH_2), at 44.9 ppm for quaternary carbon and at 51.9 ppm for carbon of (—OCH_3). The literature search reveals that the peak at 44.9 ppm for quaternary carbon indicates the syndiotactic nature of polymer, whereas the peaks at 45.2 ppm and 45.8 ppm indicate the atactic and isotactic nature of the polymer respectively (21).



Sch. 1. The mechanism of polymerization reaction.

3.5 Thermal Analysis

3.5.1. *Differential scanning calorimetry (DSC)*

The glass transition temperature (T_g) of PMMA determined using DSC is 123.22°C (Fig. 12). This value is near about to the value of T_g of syndiotactic PMMA (130°C) (3). The T_g was determined at heating rate of 10°C/min under nitrogen and the weight of the polymer sample was 3.55 mg.

3.6 Mechanism

The free radical mode of polymerization of MMA is confirmed by the effect of hydroquinone (which inhibits the polymerization reaction) and also by ESR spectroscopy which gives the value of g as 2.129 (Fig. 13). As reported in the literature (22) the ylide dissociates in the following manner, yielding a phenyl free radical which is responsible for the initiation of polymerization reaction. The mechanism is given in Scheme 1.

4 Conclusions

The polymerization of MMA, initiated by selenonium ylide in dioxan at 60 ± 1°C for 90 min followed non ideal kinetics, due to primary radical termination, as well as degradative chain transfer reaction. Spectroscopic results confirmed the syndiotactic nature of polymer.

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