

Synthesis of Tellurium Containing Syndiotactic Polymethyl Methacrylate Using Diphenyl Ditelluride as a Novel Initiator

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ABSTRACT: The synthesis of syndiotactic polymethyl methacrylate containing tellurium by using diphenyl ditelluride in the dioxan at $(60 \pm 0.1)^\circ\text{C}$ for 2 h has been carried out. The presence of tellurium in the polymer has been confirmed qualitatively as well as by induced coupled plasma mass spectroscopy (ICP-MS). The electron spin resonance spectrum shows the presence of TèPh , and value of gyromagnetic constant g has been calculated as 2.2203. The

T_g of the polymer, measured by DSC, is 105°C . The syndiotactic nature has been confirmed by FTIR and NMR spectroscopy and DSC. The system follows ideal kinetics with activation energy 66 kJ mol^{-1} . © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1017–1022, 2006

Key words: diphenyl ditelluride; free radical; kinetics and mechanism; PMMA; syndiotactic

INTRODUCTION

Applications of tellurium compounds in the field of organic chemistry has been well documented,^{1–6} e.g., Kambe et al.³ reported carbottelluration of alkynes in the presence of azobisisobutyronitrile (AIBN) and concluded that diorganyl tellurides add to $\text{C}\equiv\text{C}$ regioselectively to form alkenyl tellurides. A search of literature shows that sufficient reports are available on the use of DPDT in biological studies.^{7–9} However, their applications in the field of polymer science are of recent origin with limited publications. Takagi et al.¹⁰ have carried out radical polymerization of styrene using combination of AIBN or BPO as radical initiator and diphenyl ditelluride (DPDT) as a reagent to control molecular weight. They concluded that DPDT did not initiate polymerization at 90°C for 36 h, rather it suppressed bimolecular chain reaction due to its excellent radical capturing ability. Further, the polymerization at high temperature (125°C) in the presence of DPDT and in the absence of radical initiator produces polymer in high yield (87%). Yoshida et al.¹¹ also carried out organotellurium-mediated living radical homopolymerization of styrene, butyl acrylate, methyl methacrylate (MMA) by using combination of AIBN and ditellurides. The polymer possessed an organotel-

lanyl end group, which would be useful for polymer end manipulations and for block copolymer synthesis. Ogawa et al.¹² described the radical addition of organic ditellurides to acetylenes. They concluded that the reaction proceed by a radical chain mechanism that includes the addition to acetylene of phenytelluro radical (PhTè).

Recently few initiators like $p\text{-TsCl/CuBr/BPY}$,¹³ iron(II) pridinumbisimine complexes,¹⁴ Ni(II) acetylide,¹⁵ tetra-functional peroxide initiator,¹⁶ and Cu(II) benzamidinate complexes¹⁷ are used for polymerization of MMA.

The present article highlights that DPDT undergoes homolysis to produce PhTè , which is capable of adding to vinyl group and results in the polymerization of methyl methacrylate (MMA) at 60°C for 2 h.

EXPERIMENTAL

Materials

MMA (Merck) was washed with 4% NaOH and then distilled under pressure. The solvents used were purified as per standard procedures.¹⁸ DPDT was synthesized¹⁹ in our laboratory.

Polymerization procedure

The runs were performed in dilatometer for 2 h at $(60 \pm 0.1)^\circ\text{C}$ under nitrogen atmosphere. The polymer(s), precipitated with acidified methanol, were dried to constant weight followed by reprecipitation 3 times. The rate of polymerization (R_p) was calculated from

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TABLE I
Effect of [DPDT] and [MMA] on the Rate of
Polymerization

S.No.	[DPDT] $\times 10^6$	[MMA] (mol L ⁻¹)	% Conversion	$R_p \times 10^6$ (mol L ⁻¹)	P_n
1.	1.7	2.52	2.0	1.51	1187
2.	2.3	2.52	4.5	1.737	1072
3.	2.9	2.52	6.0	1.995	1004
4.	3.5	2.52	7.5	2.238	936
5.	4.1	2.52	9.0	2.34	825
6.	2.9	1.08	2.0	0.47	736
7.	2.9	1.80	5.0	1.30	780
8.	2.9	3.24	7.8	4.00	1233
9.	2.9	3.96	8.5	5.50	1351

the slopes of the linear zone of percent conversion versus the time plots. The intrinsic viscosity of polymer(s) was determined in benzene at $(30 \pm 0.1)^\circ\text{C}$ using an Ubbelohde viscometer. The average degree of polymerization (P_n) was calculated²⁰ from following equation:

$$\log \bar{P}_n = 3.342 + 1.13 \log(\eta_{\text{int}}) \quad (1)$$

Polymer characterization

¹H NMR spectrum was recorded with a Varian 100HA Jeol LA 400 spectrophotometer using CDCl₃ as a solvent and tetramethylsilane as an internal reference. The fourier transform infrared (FTIR) spectrum was recorded with Perkin-Elmer 599B, with KBr pellets. Electron spin resonance (ESR) was recorded on X-band EPR 109E-line century series spectrometer at room temperature. The ICP-MS was carried out by Perkin-Elmer optima 3000 ICP spectrometer. The DSC runs were carried out using VA OB Dupont 2100 analyzer, with a sample weight of 2.400 mg at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

The DPDT is insoluble in non-polar solvent like benzene but soluble in polar solvent like 1,4-dioxan, DMSO, and DMF. We have selected dioxan as the solvent for studies because no polymerization has occurred in DMSO, and in case of DMF as solvent, polymer dried very slowly.

The kinetics of reaction was studied by varying the diphenyl ditelluride and MMA concentration at $(60 \pm 0.1)^\circ\text{C}$ for 2 h under the blanket of nitrogen gas. The results of kinetic investigations of the polymerization of MMA are shown in Table I and Figure 1–4. The reaction proceeds with an induction period of about 5 min.

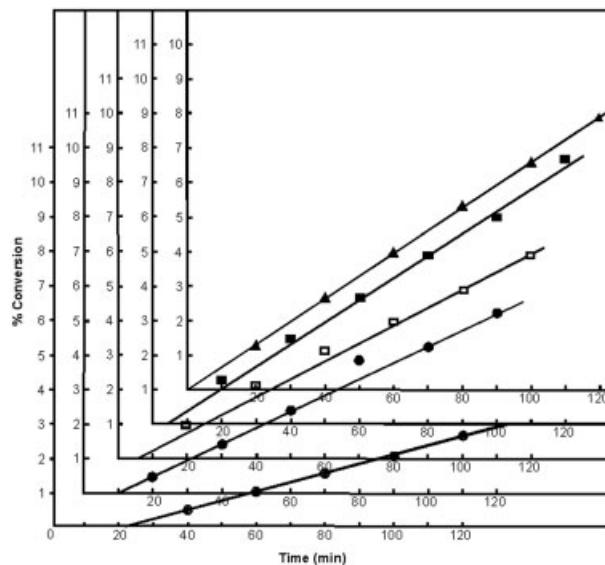


Figure 1 Percentage conversion versus time plots for homopolymerization of methyl methacrylate. [DPDT] = 2.9×10^6 mol L⁻¹; [MMA] = 1.08–3.96 mol L⁻¹; Temperature = $(60 \pm 0.1)^\circ\text{C}$; Solvent = Dioxan; Time = 2 h. ● 1.08 mol L⁻¹; ● 1.80 mol L⁻¹; □ 2.52 mol L⁻¹; ■ 3.24 mol L⁻¹; ▲ 3.96 mol L⁻¹.

Effect of the monomer concentration on R_p

The effect of [MMA] on the R_p was studied by varying the MMA concentration from 1.08 to 3.96 mol L⁻¹ (Table I). The R_p increases with [MMA], and the monomer exponent value, calculated from the slope of a linear plot of $\log R_p$ versus $\log [\text{MMA}]$, is unity (Fig. 2).

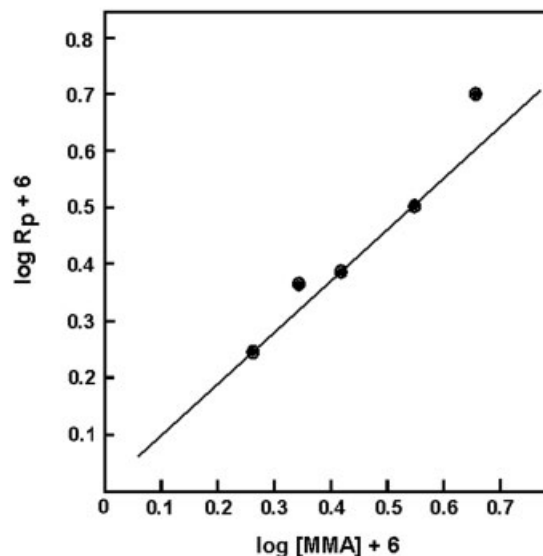


Figure 2 Relationship between $\log [\text{MMA}]$ and $\log R_p$ for the homopolymerization of MMA. [DPDT] = 2.9×10^6 mol L⁻¹; [MMA] = 1.08 to 3.96 mol L⁻¹; Temperature = $(60 \pm 0.1)^\circ\text{C}$; Solvent = Dioxan; Time = 2 h.

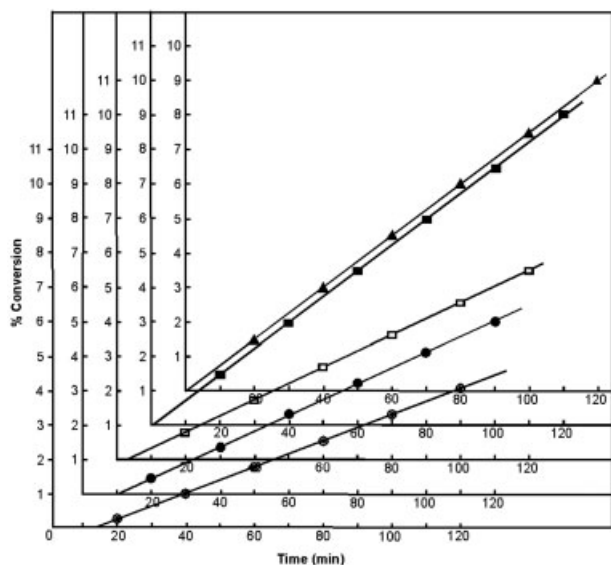


Figure 3 Percentage conversion versus time plots for the homopolymerization of methyl methacrylate. $[\text{DPDT}] = 1.7 \times 10^6$ – $4.1 \times 10^6 \text{ mol L}^{-1}$; $[\text{MMA}] = 2.52 \text{ mol L}^{-1}$; Temperature = $(60 \pm 0.1)^\circ\text{C}$; Solvent = Dioxan; Time = 2 h. \odot $1.7 \times 10^6 \text{ mol L}^{-1}$; \bullet $2.3 \times 10^6 \text{ mol L}^{-1}$; \square $2.9 \times 10^6 \text{ mol L}^{-1}$; \blacksquare $3.5 \times 10^6 \text{ mol L}^{-1}$; \blacktriangle $4.1 \times 10^6 \text{ mol L}^{-1}$.

Effect of initiator concentration on R_p

The polymerization reaction does not take place below $1.76 \times 10^{-4} \text{ mol L}^{-1}$ $[\text{DPDT}]$ and the polymerization rate decreases as the $[\text{DPDT}]$ is increased beyond the $4.1 \times 10^{-4} \text{ mol L}^{-1}$. Therefore, the effect of $[\text{DPDT}]$ on the rate of polymerization has been studied from 1.76×10^{-4} to 4.1×10^{-4} (Table I). The R_p increases with $[\text{DPDT}]$ (Table I) and the exponent value has been calculated as 0.50 from the slope of the linear plot of

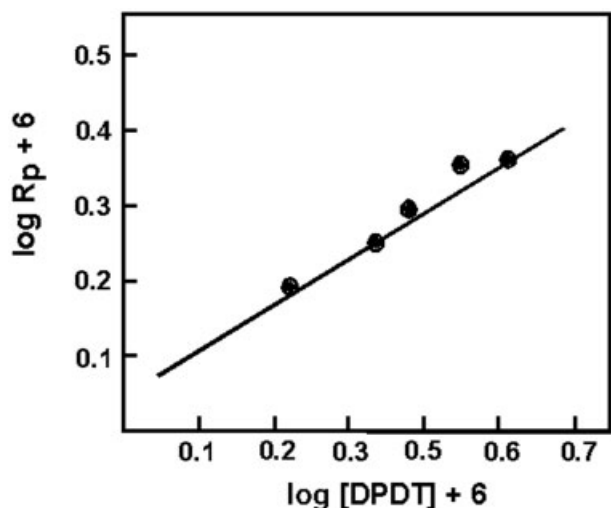


Figure 4 Relationship between $\log R_p$ and $\log [\text{DPDT}]$ for the homopolymerization of MMA. $[\text{DPDT}] = 2.9 \times 10^6 \text{ mol L}^{-1}$; $[\text{MMA}] = 2.52 \text{ mol L}^{-1}$; Temperature = $(60 \pm 0.1)^\circ\text{C}$; Solvent = Dioxan; Time = 2 h.

$\log R_p$ versus $\log [\text{DPDT}]$ (Fig. 4). The polymerization reaction was inhibited by the presence of hydroquinone ($4.5 \times 10^{-5} \text{ mol L}^{-1}$). This confirmed the radical mode of polymerization. The average degree of polymerization (P_n) of PMMA decreases as $[\text{DPDT}]$ increases.

The initiator and monomer exponent shows that the system follows the ideal kinetics, i.e., $R_p \propto [\text{MMA}]^{1.0}[\text{DPDT}]^{0.5}$.

Effect of temperature

The rate of polymerization was measured at five different temperatures at a fixed monomer and initiator concentration. The rate of polymerization increases with the temperature and overall activation energy (ΔE), calculated from the corresponding slope of the Arrhenius plot of $\log R_p$ versus $1/T$, is 66 kJ mol^{-1} (Fig. 5).

Spectral analysis

Fourier transform infrared spectroscopy

The FTIR spectrum of the PMMA (Fig. 6) shows the following bands

1. IR (KBr) 1730 cm^{-1} (s, OCH_3)
2. The bands in the region of the 1100 – 1300 cm^{-1} indicate the syndiotactic nature of the polymer.²¹ In the region 1100 – 1300 cm^{-1} of IR intensities for C—O stretching bands of PMMA, we found that each band represents single conformational state of the ester group. The bands at 1273 and 1242 cm^{-1} are assigned to the trans and cis conforma-

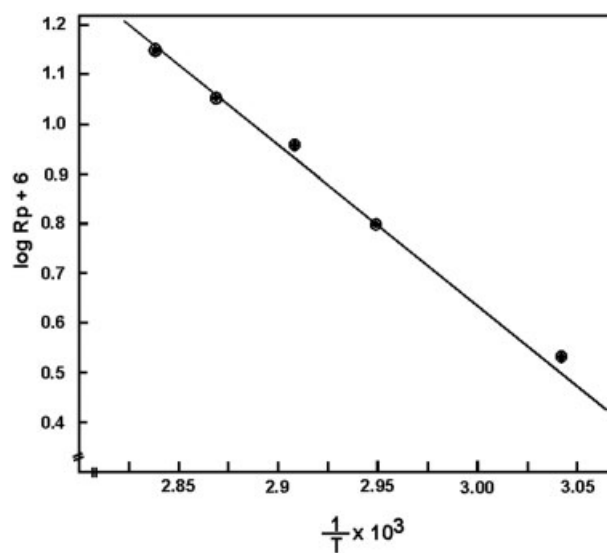


Figure 5 Plot of $\log R_p$ versus polymerization temperature (Arrhenius plot).

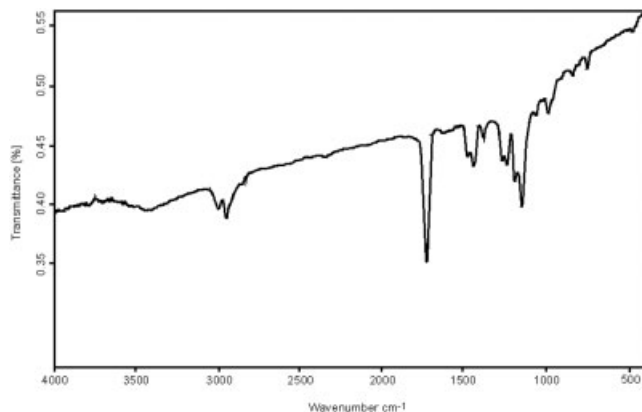


Figure 6 FTIR spectrum of the PMMA (sample 3).

tion of ester group, respectively (for isotactic PMMA these bands appeared at 1265 and 1239 cm^{-1} , respectively). The band at 1193 cm^{-1} are ascribed to the cis and trans conformation of methoxy group, respectively, and the band at 1149 cm^{-1} is due to the backbone of PMMA.

Nuclear magnetic resonance spectroscopy

The NMR spectrum of the PMMA²² shows following peaks (Figs. 7–10)

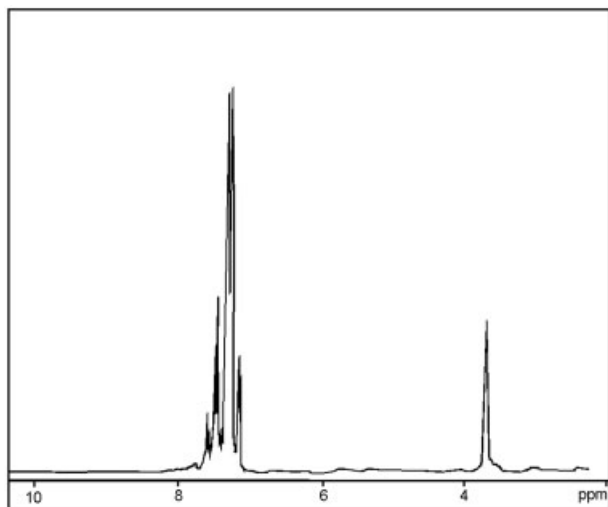
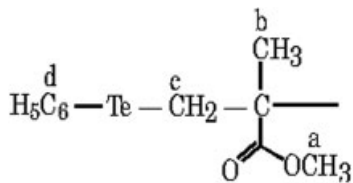


Figure 7 ^1H NMR spectrum of PMMA (sample 3; in solvent CDCl_3).

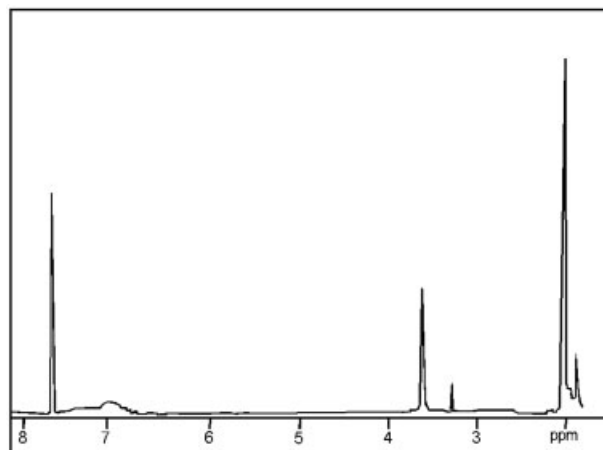


Figure 8 ^1H NMR spectrum of PMMA (sample 3; in deuterated acetone).

- ^1H NMR, δ b = 0.91 (s, α — CH_3 , syndiotactic), 1.05 (s, α — CH_3 , atactic), 1.22 (s, α — CH_3 , isotactic), c = 1.9 (s, CH_2); a = 3.8 (s, — OCH_3); d = 7.5 (m, Phenyl).

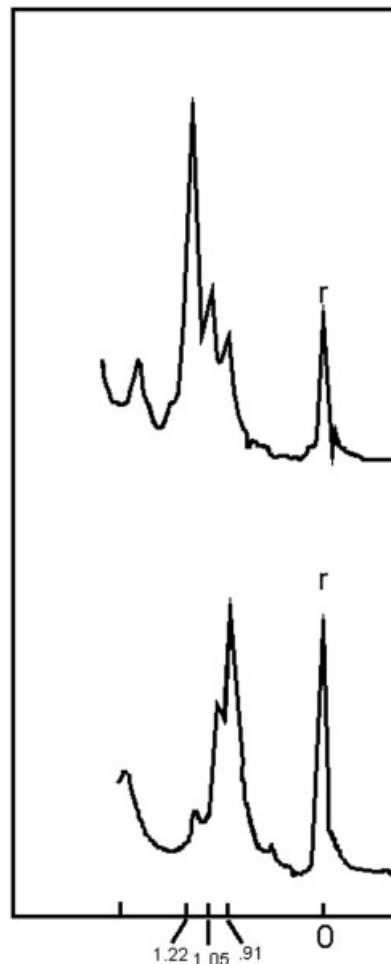


Figure 9 ^1H NMR spectrum of PMMA (sample 3; showing α — CH_3 protons for isotactic and syndiotactic PMMA).

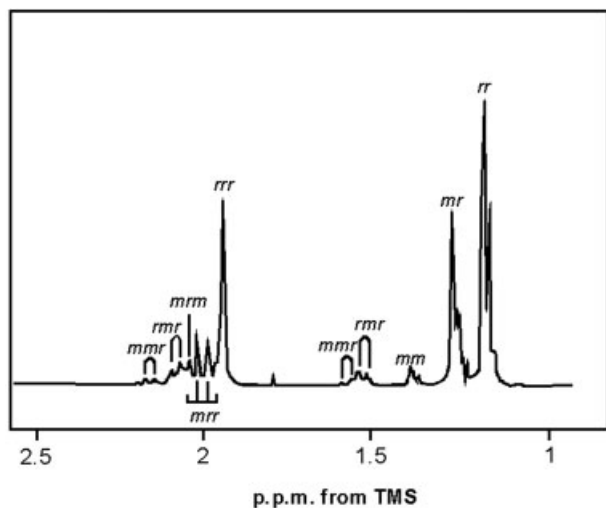


Figure 10 ^1H NMR spectrum of PMMA (sample 3; showing CH_2 protons).

2. The presence of a peak at 7.5 δ is due to Ph of TePh of polymer and also of solvent CDCl_3 . To ensure the peak due to TePh, we also run NMR in deuterated acetone (Fig. 8), when the presence of small peak at 7.5 δ confirms the presence of TePh.
3. The analysis of α -methyl region of the PMMA in ^1H NMR spectrum indicates that the polymerization leads to syndiotactic PMMA; however, very less amount of atactic and isotactic polymer is formed²³⁻²⁶ (Fig. 9).
 - a. The peak at 1.22 δ due to the α -methyl groups of MMA units, which are flanked on both sides by units of the same configuration (isotactic), i.e. ddd or lll.
 - b. The most prominent peak at 0.91 δ due to the α -methyl groups of central MMA units in syndiotactic configuration, i.e. idi, dld.
 - c. The peak at 1.05 δ due to the α -methyl groups of central MMA units in atactic configuration, i.e. ldd, dll, ddl, lld.
4. There are two possible types of dyads of chain of two monomer unit and they have different symmetry properties (Fig. 10).
 - a. The syndiotactic or racemic(r) dyad has a twofold axis of symmetry and consequently the two methylene protons are in equivalent environments. These protons, therefore, have the same chemical shift and appear as a singlet. The methylene spectrum of PMMA shows singlet at 1.9 δ , showing the predominantly syndiotactic nature.^{27,28}
 - b. The isotactic or meso dyad (m) has a plane of symmetry but no twofold axis, and so the protons are nonequivalents and have different chemical shifts (doublet at 1.6, 2.3 δ).

Electron spin resonance spectroscopy

To ensure radical nature of reaction, we have also run ESR spectrum (Fig. 11), which showed presence of a singlet, which is attributed to phenyl tellurium radical (Ph-Te^\cdot). The gyromagnetic constant g has been computed as 2.2203 (although this value is higher to the radicals, where $g = 0.8036$ ²⁹), which confirms free radical mode of polymerization.

Inductively coupled plasma-mass spectroscopy

The PMMA contains tellurium in it as suggested by the ICP-MS analysis. We have prepared solution of three different concentrations. The tellurium content of these solutions are 3731.000, 3765.000, 1953.000 ppm, respectively. The mean value is 3150.000 ppm. The standard deviation calculated and the percent relative standard deviation is 1036.000 and 32.910 ppm, respectively.

This is also confirmed qualitatively by using conc. HNO_3 and hydrazine hydrate ($\text{NH}_2\cdot\text{NH}_2\cdot\text{H}_2\text{O}$), when black precipitate is obtained.

Thermal analysis

Differential scanning calorimetry

The glass transition temperature T_g of PMMA has been determined from DSC curve (Fig. 12). The value of T_g is 105 $^\circ\text{C}$ (literature value³⁰ is 105 $^\circ\text{C}$ for syndio-

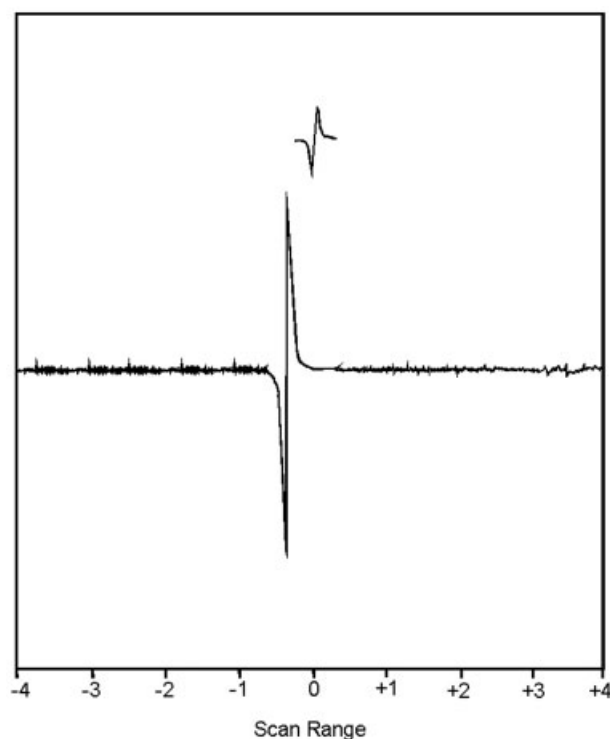


Figure 11 ESR spectrum of PMMA (sample 3).

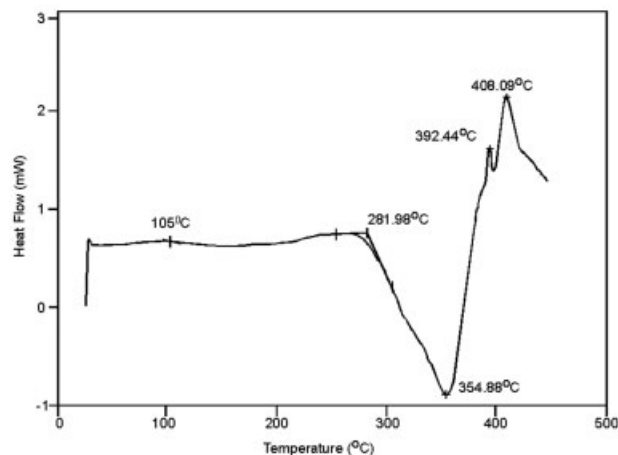


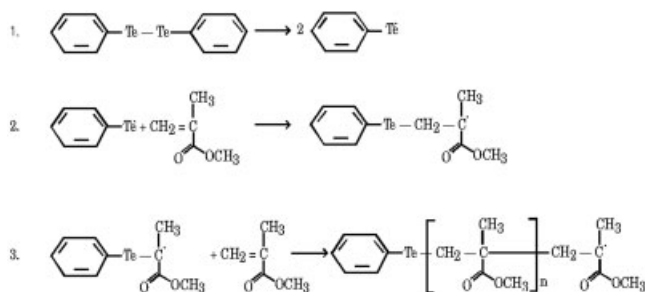
Figure 12 DSC curve of the PMMA (sample 3).

tactic PMMA) due to presence of tellurium. The T_g also depends upon the solvent used,³¹ molecular weight,³² and tacticity.³²

Mechanism:

The addition to C—C unsaturated compounds of heteroatom centered radicals arising from heteroatom—heteroatom bond homolysis is one of the basic reactions in organic chemistry.³³ It is well-known that organic dichalcogenides, e.g., organic disulphides, diselenides, and ditellurides, undergo photolysis or thermolysis to generate corresponding organic thio, seleno, and telluro radicals as labile species.^{12,34}

Based on the aforementioned discussion the following mechanism is suggested:



CONCLUSIONS

In summary, we have developed new initiating system for free radical polymerization of MMA. The obtained polymer possesses an organotellanyl end group. The system follows ideal kinetics with activation energy 66 kJ mol^{-1} . This method is convenient and is useful for the polymerization of MMA because of the simplicity of reaction procedure.

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