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Soluble conducting poly(dipropargyl ether) formation studied using ultraviolet-visible spectroscopy

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Cyclopolymerization of dipropargyl ether was carried out in nitrogen atmosphere with different initiators (KSCN/KCl/KBr/KI) in dimethyl formamide. The rate of polymerization was determined for different conditions and used for comparing the efficiency of the initiators. KSCN and KI were found to be effective initiators for cyclopolymerization. The resulting polymer exhibits good solubility in common organic solvents and exhibited solvatochromic behaviour. The results from ^{1}H NMR, FT-IR and UV-Visible spectra of poly(dipropargyl ether), PDPE supported the idea that the resulting polymer possesses polyene structure having cyclic recurring units in the polymer backbone. Conductivity, thermogravimetric analysis and electroactivity of the polymer were also studied. The results from UV-Visible, FTIR spectroscopy and conductivity measurements clearly revealed the doped nature of PDPE. *© 2001 Kluwer Academic Publishers*

1. Introduction

Studies on conjugated polymers are one of the frontier areas in macromolecular science. Polyacetylene is the simplest conducting polymer which has been studied extensively by many researchers because of its unique properties such as conductivity, paramagnetism and migration and transfer of energy. Shirakawa *et al.* [1] reported that highly conducting polyacetylene films could be formed by Zeigler-Natta catalyst through great efforts with the additional discovery of the phenomenon of doping [2]. But, the characterization of polyacetylene in its nascent state has not been fully investigated owing to its insolubility and infusibility.

To increase the processability, a study on the synthesis and characterization of substituted polyacetylene has been extensively investigated [3, 4] using a wide range of catalysts and conditions involving homogeneous and heterogeneous Ziegler–Natta catalysts, thermal polymerization, using free radical initiators, high energy radiation in solid and liquid state, cationic and anionic initiator etc [5, 6]. However, the synthesis of substituted polyacetylenes resulted in materials with very low effective conjugation lengths. Few terminal diacetylenes have been successfully polymerized to give conducting polyacetylene derivatives [7, 8]. The conditions and catalysts for the polymerization vary widely with monomer structure.

Cyclopolymerization is a type of chain growth polymerization that leads to the introduction of cyclic structure into the polymer chain via an alternating intramolecular-intermolecular chain propagation. Butler [9, 10] reported soluble, non cross-linked polymer formation from polymerization of series of symmetrical non conjugated diolefins, with a probable cyclopolymerization mechanism. The versatility of using different possible initiators adds advantage of producing these type of soluble polymers. Earlier, cyclopolymerization of substituted vinyl, divinyl and diallyl monomers were effectively performed by our research group by employing different methods of initiation [11–14].

Studies on cyclopolymerization of non conjugated diynes have been investigated in an attempt to prepare polymers that would contain alternating double and single bonds with a cyclic recurring unit [15, 16]. Polymerization of 1,6-heptadiyne and its homologues of substituted acetylenes to produce soluble polymers can now be effectively made by avoiding the difficulty associated with the formation of insoluble and intractable conducting polymers when synthesized through conventional methods. Gibson *et al.* [15, 17] reported the preparation of insoluble, free standing films with metallic lustre by the polymerization of 1,6-heptadiyne with Ziegler type homogeneous catalyst. Choi *et al.* [18–20]

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reported transition metal catalyst systems for the cyclopolymerization of 1,6-heptadiyne and its derivatives giving conjugated double bonds in the polymer backbone with cyclic recurring units. Mathias [21] provided a considerable development for factors controlling cyclopolymerization efficiency and for generating new materials. For example the incorporation of rigid cyclic structures into commercial vinyl polymers may lead to sufficient enhancement in glass transition and heat distortion temperatures to open up new markets.

The present work deals with the cyclopolymerization of dipropargyl ether, DPE, a symmetrical non conjugated diyne through different anionic initiators in an attempt to produce the soluble conducting polymer. Recently, the course of a soluble conducting polymer, poly(1,6-heptadiyne), PHDY formation was followed by UV-Visible spectroscopy [22]. A detailed investigation by following the course of cyclopolymerization of DPE with the selected anionic initiators (KSCN, KCl, KBr and KI) through UV-Visible spectroscopy would reveal the relative efficiency of the different anionic initiators. Additionally, the use of anionic initiators would systematically dope the formed polymer. In contrast to the conventional two steps method of preparing the polymers and doping with external agents. UV-Visible spectroscopy can also be used to identify the doped nature of the polymer.

Here, the authors used UV-Visible spectroscopy to monitor the course of polymerization of dipropargyl ether for the first time in an attempt to identify the relative efficiency of different initiators for cyclopolymerization and doped nature of the formed polymer. The polymer was isolated from the reaction medium and characterized for structure, solubility, conductivity, thermal transitions and electroactivity.

2. Experimental

2.1. Materials

Dipropargyl ether (Aldrich, USA) was used as received. The other chemicals used were of AnalaR grades and used as such.

2.2. Polymer synthesis

Polymerization was carried out in a polymerization tube of 80×10^{-6} m^3 capacity fitted with B_{24} ground joint head carrying inlet and outlet tubes. All experiments were carried out under oxygen free nitrogen atmosphere in dimethyl formamide (DMF). Typical polymerization procedure and method to monitor the course of polymerization is outlined below.

Suitable volumes of monomer and initiator solutions (KSCN/KBr/KCl/KI) in DMF was taken in the polymer tube and total volume was made as 20×10^{-6} m^3 by using DMF. The mixture was degassed with oxygen free nitrogen and kept in a thermostatic bath at 110°C. The top portion of the polymer tube was cooled by a condenser circulated with ice cold water to avoid loss of DMF and monomer. Nitrogen gas was passed through the reaction mixture for 15 minutes and the inlets and outlets of the polymer tubes were closed with Teflon stoppers. The course of polymerization was followed at various polymerization reaction times by recording the UV-Visible spectra of the mixture (cooled to room temperature) using a Shimadzu 2401 PC UV-Visible spectrophotometer.

After polymerization (mostly beyond 48 hours of polymerization time), the unreacted monomer and solvent (DMF) were distilled off under reduced pressure. The polymer residue was then dried under vacuum and used for characterization purposes.

2.3. Characterization of the polymer

2.3.1. UV-visible spectroscopy

A calculated amount of the polymer was dissolved in DMF and the UV-Visible spectrum was recorded using a Shimadzu UV-2401 PC UV-Visible Spectrophotometer.

2.3.2. ^{1}H NMR spectroscopy

The ^{1}H NMR spectrum of the polymer sample was recorded with a Bruker-AC-300 spectrometer and chemical shifts were recorded in ppm units with TMS as internal standard.

2.3.3. FT-IR spectroscopy

The FT-IR spectrum of the polymer sample in KBr was recorded using a Bruker 66v FT-IR Spectrophotometer.

2.3.4. Thermogravimetric analysis

Thermal properties of the dried polymer were followed using a Perkin Elmer TGA 7/DX thermal analyzer over a temperature range of 100–800°C in an inert atmosphere, at a heating rate of 20°C per minute.

2.3.5. Conductivity measurements

The conductivities of the polymer samples were determined by using four probe resistivity meter (Concord India).

2.3.6. Cyclic voltammetry

Cyclic Voltammograms (CV) were recorded using EG&G PAR Model Versastat II Potentiostat/Galvanostat. A conventional three electrode cell (10^{-5} m^3 capacity) involving SCE as reference, a platinum disk of area 2.545 mm^2 as working and a platinum foil as counter was employed. The synthesized poly(dipropargyl ether) was dissolved in acetone and cast into film on the platinum disk surface and dried under vacuum. CVs of the film coated electrodes were recorded using 2 M H_2SO_4 as background electrolyte and potentials were cycled between -0.2 V to 1.0 V vs. SCE with different scan rates.

3. Results and discussion

3.1. Polymerization

Fig. 1 represents the UV-Visible absorption spectra recorded during the course of anionic cyclopolymerization of DPE in DMF. Polymerization was carried out in nitrogen atmosphere using KSCN as initiator at 110°C. The colour of the reaction medium changed into deep brown as the polymerization time increased. UV-Visible absorption spectra were recorded for several polymerization time intervals. The spectrum of DPE in

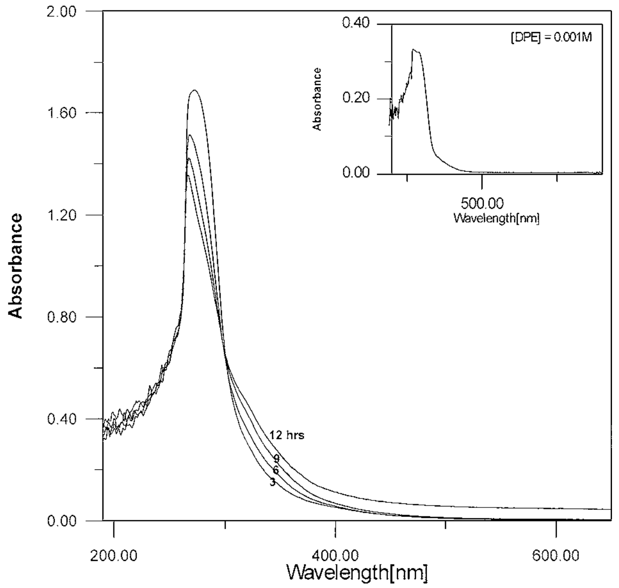


Figure 1 UV-Visible spectra recorded during the cyclopolymerization of DPE in DMF. [DPE] = 5.813 mol · m^{-3}; [KSCN] = 5.0 mol · m^{-3} (a) 3 hrs; (b) 6 hrs; (c) 9 hrs; (d) 12 hrs.

DMF (Fig. 1 (inset)) without initiator showed only a single peak at 268 nm. As time progresses, the 268 nm peak decreases simultaneously with an appearance of new absorption band at 320–340 nm with an isobestic point at 300 nm. The appearance of band at 320–340 nm is assigned for π–π^* electronic transition of polyene units in the polymer backbone. After 72 hours of polymerization time, the deep brown coloured reaction mixture was vacuum evaporated to obtain poly(dipropargyl ether), PDPE. The brown residue was again redissolved in DMF and the UV-Visible absorption spectra were recorded for different [PDPE] in DMF (Fig. 2). The optical density values at 320 nm showed linearity with [PDPE]. This calibration was used to estimate the amount of PDPE formed during polymerization while following the course of polymerization. The amount of polymer formed was then determined by estimating the molar extinction coefficient at $\lambda = 320$ nm. This value was found to be 1330 kg^{-1} · m^2.

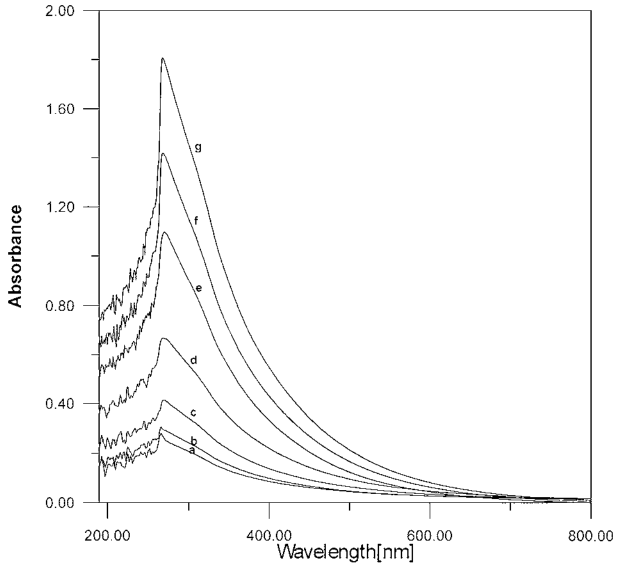


Figure 2 UV-Visible absorption spectra of PDPE in DMF for various concentrations. [PDPE] = 1.33 × 10^{-2} kg · m^{-3} (a); 1.47 × 10^{-2} kg · m^{-3} (b); 2.22 × 10^{-2} kg · m^{-3} (c); 2.48 × 10^{-2} kg · m^{-3} (d); 3.69 × 10^{-2} kg · m^{-3} (e); 6.14 × 10^{-2} kg · m^{-3} (f); 7.68 × 10^{-2} kg · m^{-3} (g).

An interesting observation was noticed on comparing the spectrum during the course of polymerization and the spectrum corresponds to the concentration of monomer used for polymerization. The monomer spectrum showed only a single peak at 268 nm with negligible absorption in the visible region. On the other hand, the polymer showed a broad band at 320–340 nm with progressive increase in absorption in the visible region with increase in [PDPE] (Fig. 2). Besides that, the distinct increase in absorbances at longer wavelength region (550–720 nm) during polymerization indicates the possible simultaneous doping for PDPE. The rate of polymerization R_p, (amount of polymer formed per unit time) was then calculated using optical density values at $\lambda = 320$ nm observed for various polymerization time intervals. R_p was found to decrease with increase in time. A comparison of R_p with changes in [KSCN] and [DPE] was made at different polymerization time. At any time of polymerization, R_p was found to increase with increase in [DPE] and also with increase in [KSCN] when [DPE] was kept as constant (Table I). The increase in rate was greater with increase in monomer concentration than with increasing initiator concentration (Table I).

Cyclopolymerization of DPE was also done with other initiators like KCl, KBr and KI. UV-Visible absorption spectra recorded during the course of polymerization showed variations in the visible region. The shoulder occurring at 320–340 nm, was found to be shifted to 295–310 nm, 285–305 nm and 350–400 nm for polymerization with KBr, KCl and KI as initiators respectively. Besides that, R_p was also found to be different in the four cases (Table II). Also, the initiator efficiency of the four initiators

TABLE I Effect of [KSCN] on rate of polymerization of dipropargyl ether $\lambda_{max} = 320$ nm. [DPE] = 5.81 mol · m^{-3} (a, b, c); 8.72 mol · m^{-3} (d). [KSCN] = 5.0 mol · m^{-3} (a, d); 7.50 mol · m^{-3} (b); 10.0 mol · m^{-3} (c)

Time in hours	$R_p{}^a \times 10^7$ kg · m^{-3} · s^{-1}	$R_p{}^b \times 10^7$ kg · m^{-3} · s^{-1}	$R_p{}^c \times 10^7$ kg · m^{-3} · s^{-1}	$R_p{}^d \times 10^7$ kg · m^{-3} · s^{-1}
3	12	13	16	21
6	6.4	8.3	9.3	13
9	5.6	5.7	8.7	9.7
12	4.3	4.8	6.7	8.0
15	3.4	4.7	6.2	6.9
18	3.0	4.2	4.6	6.4

TABLE II Effect of initiators on rate of polymerization of dipropargyl ether $\lambda_{max} = 320$ nm. [DPE] = 5.81 mol · m^{-3} (a, b, c, d). [KSCN] = 5.0 mol · m^{-3} (a); [KI] = 5.0 mol · m^{-3} (b); [KBr] = 5.0 mol · m^{-3} (c); [KCl] = 5.0 mol · m^{-3} (d)

Time in hours	$R_p{}^a \times 10^7$ kg · m^{-3} · s^{-1}	$R_p{}^b \times 10^7$ kg · m^{-3} · s^{-1}	$R_p{}^c \times 10^7$ kg · m^{-3} · s^{-1}	$R_p{}^d \times 10^7$ kg · m^{-3} · s^{-1}
3	12	4.9	3.0	2.9
6	6.4	4.5	2.4	2.4
9	5.6	3.0	2.0	2.2
12	4.3	2.4	1.9	1.9

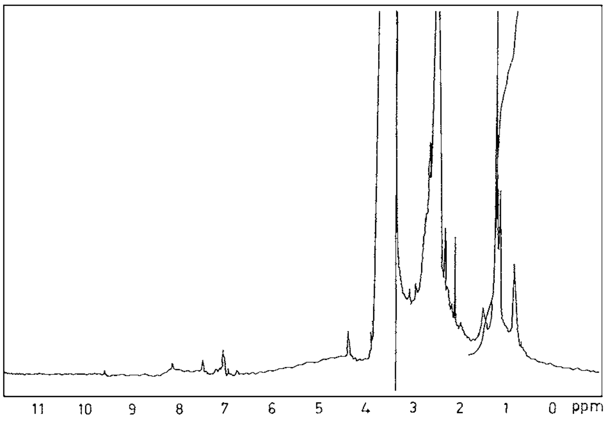


Figure 3 ^{1}H NMR spectrum of PDPE.

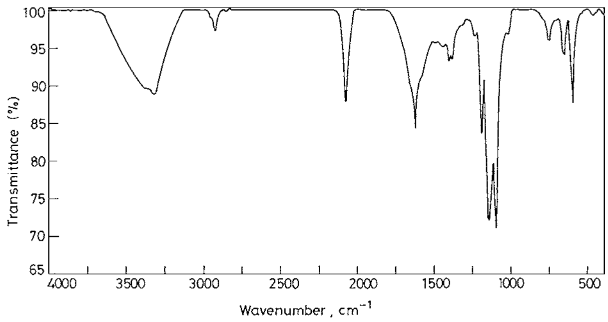


Figure 4 FT-IR spectrum of SCN doped PDPE.

on cyclopolymerization were found to be in the order KSCN > KI > KBr ≈ KCl. This trend was evident when R_p was compared with various polymerization time intervals (Table II).

3.2. Polymer structure

The polymer structure was identified by ^{1}H NMR, FT-IR, UV-Visible spectroscopic analysis. The ^{1}H NMR spectrum of PDPE in DMSO-d_6 is shown in Fig. 3. PDPE showed the acetylenic proton peaks at 2.0 ppm disappeared. The peaks at 6.6–7.5 ppm are assigned for the protons on the conjugated double bond [23]. The peak at 4.4 ppm is assigned to the allylic protons present in the cyclic ring.

The FT-IR spectrum of the PDPE (Fig. 4) showed shoulders at 2925 cm^{-1} and 3000 cm^{-1} which can be assigned for —C=C—H stretches in the backbone. Methylene scissor vibrations are also observed at 1405 cm^{-1}, 1430 cm^{-1} and 1450 cm^{-1} whereas in poly(1,6-heptadiyne) [22] the methylene scissor vibrations were observed at 1420–1450 cm^{-1}. An intensive band at 1625 cm^{-1} (—C=C— stretching) indicates the extended conjugation in the polymer backbone [19]. The doping nature of the polymer was evident from the appearance of 1420 cm^{-1} and 1099 cm^{-1}. These IR bands are also indicative of the cyclic six membered type ring structure with alternative double bonds in the polymer backbone [24].

Fig. 5 represents the UV-Visible absorption spectra recorded during the course of polymerization of DPE using KI as initiator in DMF. The appearance of broad band at 350–450 nm is due to the characteristics of π–π^* transition of conjugated polyenes. From these spectroscopic results, it was concluded that the resulting polymer possesses conjugated backbone with cyclic recurring units (Scheme 1).

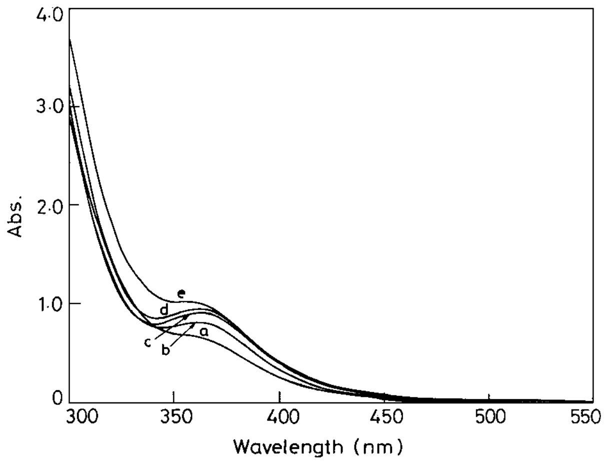
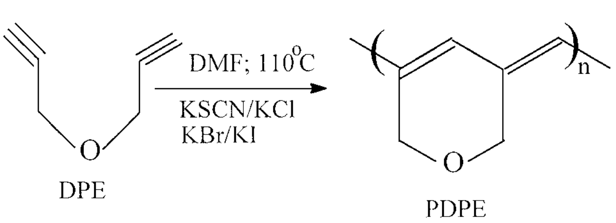


Figure 5 UV-Visible absorption spectrum recorded during polymerization of DPE in DMF using KI as initiator. [DPE] = 5.813 mol · m^{-3}; [KI] = 5.0 mol · m^{-3} (a) 3 hrs; (b) 6 hrs; (c) 9 hrs; (d) 12 hrs; (e) 15 hrs.



Scheme 1 Cyclopolymerization of DPE

3.3. Polymer properties

Fig. 6 represents the UV-Visible absorption spectra of PDPE recorded in various organic solvents. PDPE was found to be completely soluble in DMF, tetrahydrofuran (THF) [19], *N*-methyl pyrolidone (NMP), dichloromethane and acetone. The shoulder at $\lambda_{max} = 320$ nm which was observed in DMF was found to be red shifted to 356 nm for dichloromethane, 366 nm for NMP and 361 nm for THF. In the case of acetone the shift was found to be to 335 nm. These kinds of

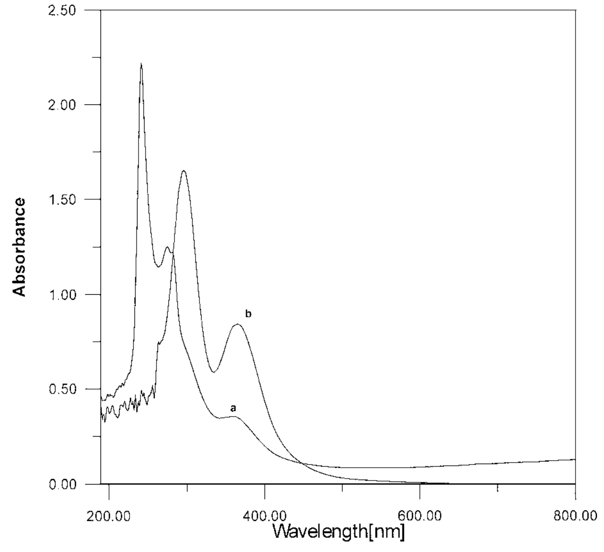


Figure 6 UV-Visible absorption spectra of PDPE in different organic solvents (a) *N*-methyl pyrolidone; (b) dichloromethane.

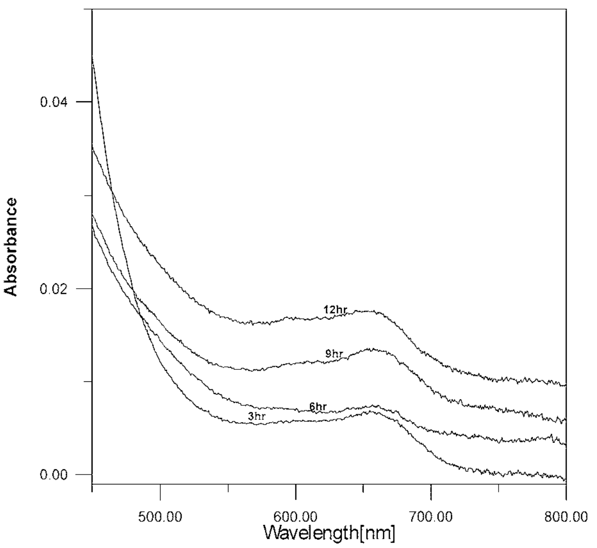


Figure 7 UV-Visible absorption spectra of iodine doped PDPE in DMF.

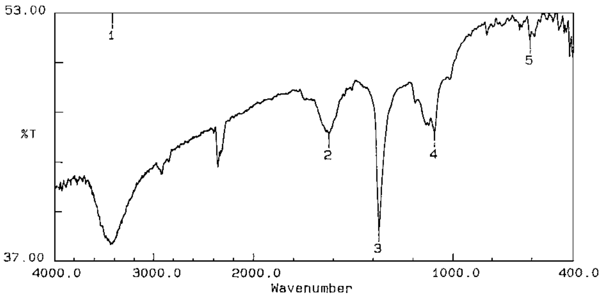


Figure 8 FT-IR spectrum of iodine doped PDPE.

solvatochromic shifts have been explained in the cyclopolymerization of N-substituted dipropargyl amine derivatives [25, 26].

The observation of a band at 550–720 nm in the UV-Visible spectra (Fig. 7) is indicative of the doped nature of the polymer. FT-IR spectrum of I^- doped PDPE showed a characteristic stretching band at 1347 cm^{-1} (Fig. 8) compared to the FT-IR spectru m of SCN^- doped PDPE (Fig. 4), in addition to the stretching bands at 1420 cm^{-1} and 1099 cm^{-1}.

The thermogram of PDPE is presented in Fig. 9. TGA results showed that 98% of weight was retained at 220°C, 90% at 400°C, 85% at 520°C and 80% at 600°C for PDPE. The first thermal process at 220°C is attributed to the exo-double bond rearrangement from a helical structure to nearly planner polyene backbone configuration [27]. The thermal process at 550°C arises from the loss of backbone configuration, which involves the rearrangement of exo-cyclic to endocyclic double bonds, proton migration, cross-linking and bond scissoring [24].

Poly(1,6-heptadiyne), PHDY posses enhanced electrical conductivity from the undoped (10^{-12} S cm^{-1}) to a maximum value in the range 10^{-2}–10^{-1} S cm^{-1} with different dopants [17]. Here, PDPE, a cyclic anolog of PHDY was found to have conductivity in the order $0.09–0.12 \times 10^{-1}$ S cm^{-1} which indicated the doped nature of the formed polymer in the present study [28].

Further, the electroactivity of the PDPE was tested by recording the cyclic voltammogram (CV) of the polymer film coated platinum electrode for various sweep rates (Fig. 10)

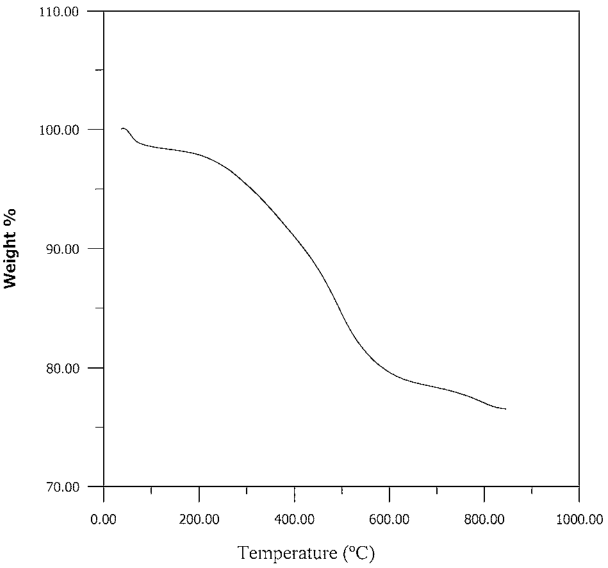


Figure 9 Thermogravimetric analysis of PDPE.

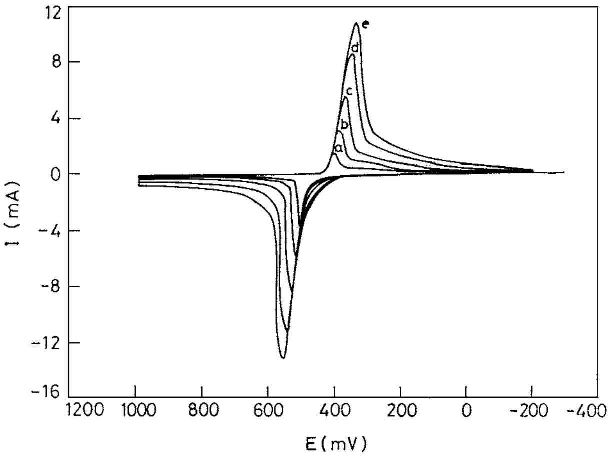


Figure 10 Cyclic voltammograms of PDPE film coated platinum electrode. Scan rate = (a) 50; (b) 100; (c) 200; (d) 400; (e) 600 mV/s.

The CVs of the PDPE film coated platinum electrode had an anodic peak at 506 mV at the scan rate (ν) of 50 mV/s which showed shifting to more anodic values, whilst the cathodic peak at 404 mV showed movement to less positive values with increase in ν. This resulted an increase in $E_p^a - E_p^c$ with increase in ν. The current values of anodic (I_p^a) and cathodic (i_p^c) peaks showed increase with ν suggesting the electrochemical characteristic of this film surface as similar to bound electroactive film on working electrodes [29].

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