

A new route to synthesize high degree polythiophene in a room temperature melt medium

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Abstract

Conducting polymers suffer from folds and kinks because of random nucleation and solvation of a free radical cation to yield a cross linked/disordered polymer and therefore a solvent free electrochemical polymerization in a room temperature melt medium is adopted to yield a high degree polymer with high electronic conductivity. Electropolymerization of thiophene was performed on platinum/ITO substrates using cyclic voltametry or galvanostatic mode in chloroaluminate room temperature melt medium to obtain a reddish brown free standing film which can be peeled off from the electrode surface after a minimum of 10 cycles. The conductivity was found to be around 10^2 S/cm. The degree of polymerization was calculated to be around 44 from IR studies. A layered structure supportive for high degree of polymerization was witnessed from potential step technique. From UV spectra the charge carriers were found to be bipolarons. The morphology of the film was found to be crystalline from SEM and XRD studies. Capacitative impedance properties for doped samples were interpreted from impedance spectroscopy. © 2005 Elsevier B.V. All rights reserved.

Keywords: Polythiophene; Room temperature melt; Conductivity; Electrosynthesis

1. Introduction

Among the numerous conducting polymers, polythiophene (PT) has rapidly become the subject of considerable interest. From a theoretical viewpoint, polythiophene has been considered as a model for the study of charge transport in conducting polymers with a non degenerate ground state, while on the other hand the high environmental stability of both its doped and undoped states together with its structural versatility have led to multiple developments aimed at applications such as conductors, electrode materials and organic semiconductors.

PTs have been considered in several reviews devoted to conducting polymers in general or to some of their more specific aspects such as electropolymerization [1–3], electrochemistry [4,5], environmental stability [6] and optical properties [7]. A more updated review of the polythiophenes stating the considerable progress accomplished in their preparation and characterization of their structure and electronic and electrochemical

properties is that of Roncali [8]. The electropolymerization of bithiophene was initially mentioned in 1980 [9] whereas the first report of the electropolymerization of thiophene appeared 2 years later [10]. Following these initial works a large number of studies have been reported to the analysis of the electropolymerization reaction and to the optimization of electrosynthesis conditions.

PT has been considered for various applications in nonlinear optical response [11–14], batteries [15–17], electrochromic devices [18–20], electrochemical sensors [21], modified electrodes, etc. [22–24]. Here, we discuss electropolymerization of thiophene to obtain a polythiophene with less number of defects due to solvent by polymerizing in a room temperature melt to yield a polymer with comparatively high conductivity.

2. Experimental

2.1. Reagents

Anhydrous aluminum chloride (98% Sigma Aldrich) recrystallized cetyl pyridinium chloride (98% Sigma Aldrich) and vacuum distilled thiophene (99% Sigma Aldrich) were used. Each time the aluminium chloride was sublimed before use.

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2.2. Preparation of electrolyte

Cetyl pyridinium chloride (33%) and aluminum chloride (67%) were mixed together thoroughly inside a dry box to get a highly viscous liquid (melt). The proportion of aluminum chloride is always maintained to be higher than cetyl pyridinium chloride to get the acidic melt. This viscous melt is dissolved in thiophene (monomer) to reduce the viscosity [25–28].

2.3. Electrochemical polymerization

The electropolymerization of thiophene was carried out by potentiodynamic technique at room temperature. A three-compartment sealed glass electrochemical cell was used with platinum 0.25-cm² foil as the working electrode and platinum wire as the counter electrode. A high purity aluminum wire was used as the reference electrode. The electro deposition of PT was carried out by sweeping potential at 50 mV/s in the potential range of 0 and 2 V versus Al wire from the 0.1 M electrolyte prepared by adding the room temperature melt in thiophene.

2.4. Characterization

The characterization of PT film was carried out under anhydrous conditions by electrochemical techniques, spectroscopic methods, conductivity measurements, thermal analysis and scanning electron micrograph.

The electrochemical characterization was carried out by cyclic voltammetric experiments at various sweep rates, electrochemical growth by step potential techniques and impedance studies under open circuit potential in the ac frequency range 100 kHz to 0.1 Hz with an excitation signal of 10 mV using IM6 Bioanalytical Systems, USA at room temperature. The electronic conductivity measurements were carried out by four probe method using Keithley Model 2400 series Source meter and Keithley Model 2182 Nano voltmeter equipment under nitrogen atmosphere. The electrical contacts were made with a mercury drop between the polymer film and the four probes.

The electronic spectra of the polythiophene as deposited on electrode surface were recorded on Cary 500 scan UV–vis–NIR spectrophotometer using high alumina pellet as reference in the range 200–1500 nm. FTIR spectra were registered using Perkin-Elmer Paragon –500 FTIR spectrophotometer using KBr pellets in the region between 400 and 4000 cm⁻¹.

The thermal studies were carried out in the air at the heating rate of 10°/min using Simultaneous Thermal Analyzer (model No. STA 1500, PL Thermal Sciences, UK). Scanning electron micrographs were recorded at various magnifications using Hitachi-S-3000H SEM machine.

3. Electrochemical polymerization of thiophene—CV Studies

It is an advantageous technique for detailed electrochemical analysis of redox characteristics of the polymer can be moni-

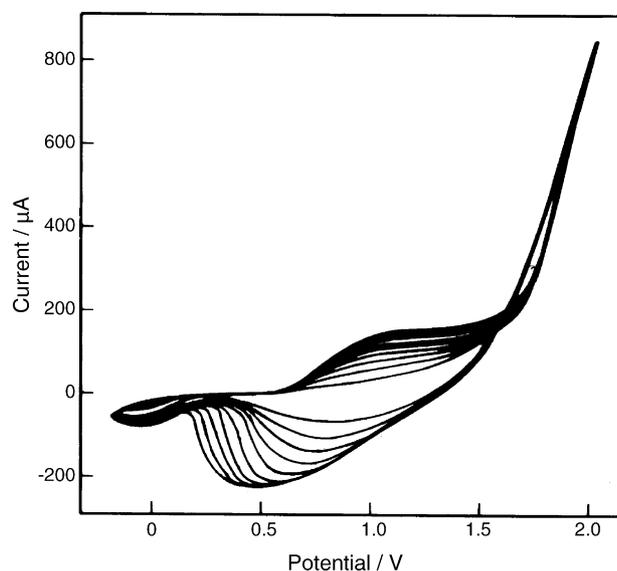


Fig. 1. Electrochemical growth pattern of polythiophene in the presence of 0.1 M chloroaluminate room temperature melt as the electrolyte, potential range 0 to 2 V vs. Al at sweep rate of 50 mV/s.

tored during film growth. The polymer growth pattern is given in Fig. 1. After deposition the working electrode was removed from the growth solution, washed with ether and placed in a monomer free solution of the room temperature melt for post polymerization CV analysis. It is common feature of the post polymerization CV that the first curve is slightly different from the subsequent cycles. The origin of this is not understood but it is evident that it takes the first electrochemical cycle for the film to fully re-establish its normal electrochemical activity following transfer from the growth solution into the fresh electrolyte. There is extensive and inconclusive discussion in literature regarding the possible origin of the multiple redox peaks sometimes observed for polythiophene species. It has been proposed that these peaks are due to the transitions between the neutral, polaron, bipolaron and metallic states of polymer [29] which may also be influenced by the rate of continuation transport [30] the reduction of different areas of the polymer film or of polymer chains of significantly different lengths [31,32], the effect of charge trapping [33], conformational changes accompanying radical cation formation [34] or consideration of the mechanical strain on the polymer that results from the forced intrusion of anions into the film [35].

All CVs indicate a significant dependence on the nature of the melt. The growth CVs show the increase in current with successive cycles indicative of successful electroactive film growth. As the film thickness during polymerization increases the voltammetric wave associated with oxidation of the polymer becomes slightly more cathodic and reduction becomes more anodic with successive scans, which is due to heterogeneous electron transfer kinetics and a increase in kinetics consequently an increase in conductivity, counter ion mobility and possibly the conjugation length. Fig. 2 shows the post-polymerization CV characterization of polythiophene film.

Usually thiophene requires a high potential of 2–2.5 V which can result in side reactions involving solvent molecule with

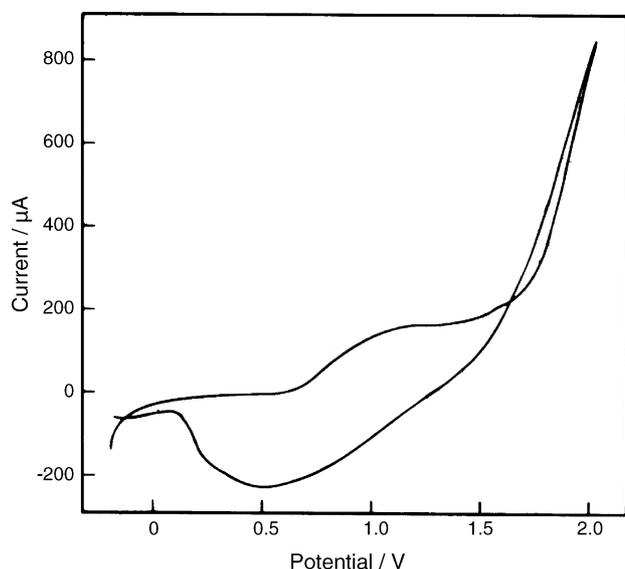


Fig. 2. Cyclic voltammogram of polythiophene in the absence of monomer, in chloroaluminate room temperature melt medium in the potential range of 0 to 2 V vs. Al at a sweep rate of 50 mV/s.

free radical generated during the oxidative polymerization of a monomer and possible overoxidation of the polythiophene polymer film, i.e. polythiophene is not stable at the potentials required for its synthesis [36,37]. But here the polymerization occurs at a lower potential of 1.6 V and to overcome to some extent the 'polythiophene paradox' [38]. The reduction of polythiophene occurs at a more negative potential, which may reflect an increase in the mean conjugation length of the polymer. To prove the high degree of polymerization we electropolymerized thiophene in 0.1 M LiClO_4 solution in acetonitrile medium (Fig. 3) and characterized its behaviour in the same medium without the monomer (Fig. 4). The oxidation potential was found to be 2.1 V versus Ag/AgCl. After synthesizing polythiophene

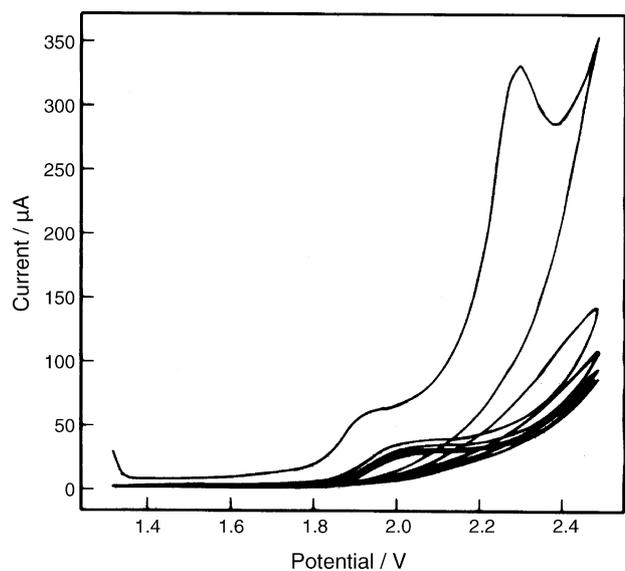


Fig. 3. Electrochemical growth pattern of polythiophene in the presence of 0.1 M LiClO_4 in acetonitrile between the potentials 0 to 2.5 V vs. Ag/AgCl at sweep rate of 50 mV/s.

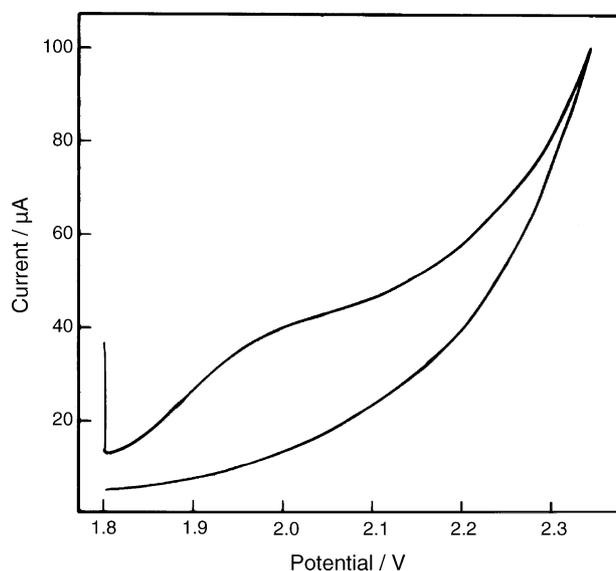


Fig. 4. Cyclic voltammogram of polythiophene in the absence of monomer, in 0.1 M LiClO_4 in acetonitrile in the potential range of 0 to 2.5 V vs. Ag/AgCl at a sweep rate of 50 mV/s.

film from the room temperature melt and dedoping we cycled the film in 0.1 M LiClO_4 for redoping. This redoped film was characterized in perchlorate medium we observed a blue shift of oxidation potential from 2.1 to 1.5 V given in Fig. 5. The current is also more comparatively which reflects that polymer obtained in room temperature melt is better ordered which reflects in its higher electronic conductivity. This infers that whenever there is an increase in the polymerization length there is a decrease in the polymerization potential. Another advantage of redoping results in the rise in the conductivity and also renders the film environmentally stable.

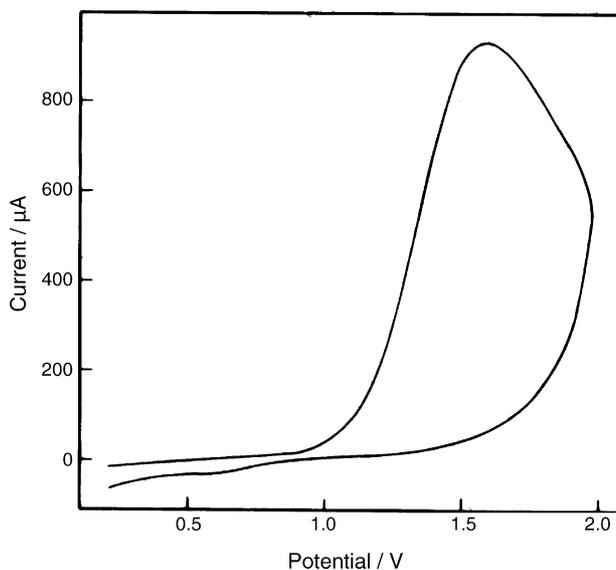


Fig. 5. Cyclic voltammogram of polythiophene (grown in chloroaluminate medium and redoped by perchlorate ion) in the absence of monomer, in 0.1 M LiClO_4 in acetonitrile in the potential range of 0 to 2 V vs. Ag/AgCl at a sweep rate of 50 mV/s.

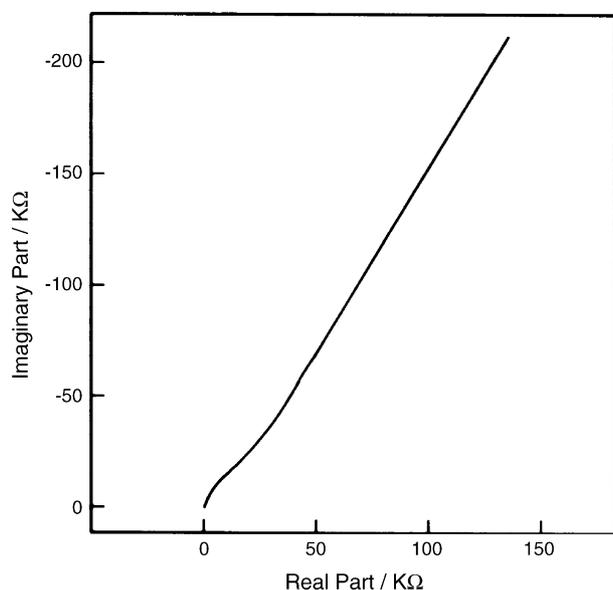


Fig. 6. Impedance spectra of doped PT film in the a.c frequency range 100 kHz to 0.1 Hz with an excitation signal of 10 mV.

4. Impedance studies

For CP modified electrodes, electrochemical impedance spectroscopy (EIS) has proved to be quite a useful tool for studying the charge transport inside the polymer coating and the charge transfer at the metal/polymer and polymer/solution interfaces [39–54]. EIS data were obtained for doped and undoped films at ac frequency varying from 0.1 Hz to 100 KHz corresponding to their electroactivity (p-doping) for 0.1 M melt solution. Figs. 6 and 7 show the impedance spectra of doped and undoped species. The spectra of the doped sample shows a 90° trend at the lowest frequency region, due to capacitive impedance, accounts for the charge transport process inside

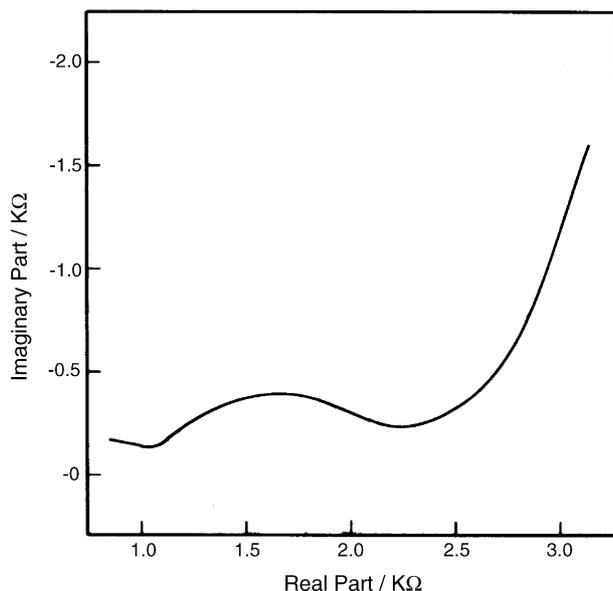


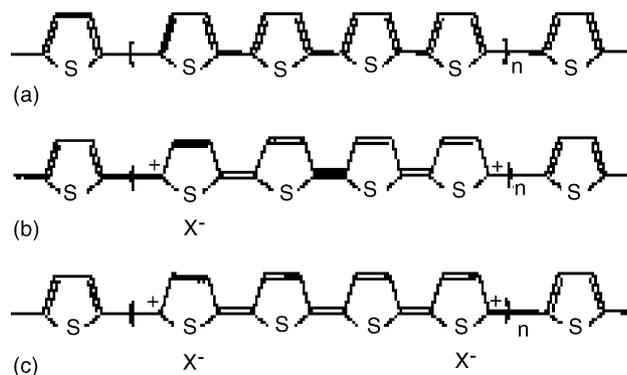
Fig. 7. Impedance spectra of undoped PT film in the a.c frequency range 100 kHz to 0.1 Hz with an excitation signal of 10 mV.

the bulk of the film. The undoped sample constitutes of a depressed semicircle due to the non-homogenous separation surfaces. There is also mid-frequency Warburg impedance quasi-45°-slope segment that reflects the diffusion migration of ions at the boundary surface between solution and polymer inside the latter medium. A key point is that ion transport is the slow process in the neutral state. Neutralization of p-doping process is completely in-charge of the AlCl_4^- exit. As a consequence in the potential region where the polymer is neutral the ion concentration is negligible and the ionic conductivity is consequently very low, so that the generalized transmission circuit model can be simplified into the classified Randle's circuit. On the other hand, in the oxidized state the conductivity due to the presence of counter-ions inside the polymer is much higher and the impedance behavior can be described by a different simplification of the same equivalent circuit, which is now coincident with Albery's model described in reference [42].

5. Mechanisms of electropolymerization

The electrochemical formation of conducting polymers is an unique process. Although it represents some similarities with the electrodeposition of metals since it proceeds via a nucleation and phase growth mechanism [55–58], the major inference lies in the fact that the charged species precursors of the deposited materials must be initially produced by oxidation of the neutral monomer at the anode surface. The consequence of this is that various electrochemical and chemical follow-up reactions are possible making the deduction of the electropolymerization mechanism a very complex. An important aspect of the electropolymerization reaction is that it proceeds with electrochemical stoichiometry with ' n ' values in the range of 2.07–2.5 F/mol [59]. The oxidation of the monomer requires two electrons per molecule while the excess of the charge corresponds to the reversible oxidation or doping of the polymer. Scheme 1 gives the different forms of thiophene obtained during electropolymerization.

The first electrochemical step consists of the oxidation of the monomer to its radical cation. Since the electron transfer reaction is much faster than the diffusion of the monomer from the bulk solution, it shows that a high concentration of radicals is



Scheme 1. Different redox forms of polythiophene: (a) reduced, (b) half-oxidized (polaronic), and (c) oxidized (bipolaronic).

continuously maintained near the electrode surface. The second step involves the coupling of two radicals to produce di-hydro-dimer-dication which leads to a dimer after loss of two protons and rearomatization. This rearomatization constitutes the driving force of the chemical step. Due to the applied potential, the dimer which is more easily oxidized than the monomer occurs in its radical form and undergoes a further coupling with a radical. Electropolymerization proceeds then through successive electrochemical and chemical steps until the oligomer becomes insoluble in the electrolytic medium and precipitates onto the electrode surface.

6. Potential step technique—nucleation studies

The potential step technique has been used to investigate nucleation and growth of PPP. In this experiment, a sudden high potential is applied to the working electrode and the current and time transients are recorded. The shape of the transient indicates how the nucleation for the growth of polymer takes place. The nucleation gets influenced by following factors:

- (i) nature of anion present,
- (ii) concentration of the monomer, and
- (iii) preparation of the electrode surface.

After each experiment the electrode surface has to be cleaned and reconditioned. The polymer growth was studied by fixing potential and time scale. The experimental set-up was the same as that for CV studies. The growth of the conducting polymer can be compared with the electrodeposition of metals, the difference being that the former is an anodic reaction. In 1981, the diffusion limited aggregation (DLA) model was introduced by Witten and Sanders [60]. In this model, particles are added one at a time, to a cluster or aggregate of particles via random walk trajectories. According to this model, there is competing growth of polymer chains from a surface which leads to the formation of independent clusters. Meakin [61] modified the DLA model, in which the growth process is in a direction perpendicular to the surfaces of growth sites. Initially, each site at the electrode surface is active. Random walkers (radicals) are launched one at a time and eventually either move a long distance from the growing deposit and are terminated or find an active site. If an active site is found this site becomes inactive and the site occupied by the random walker before it enters the active sites become the new active site. That is how the surface of an electrode becomes covered progressively. Electrodeposition of conducting polymers is a polynucleation process and transients are triggered by single potential step. Nucleation is independent of the size and shape of the electrode and polynucleation starts in synchronism with the potential step and is illustrated in Fig. 8. The current–time transient can be replotted using various equations as given by Li and Albery [62]. Fig. 8 shows the potential step growth of PT at 1.7 V versus Al wire, as per CV curve (Fig. 1) where the growth of the polymer occurs at 1.6 V and shows the maximum current. To observe proper growth transients, time scale was fixed at 5 s/cm with a total growth time of 180 s. There is rise in the current from 166 to 229 μA in steps. The steps in the growth

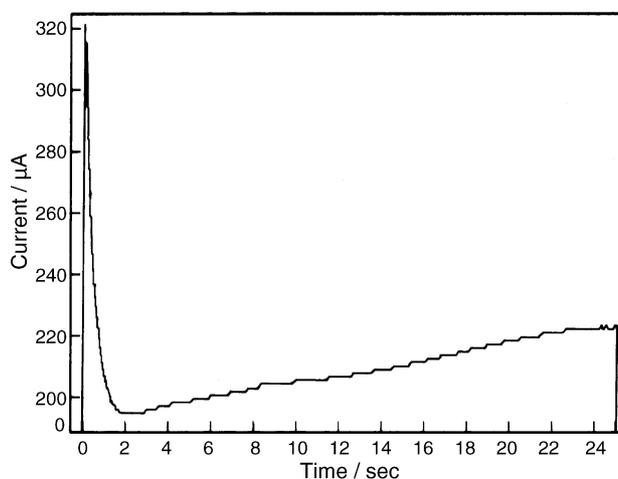


Fig. 8. Current versus time response of a polythiophene growth in the presence of room temperature melt at 1.7 V vs Al wire for 30 s.

curve indicates the formation of a polymer with a layered structure which is uncommon in conducting polymers. The growth processes depend upon the following factors:

- (i) monomer concentrations,
- (ii) oligomerizations,
- (iii) diffusion of monomer into polymer film, and
- (iv) formation of critical cluster and nucleus.

In CV curve the random adsorption of monomer on a bare electrode surface is seen more clearly in a deposition curve where relatively a broad peak appears at potentials significantly less positive than required for bulk oxidation of monomer and is followed by sharp peaks resulting from nucleation and monolayer spreading. The sharp rising edge of these peaks is linear with time which suggests that two-dimensional patch has been expanding in a shape preserving way. The close similarity of the peaks shape suggests that nucleation has occurred repeatedly on the same site.

7. Conductivity measurements

The conductivity of freshly deposited doped PT film was around 10^2 S/cm. Multiple experiments showed the conductivity range to be around $3\text{--}4 \times 10^2$ S/cm. When exposed to air the conductivity slowly decreases to 0.06 S/cm, because exposure to air dopant in a polymer film reacts with moisture to yield aluminum oxychloride and aluminum hydroxide, thereby to large extent undoping occurs, however, polymer film can be redoped. The conductivity of undoped PT was observed to be in 10^{-9} S/cm.

8. Vibrational spectroscopy

The peaks at 842 cm^{-1} (medium), $785\text{--}788\text{ cm}^{-1}$ (strong), and 701 cm^{-1} (weak) are attributed to C–H out-of-plane vibrations. The strong intensity of the $785\text{--}788\text{ cm}^{-1}$ band which is characteristic of 2,5-disubstituted thiophene rings indicates that the electrochemical coupling of thiophene ring occurs

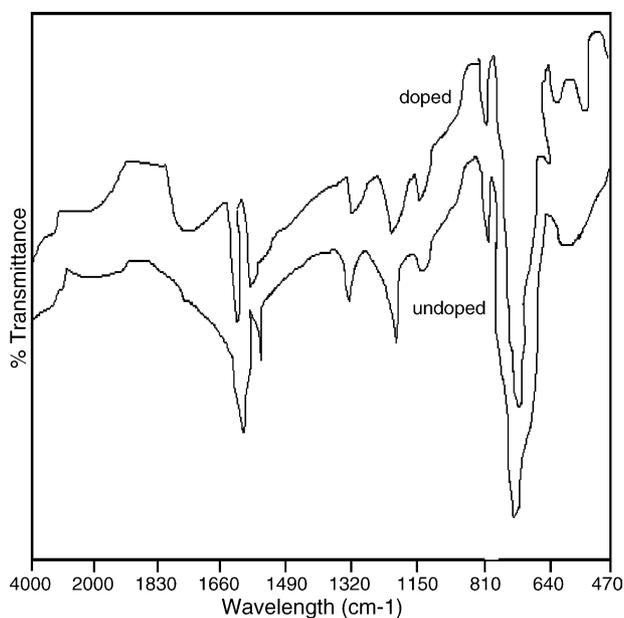


Fig. 9. FTIR spectra of doped and undoped PT in the region 4000 cm^{-1} to 400 cm^{-1} in the KBr medium.

preferentially at 2,5 positions [63]. Two medium bands at $1490\text{--}1491$ and $1437\text{--}1439\text{ cm}^{-1}$ are assigned to stretching vibrational modes of the thiophene ring [63]. For the IR spectrum of doped polythiophene film a wide band occurs at 3460 cm^{-1} , which is probably due to OH stretching vibrations resulting from the hygroscopic nature of the dopant.

The degree of polymerization (DP) of the PT films was evaluated as 44 using the procedure given by Furakawa et al. [64] and Sauvajol et al. [65] according to the expression, see Eq. (1).

$$\text{DP} = 2 \left(\frac{R_0}{R + 2} \right) \quad (1)$$

where R is the ratio of the integrated intensity of the IR bands at 701 and 788 cm^{-1} . Fig. 9 gives the FTIR spectra for doped and undoped polymer films.

9. Electronic spectroscopy

Fig. 10 shows the UV–vis–NIR spectra of polymer samples. Oxidized polymer shows a red shift in the blue range at 490 nm compared to previously observed band at 480 nm . The tail of this band extends to the infrared region indicating that the charge carriers are bipolarons or otherwise called as trapped excitons.

10. XRD studies

The undoped PT observed by X-ray diffractometer appears to be completely amorphous, which reflects great local disorders. An amorphous sample yields a diffused halo and a partially crystalline sample may yield some high intensity rings superimposed on such a halo. These disorders must be correlated with structural defects ($\alpha\text{--}\beta\text{-coupling}$), which affects the conjugation. AlCl_4^- doped film shows partial crystallinity with a 2θ value around 25° for conducting thiophenes [66].

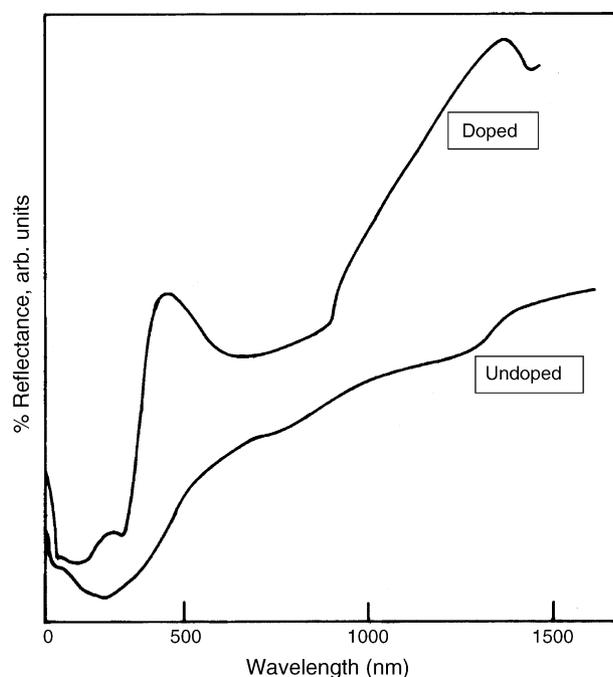


Fig. 10. The diffused reflectance UV spectra of doped and undoped PT using high alumina as reference in the range 200 to 1500 nm .

11. Thermal studies

The results of differential thermal analysis show that both the polymer films show an exothermic peak at 350°C in air which implies the breakdown of the polymer backbone. On the other hand there is a peak around 230°C in the doped species, which is due to the expulsion of the dopant. The thermo gravimetric analysis (TGA) curve of doped polymer shows initial weight loss of 10% around 78°C due to the expulsion of benzene. This elimination of benzene is due to the fact that the specimens are stored under benzene and given for analysis for avoiding the contact with moisture. There is a weight loss between 190 and 300°C due to expulsion of dopant and thereafter polythiophene begins

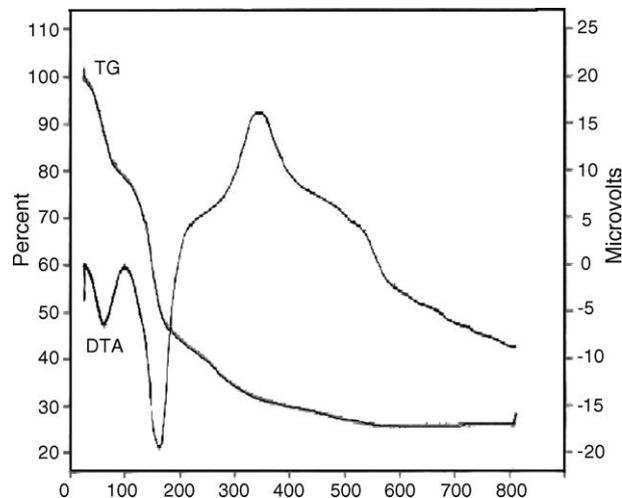


Fig. 11. TG/DTA curve for doped PT.

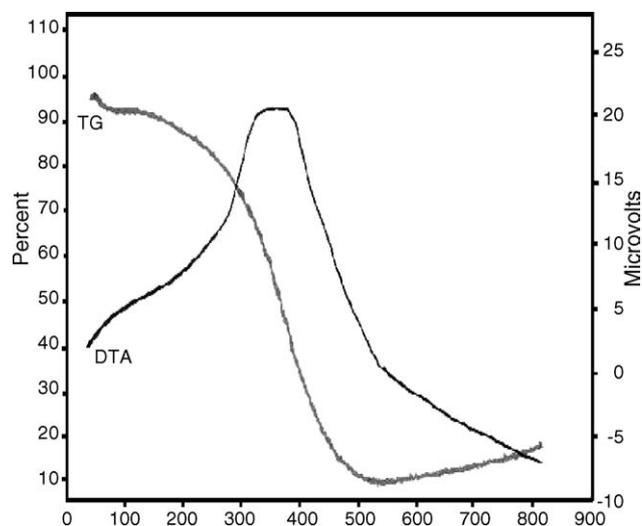


Fig. 12. TG/DTA curve for undoped PT.

to decompose. However for undoped there is no decomposition till 500 °C.

Figs. 11 and 12 give the TG/DTA curves for doped (Fig. 11) and undoped PT (Fig. 12), respectively.

12. Morphology and particle size studies

Figs. 13 and 14 are the scanning electron micrographs of doped and undoped polythiophene, respectively. Fig. 13 shows that doped polymer has a hexagonal geometry. The study shows that the size of the largest hexagon is 6.8 μm and that of smallest is 0.8 μm in the doped sample and the undoped polymer has globular structures with a size ranging from 4 to 15 μm . The brightness of hexagon in a uniform way indicates the homogeneity of doping. The particle size analysis also confirms that the particle size is in the range between 1 and 10 μm .

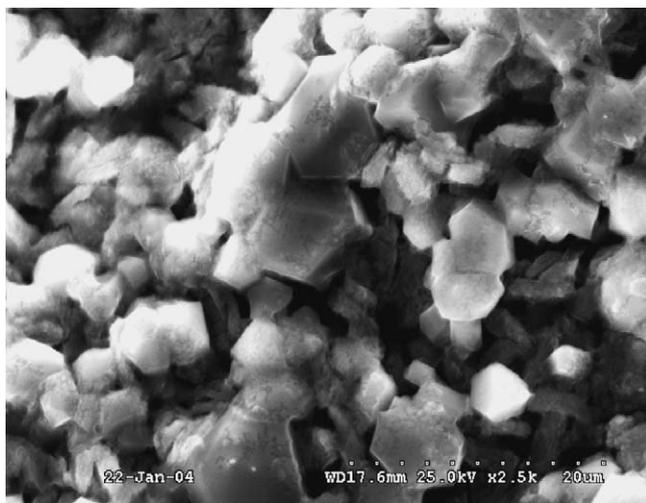


Fig. 13. Scanning Electron Micrograph of conducting PT film showing crystalline structure.

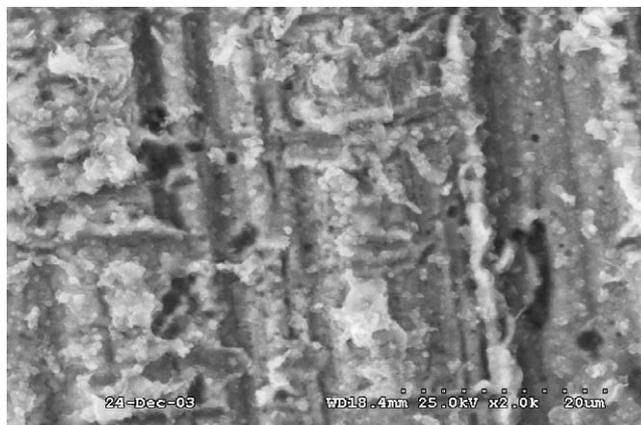


Fig. 14. Scanning Electron Micrograph of undoped PT film showing non-conducting dark portions.

13. Conclusion

Our study reveals that thiophene can be polymerized at a lower potential in a room temperature melt medium to yield a more ordered polymer with a layered structure. Our CV studies show that the polymer has comparatively high degree of conjugation and can be redoped with any dopant to obtain an environmentally stable polymer for various applications. The conductivity improved due to increase in conjugation length, which also reflects in the capacitive properties obtained from impedance studies. The XRD and SEM analysis indicate a crystalline morphology for the doped polymer. A staircase type of curve in the potential step technique shows the formation of a layered structure.

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