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Energy Procedia 18 (2012) 1059 – 1067

Energy Procedia

Some electrical properties of soluble conducting polymer polyHexylthiophene (PHT) prepared by Electrochemical polymerization

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Abstract

Thin films of soluble conducting polymer, polyHexylthiophene (PHT) doped with ClO_4 anion have been prepared by anodic polymerization of Hexylthiophene monomer on stainless steel electrode. These films characterized by FTIR. The electrical conductivity is measured by two –probe method .The quality of the films were influenced by many parameters such as current density , concentration of supporting electrolyte tetrabutylammonumtetraperclorate($TBAClO_4$) .The electrical conductivity of the films is studied as a function of current density and a concentration of $TBAClO_4$. The best electrical conductivity was found at current density about 9.3 mA/cm^2 and $TBAClO_4$ concentration 0.1M.The conductivity of PHT films decreased when immersing in ammonia solution. The effect of temperature on electrical conductivity was also investigated.

Keywords: soluble conducting polymer, polyHexylthiophene (PHT),electrochemical polymerization, electrical properties

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1. Introduction

Organic polymers are normally insulators; it can be presumed that conducting polymers must have an unusual structure. Polymers with conjugated π - electron, backbones display unusual electronic properties such as low energy optical transition, low ionization potentials, and high electron affinities.

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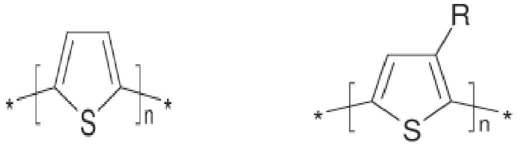
doi:10.1016/j.egypro.2012.05.120

Conducting polymers are obtained by reduction or oxidation (called doping), convert on insulating polymer to conducting one near metallic conductivity [1].

Conducting polymers have attracted great attention because of their application such as photovoltaic [2], secondary batteries [3], optical switching element [4], sensors [5] field effect transistor [6] and light emitting diode [7. Polythiophene is the first class of conducting polymers with a good stability toward oxygen and moisture both in their oxidized state (conducting state) and in their reduced state (non-conducting state) [8].



(a) PT (b) PHT (when R= C_6H_{13})

Figure 1: (a) is polythiophene and (b) is polyhexylthiophene

While polythiophene is insoluble, infusibility , poor mechanical properties and not easily processable .The incorporation of flexible alkyl substitutes at the poison 3 or 4 of the thiophene ring imparts good solubility in common organic solvents such as THF , Taluene , CHCl or NMP .[9,10].

In the present work polyhexylthiophene was prepared by electrochemical polymerization of hexylthiophene on stainless steel electrode . The quality of the film is very sensitive to various parameters such as current density, electrode space, type of solvent, type and concentration of supporting electrolyte [1]. The preparation films characterized by FT-IR .The electrical properties of doped films and the effect of temperature on electrical conductivity were investigated .

2.Experimental

Polyhexylthiophene doped with ClO_4 anion was synthesized by electrochemical polymerization in an electrochemical cell with pair of electrodes, working electrode and counter electrode, connected to constant current power supply as shown in Fig. (2). The working electrode is one where the polymer film deposits on it and it was made of stainless steel, the counter electrode was made of plantum (Pt) .The distance between these electrode was 0.3cm [11]

Different current density from (5.88 – 12.44) mA/cm² and concentration of supporting electrolyte ($TBAClO_4$) from (0.001 to 0.25) mol/L were used in order to choose the proper current density and concentration of ($TBAClO_4$) of polymerization ,that give a good quality films(highly conducting films) .

The best quality films were obtain at current density (9.3) mA/cm^2 with solution mixture at 0.1 M $TBAClO^4$ and 0.2 M hexylthiophene in CH_2Cl_2 solution . The temperature of mixture was controlled by using water circulation through a chiller . the chiller was used to maintain the reaction temperature constant at 10 C° throughout the polymerization process . The doped PHT films can be brought to undoped films by immersing them in ammonia solution, then washed with tetrahydrofurane (THF)by using Ultrasonic. The characterization of undoped and doped (PAni) film have been carried out using FTIR analyzing technique. The electrical conductivity, σ, measured by two probe method at temperature range (350-475) °K.

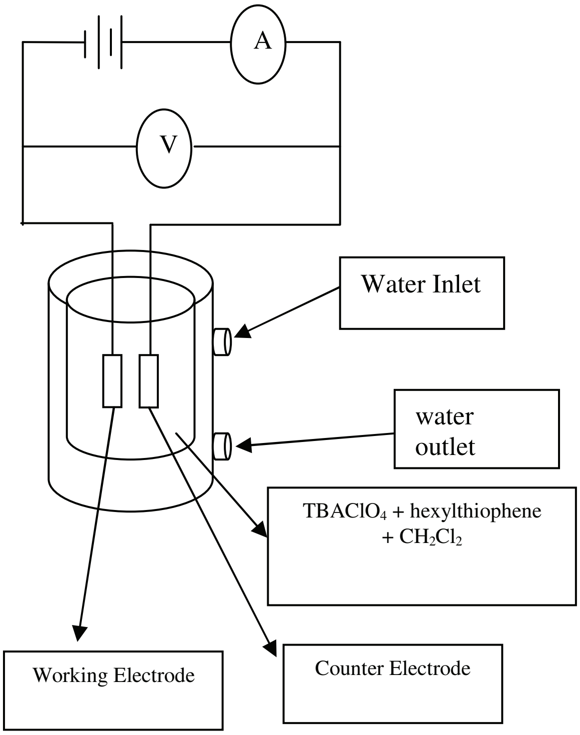


Figure (2) The electrochemical polymerization cell.

3. Results and discussion

The (FT-IR) spectrum of PHT film was measured by FT-IR-8400s Fourier transform Infrared Spectrophotometer as shown in figure (3) and(4) .The FT-IR spectrum of PHT shows bands at 1381, 1100, 1080, 798 cm^{-1}. These bands can be attributed to the thiophene monomer unit (CH bending and stretching, heterocyclic vibration). the bands 1100 and 623 cm^{-1} were characteristics of ClO_4 ion (doping) and the bands 2965, 2936 , 2836 and 926 cm^{-1} were characteristics of hexyl group . The some result has been obtained by [12-15].

The electrical conductivity for each sample, is calculated with following eq [16]

$$\sigma = \frac{\mathbf{d}}{\mathbf{A}} \times \frac{\mathbf{I}}{\mathbf{V}}$$

Where d was the thickness of the films, I was the current between the probe and substrate, V was the voltage between the probe and substrate and A was the Area of the probe. The quality of the films was examined by measuring the conductivity, σ, as a function of current density, J, and concentration of the supporting electrolyte $TBAClO_4$. Figure (5) shows the variation of conductivity with current density of polymerization. the optimum current density was found to be 9.3 mA/cm^2 ,this was carried out by

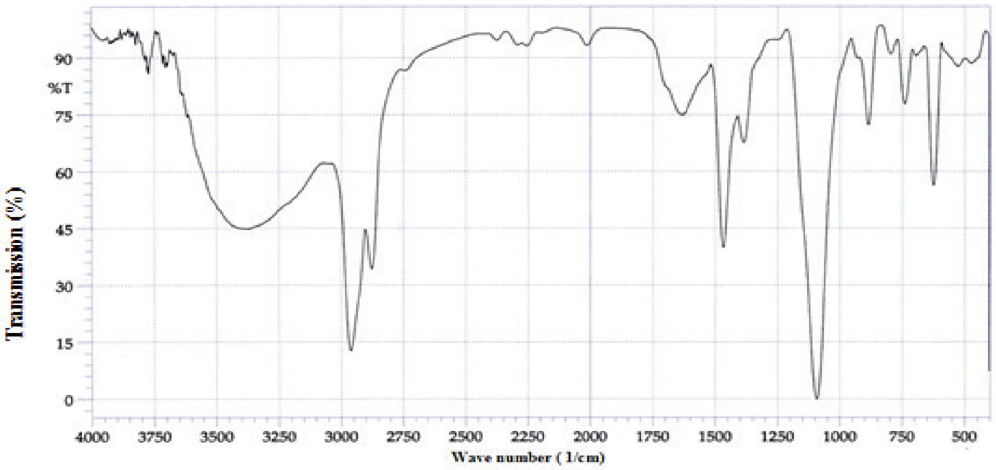


Figure 3: FT-IR spectrum of doped PHT film at temperature (80°C).

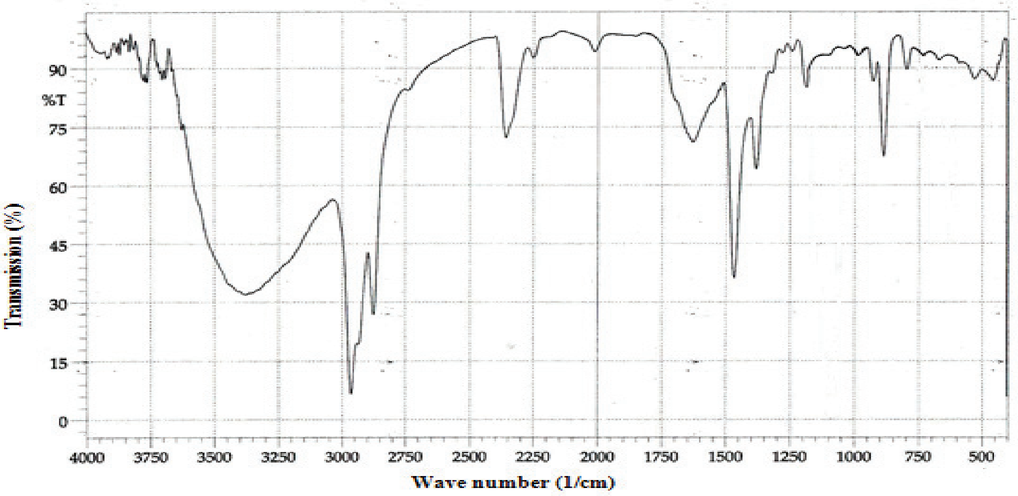


Figure 4: FT-IR spectrum of undoped PHT film.

using 0.1 M $TBAClO_4$ supporting electrolyte and 0.2 hexylthiophene monomer in CH_2Cl_2. the maximum value of conductivity for PHT is 10^{-5} S/cm .At low current density values the conductivity was low , this can be attributed to the fact that the current density is not enough to give high doping for PHT with ClO_4 anion , while the high value of current density gave low conductivity because the high current density makes the polymerization too fast . So that some polymer fragments fail in the solution [12].

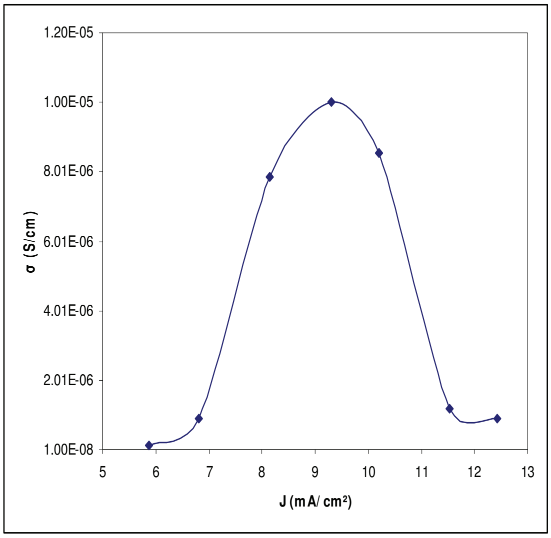


Figure (5): The Conductivity as a function of current density.

Fig (6) shows the dependence of conductivity on the $TBAClO_4$ concentration, the saturation in conductivity observed at concentration larger than 0.1mol/L, because the conductivity depends on the degree of oxidation or reduction in π – electron system and which is determined by number of conjugate carbon [17].

The conductivity of undoped film .was measured after immersing the PHT in ammonia solution. figure(7) shows the conductivity of PHT as a function of immersing time , the conductivity decreased when immersed in ammonia solution which drops the conductivity of the film to (10^{-5} to 10^{-8}) S/cm . This can be explained in the terms of compensation process [17].

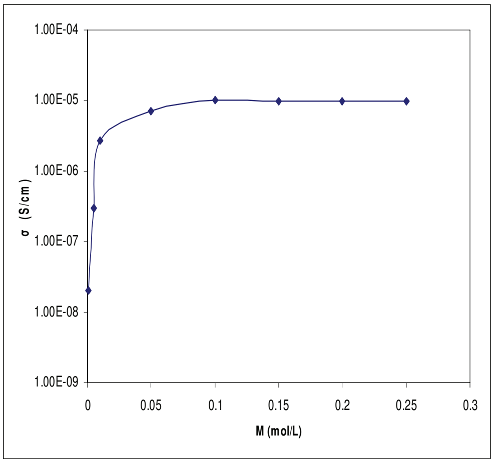


Figure (6): The Conductivity as a function of concentration.

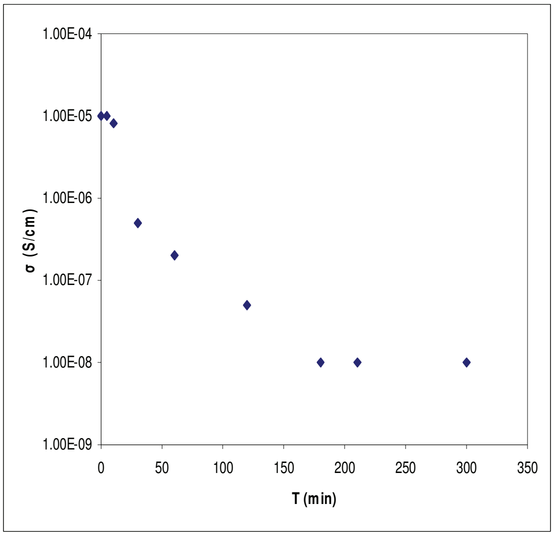


Figure (7): The conductivity as a function of immersing time in ammonia solution.

Figures (8) show the current – voltage characteristic for(Al/PHT-ClO$_4$/Al) with different at concentration of TBAClO$_4$ at room temperature. The electrical conductivity was increase as concentrations of the supporting electrolyte (TBAClO^4) increases. The mechanism of conduction carriers was studied .it was found that films which prepared at supporting electrolyte concentration larger than(0.1 M) abuse ohmic behavior at voltages larger than 20V , but the films which prepared at supporting electrolyte concentration less than (0.05 M) abuse ohmic behavior at voltages larger than 5V.this result argument with[18-21]

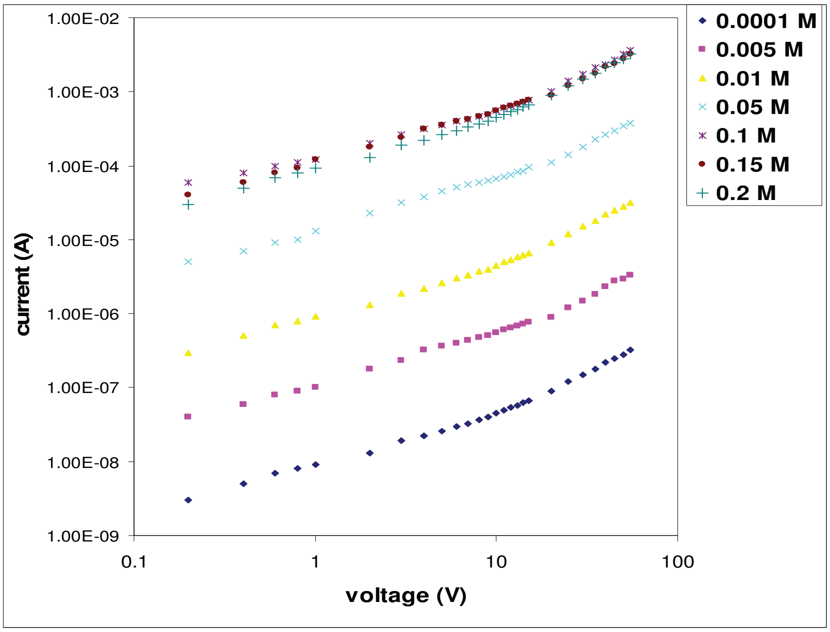
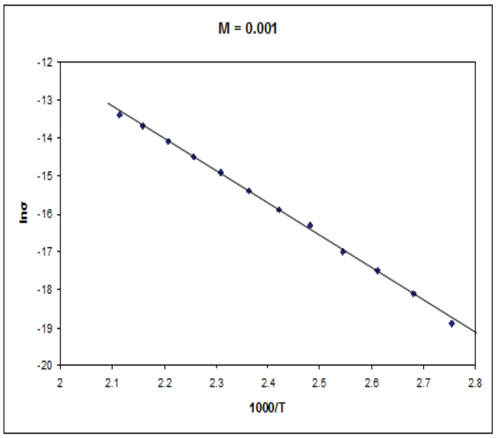
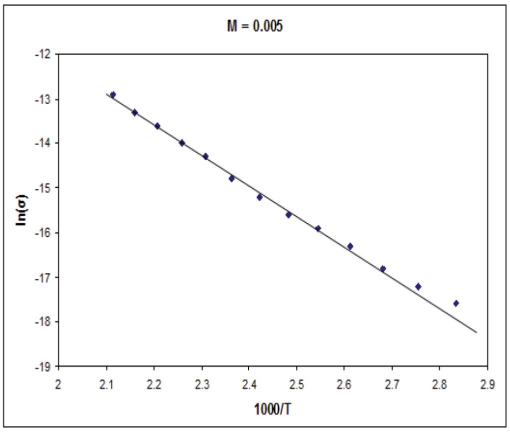
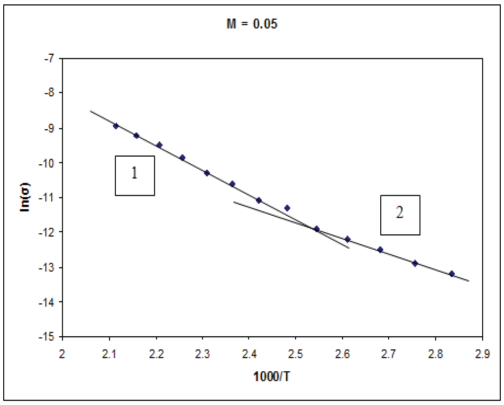


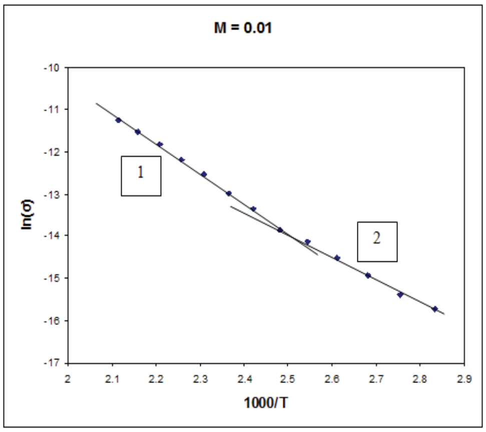
Figure (8): The conductivity of PHT as a function of concentration of TBAClO$_4$.

Figure (9) and (10) show the relation between logarithm electrical conductivity and inverse









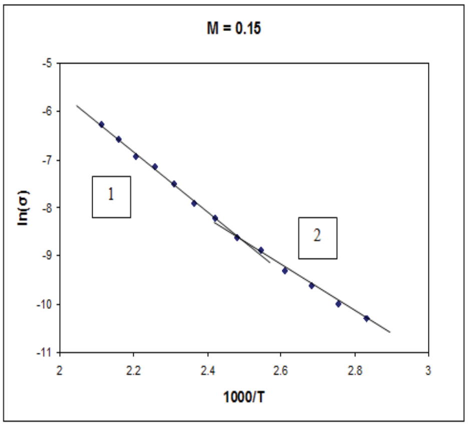


Figure (9): The electrical conductivity as a function of Inverse temperature for different doping level of PHT

Table (1) the activation energy of PHT

Concentration of $TBAClO_4$)	Ea_1 (eV	Ea_2 (eV
Undoped PHT	0.88472	----
0.001	0.74673	----
0.005	0.6565	----
0.01	0.56222	0.44322
0,05	0.54756	0.43631
0.1	0.543	0.43631
0.15	0.55172	0.48392
0.2	0.578	0.46392

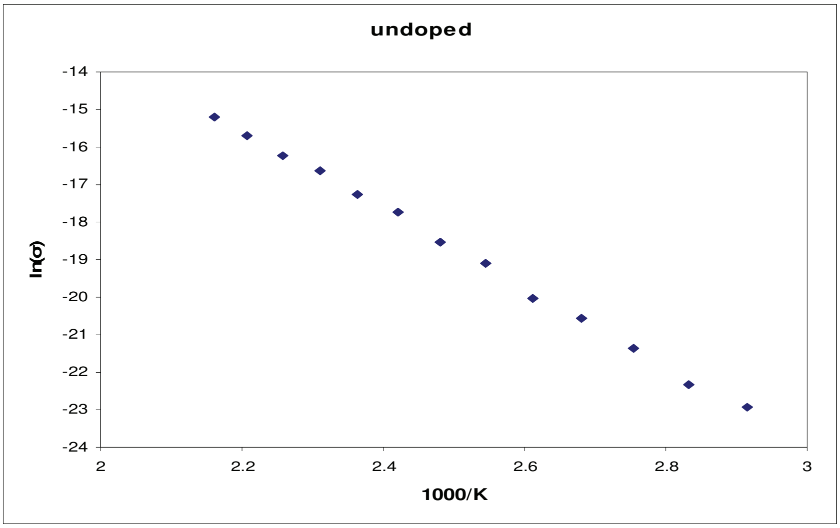


Figure (9): The electrical conductivity as a function ofInverse temperature for undoped PHT

4.Conclusions

1. The doped PHT and undoped PHT is solubility in common organic solvents.

2. The good quality films of PHT was prepared by electrochemical polymerization at current density 9.3 mA/cm^2 and $TBAClO_4$ concentration 0.1 mol/L

3. The doped films of PHT can be changed into undoped films when immersed in ammonia solution.

4. The conductivity of these films drop from (10^{-5} to 10^{-8}) S/cm when the immersing time is about 210 min.

5. The electrical conductivity increased with increasing doping level.

6. Two activation energies have been observed for the films prepared at supporting electrolyte concentration larger than (0.05 M) and one activation energy has been observed for the films prepared at supporting electrolyte concentration less than (0.05 M).

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