



Optical and Electrical Properties of Organic Conducting Polymers

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ABSTRACT

Novel electrically conducting polymeric materials are prepared in this work. Polythiophene (PT) and poly (3-Methylthiophene) (P3MT) films were prepared by electro-polymerization method using cyclic voltammetry in acetonitrile as a solvent and lithium tetrafluoroborate as the electrolyte on a gold electrode. Electrical properties of P3MT have been examined in different environments using UV-Vis absorption spectroscopy and quantum mechanical ab initio calculations. The observed absorption peaks at 314 and 415 nm, were attributed to the $n-\pi^*$ and $\pi-\pi^*$ transitions, respectively in the conjugated polymer chain, in contrast, the observed absorbance peak at 649 nm, is responsible for electric conduction. The temperature dependence of the conductivity can be fitted to the Arrhenius and the VTF equations in different temperature ranges.

Indexing terms/Keywords

polymerization of poly (3-Methylthiophene); Electrical conductivity; UV-VIS; ab initio calculations

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1. INTRODUCTION

Since the first preparation of a new class of materials, organic conducting polymer, polyacetylene [1, 2], a lot of attention has been paid to synthesize Polypyrrole, Polythiophene and Poly (3-methylthiophene). These conducting polymers can be electrochemically synthesized and have high electrical conductivity [5], they have good environment stability in Oxygen [6], there is also the possibility of application in solar energy field [7-10], and electrochromic display devices [11]. The charge carriers of these polymers have been proposed as bipolarons [12], these bipolaron are mobile along the conjugated system of a polymeric chain. The energy gap of each of PT and P3MT polymers is about 2 eV [13, 14]. The rate of change of conductivity with respect to temperature leads to two activation regions the first one shows a curvature type behavior below room temperature, called knee temperature, and above where the curves are nearly linear in behavior [13]. These activation energies are in the range of 18.92–59.27meV [15, 16]. In this work, we observed very interesting properties for these polymers, that they can be reversibly doped in an aqueous medium from a semiconductor state ($\sigma = 10^{-7} (\Omega \text{ cm})^{-1}$) to a conducting state ($\sigma = 10^{-2} (\Omega \text{ cm})^{-1}$) [17], and show a high stability, these values of conductivity depend on the order in conjugated polymers [18]. The conduction mechanism of these polymers has been widely investigated [12, 19, 20]. In these polymers, the charge carrier might hop not only across the defects in the conjugated system but also across the interchain and interfibrill gaps, many authors interpret their conductivity data in terms of variable range hopping (VRH) of carriers among atomic sites [21, 22].

2. POLYMERIZATION OF POLYMERS

We have electrochemically synthesized PT, PMT, PPY, and PANi Films, the electrolytic medium consisted of acetonitrile, LiBF_4 and monomers. When the polymerization potential value reached to its constant value, the current increases sharply and stabilizes after some minutes, then the surface of the working electrode is seen to be covered with a black highly adhesive deposit. Its conductivity allows the fast growth of a film of many μm thicknesses, preparation details are listed in Table.1 The doping process of the polymer is accompanied by a change in color from red to deep metallic green for (P3MT), from yellow to brown for (PPY) and from black to dark blue for (PANi). The dc conductivity was measured using the standard four-point method.

3. RESULTS AND DISCUSSION

3.1 Electrical properties

From figure 1, we observe an increase in the current as a function of time, indicating the formation of polymers and the polymerization reaction begin to form on working electrode. DC electrical conductivity of the samples was measured in the temperature range 300–400 K. We obtained PT and PMT films with electrical conductivities of about 80 and 35 $(\Omega \text{ cm})^{-1}$ respectively with BF_4^{-1} doping, the theoretical doping levels are approximately 0.25% or 0.33 % (one Tetrafluoroborate anion per four or three Pyrrol monomer in (PPY) units, [23]. It has been observed that the PMT conductivity increased with temperature indicating that these materials are semiconducting in nature (see figure.2). The non-linearity in Arrhenius plot for this polymer film are similar as appearing in case of electrolytes in which the ionic transport facilitates due to the segmental motion of polymer chains [24]. The electrical conductivity curve indicates two regions; this indicates that there are two conduction mechanisms associated with two activation energies and thus, we can analyze using the well-known Arrhenius equation. The activation energy values for conductivity regions (σ_I for region I, σ_{II} for region II), were found to be 10 and 58 meV respectively. From the temperature dependence results, as depicted in figure 2, it is seen that there exists a temperature, T_c , below which the conductivity plot has a curvature and above which it is linear, the region below T_c fits the empirical Vogel–Tammann–Fulcher (VTF) equation [25, 26].

$$\sigma = (A/T^{1/2}) \exp [- B/k (T - T_0)] \quad (1)$$

Where T is the absolute temperature and, T_0 the is the ideal glass transition temperature which is usually 30–50 degrees below T_c , B is an apparent activation energy, A a pre-exponential factor related to the number of carriers [27], where in high temperature fits the Arrhenius equation:

$$\sigma = \sigma_0 \exp [- Ea/ kT] \quad (2)$$

Where symbols have their usual meanings, the crossover between Arrhenius and VTF behavior of $\sigma (T)$ is widely reported and discussed in the literature [28- 31].

3.2 Optical properties

Figure 3 (a, b) represents the UV-visible absorption spectra of doped and non doped P3MT respectively, two mainly absorption bands are observed at 300-400 nm and 750-1000 nm. The absorption peak at 416 nm (2.9 eV) is attributed to the transition of electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), which is related to $\pi \rightarrow \pi^*$ electronic transition [32-34]. The other bands at 754nm (1.64eV) [35-37], and 905nm (1.36eV) are attributed to polaron and bipolar states of (P3MT), which is thought to be responsible for the electronic conduction also. In addition the absorbance at 314 nm, which has been assigned to an $n-\pi^*$ transition [38]. In the case of Polythiophene, same results have been found as shown in figure 4. We also performed theoretical calculations to justify the interpretation of our results using hyperchem program for theoretical calculation of the electronic structures of pyrrole and aniline and their radical cations by using Density Functional Theory (DFT) calculations at the B3LYP [28, 29, 39] level



combined with the 6-31+G (d, p) basis set. The simulated UV-Vis absorption peaks are in good agreement with the experimental data as shown in table 2.

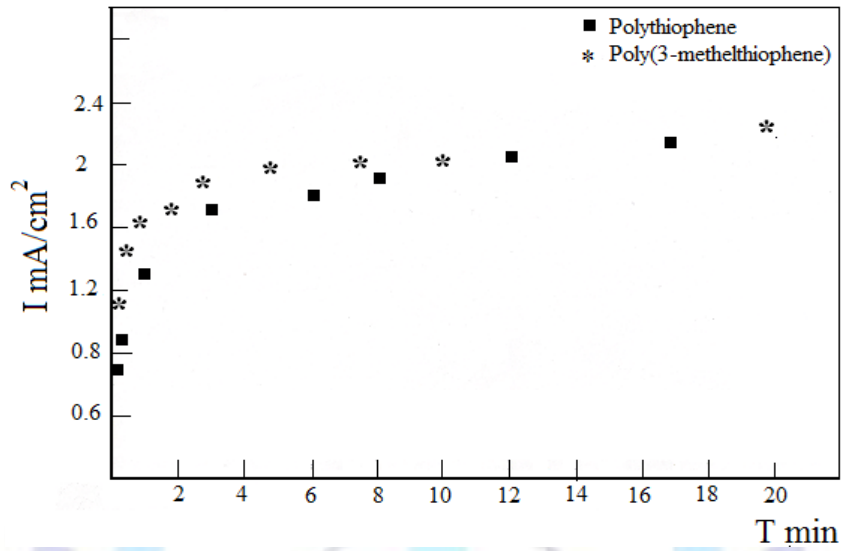


Fig 1: Polymerization time versus Current on working electrode

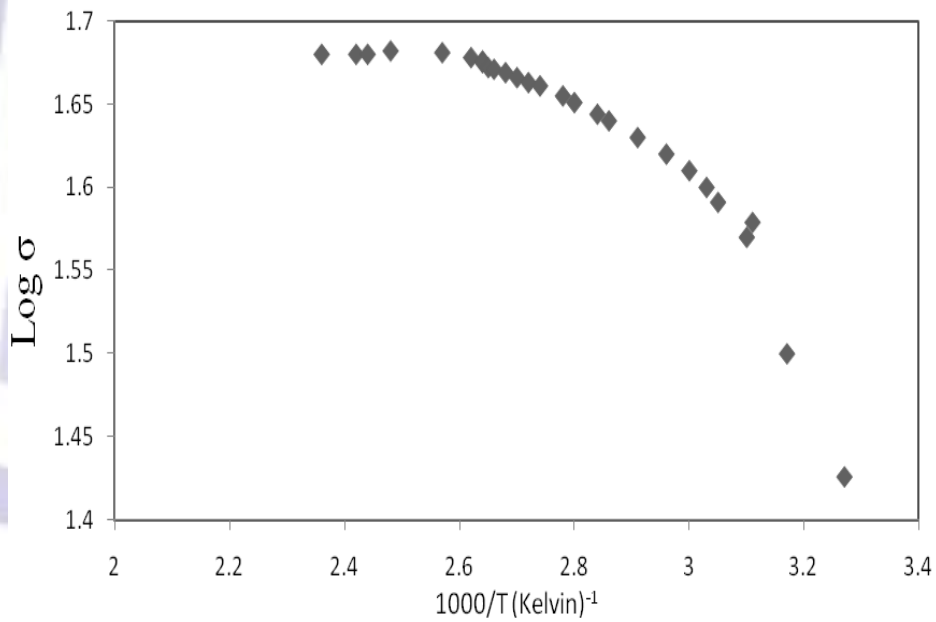


Fig 2: Variation of Electrical conductivity of poly (3-methylthiophene) with inverse temperature.

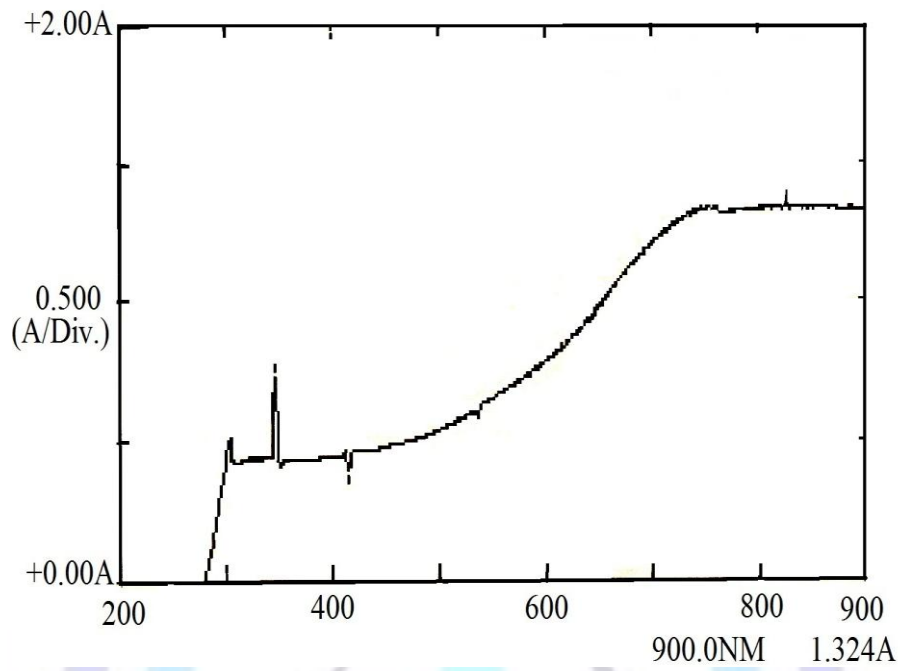


Fig 3a: UV-Vis of doped poly (3-methylthiophene)

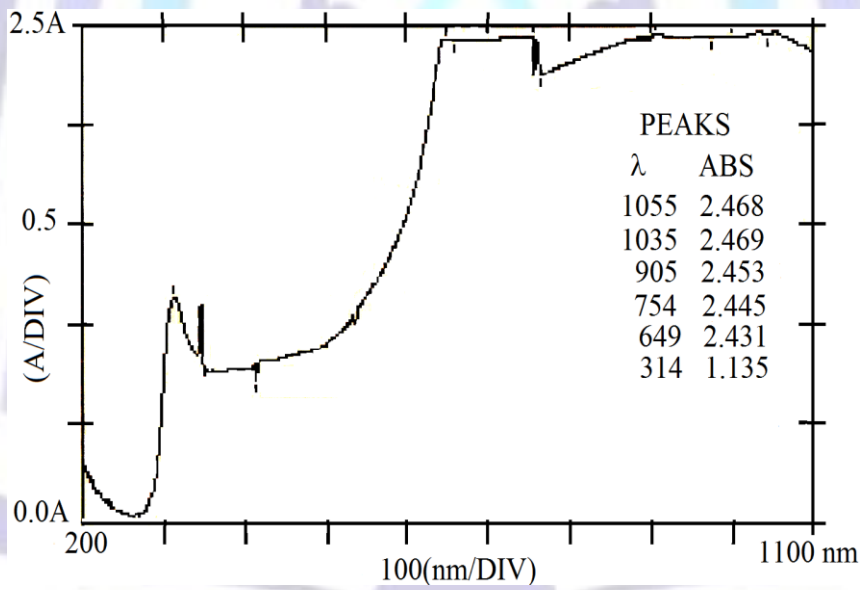


Fig 3b: UV-Vis of non-doped poly (3-methylthiophene)

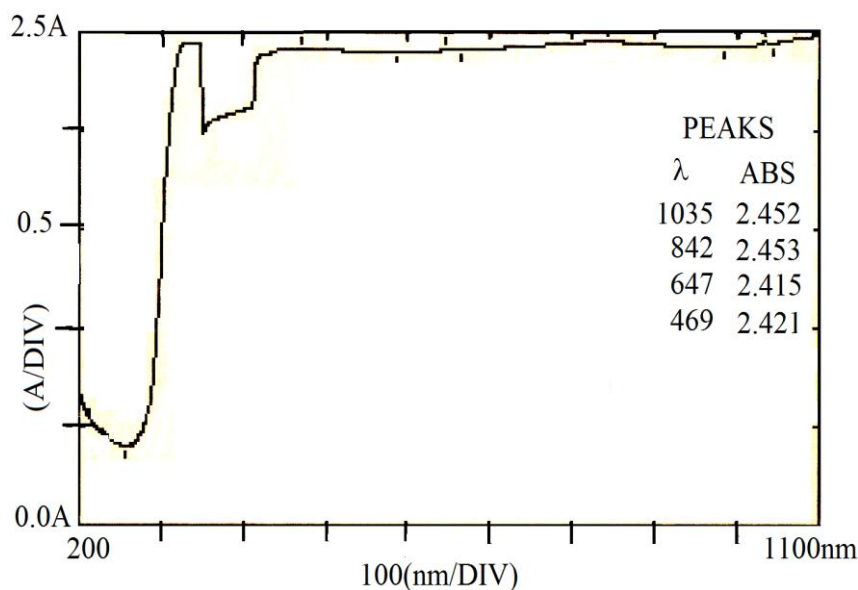


Fig 4: UV-Vis of doped polythiophene

Table 1 Oxidation Potential of various Monomers, and there polymers conductivities

Compound/Concentration	Salt/Concentration	V(SCE)/V	Solvent	$\sigma_{300k}(\Omega \text{ cm})^{-1}$
Methlthiophene/ 5×10^{-1} M	10^{-1} M	1.3	CH ₃ CN	10^2
Thiophene/ 10^{-1} M	10^{-1} M	1.3	CH ₃ CN	10^2
Pyrrole/ 10^{-1} M	10^{-1} M	1	CH ₃ CN	10
Analine/ 10^{-2} M	10^{-1} M	1.3	CH ₃ CN	5×10^2

Table 2 Theoretical and Experimental optical frequencies of monomer and polymer

Theoretical calculation of frequencies(nm)	Experimental frequencies(nm)		Assignments
	PT	P3MT	
3MTh			
313 or 349	469	415	$\pi \rightarrow \pi^*$
440	647	649	polaron
972	1035	1035	bipolaron

Abbreviations: Th=thiophene; 3MTh=3-Methelthiophen; PT = polythiophene; P3MT = poly(3- Methelthiophene)

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