

The Electronic transitions of polyaniline doped with p-toluene Sulfonic acid

الانتقالات الالكترونية للبولي أنلين المشوب بحامض الباراكولون سلفونك PAni-PTSA

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Conducting polymer application

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Abstract:

Polyaniline doped with p-toluene Sulphonic acid PAni-PTSA was synthesized by using a new oxidative chemical polymerization method. The polymer solution deposited on, glass and Aluminum substrate by spin coating technique. Fourier Transform Infrared (FTIR) spectra, and ultraviolet visibility (uv- vis. absorption) spectra, were used to characterize the molecular structures of PAni-PTSA and electronic transition of polymer. The optical analyses indicated that the transition was direct transition with energy gap about 2.5eV. The electrical properties were measured by two probe method. The conductivity values of this polymer is about $(8 \times 10^{-4} \text{ S/cm})$.

Keyword: Polyaniline doped with p-toluene Sulphonic acid, Electrical properties, optical properties.

المستخلص

حضرت مادة البوليانلين المشوب بحامض الباراكولون سلفونك بالطريقة الكيميائية مستخدم مادة مؤكسدة جديدة. المحلول لبوليمري PAni-PTSA رسبت على قواعد من الزجاج والألمنيوم بواسطة الطلاء بالبرم. جهاز مطياف FTIR ومطياف UV استخدمت في تشخيص التركيب الجزيئي والانتقالات الالكترونية للبوليمر PAni-PTSA. تحليل النتائج الضوئية تشير إلى انتقالات الكترونية مباشرة بفجوة طاقة حوالي 2.5 إلكترون فولت. الخواص الكهربائية قيست بطريقة المجسين. التوصيلية الكهربائية لهذا البوليمر المحضر حوالي $(8 \times 10^{-4} \text{ S/cm})$.

Introduction

Poly aniline (PAni), occupies the most important place among the conducting class of polymers[1]. It has attracted great attention in the field of active materials for solar cell applications such as in organic light emitting diodes (OLEDs) [2], field-effect transistors (OFETs) [3] and solar cells [4-6], gas sensor [7,8] and Protection against corrosion[9]

Polyaniline is a typical phenyl based polymer having chemically flexible-NH-group in the polymer chain flanked by phenyl ring on either side[10]. It represents a class of macro molecules whose electrical conductivity can be varied from insulator to conductor by the redox process[11]. The conducting state of polyaniline is easily obtained by simple protonation by reacting with acids and the process is also reversible. The availability of wide range of dopant such as. Mineral, carboxylic and sulfonic acids make the polyaniline chemistry much more interesting for controlling the various properties such as solubility, solid state, ordering, micro and nano-sized materials etc[12,13]. Recently, polyaniline PAni (prepared by chemical method) is dissolved in water or organic solvent and then used as hole injection layer on fabrication organic solar cells[14,15].

In the present work, (PAni) doped with p-toluene Sulphonic acid PAni-PTSA was synthesized by chemical method. This polymer characterized by (FTIR) spectra and ultraviolet visibility (UV-VIS) absorption spectra. The optical and electrical properties were studied.,

Experimental Syntheses of PAni-PTSA

polyaniline was synthesized by the oxidation polymerization of aniline in acidic media. Using a method similar to the reported by (M.Jayakannan (2006)[16].

The polymerisation was initiated by the drop wise addition of the oxidizing agent $(\text{NH}_4)_2\text{SO}_4$ in an acidified solution (Para-Toluene sulphonic acid (PTSA)) under constant stirring at $(0-5\text{ }^\circ\text{C})$. (PTSA) was prepared from dissolving 28.5gm of Para-Toluene Tosyl chloride in 15ml of distilled water. The mixture was heated up to $90\text{ }^\circ\text{C}$ for 3.5 hr, then condensed and dried by oven at temperature $50\text{ }^\circ\text{C}$. The melting point of (PTSA) was measured and it was found to be $(103-106)\text{ }^\circ\text{C}$. The monomer to oxidizing agent ratio was kept as (1:1). After complete addition of the oxidize agent the reaction mixture was kept under constant stirring for 24hr's . Precipitated polymer was filtered and washed with distilled water until the filtrate was colorless. Finally, the polymer was dried in oven at $70\text{ }^\circ\text{C}$ for 12 hr .

Thin films preparation

After the syntheses(PAni) by chemical oxidation method . (PAni) powder was added to formic acid solvent and mixed under constant stirring at room temperature. After completion the mixing process, the polymer was filtered under vacuum, Then the mixture was deposited on another glass for measured optical properties or Aluminum for electrical properties ,using spin coating method. The spin speeds in the range $(1000-5000)$ rpm and spin time of 60 sec. Thin films were then placed on a hotplate with temperature of $90\text{ }^\circ\text{C}$ for a period of 15 min for drying substrates. The thickness of the obtained (PAni-PTSA) films is found to be $15\mu\text{m}$ for structure glass/polymer for optical properties. The thickness for electrical properties about $(\sim 50\mu\text{m})$ and area (0.0314 m^2) for structure AL/polymer/AL .

Results and Discussion

The preparation PAni-PTSA powder was characterized by (FTIR) spectroscopy kind Unicam Spectrophotometer (Sp3-3005) .ThisFTIR spectrum is record of the absorption of electromagnetic radiation by the sample in the range 4000 to 400 cm^{-1} .

The absorption of infrared radiation results in changes in the amplitude of vibration of various parts of an organic molecule . Each band in the spectrum results from the absorption of radiation of a specific frequency which excites a particular bond or group of bonds in the molecule causing the atom, to vibrate with respect to each other . Most of the important peaks in infrared spectra result from changes in the frequencies of the bond stretching or bonding . The amount of energy required to excite the stretching and bonding modes depends upon the strength of the bond and the masses of the atoms attached to the bond.

Figures (1&2) show the presence of the expected functional groups of PAni doped with PTSA and undated PAni were tabulated at Table 1. For example the band at 3463cm^{-1} related to hydrogen bonding (NH). The two bands appeared at 1569cm^{-1} , and 1475cm^{-1} corresponding to the stretching vibration of the quinoid and benzenoid ring, respectively. The bands at (1310cm^{-1}) can be assigned to the (C-N) mode. The band appearing at (810 cm^{-1}) , was attributed to an out of plane (C-H) vibration of quinoid rings.

The effect of PTSA doping with PTSA on the FT-IR spectrum (Figure (1)) show the same spectrum of undoped PAni (figure (2)) except decrease the intensity of Hydrogen bonding (-NH group) at (3300 cm^{-1}) which converted to salt $(-\text{N}^+\text{H}_2\text{CH}_3\text{phSO}_3^-)$ [17]. The group of PAni agreement with [17-19] .

Table (1): The location of the most important peaks of (FTIR) spectrum Of doped and undoped PAni

Functional group of PAni	C-H cm ⁻¹	C=O cm ⁻¹	C-C cm ⁻¹	C-N cm ⁻¹	C=C Quinod cm ⁻¹	C=C Benziod cm ⁻¹
PAni-PTSA	810	-	1132	1301	1569	1475
undoped PAni	831	-		1303	1587	1500
Ref.[18]	-	-		1250	1583 1567	1500 1483
Ref.[17]	805	-		1299	1572	1485
Ref.[19]	783	1744		1308	1599	1503

The absorption coefficients (α) have been estimated after correction for the reflection losses. The absorption coefficient is given by [20,21].

$$\alpha = \frac{(2.303) A'}{d} \quad \text{-----} 1$$

where d is the thickness of the sample and A' is the absorption after correction which can be estimated as:

$$A' = A - A^0$$

where A is the absorbance ,A₀ is the correction for the reflection.

The absorption coefficient was estimated after correcting for reflection losses[20]. Fig .(3) show the absorption coefficient(α) as a function of photon energy ,hv, . The absorption data were analyzed for evidence of inter band transition in fundamental absorption region. The data was fitted to one-electron theory of Bardeen et al [22] in order to obtained information about the direct and in direct band gap. For high absorption coefficient $\alpha > 10^4$ that refer to direct transition[22-23].

The optical band gap energy (Eg) is determined using the fundamental law[22] .

$$\alpha = \frac{A (Eg - hv)^n}{hv} \quad \text{-----} 2$$

Where α is the absorption coefficient, (hv) is photon energy, A is a proportionality constant, and (n=1/2) for direct transitions and n=2 for indirect allowed transition.

The optical band gap energy (Eg) can be determined by plotting $(\alpha hv)^2$ versus (hv) as shown in fig. (4) . The plot of $(\alpha hv)^2$ agent hv yields a straight line ,for value of $\alpha > 10^4$ which show good fit with eq(2) , extrapolation of the straight line to $(\alpha hv)^2 = 0$ gives the direct energy gap The allowed direct transition optical gap is found about 2.5 eV for the (PAni-PTSA) films. That is argument with [17]

Fig(5) shows current –voltage characteristic of AL/Polymer /AL device at room temperature.The figure. shows ohmic behavior dominant at voltage rang (2 – 10)V

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($2 < V < 10$) . At a high voltage larger than 10V ($V > 10$)V The current deviate than ohmic law, ($I = KV^n$) Where K and n are constant ,one of that mechanism of charge transport, space charge limited conduction SCLC[24] . The electrical conductivity at ohm law $2 < V < 10$ about 8×10^4 S/cm .

Conclusions

- 1- PANi-PTSA , was characterize by FTIR spectrophotometer and the result agreement with other research.
- 2- the energy gap of material about 2.5 eV
- 4- current -voltage characteristic of AL/PAni-PTSA/AL show ohmic behavior at voltage between 2 V and 10V ($2 < V < 10$) with electrical conductivity about 8×10^4 S/cm²

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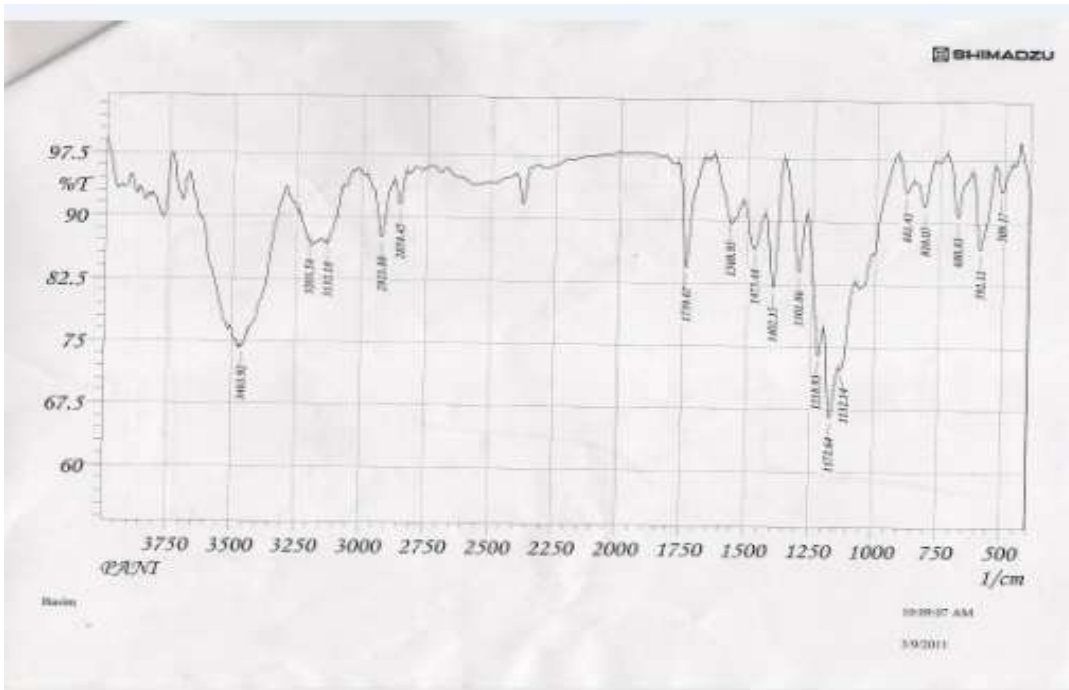


Fig .(1) FTIR spectrum for doping PANi –PTSA

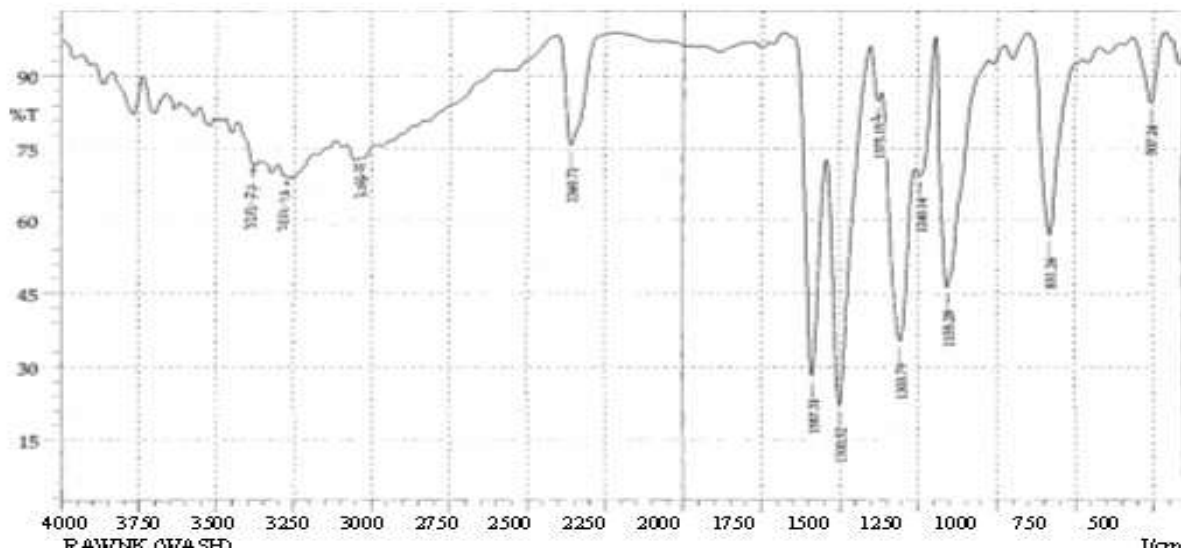


Fig .(2) FTIR spectrum for undoped PANi

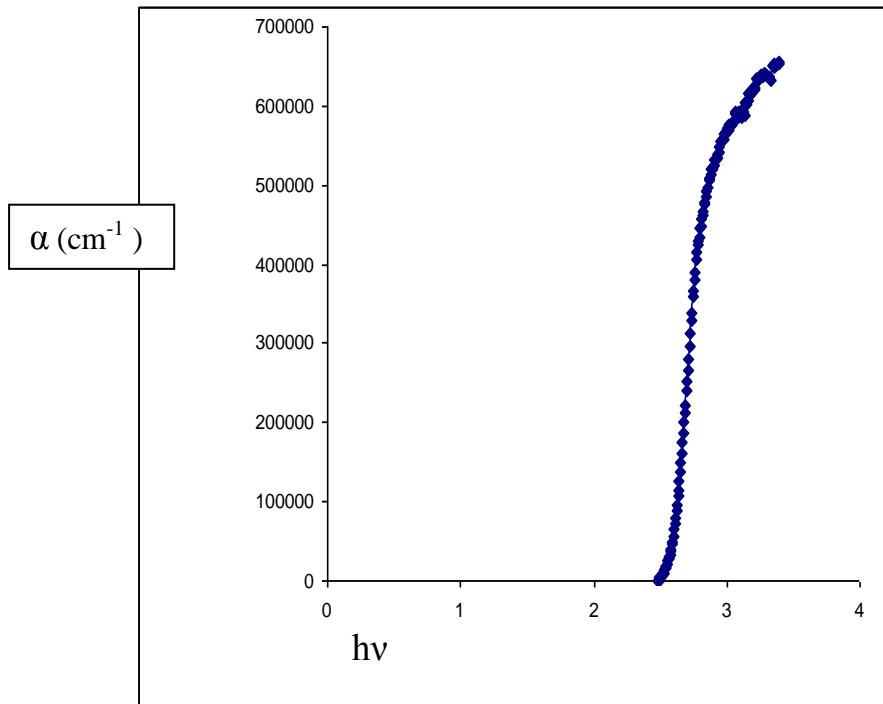


Fig.(3): Absorption coefficient(α) as a function of photon energy ($h\nu$) of PANi- PTSA

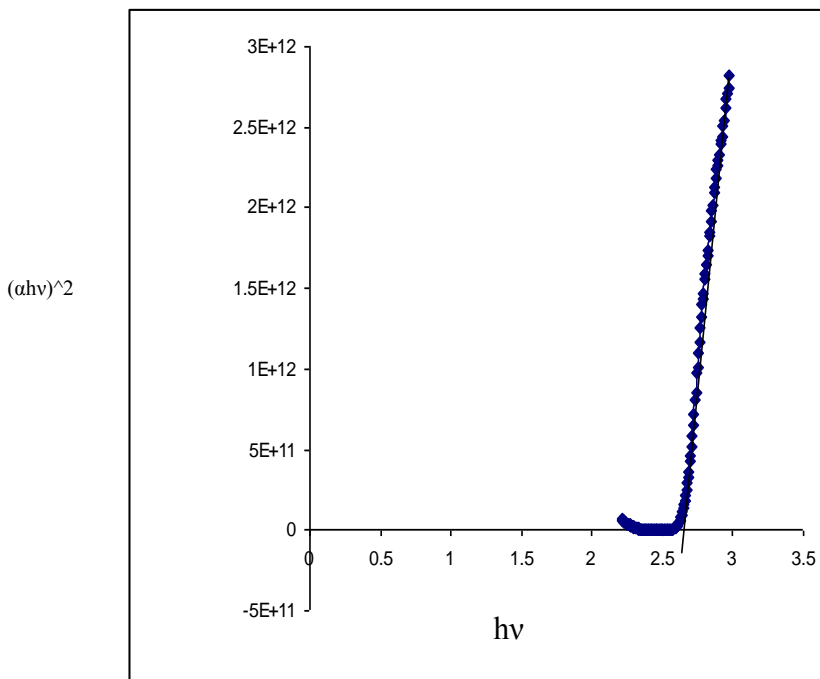
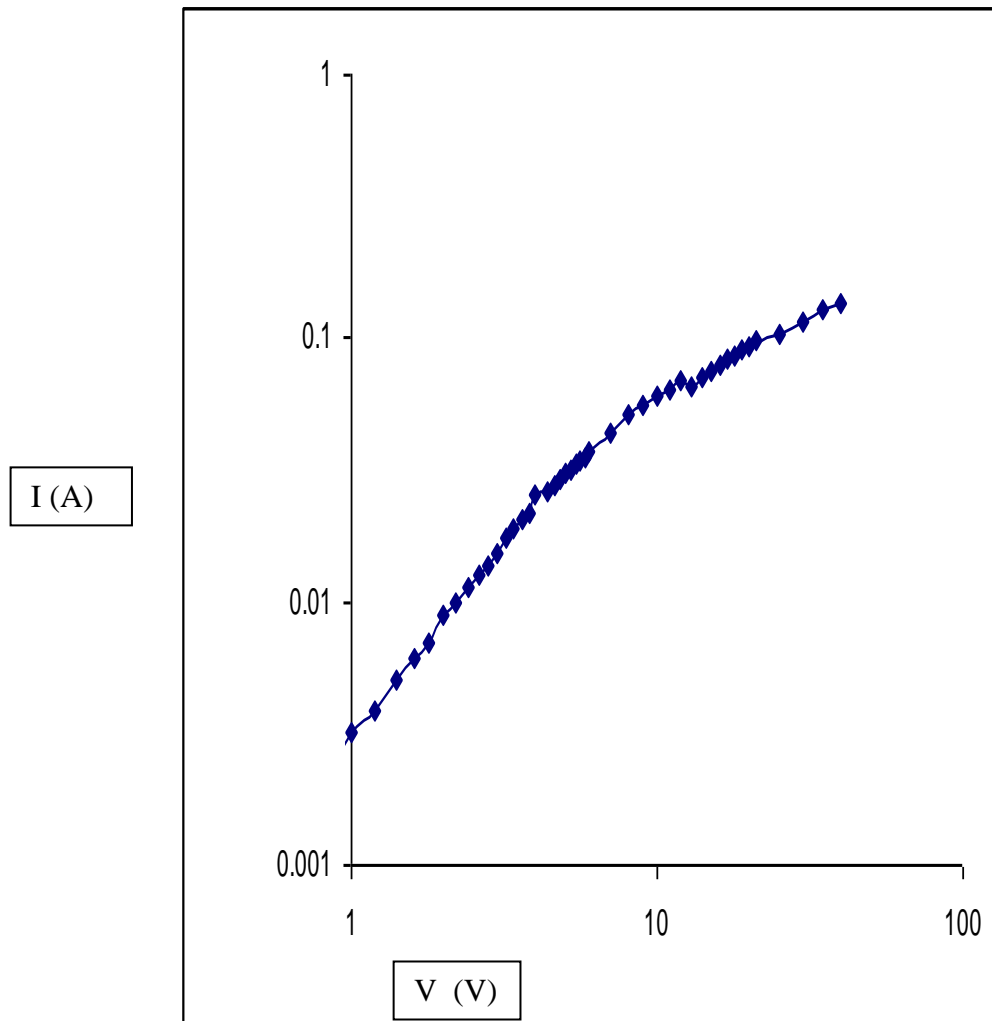


Fig.(4): $(\alpha h\nu)^2$ as a function of $h\nu$ of (PANi) doped with PTSA



Fig(5):I-V characteristic of PANI doped with PTSA at room temperature.