Synthesizes and study some electrical properties of poly(o- toluidine) doped with Para toluene sulfonic acid (POT-PTSA).

H. F. Hussein *, K. M. Ziadan **,and K. I. Ajeel *

****Dep.of physics, college of Education university of Basrah-Iraq***

***** Dep.of physics, college of Science university of Basrah-Iraq***

Abstract:

poly(o-toluidine) doped by p-toluene sulphonic acid (POT-PTSA) was synthesized by using oxidative chemical polymerization method. The polymer solution deposited on, Aluminum, interdigitated finger electrode, and silicon wafer by the use of spin coating technique. The thickness of the samples is measured by the use of Ellipseometry spectroscopy.

Transform Infrared (FTIR) spectra, Raman spectroscopes, and ultraviolet visibility functional group (UV-VIS. absorption) spectra, were used to characterize the molecular structures of (POT-PTSA). The surface imaging technique of AFM is used to get information about film's morphology. The electrical properties were investigated . The conductivity values of this polymer is ($2.46x10^{-5}$ S/cm), and increasing with increase temperature. The activation energy was determined from this curve was 0.211eV for POT-PTSA.

Introduction

Polymers have been used extensively as passive components in electronic devices because of their light weight, flexibility, corrosion resistance, high chemical inertness, electrical insulation and ease of processing. In 1975, an inorganic conjugated polymer, polythiazyl, (SN)x, was discovered, which possesses metallic conductivity and becomes a superconductor at 0.29 K [Birks, (1973)]. As a result, other polymers having a π-electron conjugated structure, such as polyaniline (PANI), poly(o-tolidine) ,polypyrrole (PPy), polythiophene (PT), polyfuran (PFu), poly(p-phenylene) (PPP) and polycarbazole (PCz) [Phillips et al, (1993), Pethrick et al, (1993)] have been synthesised and studied.

Electrically conducting polymer composed of macromolecules having fully

conjugated sequences of double bonds along the chains.

The bulk electrical conductivity of an intrinsically conducting polymer is comparable to that of some metals and results from its macromolecules acquiring positive or negative charges through oxidation or reduction by an electron-acceptor or -donor (charge transfer agent), termed a dopant. Examples of intrinsically conducting polymers are polyacetylene, polythiophene, polypyrrole, or polyaniline. Unlike polymeric electrolytes, in which charge is transported by dissolved ions, charge in intrinsically conducting polymers is transported along and between polymer molecules via generated charge carriers (e.g., holes, electrons). An intrinsically conducting polymer should be distinguished from a conducting polymer composite and from a solid polymer electrolyte[Bansi, (2002)].

In this article, the polymer thin films prepared were analysized by the use of (FT-IR) and Raman spectroscopes to determine the active groups of the chemical bonds. To identify the nature and structure of the surfaces of the prepared samples and to measure the partial size of the grain, Atomic force Microscopy was used.

Experimental

(O-Toluidine) monomer was purified by distill at under reduced pressure. The monomer was polymerised by drop wise addition of the oxidizing agent $(NH_4)_2SO_4$ in an acidified solution (P-Toluene sulfonic acid), (PTSA) which prepared by dissolving 28.5gm of P-Toluene Tosyl chloride in 15ml of water. The mixture was heated up to 90 ºC for 3.5 hr's, then condensed and dried by oven with temperature of 50 ºC for 24 hr's. The (MP point) of (PTSA) (103-106)ºC. (POT-PTSA) was synthesized by disolved (0.27 mol) of (O-toluidine) in 1M PTSA and cooled to (0 ^{o}C). Oxidizing agent ammonium persulphat $(NH_4)_2SO_4$ dissolved in 1M PTSA, added slowly and very carefully to the flask. After that, the reacter mixture was kept under constant stirring for 24hr's.

The resultant greenish emeraldine base was filtered, washed successively with water, methanol and acetone to remove the un-reacted starting materials and oligomers, then was dried in vacuum oven at 80 °C for 12 hr's.

10mg of (POT-PTSA) was dissolved in (1m) formic acid (HCOOH), the polymer deposited on silicon wafer, Aluminum, and interdigitated finger substrates by spin coating method with (2000rpm) spin speed and (35nm) thickness is measured by the use of Ellipseometry spectroscopy. Interdigitated comb-like electrode structures have frequently been suggested as ultra sensitive for chemical structure films. Electrode consist of interdigitatted Aluminium lines on an glass substrate . It can be achieved using interdigitated electrodes to measure the

surface conductivity of the samples. The samples were put on hotplate (heater) to raise a temperature from room temperature (R.T) to (90°C) .The measurement was carried out using digital Thermometer. The electric properties were measured by two probe method. Interdigitated electrod used to measured surface conductivity. Fig (1) show Interdigitated electrode.

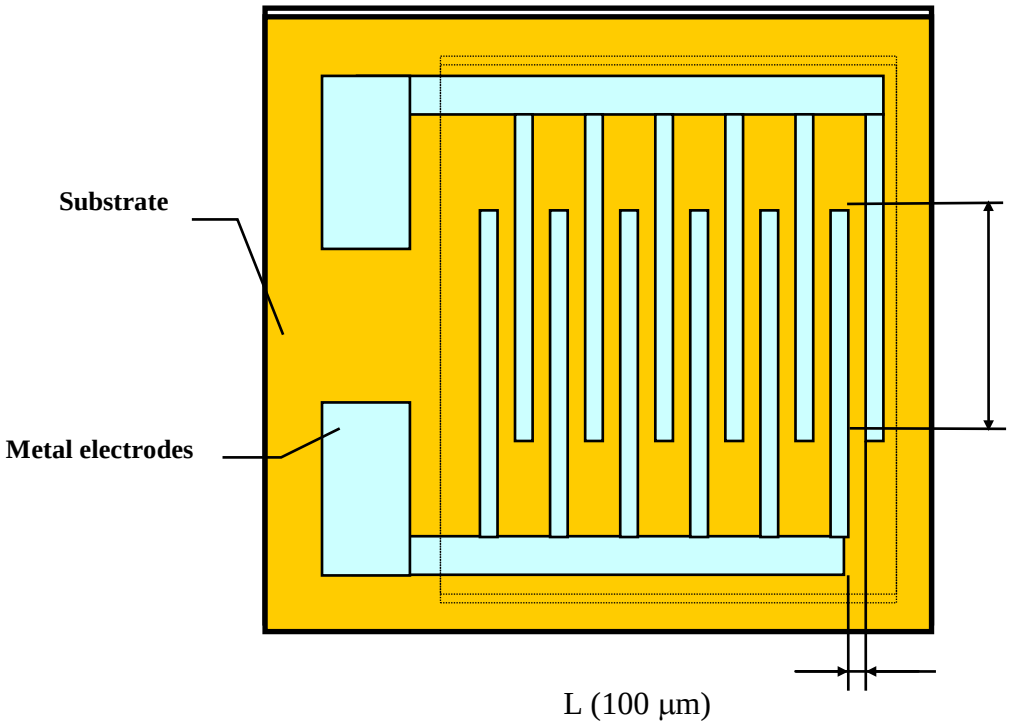

Fig. (4-1): A schematic diagram of interdigitated finger electrode.

mode of aromatic rings. Normally, at lower electrode potential ,this band is considered to be the characteristic of (C-H) bending vibration mode of benzoid ring [Quillard et al, (2005), Boyer et al, (2000)]. However the absence of this band at lower potentials in the present case and its appearance and gradual increase the intensity with the anodic sweep suggest this to be the feature

Result and discussion

The Raman spectra of (POT-PTSA) was recorded from (200 to 2000cm^{-1}) is shown in figure (2) and in table (1). A weak band appearing at (1100cm^{-1}) which corresponds to the (C-C) stretching vibration in the methyl substituted semiquinone and quinine rings [Savitha and Sathyanarayana, (2004)]. Another band at (1177 cm^{-1}) can be attributed to the (C-H) bending vibration

groups	Vibrations(cm^{-1})	Reference [10]
C-C stretching	1100	1122
C-H bending vibration mode of aromatic rings	1177	1177
C-N stretching vibration	1269	1269
C-n stretching vibration	1330-1370	1338, 1369

Table (1): Showed that Raman wave number for selective bands of (POT-PTSA).

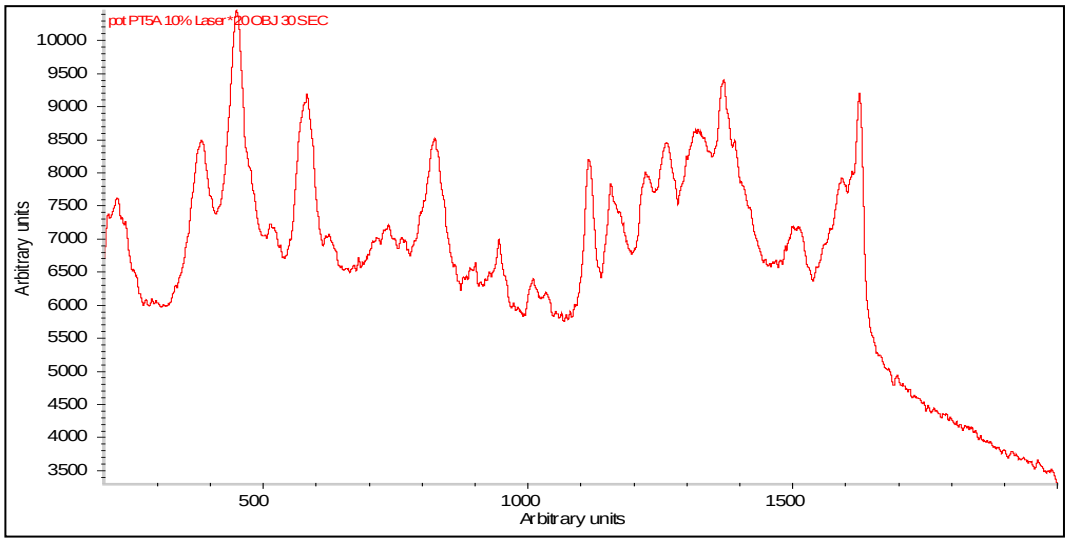

Fig. (2): Raman spectra of (POT-PTSA).

The polymer was characterised by (FTIR) spectroscopy as a powder, the FTIR spectra were recorded in figure (3), and showed that the presence of the expected functional groups, for example the band at 3300cm^{-1} related to hydrogen bonding (NH), band at 2910 cm^{-1} can be assigned to the stretching vibrat of the ($-CH_3$) alphatic[Abdiryim et al, (2005), Mucuk et al, (2009)]. The two bands appearing at (1590cm^{-1}, and1480cm^{-1}) corresponding to the stretching vibration of the quinoid and benzenoid ring, respectively. The bands at (1375cm^{-1}) is due to the symmetric deformation of methyl group. The bands at (1320cm^{-1}, and1210cm^{-1}) can be assigned to the (C-N) mode. Whereas the bands at (1150cm^{-1}, 1110cm^{-1}, and1105cm^{-1}), are the

characteristic bands of(C-H) vibration, The three bands appearing at(810cm^{-1}, 880cm^{-1}, and 940cm^{-1}) were attributed to an out of plane (C-H) vibration of quinoid rings. The presence of bands at (1590cm^{-1}, and1480cm^{-1}) clearly shows that the polymer is composed of amine and imine units. The spectrum decrease the intensity of Hydrogen bonding (-NH group) at (3300 cm^{-1}) which converted to salt (-$N^{+}H_2CH_3phSO_3$) [Savitha and Sathyana (2004)].

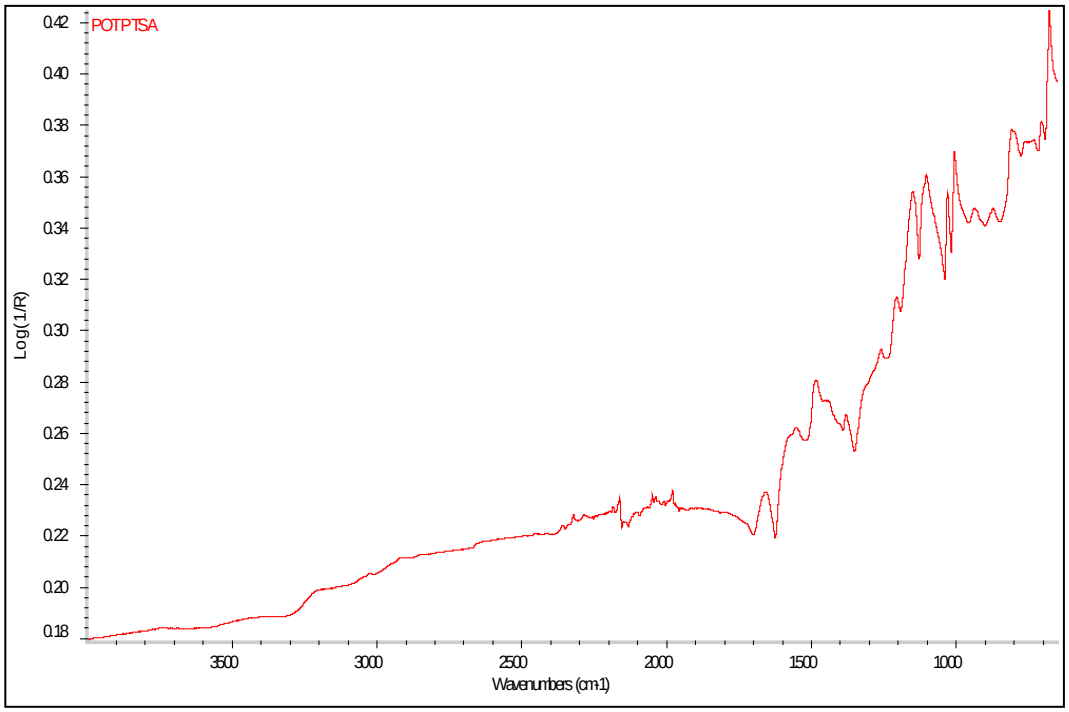

Fig. (3): FT-IR spectra of (POT-PTSA)

It can be achieved using interdigitated electrodes to measure the surface conductivity of the samples from the following relationship.

$\sigma_s = [I/V]\,[L/Wt\ell]$ …….. (1)

where, t is thickness of polymer, W is the distance fingers (10mm), ℓ is number of fingers is to be (10), and L is the space between electrodes (100μm).

So that;

$$\sigma_s = \frac{I}{Vt}\left(\frac{100\times10^{-6}}{10\times10\times10^{-3}}\right) = \frac{I}{Vt}(10^{-3}\,S/m) \quad \ldots\ldots(2)$$

The electrical properties of conducting polymer measured by two probe method. The circuit for the electrical properties consist of:

1- keithley electrometer (Model 65174) was used, to measure a current as a function of the applied voltage.
2- The electrometer is capable of supplying a voltage in range (1-100V) in steps of (1 or 5V) and used to measure currents.

3- Intelligent temperature controller (Model ITCU).
4- A cryostat (oxford instrument) contains the sample holder and connected with the temperature control.
5- The measuring system was interfaced to a computer

Figures (4) shows the current – voltage characteristic for POT doped with PTSA (Al/POT-PTSA/Al) at temperature range of (293-333)K, the thickness of POT-PTSA was 35nm. The Ohmic behavior was noticed for all applied voltage.

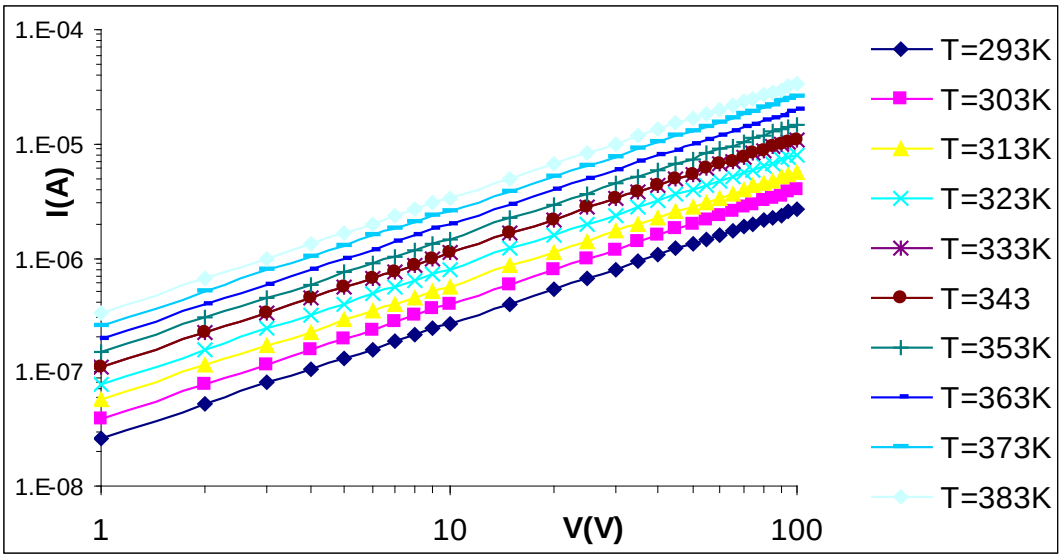

Fig. (4): The (current-voltage) characteristic for (POT-HCL) at different temperatures (293-383K).

The electrical conductivity was calculated by equation (1) for different temperature. Figure (5), show the electric conductivity as function of reciprocal temperature for POT-PTSA.

The electrical conductivity , in POT-PTSA was 2.4 x 10^{-5} S/cm at room temperature. This behaviour is showing that the doping created a bipolaron state in energy gap [Ziadan, (1997)].

The activation energy was determined from this curve was 0.211eV for POT-PTSA. The value of activation energy for POT-PTSA was small which indicates that the localized slate in POT-PTSA, so that need lower energy for transition [Jacqueline, (1989)].

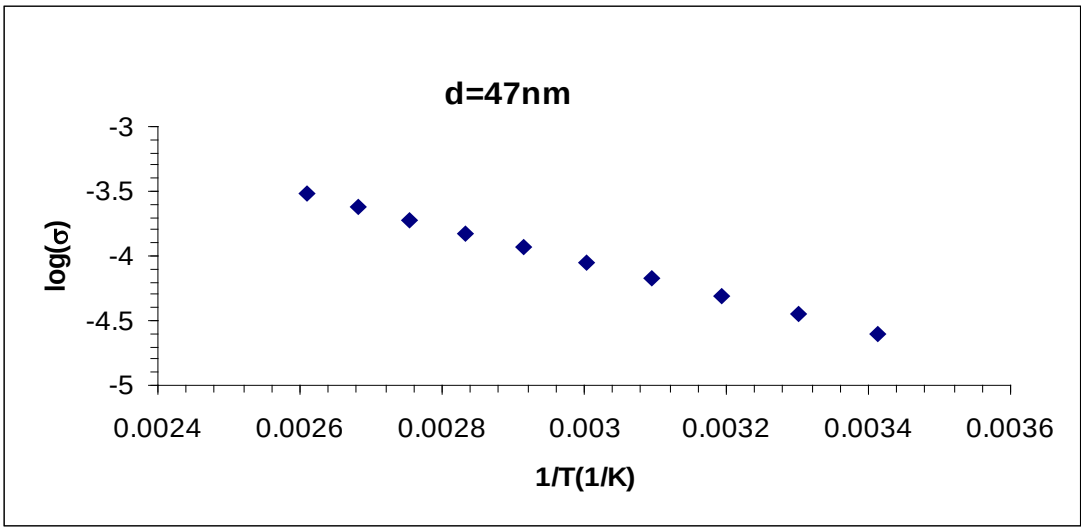

Fig. (5): The conductivity as a function of (1/T) for (POT-PTSA) film.

conclusion

Poly(o-tolidine) doped with para toluene solphonic acid (POT-PTSA) was synthesized by chemical oxidation polymerization method under typical conditions such as low temperature and well purified. The samples were prepared by spin coating method. The films were homogenous with relatively smooth surfaces. The thickness of the samples is measured by the use of Ellipseometry spectroscopy.

The polymer analyzed by Raman spectroscopy, and FTIR, to determine the active groups of the chemical bonds. Also, the structure of the surfaces of the prepared samples measured by force Microscopy was used.

The electric conductivity was studed and was found that the thin films correlate with the ohmic behaviour at the measured voltage range (1-100V) for the polymer (POT-PTSA). The effect of temperature on the electric properties of these thin films is also studied.

The study shows that the electric conductivity increases with increases temperature. This study shows that the activation energy (0.211 eV) for POT-PTSA.

References

* J.B. Birks, *Organic Molecular Photophysics*, John Wiley & Sons, London,1973.
* J.E. Guillet, Polymer Photophysics and Photochemistry, Cambridge University Press, Cambridge, UK, 1985.
* D. Phillips in Photochemistry and Polymeric Systems, Eds., J.M. Kelly, C.B. McArdle and M.J.de F. Maunder, The Royal Society of Chemistry, Cambridge, UK, 1993, 87.

* P.J. Flory, Principles of Polymer Chemistry, Cornel University Press, Ithaca, NY, USA, 1953.
* R.A. Pethrick, B. Wandelt, D.J.S. Birch, R.E. Imhof and S. Radhakrishnan in Photochemistry and Polymeric Systems, Eds., J.M. Kelly, C.B. McArdle and M.J.de F. Maunder, The Royal Society of Chemistry, Bath, UK, 1993, 68
* Bansi D. Malhotra," Handbook of Polymers in Electronics", First Published in Rapra Technology Limited, Shawbury, Shrewsbury, Shropshire, SY4 4NR, UK, 2002.
* Savitha, P. and Sathyanarayana. D," Copolymers of aniline with o- and m-toluidine: synthesis and characterization",Volume 53, Issue 1, 106–112, 2004.
* S. Quillard, K. Berrada, G. Louam, S. Lefrant, M. Lapkowski, and A. Pron, New. J. chem. 19, 365, 1995.
* M.Boyer,S.Quillard,G.Louarn,G.F royer,and S.Lefrant, "Vibrational study of the FeCl3-doped dimer of polyaniline; A good model compound of emeraldine salt", JOURNAL OF PHYSICAL CHEMISTRY B 104: 38. 8952-8961 ,2000.
* S. Bilal, A. ul- Haq Ali Shah, and R. Holze, "A correlation of electrochemi" Electrochimica Acta, 54, 4851-4856,2009.
* T .Abdiryim, Z. Gang, and R. Jamal, “Synthesis and characterization of POT Doped with Organic sulfonic acid by solid-state polymerization”, Journal of Appl. Polymer science, Vol.96, 1630-1634(2005).
* Z. Mucuk, M. Karakisla, and M. Sacak, International Journal of polymer Anal," synthesis of poly(O-Toluidine) in DMF/ water Mixture using Benzoyl peroxide", Charact, 14, 403-417, 2009.
* P.Savitha, and D.Sathyarayana, “ Donor- Acceptor- based poly(tolidine-Co-Chloroaniline)s synthesis and characterization”, Indian Instiute of scince, Bangalore,560012, 2004.
* K. M. Ziadan " Electrical & optical properties of conducting polymers (PT, PT/ PTFE, PT/ PVC and application in rechargeable behavior". PhD thesis Basrah university, Iraq 1997.
* Jacqueline.I.Kroschize, “Electrical and Electronics properties slate of the Art-componcluding encyclopedia repnnl", john wiley &suns new jurn.(1983).

تصنيع ودراسة بعض الخواص الكهربائية لـ (Poly (o-toluidine المشوبة بالـ باراتلولوين سلفونيك أسد (POT-PTSA)

*حسين فالح * - كريمة مجيد ** - خالد عجيل **

* قسم الفيزياء – كلية التربية – جامعة البصرة – العراق*

** قسم الفيزياء – كلية العلوم – جامعة البصرة - العراق*

الملخص

حضرت المادة البولمرية بولي تلوين المشوبة بحامض الباراتلوين سلفونيك بطريقة البلمرة بالاكسدة الكيمياوية . رسب المحلول البولمري على الالمنيوم والسليكون بطريقة الـ Spin Coating . تم قياس السمك للعينات بطريقة مطياف الـ Ellipsoemetry . شخصت العينات بواسطة FTIR والرامن Raman ومطياف (UV-VIS) . تم استخدام AFM للتعر على طبيعة سطح الغشاء . درست الخواص الكهربائية للاغشية وكانت التوصيلة الكهربائية (2.46×10^{-5} s/m) وهذه تزداد بزيادة درجة الحرارة حسب طاقة التنشيط وكانت حوالي 0.211 الكترون فولت .