

**Synthesis and study some optical properties of conducting polymer poly
P-anisidine(PPANS)) doped with camphor
sulphonic acid (CSA)**

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Abstract

Poly(p-anisidine) (PPANS) was prepared by chemical methods. Camphor sulphonic acid with weight ratio (0-40)% used to doped P(P-anisidine). Thin films of the doped each ratio of Poly (P- anisidine) conducting polymers were prepared by spin coating method on glass slid , then placed on a hotplate with temperature of 90°C for a period of 15 min for drying. The polymer was characterized by FT-IR spectroscopy and DXR . The optical properties was measured by UV-VIS spectrophotometer. The optical data analyses indicated that the transition was direct transition . All these results were discussed.

Keyword :Conducting polymer , Poly(p-anisidine (POANS) doped with Camphor Sulphonic acid , optical properties.

Introduction

Intrinsic conducting polymers (ICPS) offers great technological application such as, static films for transparent packaging of electronic components [Karicheldorf, (1992)]. Electromagnetic shielding [Apstein *et al.*, 1992]. Rechargeable batteries [3] light-emitting diodes [4 Yang *et al.*, 1995]. Protection against corrosion Kinllen P.J 2002 [5]. Conducting paints and glues [Hang W.S *et al.*, 19916]. Among the aniline (ANI) family, O-anisidine, M-anisidine and P-anisidine (PANS) are shown in figure 1

P-anisidine appears as a good candidate for polymerization and characterization, particularly, for data acquisition leading to establish monomer/polymer structure correlations. [7-9 Mazur 2007, Mazur *et al.* 2007] Table 1. show The chemical properties of P-anisidine

Its synthesis may be accomplished either by chemical or electrochemical [10-12 Kareema & Wejood 2012, Otero *et al.* 1993, del Valla, *et al.* 2009], means, each possessing advantages and disadvantages. Poly(O-anisidine) is an important conjugated conducting polymer. It is relatively easy to be prepared. The major problem of its successful utilization is poor mechanical properties like lower conductivity and poor solubility in common organic solvents. Recently much progress has been made to improve these poor mechanical properties by using different organic acids as dopant or stabilizer. This dopant, like organic acid and acrylic acids, is introduced by simple secondary doping or by blending the polymer with doping species such as acrylic acid. This chemical oxidative polymerization method provides polymers better solubility in

common organic solvents such as m-cresol, NMP, DMF, etc(13.14 Roza A. Salih 2012. del Valle M.A, 2012].

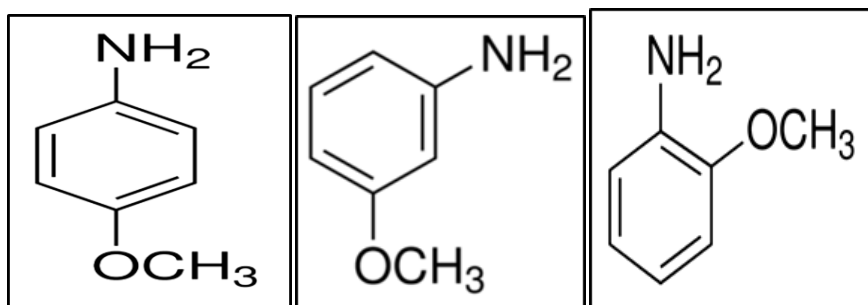


Fig.1 anisidine (PANS)

(A) O-anisidine (B) -M-anisidine (C)- P-anisidine

Table 1.The chemical properties of P-anisidine

Chemical structure	NH₂,C₆,OCH₅
Molecular Weight	123.2g/mol
Melting point	57⁰C
Boiling point	246⁰C
Density	4.3 g/cm³

Experimental

Poly(P-anisidine) was synthesized by the oxidation polymerization of P-anisidine in acidic media. Using a method similar to the reported by (M.Jayakannan (2006)[15].P-anisidine (0.0274 mol) was dissolved in (0.1 M) HCL and taken in a three necked flask and cooled to (0°C) using ice. to this a pre-cooled solution of (0.0343 mol) ammonium persulphate in (0.1M) HCl was added dropwise after 5 min green colored poly (P-anisidine) ,HCl was obtained precipitate from the solution. The polymerization was further proceeded by stirring at 30°C for 24h.

The precipitate was filtered washed with (0.1M) HCL for three time and stirred in a flask containing (0.1M) a aqueous ammonia solution (112.5 ml) in order to naturalized the blue

precipitate was stirred for 3h at room temperature to ensure the completion of de-doping the resultant blue emeraldine base was filtered, washed successively with water , methanol and acetone .It was dried in a vacuum oven at 80°C for 12h . Powder poly-P-anisidine was dissolved in Chloroform CH₂Cl₂ the solution of (PANS) added on the camphor sulphonic acid (CSA)solution as drops with moving stirrer, the weight ratios of CSA were (5%,10%,15%,20%,25%,30%,40%) .

The last process was dropping the mixture on glass slide and kept for dry for 48h at room temperature . The absorbance and transmittance before and after doping were studied at the range(200-900nm) using the (UV) spectrophotometer.

Result and discussion

The structure of the various samples was investigated by X-ray diffraction. All the scans were recorded in 2θ region of $(0-60)^\circ$. Structural information and crystallinity of the pure PANS, and doped PANS-CSA are seen in Figs.2(a), (b). X-ray diffraction pattern of pure powder of POANS and doped PONS-CSA are shown. Characteristic peaks of semi-crystalline at $2\theta = 20$ and weak peak at 29° . The structure of POAS is not affected with doping.

The d-spacing values were calculated using Bragg's equation [Jeno S 2007].

$$2d \sin \theta = n\lambda \text{ -----(1)}$$

The results are tabulated in Table 2. The d-spacing was calculated from 2θ and reported to be

characteristic distance between the ring planes of benzene ring in adjacent chains or the close contact distance between the two adjacent chains [MacDiarmid A.G. and A.J. Epstein 1993].

The average grain size (G.S) of the semi-crystalline material can be calculated from the X-ray spectrum by means of Full Width at Half Maximum (FWHM) method (Scherrer relation) [Cullity B.D. and S.R. Stock 2001]:

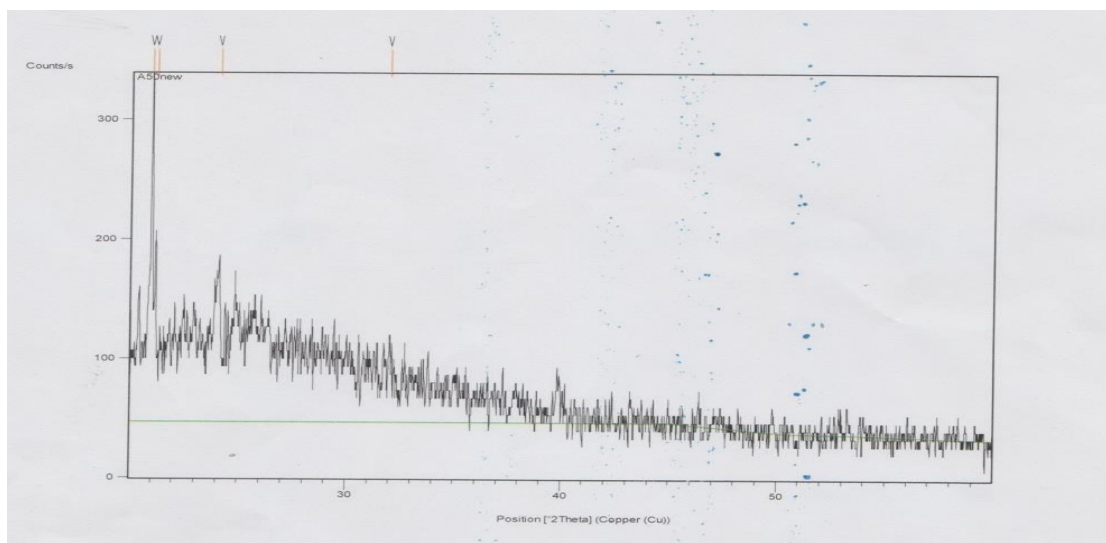
$$GS = \frac{A\lambda}{\Delta\theta \cos \theta} \text{ -----(2)}$$

Where $\Delta\theta$ is the full width at half maximum of the XRD peak appearing at the diffraction angle, θ is a Scherrer constant, usually assume $A = 1$.

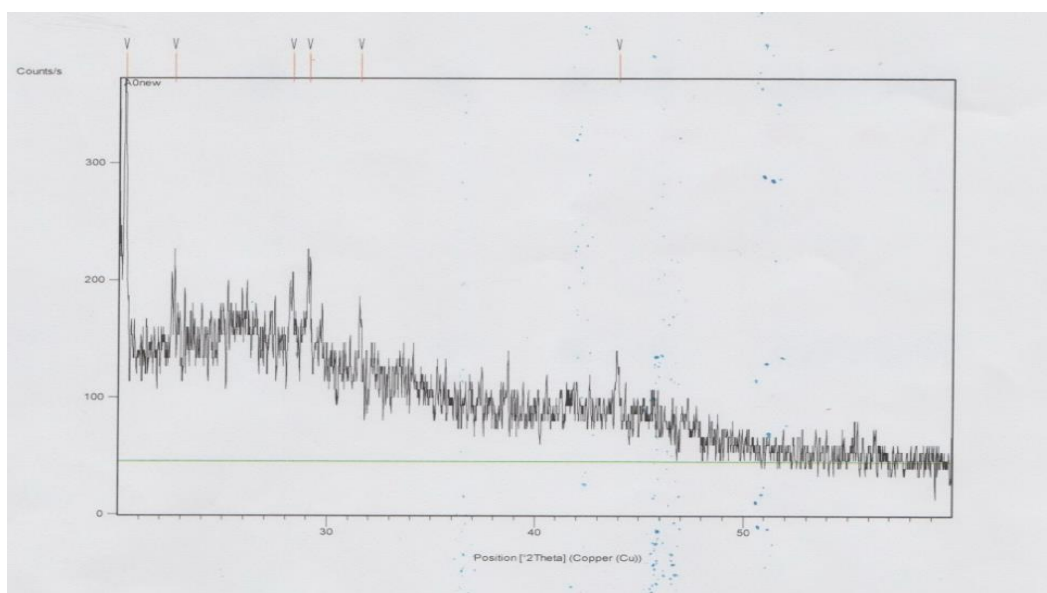
The results of doped and undoped grain size (GS) are tabulated also in Table 2

Table.2 The grain size of doped and undoped poly p-anisidine

polymers	2θ	FWHM Deg..	d- space Drg..	Grin Size A°
PANA	20.2783	0.1181	4.379 34	28.4
PANS-CSA	20.9297	0.0590	4.24052	75.78



a



B

Fig.2 XRD of poly (P-insidene),(a)pure PPANS (b) PPANS-CSA

Infrared spectroscopy is one of the most powerful analytical techniques, that its provides useful information about the structure of the molecules and bonding quickly.

The characterization of undoped and doped poly (P- anisidine) are show in Figure (3)&(4) . These were recorded in the wave number range

4000-500 cm^{-1}

Table (3 tabulated the wave vector of functional groups of (PANS & PANS-CSA). The doping with camphor sulphonic acid (CSA) appear at wave vector(1172) cm^{-1} Which is refe to S=O and 1737.74 to C=O . The group at POANS agreement with[20,21]

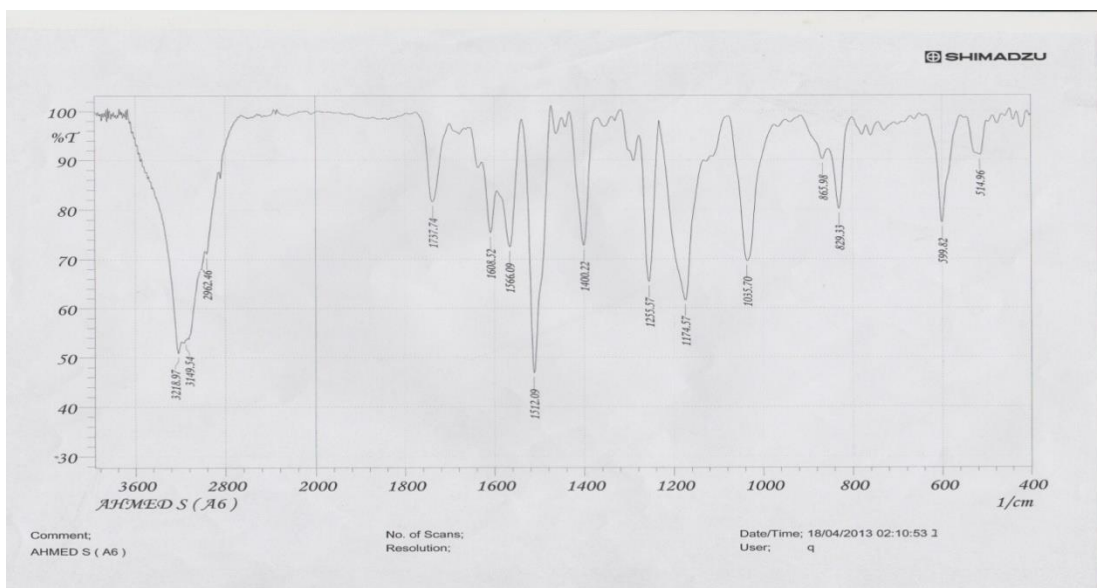


Fig.(3) : FTIR for pure poly (o-anisidine)

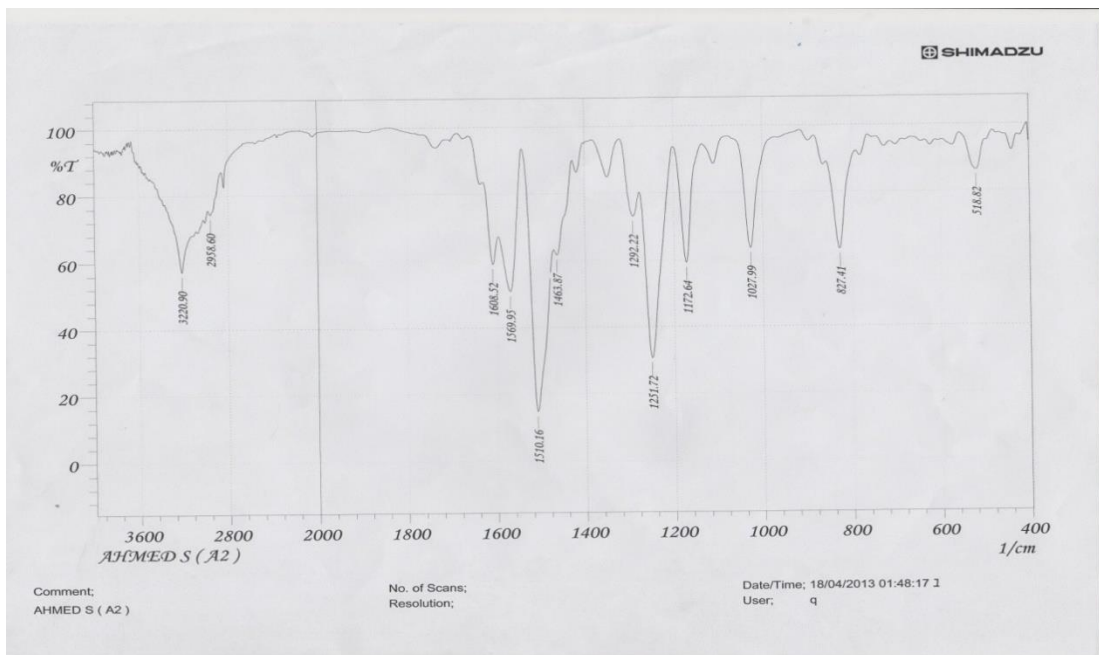


Fig.(4): FTIR for doping poly (P-anisidine)

Table (3) The functional group of P0l(P-ainisdine)

Functiona l group of POANS	N-- H str.	C- H Ali p.	C= O	N-H blen d	C=C Quin od	C= C Ben z	C-N	C-N- S-O	C-O- C	C-H
Functiona l group of undoped POANS	322 0	295 4 283 8	-	160 8	1569	146 3	1251	-	1027	827
Function groups of doped POANS	321 8 314 9	296 9	173 7	160 8	1569	146 3	1251	1174	1023	865
[Roza A. Salih 2012]	306 8	297 0		161 0	1524	145 4	1259	1100-		826
[Vuayan M. and V. Krishnan 1992]	322 0	299 2		160 0	1550	145 5	1250	1120		800 850

The absorption coefficients (α) have been estimated after correction for the reflection losses. The absorption coefficient is given by[wosr T.S. 1959]:

$$\alpha = \left(\frac{2.303}{d}\right) * A' \quad \text{----(3)}$$

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

$$A' = A - \frac{A^0}{d} \dots\dots\dots(4)$$

where A is the reflection. A^0 is the correction for the absorbance

The thickness of samples measured by coating thickness measurement equipment provide from oxford instruments[Ali S.Alis & Karema M.Ziadan 2007]

Fig.(5 show the absorption coefficient(α) as a function of photon energy , $h\nu$, of different specimen (undoped PANS and PANS-CSA, 10%,20%, ,30%,40%. All specimen show systematic behavior varies photon energy, $h\nu$, .

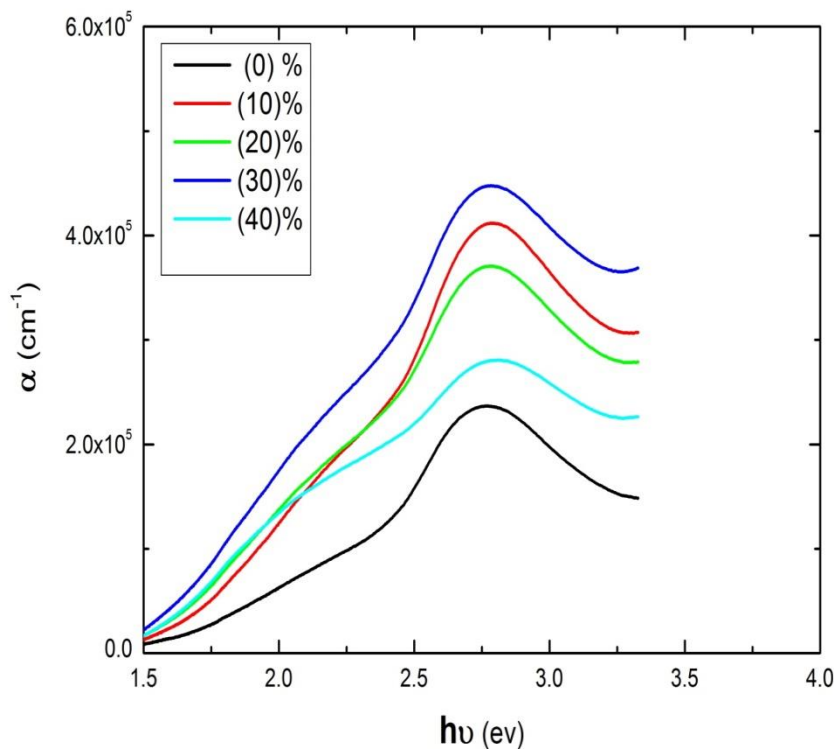


Fig. 5 the absorption coefficient as a function of the photon energy for all doping ratio

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 [Bardeen *et al.* 1956] 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[Bardeen *et al.* 1956, Kareema *et al.* 1998].

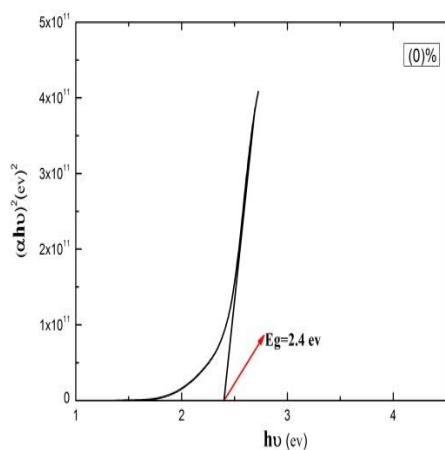
$$\alpha = \frac{B(h\nu - E_g)^{1/2}}{h\nu} \text{ -----(5)}$$

where B is constant in depended of photon energy and depending on the probability of transition and E_g direct energy gap. Fig.(6show the photon energy dependence on $(h\nu\alpha)^2$ for undoped and doped PANS

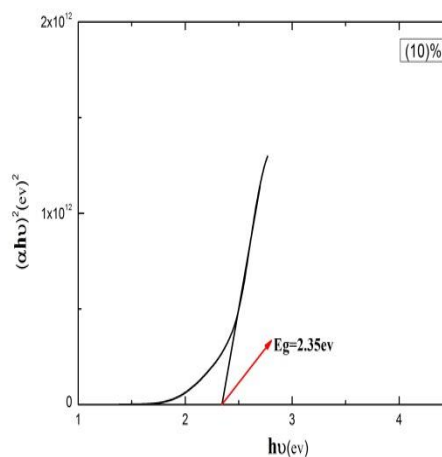
respectively . The plot of $(h\nu\alpha)^2$ against $h\nu$ yields a straight line for value of $\alpha > 10^4$ which show good fit with eq(5) , extrapolation of the straight line to $\alpha = 0$ gives the direct energy gap , which are tabulated at (Table 4).

Fig7 shows direct energy gap as a function different weight ratio of camphor sulphonic acid. The curve show that the energy gap decrease with increase the weight rate of doping (camphor

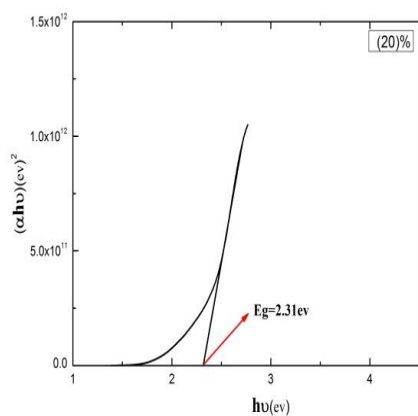
sulphonic), because the doping create polaron states in band gap and that is increase with increase doping then become a polaron band between valance band a conduction band for all details about a mechanism of conductivity in conducting polymers [Kareema M.ziadan,2012].



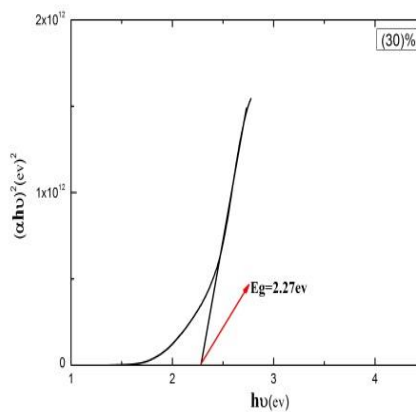
A



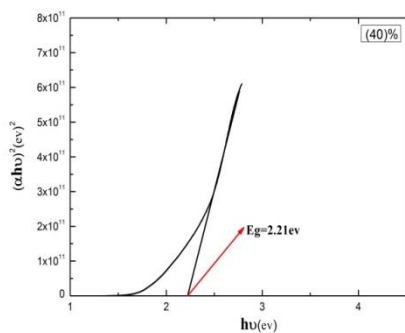
B



C



D



E

Fig6 :the direct energy gap of doped and undoped PPANS

A undoped,,B doped with 10%,C doped with 20%,D doped 30% And E 40%

Table (4) Show the E_g of doped PPANS

Weigh ratio W%	E_g (eV)
0%	2.4
10%	2.35
20%	2.31
30%	2.27
40%	2.21

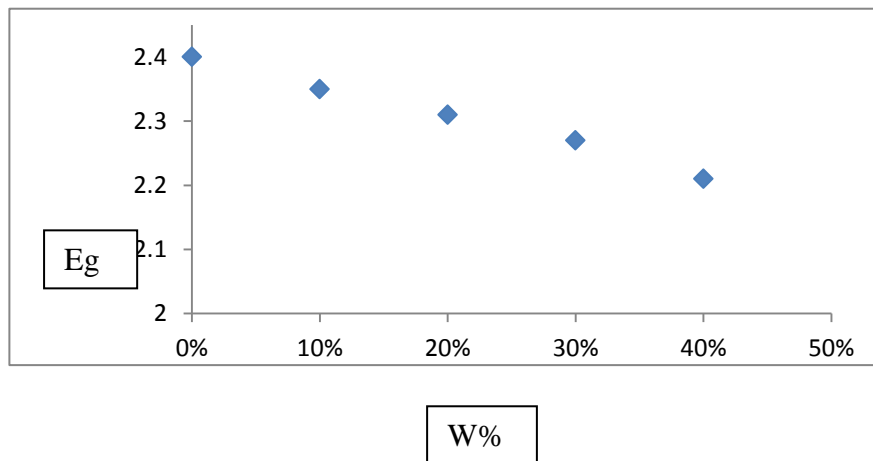


Fig.7:Direct energy gap as a function of Weigh ratio for P(P-anisidine)

Conclusion:

Poly (P-anisidine) synthesis by chemical polymerization, then doped with different ratio of camphor sulphonic. The polymer was characterizes by XRD and FTIR in order to show doping with CSA . The optical properties analyses show direct energy gap .This gap decreases as doping increases. So that the doping increase localized stat and the conductivity in poly (P-inisidine).

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تحضير ودراسة بعض الخواص الضوئية للبوليمر الموصل بولي بارا انسدين المشوب بحامض
الكامفورسلفونيك (PPSNs-CSA)

احمد سعود عبد ، كريمه مجيد زيدان و علي قاسم عبد الله
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الملخص

تم تحضير البولي بارا انسدين بطريقة كيميائية زحامض الكامفوريك بنسب وزنية (0-40)% استخدمت في تشويب البولي بارا انسدين . الاغشية الرقيقة لكل نسبة تشويب من البوليمر الموصل بولي بارا انسدين حضرت بطريقة الطلاء البرمي على صفائح من الزجاج وبعدها تتوضع على صفيحة ساخنة بدرجة 90 درجة مئوية لمدة 15 دقيقة للتجفيف.البوليمر شخص بواسطة اشعة السينية ومطياف الاشعة تحت الحمراء FTIR.الخواص الضوئية قيست بواسطة مطياف ال (UV-VIS). القاسات حلت و اشارت الى انتقالات مباشرة .وكل النتائج نوقشت.