دراسة بعض الخواص البصرية للبوليمر المشترك بولي (انلين – مشترك – الكحول الاليلي)

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Study of Some optical properties of Copolymer Poly (Aniline-CO-Ally Alcohol)

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Abstract:

Thin films of poly (Aniline-CO-Ally Alcohol) and poly (Aniline-CO-Ally Alcohol) doped with HCl of thickness (135,185)nm respectively were prepared by Casting method.

Absorption and transmittance spectra were obtained at room temperature.

These measurements have been recorded in the wave length range (200-900) nm using the (UV) spectrophotometer.

The optical properties measurement included optical absorption coefficient (α), direct energy gap (E_g), non linear optical susceptibility (X^3), single oscillator energy (E_0), dispersion energy (E_d), moment of dielectric constant (M_{-1},M_{-3}).

The allowed direct transition band gab is found (2.83eV) for poly (Ain-CO-AA) and (2.25eV) for poly (Ain-CO-AA-HCl).

Key words: Poly Aniline, copolymer, Ally Alcohol, optical properties, thin films.

الملخص:

تضمن هذا البحث دراسة غشاء للبوليمر المشترك بولي (انلين –مشترك – الكحول الاليلي) و بولي (انلين –مشترك – الكحول الاليلي) المشوب بحامض HCl بسمك (135،185) نانومتر على التوالي حيث تم ترسيب الأغشية الرقيقة على قواعد من الزجاج بطريقة الصب.

تضمنت القياسات البصرية على قياس الامتصاصية و النفاذية لمدى الاطوال الموجية (200–900) نانومتر باستخدام جهاز UV.

تم حساب معامل الامتصاصα ، فجوة الطاقة المباشرة Eg كما تم حساب بعض الثوابت البصرية المتمثلة بطاقة التفريق Ed و طاقة التذبذب الاحادي E0 و معاملات الزخم (M−1 , M−3) والتأثرية اللاخطية من الرتبة الثالثة X3 للبوليمر النقي والمشوب بحامضHCl .

لاحظنا وجود فجوة طاقة مباشرة مقدارها 2.83eVللبوليمر النقي(poly (Ain−CO−AA بينما اصبحت 2.25eVللبوليمر المشوب poly (Ain−CO−AA−HCl).

الكلمات المفتاحية: بولي انلين، البوليمر المشترك، الكحول الاليلي، الخواص البصرية، أغشية رقيقة.

Introduction:

The study of optical absorption, particularly the absorption edge has proved to be very important for elucidation of the electronic structure of the materials. It is possible to determine indirect and direct transition occurring in band gap by optical absorption spectra [1]. The refractive index of the optical materials plays an valuable role in the optical devices and the changes in refractive index and optical band gap are the fundamental parameters of an optical material, because these are closely related to the electronic properties of the material. The evaluation of refractive index and absorption edge of optical materials are of considerable importance for applications in integrated optic devices such as

switches, filters, and modulators, etc., where the refractive index of an optical material is the key parameter for device design [2].

The study of copolymer polymerization is one of the important studies in the development of new polymers with different specifications than the original materials, and it is considered the source of many of the currently known industrial polymers [3].the polymer under study poly (Aniline-CO-Ally Alcohol) is a polymer that was prepared using chemical polymerization method, study of its electrical properties and determination of the conductivity mechanism as well as the study of adhesion of the polymer membrane with different bases [4].

Synthesis of poly(Aniline-CO-Ally Alcohol):

Three-necked flask equipped with thermometer and stirrer, charged with (1.25mol) of (aniline) monomer provided by(BDH chemical Hd.UK), which dissolved with 0.1M HCl provided by (ANALYT) and cooled to (0°C) using ice, (7.8gm) of Ammonium persulphat $(NH_4)_2S_2O_8$ provided by(MERCK) (oxidizing agent) dissolved in (0.1M) HCl, added slowly and very carefully to the flask. Then we add (0.79mol) of ally alcohol provided by (SHER MAN chemicals LTD) dissolved with (0.1M) HCl from one of the Three-necked flask. After completion of adding the oxidizing agent to the reactor mixture was kept under constant stirring for 24hr's. The product of the greenish-black precipitate of the polymer was isolated by filtration and washed (15 mol) ammonia solution (NH_3) provided by (Fluka) was added to the polymer and stirred for (3hr's) at room temperature to ensure the completion of de-doping. The resultant blue emeraldine base was filtered, washed successively with water, methanol and acetone to remove the unreacted starting materials, then was dried in vacuum oven at (60°C)for (12hr's). the general structure of the poly (Aniline-CO-Ally Alcohol) is given in figure (1).

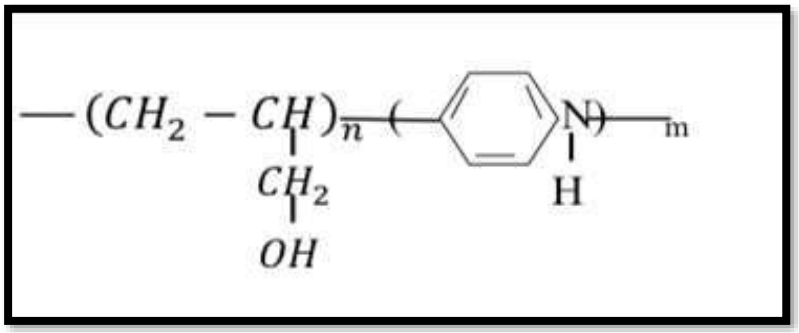

Fig (1) The chemical structure of poly (Ain-CO-AA) [4]

The FT-IR spectra were obtained using FT-IR model (s8400). FT-IR spectra were recorded in order to investigate the interaction between the poly aniline and poly allay alcohol Fig (2) show the spectra of the polymer before adoption. Fig (3) show the spectra of polymer after adoption.

There are a number of important differences between FT-IR spectrum of pure polymer and adopted polymer with HCl. Strong evidence of adoption was found when stretching vibrations of C=C, C-N and N-H groups were shifted as shown in table (1)

Table (1) The fictional group of poly (Ain-CO-AA) and poly (Ain-CO-AA-HCl)[4].

polymer	C=C Benzoide	C=C Quinoide	C-N	C-H Aromatic	C-H Aliphatic	N-H	O-H
poly(Ain-CO-AA)	1505	1588	1304	3350	2800	3386	3386
poly(Ain-CO-AA-HCl)	1481	1559	1304	3150	2900	3432	3432

Infrared spectrum showed that the absorbance at (1505,1588, 3386) Cm^{-1} as it shown in Fig (2). Fig (3) showed that the absorbance at (1481,1559, 3432) Cm^{-1}.

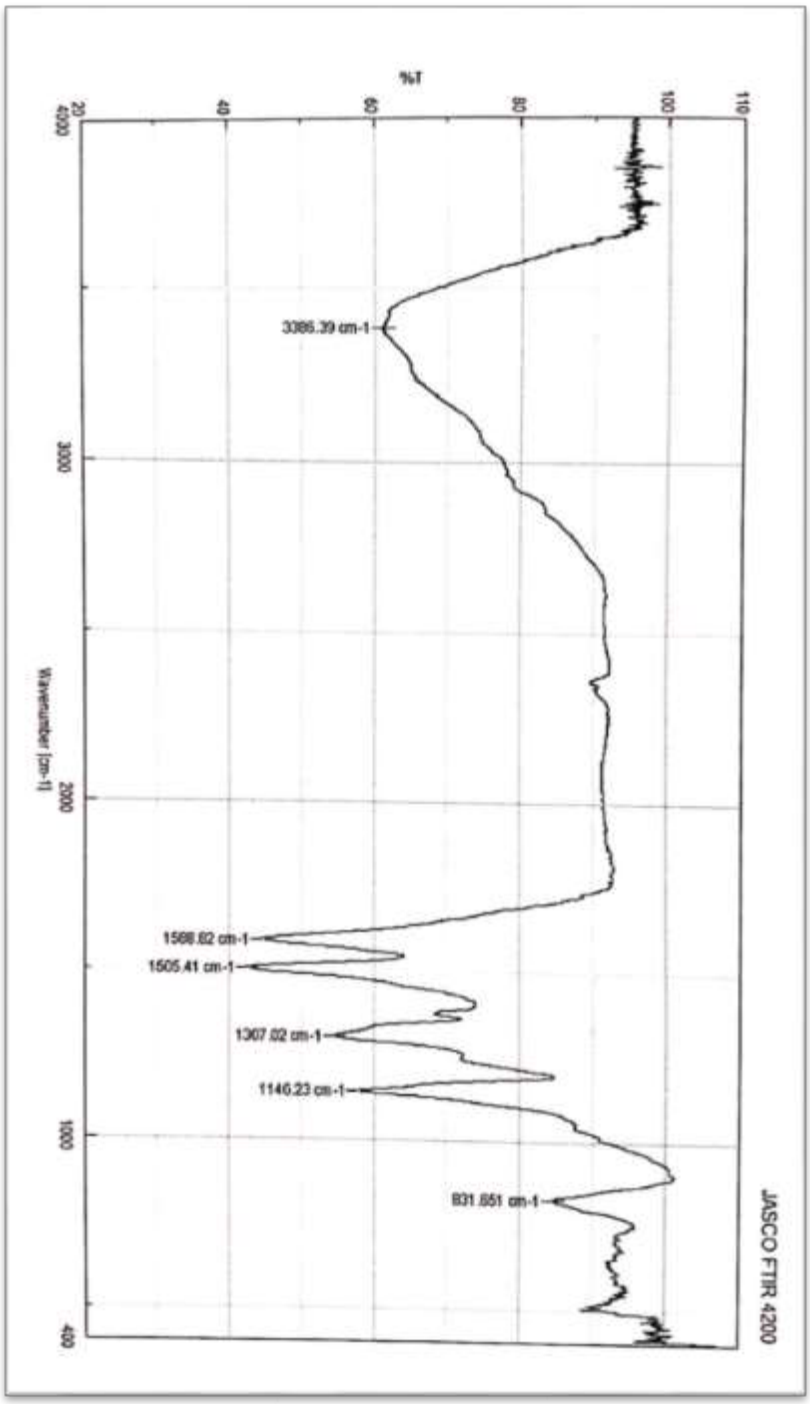

Fig (2) FT-IR spectrum of poly(Ain-CO-AA)[4]

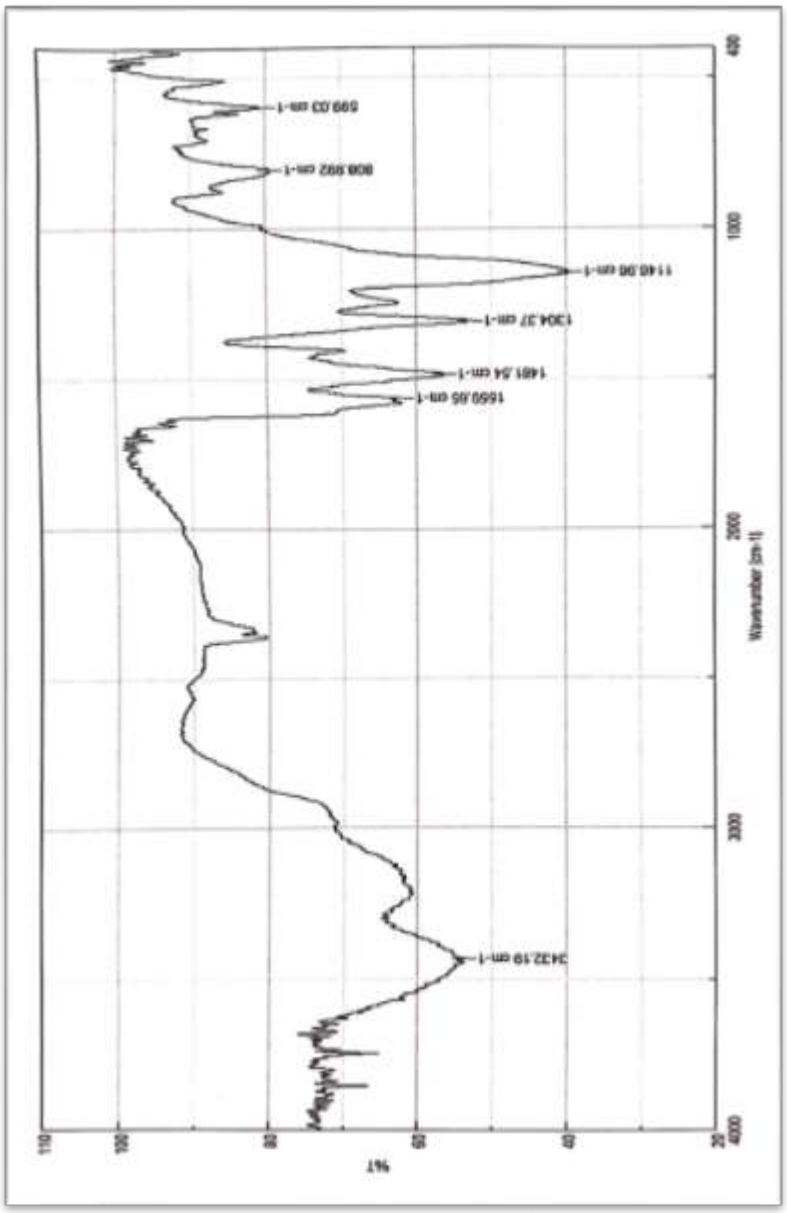

Fig (3) FT-IR spectrum of poly(Ain-CO-AA-HCl)[4]

Experiential details:

The powder of poly (Ain-CO-AA) and poly (Ain-CO-AA-HCl) were dissolve in (2ml) from formic acid (HCOOH) then put on the electric mixer for 3hours and at room temperature. After that the mixture was filtered under vacuum (10^{-2}toor). the mixture deposited on the glass substrates using the casting method. the thin film was homogeneous, the thickness of the films was (135,185) nm for poly (Ain-CO-AA) and poly (Ain-CO-AA-HCl) respectively. the thickness obtained from equation on below [5].

$$t = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where (λ_1) the wavelength corresponding to the maximum refractive index value (n_2) and (λ_2) the wavelength at the lowest value of the refractive index(n_1).

Result and discussion:

Optical Absorption spectra were recorded by a double beam UV/vis spectrophotometer (UV-1800)(SHIMADZU Company Japan) in the wave length rang (200-900) nm.

The Absorption (A) of poly(Ain-CO-AA) and poly (Ain-CO-AA-HCl) are measurement at room temperature as function of wave length (290-800) nm.The absorption spectra of both polymers on the glass substrate is shown in figure (4).The value maximum of the absorbance was observed for poly (Ain-CO-AA) at wave length (309nm) while for poly (Ain-CO-AA-HCl) two peakes appear at wave length (303,350) nm the first peak corresponding to the bonding to anti-bonding (π-π^*) transition of polarons, the second peak is shorter at about (350nm) is assigned to the excitonic transition from the (non –bonding) to the anti-bonding orbital (n-π^*) between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) [6].

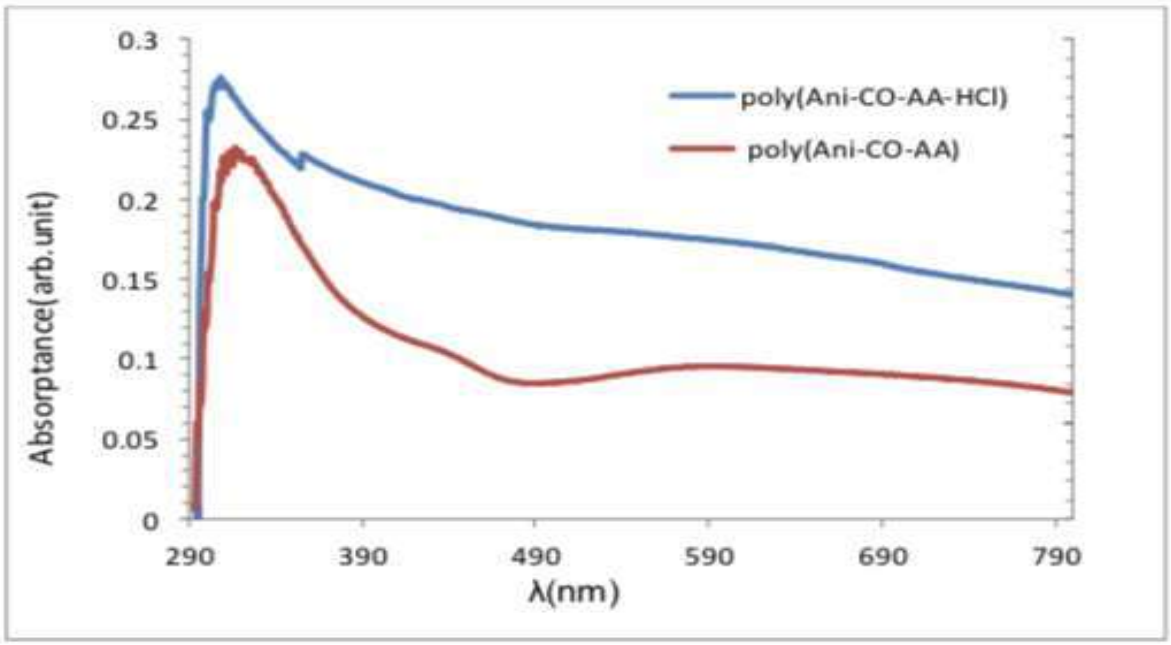

Fig (4)The relationship between optical absorption versus wavelength of poly (Ain-CO-AA), poly (Ain-CO-AA-HCl)

Figures (5), (6) shows the relationship between absorption coefficient and photon energy of poly (Ain-CO-AA), and poly (Ain-CO-AA-HCl) respectively. The value of absorption coefficient plays an important role in the limitation of the type of transition. From the figures the value of the (α) was greater than ($10^4 cm^{-1}$) indicating that the transition was direct electron transmission [7].

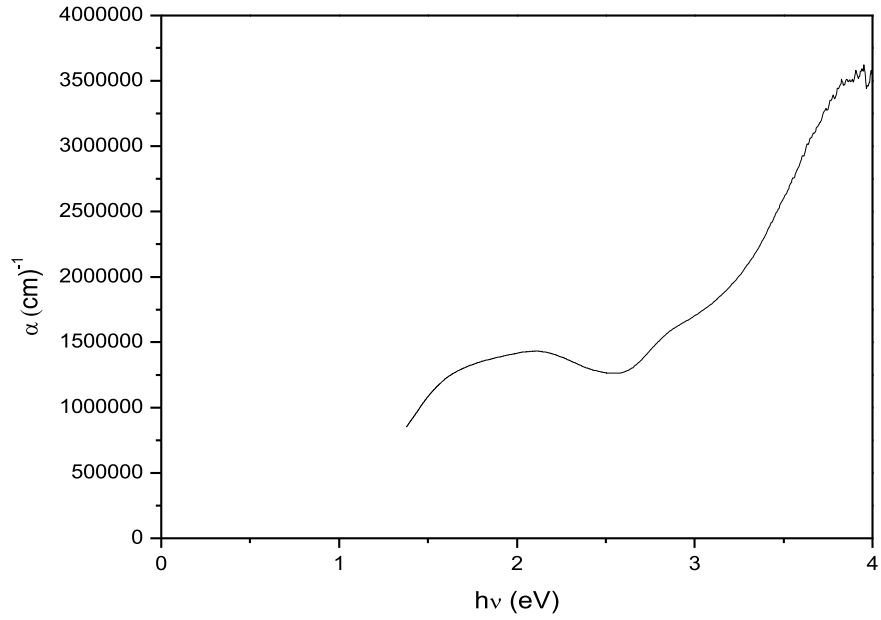

Fig (5)The relationship between absorption coefficients versus photon energy of poly (Ain-CO-AA)

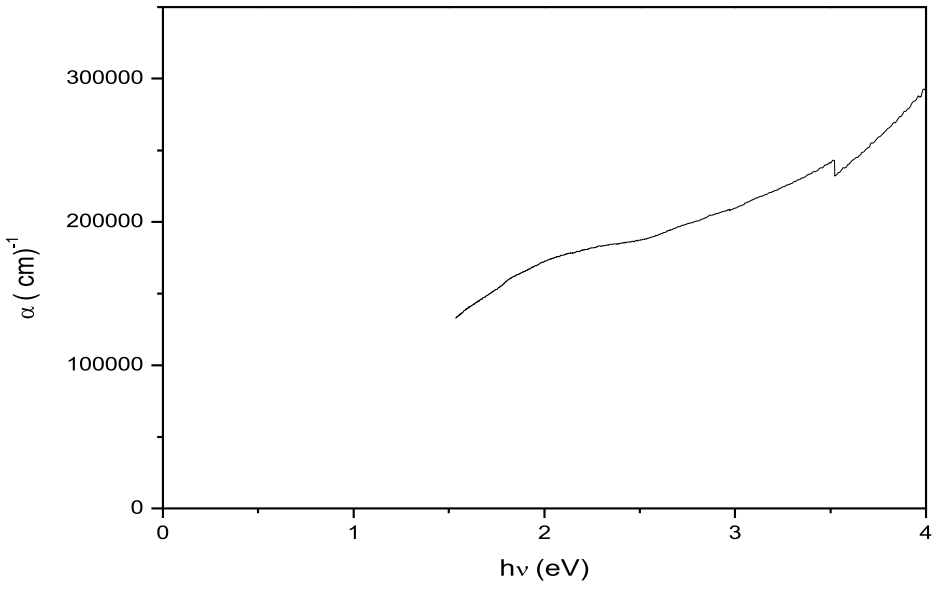

Fig (6)The relationship between absorption coefficients versus photon energy of poly (Ain-CO-AA-HCl)

The absorption coefficient (α) is given by the following relation [8].

$$(\alpha h\upsilon) = B(h\upsilon - E_g)^r \ldots\ldots(2)$$

Where (B) is substance parameter which depends on type of material , (hν) is the photon energy and (E_g) is the optical band gap in eV.r Factor govesing the direct /indirect ,etc transitions of the electronic from the valence band to the conduction band [9].The spectral variation of absorption coefficient

plotted as $(\alpha hv)^2$ versus the photon energy (hv) for poly (Ain-CO-AA), poly (Ain-CO-AA-HCl) is shown in figure (7) and figure (8).

The optical energy gap (E_g) for direct allowed transitions can be obtained by extrapolating the linear portions of the curves to $(\alpha hv)^2 = 0$. The allowed direct transition optical gap is found about (2.83eV) for poly (Ain-CO-AA) and (2.25eV) for poly (Ain-CO-AA-HCl). this is the behavior obtained from doping of the copolymer poly(Aniline-CO-O Ansidine-CO-O Toluidine) with HCl, It was observed that the amount of energy gap decreased (3.2eV), (2.62eV) for P (Ain-CO-OA-CO-OT) and P (Ain-CO-OA-CO-OT-HCl) respectively [10].

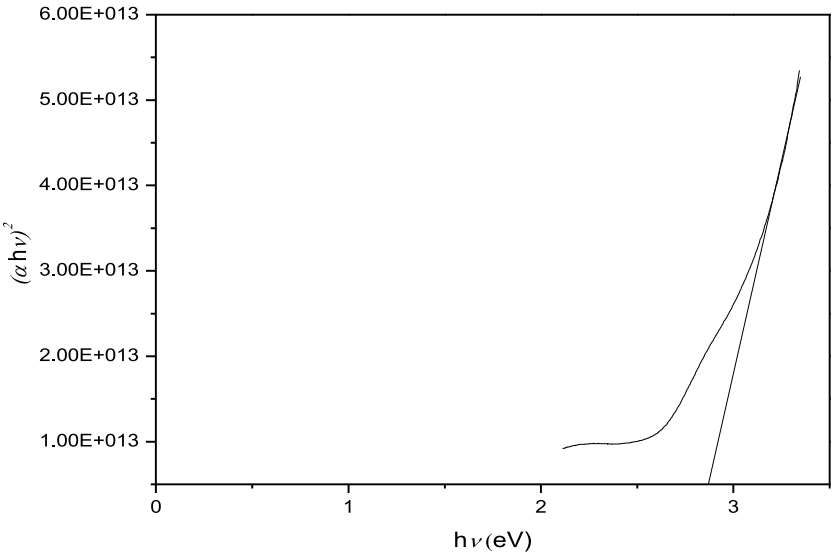

Fig (7) The relationship between $(\alpha hv)^2$versus photon energy for poly (Ain-CO-AA).

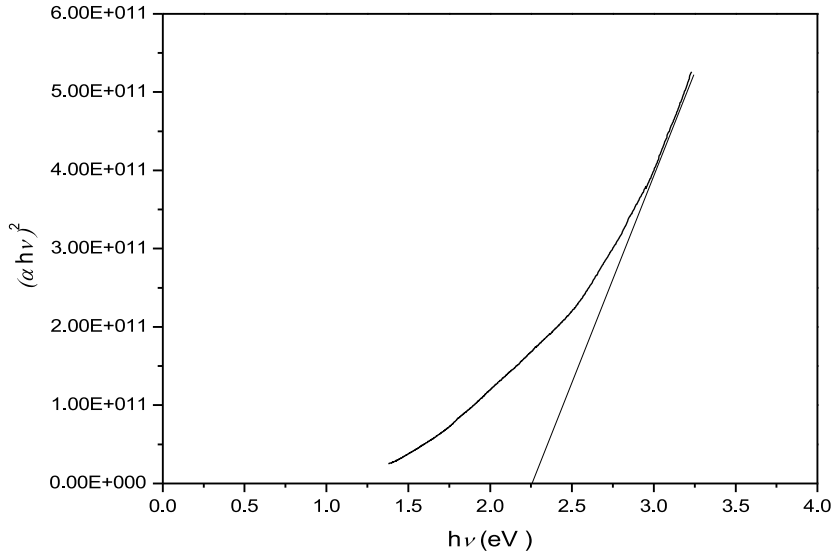

Fig (8) The relationship between $(\alpha hv)^2$versus photon energy for poly (Ain-CO-AA-HCl).

According to the single effective oscillator model proposed by wimple and Didomenico. The optical data can be described to an excellent approximation by the relation [11]

$$n^2 - 1 = \frac{E_d E_0}{E_0^2 - E^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Where (E=hv) is the photon energy ,(n) is refractive index,(E_0) is the single-effective oscillator energy and (E_d) is the dispersion energy which is a measure of the average strength of the inter –band optical transitions.Plotting $(n^2-1)^{-1}$ against (E^2) gives the oscillator parameters by fitting a straight line. Figure (9) and figure (10) show is the plot $(n^2-1)^{-1}$ versus (E^2) of poly (Ain-CO-AA) and poly (Ain-CO-AA-HCl) samples. The values of (E_0) and (E_d) can be then calculated from the slope $(E_0E_d)^{-1}$ which is the intercept on the vertical axis (E_0/E_d).Using the curve above the determined the values of (E_0) and (E_d) were found to be (4.8, 2.18, 10.3and 4.31) eV respectively. It is known that inter-material boundaries contain structural defects and impurities. These factors have a strong influence on the absorption process [12].

The M_{-1} and M_{-3} moments of the optical spectra can be obtained from the relationship [13].

$$E_0^2 = \frac{M_{-1}}{M_{-3}} \quad , \quad E_d^2 = \frac{M_{-1}^3}{M_{-3}} \quad \ldots\ldots\ldots(4)$$

The relationship between the refractive index (n) and ratio of the carrier con centration to the effective mass (N/m) is given by[14].

$$n^2 = \varepsilon_L - [\frac{e^2}{4\pi^2 \varepsilon_\circ c^2}][\frac{N}{m*}]\lambda^2 \ldots\ldots\ldots(5)$$

Where(e =1.6*10^{-19} C) is the electronic charge, (c) is the velocity of light, (ε_0) is the permittivity of free space (8.85*10^{-12}F/m) and (ε_L) is lattice dielectric constant.

From the intercept the light-frequency dielectric constant ($\varepsilon_\infty=n^2$) equals (46.24, 7.84) for poly (Ain-CO-AA) and poly (Ain-CO-AA-HCl) respectively.

The refractive index was also fitted using a function for extrapolation to wards shorter wavelengths. The means data corresponding to the wavelength range lying below the absorption edge, of the material are to be used.

The properties of the investigated sample could be treated as a single oscillator at wavelength (λ_0) at high frequency. The high frequency dielectric constant can be calculated by applying the following simple classical dispersion relation [15].

$$\frac{n_\infty - 1}{n^2 - 1} = 1 - (\frac{\lambda_\circ}{\lambda})^2 \ldots\ldots\ldots(6)$$

Where (n_∞) is refractive index at infinite wavelength (λ_0) (average inter band oscillator wavelength), (n) the refractive index and (λ) the wavelength of the incident photon. Plotting $(n^2-1)^{-1}$ against (λ^{-2}) which showed linear part, was below the absorption edge as shown in fig (11)and fig (12).

The nonlinear refractive index and susceptibility (X^3)can be calculated by combining Miller`s generalized rule [16].

The third-order nonlinear optical susceptibility, (X^3) is important parameter, because it gives a measure about the possibility of using the films in optical switching. Due to fast response time on laser excitation and laser value of the third order nonlinear (X^3) semiconductors thin films are of considerable interest. The Miller rule provides a convenience and straight evaluation of third-order nonlinear susceptibility for visible, nonlinear and near infrared frequencies [17]. It relates the third-order of nonlinear polarizability parameter and the linear optical $\lambda^{(1)}$ through the equation [18].

$$X^3 = A\{E_0 E_d/4\pi(E_0^2 - (h\nu^2)\}^4 = A/(4\pi)^4(n-1)^4 \quad .....(7)$$

Where A is constants equal to 1.7 $*10^{-10}$

We note that the value of the third order nonlinear (X^3)decreases when the polymer is doping with HCl. This is similar to what the researcher Hui and his group [19] poly (methyl methacrylate)(PMMA). this decrease because bond (π-electron).

Table (2) shows some results for (E_0 ,E_d ,E_∞,n_0,M_{-1},M_{-3},X^3).These values are compared to those of poly (Ain-CO-AA) and poly (Ain-CO-AA-HCl) thin films. the all values in table (2) of poly (Ain-CO-AA) large than compared to those of poly (Ain-CO-AA-HCl).

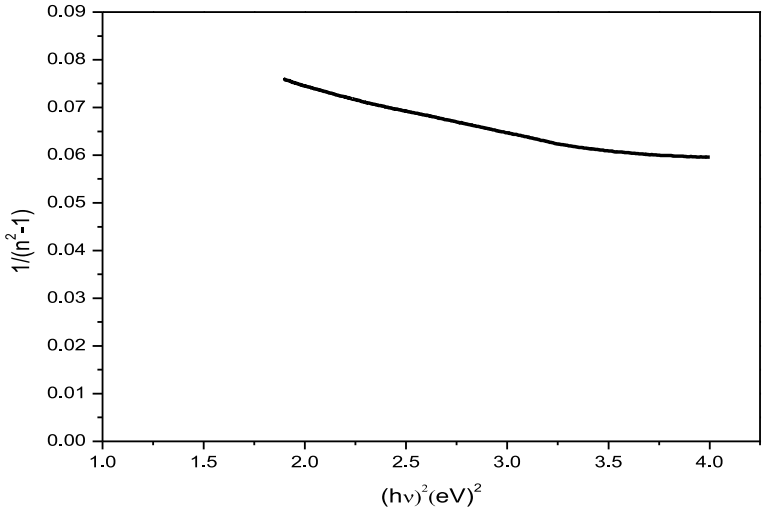

Fig (9) The relationship between $(n^2-1)^{-1}$ versus $(hv)^2$ for poly (Ain-CO-AA).

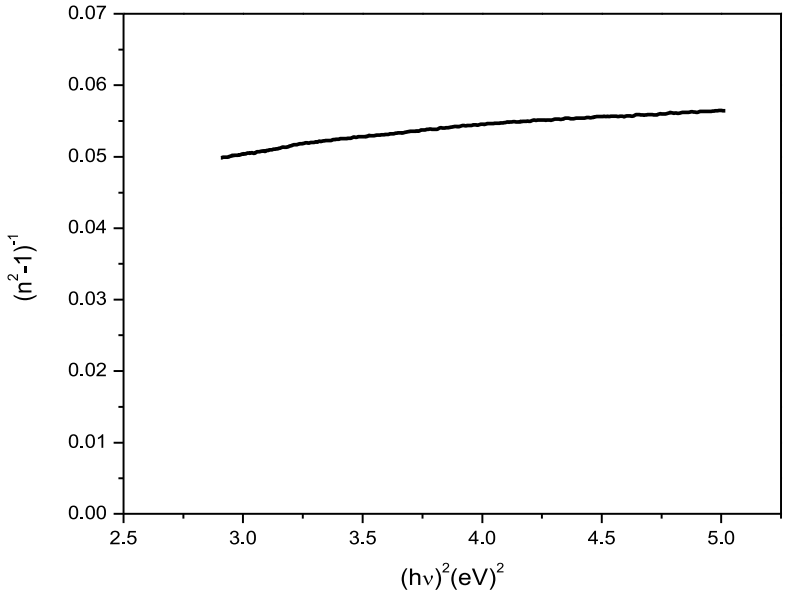

Fig (10) The relationship between $(n^2-1)^{-1}$ versus $(hv)^2$ for poly(Ain-CO-AA-HCl).

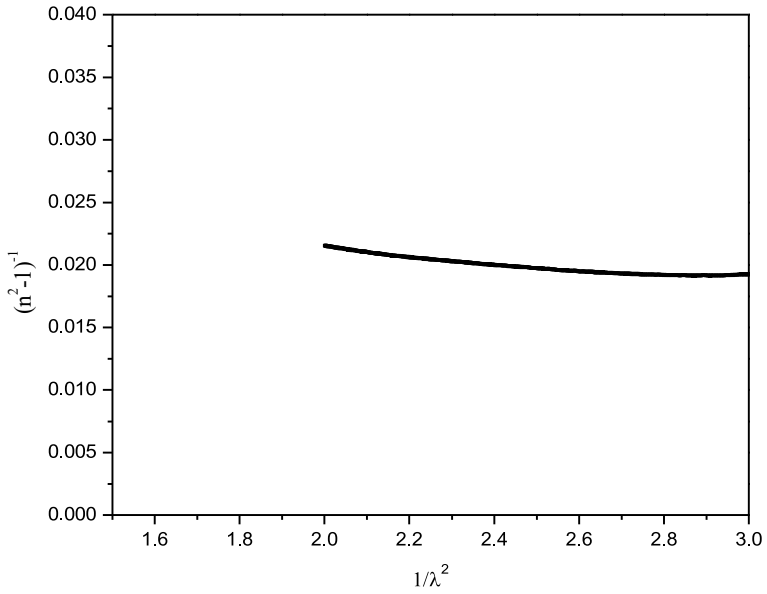

Fig (11) The relationship between $(n^2-1)^{-1}$ versus $(1/\lambda^2)$ for poly (Ain-CO-AA).

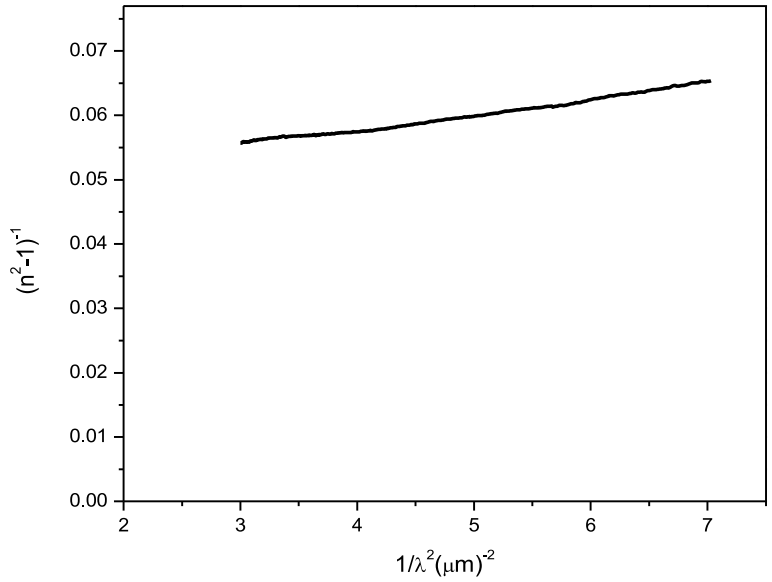

Fig (12) The relationship between $(n^2-1)^{-1}$ versus $(1/\lambda^2)$ for poly (Ain-CO-AA-HCl).

Table (2) The calculated optical constant parameters of poly (Ain-CO-AA) and poly (Ain-CO-AA-HCl).

polymer	E_0 (eV)	E_d (eV)	E_∞	$n0$	$M-1$	$M-3$	$X^3(esu)$
Poly (Ain-CO-AA).	4.8	10.3	46.24	6.8	2.14	0.9	$1.87*10^{-12}$
Poly (Ain-CO-AA-HCl).	2.18	4.31	7.84	2.8	1.97	0.4	$1.42*10^{-12}$

Conclusions:

In the present study, it was found that the polymer poly (Ain-CO-AA) and poly (Ain-CO-AA-HCl) deposited on the glass substrates using the casting method have direct electronic transition and that the effect of doping with HCl on the polymer reduced the energy gap (E_g=2.83,2.25) eV for poly (Ain-CO-AA) and poly (Ain-CO-AA-HCl) respectively. All values (E_0 ,E_d ,E_∞,n_0,M_{-1},M_{-3},X^3) table (2) of poly (Ain-CO-AA) high than for poly (Ain-CO-AA-HCl).

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