Electrical properties of terpolymer of poly[aniline-co-(o-anisidine)-co-(o-toluidine)]

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ABSTRACT:

Terpolymerpoly[aniline-co-(o-anisidine)-co-(o-toluidine)]was prepared by chemical method. The polymer solution deposited on interdigitated finger electrode by the use of spin coating technique. The thickness of the samples is measured by micro meter digital , Transform Infrared (FTIR) spectra, were used to characterize the molecular structures of copolymer.The electrical properties were investigated. The conductivity values of this polymer is $(3.6 \times 10^{-10}, 1.5 \times 10^{-7}$ S/cm) for both pure and doped polymers respectively, and increasing with increase temperature. The activation energy was determined from this curves were (0.34 ev, 0.24 eV) for copolymerpoly[aniline-co-(o-anisidine)-co-(o-toluidine)]and poly[aniline-co-(o-anisidine)-co-(o-toluidine)-HCl] respectively .

KEYWORDS: Terpolymer, chemical method, interdigitated finger, conductivity

INTRODUCTION

Copolymers, conducting polymers, such as other polymer can be prepared by chemical or electrochemical polymerization. Although the chemical method offers mass production at a reasonable cost, which are suitable for application in electronic devices. The most widely used laboratory techniques for the preparation of conducting polymer thin films[1].

Although it is established that the conducting properties of the polymer films greatly depend on the mode of synthesis such as type of monomer, concentration, and synthesis temperature, in order to improve conducting properties of polymer films suitable for a desired application, it is necessary to critically control and optimize the various synthesis parameters. Polyaniline (PA) and its derivative occupies the most important place among the organic conducting polymers. Its unique properties, such as ease of preparation in aqueous medium, good stability in air[1], simplicity in doping[2], improved electronicproperties[3], electrochromic effects[4], well behaved electrochemistry[5,6], Polyaniline and its derivative can be prepared either chemically or electrochemically. Chemical synthesis methods require a strong oxidant such as persulfates[7] or perchlorates and hydrogen peroxide[8]. The present study include the preparation of terpolymer(ANI-CO-OA-CO-OT-HCL) doped with HCl. The polymer solution deposited on interdigitated finger electrode by casting technique, in order to study electrical properties of copolymer. The polymer thin films prepared were analysized by the use of (FT-IR) to determine the functional groups of the chemical bonds.

EXPERIMENTAL PROCEDURES

1-preparation of poly [aniline-co-(o-anisidine)-co-(o-toluidine)]

(Aniline, O-anisidine, O-toluidine) Distilled, each monomer (25ml.,0.274mol) was dissolved in HCL(1M,500ml.)and taken in a 200ml three neeked flask and then cooled to (0°c) using ice.To this apre-cooled solution of ammonium persulphate(78.1g,0.343mol) in HCL (1M,250ml) was added slowly very carefully (exothermic reaction). Immediatappearane of pink color which turned into deep blue.After (5min),green colored [aniline-co-(o-anisidine)-co-(o-toluidine)-HCl] The resulant was started to precipitate from the solution.After complete adition of the oxidizing agent reaction mixture was kept under constant stirring for (24 hr·s) was filtered ,washed with (1M HCL)for three times and stirred in a flask containing (1M) aqueous ammonia solution (112.5ml 2% solution) in water.The blue precipitate was stirred for 3 hr·s at room temperature to ensure the completion of de-doping. The resulant blue was filtered, washed successifely with water ,methanol and aceton to remove the un-reacted starting materials and oligomers, then was dried in vacuum oven at 80 °c for 12 hr·s.

2-Preparation of samples:

After the synthesised terpolymer by chemical polymerization method. The copolymer powder was added to formic acid solvent and mixed under constant stirring at room temperature. After completing the mixing process, the copolymer was filtered under vacuum, then the mixture was deposited on interdigitated finger - glass substrates as a thin films using cast method. The thickness of films was (5μm),thickens measured by the use of (micro meter digital type of INSIZE).Interdigitated comb-like electrode structures have frequently been suggested as ultra-sensitive for chemical structure films.Electrode consist of interdigitattedAluminiumlines on an glass substrate. It can be achieved using interdigitated electrodes to measure the conductivity of the samples. The samples were put on hotplate (heater) to raise a temperature from room temperature (R.T) to (80°C).The

electric properties were measured by two probe method. Figure(1) show

Interdigitated electrode.
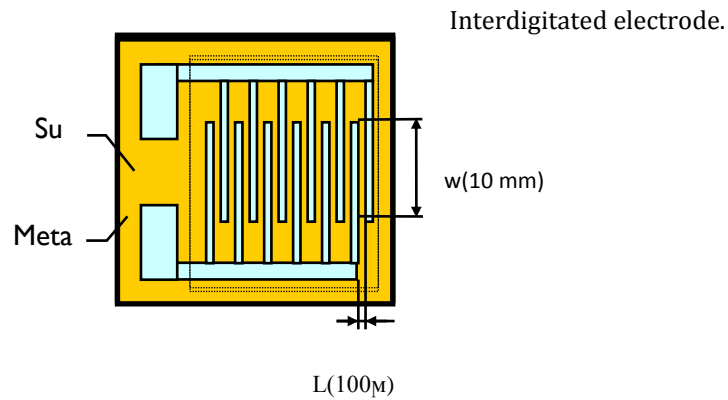
Figure (1): A schematic diagram of interdigitated finger electrode.

Electrical measurements were carried out by inserting the interdigitated finger electrode in circuit consisting of DC. Source, electrometer, and voltmeter. The samples were enclosed in grounded aluminum screen box with temperature controller system.

The sample temperature was measured with a thermocouple placed near the sample. Regulated voltage ranging from 1 to 80V were supplied by a power supply type phywe 2592.The current was measured by electrometer type(Digital-Multimeter , PM2421). Results and discussion FT-IR spectra of Ter-polymers are identical and a representative spectrum is given in Figure 2. Strong due to (3406) stretching, (1124)bending and stretching vibration of C-O group of urea combined with (1247)group respectively.

In addition to these vibrations of urethane functional group, the Ter-polymers also showed (C - O), in-phase),(1209)cm-1.
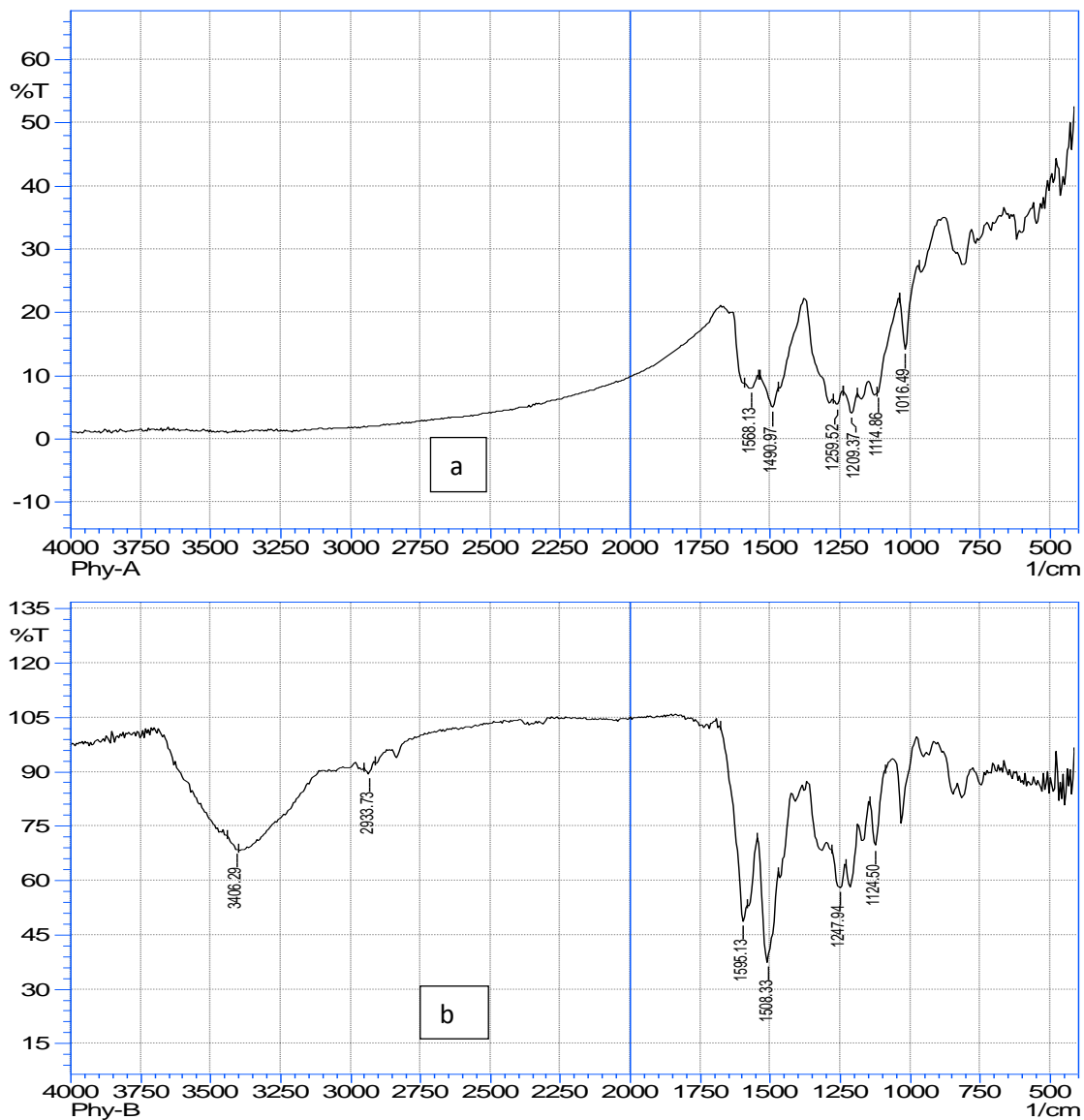
Figure (2) : FT-IR for :a-Poly [aniline-co-(o-ansidine)-co-(o-toluidine)]& b- Poly [aniline-co-(o-ansidine)-co-(o-toluidine)-HCl]

| Type of polymer	C-H Cm $^{-1}$	C-N cm^{-1}	C-O cm^{-1}	C-H Bonding vibration cm^{-1}	Quinoide cm^{-1}
poly[aniline-co-(o-anisidine)-co-(o-toluidine)]	2933	1247	1247	1124	1568
Ref	[9] 2936				[10] 1587.31
poly[aniline-co-(o-anisidine)-co-(o-toluidine)-HCl]	___	1259	1209	1114	___
Ref	[11] (I) 1277				

Figure (3), shows the AFM image of sample which indicates the formation of grains, hence revealing the organic nature of the thin films.

The surface morphology of the copolymers films as observed from the AFM micrographs figures (3) the

pictures proves that the grains are uniformly distributed within the scanning area (100nm x 100nm), with individual columnar grains extending upwards. The root mean square (RMS) surface roughness of poly[aniline-co-(o-anisidine)-co-(o-toluidine)] films are found to be(2.313 nm) in fig.(3-a). The 3D-AFM are shown in figure (3-b).

The higher the root mean square (RMS) roughness is found in (6.058 nm).
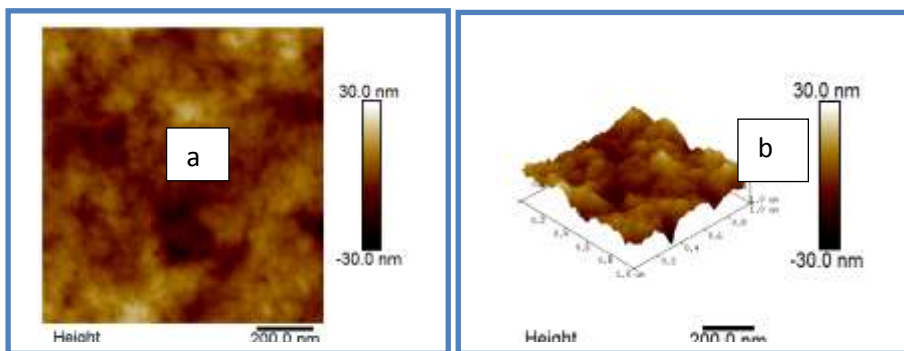
Figure (3) : AFM images to Poly [aniline-co-(o-ansidine)-co-(o-toluidine)]

a- in one dimensional.
b- in three dimensional.

The steady-state currents were measured with respect with time for poly[aniline-co-(o-anisidine)-co-(o-toluidine), poly[aniline-co-(o-anisidine)-co-(o-toluidine)-HCl) at different voltage (1,10,20,30)v as shown in figures (4), (5).The current still steady state with all time. This is behavior observed in (PPAB) doped .

Figures (6,7) are shown the relationship between steady state current and voltages at different temperatures

$(293,303,313,323,333,343,353)$°C. the relationship between voltage andcurrent shows ohmic behavior, indicates that thermally generated charge carries are effected by the current limits[10], The current increased with increasing temperature and applied voltage that means, copolymer films has conductivity of positive temperature coefficient. This is behavior was also noticed in previous new polymers synthesis in our laboratories for electronic application [14,15]
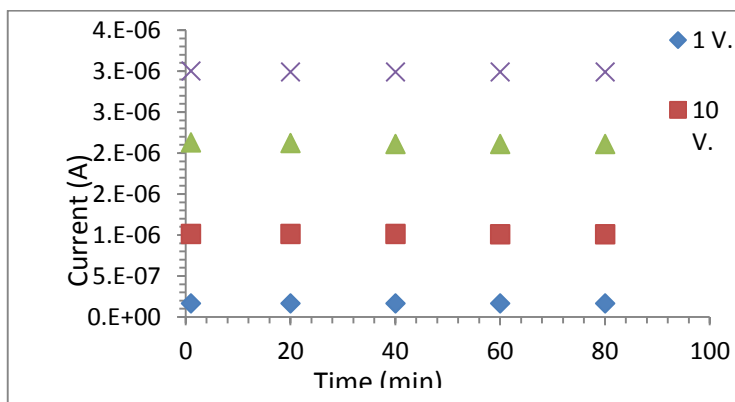
Figure(4): The Relationship between current vs. time for poly[aniline-co-(o-anisidine)-co-(o-toluidine)].
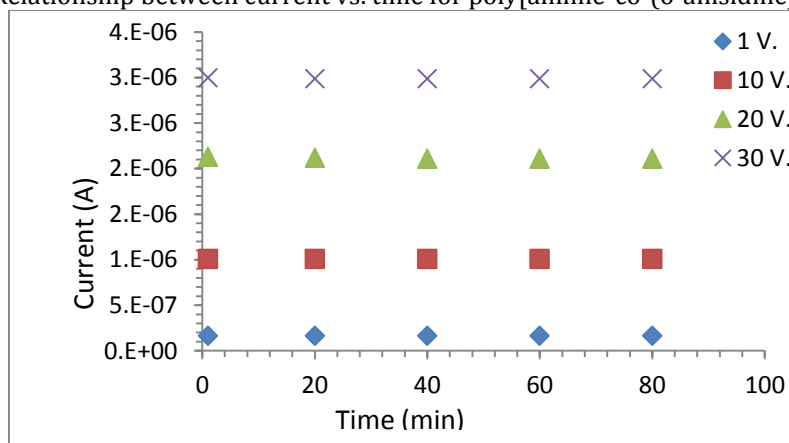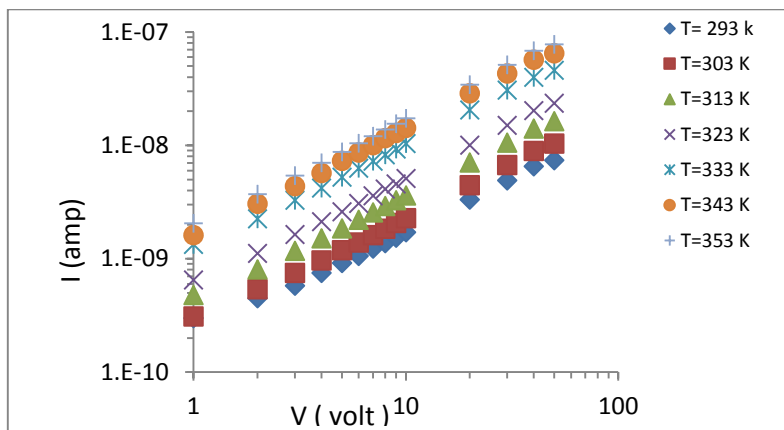

Figure(5): The Relationship between current vs. time for poly[aniline-co-(o-anisidine)-co-(o-toluidine)-HCl]
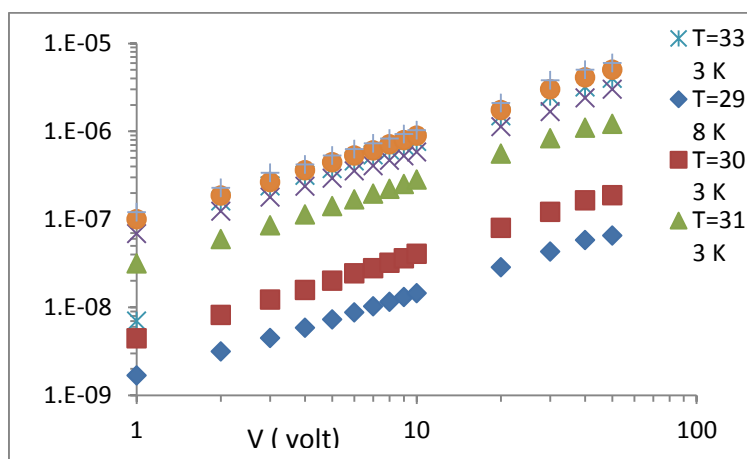
Figures (6,7) are shown the relationship between steady state current and voltages at different temperatures (293,303,313,323,333,343,353)°C. the relationship between voltage andcurrent shows ohmic behavior, indicates that thermally generated charge carries are effected by the current limits[10], The current increased with increasing temperature and applied voltage that means, copolymer films has conductivity of positive temperature coefficient.

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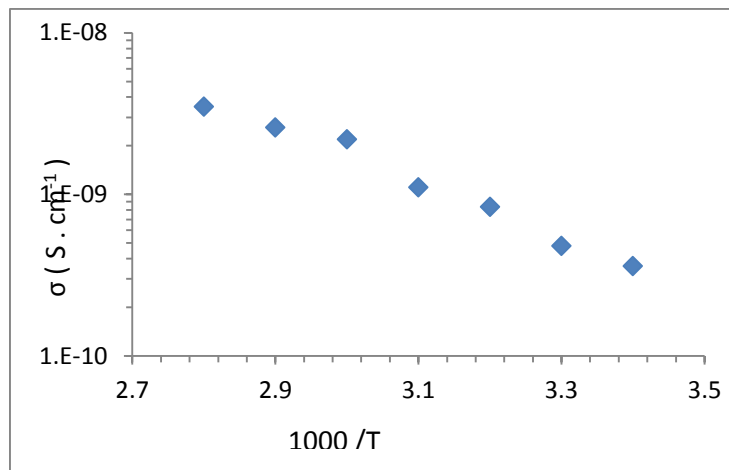

Figure (6): The relationship between current vs. voltage for poly[aniline-co-(o-anisidine)-co-(o-toluidine)]at different temp.(293,303,313,323,333,343,353)°c
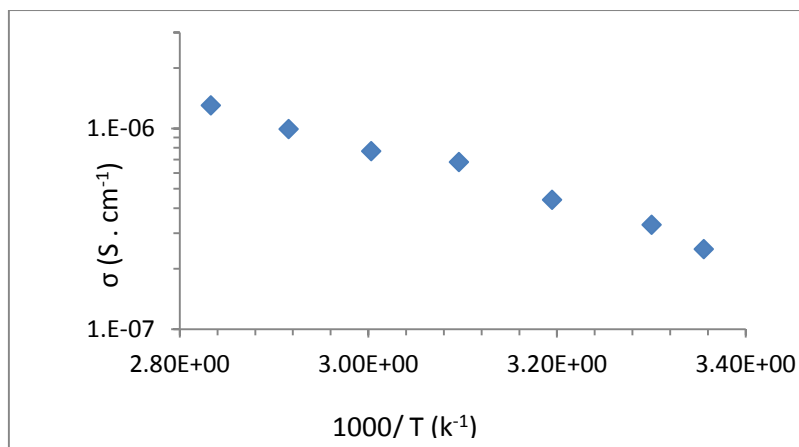

Figure (7): The relationship between current vs. voltage for poly[aniline-co-(o-anisidine)-co-(o-toluidine)-HCl]at different temp.(293,303,313,323,333,343,353   )°c

Figures (8,9) are shown the temperature dependent of conductivity for each copolymers pure and doped by Hcl. It is clear from the figures that increasing temperature, that mean polymers has a conductivity of positive temperature coefficient which is identical to the characteristics of semiconductor materials.

The activation energy calculated from slope for both figures according to equation(1), the activation energy was (0.34 , 0.24 eV) for both terpolmerpoly[aniline-co-(o-anisidine)-co-(o-toluidine)],poly[aniline-co-(o-anisidine)-co-(o-toluidine)-HCl].

Figure (8): The relationship between conductivity vs. (1000/T) for poly[aniline-co-(o-anisidine)-co-(o-toluidine)]

Figure (9):The relationship between conductivity vs. (1000/T) for poly[aniline-co-(o-anisidine)-co-(o-toluidine)-HCl]

Figure(10) shows the relationship between current and $(V)^{1/2}$.At high applied filed region the curves showed a clear fit to a straight line quite nicely and display the familiar Schotty emission characteristics. These data lead us to speculate that the expected mechanism "Schottky effect or poole –frenkel effect". Poole frenkel emission (internal Schottky effect) describes the trapped electrons in to conduction band of the solid[11]. The frenkel expression is given by[16].

$$J=J_o\exp[(\beta E^{1/2}-e\Phi)/KT] \quad \dots \qquad (1)$$

$$\beta = (\frac{e^3}{\pi\epsilon\epsilon_\circ})^{1/2} \dots\dots \qquad (2)$$

$$\alpha_f = \beta_r/kT \dots\dots \qquad (3)$$

E, eΦ , k, π, ϵ_o ϵ are the applied electric field , the work function of metal-polymer interface, Boltzman constant and the polymer dielectric constant . Schottky expression has a similar Formula like eq. (1) with small difference that is

$$\alpha_s=\alpha_f /2 \qquad \dots\dots\dots \qquad (4)$$

where are α_s , α_f schottky constant value and pool-frenkel constant value , respectively .

the theoretical values of α_s and α_f be calculated with the help of eq (3) and (4) . theoretical values of α_f and α_s along with experimental values of α_{exp} can be obtain from the slope of fig (10) measured in the high field region are listed in the following table
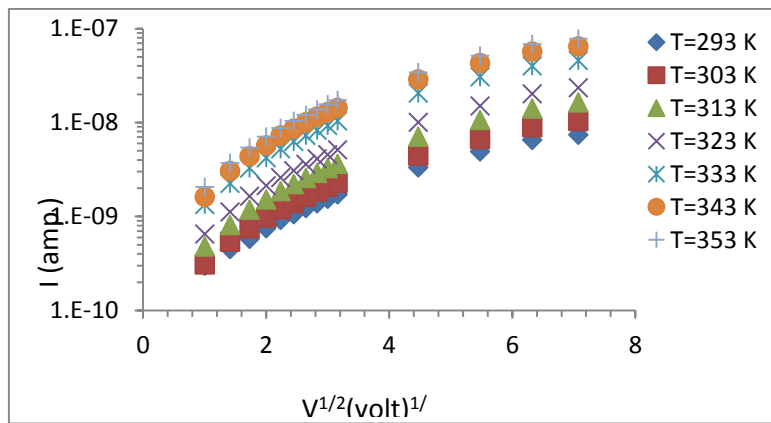
Figure (10): The relationship between current vs. voltage for poly[aniline-co-(o-anisidine)-co-(o-toluidine)]. at different temp.(293,303,313,323,333,343,353)K
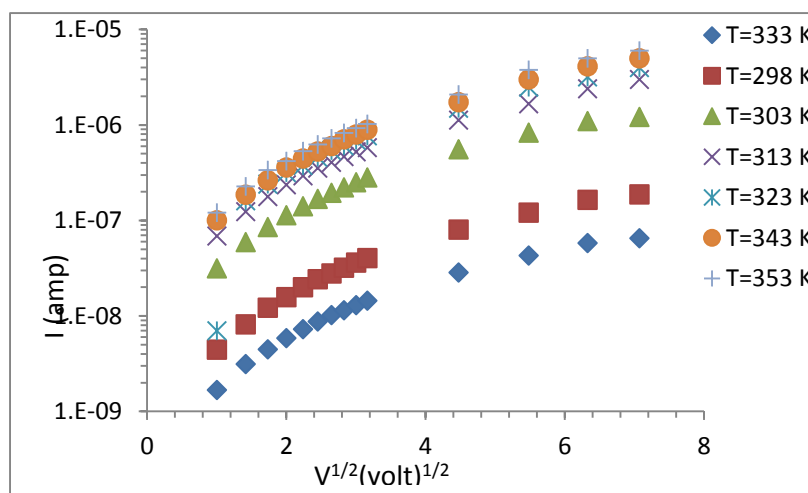
Figure (11): The relationship between current vs. voltage for poly[aniline-co-(o-anisidine)-co-(o-toluidine)-HCl] .at different temp.(293,303,313,323,333,343,353)K

Table (I): experimental and calculated αs and αf values from schottky and frenkel theories for poly[aniline-co-(o-anisidine)-co-(o-toluidine)]

T(K)	α_{exp}	α_s	α_f	ϵ
293	0.090	0.090	0.17	0.7
303	0.087	0.087	0.17	0.7
313	0.082	0.082	0.16	0.8
323	0.079	0.079	0.16	0.9
333	0.086	0.068	0.13	1.2
343	0.066	0.066	0.14	1.3
353	0.063	0.063	0.13	1.4

Table (II): experimental and calculated αs and αf values from schottky and frenkel theories for poly[aniline-co-(o-anisidine)-co-(o-toluidine)-HCl]

T (k)	α_{exp}	α_s	α_f	ϵ
293	0.08	0.08	0.16	0.8
303	0.079	0.079	0.158	0.9
313	0.075	0.075	0.15	1
323	0.074	0.074	0.148	1
333	0.067	0.067	0.134	1.2
343	0.066	0.066	0.132	1.3

| **353** | 0.056 | 0.056 | 0.112 | 1.8 |

The experimental values of α for the examined films indicated that schottky effect is the dominated process mechanism .

fig (12) shows the variation ØΔ versus applied electric field according to eq(5). from the figure observed a linear relationship.
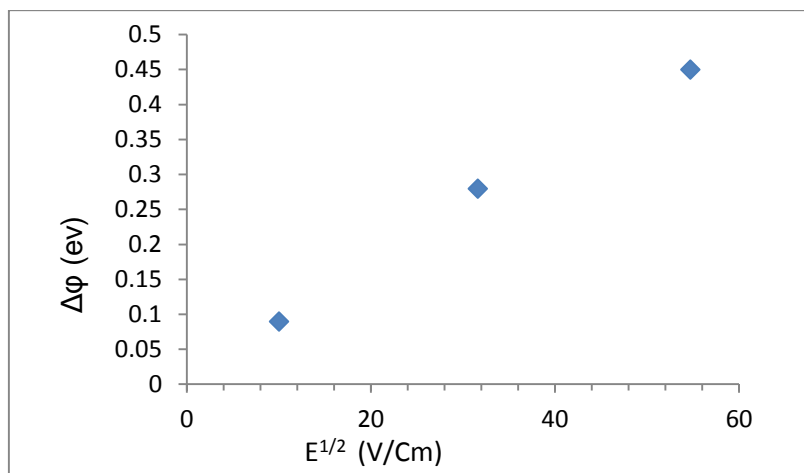
E/4πεr)1/2   ……………   (5)
e) =ØΔ

Where εo , εrthe primitive free space and dielectric constant of polymer.

Though both poole-frenkel and from the schottky emission yield a straight line on plots of log J versus $\sqrt{E}$ over the range of fields employed experimentally the employed direct analysis to distinguish between them was assisting by other criteria based on possible electrode effect .

Other mechanism such as ionic , space charge limited current were also tested before excluded from our discussion. nonionic conduction mechanism because polts between ln ($\sigma T^{1/2}$) verus (1/T) is not linear . also , non-space charge limited because the value of slope for eq.(6) is not equal to (-3)
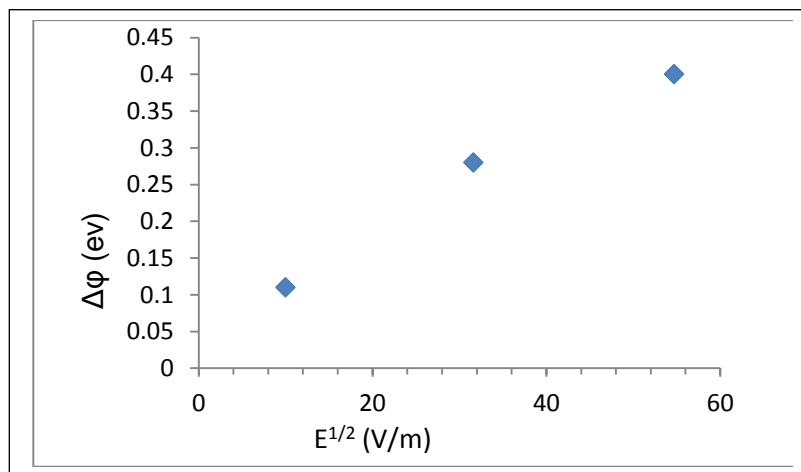
Figure (12): The relationship between Δφ vs. $E^{1/2}$ for poly[aniline-co-(o-anisidine)-co-(o-toluidine)]

Figure (13): The relationship between $\Delta\varphi$ vs. $E^{1/2}$ for poly[aniline-co-(o-anisidine)-co-(o-toluidine)-HCl]

CONCLUSION

poly[aniline-co-(o-anisidine)-co-(o-toluidine)] was synthesized by chemical oxidation polymerization method under typical condition such as low temperature and well purified the samples were prepared by casting method . the polymer analyzed by FT-IR spectroscopy to determinc the active groups of the chemical bonds . the electric conductivity was studied and was found that the thin films correlate with the ohmic behavior at the measured voltage range (1-80v) from the polymer poly[aniline-co-(o-anisidine)-co-(o-toluidine)]and poly[aniline-co-(o-anisidine)-co-(o-toluidine)-HCl].

The effect of temperature on the electric properties of these thin films is also studied . the study shows that the electric conductivity studied . the study shows that the electric conductivity increases with increases temperature. this study shows that the activation energy (0.34) for poly[aniline-co-(o-anisidine)-co-(o-toluidine)]and (0.24) for doped polymer and it's the same result to (Asaad F. KhattabSa'ad F. MahmoodYousif A. Shahab)that study (The Effect of the Chain Sequence Distribution, Nature of Monomersand Temperature on the Electrical Conductivity of someUnsaturated Amide-Ester Copolymers)[17], and schottky mechanism effect was shown to be dominat process at electric filed .

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