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Electrical conductivity study of starch grafting with Poly2-ChloroAniline and 3-Chloro-2-methyl Aniline

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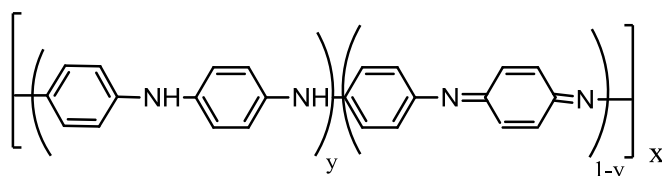
Abstract—In this paper the grafting polymerization of starch with Poly2-Chloro -2-Methyl Aniline were prepared and characterized using infrared spectroscopy .The solid state electrical conductivity of copolymers were studied by I-V Characteristic in the range (0-60)V at room temperature and found that enhancement of electrical conductivity for grafting copolymer rather than starch and polyaniline derivatives

Keywords Terms—Conductive polymer, grafting , copolymer.

I. INTRODUCTION

Conducting polymers are special class of organic polymers that have alternate single –double bond conjugation and conduct electricity .Among all the conducting polymer poly aniline (PANI)/polymer have attracted considerable research interest because of their potential applications as electrodes ,biosensors ,batteries ,antistatic coatings, gas sensors ,membranes , light emitting diodes and the magnetic properties of high –modular poly conjugated compounds-electrically conductive polymers⁽¹⁻³⁾ .Insulating polymeric materials and with excellent physical properties, plastics and textile are seldom used to make PANI composites^(4,5) .

Poly aniline consists of monomer units built from reduced (y)oxidized (1-y)blocks ,where($0 \leq y \leq 1$)

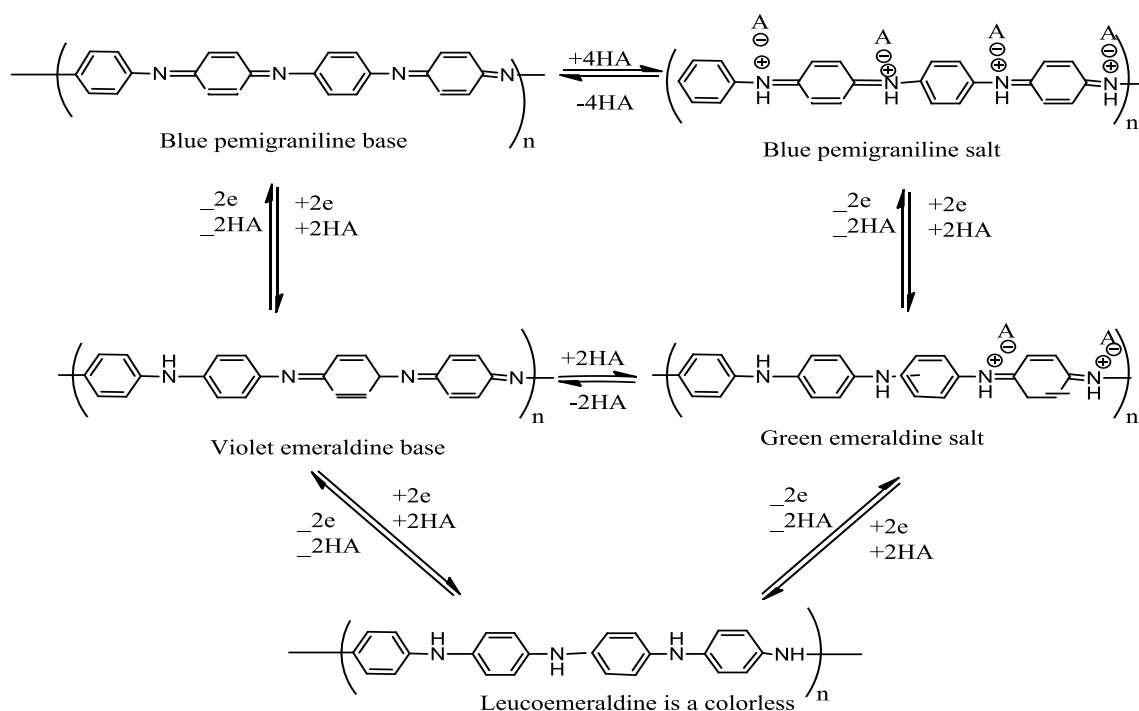


The redox state of the polymer is determined by the value of y, which may vary continuously from zero to unity .At y=0.5 polyaniline occurs in the form of emeraldine ,y=0 corresponds to the fully oxidized form, Pernigraniline while y = 1 corresponds to the fully reduced form, leucoemeraldine.



Pernigraniline and emeraldine may occur as either salts or bases. The forms of PANI have different colors, stabilities, and conductivities. Leucoemeraldine is colorless⁽⁶⁻⁸⁾.

Graft polymerization is a process in which monomers are covalently bonded and polymerized as side chains onto the main polymer chain (the backbone). Starch is a polysaccharide by higher plant as a mean of storing energy. It is stored intracellular in the form of spherical granules that are 2-100µm in diameter. Most commercially available starches are isolated from grains such as corn, rice, wheat, and from tubers such as potato and tapioca. Chemically, starch is a heterogeneous substance and contains both linear (amylose) and branched (amylopectin) structures⁽³⁻⁶⁾. Starch has been long used in preparation of PANI composites. Additionally, the use of viscous and lyocell (regenerated cellulose) in combination with conductive polymers for the preparation of conductive publications⁽⁷⁾.



Conducting polymers belong to a peculiar family of compounds composed of monomer units with conjugated chemical bonds that, under certain conditions (doping), ensure the electron conductivity of the polymer. For various applications, they can replace metals and semiconductors, because they feature conductivity, low density and easy processability. Polyaniline (PANI) — a representative from the family of conducting polymers is distinguished by easy synthesis and high environmental stability⁽⁹⁻¹³⁾.

II. EXPERIMENTAL

Materials

Aniline and ethanol absolute were supplied by (RDH), 3-chloro-2-methylaniline and 2-chloro aniline were supplied by (Aldrich), starch, hydrochloric acid, ammonium persulphate and sodium hydroxide were supplied by (Fluka).

A-synthesis polyaniline derivatives

0.5 M of monomer was dissolved in 200ml of aqueous solution of 1M HCl was brought to a temperature of 273-277°K in an ice bath . 0.54M of ammonium persulphate was dissolved in 200ml of 1N HCl second solution was added to the first solution drop by drop .A few minutes solution of the oxidant , the solution turned bluish –green color .the color of the reaction become darker green by the time the color of the reaction became darker green by the time . After 5 hours of stirring was filtered through filter paper and washed with 1N HCl till the to colorless .Greenish black deposits remaining on the filter paper was water until the filtrated become acid free and was dried in an electric oven 12 hours .The polymer was ground to a fine powder .Dissolved in formic acid and coating on glass and aluminum plat ,after that drying in room temperature to give films to measuring conductivity .

B-Synthesis of starch grafting polyaniline derivatives

1g of starch dissolved in 20ml of 1N HCl at 150 ml flask 3ml .A mixture of 3ml monomer (aniline ,2-chloro aniline and 3-chloro 2-methyl aniline) which dissolved in 20 ml of 1NHCl was added to the flask .The reactant stayed at 298°K by using thermostat at 298°K and continuously stirred . After 30 minutes ,5g of ammonium persulphate at once with stirring for (1hr). The reaction mixture neutralized by 5% aqueous NaOH the copolymer precipitated with absolute ethanol.

C-Preparation samples

.Glass substrate and Aluminum plate were thoroughly cleaned before deposition process by immersion it in cleaning solution. Them washed several times by distilled water and dried. Finger Aluminum electrodes deposited on glass substrate by evaporation method under low pressure (10^{-6} torr). Three thin films polymers were prepared by dissolving (0.1gm) of each polymer in 10ml of formic acid solvent and mixed under constant stirring at room temperature, after completing the mixing process. The mixture was filtered under vacuum then deposited on electrodes from Aluminum deposited on glass substrate and aluminum plat as a thin films using casting method, after that drying in room temperature to measure the electric conductivity of the samples.

ii. Result and dissection

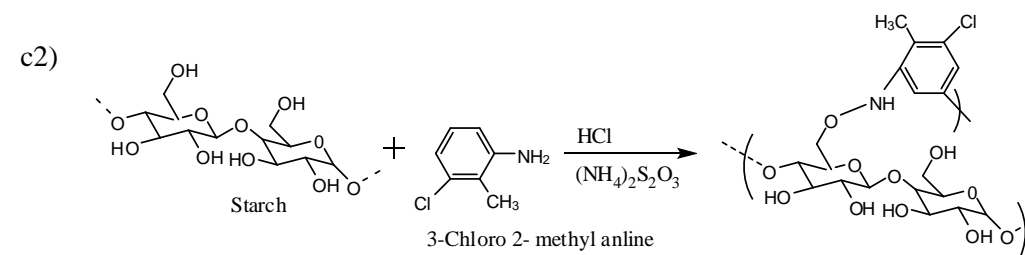
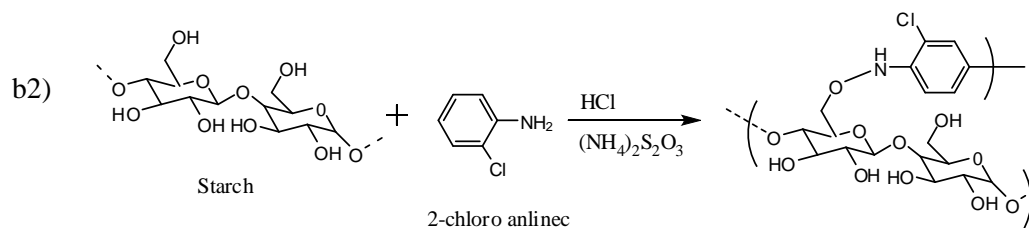
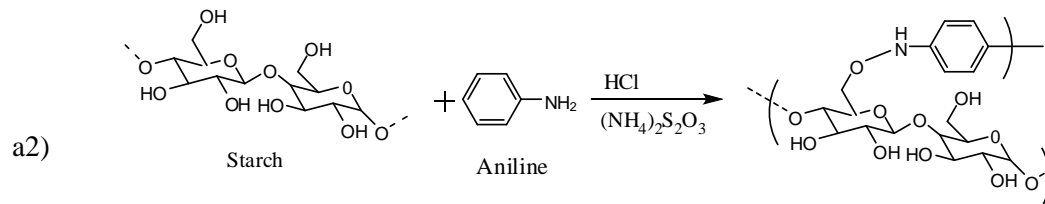
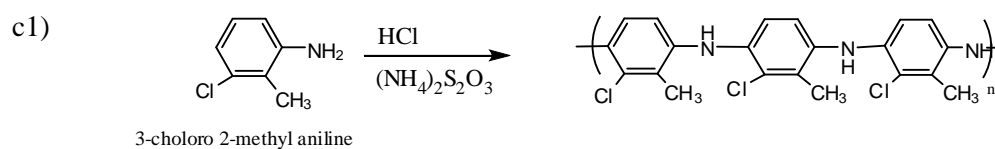
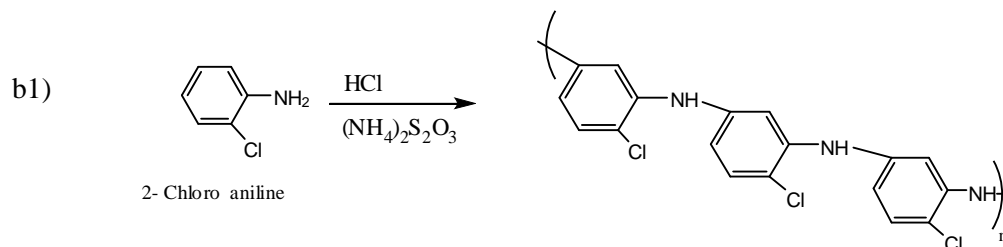
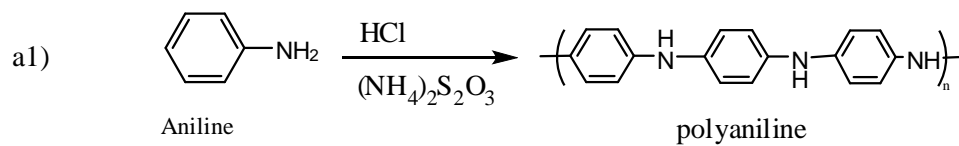
A-FTIR Analysis

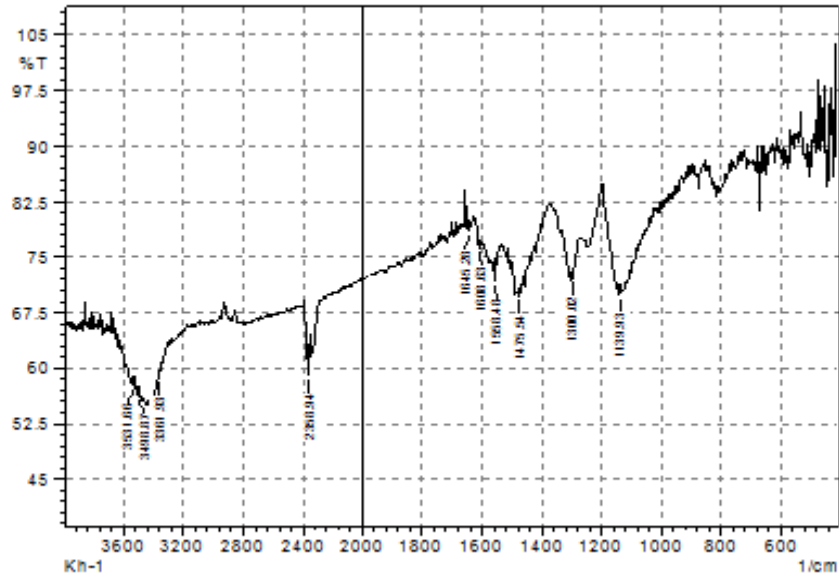
The FTIR spectra of (a1)poly aniline and (a2) poly aniline / starch are shown in figure (1) , the peaks around 1475.5cm^{-1} and 1558.48cm^{-1} results from stretching vibrations of(N-Benzenoid –N) and(N=quinoid =N)moieties in the poly aniline chains structures respectively .The peaks at 1139.93cm^{-1} and 1300.02cm^{-1} due to vibrations of C-H and C-N stretching bands in benzene ring are bending observed .

In poly aniline / starch we find that the band of the starching vibration of O-H the composite is apparently weaker in 3421cm^{-1} in spectrum of pure starch¹⁴ is blue shifted to 3432cm^{-1} in the spectrum of the composite these confirm that starch is successfully activated by superfluous acids the intermolecular hydrogen bonds are broken and the more hydrogen groups become accessible.

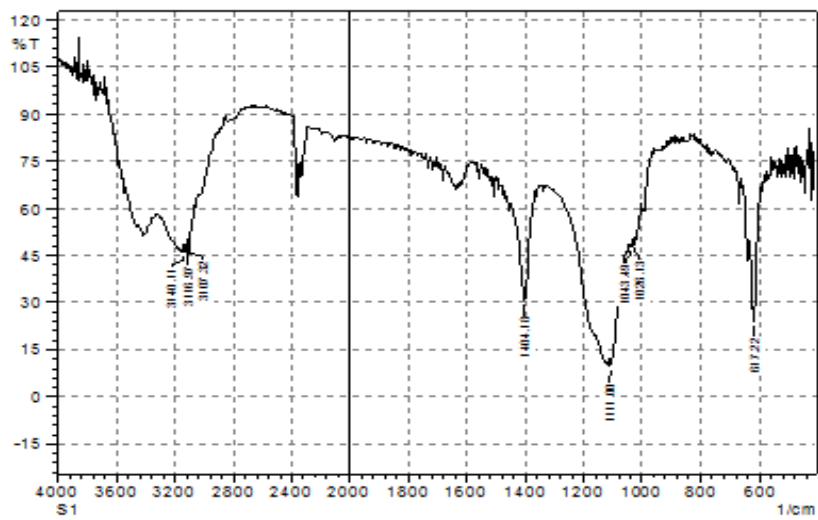
In Figure (2) spectra of (b1) poly 2-chloro aniline (b2) copoly 2-chloro aniline /starch, The peaks for 1400.32cm^{-1} and 1558.57cm^{-1} results from stretching vibration of (N-Benzenoid –N) and(N=quinoid =N)moieties in the poly2-chloroaniline and poly2-chloroaniline\starch .The peaks in b1 find that the band of the starching vibration of O-H the 3398.57cm^{-1} ,and 3468.01cm^{-1} for b2\starch copolymer.

In Figure (3) spectra of (c1)) poly 3-chloro 2-methyl aniline (c2)copoly3-chloro2-methylaniline /starch peak at 1680cm^{-1}



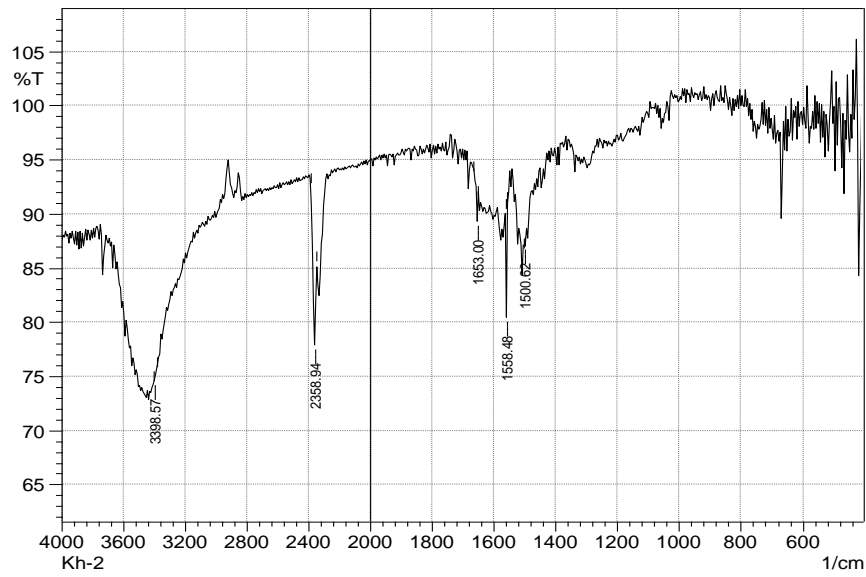


(a1)

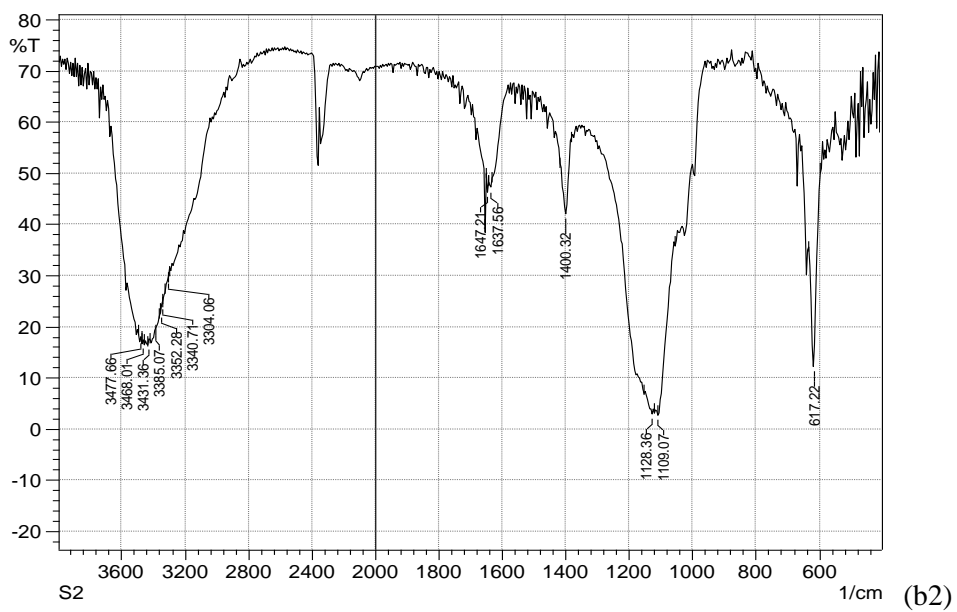


(a2)

Figure 1. FTIR Spectra of (a1) polyaniline (a2) copolyaniline/starch

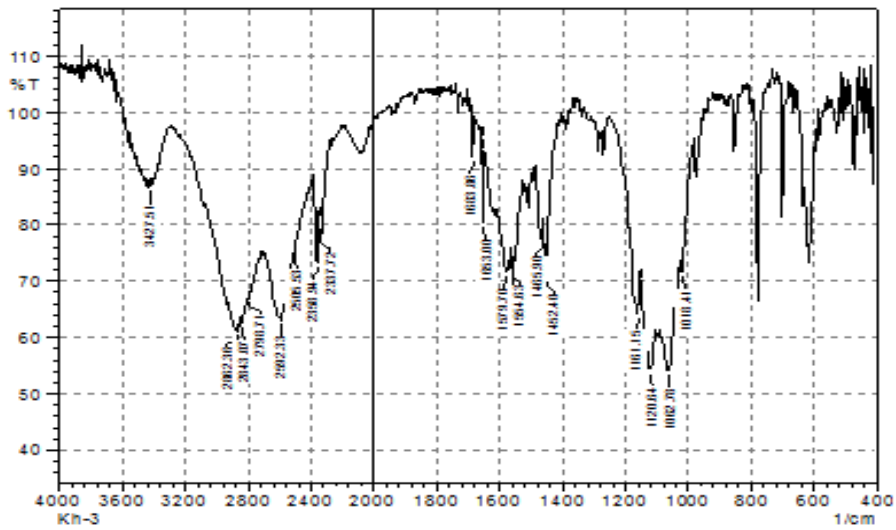


(b1)

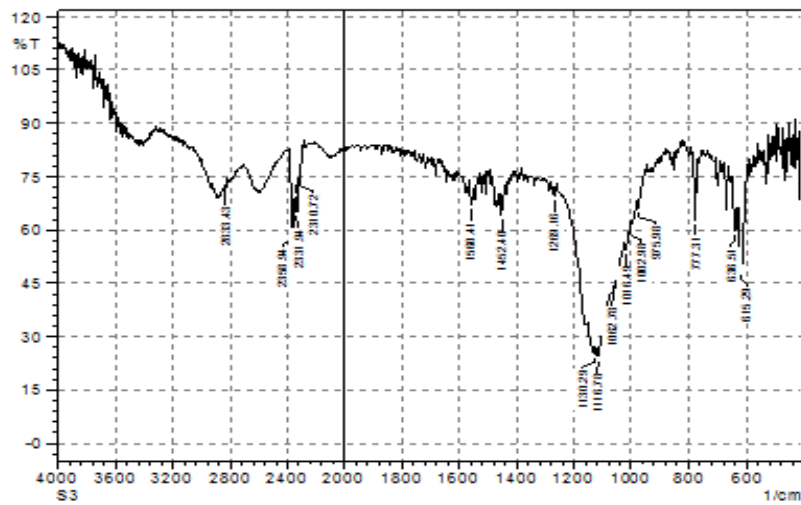


(b2)

Figure(2). FTIR Spectra of (b1) poly 2-chloro aniline (b2) copoly 2-chloro aniline /starch



(c1)



(c2)

Figure (3) :FTIR Spectra of (c1) poly 3-chloro 2-methyl aniline (c2)copoly3-chloro2-methyl aniline /starch

d-Conductive results

The variation of dark current with applied voltage was measured considering steady state condition. In order to obtain the reproducible results, one minute current value after applied voltage was adopted for all measurements. Fig. (4) Shows the current versus voltage on a log- log scale for (poly Aniline, co-poly (3cloro-2methelaniline,co-poly(2-cloroaniline)))deposit on Aluminum plat, at room temperature. At low region (1-10V) the current shows ohmic behavior. The bulk conductivity of theirs polymers films in the ohmic region was at room Temperature .From their figure, the current increased with increasing applied voltage.

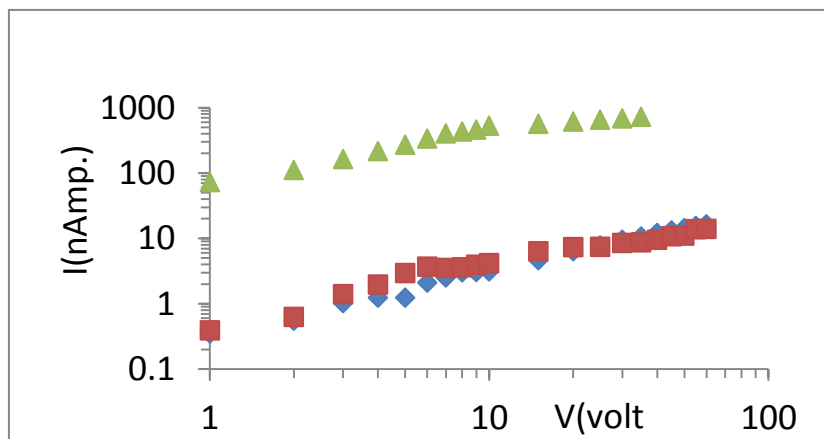
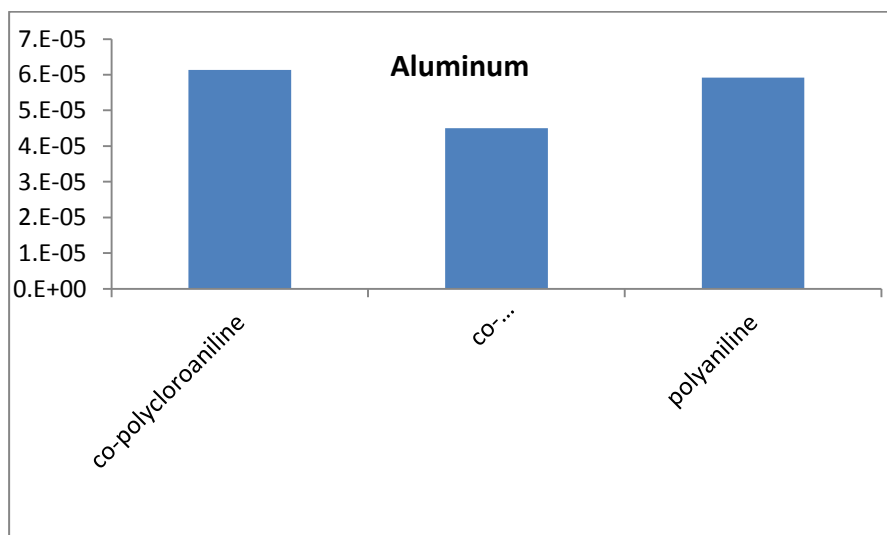


Fig.(4) shows the current versus voltage on a log- log scale for (poly Aniline, co-poly(3cloro-2methelaniline,co-poly(2-cloroaniline)))deposit on Aluminum plat, at room temperature

Fig(5) shows the conductivity for for (poly Aniline, co-poly(3cloro-2methelaniline,co-poly(2-cloroaniline))),deposed on Aluminum substrate, it is clear from the figure that increasing conductivity for co-poly(cloroanile) that mean this polymer have small activation energy



Fig(5) shows the conductivity for for (poly Aniline, co-poly(3cloro-2methelaniline,co-poly(2-cloroaniline))) deposited on Aluminum substrate

The electric properties of polymeric materials depend not only on the type polymer but also on the type of substrate .The current were measured as a function of voltage after a period of time for three

polymers(poly Aniline, co-poly(3cloro-2methelaniline,co-poly(2-cloroaniline)))deposit on glass substrat, at room temperature.as shown in figure (6).Three Curves can be distinguished on the curves at low voltage, from the straight line in homic regain limited conductivity for polymers(poly Aniline, co-poly(3cloro-2methelaniline,co-poly(2-cloroaniline))).

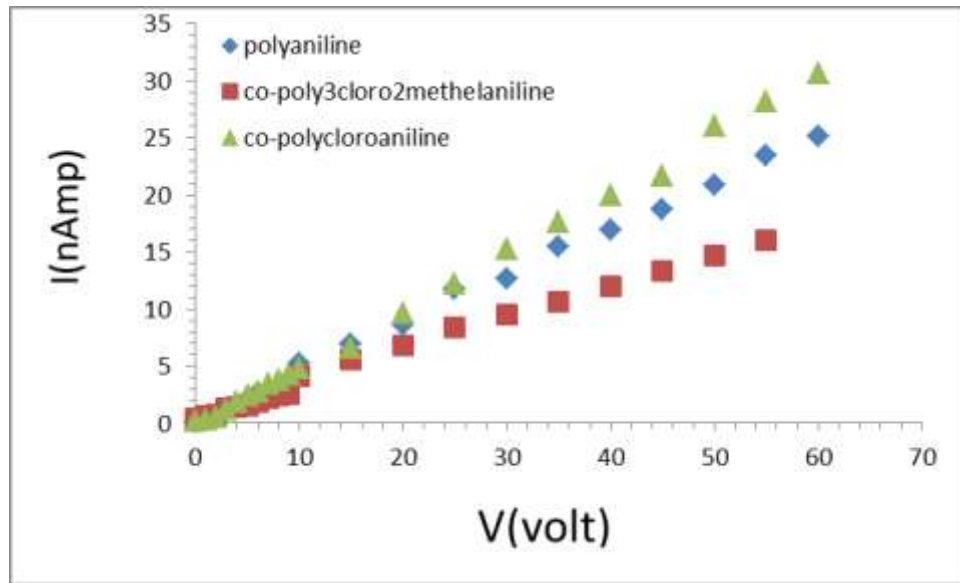
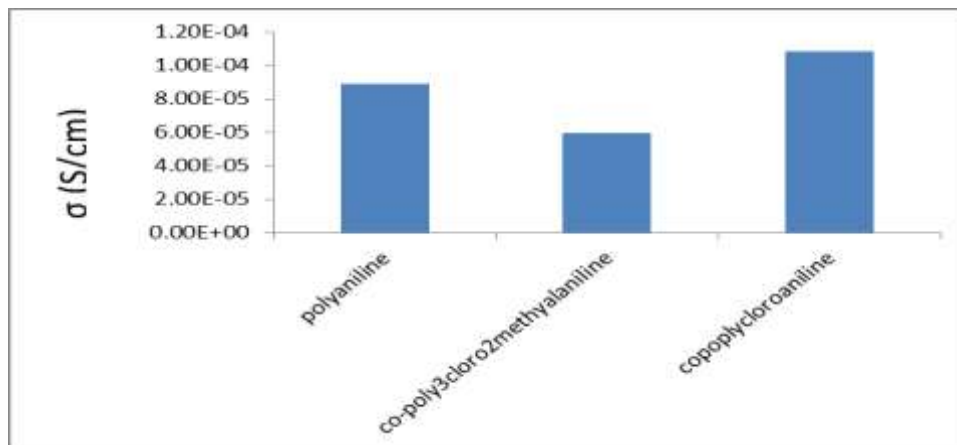


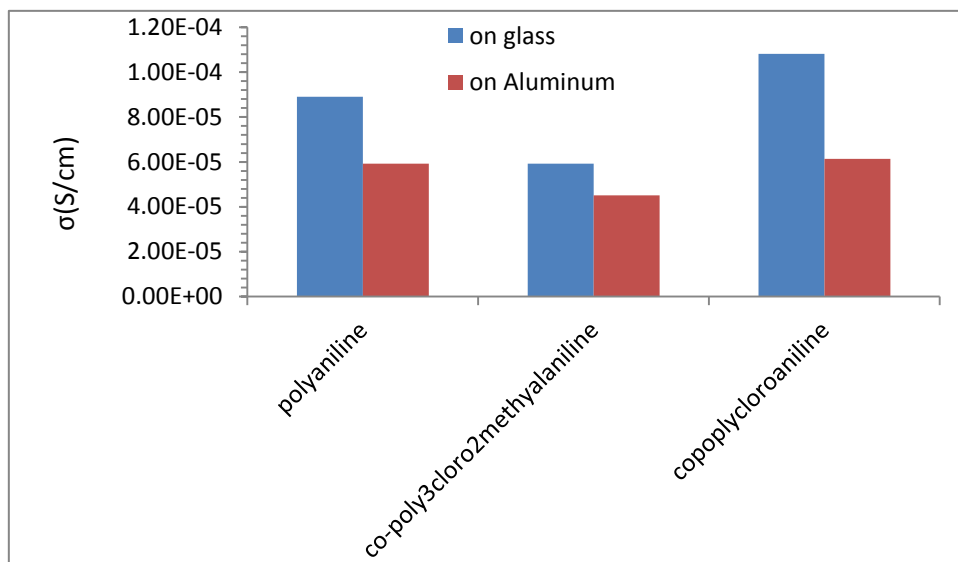
Fig.(6) shows the current versus voltage on a log- log scale for (poly Aniline, co-poly(3cloro-2methelaniline,co-poly(2-cloroaniline)))deposit on glass substrate, at room temperature.



Fig(7) shows the conductivity for (poly Aniline, co-poly(3cloro-2methelaniline,co-poly(2-cloroaniline))),deposited on glass substrate clear from the figure that increasing conductivity for co-poly(2-cloroaniline) this behavior same the behavior in figure (5)

Fig(7) shows the conductivity for for (poly Aniline, co-poly(3cloro-2methelaniline,co-poly(2-cloroaniline)),deposited on glass substrate.

Fig(8) shows the conductivity for (poly Aniline, co-poly(3cloro-2methelaniline,co-poly(2-cloroaniline)),deposited on finger electrode Aluminum deposited on glass and Aluminum substrate , from this figure we observed ,the samples deposited on finger electrode Aluminum deposited on glass substrate have high conductivity compared with the samples deposited on Aluminum plat. We show method to differentiate conductivities from the surface states and the coexisting bulk states in films polymers. Using this method, we demonstrate the separation of 2D and 3D conduction in topological insulators by comparing the conductance surface and bulk by using substrate deposition. The method offers a means to understanding different between surface and bulk conductive. Here we report a new method to account for both surface and bulk conduction for both 2D and 3D. After validation in both the 2D and 3D limits, we employ this method to differentiate conductivities from the surface states



Fig(8) shows the conductivity for for (poly Aniline, co-poly(3cloro-2methelaniline,co-poly(2-cloroaniline)),deposited on finger electrode Aluminum deposited on glass and Aluminum substrate

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