The Effect of the Solvents on Electrical Properties of POT Conducting Polymer

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K E Y W O R D S

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Activation energy

A B S T R A C T

In this research, the preparation conducting polymer poly(O-Toluidine) emeraldine salt (ES) doped with HCL (POT/HCL) by oxidizing polymerization external doping by DBSA the effect of the solvent on the electrical characterization of Poly (O-toluidine) was studied.POT (EB) powder was completely dissolving in all solvents such as chloroform, formic acid, Toluene, and meta-cresol. The morphology and composition of POT were measured by SEM and EDX. Two-probe techniques were used to calculate electrical conductivity; an interdigitated finger electrode was used to measure electrical conductivity. The effect of temperatures on electrical conductivity was also studied to provide heating in the range of (303-373 K) and used to the found activation energy of (POT) in a different solvent.

1. Introduction

Polyaniline (PANI) and Poly (O-Toluidine) (POT) are known to be more effective polymer conductor. The area of conducting polymer has been booming quickly, day by day, and all of these products are essential for this century. Polyaniline, one of the two naturally best polymer conductors A sluggish and low processability due to its insolubility Organic special solvents [1, 2]. Polymers of the substitution aniline show greater solubility, than the conductivity found is noticeably smaller. Nonetheless, In the past few years, attempts are being made to enhance the processability of these polymers. Utilizing the Protonic acid functionality also permits the conduct of polyaniline. The production probably results in soluble polyaniline compound organic solvents such as Chloroform Formic-acid Toluene and Meta-cresol [3,4]. Once adding formic-acid the energy level would be present will be between the valence band and the conduction band and increase the energy level with increased doping (formic acid), which produces polaron bands within the energy gap naturally special bonding structure around the conjugated polymer, consists of the double alternate structure (π) and single (π) bonds (Conjugated polymers).

Suppose an electron is adjusted to the conjugated polymer column (reduction, n-type doping) or removed from it (oxidation, p-type doping). In that case, the chemical or electrochemical doping procedure has followed the charge can freely move the conjugation routes anyway when the electrical potential is applied.

The electrical conductivity of the entire dielectric (10-7S/cm) semiconductor (10-5-10-1S/cm)-metal (102-105 S/cm) scope is based on the degree of doping [5]. The oxidized state-related charge is usually delocalized over many units of such polymers and can create either a radical cation (polaron) or a dication (Bipolaron); adding charge to the chain may change the aromatic arrangement into a lower bandgap of the quinoid arrangement [6].

Activation energy is suitable for several other time scales, chemical reaction rate constants, and intrinsic disputes. It could be necessary to pick a sufficient temperature range especially dominant in these cases. Coefficients of diffusion, Period of reorientation, viscosity, and dielectric relaxation. There are only a few kinds of time scales that may be represented the Arrhenius equation is similar to Equation (4) [7].

Strong Conjugate polymer string, unique doping and de-doping cycle, and redox electrical reversibility contribute to the special properties of conductive polymers, such as strong non-linear

optical properties of metal or semiconductor and electrical properties. Maintaining mechanical properties like those used for conventional polymers opens up new growth opportunities.

All promising discoveries of development are compatible with their properties. As regards, for example, their semi-conductive behavior, polymer-based electronic devices (e.g., Schottky rectifier, field-effect resistance, LEDs, etc.) [8]

In this work, we dissolve POT (EB) in different solvents. One of these meta-cresol solvents is at a disadvantage in the first case.

The implementation of adhesives is confined to glass and other substances resistant to m-cresol, and the toxic effects of m-cresol solutes are very hard to apply in practice. M-cresol acts as a "secondary doping," especially useful for coatings and films requiring quality. A wide selection of articles is eligible to publish works on substituted polyaniline derivatives [8-11].

These conductive polymers have amazing mechanical and electrical properties and can be produced continuously as efficient films using electrochemical techniques. In some PANI application areas, electrical conductivity has been among $(10-10 – 10-2)(\Omega$ cm$)-1$ and is used as a hole injection layer for versatile light-emitting diodes. [12-15].

This paper introduces a novel polymerization process for chemical processing poly (O-toluidine) secondary dopant with HCL and dissolved in chloroform $CHCl_3$, Formic acid CH_2O_2, Toluene $C_6H_5CH_3$, and meta-cresol C_7H_8O (Fig. 1) and calculating the electrical conductivity for each solvent and calculate the activation energy.

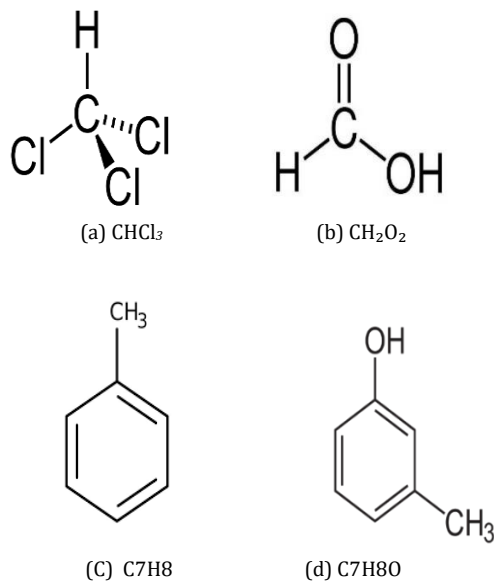(a) $CHCl_3$ (b) CH_2O_2

(C) C7H8   (d) C7H8O

Fig. 1. Structures of Solvents (a) Chloroform (b) Formic acid (C) Toluene (d) Meta-Cresol

2. Experimental

Materials: (O-Tolidine) monomer was provided by Fisher scientific company. Fluka Company provided hydrochloric acid (HCl). Dodecylbenzene sulfonic acid (DBSA) and ammonium persulfate $(NH4)2S2O8$ were obtained from the Aldrich company. Different solvents were used to dissolve POT such as Chloroform, Formic acid 99-100% analar normapur from slaughter, Toluene from Reagent, water <0.2, Assay>99.5, weight Per ml(g) 0.865,0.875, Meta Cresol 99%, ACROS Organics from fisher.

3. Preparation of Conducting Polymer (POT)

Poly(o-toluidine) (POT) doped with hydrochloride was synthesized using a chemical polymerization technique. The same method of preparing for researcher Kareema was followed [16] Were using ammonium persulphate as an oxidizing agent. The polymerization of 2.4g from the monomer (O-Toluidine) dissolving in 4 ml (1M/HCL) Initiated by a small dropwise addition of oxidizing agent (4.3 g APS) in 24ml (1M/HCl) Under mechanical continuous stirring at (0-5 ° c). When the oxidizing agent was completely added, the reaction mixture was kept constant stirring for 24 hours. The polymer was filtered and washed with distilled water filtrate. Finally, the polymer was dried in an oven at 50 °c for 12 hr. The result was black-green powder (POT/ES).

POT (ES) emeraldine salt transforms to emeraldine base by adding ammonia and left for about 8h, then filtered and dried in a vacuum oven at 50 °C. 0.1 g from POT (EB) dissolved 2ml of a suitable solvent (chloroform formic acid, Toluene, and meta-cresol. The solution was put under the starrier for 2 h after adding 0.13g Dodecylbenzene sulfonic acid (DBSA) and remains on mechanical stirrer 1 h [16]. Thin films of (POT-DBSA) prepared using the Process of Spin Coating.

4. Results & Discussion

EDX: the technique was performed to find the chemical composition of POT. Figure 2 shows The EDX patron of POT-DBSA material dissolved in Chloroform $CHCl_3$. The curve confirms the existence of C, Cl, and O for Chloroform and displays that the ratio of C, Cl, and O is 71.56, 0.64, and 21.52, respectively. The element Si, S, Al from the substrate of the device.
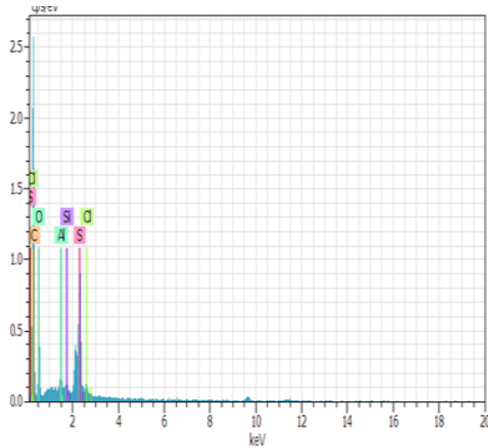
Fig. 2. The EDX patron of POT-DBSA material dissolved in Chloroform CHCl3

SEM: The SEM technique was used to study surface morphology; the thin film was designed by deposition on a glass plate SEM POT-DBSA thin-film graphics. Figures 3 show the image of POT dissolved in Chloroform. The figure shows the surface morphology of the film is smooth and has spherically formed grains. No holes or cracks are observed in the sample. The surface morphology also shows the average grain sizes of the films were approximately (14.31) μm in diameter.
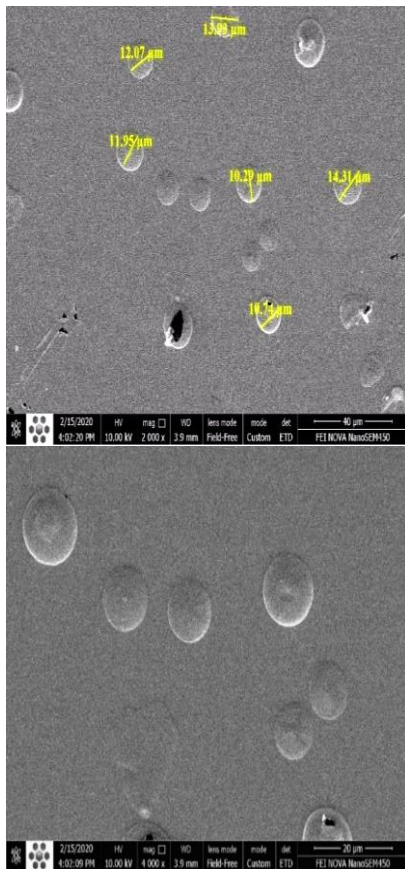

Fig. 3. Graphics of POT-DBSA dissolved in Chloroform obtained by scanning electron microscopy SEM Morphology of (POT-DBSA CHCl3)

5. The Electrical Characterization

The polymer POT(EB) +DBSA was dissolved in chloroform, formic acid, Toluene, and Meta-cresol. Each one of them deposited on the interdigitated finger electrode is shown in Figure 4. The conductivity can be calculated from this equation [16]:

$$\sigma_s = \frac{I}{V}\frac{L}{Wt} \tag{1}$$

t: is polymer thickness, W is finger range (10 mm), l is the number of fingers (10), and L is the space between electrodes (100μm).[17]

$$\sigma_s = \frac{I}{V\,t}\frac{100*10^{-6}}{10*10*10^{-3}} \tag{2}$$

$$\sigma_s = \frac{I}{V\,t}10^{-3}\ \text{s/cm} \tag{3}$$

Figure 5 Shows I-V characteristics for (POT/EB) with different solvents at room temperature. The current increases linearly with the applied voltage between 0.5 V and 20V for all samples. All these curves are referred to the ohmic behavior.

The electrical conductivity was calculated from equation (1) and tabulated in Table 1.

The higher conductivity of samples found using chloroform and Formic-acid solvents is about (0.38 *10-1 and 0.19*10-1 S/cm) respectively. The lowest electrical conductivity at Meta-cresol solvent is about $0.23*10^{-4}$. The difference in electrical conductivity is about four orders. This conductivity indicates that chloroform and formic acid interact more strongly with polymer chain and DBSA dopant anions than with meta –cresol.

That increases in electrical conductivity may be caused by secondary doping so that the bipolaron sites increase in POT-DBSA conducting polymer chins [18].

The high conductivity in chloroform because the sample drying time is the fast and chemical structure of chloroform. This increases the possibility of charge carrier hopping between macromolecules within domains and better film conductivity [19].
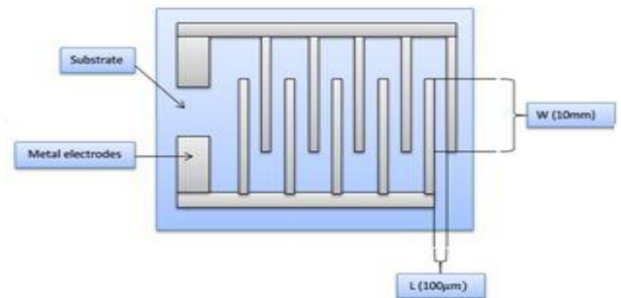

Fig. 4. A schematic of an interdigital electrode for fingers [20].

Table 1. Electrical conductivity for POT -DBSA with solvent

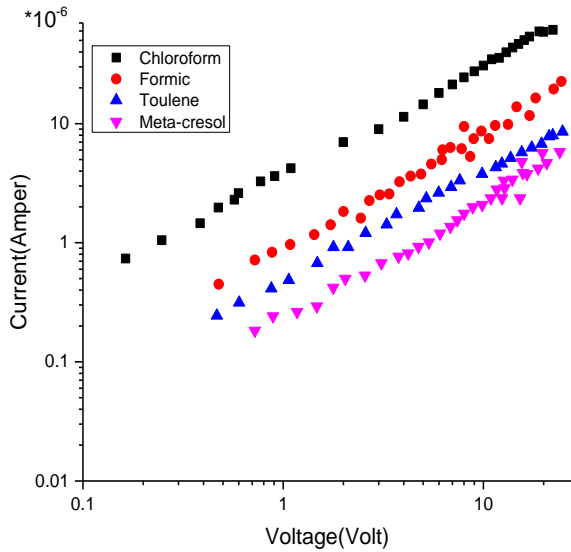| The polymer (POT)	Solvents	Conductivity (σ) (mS. Cm^{-1})
POT(EB)+DBSA	Chloroform	$380*10^{-1}$ [3]
POT(EB)+DBSA	Formic-acid	$190*10^{-1}$ [3]
POT(EB)+DBSA	Toluene	$430*10^{-2}$ [4]
POT(EB)+DBSA	Meta-cresol	$230*10^{-4}$ [3]

Fig. 5. I-V Characteristic for (POT/All Solvents)

6. The Effect of Temperatures on The Electrical Conductivity

Current-voltage characteristics of POT-DBSA dissolved in various solvents and at temperature range (303-373 K) can be seen in Figure 6. All figures (different in solvent) detect ohmic behavior, the current increases as voltage increases at a constant temperature. At a constant voltage, the recent increases as temperature increases. As temperature increases, the number of charge carriers increases, leading to increases in electrical conductivity [17].

The relation between electrical conductivity and temperature Can be described by using the Arrhenius equation:

$$\sigma = \sigma_0 \exp -Ea/KT \qquad (4)$$

Ea: is the activation energy, and K: is the constant Boltzman.

Figure 7 Indicates the ln σ as a component of ($10^3/T$) for (POT-DBSA) thin films prepared by dissolved in different solvents.

Figure 7 indicates that electrical conductivity increases with increased temperature; this means the POT-DBSA has a negative thermal

coefficient for all solvents. It can also be seen that POT-DBSA dissolved in Chloroform and meta-cresol has two activation energy: one at low temperature (303-323K) and second at high temperature (353-373K). The activation energy for chloroform and meta-cresol (0.90, 0.85 eV) and (1.56, 0.34 eV) for chloroform and M-cresol, respectively, an approximate value for a previous study [19]. The activation energy for Formic acid is about (1.2) eV, and Toluene is about (0.97) eV. Via the activation energy, the temperature sensitivity of polymer melt viscosity can be measured. The molecule's thermal movement is dictated by an increase in temperature, which results in their displacement based on the free motion of the molecules and the overcoming of the intermolecular interaction forces.

The Arrhenius form of the equation is based on the absolute principle of the rating phase. Activation energy can say how much energy is required for the melt flow as the temperature increases from one temperature to another at a higher temperature. As a result, lower activation energy would mean that the polymer melt would flow more effectively. [21]

At rang (353-373) K, the temperature is sufficient to move the charge carrier from the valence band to the bipolaron conduction band; the electrical conductivity follows the free carrier transition in an extended state over the chain.

Length in addition to the interchain transition as a temperature lowered (303-323K), the number of holes in the valence band decreases and shifts to the localized bipolaron state. This region can be mentioned by hopping (charge transfer) through tail states between adjacent sites. When the valence band merges the conduction band, the valence electrons are free to pass and scatter in the conduction band. Charges are shifted with the ensuing establishment of charge carriers. The task of the dopant is not only to remove electrons from the conducting polymer but also to add electrons to the conducting polymer spine [22]. The ohmic behavior at low temperature under 333 K and higher than that is not linear.

The activation energy is tabulated in Table 2.

Table 2. The activation energy produced from I V characteristic with solvent

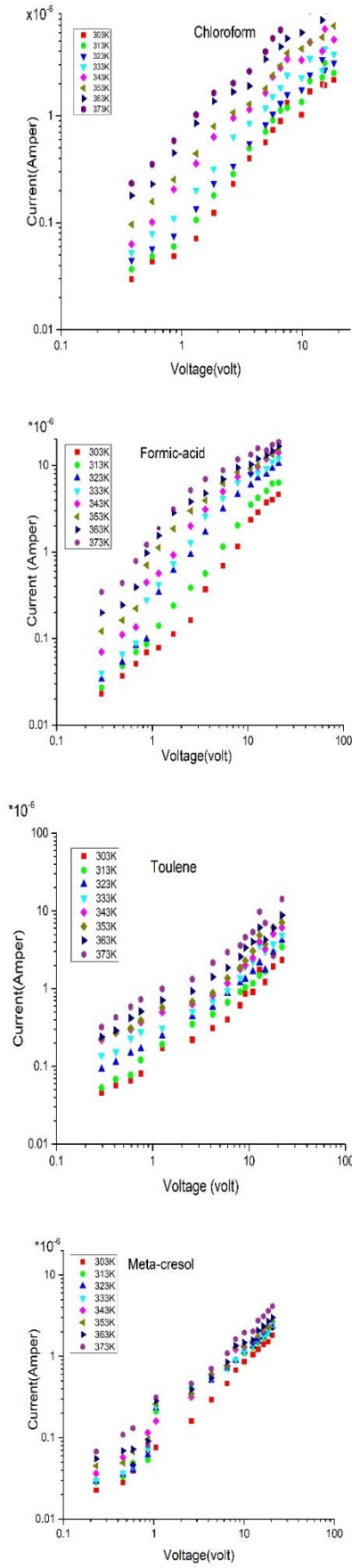| The Solvent	Activation of energy	Activation of energy
Chloroform	0.90 eV	0.85 eV [20]
Formic-acid	1.2 eV	
Toluene	0.97 eV	
Meta-cresol	1.56 eV	0.43 eV

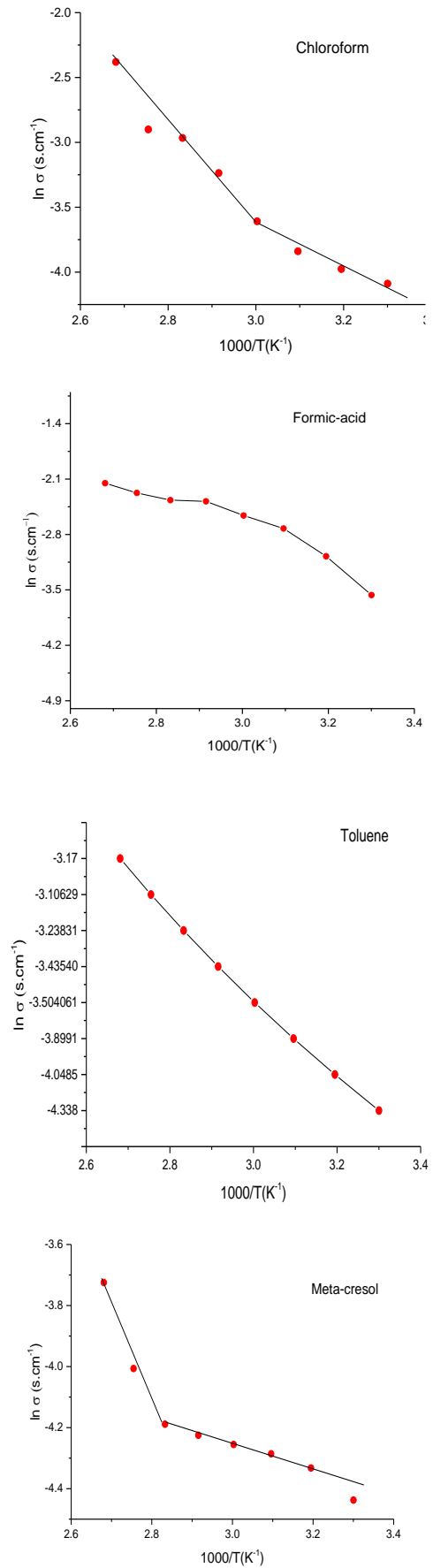**Fig. 6.** I-V characteristic POT-DBSA at different Temperature and different solvent

Fig. 7. Electrical conductivity ln σ as a temperature factor T(K^{-1}) for solvents (a) chloroform (b)Formic-Acid (c)Toluene (d) meta-cresol

7. Conclusion

The purpose of this research is to study electrical properties for POT secondary doping with DBSA by dissolving in several organic solvents after deposition of the solution (POT+DBSA/solvent) on the interdigitated finger electrode. The electrical measurement found the highest electrical conductivity by using chloroform solvent $0.38*10^{-1}$ s/cm after that Formic-acid, Toluene, and lower conductivity at meta-cresol $0.23*10^{-4}$ s/cm. and the activation energy 0.90 eV chloroform, 1.56 eV in meta cresol. As well as calculating the I-V characteristic with different temperatures, we find the activation energy for each solvent.

8. Acknowledgments

9. References

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