D.C electrical conductivity of prepared pure and doped polyaniline salt

Mustafa N. Obaid and Salma M. Hassan

Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq

E-mail: salma.mhammed@yahoo.com

Abstract

Pure Polyaniline salt, and protonation PANI by H_2SO_4 were synthesized by electro-chemical oxidative polymerization of aniline with acidity of H_2SO_4. The solution was prepared in reaction temperature equal 291 K and the acidity of aqueous solution was 1 molarities. The prepared polyaniline was characterized by FT-IR, the result indicate that the intensity is increase with increasing of applied voltage. The dc conductivity has been measured for bulk polyaniline pure and doped in the form of compressed pellet with evaporated Ohmic Al electrodes in temperature range (303-423) K. The E_{av} energy of the thermal rate process of the electrical conductivity was determined. The results indicate that the dc conductivity of doped samples are two or three orders of magnitude higher by comparison with the pure sample and found that the increasing in conductivity of prepared samples with applied voltage is systematic.

<div dir="rtl">

التوصيلية الكهربائية المستمرة لملح البولي انيلين المحضر النقي و المطعم

مصطفى نجم عبيد و سلمى محمد حسن

قسم الفيزياء، كلية العلوم، جامعة بغداد، بغداد، العراق

الخلاصة

حضر ملح البولي أنلين النقي والبولي انيلين المطعم بحامض الكبريتيك باستخدام بلمرة الاكسدة الالكتروكيميائية للانلين مع حامض الكبريتيك بدرجة حرارة 291 كلفن وفي وسط حامضي ذو مولارية مساوية الى 1 مولاري. وقد استخدم طيف الاشعة تحت الحمراء لتشخيص البولي أنلين المحضر حيث أظهرت النتائج الشدة مع زيادة الفولتية المسلطة، كما قيست التوصيلية المستمرة لنماذج البولي انلين النقي و المطعم المحضرة على شكل قرص وتم استخدام تقنية التبخير لترسيب اقطاب المنيوم لهذه النماذج وكانت القياسات ضمن مدى درجات الحرارة 303-423 كلفن. أظهرت النتائج ان التوصلية للبوليمر المطعم أعلى بمرتبتين مقارنة بالنموذج الغير مطعم ووجد أيضا ان زيادة التوصيلية للبوليمر المحضر مع الجهد المسلط كانت بصورة منتظمة.

</div>

Introduction

Traditionally polymers were seen as good electrical insulators and most of their applications had relied on their insulating properties [1]. The use of PANI as logic or switching elements is of key importance in the development of new electronic devices, PANI also have many applications in (Chemical Sensor, Biosensor, Data Storage, Super capacitor and Photovoltaic Cell etc.) [2]. However, until three decades ago researchers showed that certain class of polymers exhibits semiconducting properties [3]. Early studies showed that polypyrroles exhibit signs of conductivity [4].

Polyaniline is one of the most studied materials because of its high conductivity upon doping with acids, well behaved electrochemistry, and easy preparation under reproducible conditions by electro polymerization and chemically oxidation of aniline, chemical and electrical stability, and good environmental stability [5, 6].

A key property of a conductive polymer is the presence of conjugated double bonds along the backbone of the polymer. In conjugation, the bonds between the carbon atoms are alternately single and double. Every bond contains a localized "sigma" (σ) bond which forms a strong chemical bond. In addition, every double bond also contains a less strongly localized "pi" (p) bond which is weaker. However, conjugation is not enough to make the polymer material conductive. In addition, and this is what the dopant does, charge carriers in the form of extra electrons or holes have to be injected into the material. A hole is a position where an electron is missing. When such a hole is filled by an electron jumping in from a neighboring position, a new hole is created and so on, allowing charge to migrate a long distance. The conducting mechanisms are well understood by considering their conjugated carbon backbones the conducting mechanism in the polyaniline forms is more complex and not very well established. Polyaniline acts as an electrically conductive material only in the protonation form of emeraldine salt. It can changes the electronic conductivity about (10) orders of magnitude, passing from insulator state (emeraldine base with s <10-10 S/cm) to metallic conduction (emeraldine salt with s ~10^{-1}-10^{2} S/cm), depending upon the protonation degree [7, 8]. These properties are optimal at stoechiometrical ratio between the oxidant, hydrochloric/ sulfuric acid and aniline [9, 10].

The aspect which attracted our interest is the protonated structure of polyaniline in the acidic media (Fig.1) Polyaniline in its sulfonated form shows a close structure with the ion conducting polymers, where the inorganic anions are represented by HSO_4^- species.
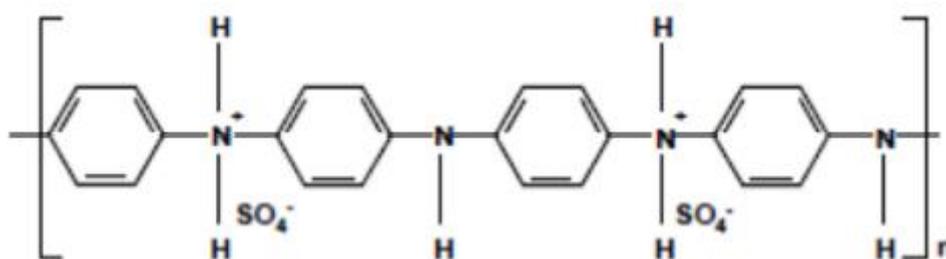

Fig.1: Polyaniline as Emeraldine Salt (ES), in sulfuric acid media.

In the emeraldine salt (ES), the HSO_4^- species are ionically bonded with the -NH groups presented in the polymer chain. Actually, these kinds of bonds are very weak and can be removed very easy by changing the system's pH. By supplementary doping of polyaniline in sulfuric acid media, actually we introduced multiple charge carriers which determine an improvement of the electrical conduction along the polymer chain. Moreover, it was assume that the total conduction in SPANI is given by summing the electrical conduction and ionic conduction that occurs by sulfonic groups on the aromatic rings and transition of electrons as shown in Fig. 2.
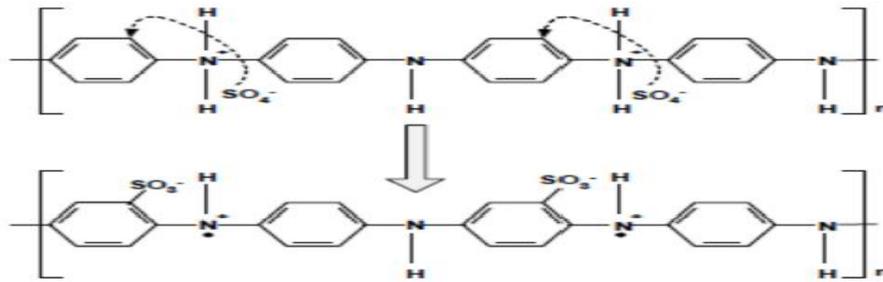
Fig. 2: The designed transition of electron conducting PANI (ES) to SO_3^- doped polyaniline (SPANI).

Experimental

Generally, experimental set-up for electrochemical synthesis of electro conducting polymers in laboratory conditions is simple. It involves, in majority of cases, standard three-electrode electrochemical cell, although in some cases of galvano static polymerization, two electrode cell can be used [11]. The polymer obtained by this procedure is deposited directly on the electrode. Novel experimental set-up, enabling electrochemical generation of polyaniline colloids, using flow-through electrochemical cell, was also reported [12]. In this novel electrochemical cell, anode was separated from two and cathodes by ion exchange membrane the anodic electrode was Graphite rod and the two cathodic electrodes was plates of stainless steel. The anodic and cathodic electrolytes were passed through electrode compartments at specified flow, while polymerization was achieved at constant potential.

Preparation of PANI

Pure polyaniline was prepared by dissolving of (2.59 g) of aniline hydrochloride in (50 ml) of distilled water and mixed with (5.71 g) from ammonium peroxy disulfate that dissolved in (50 ml) of distilled water in the Container of electrochemical cell at room temperature and the doped sample was prepared in the same way but both of aniline hydrochloride and

ammonium peroxy disulfate was dissolved in (1 M) of H_2SO_4 and then constant voltage was applied for a certain sample for two hours. The same process was repeated for (0.5, 1, 1.5, and 2) volt. The deposited Polyaniline has been collected from stainless steel electrode and washed with distilled water. Polyaniline (emeraldine) hydrochloride powder is dried in air for about one hour then in vacuum oven about (80 ℃) for (6 hours) the average yield is (2.29g).

The D.C electrical measurements are used to investigate polyaniline samples doped and pure during polymerization with various voltages. The polyaniline powder was thoroughly grounded in a mortar to obtain very fine particles, and then it was compressed under a pressure of (3 tone) in the form of a pellet. The resulting pellet has a diameter of (10 mm and thickness of 1.68 -1.98mm). To improve the electrical contact the faces of the pellet were coated with aluminum by thermal evaporation. Series circuit method was used for the D.C measurements. The sample was placed in a holder specially designed to minimize stray capacitance. The range of temperature was (303-423) K. The measurement give as, current and resistance.

The total conductivity was calculated from the following equation:

$$\sigma = L/RA \qquad (1)$$

where (L) thickness, (A) cross section and (R) resistance is given by:

R= V/I　　　　　　　　　(2)

where (V) applied voltage and (I) is current.

We used Arrhenius equation to obtained the (E_a) Activation Energy in J by the following formula [13],

$$\sigma = A \exp (-E_a / K_B T) \qquad (3)$$

K_B is the Boltzmann's constant which is 1.3806×10^{-23} J/K, T is the temperature in Kelvin. The E_a is in practice taken to be the slope of an Arrhenius plot of ln (σ) versus $1/T$ in Kelvin [13].

Results and discussion
1. Fourier Transform Infrared (FT-IR)

The FTIR spectra of protonation PANI by H_2SO_4 is shown in Figs. 3,4 and 5 The main characteristic peaks of PANI can be interpreted as: the peaks at 1564 and 1479 cm^{-1} is due to C=C* stretching mode of the quinoid rings and C=C stretching mode of benzenoid rings respectively. The peak at about 1301 cm^{-1} is due to the C–N stretching mode, the peaks at 1145 cm^{-1} Q=NH^{+} or B–NH^{+}–B/C–H bending mode of Q ring [14,15] and a shoulder-like band at 1120 cm^{-1} ascribed to Q=NH^{+}, B–NH^{+}–B, and C–H bending mode of the Q ring in the ES [13], the peak at 1118 cm^{-1} is due to S–O bond stretching of SO_3^- [15] and the peak at 885 cm^{-1} is HSO_4^- in ES, or C–H in 1,2,4-trisubstituted B ring (2-substituted phenazine ring)[16] and the peaks 466 cm^{-1} naphthalenes Out of plane ring bending these values are listed in Table 1.

Quinoid and benzenoid rings are shifted with increasing of applied voltage as shown in Figs. 3, 4 and 5, it's clear from these figures that the intensity is increase with increasing of applied voltage.
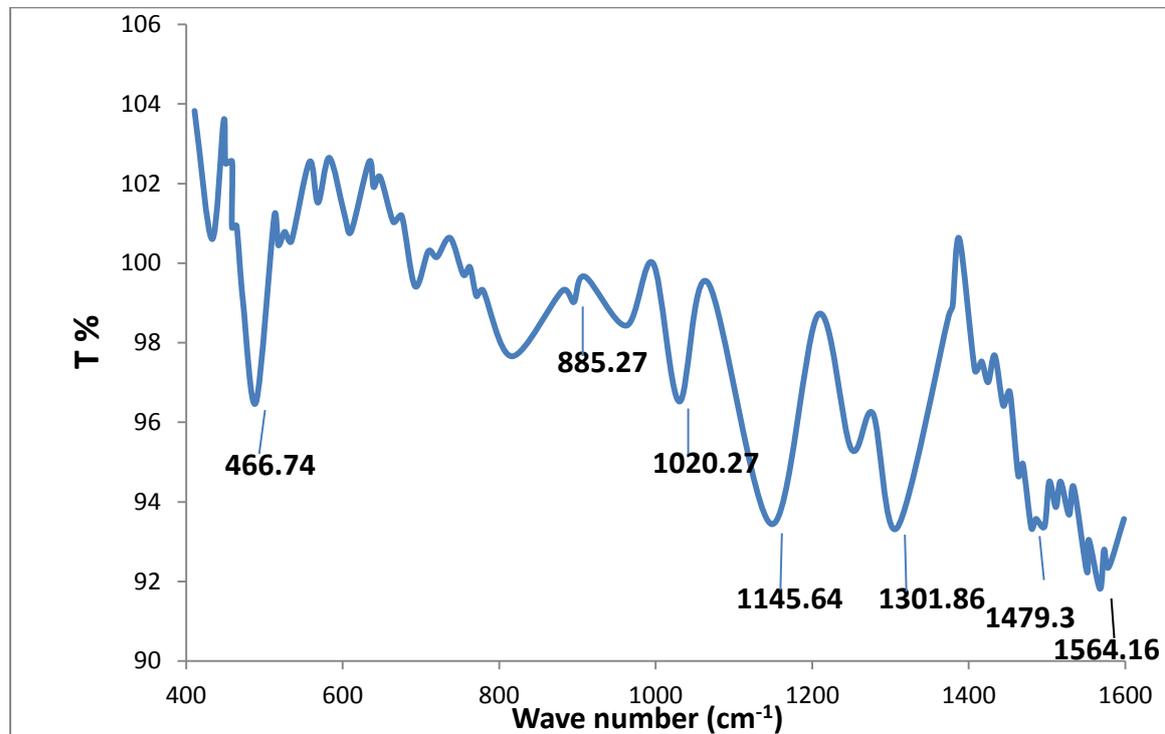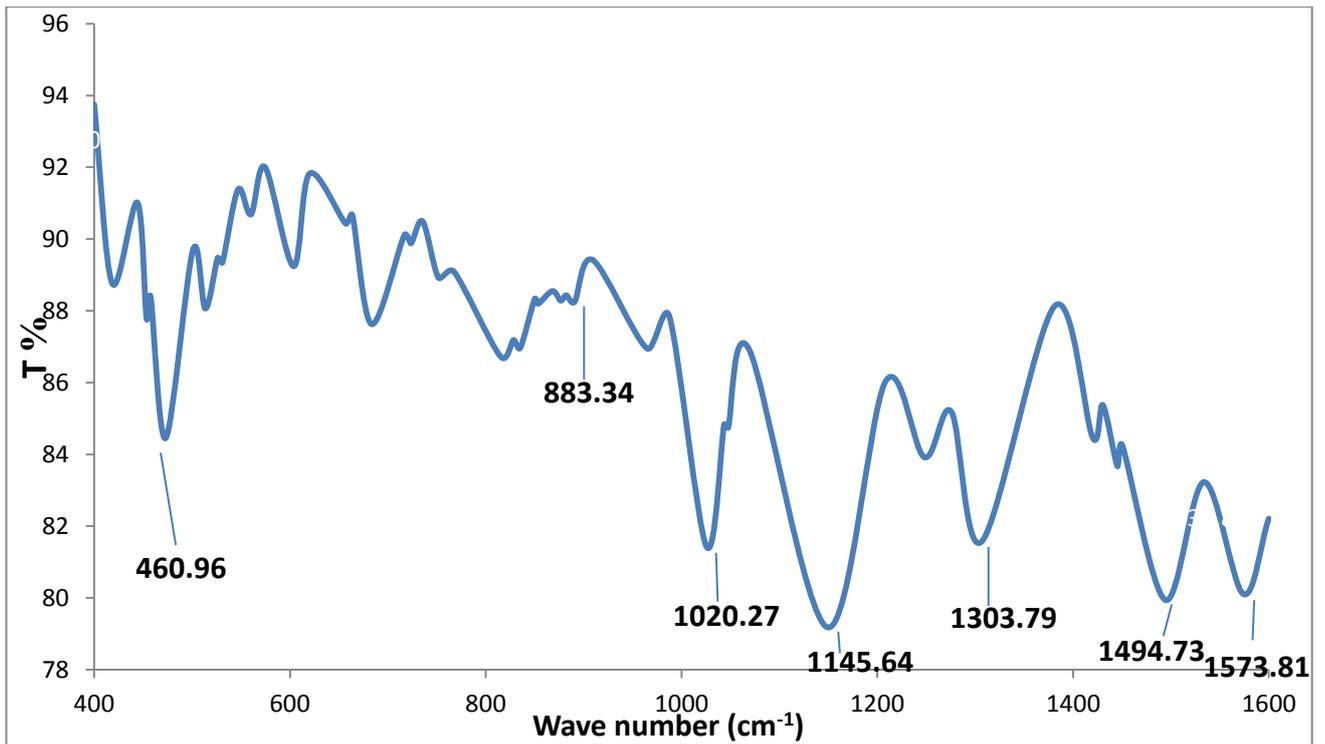

Fig.3: The FT-IR spectrum for 0.5 V polyaniline.
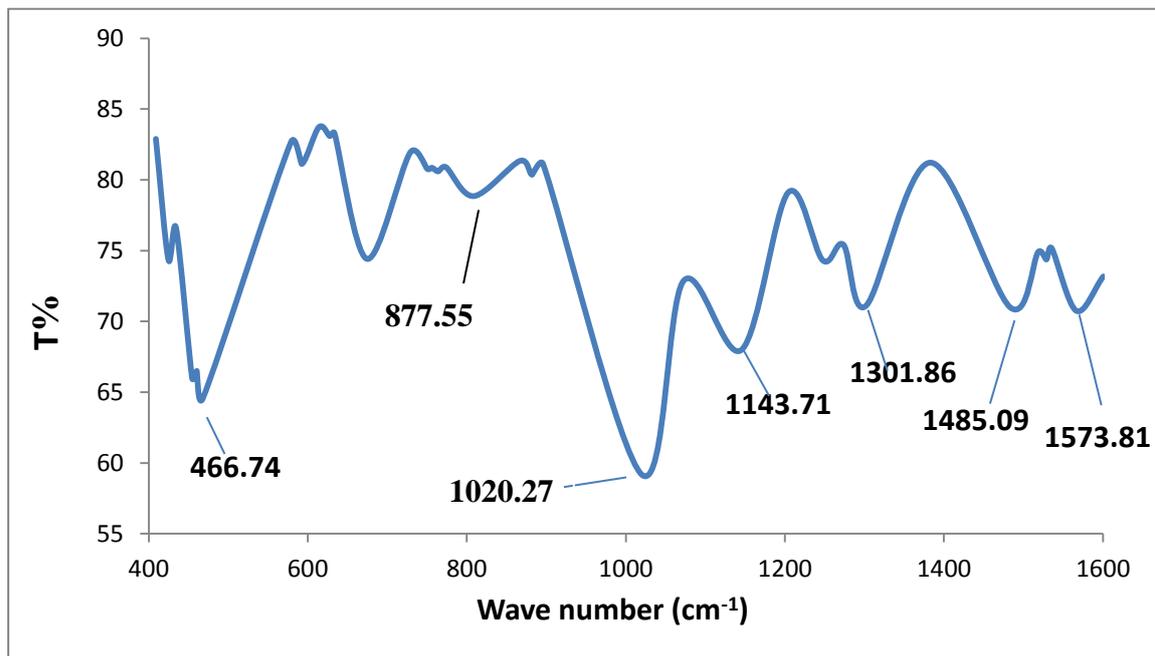
Fig.4: The FT-IR spectrum for 1 V polyaniline.

Fig. 5: The FT-IR spectrum for 2 V polyaniline.

Table 1: General list of FTIR band positions and proposed assignments for PANI.

Wave number (cm^{-1})	Assignments
1564	C=C stretching/C–H bending modes of Q ring
1479	C=C stretching/ C=N asymmetric stretching/C–H bending modes of B ring
1301	C–N stretching of secondary aromatic amine
1145	Q=NH+ or B–NH+–B/C–H bending mode of Q ring
1020	A shoulder-like band at ascribed to Q=NH+, B–NH+·–B, and C–H bending mode of the Q ring in the ES.
885	HSO$_4^-$ in ES, or C–H in 1,2,4-trisubstituted B ring (2-substituted phenazine ring)
466	naphthalenes Out of plane ring bending

2. DC-electrical conductivity

To illustrate the effect of change in applied voltage on the DC-conductivity of polyaniline, a comparison of pure PANI and protonation PANI by H$_2$SO$_4$ was made. Fig. 6 shows the temperature dependence of DC-conductivity in the temperature range 303 - 423 K for pure PANI and protonation PANI by H$_2$SO$_4$ at 2V. From the Fig. 6, it is evident that the DC-electrical conductivity of protonation PANI by H$_2$SO$_4$ is higher than that of pure PANI.
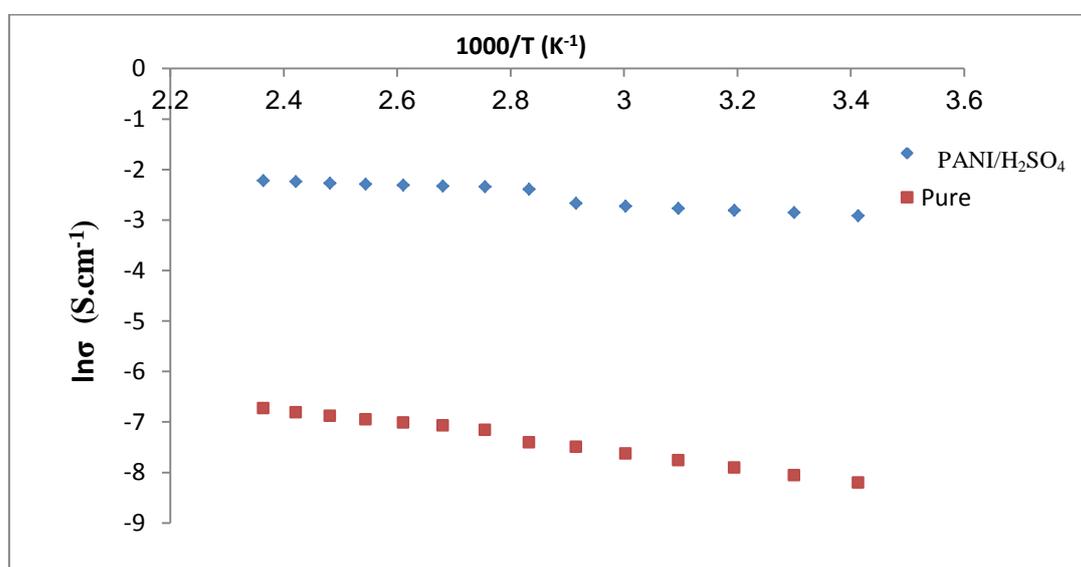

Fig.6: Effect of temperature on DC-electrical conductivity for pure and protonation PANI at 2 V.

Fig. 7 shows that the conductivity is increase with increasing of applied voltage because increasing of polymer growth and this leads to increase the concentration of charge carriers.
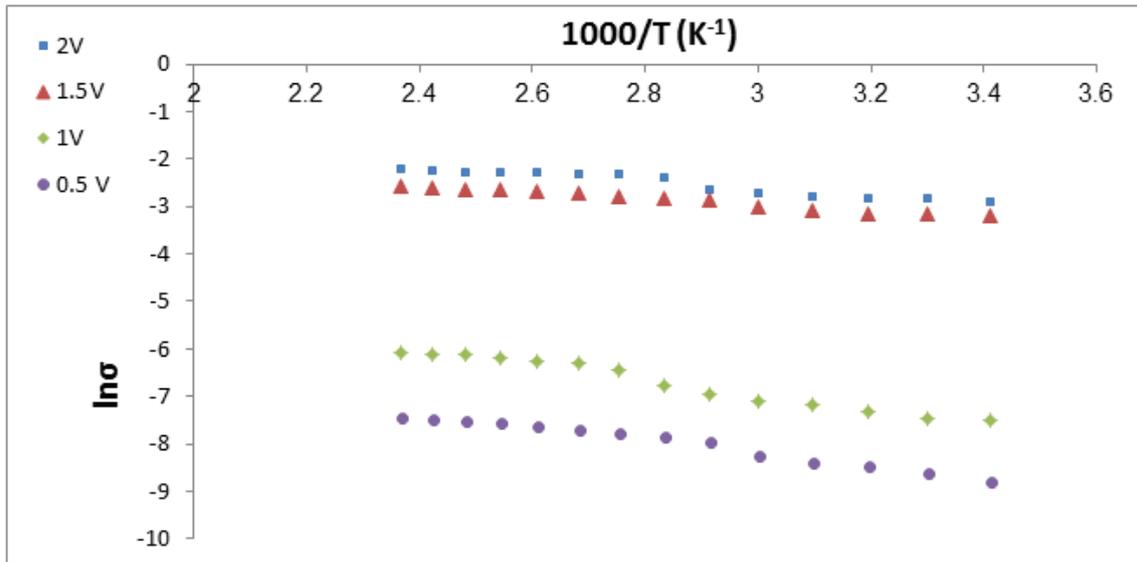
Fig.7: Effect of temperature on DC-electrical conductivity for protonation PANI at different voltage.

It is clear from the Figs. 6 and 7 that samples possessed two mechanisms at low and high temperatures, the plots of ln σ_{DC} vs. 1000/T shows that all samples are nearly straight lines at low and high temperatures, indicating that the conduction in these samples through an activated process having two activation Energies, the range of first region temperature is (303 -343 K) and second region is 373-423 K. The activation behaviors of the samples are studied by using Arrhenius Equation [17]. The values of activation energy calculated from Figs. 6 and **7** as shown in Table 2. It was found that the activation energy for pure PANI is higher than that of protonation PANI; also it was found that the activation energy is decrease at high temperatures. An increase in D.C conductivity with corresponding decrease in activation energy is found to be associated with a shift of Fermi level in doped samples [17].

Table 2: Activation energy data for all investigated samples.

Sample	Activation Energy(ev) low temperature	Activation Energy(ev) high temperature
Pure	0.1232	0.0935
0.5 V	0.1031	0.0653
1 V	0.1087	0.0665
1.5 V	0.0301	0.0256
2 V	0.0451	0.0423

From the value of activation energy it is clear that the conduction is through the carrier concentration at the Fermi level. But the activation energy (Ea) alone does not provide any information whether the conduction takes place in extended states or by hopping in localized states. This can be explained on the basis of the values of pre-exponential factor (σ_o). According to Mott and Davis [18] the value of σ_o in the range 10^3 - 10^4 S.cm^{-1} indicates that the conduction takes place mostly in extended states. A smaller value of σ_o indicates a wide range of localized states and the conduction is taking place by the hopping process. In our case, the values of σ_o are listed in Table

3, therefore the conduction takes place by the hopping process due to the wide range of localized states present in the sample. From the above results we can conclude that the hopping mechanism is responsible for an increase in the conductivity of the samples.

It has been observed from the Fig. 8 that conductivity of the protonation PANI was found to be increased with the increase in temperature as that of pure PANI, representing the semiconducting nature of the protonation PANI. The increase in the conductivity is due to the increase of efficiency of charge transfer by contribution of polaron and bipolaron bands and to the effect of dopant ions. As can be seen, the undoped sample has conductivities in the range of 10^{-4} and the highest conductivity in the range of 10^{-1} was exhibited by the (2V) doped sample.

Table 3: D.C Conductivity data for all investigated samples.

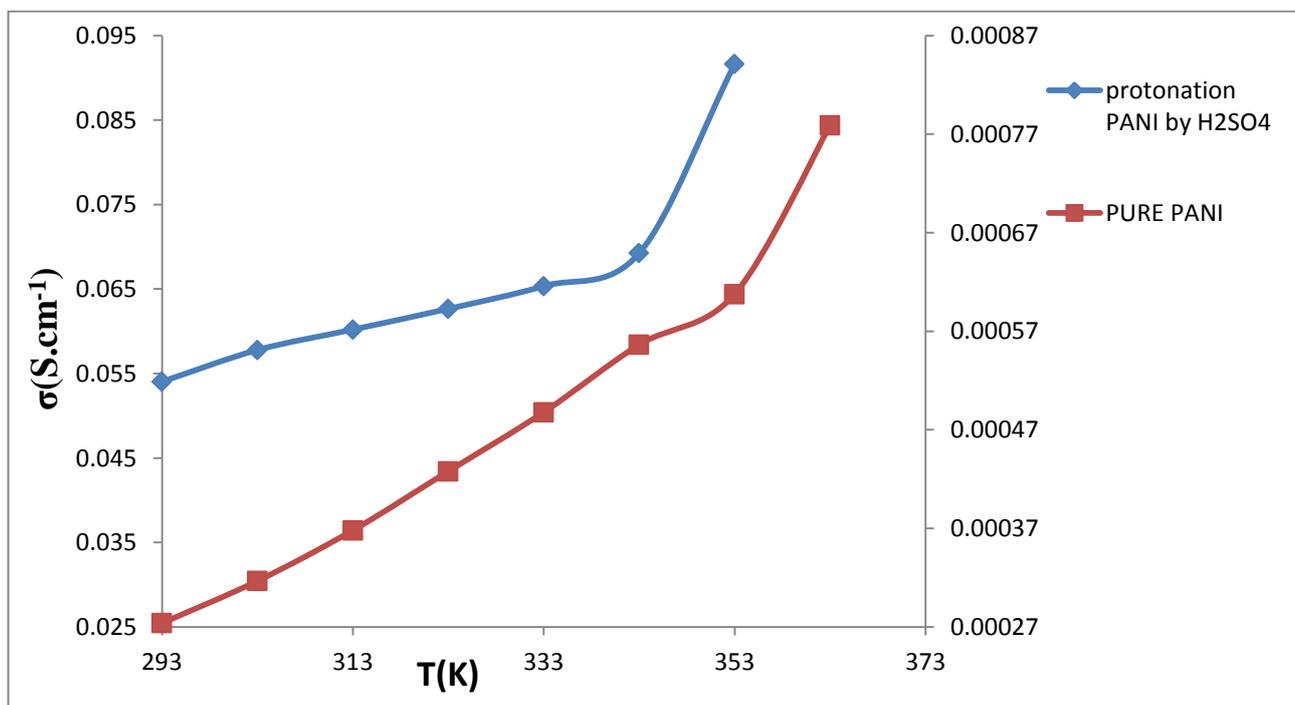| Sample	Minimum conductivity S.cm^{-1}	Maximum conductivity S.cm^{-1}
Pure	2.73×10^{-4}	1.2×10^{-3}
Doped PANI (0.5V)	1.58×10^{-4}	6.07×10^{-4}
Doped PANI (1V)	5.4×10^{-4}	2.32×10^{-3}
Doped PANI (1.5V)	4.17×10^{-2}	7.57×10^{-2}
Doped PANI (2V)	5.4×10^{-2}	1.08×10^{-1}

Fig. 8: Electrical conductivity of pure and protonation PANI by H_2SO_4 at 2 volt.

Fig. 9(a) and 9(b) shows that conductivity of doped samples with different voltage are also increase with increase in temperature; it's clear from above that the increasing in conductivity of prepared samples are systematic.
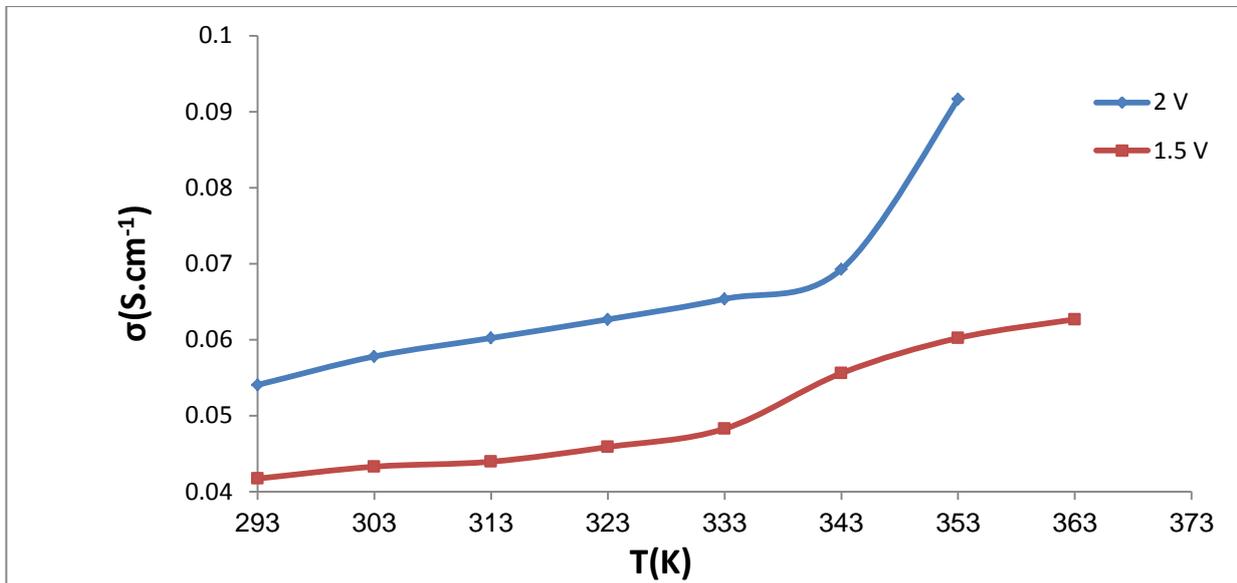
(a)
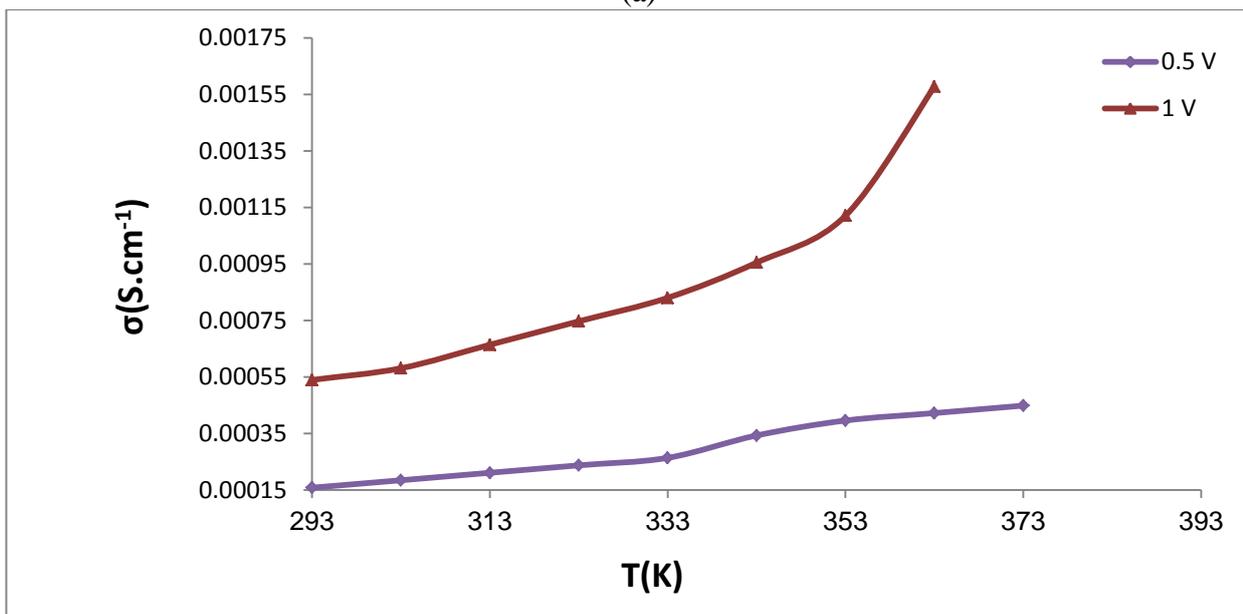
(b)

Fig.9: Electrical conductivity of protonation PANI by H_2SO_4 for (a) 1.5 and 2 volt (b) 0.5 and 1 volt.

Conclusion

The protonation PANI by H_2SO_4 exhibit remarkable improvement of electrical conductivity by increasing of applied voltage when compared with pure PANI the conductivity increase by three orders. The FTIR spectroscopy shows shifting of quinoid and benzenoid rings so, this is a simple way by which electrical properties of other conductive polymers may be enhanced by use different acid and by changing concentration of H_2SO_4 and electrode properties.

References

[1] A.J. Epstein, J.M. Ginder, F. Zuo, R.W. Bigelow, H.Woo, D.B. Tanner, A.F. Richter, W. Huang, G.A. MacDiarmid, Synth. Met., 18 (1987) 303-309.

[2] Jyongsik Jang, Adv. Polym. Sci., 199 (2006)189–259.

[3] A. Heeger, Synth. Met., 125 (2001) 23-42.

[4] B. Bolto, R. McNeill, D. Weiss, Aust. J. Chem., 16 (1963) 1090-1103.

[5] J. J. Huang and B. R. Kaner, J. AM. CHEM. SOC., 126 (2004) 851-855.

[6] A. S. Bitencourt, U. Barros, C. C. Maria, D. S. Leite, International Journal of analytical Chemistry 116, (2012) 1567-1577.

[7] Ali, E.Saion, N. Yahya, A Kassim, K.M. Dahlan, S.Hashim, Journal of Engineering Science and Technology 2, 1 (2007) 111-118.

[8] J. Dumitrescu, C.A Nicolae, A. Maria, R.A. Gabor, M. Grigorescu, M. Mihailescu, U.P.B. Sci. Bull., Series A, 71 (2009) 63-72.

[9] J.E.P. Da-Silva, M.L.A. Temperini, S.I.C. De-Torresi, J. Braz. Chem. Soc.,16, 3A (2005) 322-327.

[10] S. Hdeshmukh, D. Kburghate, V. P. Akare, Journal of Mater. Sci., 30, 1 (2007) 51–56.

[11] G. Wallace, G. Spinks, L. Kane-Maguire, P. Teasdale, CRC Press, (2009) Taylor & Francis Group, ISBN 978-1-4200-6709-5, Boca Raton.

[12] V. Aboutanos, J. Barisci, L. Kane-Maguire, G. Wallace, Synthetic Metals,106, 2 (1999) 89-95.

[13] L.K Sudha, Sukumar Roy, K. Uma Rao, International Journal of Materials, Mechanics and Manufacturing, 2, 1 (2014) 96-100.

[14] Y. N.Qi, F. Xu, L. X. Sun, J. Therm Anal Calorim, 94 (2008) 137-141.

[15] E.N. Konyushenko, J Stejskal, M, Trchová, J. Hradil, J. Kovářová, J. Prokeš, M. Cieslar, J.Y. Hwang, K.H. Chen, I. Sapurina, Polymer , 47 (2006) 5715-5723.

[16] A. Kellenberger, E. Dmitrieva, L.J. Dunsch, Phys. Chem. B, 116 (2012) 4377-4385.

[17] G. B. Shumaila, V. S. Lakshmi, M. Alam, A. M. Siddiqui, M. Zulfequar, M. Husain, Current Applied Physics, 11, 2 (2010) 217-222.

[18] N. F. Mott, E. A. Davis, Clarendon Press, Oxford, 1979.