DC Conductivity in P-Toluenesulphonic Acid Doped Poly (2-Methylaniline)

Atul Kapil, Navdeep Sharma

Abstract: Para-toluenesulphonic acid doped Poly(2-methylaniline) (PmANI) was synthesized by chemical method using ammoniumpersulphate (APS) as an oxidant. It was synthesized along with optimization studies w.r.t. varied dopant-monomer ratios for better DC conductivity. Various spectroscopies like XRD, UV-Vis and FT-IR were used to characterize the polymer. The behavior of DC conductivity with variation in temperature was studied with in the temperature range of 300 - 425 K and it was observed that conductivity rised to ~four orders with the surge in temperature. The experimental conductivity data was fitted with various conduction models to find the proper charge transport mechanism in this polymer.

Keywords: Poly(2-methylaniline), Electrical Conduction, VRH Model, Arrhenius Model

I. INTRODUCTION

Polyaniline (PANI) is the most studied conducting polymer (CP) over worldwide in past few decades due to its excellent properties. Polyaniline is considered a prime choice in all conducting polymers because of its low cost, ease of synthesis, good environmental stability, non-toxicity, high electrical conductivity etc. [1]. It has been widely used as rechargeable batteries, energy storage devices, electromagnetic interference shielding, electronic and optical devices, light emitting diodes (LED's), sensor and super capacitors etc. [2,3]. There are a lot of reports regarding the synthesis of polyaniline by using different dopants, but the weak processibilty and lack of solubility of PANI in common organic solvents shortened its applicability [4]. To overcome these limitations, researchers have adopted two major routes: derivatization of the polymer backbone by using a substituted monomer of PANI and incorporation of bigger organic acids as dopants into the polymer backbone [5].

The synthesis route of polyaniline (PANI) with different dopants has been stated by many researchers worldwide. However, the major drawback of conducting polymers including PANI is the low value of conductivity, processabilty and its weak solubility. It is reported that derivatives of aniline for example anisidine, N-methylaniline or N-ethylaniline, Poly(2-methylaniline) (PmANI) etc have good or moderate solubility in spite of the low observed conductivity [5].

PmANI was prepared chemically by polymerizing 2-methylaniline doped with p-toluenesulphonic acid. Polymerization was initiated by using APS as oxidant. Various spectroscopic characterization techniques were used to confirm the formation of polymer in the doped state. The variation of DC electrical conductivity with the temperature was examined by varying the temperature from 300 to 425K. The charge transport was studied by fitting our experimental data with pre-existed conductivity models. The results were repeated many times to reduce the errors and to increase the reproducibility.

II. EXPERIMENTAL

A. Materials

p-toluenesulphonic acid (p-TSA), 2-methylaniline, Ammoniumperoxydisulfate (APS)and dimethylsulphoxide (DMSO)were used in the present investigation in the form as received from Alfa Aesar.

B. Synthesis

The monomer 2-methylaniline was chemically polymerized to prepare Poly(2-methylaniline) in acidic medium. p-TSA was used as dopant during the polymerization. All the solutions were prepared using distilled water. Monomer 2-methylaniline (0.01mol) dissolved in water was stirred at temperature 0-5 ^oC. This was further mixed with p-TSA which was already dissolved in distilled water. Polymerization process was continued for next 5 hrs after the complete addition of 100ml oxidant solution containing 10 ml of APS. The precipitates were separated by vacuum filtration. This filtrate was placed in a vacuum oven at 50^oC for 10hrs. A hydraulic press with a steel die was used to compress this powder to pellets of diameter ~ 10 mm and thickness < 1 mm.

C. Materials

A standard linear four point -probe technique was used to record the DC electrical conductivity data. The relation used to calculate the conductivity (σ) is given as [6].

$$\sigma = \frac{\ln 2}{\pi d}\left(\frac{I}{V}\right) \quad (1)$$

Where V, I are voltage and current measured as per four probe set-up and 'd' is the pellet thickness. Perkin-Elmer spectrum 2000 spectrophotometer in the wave number range of 600-4000 cm^{-1} was used to record the spectrum in the pellet form mixed with KBr powder.

Manuscript published on 30 September 2019
* Correspondence Author
Atul Kapil*, School of Sciences, Former Faculty of Department of Physics, Career Point University Hamirpur (H.P.) 176041 INDIA Email: atulnit@gmail.com
Navdeep Sharma, Department of Applied Sciences, Alakh Prakash Goyal Shimla University (H.P.) 171013 INDIA Email: sharmanavdeep1@gmail.com

UV-visible spectroscopic study of PmANI in the wavelength range of 200–800 nm was carried out by using Perkin –Elmer spectrophotometer. The effect of doping on the crystallinity of PmANI was verified by x-ray diffraction pattern using Philips diffractometer.

III. RESULT AND DISCUSSION

A. Spectroscopy

FTIR spectrum of p-TSA doped Poly(2-methylaniline) is shown in Fig. 2. The formation of the polymer is confirmed by the peak at ~808 cm^{-1}. The aromatic amine group is confirmed by the C-N stretching at 1314.28 cm^{-1}. The peak at 1156 cm^{-1} in FTIR spectra is attributed to the C-H in plane bending vibrations in conducting PmANI. The stretching vibrations in C-ring belong to the peaks at ~1490 and ~1590 cm^{-1}. The peak because of the sulphonic group of the dopant occurs at 1012 cm^{-1}.

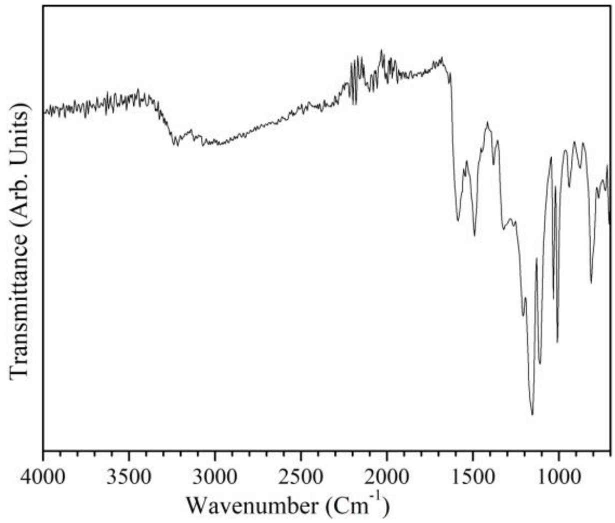

Fig. 1 The FT-IR spectrum of Poly(2-methylaniline)

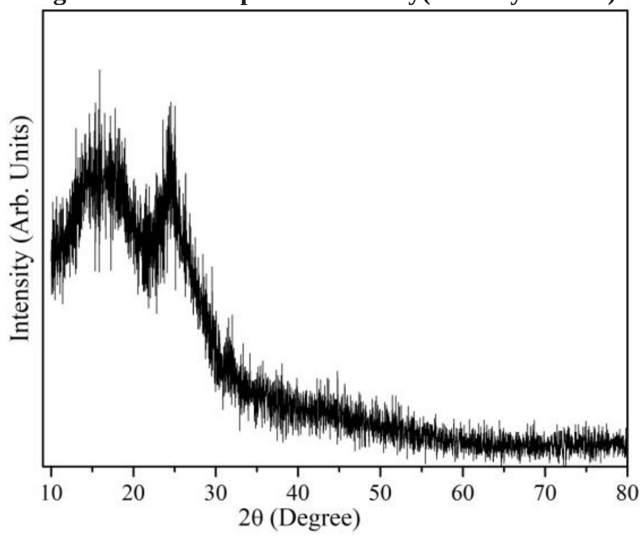

Fig. 2 XRD of Doped PmANI

The bands at 1490 cm^{-1} are due to C-N stretching of benzoid rings and bands at 1587 cm^{-1} are due to C-N stretching of quinoid rings. Thus the presence of vibration band of the dopant ion confirms the presence of conducting emeraldine salt phase of PmANI. The occurrence of these peaks clearly shows that the polymer is composed of amine units. The peak at 3217.13 cm^{-1} shows aromatic C-H stretching [7].

The XRD pattern of Poly(2-methylaniline) doped with p-TSA is displayed in Fig. 2. The structural information of polymers is provided by the diffractometric studies. The peaks at 2θ ~15^0 and 25^0 are in good agreement with the reports explaining either semi crystalline or amorphous structure of the conducting polymers [8]. Fig. 3 shows the absorption spectrum of p-TSA doped PmANI. Different oxidation states of any polymer can be explained by UV-vis absorption spectroscopy. The doped state spectra are categorized by the presence of small peak at 425 nm. The peak at 313 nm is assigned to the π- π* transition of the bezenoid rings, whereas the peak occurred at 425 nm can be assigned to the localized polarons which are the characteristics of doped PmANI [9].

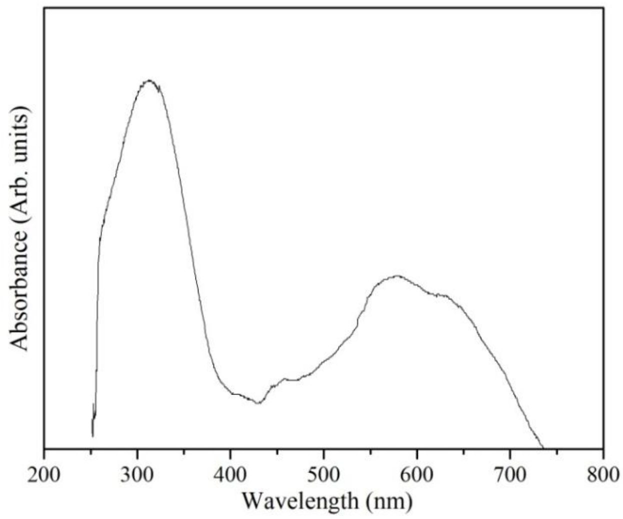

Fig. 3 Absorption spectrum of doped PmANI

B. DC Conductivity

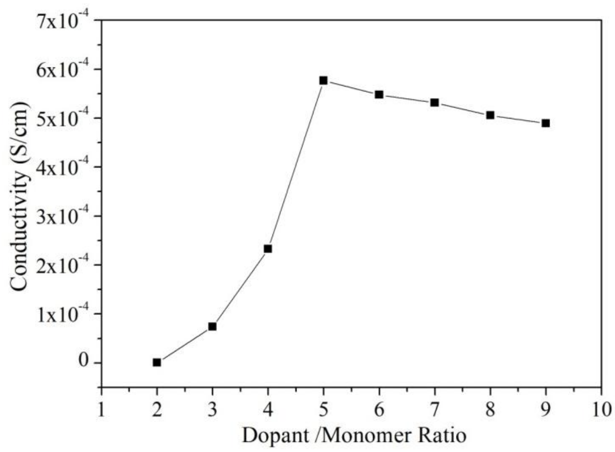

Fig. 4 Variation in electrical conductivity with dopant-monomer ratio

The concentration of the dopant plays a very important role in defining the electrical conductivity in polymers. Fig. 4 shows the variation in conductivity with different dopant-monomer molar ratios. It is observed that conductivity increased on increasing the dopant-monomer ratio and attained maxima at 5 ratio with further slight decrease in conductivity.

This increase in the dopant concentration accounts for the surge in conductivity [10]. We have chosen three samples namely, S2 (for dopant/monomer ratio = 2), S4 (for dopant/monomer ratio = 4), and S7 (for dopant/monomer ratio= 7) in our study to analyze the temperature dependence of DC conductivity. The conductivity increased with increase in the temperature as depicted in Fig. 5. This may be for the reason that some molecular rearrangements may occur on heating the polymer which make the electronic delocalization more favorable.

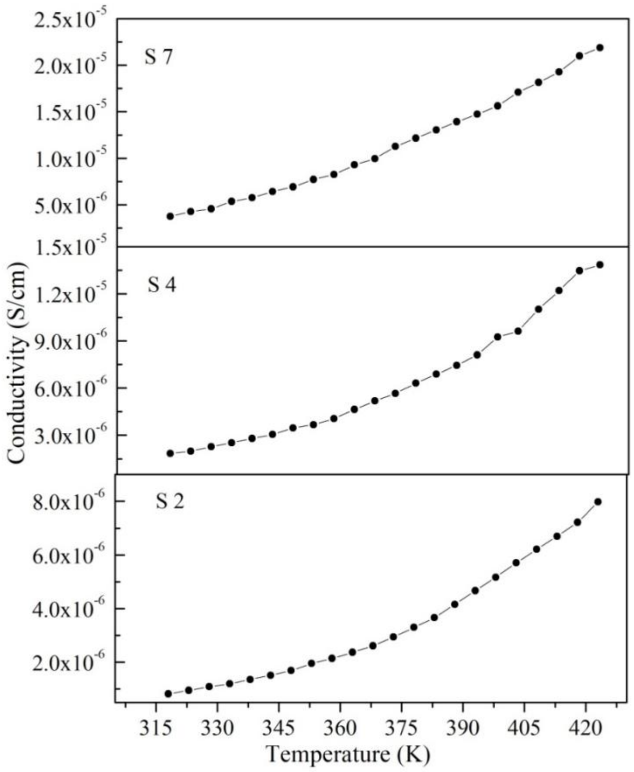

Fig. 5 Variation in conductivity for three samples in the temperature range 300-430 K

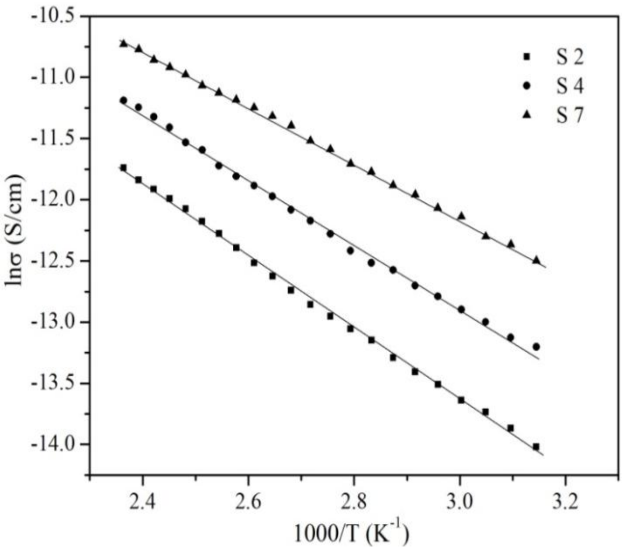

Fig. 6 Conductivity variation of PmANI with 1000/T

Temperature vs conductivity data can be inferred analytically to speculate the most appropriate conduction model in these polymers. The electrical conductivity can be given in the following relation [11]:

$$\sigma_{d.c.}(T) = \sigma_0 \exp(-E_A/kT) \qquad (2)$$

Where E_A, k and σ_0 are activation energy, Boltzmann constant and conductivity at infinite temperature, respectively.

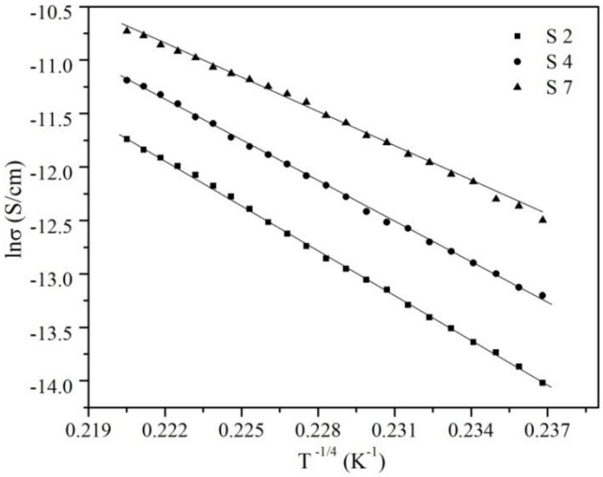

Fig. 7 DC conductivity behavior of PmANI with $T^{-1/4}$

Electrical conductivity data was analyzed with the inverse of temperature (Fig. 6). Experimental data is observed to show a good linear fit in the plot and thus indicated the band gap model of charge transport in this polymer.

The VRH model given by Mott can also describe the temperature dependent DC conductivity and the conduction mechanism in disordered polymers. The conductivity equation in Mott's VRH model is given as follows [12-13].

$$\sigma(T) = \sigma_0\ exp\left[-\left(\frac{T_o}{T}\right)^{\frac{1}{n+1}}\right] \qquad n=1,2,3 \qquad (3)$$

Where T_o is the Mott temperature parameter, σ_0 is the conductivity value at infinite temperature and 'n' corresponds to one- dimensional, two- dimensional and three-dimensional mode of conduction process

Fig. 7 depicts the validity of the VRH model. In our observations, conductivity data was found to linearly fit for Arrhenius model and Mott's VRH model in the whole range of temperature. Thus, variable range hopping model and band conduction model is best explained by the nice linear fit of temperature dependent conductivity data in PmANI.

IV. CONCLUSION

PmANI in doped form was chemically prepared in the presence of p-TSA. The optimization studies for better conductivity were performed for various doping levels. It was observed that conductivity increased on increasing the dopant-monomer ratio and showed maxima for 5 ratio. Spectroscopic characterization studies confirmed the formation of PmANI in doped form. Temperature dependent DC electrical conductivity data was found to fit well with Arrhenius model and Mott's VRH model of charge transport, further signifying a diverse electrical conduction mechanism in this polymer.

REFERENCES

1. J. Heeger, "Semiconducting and metallic polymers: the fourth generation of polymeric materials," Synthetic Met. 125 (2002) p.p. 23-42

2. H. Zhuan, J. Kan, "Studies of Zn-Poly(aniline-co-5-aminiosalicylic acid) aqueous battery with graphite paper current collector," International Journal of Electrochemical science 12, 9 (2017) p.p.7977-7988
3. K. Jin, W. Zhang, Y. Wang, X. Guo, Z. Chen, L. Li, Y. Zhang, Z. Wang, J. Chen, L. Sun, T. Zhang, "In–situ hybridization of polyaniline nanofibers on functionalized reduced graphene oxide films for high-performance supercapacitor," Electrochimica Acta 285 (2018) p.p. 221-229
4. Shumaila, G. B. V. S. Lakshmi, M. Alam, A. M. Siddiqui, M. Zulfequar, M. Husain, "Synthesis and characterization of Se doped polyaniline," Current Applied Physics 11 2 (2011) p.p. 217-222
5. V. Chabukswar, S. Bhavsar, A. Horne, "Organic synthesis and characterization of electrically conducting poly(o-Toluidine) doped with organic acid," Chemistry and Chemical Technology 5 (2011) p.p. 37-40
6. N. Colak, B. Sokmen, "Doping of chemically synthesized polyaniline," Designed Mono. Polym. 3 (2000) p.p. 181-189
7. C. Uchoyuk, M. Karakisla, M. Sacak, "Preparation of poly(o-toluidine)/Polyacrylonitrile composite fibres using CrO_3," Indian J. of Fibre and Textile Res. 37 (2012) p.p. 120-126
8. S. Kalyane, "Conductivity study of polyaniline–PbO composites," International Journal of Pure and Applied Physics 13 (2017) p.p.109-116
9. C. Hu, Y. Li, Y. Kong, Y. Ding, "Preparation of poly(o-toluidine)/nano ZnO/epoxy composite coating and evaluation of its corrosion resistance properties," Synthetic Metals 214 (2016) p.p. 62-70
10. M. G. Han, S. S. Im, "X-ray photoelectron spectroscopy study of electrically conducting polyaniline/polyimide blends," Polymer 41 9 (2000) p.p. 3253-3262
11. A. Kapil, M. Taunk, S. Chand, "Preparation and characterization of chemically synthesized poly(N-methylaniline)," Synthetic Metals 159 (2009) p.p. 1267-1271
12. Y. A. Ismail, A. Ahmad, F. Mohammad, "Synthesis, Electrical, Electronic, and Charge Transport Properties of Poly(aniline-co-p-toluidine)," Journal of Macromolecular Science Part A: Pure and Applied Chemistry 45 (2008) p.p. 650-657
13. R. Ratheesh, K. Viswanathan, "Charge transport study in para-toluene sulfonic acids," International Journal of Innovative Research in Science, Engineering and Technology 3 (2014) p.p. 10646-10658

AUTHORS PROFILE

Dr. Atul Kapil is currently working in Department of Higher Education Shimla, Himachal Pradesh (INDIA). He is former faculty of School of Sciences, Department of Physics, Career Point University Hamirpur (H.P.). He got his Ph. D in the field of organic semiconductors from National Institute of Technology Hamirpur (H.P.) India and later served as faculty in the same institution. He has more than 15 Years of academic and administrative experience in various renowned organizations of India. He has written more than 20 research manuscripts in International journals and conferences of repute. He has been awarded with "Young Researcher" by Asian Polymer Association in 2009 for his research work on Conducting Polymers. He has been the reviewer of many journals of repute in India as well as abroad. He is member of many Scientific Societies like Indian Physical Society, Materials Research Society of India etc.

Navdeep Sharma received Master's in Physics from Dr. B. R. Ambedkar University, Agra, India and M. Phill. degree in Physics from Chaudhary Devi Lal University, Haryana, India. He has more than 12 years of academic experience in various distinguished organizations of India. He has also participated and presented his research work in various National/International conferences and workshop/seminars. He is currently pursuing his Ph.D. degree in the field of conducting polymers from Department of Physics, Career Point University, Hamirpur, India. He has also published his research work as a chapter in a book titled "The Physics of semiconductor Devices" published by Springer.