

Structure and Temperature Dependence of Electrical Conductivity in Polythiophene Nanoparticles

Jyoti Kattimani, T. Sankarappa*, K. Praveenkumar, J. S. Ashwajeet, R. Ramanna, Chandrababha G. B, T. Sujatha

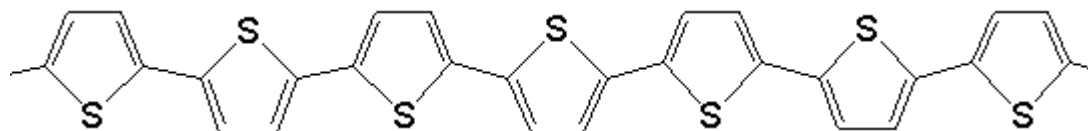
Department of Physics, Gulbarga University, Gulbarga, Karnataka, India
*sankarappa@rediffmail.com

Abstract: Polythiophene (PTh) has been synthesized at three different temperatures by oxidation process with ferric chloride as an oxidizing agent. Samples were confirmed to be non-crystalline by XRD studies. SEM images showed an agglomeration of particles in the samples made at 278K and 305K and tubes like structures were observed for sample made at 323K. The optical absorption (UV-Vis) studies indicates two bands for PTh samples synthesised at 278K & 305K and three bands for the one made at 323K. Temperature dependence of DC conductivity has been measured and data analyzed using Mott's small polaron hopping and variable range hopping models. Activation energies for DC conduction were determined. Density of states obtained by Mott's (VRH) model fits were found to be quite high compared to elemental semiconductors and polymers.

Keywords: Polythiophene, conductivity, activation energy.

1. INTRODUCTION

Conjugated polymers in general and thiophene based polymers in particular are considered to be the most desired ones for electrical applications as they exhibit useful electrical, dielectric and optical properties besides the fact that they are environmentally stable and can be prepared with ease in laboratories [1]. Materials with a combined character of high performance and lightweight are required in space applications. They can be realized by synthesizing composites made of polythiophene like polymers doped with carbon nanotubes (CNTs). Such materials exhibit useful mechanical, electrical and multi-functional properties. Furthermore, conducting polymers as electrode materials in electrochemical supercapacitors has been widely studied in the recent years [2]. For this, of all the conducting polymers, polythiophenes in nanoforn are best suited due to their environmental stability, high electrical conductivity etc. Nano sizes offer high surface areas which results in uniform porosity in the material and that in turn gives a good supercapacitor performance [3-5]. Polythiophenes consist of a chain of alternating double and single bonds. Each first and fourth carbon atom are connected by a sulfur atom forming a thionyl ring [6,7]. Therefore, the bond between the second and the third carbon atom gets more single bond character than other C-C bonds and consequently the bonds connecting the thionyl rings are more of single bond character. In addition to the structure defining function, the sulfur atoms will also influence the electronic and optical properties of a polythiophene. The conjugation of C atoms will dominate the spectroscopic properties of the polythiophenes.



Chemical structure of Polythiophenes.

Polythiophene exhibit superior properties such as low density and ease of fabrication [8] as compared to other polymers. Also this can be manipulated from conducting to the insulating range using different routes of polymerisation. Though there are several methods by which PTh can be prepared, the chemical oxidative technique is considered to be suitable as it produces high

yield [9, 10]. The room temperature conductivity of pure PTh was reported to be $3.2 \times 10^{-5} \Omega/\text{m}$ by chemical oxidative technique [11]. Polythiophene thin films prepared by chemical oxidative method exhibited electrical conductivity in the order of $10^{-5} \Omega/\text{m}$ [12,13]. The conductivity of PTh measured in nitrogen gas atmosphere at 318K was found to be $7.2 \times 10^{-1} \Omega/\text{m}$. It has been reported that conductivity and yield of PTh in a preparation method depends on the type of solvent, type and ratio of oxidant, reaction time and temperature. [14, 15]. There have been other reports on the conductivity of polythiophene [16, 17] but very few attempted to understand conduction mechanism in polythiophene nanoparticles. Here, we report on synthesis of PTh (Particles prepared by oxidation method at three different temperatures.) XRD, SEM, UV-visible spectroscopy and DC conductivity results.

2. EXPERIMENTAL

Analytical grade Thiophene, Ferric chloride, Methanol and Chloroform were used as starting materials in the preparation of PTh. Aqueous solution of thiophene was prepared and stirred. Aqueous chloroform and ferric chloride solution were added drop wise to the homogeneous PTh solution. The mixture was magnetic stirred for 24 hours and the black precipitate obtained was washed first with chloroform and then with methanol. During this procedure, the precipitate became brown indicating the formation of polythiophene [11]. The powder was dried and grinded. The synthesis was carried out at three different temperatures of 278K, 305K and 323K and the products were labelled as PTh1, PTh2, and PTh3 respectively.

In order to understand the structure of the samples they were subjected to powder XRD studies using X'Pert Pro X-Ray diffractometer. To observe surface structure, the SEM images of the samples were collected. The colloidal solution of PTh was investigated for optical absorption using T90+ UV-VIS Spectrophotometer. Electrical conductivity has been measured in the temperature range from 303K to 473K by following two probe method. A constant voltage of 5V has been applied across the two-side silver painted PTh pellet. The current passing through the pellet was measured using a picoammeter. Resistivity, ρ , has been determined as per, $\rho = (V/I) (A/t)$, where A is surface area and t the thickness of the pellet. Conductivity, $\sigma = 1/\rho$ was determined. The errors on σ were estimated to be within 2%.

3. RESULTS AND DISCUSSIONS

XRD: A typical XRD pattern obtained for PTh1 is shown in Fig. 1. In the figure, we see no sharp peaks. This indicates that the polymer under investigation is noncrystalline in nature [11, 18]. XRD patterns of other two samples also indicated the same.

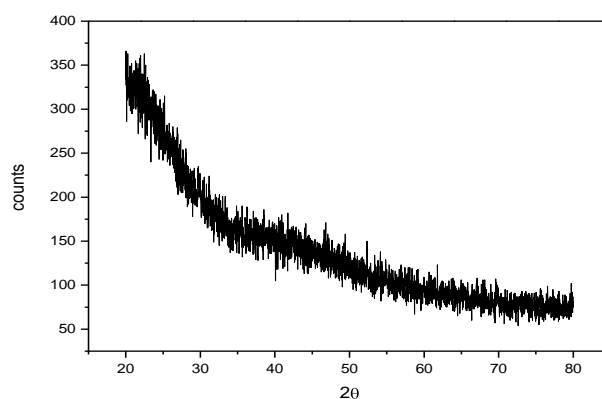


Fig 1. X-ray diffraction pattern of PTh1 sample

SEM: The SEM images of the samples are shown in Fig.2 (a-c). The Fig.2(a) shows nanoparticles agglomerated with micropores in between [19]. In Fig. 2(b), the size of the agglomeration is found to be increased. In Fig. 2(c), a tube like structure formed by the nanoparticles. The average sizes of the nanoparticles are found to be 41 nm, 50 nm and 71 nm for PTh1, PTh2 and PTh3 respectively. It may be noted that SEM image shown in Fig. 2(c) correspond to the sample prepared at 323K. This imply that PTh prepared at higher temperature produces tube like structure

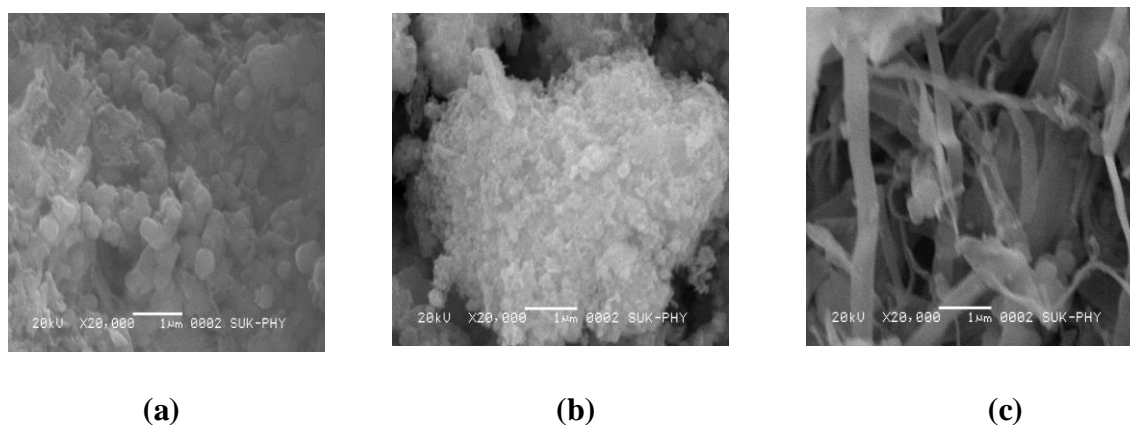


Fig 2. SEM images of PTh samples (a) PTh1, (b) PTh2 and (c) PTh3

Optical Absorption: The absorption spectra in the UV-visible region were recorded at room temperature. The UV-visible spectra of the present samples collected in their colloidal form are shown in the Fig. 3. The spectra of PTh1 shows two distinct bands at 306nm and 377nm. The band at 306nm is associated with $\pi-\pi^*$ inter band transition and band at 377nm is associated with $n-\pi^*$ transition [12,20,21]. For PTh2 and PTh3 the absorption bands are observed at 320nm and 360nm respectively. PTh3 also exhibited an additional weak band at 480nm. It is worth nothing that the surface morphology and UV-Vis spectra of all the three samples are differing from one another. It may be due to the fact that they are prepared at different temperatures. This implies that temperature of making the polymer affects the properties such as structure and optical properties.

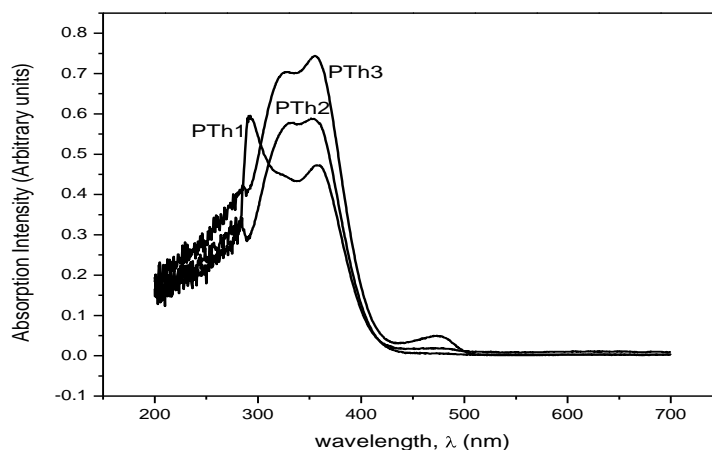


Fig 3. UV-Vis. Spectra of three systems of PTh.

Conductivity: The measured room temperature conductivities for PTh1, PTh2 and PTh3 are $2.43 \times 10^{-5} (\Omega m)^{-1}$, $0.95 \times 10^{-5} (\Omega m)^{-1}$ and $1.65 \times 10^{-5} (\Omega m)^{-1}$ respectively. The room temperature conductivity of Polythiophene prepared by chemical oxidative method has been reported to be $1.67 \times 10^{-4} \Omega/m$ [20]. Conductivity of the present samples increased with increasing temperature, which indicates their semiconducting nature.[22, 27]. The temperature variation of conductivity has been fit to conductivity expression derived by Mott in the case of Small polaron hopping (SPH) in noncrystalline semiconductor solids.[12, 13, 23]. The plots of $\ln(\sigma T)$ versus $(1/T)$ were plotted according to Mott's (SPH) conductivity expression and shown in Fig. 4(a). The linear lines were fit to the data in the high temperature region where the data appeared linear. The slopes were used to determine the activation energy, E_a (Table. 1). Activation energy is found to be highest for PTh2 and lean for PTh1.

Table 1. Activation energy, E_a , of PTh nanoparticle systems.

Systems	PTh-1	PTh-2	PTh-3
E_a (meV)	0.07 ± 0.01	0.53 ± 0.02	0.30 ± 0.02

The data deviated from SPH model has been fit to Mott's 3D VRH model. Mott's (VRH) model has been used for analysing conductivity of polypyrrole and polythiophen [25, 26]. The plots of $\ln(\sigma)$ versus $(T^{-1/4})$ were made according to this model and shown in Fig. 4(b). The linear lines were fit through the data. Certain range of data appeared to be in agreement with the model fit. However, the data corresponding to lower temperature has deviated from Mott's VRH model fit [28, 29]. Density of states $N(E_F)$ were determined to be $8.83 \times 10^{31} \text{ (eV}^{-1} \text{ m}^{-3}\text{)}$, $0.10 \times 10^{31} \text{ (eV}^{-1} \text{ m}^{-3}\text{)}$ and $3.80 \times 10^{31} \text{ (eV}^{-1} \text{ m}^{-3}\text{)}$ for PTh1, PTh2 and PTh3 respectively. The phonon frequency, $\nu = 10^{13} \text{ Hz}$ and $\alpha = 1.2 \text{ \AA}$ were used to calculate $N(E_F)$ [24]. These values of $N(E_F)$ are much greater than that reported for elemental semiconductors and polymers. So, it can be concluded that though Mott's (VRH) model fit appeared to be in agreement with data, the obtained results are far off from the expected values of $N(E_F)$ and hence this model is not suitable for explaining the present data.

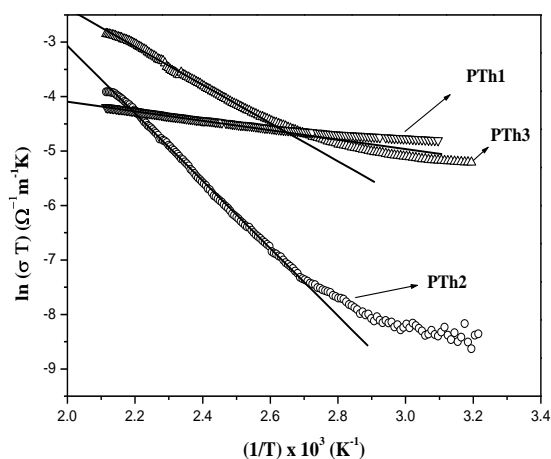


Fig 4(a). Plots of $\ln(\sigma T)$ versus $(1/T)$ for three PTh nanoparticles systems. Solid lines are linear fits as per Mott's SPH model

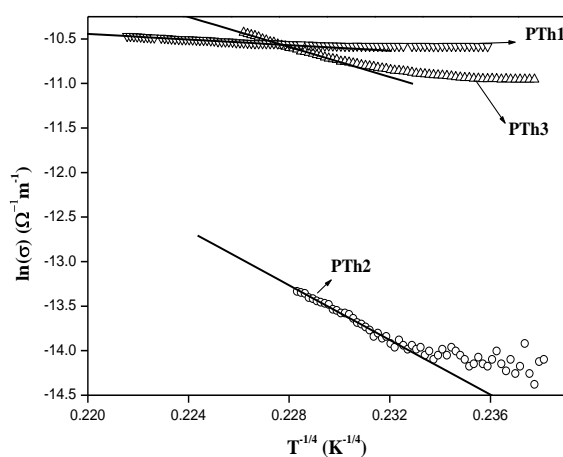


Fig 4(b). Plots of $\ln(\sigma)$ versus $(1/T^{1/4})$ for three PTh nanoparticle systems. Solid lines are linear fits as per Mott's VRH model.

4. CONCLUSIONS

Polythiophene samples have been synthesised at three different temperatures and their non-crystalline nature have been confirmed by XRD. Small differences in particle sizes have been noted between the samples made at different temperatures. SEM images showed tubular structure for PTh sample made at 323K. UV-visible spectra of all the three samples revealed the characteristic peaks of polythiophene in colloidal solution. The sample made at 323K exhibited additional peak at 480nm. The temperature dependent electrical conductivity has been measured and analyzed using Mott's SPH and 3D VRH models. Activation energies for conduction were determined. The density of states of carriers at Fermi level were found to be quite high.

REFERENCES

- [1] D.C.Tiwari, Vikas Sen and Rishi Sharma, *Indian J Pure & Appl Phys.* 50, 49 (2012).
- [2] S. Richard Prabhu Gnanakan, M. Rajasekhar and A. Subramania, *Int. J. Electrochem. Sci.*, 4 1289 (2009).
- [3] V. Gupta, N. Miura, *J. Power Sources* 157, 616 (2006).
- [4] K. Jurewicz, S. Delpeux, V. Bertagna, F. Beguin, E. Frackowiak, *Chem. Phys. Lett.* 347, 36, (2001).
- [5] Kerileng M. Molapo, Peter M. Ndangili, Rachel F. Ajayi, Gcineka Mbambisa, Stephen M. Mailu, Njagi Njomo, Milua Masikini, Priscilla Baker and Emmanuel I. Iwuoha, *Int. J. Electrochem. Sci.*, 7 11859, (2012).
- [6] V. Gupta, N. Miura, *Electrochem. Commun.* 7 (2005) 995.
- [7] *Conjugated polymer-An introduction*, Chemical Physics:Research, Lund University.
- [8] X.S.Wang, Y.H. Deng, Y.Q. Li, *J. Mat. Sci.* 37, 4865 (2002).
- [9] A.K. Narula, R.J.Singh, *App.Bioc. & Biot.*, 96, 109 (2001).
- [10] O. Yu Posudievskii, N.V. Konoshchuk, A. L. Kukla, A. S. Pavlyuchenko, G. V. Linyuchev, V. D. Pokhodenko, *Thero. and Exp. Chem.* 42, 339 (2006).
- [11] Kowsar Majid . R. Tabassum . A. F. Shah .S. Ahmad .M. L. Singla, *J Mater Sci: Mater Electron* 20:958 (2009).
- [12] S. V. Kamat, S. H. Tamboli, Vijaya Puri, J. B. Yadav, Oh Shom Joo *Arch. Phy. Res.*, 1 (4):119 (2010).
- [13] S. V. Kamat, S. H. Tamboli, Vijaya Puri, R. K. Puri, J. B. Yadav, Oh Shom Joo, *Journal of optoelectronics and advanced materials*,12,11, 2301 (2010).
- [14] O. Yunus Gumus, H. Ibrahim Unal, Ozlem Erol, Bekir Sari, *Polymer Composites* -10. 1002,418 - 426 (2011).
- [15] N.K. Guimard, N. Gomez, and C.E. Schmidt, *Prog. Polym. Sci.*, 32, 876 (2007).
- [16] G. I. Rusu, A. Airinei, M. Rusu, P. Prepelita, L. Marin, V. Cozan, I. I. Rusu, *Acta. Mat.*, 55, 433 (2007).
- [17] G. I. Rusu, V. Sunel, D. Sirbu, A. Amariei, I. Caplanus, G. G. Rusu, *Mat. Res. Innovat.*, 06, 247 (2002).
- [18] S. A. Waghuley, R. S. Bobade, A. V. Kohle, G. G. Muley, S. S. Yawale, F. C. Raghuvanshi, B. H. Pawar, S. P. Yawale, *optoelectronics and advanced materials – rapid communications*, 4, 1, 97 (2010).
- [19] Deepali Kelkar and Ashish Chourasia, *Chemistry & Chemical Technology*, 5, 3, 309 (2011).
- [20] Mohammad Rezaul Karim, Chul Jae Lee, Mu Sang Lee, *Journal of Polymer Science: Part A: Polymer Chemistry*,44, 5283 (2006)
- [21] Zhiyue Han. Jingchang Zhang. Xiuying Yang. Hong Zhu. Weiling Cao *J Mater Sci: Mater Electron* 21:554 (2010).
- [22] F.Samir, M. Morsli, A. Bonnet, A. Conan and S. Lefrant, *journal de physique IV*, 3, 1565 (1993).
- [23] N.F. Mott, *J.Non-Cryst.Solids* 1, 1 (1968).
- [24] Ishpal Rawal, Amarjeet Kaur, *J.Appl.Phys.* 115, 043717 (2014).
- [25] Gholamreza Kiani, Hossein Sheikhloie, Ali Rostami; *Iranian Polymer Journal*, 20, 8, 623 (2011).
- [26] N.Othman, Z.A.Talib, A.Kassim, A.H.Shaari and J.Y.C.Liew, *J.Fundamental Sciences*, 5, 29 (2009).
- [27] V. Shaktawat, N. Jain, R. Saxena, N. S. Saxena, K. Sharma, T. P. Sharma, *Polymer Bulletin* 57, 535 (2006).
- [28] J J Hauser, *Phys. Rev.* B9, 2623 (1974).
- [29] N. Motts, E. A. Davis, *Electronic Processes in Non-Crystalline Materials* 2nd Ed. Oxford, Clarendon, Ch. 2.(1971).