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# Studies On Polythiophene Nanoparticles

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ABSTRACT

Polythiophene (PTh) was synthesized at three varying temperatures by an oxidation method with ferric chloride as an oxidizing agent. Samples have been reported to be non-crystalline in XRD experiments. SEM images showed agglomeration of the particles in samples made at 278 K and 305 K, and loops identical to structures were found in samples made at 323K. The optical absorption (UV-Vis) studies show two bands for PTh samples synthesized at 278 K & 305 K and three bands for 323K. Temperature dependent DC conductivity was calculated and data analyzed using Mott's small polaron hopping and variable range hopping models. Activation energies for DC conduction have been established. The density of the states produced by the Mott (VRH) model fits was observed to be quite high compared to the elemental semiconductors and polymers.

KEYWORDS: Polythiophene, conductivity, PTh nanoparticles

## 1. INTRODUCTION

Conjugated polymers in general and thiophene-based polymers in particular are known to be the most suitable for electrical applications because they exhibit valuable electrical, dielectric and optical properties, in addition to being environmentally friendly and easy to prepare in laboratories. High-performance and lightweight composite materials are needed in space applications. These can be realized by synthesizing composites made of polythiophene, including carbon nanotubes (CNTs) doped polymers. Such products possess valuable mechanical, electrical and multi-functional properties. In fact, the use of polymers as electrode materials in electrochemical supercapacitors has been extensively studied in recent years. For this reason, polythiophenes in nanoform are best suited to conductive polymers due to their environmental resilience, strong electrical conductivity, etc. Nano sizes give a high surface area which results in a uniform porosity of the material and which in effect gives a good supercapacitor efficiency. Polythiophenes consists of a series of alternating double and single bonds. Each first and fourth carbon atom is bound by a sulfur atom creating a thionyl ring. As a consequence, the bond between the second and third carbon atoms has more of a single bond character than other C-C bonds, and therefore the bond between the thionyl rings has more of a single bond character. In addition to the defining feature of the structure, the sulfur atoms will also affect the electrical and optical properties of the polythiophene. The conjugation of C atoms is regulated by the spectroscopic effects of polythiophenes.

## Conduction mechanisms in polythiophene

Polythiophene (PTh) has been extensively studied by many researchers. It is a conjugated polymer like polyacetylene (PA), poly (p-phenylene)(PPP) and polyaniliane (PANi). PTh has a heterocyclic structure similar to polypyrrole (PPY). PTh is obtained from the polymerization of thiophene a sulphur heterocycle that can be made into conducting by adding or removing an electron from the orbitals via doping process [1, 2]. PTh and its derivatives are attractive more due to their high electrical conductivity, environment and thermal stability. Conducting polymers are used in combination of other polymers or inorganic materials as composites or blends [2, 3]. PTh consist of alternating double and single-bonds in which each first and fourth carbon atom connected by sulphur atom forming a thionyl ring. The bond between the second and third carbon atoms therefore has more single bond character than the other C-C bonds and therefore the bonds linking the thionyl rings have more single bond character[4].

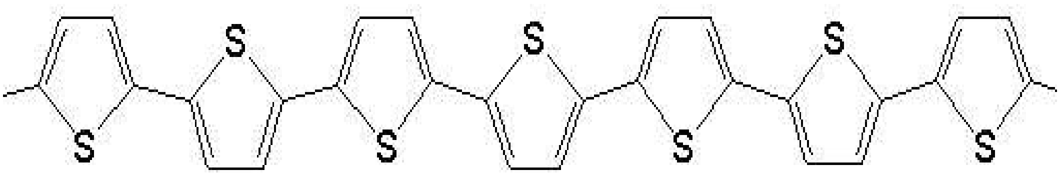


Fig 1 Structure of Polythiophene.

When the conductivity is below $10^{-10}$ $\Omega^{-1}m^{-1}$ the materials are observed to be insulators and if conductivity was between $10^{-9}$ and $10^{-2}$ $\Omega^{-1}m^{-1}$ then the materials are said to be semiconductor. If conductivity is greater than 1 $\Omega^{-1}m^{-1}$ the material is considered as conductor. In their neutral states most of the conducting polymers are insulators or weak semiconductors. The conductivity of these polymers can be increased by the process of doping. The doping can be carried out chemically by either exposing of the polymer to the dopant or by electrochemical oxidation or reduction methods. These dopants works as charge transfer agents in the polymerization process. They occupy interstitial sites between the polymer chains and during this reaction they donate charges to or accept charges from the polymer backbone. Generally, soliton or polaron and bipolaron structures are formed due to the redox reaction. These entities are responsible for the intramolecular conductivity.

Upon doping Polythiophene, polarons and bipolarons are formed. In polymer backbone when a $\pi$- electron is removed, it becomes a radical cation that is polaron which itself get stabilised by polarising over several monomeric units. From the polymer when a second electron is removed, two polarons or one bipolaron are formed. A bipolaron usually stretches from 1 to 6 carbon atoms and has a structural deformation associated with it. Therefore bipolarons are energetically more favourable than the separate polaronic states. Polarons and bipolarons become mobile in external electric field and act like charge carriers and hence become responsible for electrical conduction in the polymer chains [5, 6].

From the existing literature survey, it is learnt that transition metal ions plays an important role in tuning structural and electrical properties of polymers. There were only very few reports on conductivity studies of PTh-$V_2O_5$ and PTh-CoO nano composites.

## 2.EXPERIMENTATION

### 2.1 SYNTHESIS OF SAMPLES

In research, the Polymers are prepared by the variety of techniques. The chemical oxidative polymerization technique is most widely used, as it is easy has high yield, allows to modify with different chemical groups and is economic [7-9]. Samples of this thesis were prepared using a chemical method. The chemicals used for the sample preparation were analytical grade Thiophene, Ferric chloride, Methanol and Chloroform. The PTh nanocomposites were prepared by mechanical mixing analytical grade vanadium pentaoxide $V_2O_5$/CoO PTh.

### 2.2 SYNTHESIS OF POLYTHIOPHENE

Thiophene and chloroform solution was prepared and stirred well. Chloroform and ferric chloride solution were prepared and magnetic stirred for half an hour. To the homogeneous PTh solution, the chloroform , ferric chloride solution was added in drop wise. For 24 hours, the whole mixture was stirred magnetically and the black precipitate was obtained. It was first chloroform washed and then methanol washed. Throughout this procedure, the precipitate became brown indicating the formation of Polythiophene [10-13].

The collected precipitate was filtered and washed repeatedly with double distilled water and methanol for removing unreacted oxidants and thiophene monomer until the filtrate was colourless. The powder was dried and grinded. The synthesis was carried out at three different temperatures of 278K, 305K and 323K and the products so obtained were labelled as PTh1, PTh2 and PTh3 respectively.

## 3. RESULTS AND DISCUSSIONS

### 3.1 STUDIES ON PTH NANOPARTICLES

The results of XRD, SEM, UV-VIS, electrical conductivity and dielectric measurement studies on PTh and PTh-composites are discussed below.

### 3.1.1 **X-Ray Diffraction (XRD) results**

A typical XRD pattern obtained for PTh1 is shown in Fig. 2 In the figure, we see no sharp peaks. This indicates that PTh1 is noncrystalline in nature [14, 15]. XRD patterns of other two samples also revealed same information.

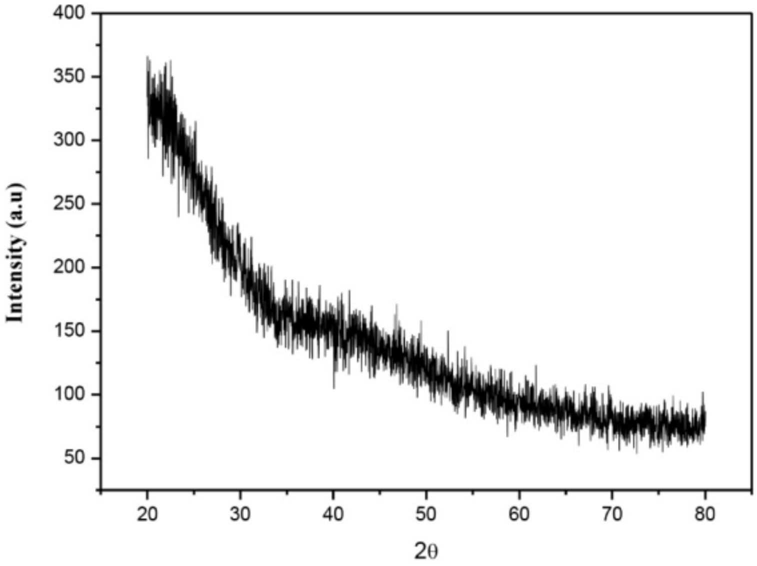
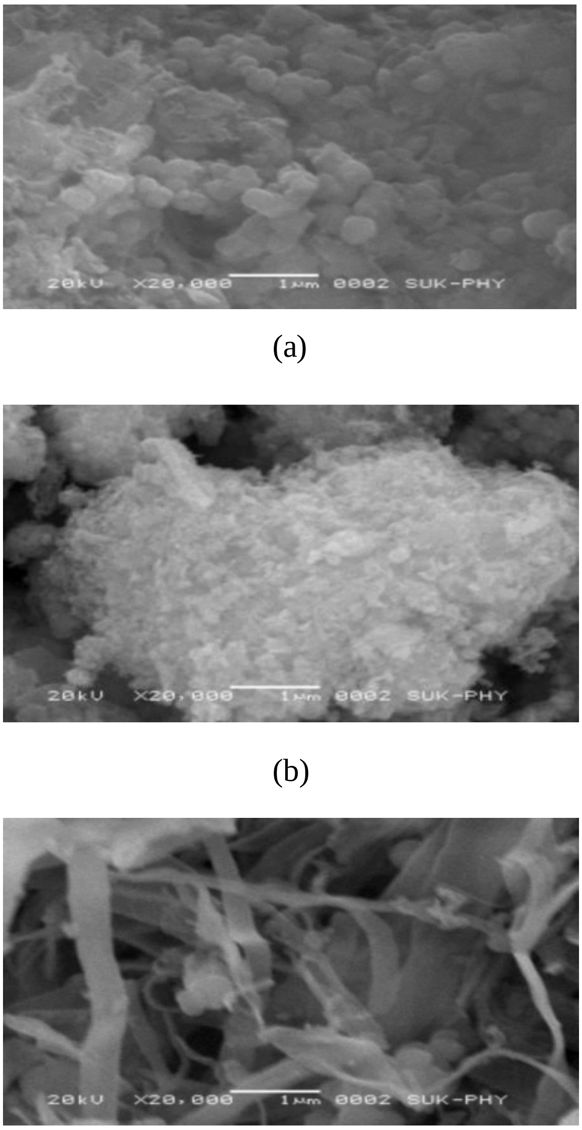


Fig 2. X-ray diffraction pattern of pure PTh1.

### 3.1.2 SCANNING ELECTRON MICROSCOPY (SEM) RESULT

To understand the surface morphology, samples were subjected to Scanning Electron Microscopy. The SEM images of three PTh samples are shown in Fig.3 (a-c). The Fig.4 Shows agglomerated nanoparticles with micropores within them.

In Fig. 3(b), It is found that the agglomeration rate is increased. In the figure. 3(c),the nanoparticles formed a tube-like structure. The average nanoparticles sizes are 41 nm, 50 nm and 71 nm respectively for PTh1, PTh2 and PTh3. The SEM image displayed in Fig. 3(c) corresponds to the prepared sample of 323 K . This means that PTh formed tube-like structure at higher temperatures.



(a)

(b)

(c)

Fig 3. SEM images of (a) PTh1, (b) $PTh_2$ and (c) $PTh_3$ samples.

### 3.1.3 OPTICAL ABSORPTION RESULTS

The UV-visible spectra of PTh samples in their colloidal form are shown in Fig.4. These spectra in the UV-visible region were recorded at room temperature. The spectra of PTh1 show two distinct bands at 306 nm and 377 nm is associated with n–π* inter band transition and band at 377 nm is associated with n–π* transition [17-19]. For PTh2 and PTh3, the absorption bands are observed at 320nm and 360nm respectively. At 480 nm, PTh3 also had an additional low unit. It's useless that the morphology of the surface and UV-V are spectra of all three samples that vary from each other. It may be due to the fact that at different temperatures they are prepared. This indicates that the temperature of the polymer preparation impacts properties such as structure and optical properties.

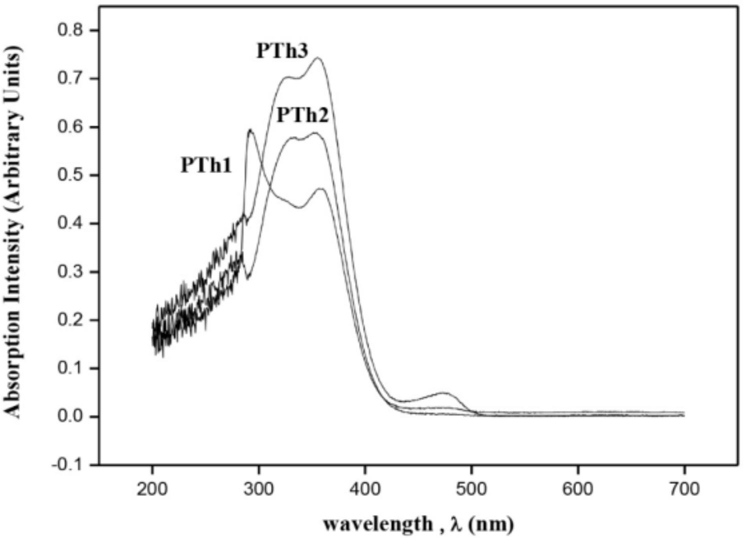


Fig 4 UV-Vis. spectra of three systems of PTh.

### 3.1.4 DC ELECTRICAL CONDUCTIVITY RESULTS

The calculated room temperature conductivities for PTh1, PTh2 and PTh3 samples are $2.43\times10^{-3}$ $(\Omega m)^{-1}$, $0.95\times10^{-5}$ $(\Omega m)^{-1}$ and $1.65\times10^{-5}$ $(\Omega m)^{-1}$ respectively. The room temperature conductively of Polythiophene prepared by chemical oxidative method has been reported to be $1.67\times10^{-4}$ $(\Omega m)^{-1}$ [18]. Conductivity of the present polymer samples increased with increasing temperature, indicating semiconducting nature of them (Fig 5) [20, 21]. In the case of Small Polaron Hopping (SPH) in non-crystalline semiconductor solids [17, 22, 23], the temperature variance of conductivity was conform to the conductivity term obtained by Mott. The plots of ln(σT) versus (1/T) were plotted using the conductivity expression of Mott (SPH) and shown in Fig 6. In the high temperature region where the data appeared linear, the

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linear lines fitted the data. The slopes used to evaluate the energy of activation, $E_a$ (Table 1). For PTh2 and at least for PTh1 , activation energy is found to be the highest.

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 | 0.300 ± .02 |

Mott's 3D VRH model designed the data deviated from the SPH model. Mott's (VRH) model was historically used to evaluate polypyrrole and polythiophene conductivity[24, 25]. The ln($\sigma$) versus ($T^{-1/4}$) plot were created using this model and shown in Fig. 7. Through the data, the linear lines fit. Some data range seemed to be in line with the fit model. Data for lower temperatures, however, have deviated from Mott's VRH model fit [26, 27] Density of states $N(E_F)$ were determined using slope intercept and they were found to be $8.83\times10^{31}$ ($eV^{-1}$ $m^{-3}$), 0.10 $\times10^{31}$ ($eV^{-1}$ $m^{-3}$) and $3.80\times10^{31}$ ($eV^{-1}$ $m^{-3}$) for PTh1, PTh2 and PTh3 respectively. The phonon frequency, $\nu=10^{13}$ Hz and $\alpha=1.2$ Å were used to calculate $N(E_F)$ . 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 result are far off from the expected values of $N(E_F)$ and hence this model may be considered to be not suitable for explaining the present data.

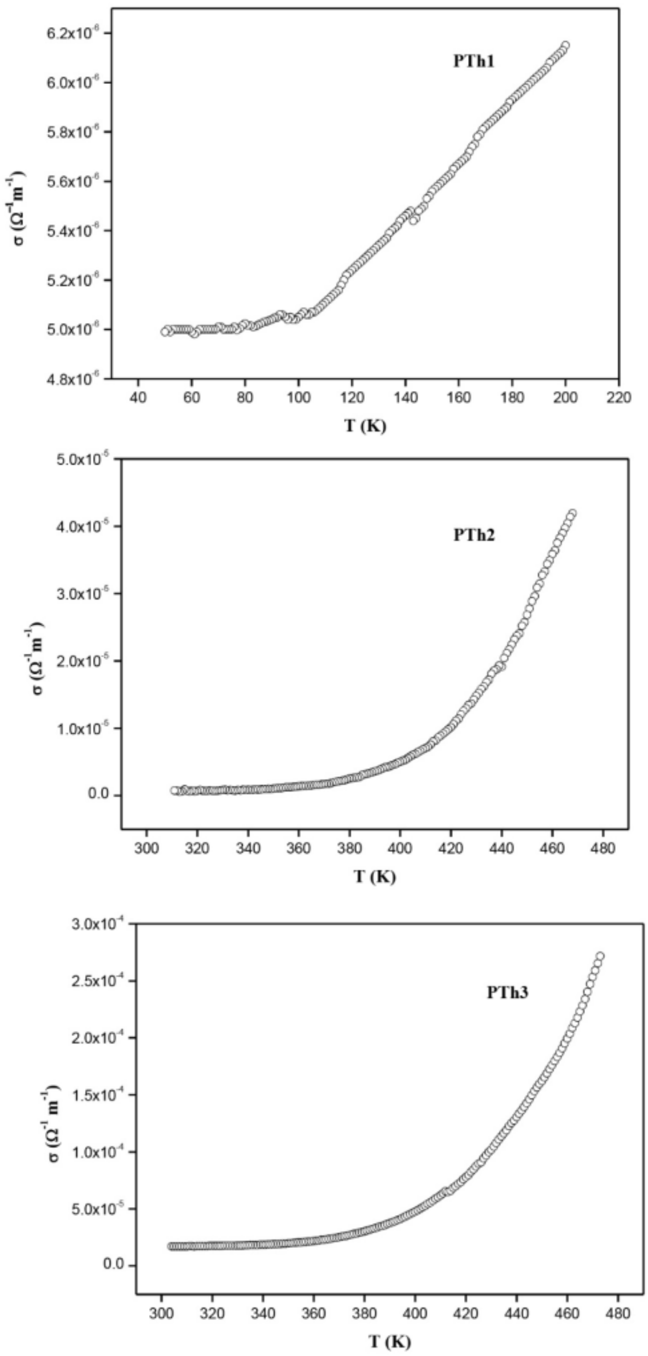

Figure 5 Conductivity versus temperature for PTh systems.

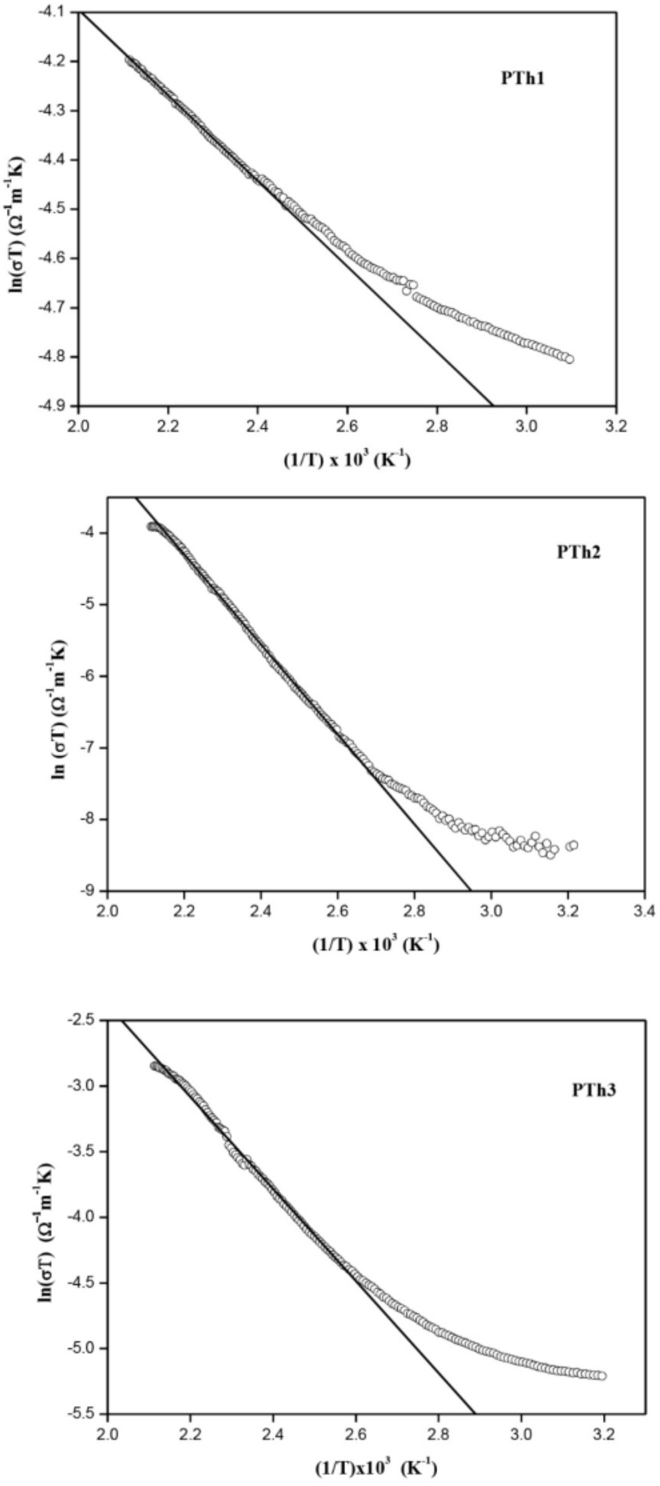

Figure 6 Plots of ln(σT) versus (1/T) for PTh systems. Solid lines are linear fits as per Mott's SPH model

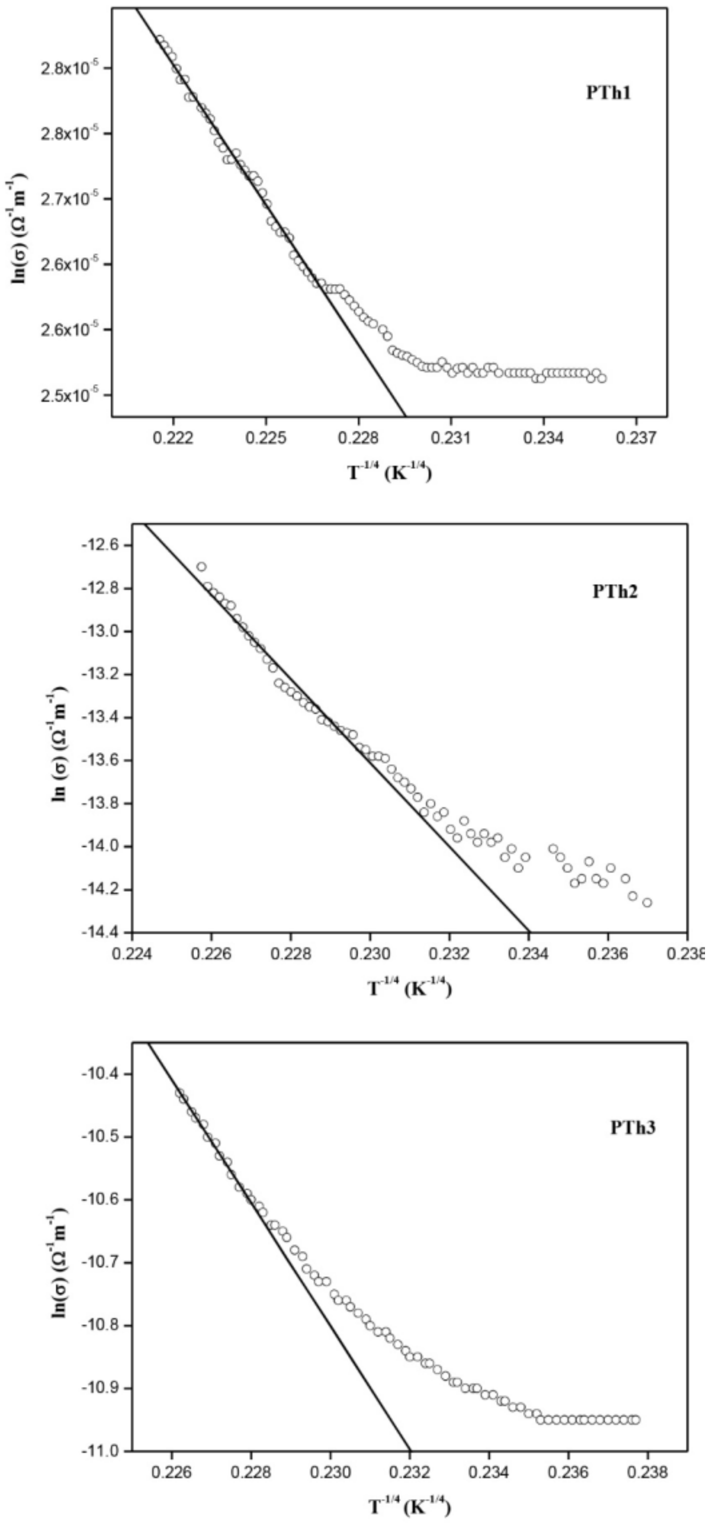

Figure 7 Plots of ln(σT) versus ($T^{-1/4}$) for PTh systems. Solid lines are linear fits as per Mott's SPH

## 4. CONCLUSION

Polythiophene samples have been synthesized 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 calculated 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.

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