

# Synthesis and Preparation of Polythiophene Thin Film by Spin Coating Method

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**Abstract:** Polythiophene (PT) Nanoparticles have been synthesized by oxidative emulsion polymerization of Thiophene monomer in the presence of copper nitrate catalyzed. In the copper nitrate catalyzed increased with high yield of polythiophene in short time period of polymerization reaction. In this polythiophene nanoparticles dispersed in organic solvent to prepare thin film coated with glass substrate by spin coating method. The prepared thin film characterization studies was carried by using Fourier Transform Infra Red spectroscopy (FTIR) and Raman spectroscopy measurements to conformed by the formation of polymer material of polythiophene. The structural optical and surface morphology studies by using X- ray diffraction (XRD) spectroscopy, UV visible spectroscopy and Scanning Electron Microscopy (SEM).

**Keywords:** Polythiophene, Oxidative emulsion Polymerization, Conducting Polymers, FTIR, SEM, XRD, Raman Spectrum

## 1. Introduction

Conjugated conducting polymers such as Polypyrrole (PPy), Polyaniline (PANI), Polyacetylene (PAC), Polythiophene (PT), and so forth are the most interesting conducting polymers due to their excellent chemical and electrochemical stability. They are easy to prepare in the form of large area thin films and are capable of storing charge throughout their entire volume [1, 2]. Polythiophene are one of the most valuable types of conducting polymers that may be easily modified to afford a variety of useful electrical and physical properties such as solubility, electrical conductivity, mobility and others [3]. Polythiophene has been widely used in environmentally and thermally stable conjugated polymer materials, such as chemical and optical sensors, light-emitting diodes and displays, photovoltaic devices, molecular devices, DNA detection, polymer electronic interconnects and transistors [4-8].

Polythiophene can be synthesized by major two types one is electrochemically by applying a potential across a solution of the monomer to be polymerized. Another one is chemically using oxidants or cross-coupling catalysts. The quality of electrochemically prepared PT thin films is affected by a number of factors. These include the electrode material, current density, temperature, solvent, electrolyte, presence of water, and monomer concentrations [9]. Two other important but interrelated factors are the structure of the monomer and the applied potential. The Chemical synthesis method offers two advantages compared with electrochemical synthesis of Polythiophenes a greater selection of monomers, and, using the proper catalysts, the ability to perfectly synthesize PT nanoparticles. The first planned chemical syntheses using metal catalyzed polymerization of 2, 5-dibromothiophene was reported by two groups independently in 1980. Yamamoto *et al.* used magnesium in tetrahydrofuran (THF) and nickel (bipyridine) dichloride, analogous to the Kumada coupling of Grignard reagents to aryl halides [10]. Unsubstituted PT was conventionally made by chemical and electrochemical polymerization. However, it cannot be melted or dissolved in common solvents, thus limiting its practical applications to a large extent. To date the most extensively used solution to address this insolubility problem

is to incorporate kinds of substituent's onto the PT backbone, such as alkyl, alkoxy, amine, and other carboxyl groups[11-14] making PT soluble or dispersible in organic solvents, water or supercritical fluids. These soluble PT derivatives are directly used as film materials but these synthetic procedures are quite complex and expansive which generally require stringent conditions and several individual steps and some toxic solvents are usually involved so which are not environmentally favourable. Bjerring *et al.* [15] successfully prepared unsubstituted PT films by solution processing thermo-cleaving method, in which the solubilising side chains were removed after formation of the film. Recently researchers started the effort of preparing PT Nanostructures by using various surfactants and oxidant of ferric chloride (FeCl<sub>3</sub>) as in traditional oxidative polymerization methods[16,17] and also using hydroxyl peroxide as a co-oxidant to regenerate the Fe<sup>3+</sup> from Fe<sup>2+</sup> formed during the polymerization, high yield could be achieved using only a small amount of FeCl<sub>3</sub>. The synthesized PT nanoparticles could be easily redispersed in various organic solvents [18].

In the present work we are preparing polythiophene thin film by using spin coating technique. First up all polythiophene nanoparticles is synthesised by new traditional oxidative emulsion polymerization method. In this traditional method contain only using co-oxidant of hydroxyl peroxide solution and another one factor of during this polymerization process thought atmospheric pressure and temperature conditions. Thin film sample are characterized by using different techniques such as FTIR, Raman Spectroscopy analysis, UV-Visible spectroscopy, analysis of X-ray diffraction, and scanning electron microscopy technique have also been carried out.

## 2. Experimental

### 2.1 Materials

The Thiophene(C<sub>4</sub>H<sub>4</sub>S) was obtained from Sigma-Aldrich distilled prior to use, Sodium Dodecyl Sulphate (SDS) Thermo fisher scientific India. Hydroxyl peroxide (H<sub>2</sub>O<sub>2</sub>, 30%), Copper (II) nitrate trihydrate (Cu (NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O) Merck Specialities Mumbai India, Tetrahydrofuran (THF) E.Merck

Mumbai India are all analytical grade reagents were used as received.

## 2.2 Synthesis of Polythiophene Nanoparticles

Here 2ml of Thiophene monomer was taking 250ml beaker and addition of 100ml deionised water and sodium dodecyl sulphate 1g was adding and the mixture was stirred for 30 min. After that solution of 50ml 30% hydroxyl peroxide ( $H_2O_2$ ) was introduced by the above mixture of solution then stirring for 5min. The determinant quantity of copper (II) nitrate trihydrate catalyst salt before dissolved in 10ml deionised water and this adding with solution mixture. The reaction was allowed to proceed for 7 hours after that solution diluted with deionised water and the polymer was precipitated by adding sodium hydroxide solution followed by centrifugation. The brown colour polythiophene nanoparticles precipitated then the precipitate washed with deionized water for several times and dried with room temperature for two days.

## 2.3 Preparation of PT Thin Film by Spin coating

The synthesized polythiophene nanoparticles were using preparation of PT thin film. The polythiophene nanoparticle is fully dispersed with organic solvent of Tetrahydrofuran (THF) at constant stirring to make a homogenous solution. Then the homogenous dispersed PT solution was deposited on glass substrate using spin coating technique at a speed of 3000 rpm on glass substrate. Then PT thin film was dried in air with room temperature.

## 2.4 Characterization of PT Thin Film

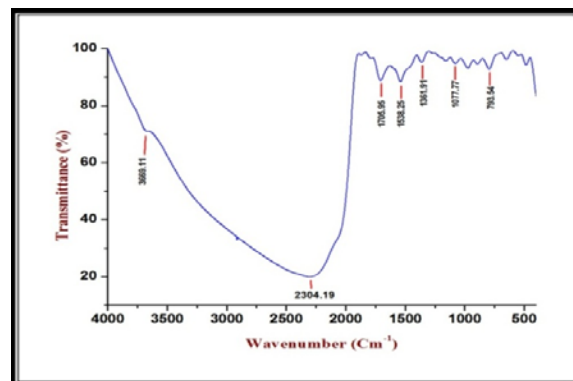
Analysis of FTIR and XRD were used to confirm the formation of PT. The chemical bonding was analyzed by using FTIR – Perkin Elmer make-model Spectrum RXI spectroscopy. UV-Visible measurements were carried out on Perkin Elmer make-Lambda 35 model and absorption spectra were obtained by depositing of thin film PT on glass substrate. X-ray diffraction (XRD) studies were carried out using Rigaku X-ray Diffractometer. Raman spectroscopic studied by Raman Systems RSIQ model. And Scanning Electron Microscope (SEM) studied by SEM TESCAN Vega-3 SBU model using acceleration voltage of 5.0 kV.

## 3. Results and Discussion

### 3.1 FTIR Spectroscopy Analysis

The chemical structures of PT thin film sample were determined by FTIR Spectroscopy study is represented in **Figure 1**. The spectrum in the range of 400 to 4000  $Cm^{-1}$  shows the presence of expected peaks of polythiophene. The major peaks observed at 1705.95  $Cm^{-1}$  and 1538.25  $Cm^{-1}$  assigned for C=C asymmetric and symmetric stretching vibration of thiophene ring [19]. The bands 1077.77  $Cm^{-1}$  to 1361.91  $Cm^{-1}$  are due to deformation of C-H bending and C-H in-plane of vibrations [20]. The peaks 793.54  $Cm^{-1}$ , 644.98  $Cm^{-1}$ , 544.76  $Cm^{-1}$  and 481.13  $Cm^{-1}$  assigned for C-S bending vibration and C-S-C ring deformation stretching of polythiophene which is confirms the successful

polymerization of thiophene monomer and the formation of polythiophene [21].

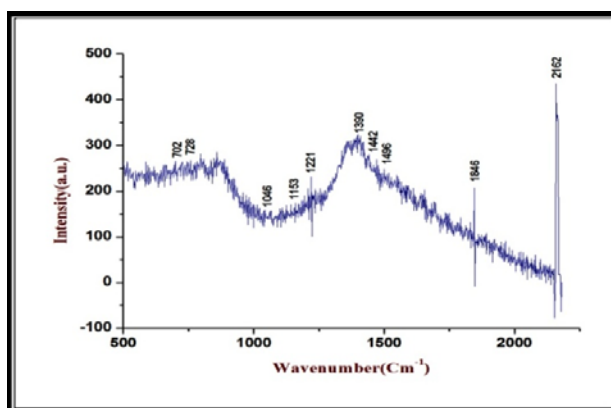


**Figure 1:** FTIR spectrum of PT thin film

### 3.2 Raman Spectroscopy Analysis

Raman spectroscopic study is one of the important tools to obtain structural information on polymers. In most cases, Raman scattering is sensitive to the degree of crystallinity in a sample. Typically, a crystalline material yields a spectrum with very sharp and intense Raman peaks, while an amorphous material shows broader and less intense Raman peaks.

The Raman spectra of PT thin film shows **Figure 2**, The most important peak at about 1422  $cm^{-1}$  which can be attributed to the  $C\alpha=C\beta$  backbone ring stretching of the neutral PT [22]. The peak at about 1390  $cm^{-1}$  is assigned to the bipolaron absorptions the band of  $C\beta-H$  bending appears at 1046  $cm^{-1}$ . The band located at about 702 and 728  $cm^{-1}$  are assigned to the C-S-C ring deformation associated with dication (bipolaron) and radical cation (polaron), respectively. The peak 1221  $Cm^{-1}$  and 1370  $Cm^{-1}$  are assigned to  $C\alpha - C\alpha'$  stretching and  $C\beta - C\beta'$  ring stretching formations [23-24].

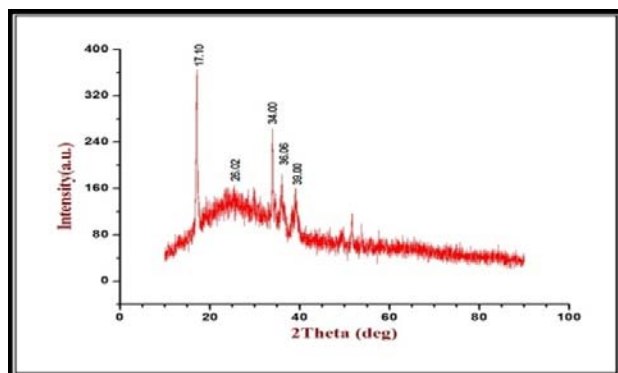


**Figure 2:** Raman spectrum of PT thin film

### 3.3 X-Ray Diffraction Analysis

The X-ray diffraction (XRD) studies of the sample were done on Rigaku X-ray Diffractometer with Cu –  $K\alpha$  radiation operating at 40kV and 15 mA. Scanning was carried out in the  $2\theta$  range from  $10^\circ$  to  $90^\circ$  at a scan speed of  $10^\circ$  per minute. A typical X- ray diffraction pattern for PT thin film prepared by spin coating method is shown in **Figure 3**. PT thin film

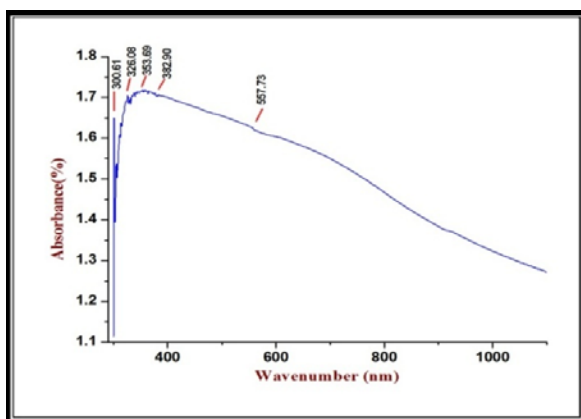
which can clearly indicated that they are amorphous nature. The broad peak observed at about  $2\theta = 17.10^\circ, 26.02^\circ, 34.00^\circ, 36.06^\circ$  and  $39.00^\circ$  which is characteristic conducting amorphous polythiophene particularly the peak appearing at  $26.02^\circ$  which is conformed in Undoped polythiophene and fully amorphous to well developed crystal depending on their method of preparation [25,26]. The average crystallite size of sharp peaks is estimated by using scherrer's formula leads to the crystallite size of about **30.63 nm** for PT thin films. The average value of d- spacing PT thin film is **8.28 Å**.



**Figure 3:** X- Ray diffraction pattern of PT thin film

### 3.4 UV – Vis Spectroscopy Analysis

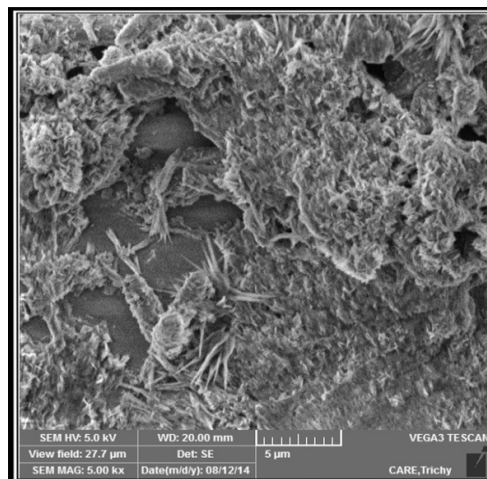
The UV- Vis spectroscopy of polythiophene thin film is shown in the **Figure 4**. These absorption spectra have been recorded over wavelength range 300 to 1100 nm using a lambda 35 UV-Vis spectroscopy model at room temperature. The absorption peak is around 353.69 nm belonging to the absorption maximum of PT and their corresponding band gap value is 3.51eV. The two absorption peaks 382.90nm and 557.73 nm indicate the formation of conjugated undoped PT. The absorption peak 326.08 nm attributed  $\pi - \pi^*$  transition for thiophene monomer [21, 27].



**Figure 4:** UV-Vis absorbance spectrum of PT Thin film

### 3.5. Scanning Electron Microscopy Analysis

The scanning electron microscopy shows the surface morphology of PT thin film images shown in the **Figure 4**. The image indicate amorphous crystalline nature of PT thin film, these film porous structure and also nano sized rod and sharp needle type formation of PT crystals presented.



**Figure 5:** SEM image of PT Thin film.

## 4. Conclusions

The Polythiophene nanoparticles was successfully synthesized by oxidative emulsion polymerization method and prepared thin film PT by using spin coating technique. The structure of PT confirmed by FTIR, XRD and Raman Spectroscopy techniques. The UV-Vis studies showed that the formation of conjugated undoped PT and band gap energy value. The SEM of surface morphology and also studied.

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