

# Study of Facile Chemically Synthesized Polythiophene Thin Films

Asst. Prof. Himmat Singh Mahor

Department of Physics

B.S.A. College, Mathura, Uttar Pradesh, India.

## Abstract

Polythiophene thin film were synthesized by using chemical polymerization technique (CBD) at room temperature and deposited on glass substrate. The chemical bonding, surface morphological and optical properties were studied using FT-IR, FE-SEM, AFM, UV-Visible spectroscopy. The study of chemical bonding nature clearly indicating the characteristic IR absorption bands of polythiophene. The surface morphological study revealed that the nanofibrous polythiophene morphology. The water contact angles were measured, shows the surface behavior of film with water.

**Keywords:** Chemical Bath Deposition, Polymer, Polythiophene-thin film, Field Emission Scanning Electron Microscopy (FE-SEM), Optical properties.

## 1. Introduction

Now a day, due to the electrical, chemical or physical properties, lot of development has taken place in the of conducting polymers such as polythiophene (PTh), polyaniline (PANI), polypyrrole (PPy) and their derivatives. One of the conducting polymers, polythiophene and its detivatives have been studied for several applications in optoelectronics i.e. supercapacitor, field effect transistors, photovoltaic and photoconductive devices, sensor, light emitting diodes, etc.[1-5]. The electronics and optical properties of the films are characteristically depend on its local structure for the operation of the devices.

In this work we report the formation of nanofibers of polythiophene by using chemical synthesis (chemical bath deposition technique). The surface morphology, optical properties and water contact angle were reported.

## 2.1 Experimental

The nanofibrous polythiophene were synthesized using the chemicals, thiophene (AR grade 99% Aldrich chem. Ltd.), ferric chloride (AR grade, 98% Thomas Baker Pvt. Ltd.), Chloroform (AR grade, 99.4%, Thomas Baker Pvt. Ltd.), and methanol (AR grade, 99.5%, Spectrochem Pvt. Ltd.)

## 2.2 Synthesis of Polythiophene thin film

By using ferric chloride as a oxidant and thiophene as monomer, nanofibrous polythiophene thin film were synthesized by using chemical polymerization. Thiophene were dispersed in chloroform to make monomer solution, however,  $\text{FeCl}_3$  was dissolved in chloroform to get oxidant solution. Thiophene prepared with different molar solution as 0.5, 1.0, 1.5, 2.0 M and oxidant with 1.5 M.

Both the solution were prepared in 50 ml anhydrous chloroform with constant stirring for 30 min. simultaneously. The oxidant solution added in monomer solution with constant volume after constant interval of time (15 min) and continuous stirring of solution. The vertically dipped glass substrate in the solution are provide the adherent coefficient to deposit thin film on the glass. With addition of oxidant the reaction is initiated and the color of solution change from brown to dark brown and at same time the film deposited on the glass substrate.

## 3. Physico-chemical characterization

Thin films were characterized by FTIR spectroscopy for nature of chemical bonding. Study of surface morphology was carried out using FESEM. Atomic force microscopy was used to study the topography of the deposited thin film. Absorption spectra of the films were obtained using UV-Visible spectrophotometer. The water adsorption study was carried by using wettability of the film.

### 3.1 Fourier Transform Infrared Spectroscopy (FTIR) analysis

Fourier Transform Infrared Spectroscopy analysis shows the nature of chemical bonding of polythiophene thin film in the range of  $500\text{-}4000\text{ cm}^{-1}$ . Fig. 1 shows the FTIR spectra of polythiophene thin films. The absorption spectra in the range  $600\text{ to }1500\text{ cm}^{-1}$  shows the fingerprint region of polythiophene. The absorption band at  $676\text{ cm}^{-1}$ (1) attributed to C-S stretching in the thiophene ring whereas at  $781\text{ cm}^{-1}$ (2) shows C-H out of plane vibration. The band at  $1089\text{ cm}^{-1}$ (3) assigned the C-H in plane stretching vibration [1,6]. The peak at  $1339\text{ cm}^{-1}$  (5) and  $1456\text{ cm}^{-1}$  (6) are shows C-C stretching vibration and C=C symmetric vibrations [7-9]. The band at  $1732\text{ cm}^{-1}$  (7) arises due to presence of small amount of C=O [10]. These peaks reveal that the polymerization of thiophene monomer.

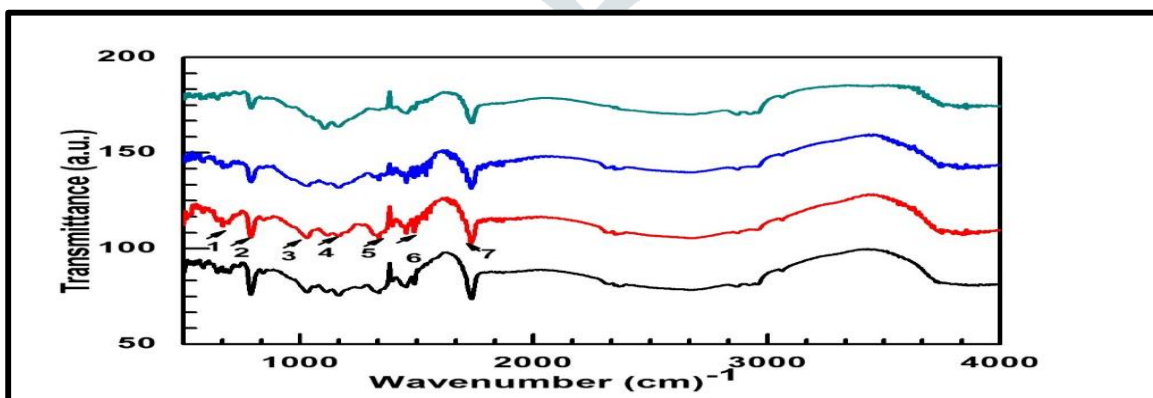
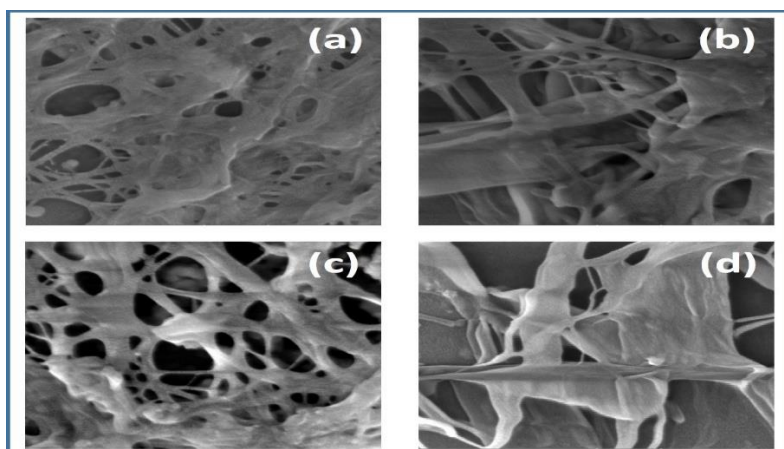


Fig. 1. FTIR spectra of polythiophene thin films deposited at (a) 0.5, (b) 1.0, (c) 1.5 and (d) 2.0 M thiophene concentration.

### 3.2 Field Emission Scanning Electron Microscopy (FESEM)

FESEM images shows the surface morphology of the polythiophene thin film. Fig 2 shows that the fibrous structure of the film of average diameter is in the range of some nanometer, which provides large surface area. The fibers are connected with each other. Hence mesh like structure is formed.



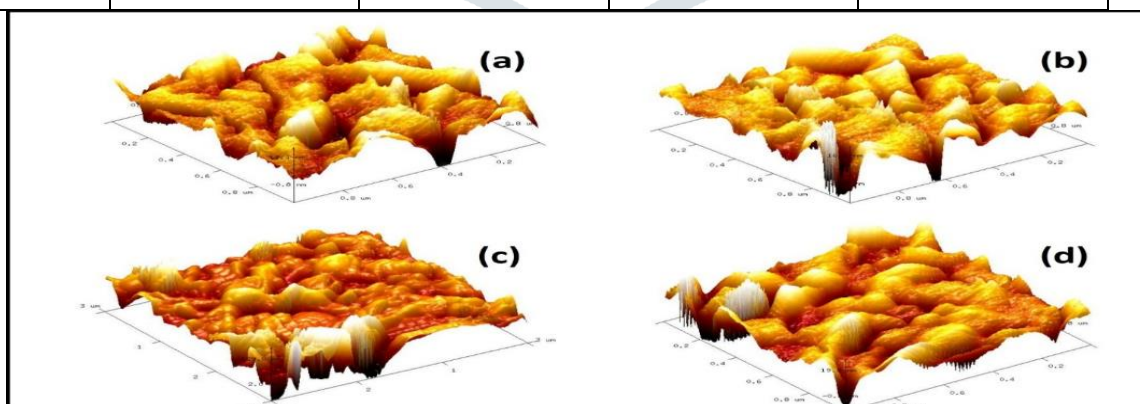
**Fig. 2** FESEM micrographs of polythiophene thin films deposited at (a) 0.5, (b) 1.0, (c) 1.5 and (d) 2.0 M thiophene concentration.

### 3.3 Atomic Force Microscopy (AFM)

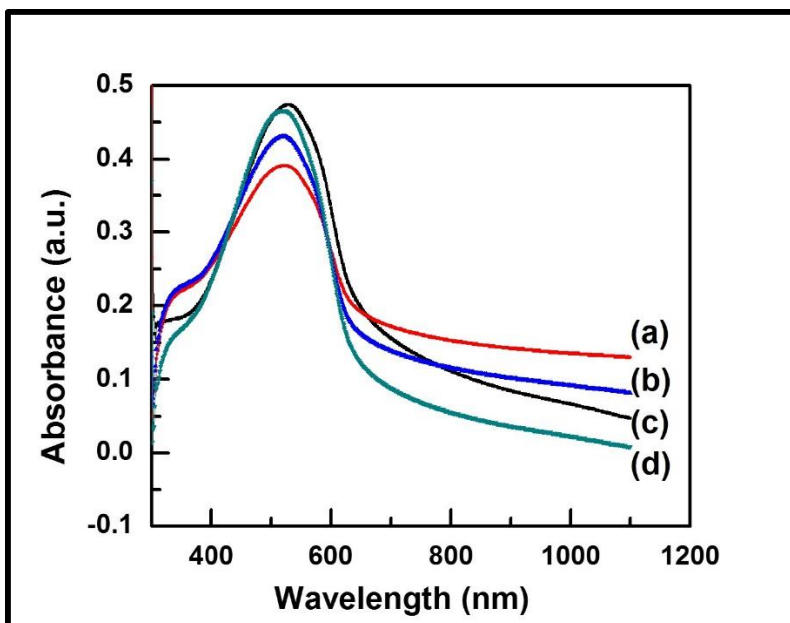
Atomic force microscopy images for all the films were recorded in non-contact mode Fig. 3. The Fig. 3 reveal that the effect of concentration variation on the film growth. The budlike structure is formed. The number of spikes increases with increase in monomer concentrations. The roughness is also vary with the concentrations shows in Table 1.

**Table 1.** Roughness of polythiophene thin films (a) 0.5, (b) 1.0, (c) 1.5 and (d) 2.0 M.

Sample	a	b	c	d
Roughness (nm)	2.78	3.27	18.1	3.66



**Fig. 3.** 3-D AFM images of polythiophene thin films deposited at (a) 0.5, (b) 1.0, (c) 1.5 and (d) 2.0 M thiophene concentration.



**Fig. 3. UV-Visible spectra of polythiophene thin films deposited at (a) 0.5, (b) 1.0, (c) 1.5 and (d) 2.0 M thiophene concentration.**

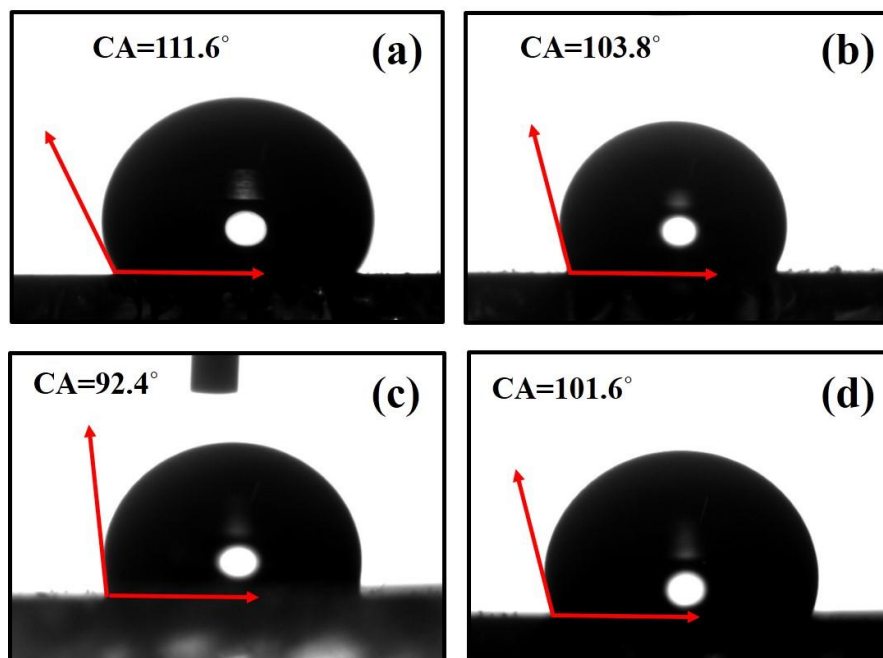
### 3.4 Optical study

Absorption spectra of polythiophene thin film were recorded over the spectral range of 400 to 1100 nm for different monomer concentration (Fig.4). With the increase in monomer concentration the absorbance of the film were increased. The UV-visible spectra shows a single wide peak at about 525 to 532 nm. The formation of peak is due to transition of electron from  $\pi$  to  $\pi^*$ .

### 3.5 Water contact angle study

The water adsorption study was carried by using wettability of the film. The hydrophobicity of the INPTh thin film was estimated by using water contact angle measurement.

The contact angle is related with the roughness of the film. According to Wenzel, a surface is termed hydrophobic when contact angle is greater than  $90^\circ$ . The water contact angle with INPTh thin film were showed in Fig. 5. The water made contact angle with INPTh thin films are  $112^\circ$ ,  $104^\circ$ ,  $92^\circ$  and  $102^\circ$  showed the hydrophobic in nature of the films.



**Fig. 5. Contact angle images of polythiophene thin films deposited at (a) 0.5, (b) 1.0, (c) 1.5 and (d) 2.0 M thiophene concentration.**

#### 4. Conclusion

Effect of monomer concentration on physico-chemical and optical properties were studied. The FTIR spectra shows that the chemical nature and composition of polythiophene which reveal that formation of polythiophene using chemical bath deposition technique. Structural characterization showed films were fibrous mesh like structure with high surface area. AFM study reveals that the average roughness increases with increase in monomer concentration. The water contact angle with polythiophene thin films shows the hydrophobic nature of the films.

#### References:

- [1] B.H. Patil, A.D. Jagdale, C.D. Lokhande, Synthesis of polythiophene thin films by simple successive ionic layer adsorption and reaction (SILAR) method for supercapacitor application, *Synth. Met.* 162 (2012) 1400.
- [2] L. Torsi, A. Tafuri, N. Cioffi, M.C. Gallazzi, A. Sassella, Regioregular polythiophene field-effect transistors employed as chemical sensors, *Sens. Actuators B Chem.* 93 (2003) 257.
- [3] P. Schottland, M. Bouguettaya, C. Chevrot, Soluble polythiophene derivatives for NO<sub>2</sub> sensing applications, *Synth. Met.* 102 (1999) 1325.
- [4] D. B. Kamble, A.K. Sharma, J.B. Yadav, V. B. Patil, R. S. Devan, A. A. Jatrakar, M.A. Yewale, V.V. Ganbavle, S.D. Pawar, Facile chemical bath deposition method for interconnected nanofibrous polythiophene thin films and their use for highly efficient room temperature NO<sub>2</sub> sensor application, *Sensors and Actuators B* 244 (2017) 522.
- [5] N.S. Sariciftci, D. Braun, C. Zhang, V.I. Srdanov, A.J. Heeger, G. Stucky, et al., Semiconducting polymer-buckminsterfullerene heterojunctions: diodes-photodiodes, and photovoltaic cells, *Appl. Phys. Lett.* 62 (1993) 585.
- [6] M. Nasrollahzadeh, M. Jahanshahi, M. Salehi, M. Behzad, H. Nasrollahzadeh, Synthesis and characterization of nanostructured polythiophene in aqueous medium by soft-template method, *J. Appl. Chem.* 8 (2013) 31.
- [7] M. A. Loi, Q. Cai, H.R. Chandrasekhar, M. Chandrasekhar, W. Graupner, G. Bongiovanni, et al., High pressure study of the intramolecular vibrational modes in sexithiophene single crystals, *Synth. Met.* 116 (2001) 321.

- [8] T. Teslaru, I. Topala, M. Dobromir, V. Pohoata, L. Curecheriu, N. Dumitrascu, Polythiophene films obtained by polymerization under atmospheric pressure plasma conditions, *Mater. Chem. Phys.* 169 (2016) 120.
- [9] O. Inganas, B. Liedberg, W. Chang-Ru, A new route to polythiophene and copolymers of thiophene and pyrrole, *Synth. Met.* 11 (1985) 239.
- [10] M. Xu, J. Zhang, S. Wang, X. Guo, H. Xia, Y. Wang, et al., Gas sensing properties of SnO<sub>2</sub> hollow spheres/polythiophene inorganic-organic hybrids, *Sens. Actuators B Chem.* 146 (2010) 8.

