



# **SYNTHESIS AND CHARACTERIZATION OF POLYTHIOPHENE NANOFIBERS**

**S. MURUGAVEL and M. MALATHI\***

Condensed Matter Research Laboratory, Materials Physics Division, School of Advanced Sciences,  
VIT University, VELLORE (T.N.) INDIA

## **ABSTRACT**

Polythiophene nanofibers have been prepared by in situ chemical oxidative polymerization method. X-ray diffraction method (XRD) and Fourier transform infrared analysis (FTIR) were used to confirm the formation of polythiophene. The synthesised polythiophene nanofibers were also characterized by energy dispersive analysis of X-rays (EDAX), transmission electron microscopy (TEM) and atomic force microscopy (AFM). Zeta potential measurement was employed to determine the surface charge of the polymer.

**Key words:** Polythiophene, TEM, AFM, Zeta potential.

## **INTRODUCTION**

In the recent years, the field of conducting polymers has been one of the most important areas of the polymer electronics research<sup>1-3</sup>. Research of polymer electronics mainly involved with the synthesis and characterization of conducting polymers<sup>4-6</sup>, because wide range applications completely based on the interplay of structure and properties of the polymers<sup>7-8</sup>. In 1977, research in electric conduction of conjugated polymers was initiated by analysing the conductivity of polyacetylene<sup>9</sup>. Since then, various conjugated polymers such as polypyrrole, polyaniline and polythiophene have been synthesized for a wide range of applications like sensors, rechargeable batteries and super capacitors<sup>10-12</sup>. Still, conducting polymers are under intense study in a various engineering applications including photovoltaic devices<sup>13,14</sup>. Owing to the high development of conjugated polymers, it has become possible to control the conductivity of the polymers over the range from non-conductivity to superconductivity<sup>15,16</sup>. Because of controllable conductivity and resistance to corrosion, conjugated polymers can replace metals in many electronics applications<sup>17</sup>. Among the

---

\* Author for correspondence; E-mail: mmalathi@vit.ac.in

conducting polymers, polythiophenes are widely utilised in a various engineering applications<sup>18-20</sup>. Polythiophene and the substituted polythiophenes are currently used as sensors and antistatic coatings because of their controllable electrical conductivity, which is produced due to the existence of an extended  $\pi$ -bonding system<sup>21</sup>. Electrical properties of polythiophene can be manipulated by doping either p or n. In order to explore the use of polythiophenes in various fields, they are prepared by chemical treatment via oxidation<sup>22</sup>. Thiophene based conducting polymers are especially important materials for theranostic gene delivery because of their thermochromism, electrochromism surfactochromism, solvatochromism, photochromism and affinitychromism<sup>23-25</sup>.

In this work, polythiophene nanofibers were prepared by in situ chemical oxidative polymerization method and the prepared polythiophene nanofibers were characterized by XRD, FTIR, EDAX, TEM, and AFM techniques. Zeta potential measurement was used to determine the surface charge of the polythiophene.

## **EXPERIMENTAL**

### **Materials**

Thiophene (Sigma-Aldrich) was used after double distillation. Anhydrous ferric chloride ( $\text{FeCl}_3$ ) and chloroform were purchased from Merck. All the chemicals used were of AR grade. Water used in this experiment was de-ionised water.

### **Measurements**

In order to determine the structure and properties of the polythiophene nanofibers, several instrumental techniques, such as XRD (XRD-Smart lab), FTIR (Spectrum RX1), EDAX (FESEM-SUPRA 55), HRTEM (JEOL 3010) and AFM (NTMDT, Ireland) were employed. Surface charge was determined by using zeta potential measurement (Horiba).

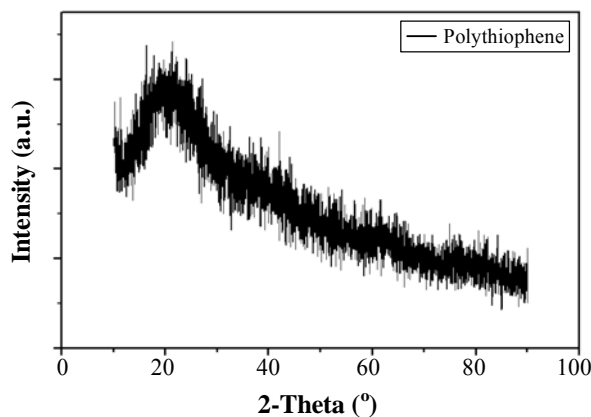
### **Synthesis of polythiophene nanofibers**

In a round bottom flask, 1 mL of thiophene was taken and mixed with 100 mL of chloroform and stirred for several minutes. Then required amount of anhydrous  $\text{FeCl}_3$  (the mole ratio of  $\text{FeCl}_3$ /thiophene was 1:2) was added to the above mixture, which was maintained under constant stirring. After stirring for 12 hr, the dispersion was filtered and a brown precipitate of polythiophene was obtained. This precipitate was extracted with methanol for 12 hr. Finally, after washing, the obtained precipitate was dried at 70°C for 5 hr.

## RESULTS AND DISCUSSION

### XRD

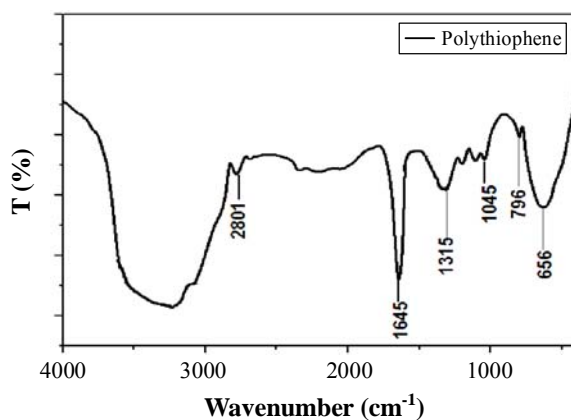
Crystalline nature of polythiophene nanofibers was analysed by using X-ray diffraction study (XRD). The XRD pattern of polythiophene is shown in Fig. 1. It shows only one broad peak centred at near  $2\theta$  value of  $21.5^\circ$ . This diffraction peak strongly associated with the  $\pi$ - $\pi$  stacking structure in polythiophene chains. In general, XRD spectrum revealed the semi crystalline nature of polythiophene nanofibers.



**Fig. 1: XRD pattern of polythiophene nanofibers**

### FTIR

The Fourier transform infrared spectrum of polythiophene prepared with oxidant  $\text{FeCl}_3$  in the region from  $4000$  to  $400\text{ cm}^{-1}$  is shown in Fig. 2.



**Fig. 2: FTIR spectrum of polythiophene nanofibers**

The characteristic absorption bands of polythiophene nanofibers are clearly observed in the FTIR spectrum (Fig. 2). The band at  $2801\text{ cm}^{-1}$  in the spectrum of the polythiophene corresponds to the C-H stretching. The band from  $1645\text{ cm}^{-1}$  is attributed to C=C characteristic peak. Absorption bands at  $1045\text{ cm}^{-1}$  and  $796\text{ cm}^{-1}$  belong to C-H in plane deformation and C-H out of plane stretching respectively. The peak situated at about  $656\text{ cm}^{-1}$  belonging to C-S thiophene stretching. Finger print region (600-1500) of the FTIR graph displayed all the characteristic peaks of polythiophene.

### EDAX

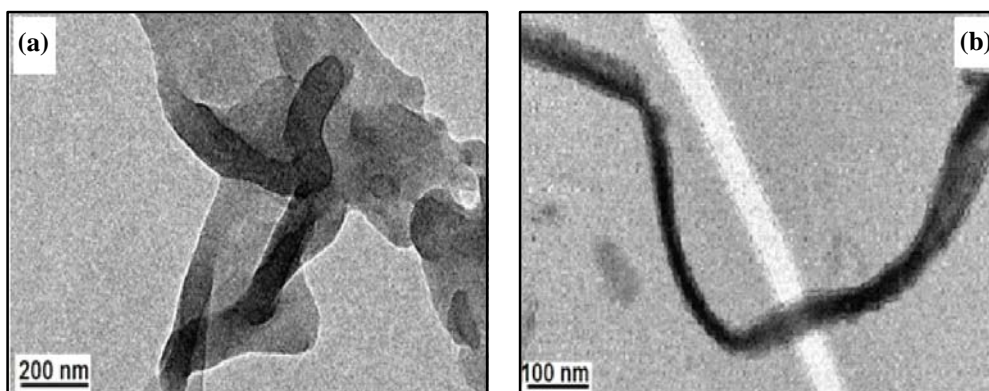
Table 1 gives the results of elemental analysis using EDAX experiment. Weight percentage of these elements of polythiophene was calculated within experimental error limit of 1%. The EDAX data confirmed that the polymer synthesized is polythiophene.

**Table 1: Weight percentage of various elements obtained through EDAX analysis**

Elements	C	O	S	Fe	H
Weight %	62.05	5.3	29.75	0.25	2.65

### TEM

The morphologies of polythiophene using TEM were investigated by many researchers but majority of nanofibers were prepared by electro spinning process. Already the utilization of polythiophene nanofibers enriched the path of organic nano electronics. In this work, nano scale images of chemically synthesized polythiophene were obtained using the transmission electron microscopy (TEM) technique.

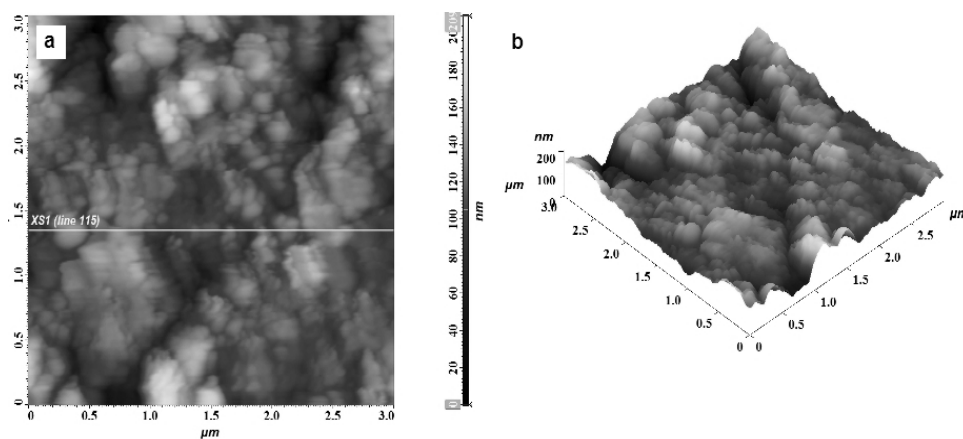


**Fig. 3: TEM images of polythiophene nanofibers (a) scale bar 200 nm, (b) scale bar 100 nm**

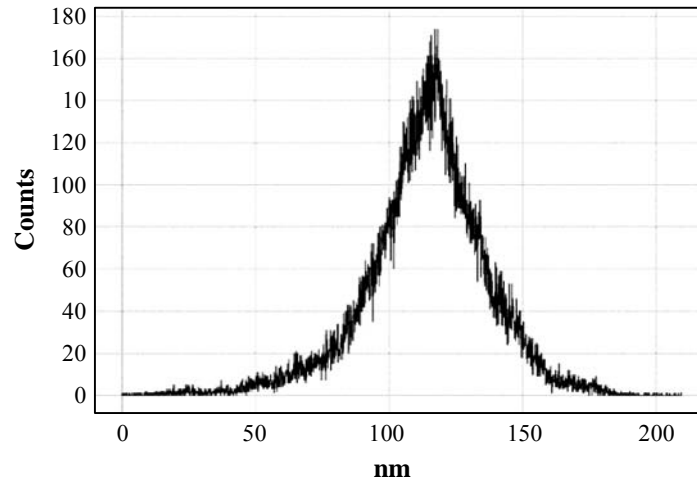
Unlike the AFM phase imaging, here, specifically, short range morphologies were analyzed (at 100 nm scale bar) for synthesized polythiophene. TEM images clearly showed the formation of nano scale polythiophene fibers with the thickness of approximately 25 nm. The TEM micrographs of chemically synthesized polythiophene nanofibers in different scale bar (200 & 100 nm) are shown in Fig. 3 (a & b).

## AFM

AFM imaging process of polythiophene coated glass slides was carried out to get understanding of the topography and roughness of the polymer. AFM images were taken using an AFM instrument NTMDT, Ireland. All imaging process were done in air at room temperature. Fig. 4a displays 3 x 3  $\mu\text{m}$  AFM image of polythiophene nano materials in 2D. Surface topography of polythiophene in 3D view is shown in Fig. 4b. The morphology of polythiophene film is looking like small globules structure ranging from 100 nm to 200 nm in diameter. Here the globules structure is the combination of long range (due to the presence of globules) and the short range (due to the region inside the globules) morphologies. Here the short range morphology is revealed in TEM images of polythiophene nanofiber (Fig. 3a and b). From Fig. 4 (a and b), it can be known that surface irregularities are only minor and smaller. The parameters  $S_q$  and  $S_a$  are the characteristic of roughness of the surface of polythiophene nano material. The average ( $S_a$ ) and root mean square ( $S_q$ ) roughness calculated for polythiophene film is 17.027 nm and 22.927 nm respectively (Table 2). Fig. 4c shows Histogram plot of polythiophene film which was used to understand the height values corresponding with the topographical images.



**Fig. 4: AFM micrographs of a polythiophene nano material (a) 2D image, (b) 3D topographic image**



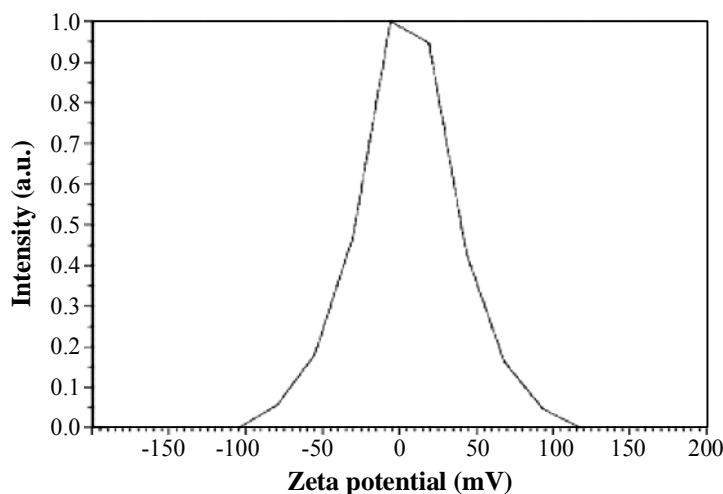
**Fig. 4c: Histograms corresponding to AFM images**

**Table 2: Results of roughness analysis from AFM experiment**

<b>Results of roughness analysis</b>	
Amount of sampling	65536
Max	209.449 nm
Min	0 nm
Peak-to-peak, Sy	209.449 nm
Ten point height, Sz	104.025 nm
Average	113.871 nm
Average Roughness, Sa	17.0277 nm
Root Mean Square, Sq	22.9273 nm
Second moment	13492.2
Surface skewness, Ssk	-0.482209
Coefficient of kurtosis, Ska	1.55895
Entropy	9.86969
Redundance	-0.281188

## Zeta potential

Stability of suspension depends on the value of net surface charge on particles in a particular liquid medium. Net surface charge is given by zeta potential measurements. Stability of suspension can be enhanced by manipulating zeta potential. The surface charge of the polythiophene nanofibers in deionised water was measured by Horiba SZ-100 nanoparticle dynamic light scattering system. Sample was prepared by dispersing 1 g polythiophene nanofibers in 100 mL deionised water. 1 mL of the sample was injected into a zeta cell, which contains two electrodes that were responsible for an induced electric field. After the application of electric field, movement of the polythiophene nanofibers were identified. This experiment was done at 25°C and an applied voltage of 100 V. Sample concentration was 1 mg/mL in deionised water. Fig. 5 shows zeta potential distribution for polythiophene nanofiber dispersion.



**Fig. 5: Zeta potential distribution for polythiophene nanofiber dispersion**

Henry's equation was used to calculate the zeta potential ( $Z$ )

$$U_e = 2\varepsilon Z f(Ka) / 3\eta$$

$$Z = U_e 3\eta / 2\varepsilon f(Ka)$$

Where  $U_e$  is the electrophoretic mobility,  $\varepsilon$  is the dielectric constant,  $f(Ka)$  is the Henry function describing the ratio of the particle radius to the Debye length, and  $\eta$  is the viscosity. Here, the experimentally determined value of mean electrophoretic mobility is  $0.000011 \text{ cm}^2/\text{Vs}$ . Based on Smoluchowski model, Henry function was approximated as 1.5.

The mean zeta potential (5.3 mV) was determined by substituting the value of electrophoretic mobility and Henry function in the above equation.

## CONCLUSION

Polythiophene nanofibers were successfully synthesized by using chemical oxidative polymerization method. The results of XRD, FTIR, and EDAX experiments confirmed that the synthesized material is polythiophene. The morphologies of the polythiophene were studied by TEM and AFM techniques. Transmission electron microscopy revealed that the short range morphology of polythiophene is in the form of nanofiber. The long range morphology of polythiophene was identified as globules structure which was shown by atomic force microscopy. The surface charge of the polythiophene nanofibers was measured by the zeta potential experiment. The results showed positive surface charge for polythiophene nanofibers.

## REFERENCES

1. K. Gurunathan, A. Vadivel Murugan, R. Marimuthu, U. P. Mulik and D. P. Amalnerkar, *Mater. Chem. Phys.*, **61**, 173-191 (1999).
2. J. Kanicki, *J. De Physique C*, **3**, 529 (1983).
3. P. Bergveld, *Sensors and Actuators B*, **4**, 125 (1991).
4. R. John and G. G. Wallace, *Polym. Int.*, **27**, 255 (1992).
5. C. R. Martin, R. M. Penner, L. S. Van Dyke, In *Functional Polymers*, D. E. Bergbreker, (Ed.) Plenum Press, New York (1989).
6. Q. Pei and O. Inganas, *J. Phys. Chem.*, **96**, 10507 (1992).
7. S. M. Yang, K. H. Chen and Y. F. Yang, *Synth. Met.*, **152**, 65-68 (2005).
8. X. Zhang, W. J. Goux and S. K. Manohar, *J. Am. Chem. Soc.*, **126**, 4502-4503 (2004).
9. C. K. Chiang, C. R. Fincher, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau and A. G. McDiarmid, *Phys. Rev. Lett.*, **39**, 1098-1101 (1977).
10. B. Winther-Jensen, J. Chen, K. West and G. G. Wallace, *Polymer*, **46**, 4664 (2005).
11. H. Kosenen, J. Ruokolainen, M. Knaapila, M. Torkkeli, K. Jokela, R. Serimaa, G. T. Brinke, W. Bras, A. P. Mankman and O. Ikkala, *Macromol.*, **33**, 8671 (2000).
12. M. Sato, T. Shimizu and A. Yamauchi, *Makromol. Chem.*, **191**, 313 (1990).



13. H. N. Kim, Z. Q. Guo, W. H. Zhu, J. Yoon and H. Tian, *Chem. Soc. Rev.*, **40**, 79 (2011).
14. A. Facchetti, *Chem. Mater.*, **23**, 733 (2011).
15. S. N. Bhadani, S. K. Sen Gupta and J. Prasad, *J. Appl. Polym. Sci.*, **47**, 1215 (1993).
16. M. Sato, S. Tanaka and K. Vama, *J. Synth. Met.*, **14**, 279 (1986).
17. G. Wegner, *Angew Chem. Int. Ed. Engl.*, **20**, 361 (1981).
18. David C. Borrelli, Sunghwan Lee and Karen K. Gleason, *J. Mater. Chem. C*, **2**, 7223 (2014).
19. S. G. Im, K. K. Gleason and E. A. Olivetti, *Appl. Phys. Lett.*, **90**, 3 (2007).
20. D. C. Borrelli and K. K. Gleason, *Macromolecules*, **46**, 6169 (2013).
21. T. Yamamoto, T. Maruyama, Z. H. Zhou, Y. Miyazaki, T. Kanbara and K. Sanechika, *Sym. Met.*, **41**, 345 (1991).
22. Y. Wei and J. Tian, *Polymer*, **33**, 4872 (1992).
23. Analyn C. Carreon, Webster L. Santos, John B. Matson and Regina C. So, *Polym. Chem.*, **5**, 314 (2014).
24. T. Shiraki, A. Dawn, Y. Tsuchiya and S. Shinkai, *J. Am. Chem. Soc.*, **132**, 13928 (2010).
25. G. Yang, H. Yuan, C. Zhu, L. Liu, Q. Yang, F. Lv and S. Wang, *ACS Appl. Mater. Interfaces*, **4**, 2334 (2012).

*Accepted : 24.01.2016*