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# SYNTHESIS AND CHARACTERISATION OF POLYTHIOPHENE AND $TiO_2$ DOPED POLYTHIOPHENE THIN FILMS BY CHEMICAL BATH DEPOSITION.

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**ABSTRACT**

In the polymer science the conducting polymers have been studied extensively during the last two decades as an important semiconductor material because of their interesting chemical and physical properties. Firstly Chemical bath deposition method is successfully used for the synthesis of polythiophene which was successfully doped $TiO_2$ composites on glass slide surface using $FeCl_3$ as an oxidant at room temperature. Effect of dopant $TiO_2$ on properties of polythiophene thin film was then studied. Chemical composition of polythiophene film was investigated by FTIR spectroscopy. Surface morphology was influenced by dopant. SEM image of composites exhibit nano size grains this is a beauty of our work. XRD analysis showed modification from fully amorphous to well developed crystalline structure .TGA-DTA results indicates composites of polythiophene with $TiO_2$ are found to be most thermally stable than undoped polythiophene.

**Keywords:** Polythiophene ,$TiO_2$ ,chemical bath deposition, morphology.



## INTRODUCTION

Advances in science and technology made in recent decades owe much to development of polymer science. Polymer science, both basic and applied, has undergone great development. In the polymer science the conducting polymers have been studied extensively during the last two decades as an important semiconductor material because of their interesting chemical and physical properties [1-3].Dopant plays an important role in conjugated polymers because these polymers become conductive when charge carriers, generated by dopants are present in their structure [4]. There are lots of conjugated polymers and one of the most widely studied conjugated polymers is polythiophene, which becomes highly conductive upon doping [5]. In polyheterocyclic particular polythiophene is one of the extensively studied electronic materials, because it exhibits relatively high electrical conductivity, good environmental stability, low toxicity and versatility of synthesis and ease of tailoring to synthesize functionalized polythiophene. The properties of polythiophene are very sensitive to fabrication conditions and to the type of preparation technique used. Therefore, study of the properties of these conducting polymers with respect to different growing as well as ambient conditions is of high importance. Stability of polythiophene in air comes from its lower oxidation potential thus polythiophene thin films have been studied by many workers, because of their special electrical properties, considerable thermal stability and oxidation resistance. It has also shown that composite material always has advantages over homogeneous material. Study of polythiophene has intensified over last three decades. It has been found that much of relevant work was carried out in recent years. Many researchers have doped polythiophene or its derivatives using $LiBF_4$, $NaAsF_6$, $NaPF_6$[6], $Bu_4NClO_4$, $Et_4NBF_4$, $Et_4NBF_6$[7], and iodine[8]. Few researchers reported doping of derivatives of polythiophene by $FeCl_3$[9,10] and fabrication of devices using $FeCl_3$ doped derivatives of polythiophene.[11, 12] An optical and electronics properties of polythiophene are useful for various device applications such as LED[2],field effect transistors[3], optical waveguides[13], in optoelectronic devices [14], photovoltaic and photoconductive devices and optical modulator devices [15]. Polythiophenes have also been exploited in sensor applications[16].

There are several routes for synthesis of polythiophene thin films the chemical bath deposition method for polythiophene thin films is important, chemical bath deposition (CBD) method appears most suitable for integration in large scale fabrication process. A single reference related to doping of $TiO_2$ was not reported in literature; hence in present research work we used $TiO_2$ as a dopant. Present work covers the chemical synthesis of conducting polythiophene and different %w/v of $TiO_2$ doped thin film. Structural investigation and characterization with their properties were determined by using FTIR analysis, scanning SEM, XRD, TGA-DTA techniques.

## EXPERIMENTAL

### Materials and Methodology

**Chemicals:** Thiophene (AR grade Merck), Iron chloride (Sd-Fine), Methanol ($CH_3OH$), $TiO_2$, and chloroform are used for the synthesis.

**FTIR:** Bruker Germany spectrometer with a resolution of 4 $cm^{-1}$ in the range 450-4000 $cm^{-1}$of SAIF IIT Mumbai.

**XRD:** Rikagu Mini Flex 300/600 instrument at Vidyabharti College, Amravati.

TGA-DTA: Rigaku thermos plus EV02 instrument at GVISH College, Amravati.

**SEM:** JSM-6380 Instrument VNIT College, Nagpur.

For Synthesis of polythiophene by chemical bath deposition method initially, substrate were washed with deionized water, boiled in chromic acid and washed with detergent, rinsed in acetone and finally ultrasonically cleaned with deionized water before deposition of thin film.Thiophene is used as monomer for preparation of polythiophene thin films. Monomer solution was prepared by dissolving 0.1 M of thiophene in chloroform, oxidant solution was prepared in a glass beaker with 0.5 M concentration of $FeCl_3$ in chloroform the ratio of monomer to oxidant was kept 1:5. 0.5%w/v and 1% w/v $TiO_2$ added in oxidant solution. Substrates were immersed in bath at room temperature at constant stirring. Monomer solution was added drop wise in an oxidant solution reaction being carried out at room temperature. During precipitation, heterogeneous reaction occurred and deposition of polythiophene took place on substrate. The substrates coated with polythiophene thin films were removed after a time interval of 1 h from the bath, washed with methanol followed by chloroform and acetone repeatedly to remove residual oxidant and unreacted monomers. Dried in air and preserved in an airtight container

## RESULTS AND DISCUSSION

### By Fourier Transform Infrared (FTIR) investigation

The IR studies of undoped polythiophene and polythiophene $TiO_2$ composites synthesized in present research work are given in Figures- 1, 2, 3 and the related absorbance are given in Table-1 determined by The FTIR spectra for pure polythiophene and $TiO_2$ complexes are shown below,

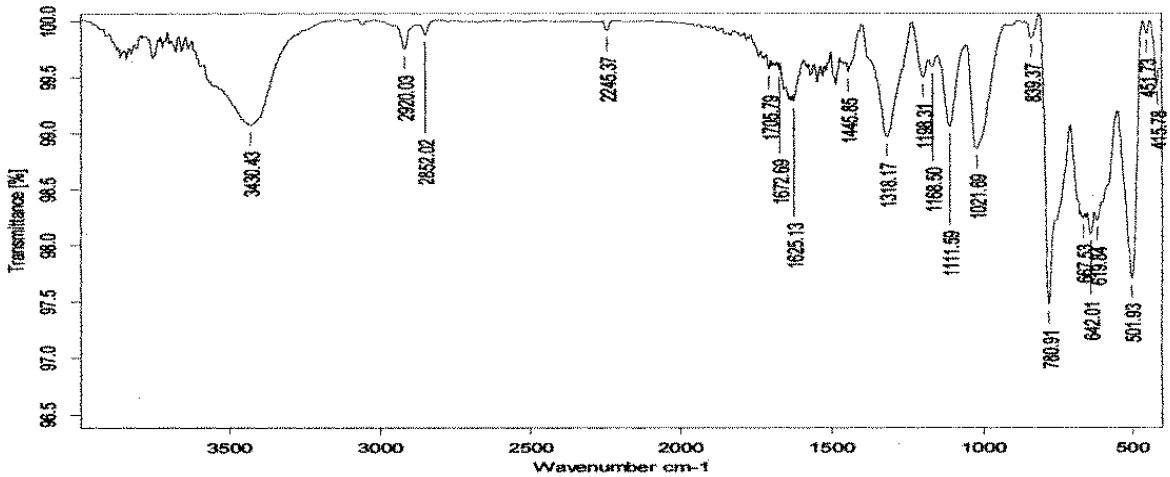


Fig.-1: FTIR of polythiophene without dopant

The observed vibrational frequencies are enclosed in Table-1.

Table-1

| Material | Frequency in $cm^{-1}$ | | | | Stretching frequency | Bending |
|---|---|---|---|---|---|---|
| | Ar-C=C-H | Ar C=C | C-C | C-S | Ti-O | Ti-O |
| Pure Polythiophene | 2920.03 | 1625.13 | 1318.17 | 780.91 | - | - |
| Polythiophene+0.5w% $TiO_2$ | 2923.03 | 1607.41 | 1313.86 | 783.46 | 721.83 | 552.74 |
| Polythiophene+1w% $TiO_2$ | 2919.64 | 1626.24 | 1320.60 | 784.05 | 726.73 | 560.42 |

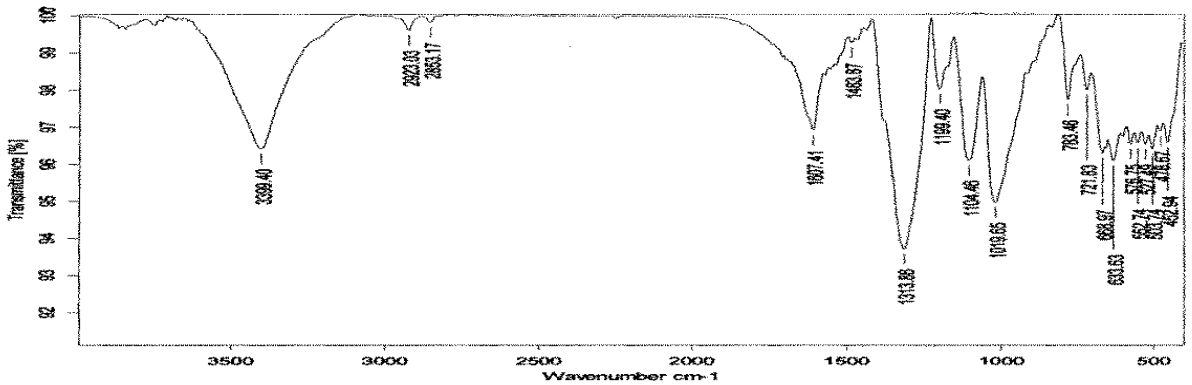


Fig.-2: FTIR of polythiophene with dopant (Dopping of $TiO_2$ (0.5 % w/v) in polythiophene thin film.)

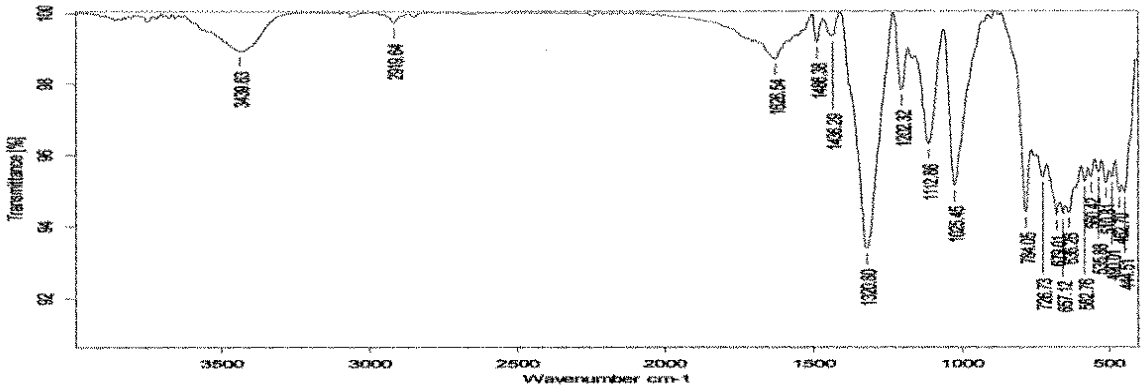


Fig.-3: FTIR of polythiophene with dopant (Dopping of $TiO_2$ ( 1 % w/v) in polythiophene thin film.)

The absorption band in region 2920.03 $cm^{-1}$ is due to aromatic C=C-H stretching frequency of undoped polythiophene which is shifted to the ranges 2923.03 $cm^{-1}$ and 2919.64 $cm^{-1}$ in Polythiophene/$TiO_2$ composite.The absorption band in region 1625.13 cm-1 is due to aromatic C=C stretching frequency of undoped polythiophene which is shifted to ranges 1607.41 $cm^{-1}$, 1626.24 $cm^{-1}$. Peak at 1313.17 $cm^{-1}$ for Polythiophene is assign for C-C stretching frequency are shifted to 1313.86 $cm^{-1}$, 1320.60 $cm^{-1}$.The absorption band in the region 780.91 $cm^{-1}$ is due to the C-S stretching frequency of undoped polythiophene which is shifted to the ranges 783.46 $cm^{-1}$,784.04 $cm^{-1}$ in polythiophene/$TiO_2$ composites.
The absorption peak at lower frequency 721.83 $cm^{-1}$ ,784.05 $cm^{-1}$ assigned for Ti-O stretching and 552.74 $cm^{-1}$ and 580.42 $cm^{-1}$ for Ti-O bending of Polythiophene+0.5%w/v and Polythiophene+1%w/v $TiO_2$ composite.

**SEM Study**

The SEM images of pure polythiophene and polythiophene/$TiO_2$ composites thin film are shown in figures-4,5 and 6.Tthe images seems to be uniform microporous on the surface and the particles were in nanometer scale. Nanoparticles agglomerated grain structure observed. The grains are highly agglomerated irregular shape but they are well interconnected each other.

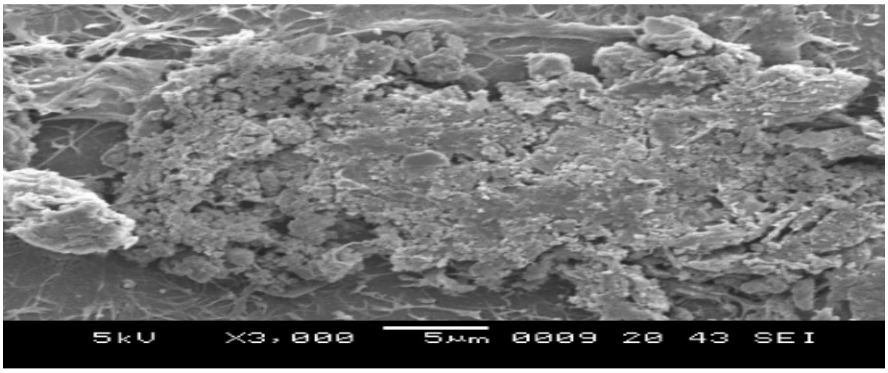


Fig.-4: SEM Image of undoped polythiophene thin film.

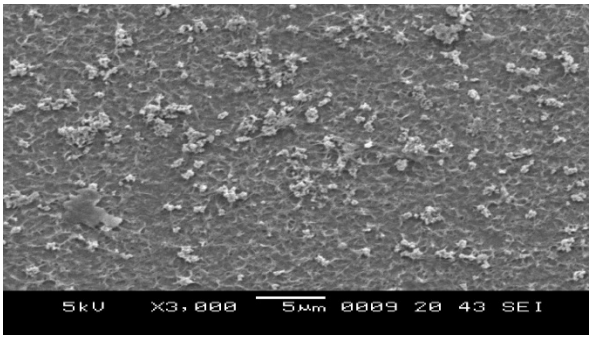


Fig.-5: SEM image of 0.5 %w/v Ti02 doped polythiophene thin film.

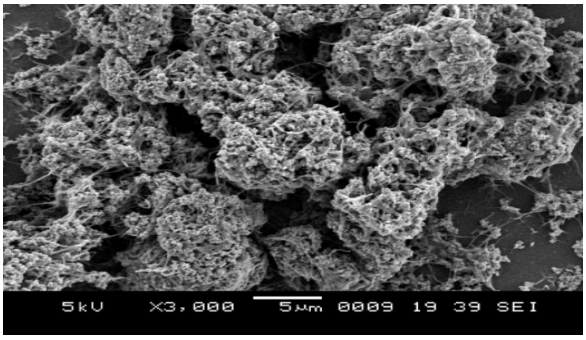


Fig. -6: SEM image of 1 %w/v Ti02 doped polythiophene thin film.

**XRD Studies**

A typical XRD pattern obtained for undoped polythiophene and $TiO_2$ doped Polythiophene composite are shown in Figures-7, 8 and 9 .In case of undoped polythiophene no sharp peak observed in figure A this indicates the polymer under investigation is nanocrystalline in nature .XRD analysis 0.5%w Tio2 doped polythiophene shows 5 peaks at 2 theta 25.507,38.00,48.199,55.36,69.01while that of 1%w of Tio2 shows 12 intense peak which was absent in pure polythiophene this shows modification of fully amorphous polythiophene to well developed crystalline structure.

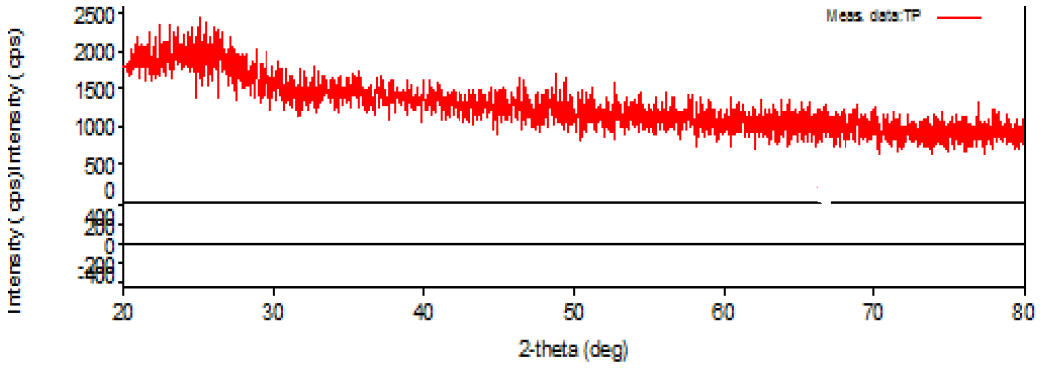


Fig.-7: XRD of undoped polythiophene

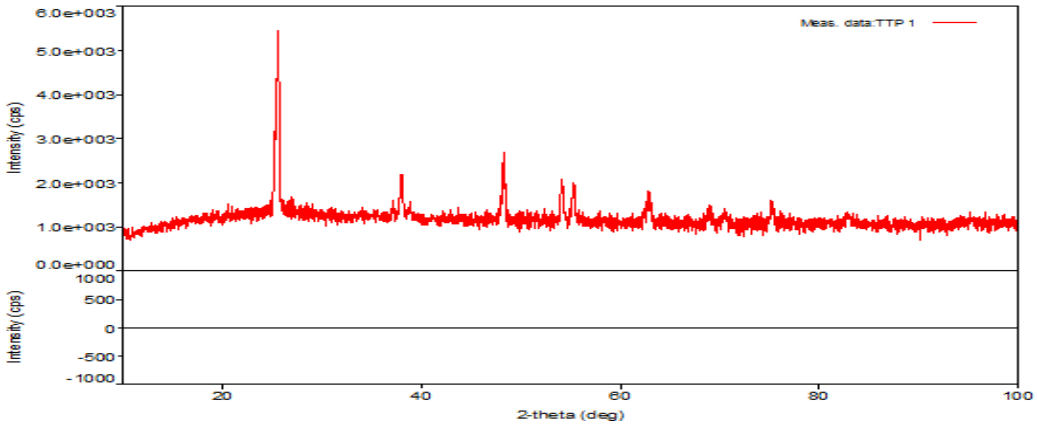


Fig.-8: XRD of 0.5% w/v $TiO_2$ doped polythiophene.

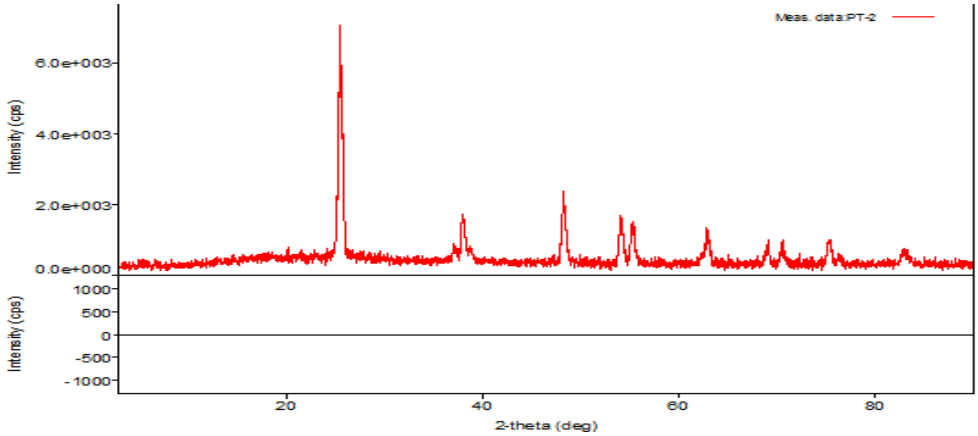


Fig.-9: XRD of 1% w/v $TiO_2$ doped polythiophene

**TG-DTA analysis**

Thermogravimetric and differential thermal analysis of Polythiophene and different %w/v of $TiO_2$ composite was carried out in air atmosphere .TGA was performed on Rigaku TG8121 thermal analyser with pt. pan in the temperature range from room tempreture to 550°C.The thermogram of polythiophene and composite as shown in Figures-10,11 and 12. Three major weight losses are observed one around 70-80$^0$weight loss is about 1-3% due to elimination of moisture,evopouration of solvent as well as unreacted monomer .second weight loss around 280-300 $^0$ is due to loss of dopant component of polythiophene. Third major drop in weight observed at 350-400$^0$ and beyond the range is due to degradation of polythiophene itself. In case of DTA shows two exothermic maxima at near about 400$^0$and 450°C.

## CONCLUSION

We have demonstrate successful synthesis of nanostructure polythiophene and polythiophene $TiO_2$ composite thin film by chemical bath deposition techniquepolythiophene can be doped by $TiO_2$ in chloroform with formation of complex .The result of FTIR proved the formation of polythiophene.Morphology of thin film were analysed by SEM it shows change in morphology after doping .XRD shows modification from amorphous to the well-developed crystalline structure thermal properties of nanocomposites were investigated by .TG-DTA analysis shows composites of polythiophene are found to be more thermally stable than pure polythiophene.

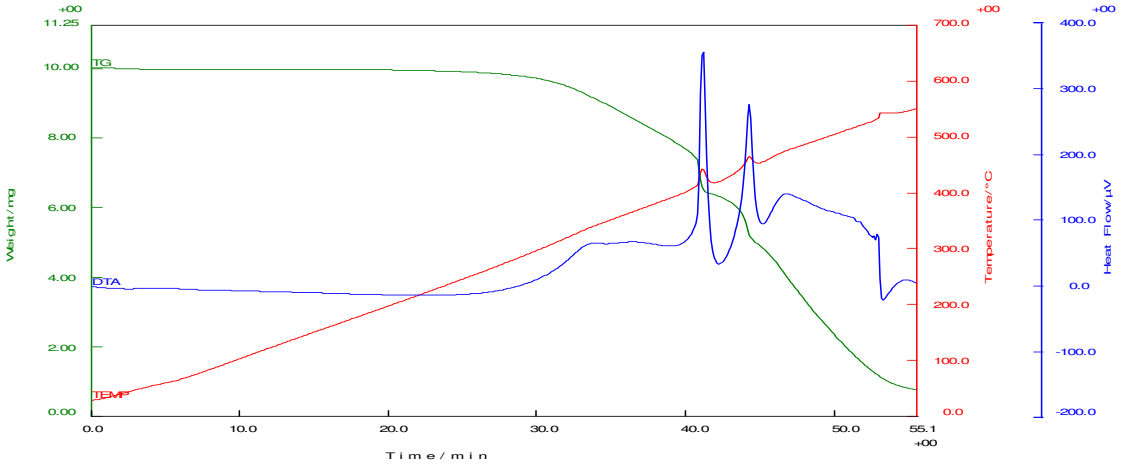


Fig.-10: TG-DTA thermogram of undoped polythiophene

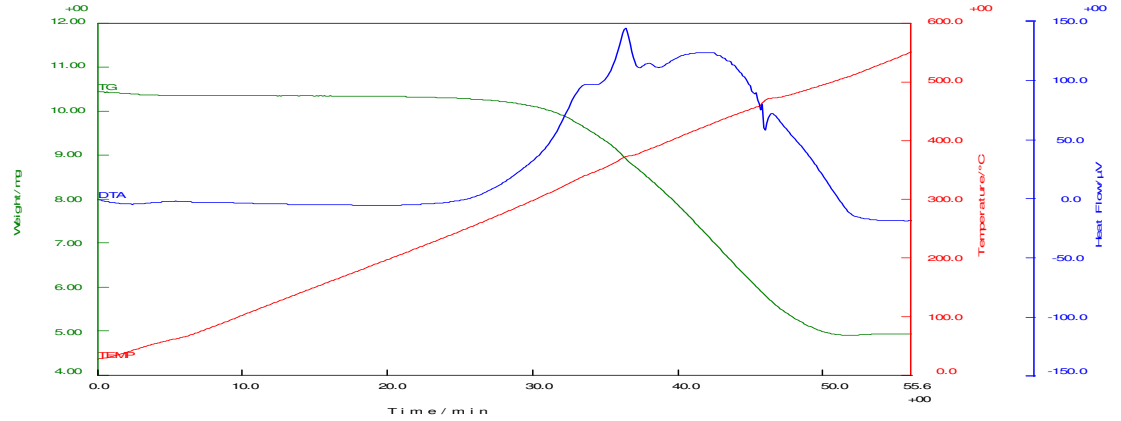


Fig.-11: TG-DTA thermogram of 0.5% w/v $TiO_2$ doped polythiophene

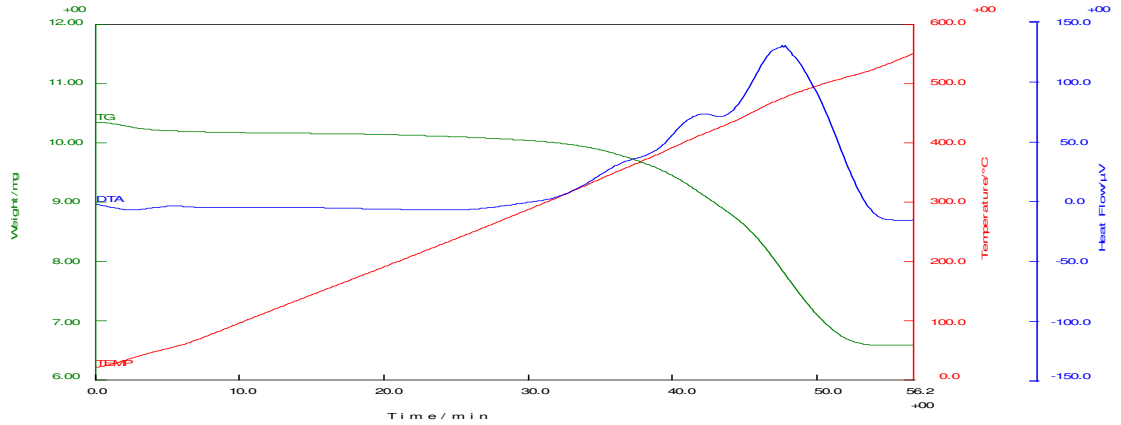


Fig.-12: TG-DTA thermogram of 1% w/v $TiO_2$ doped polythiophene

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