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Synthesis and characterization of homo and poly (Pyrrole-Co-O-Toluidine) copolymers to develop a charge transport material for solar cell applications

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The Pyrrole, O-Toluidine and its copolymer doped with H_2SO_4, HNO_3 were synthesized by chemical oxidation method with monomer ratios. The samples were characterized by FTIR, UV-Vis, X-Ray Diffraction, TGA, solubility and conductivity studies. FTIR Spectrum confirms the presence of functional groups in the copolymer structure. The UV-Vis spectrum reveals the $\pi - \pi^*$ transition in the polymer chain. The XRD pattern shows the amorphous nature of the prepared samples. The higher solubility of copolymer compared with homo polymer is confirmed from solubility studies. The conductivity studies confirm the low conductivity in the samples having equimonomer ratio. The conductivity increases with the increase in Pyrrole percentage. This establishes the conductivity dependence of monomers' ratio. The TGA graphs show that the copolymer has higher thermal stability compared with homo polymer. The results are reported.

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Keywords: Conducting polymers: Pyrrole, O-Toluidine, & Poly(Pyrrole,-Co-O-Toluidine) Copolymers, FTIR, UV-Vis, X-Ray Diffraction, TGA, solubility and conductivity.

1. Introduction

Polymers are generally insulators. But some polymers can have conductivity comparable to that of metals and semiconductors. This particular aspect has motivated the researchers in the field of polymers. These conducting polymers are used in electronic displays, telecommunications, biosensors, electrochemical storage and molecular electronics. [1-3] Among the familiar conducting polymers, Pyrrole is the most attractive one because of its easy preparation, higher performance, stability and higher oxygen and nitrogen separation factor[4].

It is an electron rich material. On the other hand, Poly (O-Toluidine) has good stability[5] but has low conductivity. It is electron deficient material. There are some reports about the copolymerization of pyrrole with aniline [5-8]. By combining these two materials, one can develop a charge transport material for solar cell applications. In this paper, an attempt has been made to synthesize pyrrole, O-Toluidine and their copolymers with different ratios and study their suitability for the above purpose.

2. Experimental

2.1. Polymer Synthesis

Pyrrole (PPY), O- toluidine(OT), 38% of Nitric acid (HNO_3), Potassium Dichromate ($K_2Cr_2O_7$) and DMSO obtained from merck (AR grade) Company were used for synthesis.

The pyrrole-orthotoluidine copolymer was synthesized by chemical oxidative method with different monomer ratios [0,1:1,2:1.etc]. A mixture of 0. 5M pyrrole and 0.5 M of O-toluidine were added to 100ml of distilled water followed by the addition of 1M of HNO_3 aqueous acid. The solution was stirred vigorously for half an hour 0.5M Potassium Dichromate ($K_2Cr_2O_7$) was dissolved in 20ml of de-ionized water separately which was then added drop by drop for a period 30 minutes to enhance the reaction. The solution became a black color. The reaction was carried out at room temperature for 6 hours. The precipitate polymer was filtered and washed with appropriate acid and distilled water until the product becomes color less. It was dried in vacuum at 60° C for 24 hours.

2.2. Characterization

The Pyrrole (PPY), O- toluidine(OT), and copolymer of Poly (Pyrrole,-Co-O-Toluidine) powder were characterized by using in FT-IR, XRD, Thermo gravimetric analysis (TGA), UV – VIS spectro photo meter, Solubility and conductivity.

The UV- Visible spectrum of homo polymer and co-polymer was studied with a jasco V-530 in range of 200 to 800 nm in DMSO solvent.

The X –ray diffraction patterns of the PPY, POT, and copolymer of Poly (Pyrrole,-Co-O-Toluidine) samples were recorded through a Bruker AXS 508 advance diffractometer with monochromatic Cu Kα radiation. The thermal studies of Pyrrole (PPY), O- Toluidine(OT), , and copolymer of Poly (Pyrrole,-Co-O-Toluidine) powders were carried out at Nitrogen atmosphere at heating rate of 20° /min on Perkin Elmer STA 6000 thermal analyzer.

The IR spectra of PPY, POT, and copolymer of Poly (Pyrrole,-Co-O-Toluidine) powders were recorded on shimadzu (model – 8201) in the KBr pellete medium at room temperature in the region 4000 – 400 $cm^{-1.}$

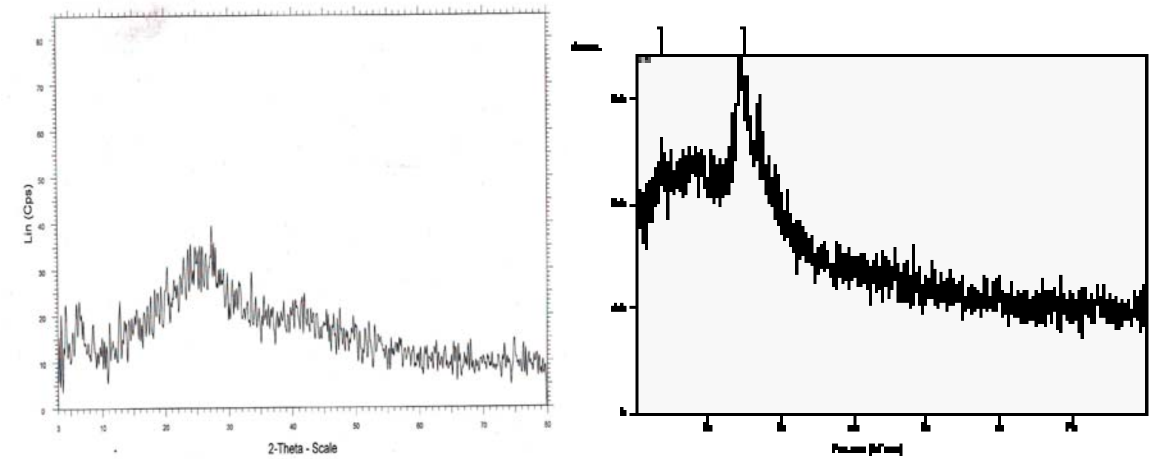
The conductivity measurements of PPY, POT, and copolymer of Poly (Pyrrole,-Co-O-Toluidine) copolymer samples were compressed into a pellete (13mm diameter and 1mm thick) with manual hydraulic press at 700 Mpa. The measurements were performed by four –probe setup(model –DFP-02) at room temperature.

The solubility of the resulting polypyrrole, poly(o)-toluidine and PPY-POT copolymer are determined by dissolving in various organic solvents. A few milligrams of the above synthesized polymers was dissolved with 2ml of solvent and kept for 24 hours at room temperature. It is found that, the PPy, poly(o)-toluidine and ppy-POT copolymer are soluble in DMSO and DMF.

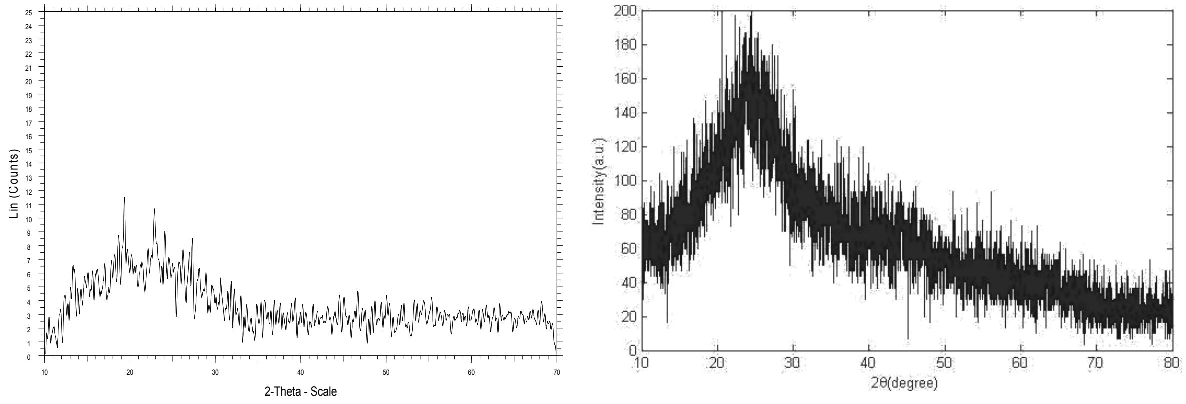
3. Results and discussion

3.1. XRD pattern of homo and copolymers

The x-ray pattern of PPY,POT, and copolymer of Poly (Pyrrole,-Co-O-Toluidine) copolymers. are shown in fig1.Fig 1 (a) the two peaks obtained at 2θ = 12.7^0 and 25º shown in fig1a shows that the PPY is in amorphous nature[9]. It is due to the scattering from ppy chains at interplanar spacing [10].



(a) PPY (b) POT



(c) (PPY – CO – POT) (1:1) (d)PPY CO – POT)(2:1)

Fig 1. XRD spectrum of (a) PPY (b) POT (c) (PPY – CO – POT) (1:1 (d) (PPY – CO – POT)(2:1)

From fig 1 (b) it can be conclude that the POT shows amorphous nature at 2θ =24.7º.

From fig1 (c) the XRD spectrum of Poly (Pyrrole,-Co-O-Toluidine) copolymers (1:1) ratio shows the sharp peaks at 2θ =20º and 2θ =23º reveals that the polymer shows semicrytalline behavior[11].

From fig 1 (d) the XRD spectrum of Poly (Pyrrole,-Co-O-Toluidine) of copolymers in the (1:1) ratio at 2θ =24.7º with broad amorphous diffraction peak. The XRD patterns homo and copolymers shows that the polymers are amorphous nature.

3.2 FTIR analysis of homo and copolymers

Pyrrole, O-Toludine and their copolymers with different molar ratios (0,1:1,2:1) were shown in the fig(2).

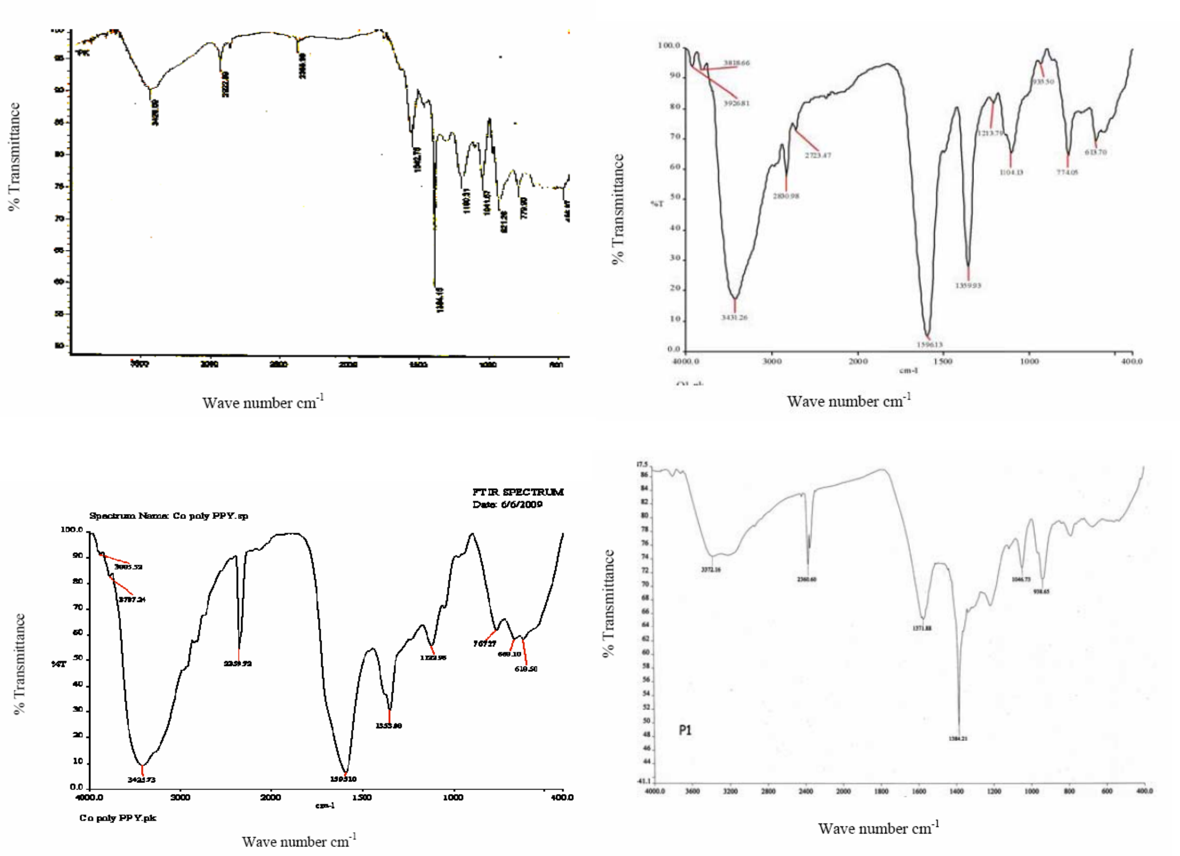


Fig . 2. FTIR spectrum of (a)PPY (b) POT (c) (PPY – CO – POT) (1:1 (d) (PPY – CO – POT)(2:1).

The peaks at 1384, 1359, 1353 and 1384.2 cm^{-1} are corresponds to CH_3 methyl group present in the structure. The peak 1384.2 is attributed to the methyl group in the structure of O-Toluidine units [12].

The peaks observed in the FTIR spectrum indicate the presence of O- Toluidine unit in the obtained copolymer structure. The peaks at 1542, 1596,1595 and 1571 cm^{-1}, attributed to C = C stretching of reduced and oxidized quinoid form benzene and pyrrole ring [13]. The spectral data of samples are given below

Table 1. FTIR data of homo and copolymers.

Polymer / Copolymer	N-H Stretching	C-H Stretching	C-C Stretching	C-H in-plane	C-H out-plane
PPY	3428	2922	1542	1041	779
POT	3431.2	2830	1596	1104	774
PPY – POT (1:1)	3425	2359	1595	1122	767
PPY – POT (2:1)	3372	2360	1971	1046.73	938

The peak 1542 cm^{-1} corresponds to delocalized π-electrons are affected by doping polymer [14]. The IR spectral results confirm the formation of PPY/POT copolymer.

The peaks at 1041, 1104.13, 1122 and 1046.73cm^{-1} are assigned to C – H inplane bending. The peak at 1041cm^{-1} is due to C-H inplane deformation of the PPY unit[15].

3.3 UV-vis Spectra of the homo and copolymers

Fig(3) shows the UV-vis absorption spectra of copolymers with different molar ratios (0, 1:1, 2:1, etc.).

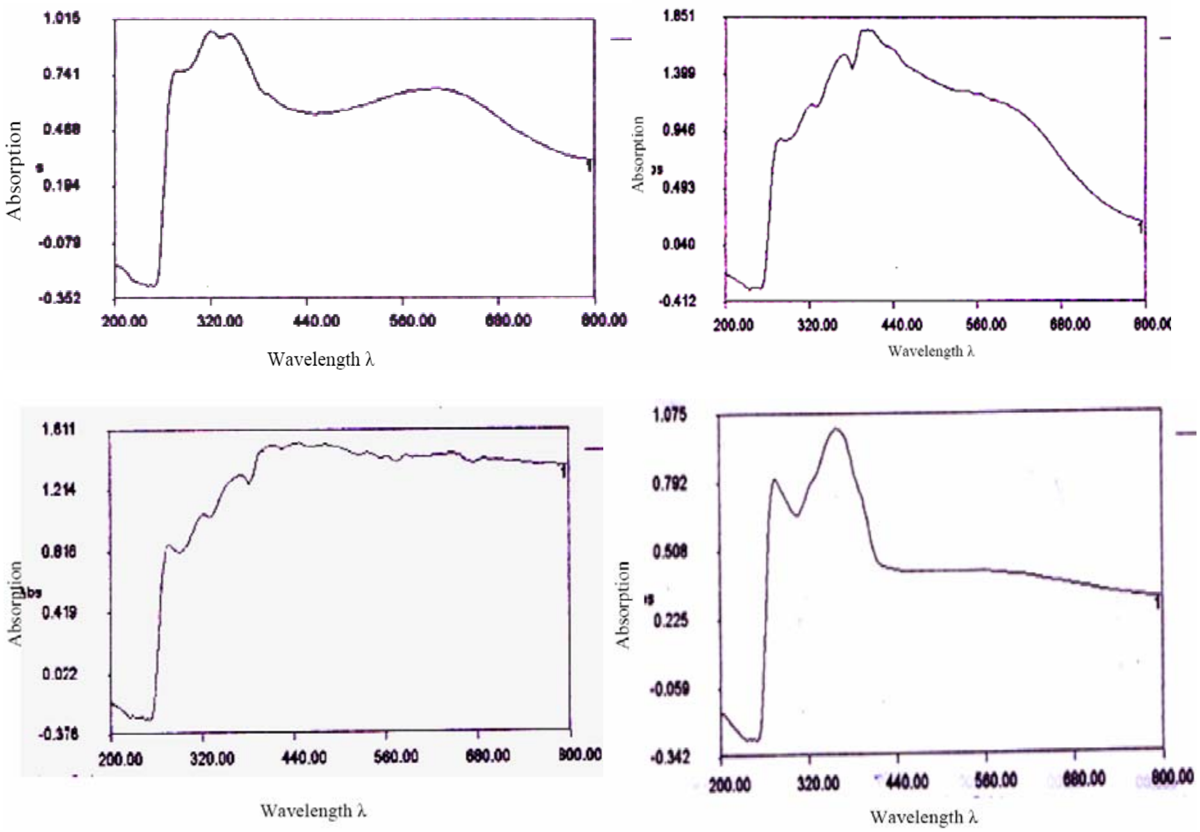


Fig 3. UV-vis spectrum of (a) PPY (b) POT (c) (PPY – CO – POT) (1:1 (d) (PPY – CO – POT)(2:1).

Table 2. UV-vis Spectral data of the homo and copolymers.

Molar Ratio	Wavelength (nm)	
	Band 1	Band 2
PPY	320	600
POT	324	396
PPY – POT (1:1)	324	413
PPY – POT (2:1)	276	276

From table2, the sharp peaks at 300 nm and 600 nm are assigned to the π – π* transition of the benzoid rings. The strong band at 600 nm is attributed to π – π* transition in poly pyrrole[16]. The band has undergone bathochromic shift owing to the extension of conjugation in the poly pyrrole chain.

The spectram of copolymer reveals that the equimolar ratio mixture of comonomers did not have linear combination of the spectrum of the obtained homopolymers[17].

The peak at 276 nm corresponds to the π – π* transition of the benzene ring. This band appearing in the spectrum of PPY –POT copolymer indicates that the O-toluidine units in the copolymers[18]. It is observed that the PPY content ratio increases. The bands move towards lower value[19].

3.4 Thermal stability of the homo and co polymers

The TGA graphs of PPY – POT copolymer with different monomer ratios are shown in the fig 4.

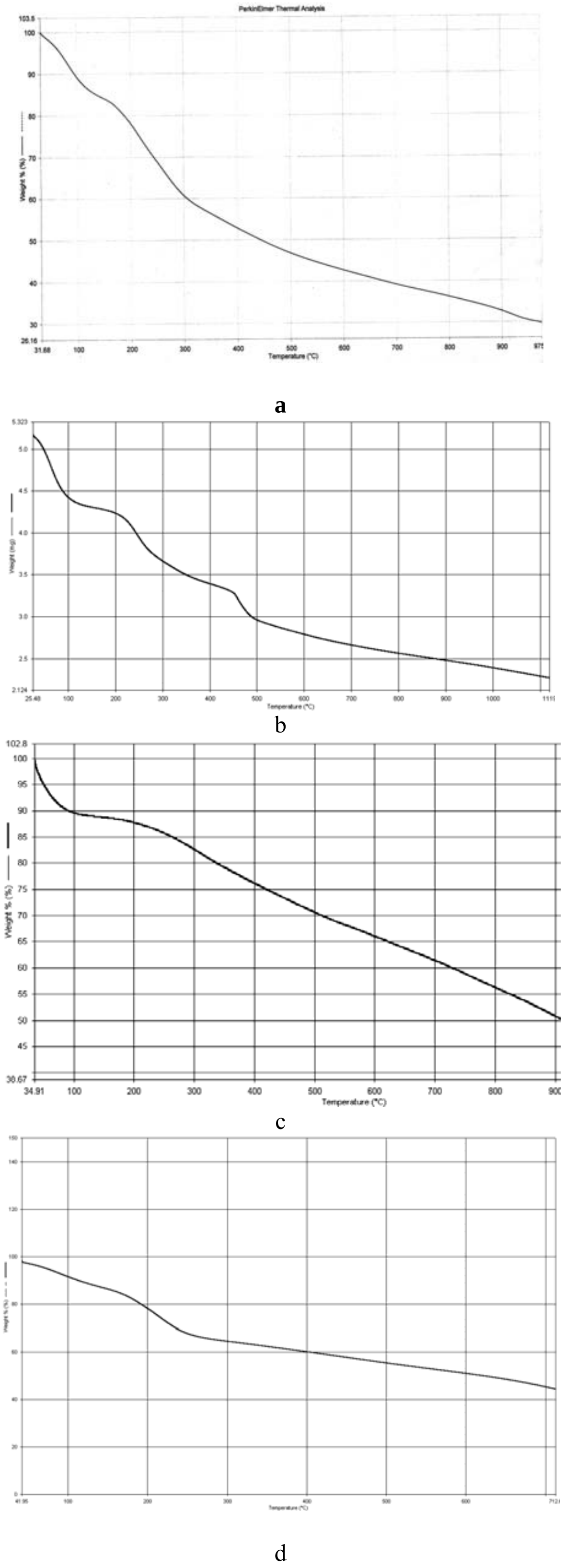


Fig 4. TGA of (a) PPY (b) POT (c) (PPY – CO – POT) (1:1 (d) (PPY – CO – POT)(2:1)

Fig 4(a) there were two major weight losses. The first weight loss observed upto 110 °C is due to lose of water or moisture from the polymer[20]. The second stage observed within the temperature range 100 – 300 °C. This is rage related to removal of dopant from the polymer structure [21]. The polymer starts to degrade above 380 °C gradually. The total weight loss is 70 %.

Fig 4(b) there were three major weight losses. The first weight loss observed upto 100°C is due to lose of water or moisture from the polymer. The second stage was observed within the temperature range 250 °C. The third stage observed within the temperature range 450 °C. This range related to removal of dopant from the polymer structure. The polymer starts to degrade above 450 °C gradually. The total weight loss is 57 %.

From Fig 4(c) copolymers of the equal ratio first weight loss was observed 150 °C and then polymer degrades rapidly. The total weight is 60 %. The compound is not stable [22].

From Fig 4(d) the decomposition did not complete upto 800 °C [23] which could be attributed the good stability of PPY – POT copolymer. This graph shows a slight variation at 250 °C. The total weight loss is 25 %.

3.5 Conductivity of the homo and copolymers

The conductivity of PPY, POT and PPY – POT with different ratios are shown in the Fig. 5.

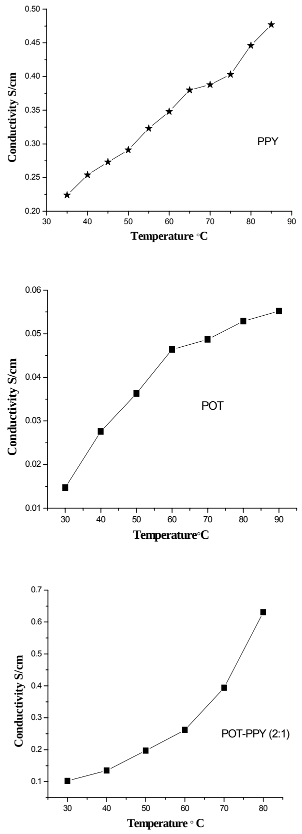


Fig 5. Conductivity of the homo and copolymers of (a) PPY (b) POT (c) (PPY – CO – POT) (1:1 (d) (PPY – CO – POT) (2:1).

The conductivity of the PPY, POT and PPY – POT are 0.477 S/cm, 0.055 S/cm and 0.63 S/cm. In the case of copolymers, the conductivity increases with the content of pyrrole which shows semiconducting nature.

3.6 Solubility of the homo and copolymers

The solubility of PPY, POT and PPY – POT with different ratios were determined by dissolving in various organic solvents in DMSO and DMF. A few milligrams of above synthesized polymers are dissolved in 2 ml of solvent kept at room temperature. The solubility of the copolymers is higher than the homopolymers in DMSO solvent.

4. Conclusion

The PPY, POT and PPY – POT with different ratios were synthesized by chemical oxidation method. The samples were characterized by XRD, FTIR, UV, TGA, Conductivity and Solubility. The XRD pattern confirms the amorphous nature of polymers. The FTIR spectroscopic information reveals the presence of O-Toluidine units in the copolymer structure. The UV spectral studies depict the electron mobility in homo and copolymers. The TGA of copolymers are higher than the homopolymers. The decomposition did not complete even at 700 ^{o}C which shows good thermal stability of copolymers. The conductivity depends upon the monomer ratio. The equal monomer ratio of the copolymer shows low conductivity.

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