

# SYNTHESIS AND CHARACTERIZATION OF POLYANILINE AND POLY-O- TOLUIDINE TERNARY COPOLYMERS

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## ABSTRACT

Homopolymers of aniline toluidines and their copolymers were synthesized by chemical oxidate polymerization using different ratios of monomers the molar feed radio of the starting aniline monomers was varied to result in copolymers with different compositions. The synthesized polymers were characterized by employing Fourier transform infrared, UV-visible, X-ray diffraction techniques for understanding the details of the structure of the synthesized polymers. Morphological of the as synthesized polymers were also studied by employing scanning electron microscopy from the SEM images .the morphology and structure of the PANI nanoparticles were observed using SEM ,PANI shows a porous irregular structure and POT nanoparticles shows a globular structure consisting of small globulas and pores.

**Keywords:** polyaniline; poly(o-toluidine);chemical polymerization, characterization.

## 1.INTRODUCTION

There is an explosive increase in the demand for composite materials in the last two decades, which are now available as materials with an unique combination of properties. However , the major problem in applying these polymers is their poor processibility by solvent or multi techniques most of them are insoluble in common solvent and undergo degradation before reaching the melting point. Copolymerization offers a way of improving the processibility of PANI. the properties of the processibility of the poly(substituted anilines)like toluidine depend on the type of substitution like electron with drawing ,electron donating groups or less affecting groups like alkyl groups. Copolymers of aniline with poly(aniline-o-toluidine) were reading synthesized in various molar ratios of comonomers by chemical and electrochemical polymerization.

Chemically oxidation copolymerization of aniline and o-toluidine with 4m ratios has been performed using ammonium per sulfate as an oxidant in HCL medium at 0-4<sup>0</sup>. The effect of different composites of monomers on the transport properties of poly(aniline-0-toluidine)by various techniques such as optical

and electrical has been investigated and compared with the homopolymers.

The polyaniline family is challenging because of its conducting and solubility in polar organic solvents that depend not only on the oxidation state but also on the degree of protonation and nature of dopants. It is also observed that polyaniline-o-toluidine. Copolymers has better solubility than homo polymers in various organic solvents.

## 2. Materials and methods

### 2.1 Materials

Aniline (fluka) was double distilled before use o-toluidine (Aldrich) and all the reagents and solvents (ethanol, methanol) were analytical grade and used after further purification. UV-visible spectra were obtained on a spectroskan, UV/visible obtained on a spectro-photometer with quartz cells of 1 cm optical path. Infrared spectra were recorded at room temperature using BLORAD EXCALIBUR.

### 2.2 Synthesis procedures

#### 2.2.1 Synthesis of polyaniline

Polyaniline was synthesized by chemical oxidative method with inset chemical polymerization of aniline in presence of sulphuric acid as dopant and potassium dichromate as an oxidant. The synthesized polyaniline was finally grinded using agate mortar and product is obtained in the form of fine powder.

#### 2.2.2 synthesis of poly (o-Toluidine)

The Poly(O-Toluidine) was synthesized by chemical oxidative method with inset chemical polymerization of O-Toluidine in presence of Sulfuric acid as dopant and potassium dichromate as an oxidant. The dark green precipitate of Poly(O-Toluidine) resulting from the polymerization reaction was filtered using Whatmann filter paper and washed with distilled water and acetone solution respectively in order to remove the excess acid and impurity. For deprotonation, Poly (O-Toluidine) was suspended in ammonium hydroxide solution and resulting.

Emeraldine base Poly(O-Toluidine) was dried under vacuum at 100 °C for 10 hours. The synthesized Poly(O-Toluidine) was finally grinded using agate mortar and product is obtained in the form of fine powder.

#### 2.2.3 Synthesis of poly(ANILINE-O-TOLUIDINE) copolymer

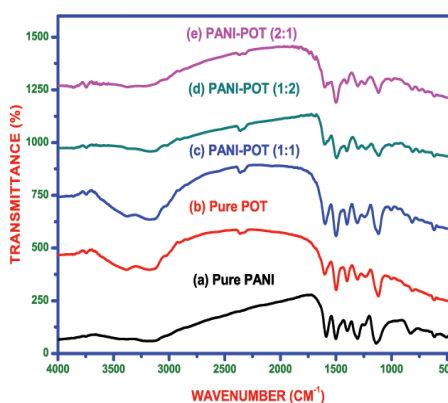
The poly(Aniline-O-Toluidine) copolymer was synthesized by chemical oxidative method with different monomer ratio [1:1, 1:2, 2:1]. The synthesized Copolymer was finally grinded using agate mortar and product is obtained in the form of fine powder.

## 3. Results and discussion

The prepared powdery samples are characterized and investigated for Optical, functional and surface morphological studies.

### 3.1 FTIR ANALYSIS:

The functional group of Polyaniline (PANI), Poly-O-Toluidine (POT) and Co-polymers (PANI-Co-POT) powders were recorded using KBr pellets. Fig 5.1 shows the FTIR spectrum of Polyaniline (PANI), Poly O-Toluidine (POT) and Co-polymers (PANI-Co-POT) in the range of 400-4000  $\text{cm}^{-1}$ . The structural information on all the electrode materials was identified by FTIR spectra. The spectrum of PANI (Fig.3.1. a) acquires the main characteristic peaks at 3414.03, 1587.43, 1501.11, 1306.3, 1246.51, 1138.49 and 827.95  $\text{cm}^{-1}$ . The strong broad peak in range 3414.03  $\text{cm}^{-1}$  corresponds to N-H band stretching vibration [1, 2].



**Fig.3.1. FTIR spectrum of (a) Pure PANI, (b) Pure POT, (c) PANI-POT (1:1), (d) PANI-POT (1:2), (e) PANI-POT (2:1) Co-polymers**

Characteristic vibration	Wavenumber (cm <sup>-1</sup> )				
	PANI	POT	PANI-POT (1:1)	PANI-POT (1:2)	PANI-POT (2:1)
N-H stretching vibration	3414.03	3383.17	3378.83	3171.96	3381.72
C=N stretching	1587.43	1602.38	1597.55	1601.89	1602.38
C=C stretching	1501.11	1498.22	1498.70	1495.81	1498.70
C-N stretching for benzenoid	1306.30	1307.27	1307.75	1299.55	1304.37
C-N and C=N cm <sup>-1</sup> stretching modes	1246.51	1236.38	1242.65	1233.01	1241.20
C-N stretching for quinoid	1138.49	1118.72	1117.76	1115.35	1117.28
C-H stretching	827.95	812.04	815.41	810.11	815.41

Table.3.1. FTIR peaks and their assignments of Pure PANI, POT and Copolymer poly (Aniline-O-Toluidine)

### 3.2. UV ANALYSIS

The electronic properties of the pure PANI, POT and Copolymers (PANI-POT) UV-visible absorption spectroscopy analyses were performed. Fig.5.2 represents the UV-visible spectra of the Pure PANI, Pure POT, and Copolymers (PANI-POT). All the powders are dissolved in DMSO solvent for UV-Visible is spectroscopy analysis.

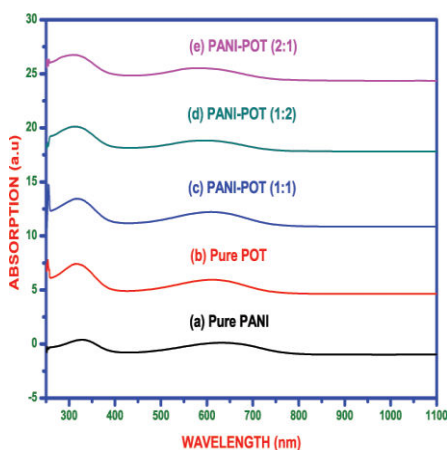


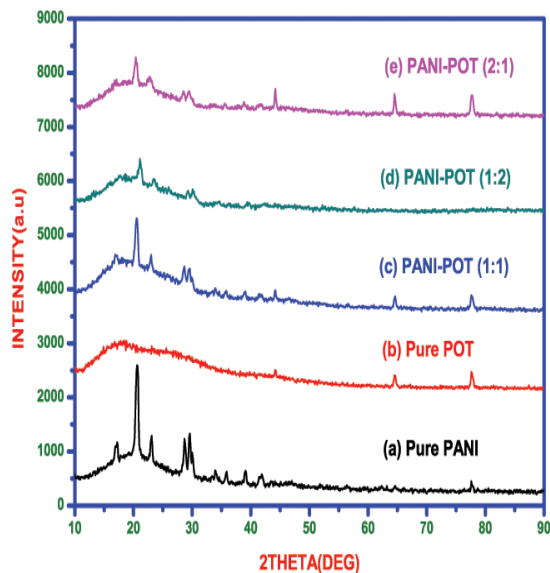
Fig.3.2. UV- Vis spectrum for (a) Pure PANI, (b) Pure POT, (c) PANI - POT (1:1), (d) PANI - POT( 1:2), (e) PANI- POT (2:1) copolymers

S.NO	Sample name	wavelength (nm)	Electron transition	Band gap energy (eV)
1	PANI	328 nm	$\pi - \pi^*$	4.60
		632 nm	n- $\pi^*$	
2	POT	315 nm	$\pi - \pi^*$	4.78
		611 nm	n- $\pi^*$	
3	PANI-POT (1:1)	315 nm	$\pi - \pi^*$	4.78
		610 nm	n- $\pi^*$	
4	PANI-POT (1:2)	312 nm	$\pi - \pi^*$	4.85
		595 nm	n- $\pi^*$	
5	PANI-POT (2:1)	311 nm	$\pi - \pi^*$	4.90
		582 nm	n- $\pi^*$	

Table 3.2 UV peaks and their electron transition and band gap energy of PANI, POT and (PANI – Co- POT) Copolymers

### 3.3 XRD ANALYSIS

X-ray diffraction (XRD) spectra of all the samples recorded by Phillips Expert PW3020 diffractometer using Cu K $\alpha$  radiation ( $\lambda=1.54056$  Armstrong) were presented for structural analysis of the samples.



**Fig.3.3. XRD Spectrum for (a) Pure PANI, (b) Pure POT, (c) PANI - POT (1:1), (d) PANI - POT( 1:2), (e) PANI – POT (2:1) copolymers**

The XRD pattern of PANI (5.3.a) shows a Sharpe peaks at  $2\theta=20.5852^\circ$  ( $d=4.31118$ ), indicates broad amorphous nature. This characteristic peak of PANI is ascribed to the periodicity in parallel and perpendicular directions of the polymer. The XRD pattern of POT (3.3.b) shows a Sharpe peaks at  $2\theta=17.5839^\circ$  ( $d=5.03968$ ) amorphous behavior, The XRD pattern of PANI-POT (1:1), PANI-POT (1:2) and PANI-POT (2:1) copolymers are shown in Fig.3.3 (c-e). The characterization peaks ascertained from the XRD pattern of copolymers are at  $2\theta = 20.4773^\circ$  ( $d=4.33365$ ) PANI-POT (1:1),  $2\theta = 20.8000^\circ$  ( $d=4.26714$ ) PANI-POT (1:2) and  $2\theta = 19.9083^\circ$  ( $d=4.45621$ ) PANI-POT (2:1), broad amorphous diffraction peak due to the presence of benzoid and quinoid rings of copolymer [18, 19]. The crystalline sizes and dislocation density are calculated and tabulated as shown in Table 5.3. As compared to pure PANI, POT, the crystallite sizes in decreased for the copolymer materials.

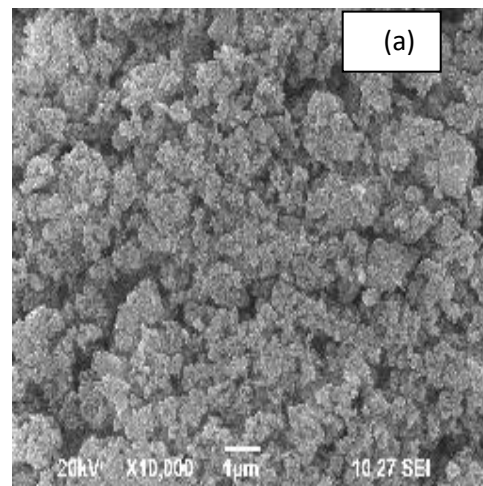
### 3.4 SEM ANALYSIS

The scanning electron microscopy (SEM) images of all the sample pellets were taken by scanning electron microscope. Scanning electron microscopy (SEM) is used here to study the surface morphology of the samples. The particle size and surface morphology were dependent on the type and

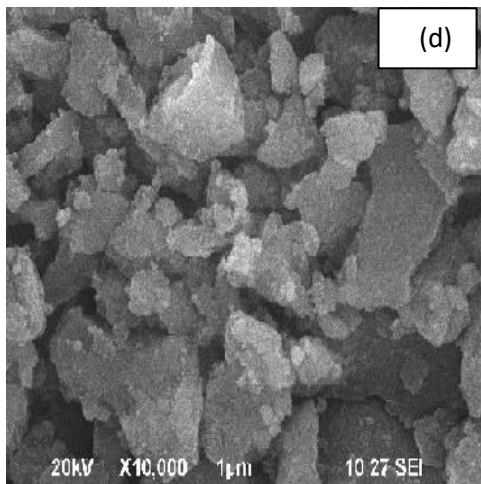
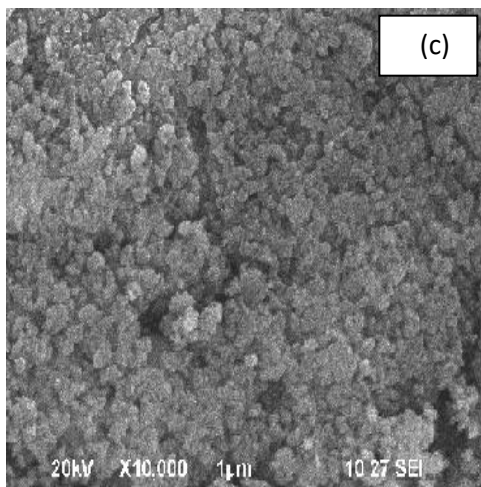
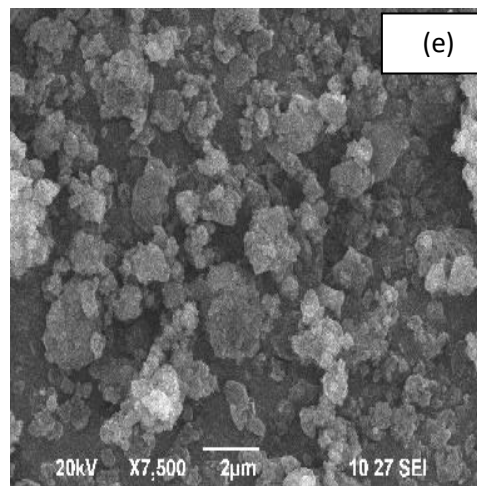
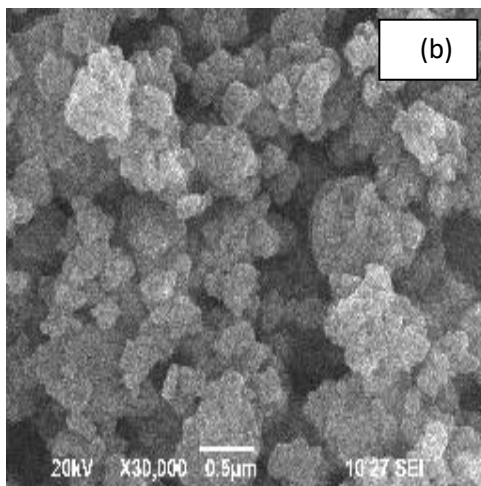
S.No	Sample name	$2\theta$ (deg)	FWHM (deg)	Intensity	d spacing (Å)	Crystal size (nm)	Dislocation density $\times 10^{15}$
1	PANI	20.58	0.62	1277	4.31	13.43	5.54
2	POT	17.58	6.71	217	5.03	1.25	0.06
3	PANI-POT 1:1	20.47	1.12	825	4.33	7.52	0.17
4	PANI-POT 1:2	20.81	2.39	271	4.26	3.53	0.79
5	PANI-POT 2:1	19.91	7.81	243	4.45	1.08	0.08

**Table.3.3. XRD Spectrum for (a) Pure PANI, (b) Pure POT, (c) PANI - POT (1:1), (d) PANI - POT( 1:2), (e) PANI – POT (2:1) copolymers**

concentration of surfactant, because the surfactant was adsorbed physically to the growing polymer [19]. Fig.3.4 shows the surface morphology of pure PANI, POT and copolymers(PANI-POT (1:1, 1:2, 2:1). However Figures 3.4(a)-(e) demonstrates the dependence of the size and homogeneity of the particles only from concentration of surfactant. Adsorption of the surface active agent on the PANI and POT are primarily due to the hydrophobic components in the surfactant, probably via a hydrogen bonding mechanism with the aniline N-H group [20]. The morphology and structure of the PANI nanoparticles were observed using SEM Fig.5.4 (a) shows a porous and irregular structure of low conductive surface of PANI.



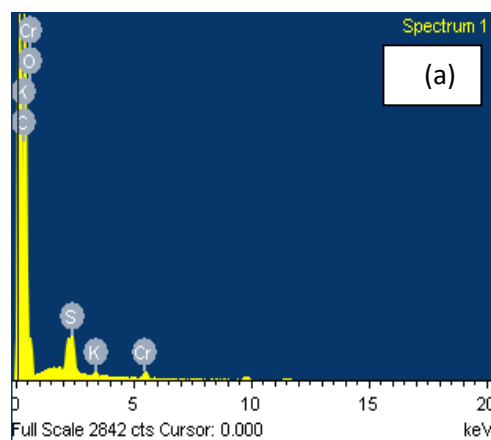


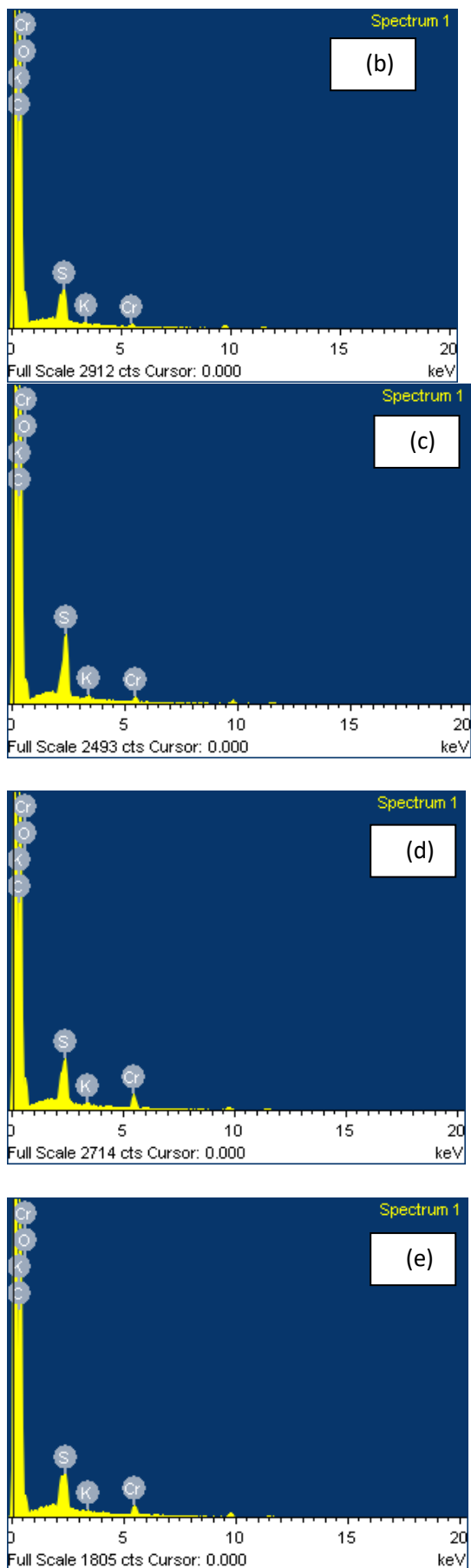


**Fig.3.4. SEM images of (a) Pure PANI, (b) Pure POT, (c) PANI-POT (1:1), (d) PANI-POT (1:2), (e) PANI - POT (2:1) copolymers**

### 3.5. EDX ANALYSIS

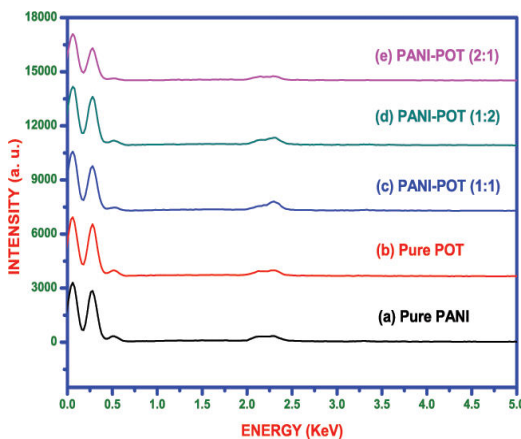
Energy dispersive X-ray spectroscopy (EDX) is an analytical technique to identify the chemical composition of the sample. The EDX of PANI, POT and Copolymers (PANI-POT) at different molar ratios (1:1, 1:2, 2:1) are shown in fig .3.5 (a-e).The characteristic peaks in Fig.3.5 (a-e) show the presence of various elements are C, O, S, K and Cr. The presence of C, O and S are in Fig .3.5. (a-b)confirms the formation of PANI and POT. The incorporation of K and Cr are in Fig.3.5. (c-e) show that the formation of PANI-POT Copolymer from Fig.3.6. The atomic weight percentage of copolymer gradually increased. The EDX spectrum gave the peaks for C, O, S, K and Cr and their weight percentage are tabulated in Table 3.4.





**Fig.3.5.EDX spectrum of (a) pure PANI, (b) pure POT, (c) PANI-POT (1:1), (d) PANI-POT (1:2), (e) PANI-POT (2:1) Copolymers**

The result indicates the existence of C, O, S, K and Cr from PANI-POT.



**Fig.3.6. Elemental composition of pure PANI, POT and Copolymers (PANI-Co-POT) nanoparticles**

Sample name	Weight % of Carbon (C)	Weight % of Oxygen (O)	Weight % of Sulfur (S)	Weight % of Potassium (K)	Weight % of Chromium (Cr)
PANI	83.16	15.19	0.70	0.22	0.73
POT	82.10	16.63	0.92	0.09	0.26
PANI-POT (1:1)	89.25	7.64	2.16	0.23	0.72
PANI-POT(1:2)	84.96	11.72	1.32	0.23	1.78
PANI-POT (2:1)	89.05	8.22	1.11	0.10	1.52

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