



# Synthesis and Characterization of Poly (p-phenylenediamine) in the Presence of Sodium Dodecyl Sulfate

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## Abstract

Conducting polymers are cation salts of highly conjugated polymers and they are synthesized by electrochemical or chemical oxidation method. Chemical oxidative polymerization has formed various functional polymers. In the present work, the chemically oxidative polymerization of p-phenylenediamine and p-phenylenediamine with surfactant like Sodium Dodecyl Sulfate was prepared at room temperature. The synthesized polymers were characterized using spectroscopic techniques like IR, UV and it confirmed the formation of the polymer. The thermal properties with their stability were studied using TGA, DTA and DTG and it was confirmed that the polymers were stable up to 700°C which is also evident from the activation analysis calculation. The X-ray analysis confirms the crystalline nature of the polymer which is also confirmed from the Scanning electron microscopic analysis. The prepared polymers were of semiconducting in nature and has the fluorescence property.

**Keywords:** Conducting polymers, polyphenylenediamine, surfactant, semiconductor, fluorescence.

## Introduction

Surfactants are compounds with molecular structure consisting of a hydrophilic and a hydrophobic part. Surfactants have been used as an additive in the polymerization reactions for it affects the inverse emulsion pathways and it improves the properties of the polymers with respect to conductivity, stability, solubility in organic solvents, and processibility. The surfactant micelles controls the distribution of the reactants between the micellar and aqueous phases, if it is an anionic surfactants, it can act as counter ions and the surfactant becomes a part of the resulting polymeric materials. Jaroslav Stejskal et al have reported that the surfactants have been used as additives in the polymerization of aniline and pyrrole and compared their electrical and thermal properties<sup>1</sup>.

Phenylenediamines belong to aniline derivatives and Poly (o-phenylenediamine) shows different properties when compared to polyaniline<sup>2</sup>. The derivatives of Polyaniline (PANI) are found applications in different fields like removal of heavy metals from the industrial effluents, anticorrosive agents<sup>3</sup>, sensor studies, microelectronic devices, electromagnetic shielding and in optics<sup>4-7</sup>. The synthesized poly-paraphenylenediamine (PpPD) by chemical oxidation method has been formed by dication units in its Pernigraniline base form and radical cations in its Emeraldine salt form<sup>8</sup>.

The p-phenylenediamine can be polymerized easily in mild acidic conditions and in the presence of an oxidant. The anionic surfactant Sodium Dodecyl Sulphate (SDS) can make electrostatic interaction with protonated  $-\text{NH}_3^+$  groups of the polymer during the oxidative polymerization of PPD.

Mahasweta Nandi et al<sup>9</sup> have prepared mesoporous poly p-phenylenediamine with SDS and studied the porosity and the magnetic property of the polymer. Ichinohe et al<sup>10</sup> have prepared poly- o, m, p- Phenylenediamines using hydrogen peroxide as an oxidizing agent in reversed micellar systems consisting of an anionic surfactant sodium di (2-ethylhexyl)sulfosuccinate and studied their magnetic properties.

## Material and Methods

**Materials:** The monomer p-Phenylenediamine, Ferric chloride, Hydrochloric acid, SDS were purchased as an AnalaR grade and used as received.

**Chemical preparation of poly (p-phenylenediamine) with and without SDS:** To the monomer p-phenylenediamine (0.5M), the oxidant  $\text{FeCl}_3$  (0.5M) and the initiator HCl (1M) were added drop wise with constant stirring and it was left for stirring for 6 hours to complete the polymerization. The synthesized polymer was filtered, washed several times with water and purified with methanol. The poly (p-phenylenediamine) was prepared with the surfactant SDS with the standard procedure<sup>1</sup>. The surfactant SDS concentration was maintained at its critical micellar concentration (*cmc*) (8mM)<sup>11</sup>.

**Characterization:** The FT-IR spectroscopy was recorded using ABB-MB-3000 FT-IR spectrometer by pelletizing polymer with KBr. The UV- Vis spectrum of polymers was taken using Perkin Elmer Lambda UV-Vis- Spectrometer by dissolving the polymers in DMSO as a solvent. The thermal properties were studied using Perkin Elmer STA 6000. The morphology of the synthesized polymers was studied using JEOL Model JSM -

6390LV model. The XRD was measured with Bruker AXS D8 Advance. A Perkin Elmer LS-45 spectrofluorophotometer was used in the fluorescence measurements using DMSO solvent. The activation energy was calculated from thermogram using Coats–Redfern and Broido’s relation models<sup>12-16</sup>.

## Results and Discussion

**FT-IR spectroscopy:** The FT-IR spectrum of the product poly (p-phenylenediamine) (PpPDA) and poly (p-phenylenediamine) with the surfactant SDS (PpPDA/SDS) are given in figure 1. The band at 3220  $\text{cm}^{-1}$  is due to the N–H stretching vibrations of the –NH– group. The peaks at 3650 and 2961  $\text{cm}^{-1}$  are belonging to the asymmetric and symmetric stretching vibrations of N–H bond of  $\text{NH}_2$  group. The presence of strong peaks at 1677  $\text{cm}^{-1}$  and 1504  $\text{cm}^{-1}$  are connected with the C=C and C=N stretching vibrations of phenazine ring. The peaks at 1407  $\text{cm}^{-1}$  and 1261  $\text{cm}^{-1}$  are ascribed with C–N–C stretching vibrations of benzenoid and quinoid imine units. The bands at 805  $\text{cm}^{-1}$  and 581  $\text{cm}^{-1}$  are the characteristic of C–H out-of-

plane bending vibrations of benzene nuclei in the phenazine skeletons<sup>17</sup>. The PpPDA prepared with SDS have all the peaks of polymer but the values are slightly shifted towards longer wave number. The comparative values of the polymers with and without the SDS are given in table 1.

**UV-Vis spectroscopy:** The UV-Vis spectrum of PpPDA and PpPDA/SDS are shown in figure 2. The PpPDA has two major peaks, one at 309 and the other at 452 nm. The band at 452 nm is due to  $\pi$ – $\pi^*$  transition associated with the phenazine ring which is conjugated to the two lone pairs of electrons on nitrogen atom of the  $\text{NH}_2$  groups and the peak at 309 nm is assigned to the  $\pi$ – $\pi^*$  transitions of the benzenoid and quinoid structures of the polymer<sup>18</sup>. The polymer PpPDA/SDS also has two bands which are slightly higher than that of polymer prepared in the absence of SDS. The peaks at 312nm and 455nm are attributed to  $\pi$ – $\pi^*$  transitions of the benzenoid and quinoid structures and  $\pi$ – $\pi^*$  transition associated with the phenazine ring respectively.

Table-1  
Comparison of FT-IR Spectral data of PpPDA and PpPDA/SDS

Polymer	$\nu(\text{S=O})$ ( $\text{cm}^{-1}$ )	$\nu(\text{N-H})$ ( $\text{cm}^{-1}$ )	$\nu(\text{NH}_2)$ ( $\text{cm}^{-1}$ )		Phenazine ( $\text{cm}^{-1}$ )		$\nu(\text{C-N-C})$ ( $\text{cm}^{-1}$ )		Aromatic $\nu(\text{C-H})$ ( $\text{cm}^{-1}$ )
			asym	Sym	$\nu(\text{C=C})$	$\nu(\text{C=N})$	Benzenoid	Quinoid	
PpPDA	-	3220	3650	2961	1677	1504	1407	1261	805,581
PpPDA/ SDS	1153	3237	3650	2967	1644	1565	1417	1266	808,595

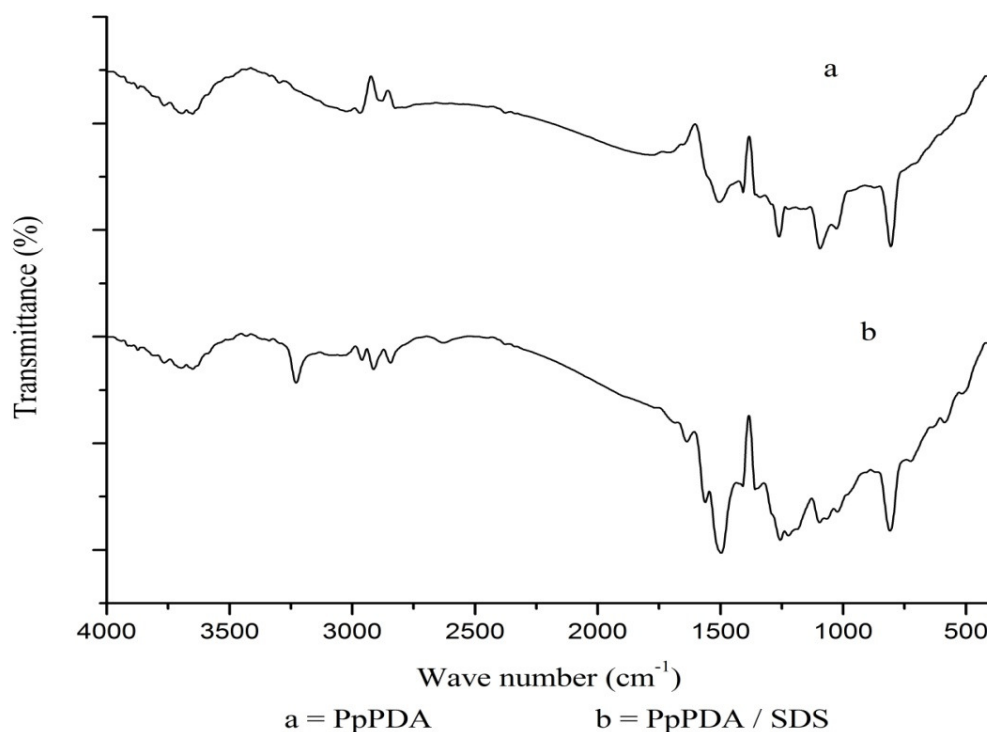


Figure-1  
FT-IR spectrum of PpPDA and PpPDA/SDS

**Thermal analysis:** The thermal degradation of PpPDA, PpPDA/SDS was studied using thermogravimetric techniques. The thermogram was recorded in the temperature ranges of 25–700°C with the heating rate of 10 degree per minute. The data from the thermogravimetric analysis clearly indicates that the decomposition of the polymer proceeds in three steps and the corresponding spectrum is shown in figure 3 and 4. In the TGA and DTG thermogram, the first weight loss around 120-240 is due to the loss of water molecules and dopant, the second decomposition in the temperature range 240-340 is due to the loss of oligomers and the third weight loss occurred from 300 – 450 is due to the degradation of polymer.

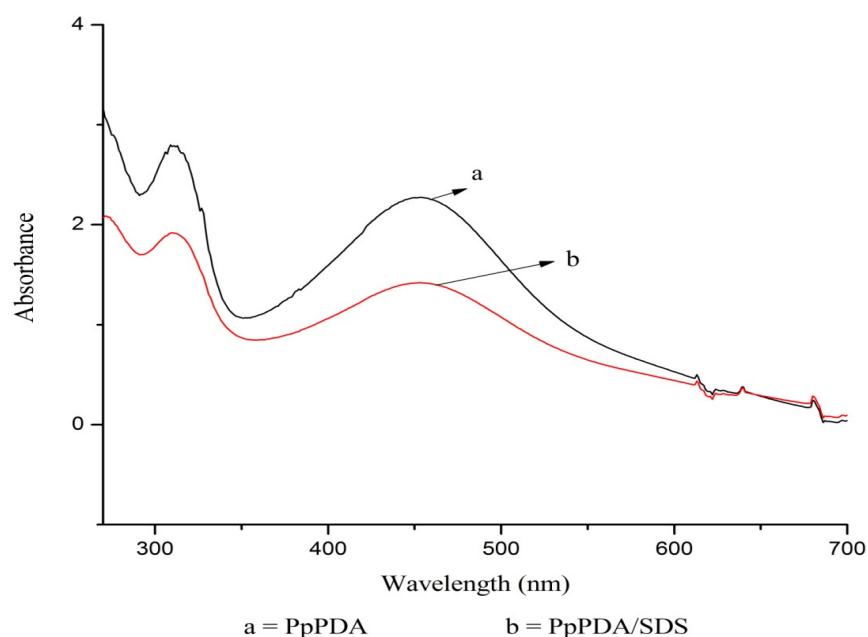
The activation energy for each decomposition step was calculated from TGA curve by broido and coats redfern methods and the results are given in table 2. For the polymers prepared with and without SDS, the second decomposition showed the least Ea of 12.625 KJ/mol and 17.848 KJ/mol by broido method and 05.139 KJ/mol, 8.219 KJ/mol by coats

redfern method. This value confirms that the polymers were thermally stable up to second stage. For the polymer PpPDA/SDS, the activation energy calculated was found to be high for the first decomposition step 150-235°C which is 33.250 KJ/mol calculated by broido method and 23.323 KJ/mol calculated by coats redfern method. The activation energy for third step calculated from the temperature 300–410°C was found to be 20.606 KJ/mol and 10.506 KJ/mol calculated by broido and coats redfern method for polymer with SDS. The linear plots with concurrency values ( $R^2$ ) are closer to one and this show that there is good correlation.

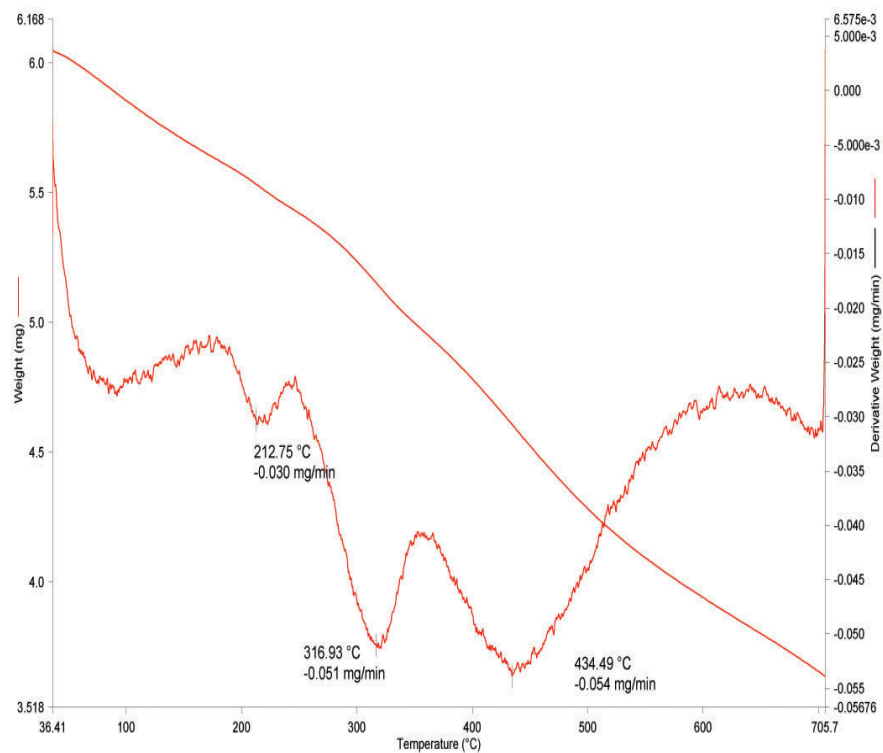
**X-ray diffraction:** The XRD spectrum of PpPDA and PpPDA/SDS shows a series of sharp lines in the regions of  $5^\circ < 2\theta < 42^\circ$  and  $5^\circ < 2\theta < 40^\circ$ , which depicts that the synthesized polymer samples has high crystallinity and long range ordering<sup>19</sup>. From the spectrum it is evident that there is no broadening of peaks due to amorphous components as shown in figure 5 and found to be crystalline in nature.

**Table-2**  
**Thermal and kinetic data of PpPDA and PpPDA/SDS by Broido and Coats Redfern method**

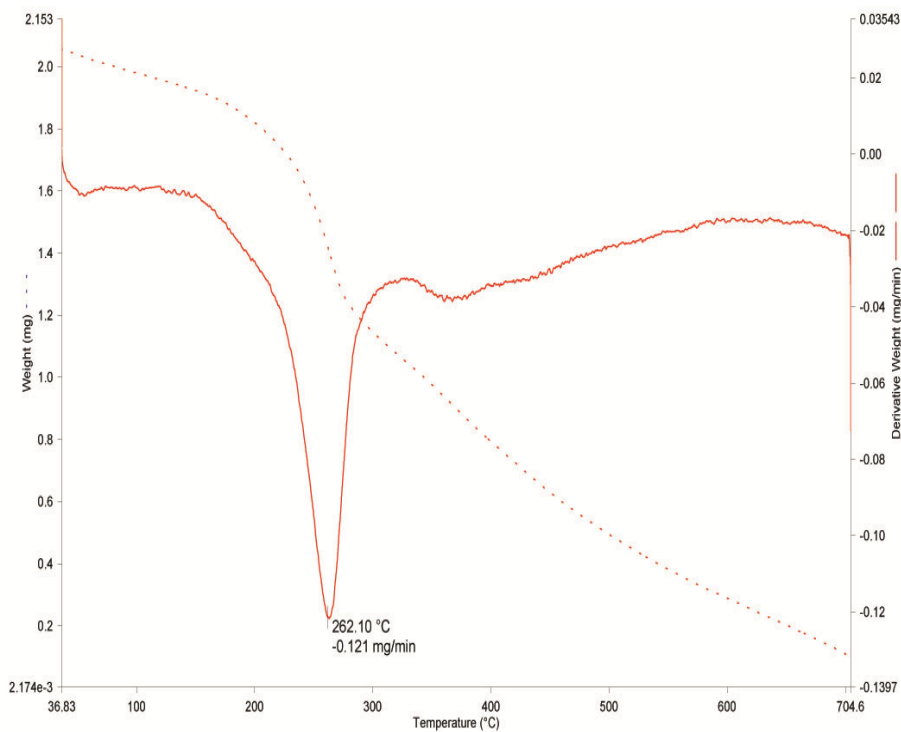
Polymer	Decomposition Range (°C)	Broido		Coats redfern	
		Ea (KJ/mol)	$R^2$	Ea (KJ/mol)	$R^2$
PpPDA	150-220	18.201	0.99	11.840	0.97
	240-340	12.625	0.95	05.139	0.80
	360-450	18.214	0.98	12.998	0.94
PpPDA/SDS	150-235	33.250	0.98	23.323	0.96
	240-280	17.848	0.99	08.219	0.95
	300-410	20.606	0.99	10.506	0.97



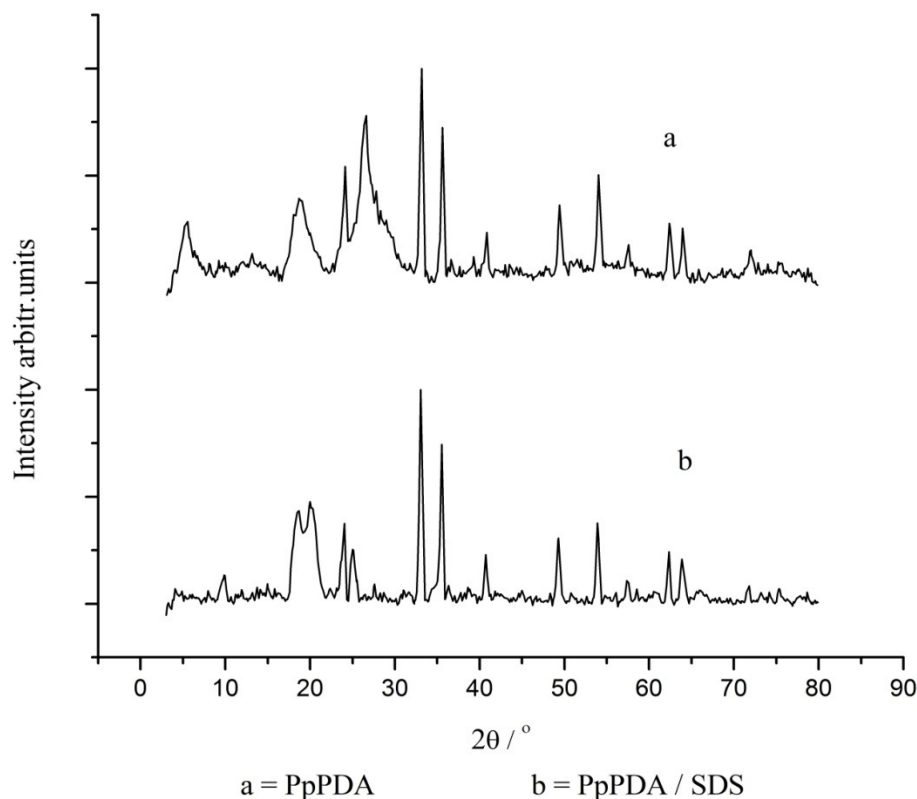
**Figure-2**  
**UV-Vis spectrum of PpPDA and PpPDA/SDS**



**Figure-3**  
**TGA/DTG thermogram of PpPDA**

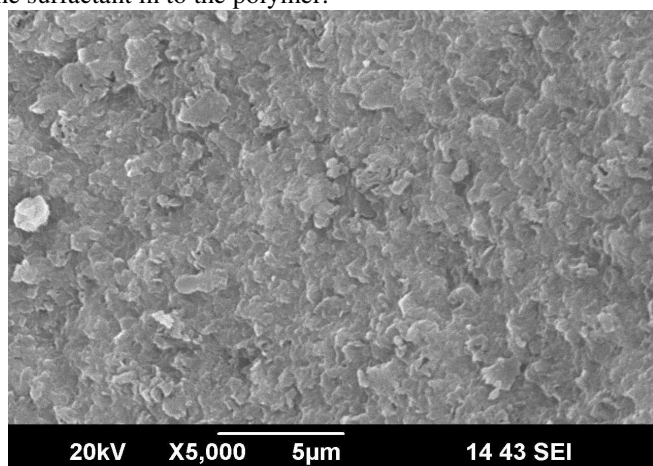


**Figure-4**  
**TGA/DTG thermogram of PpPDA/SDS**

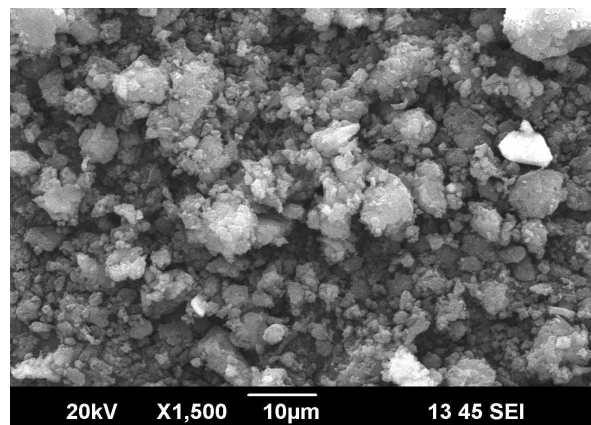


**Figure-5**  
**XRD pattern for PpPDA and PpPDA/SDS**

**Scanning Electron Microscopy:** The Scanning Electron Microscopy (SEM) analysis was carried out to study the morphology of the polymer and polymer prepared with SDS and morphology are shown in figures 6 and 7. The morphology of PpPDA shows smooth surface with flakes ordering morphology but for PpPDA/SDS, the morphology was found to be globular like arrangement. The SEM image of PpPDA/SDS result shows that the polymers are well ordered due to the incorporation of the surfactant in to the polymer.



**Figure-6**  
**SEM Image of PpPDA**



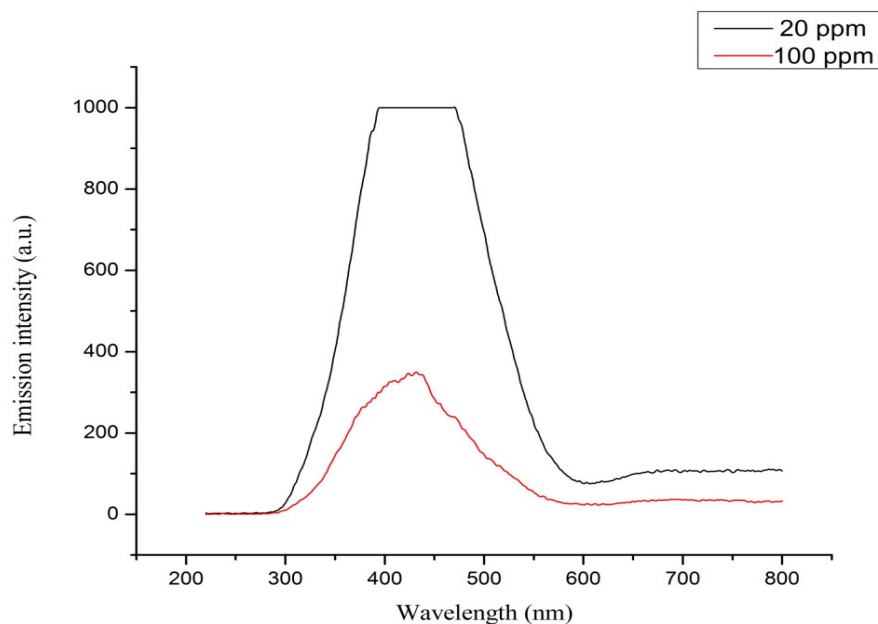
**Figure-7**  
**SEM Image of PpPDA/SDS**

**Conductivity:** The conductivity of the poly (o-phenylene diamine) prepared with and without surfactant was studied by four probe conductivity measurements at room temperature. The synthesized polymers were of semiconducting in nature and fall in the range of  $10^{-8}$  s/cm. The same result is expected in PpPDA with and without surfactant<sup>20</sup>.

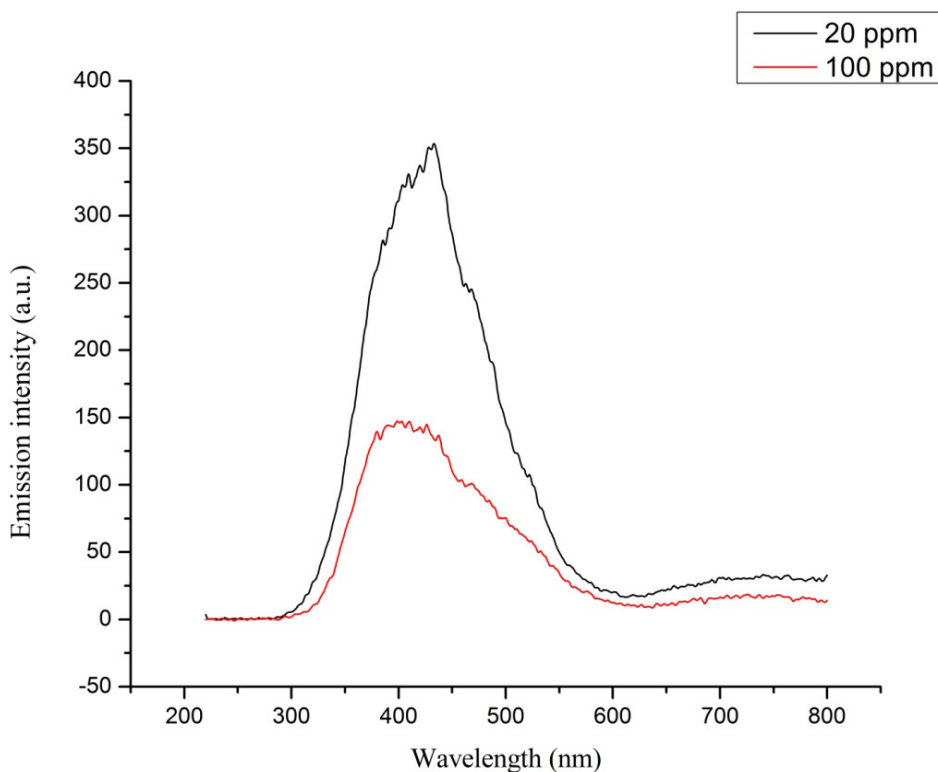
**Fluorescence measurement:** The fluorescence measurement showed that the synthesized polymers PpPDA and PpPDA/SDS were having emission spectra. The fluorescence spectrum of

PpPDA at 100 ppm exhibited the emission intensity of 250 and found to increase to 1000 with the decrease of concentration to 20 ppm and the results are shown in figure 8. The fluorescence spectrum of PpPDA/SDS shows emission intensity of 150 at

100 ppm, when the concentration is decreased to 20 ppm the emission intensity was increased up to 350 shown in the figure 9. The result also shows that the presence of surfactant decreases the emission intensity in fluorescence spectra.



**Figure-8**  
**Emission spectra of PpPDA**



**Figure-9**  
**Emission spectra of PpPDA/SDS**



## Conclusion

The PpPDA and PpPDA/SDS was prepared and the polymers were characterized using FT-IR, UV-Vis spectroscopy. The thermal properties of the polymer were studied using thermo gravimetric analysis and their activation energy was calculated using Broido and Coats Redfern method. The activation energy was found to be low in the temperature range 240-340°C. The kinetic data reveals that an enhanced thermal stability of polymers is associated with the activation energy which is responsible for the increase in degradation process. The X-ray diffraction shows that the polymers were highly crystalline in nature. The morphology of the polymer without the SDS shows flakes like structure. The PpPDA/SDS shows globular like structure. The conductivity of the polymer was recorded and the result shows that the polymers are semiconducting in nature and it shows very good fluorescence property which can be applied in different field.

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