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Effect of Surfactant on the Chemical Polymerization of o-Phenylenediamine- A Comparative Study

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ABSTRACT

The poly (o-phenylenediamine) was chemically synthesized using ferric chloride as an oxidant and hydrochloric acid as an initiator. Different concentration of the anionic surfactant like Sodium Dodecyl Sulphate was used to study their effects on the polymers. The synthesized polymers were characterized using FT-IR, UV-Vis spectroscopy and their thermal properties were study using TGA, DTG and DTA. The SEM and XRD studies show that the prepared polymers were crystalline in nature. The conductivity study was carried using four probe method in room temperature and was found to be semiconducting in nature.

Keywords: *Polyphenylenediamine, SDS, Thermal Properties, Conductivity.*

1. INTRODUCTION

Polyaniline (PANI) is one of the most important classes of conjugated polymers that possess excellent electronic, optical, and redox properties and good environmental stability, low cost, and high conductivity upon doping with acids. PANI, as a conducting polymer has showed many practical applications like battery electrodes, electrochromic devices, photoelectric cell, light-emitting diodes, biosensors and anticorrosive coatings, etc [1,2]. Various methods are available for the synthesis of PANI. However, the most widely used techniques are electrochemical and chemical oxidative polymerization methods. The chemical method is important to produce PANI on large scale. Several oxidizing agents have been used in the polymerization of the aniline [3]. It is sometimes limited in practical applications because of its intractable nature, such as its insolubility, high brittleness [4], the strong dependence of its conductivity and electrochemical activity on medium pH, acid-catalyzed oxidative degradation, and so on [5].

Polyaniline and its derivatives attract considerable attention in recent years due to their applications in different fields [6]. Phenylenediamines are a class of aniline derivatives having an extra -NH_2 group in the o-, m-, or p-positions. Poly(o-phenylenediamine) (PoPDA) has apparently shown different characteristics of molecular structure and properties when compared to PANI [7]. Poly(o-phenylenediamine), a highly aromatic polymer containing 2,3-diaminophenazine or quinoraline repeating unit, involving variable conductivity, strong electroactivity, good optical and magnetic activity and high environmental and thermal stability [8,9,10].

Polymer-surfactant mixtures are widely used for controlling the colloid stability and rheological properties of complex disperse systems in many practical applications, such as the paper, food, pharmaceutical industries, home and personal care products. Due to their wide-spread usage and complex physicochemical properties, these systems have attracted the attention of researchers and they are subject of numerous studies, aimed at revealing the role of the surfactant-polymer interactions, both in the bulk and on the solution surface, for the overall system behavior. [11] The surfactants have special properties like lowering of the surface tension of solutions and association tendency. At a concentration above a critical value named Critical Micelle Concentration (CMC), surfactants molecules tend to aggregate forming micelles. At CMC, some properties of surfactants solutions like conductivity, surface tension, and osmotic pressure suffer abrupt changes due to the micelle formation [12].

Surfactants have been used as an additive in the polymerization of aniline and pyrrole and their electrical and thermal properties have been compared [13]. Mahasweta Nandi et. al., have prepared mesoporous poly(p-phenylenediamine) with anionic surfactant Sodium Dodecyl Sulphate (SDS) as an template and their porosity and magnetic property was studied [14]. D. Ichinohe et al prepared o, m, p-phenylenediamines using hydrogen peroxide as an oxidizing agent in reversed micellar systems consisting of an anionic

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surfactant sodium di (2-ethylhexyl)sulfosuccinate and their magnetic property has been studied [15].

2. EXPERIMENTAL

2.1. Materials

o-Phenylenediamine, Ferric chloride, Hydrochloric acid, SDS were purchased as an analytical grade and used as received without further treatment.

2.2. Chemical Preparation of Poly(o-phenylene diamine)

To the monomer o-phenylenediamine (0.5M), the oxidant $FeCl_3$ (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 polymer formed was collected by filtration and washed several times with water and dried.

2.2. Chemical Preparation of Poly(o-phenylene diamine) with Surfactant

The polymers were synthesized using surfactant Sodium Dodecyl Sulphate. The surfactant concentrations were varied above and below its critical micelle concentration. The CMC value of SDS was found to be 8mM and the concentrations used in the present study are 5mM which is below CMC, 8mM which is assigned to be equal to CMC, and 50mM which is greater than CMC. The monomer, o-phenylenediamine and SDS were added and stirred with the addition of the oxidant and the initiator drop wise. After complete addition, the reactions were carried out for 6 hours. The polymer formed was collected by filtration and washed several times with water and dried [13].

2.3. 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 Lamba UV-Vis- Spectrometer by dissolving in DMSO as a solvent. The thermal properties were studied using **P**erkin 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 with Cu Kα (λ = 0.154 nm) radiation. Conductivity of the polymer was calculated by four probe method at room temperature. The kinetic parameters of thermal degradation process have been calculated using Coats–Redfern and Broido's relation [16, 17, 18, 19] models.

3. RESULTS AND DISCUSSION

3.1. FT-IR Spectroscopy

The FT-IR spectrum of the product PoPDA and PoPDA with SDS at different concentrations is given in Figure 1. The single band at around 3303 cm^{-1} is due to the N-H stretching vibrations of the -NH- group. The two peaks at 3431, 3169 cm^{-1} are ascribed to the asymmetrical and symmetrical of N–H stretching vibrations of NH_2 group respectively. Two strong peaks at 1642 cm^{-1} and 1499 cm^{-1} are associated with the stretching vibrations of C=C and C=N group in phenazine ring. The peaks at 1355 cm^{-1} and 1221 cm^{-1} are associated with C-N-C stretching in the benzenoid and quinoid imine units. Furthermore, the bands at 759 cm^{-1} and 581 cm^{-1}, which are the characteristic of C-H out-of-plane bending vibrations of benzene nuclei in the phenazine skeleton, are also observed. The polymers prepared with SDS have all corresponding peaks of polymers but the values are shifted towards longer wave number. The comparative IR spectral values are presented in Table 1.

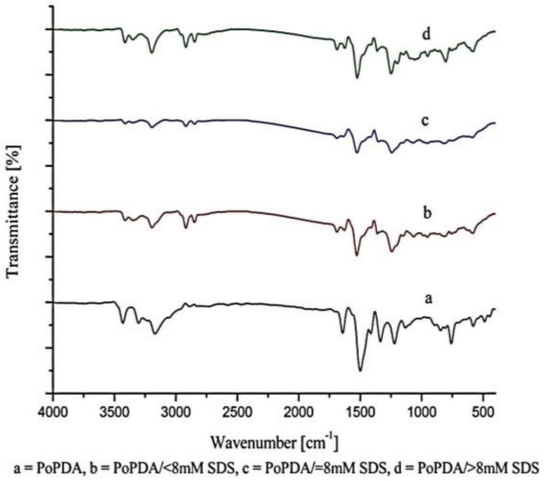

Figure 1: FT-IR spectrum of PoPDA and PoPDA with different concentration of SDS

3.2. UV-Vis Spectroscopy

The UV-Vis spectrum of PoPDA and PoPDA with SDS in different concentrations is shown in Figure 2. From the spectra it was observed two major peaks at 258 and 437 and the band near 437 nm is assigned to π–π* transition associated with the phenazine ring conjugated to the two lone pairs of nitrogen of the NH_2 groups. The other peak at about 258 nm is mainly due to π–π* transitions of the benzenoid and quinoid structures. The polymers with SDS shows two bands corresponding to π–π* transition of phenazine ring and π–π* transition benzenoid and quinoid structures and the values are shifted towards longer wave length to some extent.

3.3. Thermal Analysis

The thermal degradation of polymers PoPDA, PoPDA with different concentrations of SDS, above and below CMC values was studied using thermogravimetric techniques in the heating range of 10 degree/minute. The data from the thermogravimetric analysis clearly indicated that the decomposition of the complexes proceeds in

Table 1: FT-IR spectral data of PoPDA and PoPDA with SDS at different concentrations

Polymer	S=O	N-H	NH_2		Phenazine		C-N-C		Polymer
Polymer	S=O	N-H	NH_2	Phenazine	C-N-C	Polymer	S=O	N-H	NH_2
PoPDA	-	3303	3431	3169	1642	1499	1355	1221	759,581
PoPDA/ <8mM SDS	1150	3351	3412	3194	1688	1527	1360	1242	757,582
PoPDA/ =8mM SDS	1153	3350	3411	3201	1693	1525	1345	1244	763,595
PoPDA/ >8mM SDS	1147	3351	3413	3195	1688	1524	1361	1249	755,581

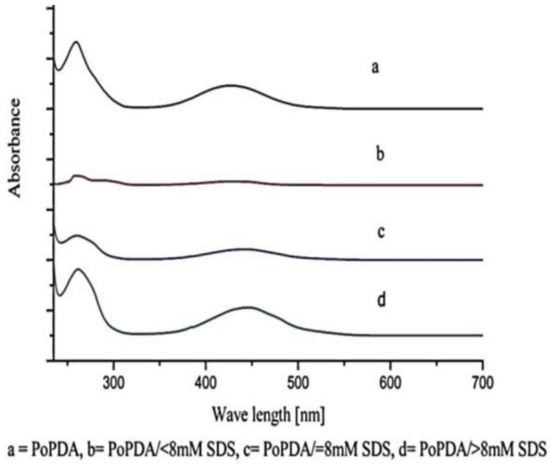

Figure 2: UV-Vis spectrum of PoPDA and PoPDA with different concentration of SDS

three steps and the corresponding spectra are shown in Figure 3, 4, 5, 6. First step decomposition is due to the loss of water molecules and dopant, the second step decomposition is mainly due to the loss of oligomers and the third step decomposition is due to the degradation of polymers.

The activation energy (Ea) for each step was calculated by Broido and Coats-Redfern methods by measuring the temperature and percentage of weight lose in each step. The linear plot with concurrency value (R^2) closer to one was obtain. The thermal decomposition with different stages and the calculated activation energies with R^2 values are listed in Table 2. For the PoPDA, the first step is absent due to the absence of water molecule in the polymer. The activation energy calculated for the entire range of temperature and found to be lowest in the temperature range of 450-625°C which has the Ea value of 20.104 KJ/mol by Broido method and 7.823 KJ/mol by Coats Redfern method. This clearly indicates that the polymer prepared without SDS is thermally stable up to 625°C.

The polymers prepared using SDS is found to start to decompose 440 °C which is lower than the polymer prepared without SDS. This may be attributed due to the less thermally stability of polymers prepared with SDS and the reason may be that the surfactant SDS molecule would have incorporated into the polymeric backbone. For the polymers PoPDA/<8mM SDS, PoPDA/=8mM SDS, PoPDA/>8mM SDS the activation energies calculated by Broido method was found to be 32.033-35.039 KJ/mol for first step (148-235 °C) and 24.448- 27.483 KJ/mol calculated by Coats Redfern method for the same temperature. The Ea values for the second decomposition temperature of 240-295°C calculated by the Broido method was found to have 47.550- 52.784 KJ/mol and 39.305-44.769 KJ/mol calculated by Coats Redfern method which conforms that the polymers are thermally stable up to the second stage. The activation energy for third step 300-440 °C is low 13.525-16.261 KJ/mol calculated by Broido and 03.900-0.6998 KJ/mol by Coats Redfern method indicates that the third step is fastest step for the decomposition of the polymers prepared with and without SDS. The Ea was found to decrease to a small extent for the polymers prepared using SDS. Among the three concentrations of the SDS studied, the polymer prepared at CMC (8mM) was found to have high activation energy when compare to other two concentrations and the Ea values are much closer to polymer synthesized without SDS.

3.4. X-ray diffraction (XRD)

The XRD spectrum of PoPDA and PoPDA/SDS(=8mM) exhibits a series of sharp lines in the region of 5°<2θ>42° and 5°<2θ>30°, which indicates the samples has high crystallinity and long range ordering. From the spectrum it is evident that there is no broad reflection due to amorphous components as shown in Figure 7.

3.5. Scanning Electron Microscopy (SEM)

The SEM analysis was carried out to study the morphology of the polymer with different concentrations of the surfactant like PoPDA/<8 mM SDS (Figure 8), PoPDA/=8 mM SDS (Figure 9) and PoPDA/>8 mM SDS (Figure 10). The SEM images shows that the polymers are flakes in shape and they are arranged in well ordered manner when the polymer are prepare with the SDS at CMC value and this shows that the effect of CMC on the polymers are much pronounced in morphology of the polymer.

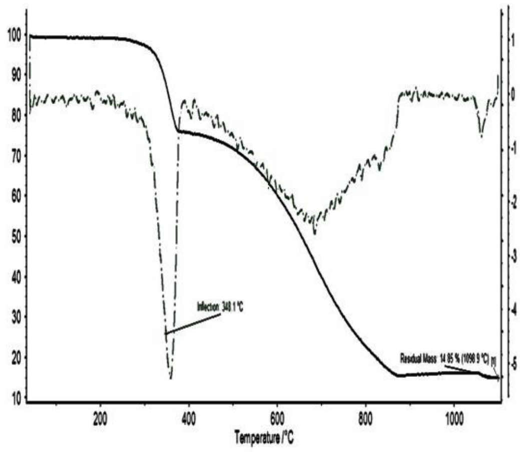

Figure 3: TGA/DTG thermogram of PoPDA.

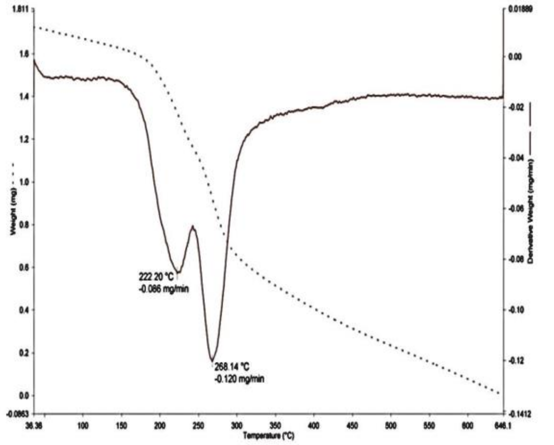

Figure 4: TGA/DTG thermogram of PoPDA with 5mM SDS.

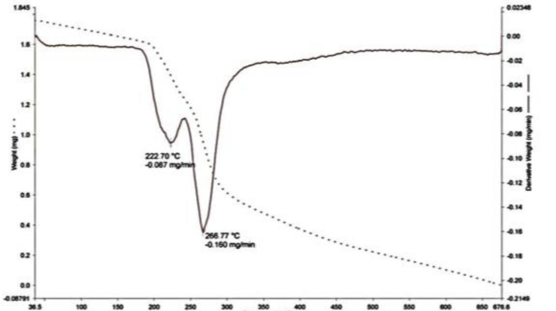

Figure 5: TGA/DTG thermogram of PoPDA with 8mM SDS.

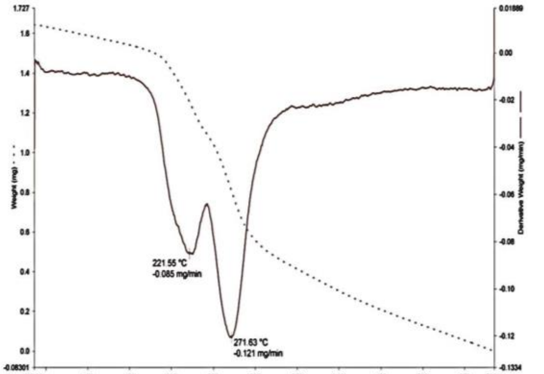

Figure 6: TGA/DTG thermogram of PoPDA with 50mM SDS.

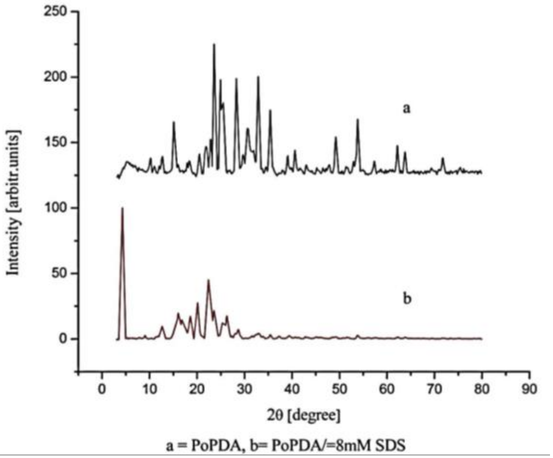

Figure 7: XRD pattern for PoPDA and PoPDA with SDS at its CMC.

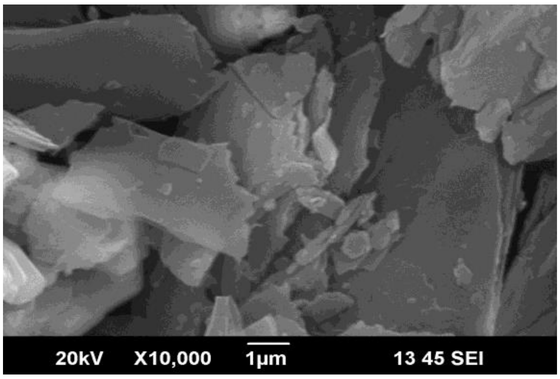

Figure 8: SEM image of PoPDA with 5mM SDS.

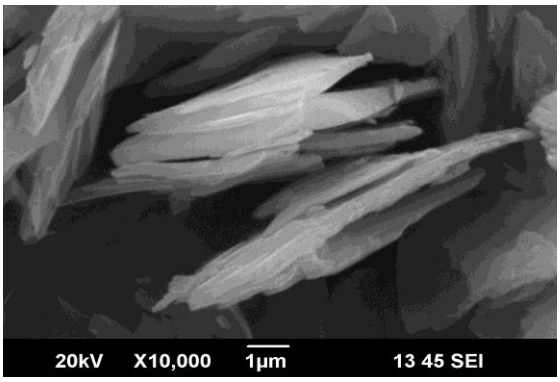

Figure 9: SEM image of PoPDA with 8mM SDS.

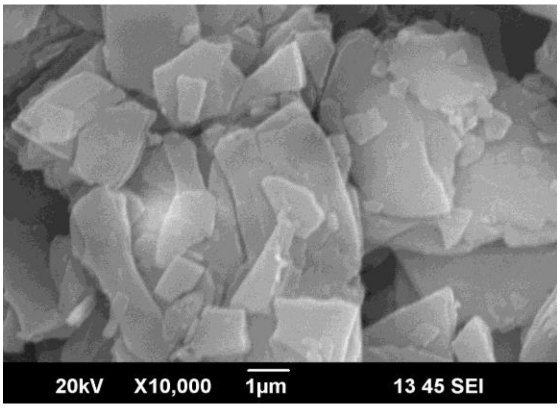

Figure 10: SEM image of PoPDA with 50mM SDS.

Table 2: Thermal and kinetic data of PoPDA and PoPDA with SDS by Broido and Coats Redfern method

Polymer	Decomposition range (°C)	Broido		Coats redfern	
		Ea (KJ/mol)	R^2	Ea (KJ/mol)	R^2
PoPDA	270-370	66.879	0.98	57.575	0.97
	450-625	20.104	0.97	07.823	0.84
PoPDA/<8mM SDS	148-230	32.033	0.99	24.448	0.98
	240-295	47.550	0.97	39.305	0.96
	315-415	15.782	0.99	06.471	0.94
PoPDA/=8mM SDS	150-235	35.039	0.99	27.483	0.99
	240-280	52.784	0.96	44.769	0.94
	300-410	16.261	0.99	6.998	0.98
PoPDA/>8mM SDS	150-230	32.569	0.98	25.000	0.97
	240-285	51.216	0.99	43.038	0.98
	320-440	13.525	0.99	03.900	0.83

4. CONCLUSIONS

The Poly o-phenylenediamine and the polymer with SDS were prepared by varying the concentration of surfactant concentration. The resultant polymers were characterized using FT-IR, UV-Vis spectroscopy. The thermal stability of the polymers was analyzed using Thermo gravimetric analysis. The kinetic parameter like activation energy was calculated for each degradation step and found the stability of synthesized polymer. The polymers prepared without the surfactant are stable up to 625°C and the polymers prepared with the surfactant are stable up to 440 °C. The less stability of the polymers prepared in the presence of surfactant may be due to the lower thermal stability of SDS.

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