



## Effect of oxidant concentration on the co-polymerization of m-aminobenzene sulfonic acid and aniline co-polymer: synthesis and characterization

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### ABSTRACT

The effect of the concentrations of the oxidizing agent (sodium persulphate) on the properties of poly (m-aminobenzene sulfonic acid -co- aniline) p(m-ABSA-co-Ani) co-polymer has been investigated. The prepared samples were confirmed by Fourier transformation infrared spectroscopy and further characterized by electron paramagnetic resonance (EPR), UV-Vis spectroscopic techniques and tested for temperature dependent stability by thermogravimetric analyses. The room-temperature conductivity measurements have been performed on all the p(m-ABSA-co-Ani) co-polymers samples and found a maximum value of conductivity of  $\sim 6.5 \times 10^{-2}$  S/cm at 168 mM concentration of oxidizing agent. The EPR studies have been shown that the variation of line width of EPR signals with oxidizing agent concentration and found a close relation with electrical conductivity. The prepared co-polymer samples are thermally stable up to 600 °C detected by TGA analysis. The synthesized co-polymer materials show around 75% solubility in chloroform, ~65 % in Dimethyl sulfoxide, ~58 % in N-methyl-2-pyrrolidinone and weakly soluble in aqueous medium.

*Keywords:* Chemical synthesis, Electron Paramagnetic Resonance, Thermogravimetric Analysis

### INTRODUCTION

During last decade, organic materials, conducting polymers were extensively investigated due to their wide range of potential applications in the fields of electromagnetic shielding, gas- and ion-sensors, and battery electrodes.<sup>1,2</sup> Among the most studied conducting polymers, polyaniline (Pani) stand out due to its tunable electrical conductivity from insulator to metal-like along with its good environmental stability. It can be doped to conducting form without changing the number of  $\pi$ -electrons through protonation by exposure to an appropriate protonic acid in aqueous solution.<sup>3-6</sup> But the main hindrance in the application of these materials is their solubility because these conducting materials have poor solubility in common organic solvents. Beside this water soluble materials are more versatile as compared to soluble in organic solvent in

regards to application.<sup>7,8</sup> Researchers are paying attention in this direction and various research groups all over the world have done some extensive work on this.<sup>9-13</sup> The most successful approach to enhance the solubility of conductive Pani in organic/aqueous solvent solutions is to attach the sulfonic ( $-\text{SO}_3\text{H}$ ) acid groups to polymer chains. This can be achieved by treating the polymer with the appropriate reagents after polymerization or by polymerizing the substituted aniline derivatives. The sulfonation of the emeraldine base with fuming sulfuric acid, to produce a polymer, soluble in aqueous alkaline solutions is the best example of the former approach.<sup>11-13</sup> Introducing a  $-\text{SO}_3\text{H}$  group on the Pani chain, affects the properties of parent polyaniline without substantially sacrificing its conductivity and is of specific interest for several reasons. The electrical, optical and thermal properties of the sulfonated Pani are incredibly altered due to electronic effects of the  $-\text{SO}_3\text{H}$  groups. This  $-\text{SO}_3\text{H}$  groups on the phenyl rings provides the good environmental stability to the parent Pani due to its strong electron withdrawing properties. Along with these improved properties, the solubility of Pani is greatly enhanced due to the presence of the  $-\text{SO}_3\text{H}$  groups.<sup>11</sup> The incorporation of the side groups to Pani chains has enhanced its solubility and processability and change its properties. Although, alkyl- and alkoxy-ring-substituted Pani after acid doping have a moderate conductivity of  $10^{-1}$ - $10^{-3}$  S/cm,<sup>14</sup> however, the poor processability of Pani, which is also true of other conducting polymers as well have limited its applications.

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A large number of reports are available on the synthesis of pure Pani but there is a dearth of data on the co-polymerization of aniline with its derivatives. Furthermore, the sulfonation of Pani co-polymers still a challenging task leading to its enhance solubility in different mediums.<sup>15-17</sup> In this present study, we have made an attempt to use both the approaches of sulfonation at the same time during the reaction by co-polymerizing the aniline with its derivative m-aminobenzene sulfonic acid in a highly sulfonated solution to explore the possibility of their easy processability.

## EXPERIMENTAL DETAILS

### 2.1. Synthesis of poly (m-aminobenzene sulfonic acid -co-aniline)

The co-polymer of aniline and its derivative, m-aminobenzene sulfonic acid, {poly (m-aminobenzene sulfonic acid -co- aniline)} or p(m-ABSA-co-Ani) has been synthesized by simple chemical oxidation method at different concentrations of oxidizing agent, sodium persulfate. A 97 mM solution of m-aminobenzene sulfonic acid was prepared in 75 ml distilled water and then 8 mM solution of aniline hydrochloride and 18 mM solution of radical initiator ferrous sulfate was added to it. The prepared mixed solution was further, stirrer for a homogeneous solution. A 67 mM solution of oxidizing agent, sodium persulfate was added to the above prepared solution of monomers. After few seconds the polymerization start and solution turns into dark green and the reaction was left for further polymerization for 6 hours at room temperature. The resultant co-polymer precipitates were filtered, washed with ethanol and distilled water several times and dried at room temperature for 24 hours. The sample was labeled as P1.6. Similar, route has been adopted for the synthesis of other samples at 84, 126, 168, 210 and 252 mM concentrations of oxidizing agent and designated as sample P2, P3, P4, P5 and P6, respectively. The persulfate group present in the oxidizing agent make the solution highly sulfonated which lead to dope the Pani chains with -SO<sub>3</sub>H groups.

### 2.2. Samples Characterizations

For the confirmation of the synthesis of p(m-ABSA-co-Ani) co-polymer Fourier transform infrared spectroscopy measurements were performed on all the prepared samples at FT-IR Spectrometer, Spectrum BX (Perkin-Elmer). The KBr pallet method has been employed for these measurements. The optical properties of the prepared samples were tested under UV-Vis spectrophotometer, CARY-100 (Varian). The band gap energy was calculated from the following equation:

$$\Delta E = hc/\lambda_{\max}$$

Where,  $h = 6.6 \times 10^{-34}$  J-s,  $c = 3 \times 10^8$  m/s

Here,  $\Delta E$  is the band gap energy,  $h$  is the plank's constant,  $c$  is the velocity of light, and  $\lambda_{\max}$  is the wave length of the absorption.

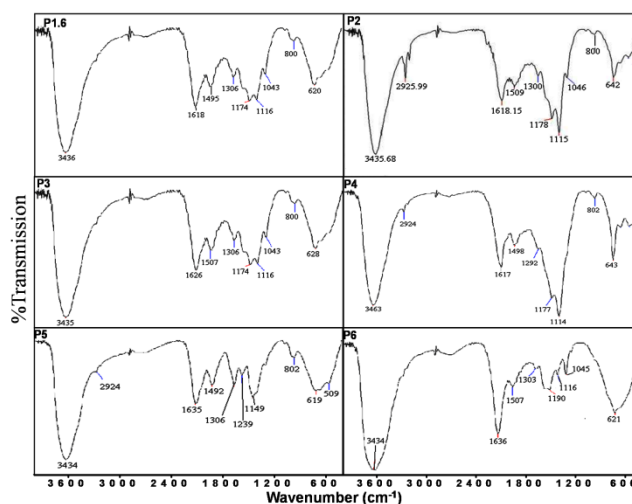
Electron paramagnetic resonance (EPR) analysis of the powder samples were carried out using EPR spectrometer ( JEOL, JES-FE3XG ) with center field 3260 G having a sweep width of 500 G. A resolution of 1000 points at

microwave frequency 9.4 GHz and microwave power 1mw was used for all the measurements. The system was standardized with 1,1-diphenyl-2-picrylhydrazyl (DPPH). The temperature dependent stability of the samples was tested under thermogravimetric analysis at TGA, SII (Perkin Elmer). The experiments were carried out under N<sub>2</sub> atmosphere from 30 to 600°C at a heating rate of 10°C/min. The room temperature DC conductivity of the samples was measured with Keithley's 236 source measurement unit (SMU) on the pallets in sandwich structure. The solubility of the prepared samples was tested in chloroform, Dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidinone (NMP) organic solvents and aqueous medium.

## RESULTS AND DISCUSSION

### 3.1. FT-IR studies

For the confirmation of the synthesis of p(m-ABSA-co-Ani) co-polymer FT-IR spectroscopic measurements have been performed on the all the sample. Figure 1 shows the characteristic FT-IR spectra of p(m-ABSA-co-Ani) at various concentrations of oxidizing agent. The FT-IR spectra of the co-polymer consist of all the characteristic bands of Pani along with some other bands including the -SO<sub>3</sub>H band which confirms the sulfonation of co-polymer.



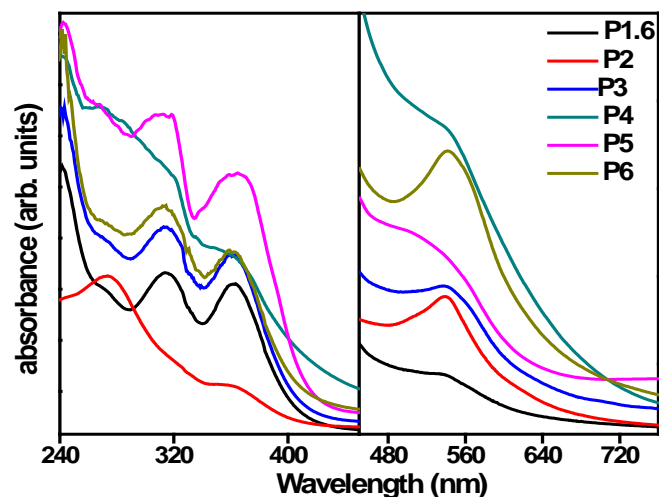
**Figure 1.** FT-IR spectra of p(m-ABSA-co-Ani) at various concentrations of sodium persulfate P1.6 = 67, P2 = 84, P3 = 126, P4 = 168, P5 = 210 and P6 = 252 mM.

The intense band located around at ~3435 cm<sup>-1</sup> in the spectrum of all the samples was attributed to the N-H stretching band while the weak doublet at the lower side at ~2854 and 2924 cm<sup>-1</sup> was assigned to the C-H bands of methyl and methylene, respectively. A strong quinoid stretching band was observed around at 1618 cm<sup>-1</sup> whereas a weak benzenoid stretching band around at 1509 cm<sup>-1</sup> with minor shifting with oxidant concentration. The band located around 1292-1309 cm<sup>-1</sup> was ascribed as the C-N stretching band of Pani with some overlapping of SO<sub>3</sub>H groups. This can be attributed to the lower electron-withdrawing capability of the SO<sub>3</sub>H group attached directly to the benzene ring 18. The presence of the absorption peak at ~1172 and 1044 cm<sup>-1</sup> characteristic of asymmetric and symmetric O=S=O stretching 19,20 with some shifting due

to different doping of SO<sub>2</sub> groups while the band at ~1115 cm<sup>-1</sup> is due to strong aromatic C-N stretching of Pani. The bands in the region between 800 and 600 cm<sup>-1</sup> are due to C-S and S-O stretching modes and these bands indicate the existence of SO<sub>3</sub><sup>-</sup> groups. Thus, the FT-IR studies confirms the synthesis of the p(m-ABSA-co-Ani) co-polymer with the doping of sulfonic groups.

### 3.2. UV-Vis spectroscopic measurements

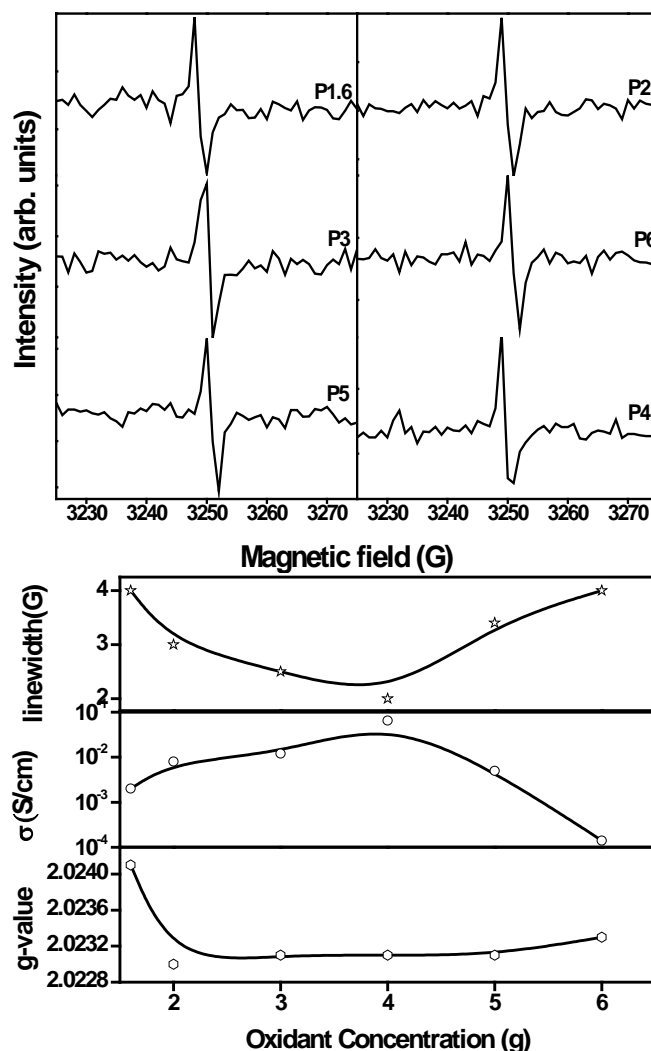
Figure 2 illustrates the UV-Vis spectra of all co-polymer samples taken in ethanol. All of spectra consist of three major absorption bands. The first one is around 310-315 nm, which is attributed to π-π\* electronic transition for the benzenoid rings in the polymer backbone. This band also provides the conjugation length. This band shows a hypsochromic shift from an emeraldine base, the insulating form of Pani to a conducting form of Pani, the emeraldine salt, for all the six samples P1.6 to P6. This transition mainly caused by the steric hindrance between large ortho substituent and neighboring phenyl hydrogen, location of charge in this type of structures due to hydrogen bonding interaction between SO<sub>3</sub>H and NH<sub>4</sub><sup>+</sup> radical cation. This also indicates the excitation of the nitrogen in the benzenoid segments.<sup>18,21</sup> The second absorption band was observed around 355-370 nm ascribed to polaron/bipolaron transition that occurs in doped Pani.<sup>21</sup> The third absorption band for exciton transition was observed in the range of 520-580 nm having a peak around 550 nm. This band mainly caused by the exciton transition between interchain or interchain charge transfer or the charge transfer between the benzenoid and quinoid rings. The steric repulsion may enhance the ring torsion angle and reduce the overlap between the two neighboring phenyl rings.<sup>8</sup> This band becomes more and more prominent with the oxidant concentration. The bands located around ~370 and 550 nm are confirm the protonated structures of the Pani samples. This confirms that all the samples maintained their conducting states with oxidizing agent.



**Figure 2.** UV-Vis spectra of p(m-ABSA-co-Ani) at various concentrations of sodium persulfate P1.6 = 67, P2 = 84, P3 = 126, P4 = 168, P5 = 210 and P6 = 252 mM.

### 3.3. EPR studies

EPR is a powerful tool used for probing the spin localization and dimensionality through the measurement of susceptibility, line width, line shape and g factor. The EPR line width is inversely proportional to the spin-spin relaxation time (T) and there are several relaxations which are tends to shortened this time (T) and caused for the line broadening of EPR line. Spin-lattice relaxation is one of the examples of such relaxation which shortens the lifetime of spins states and broadens the EPR line. While the EPR line shape generally depends upon the dipole-dipole or hyperfine interaction and spin motion. The EPR lines have a Gaussian shape if there is dipole or hyperfine broadening while the 3D spin motion or exchange altered the line shape to a Lorentzian shape. Thus, the Lorentzian line shape corresponds to the 3D spin motion or exchange while Gaussian shape corresponds to the 1D motion.



**Figure 3.** (a) EPR spectra of p(m-ABSA-co-Ani) (b) variation of g-value, conductivity and line width at various concentrations of sodium persulfate P1.6 = 67, P2 = 84, P3 = 126, P4 = 168, P5 = 210 and P6 = 252 mM.

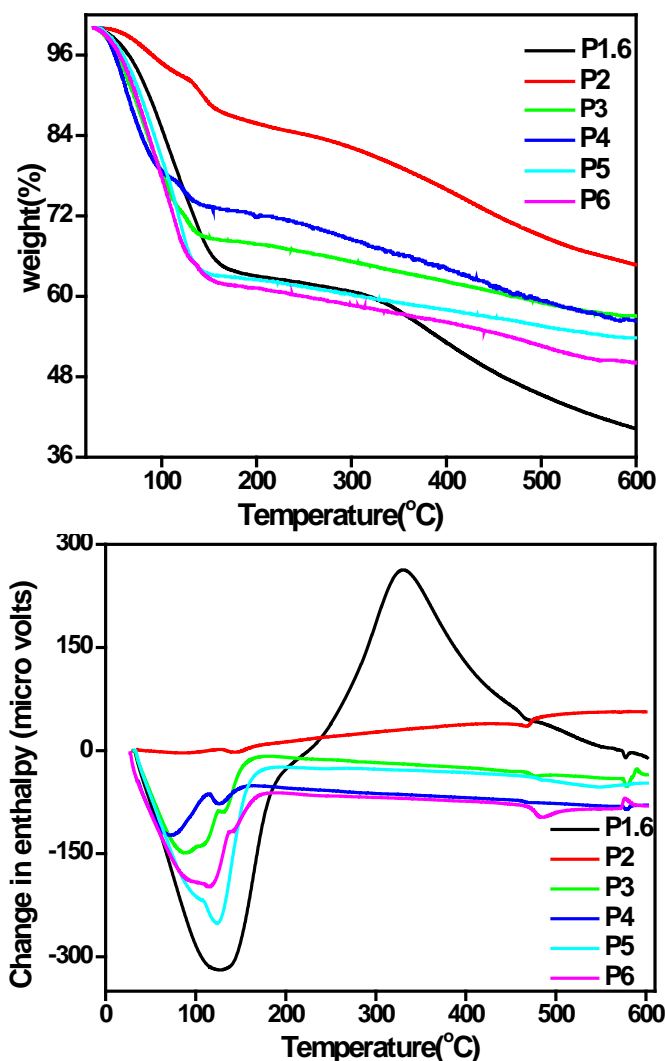
Figure 3a shows the EPR spectra of p(m-ABSA-co-Ani) co-polymer at various concentration of the oxidizing agent. All the spectra have somewhat asymmetric Lorentzian line

shape. The EPR spectra were further used for the evaluation of the line width and  $g$ -value. Figure 3b elucidates the variation of line width, conductivity and the  $g$  values with oxidant concentration. It has been found that with increase of the concentration of the oxidant the line width of the EPR spectra decreases from 4.0 to 2.0 G while the conductivity of the samples increases from  $2 \times 10^{-3}$  to  $6.5 \times 10^{-2} \text{ S/cm}^{-1}$  upto 168 mM concentration of the oxidizing agent. Beyond, 168 mM concentration of the oxidizing agent the line width and electrical conductivity show a reversal trend with concentration. However, the  $g$ -values of all the samples are approximately same except sample P1.6. The change in line width is strongly depends upon the nature of the co-polymer and the nature of the co-polymer is strongly depends on the concentrations m-aminobenzenesulfonic acid and aniline used for the co-polymerization process. It causes the hyperfine broadening and re-ordering in the structure of co-polymers and change the EPR line width.<sup>22,23</sup> If we compare the line width values with electrical conductivity of the p(m-ABSA-co-Ani) co-polymer, it has been found that electrical conductivity of the co-polymer increases with decrease in the line broadening EPR signal. This may be due to the protonation of the co-polymer with oxidizing agent concentration. The broadening of the EPR line width beyond 168 mM concentration of the oxidizing agent and decrease of the electrical conductivity influences that if we further increase the oxidizing agent concentration and decrease the electrical conductivity, the EPR line broadening increases until the disappearance of the EPR signal. Thus, the EPR line width has a direct relationship with the unpaired spin density in the co-polymer. The broadening of the EPR line width influences the formation of localized polarons or localized spins.

The  $g$ -value of the co-polymer also changes between 2.030 to 2.041 with oxidant concentration but are very close to each other and to the free radicals (electron)  $\sim 2.0023$  in the  $\pi$  system of polyenes and aromatics. This indicates that the spins are free electron type in the co-polymer. The  $g$ -value depends upon the electronic structure of the species because the applied field moves the electron through the molecule. Thus, the similar  $g$ -values of the co-polymers demonstrate that the electronic structures of all the co-polymer are same. Similar behavior of electrical conductivity with EPR line width and  $g$ -value has been demonstrated into the reported literature.<sup>24-27,31,32</sup>

### 3.4. Thermal gravimetric analysis and Differential thermal analysis

For the evaluation of the temperature dependent stability of p(m-ABSA-co-Ani) co-polymer samples TGA measurements have been performed on the prepared samples. Figure 4a elucidates the TGA plots of p(m-ABSA-co-Ani) co-polymer samples. All the samples have a two-step process of weight loss except sample P1.6 which has a three step process. The first step of weight loss is upto  $\sim 100^\circ\text{C}$  and second step above  $100^\circ\text{C}$ . The first step of weight loss upto  $100^\circ\text{C}$  is due to the loss of moisture or expulsion of loosely bounded water molecule or sulfonic acid from the polymer chain.<sup>21,28-30</sup> About 20% weight is lost in this region except sample P2 having a weight loss of about 6% only upto  $100^\circ\text{C}$ . The first step of the weight loss upto  $100^\circ\text{C}$



**Figure 4.** (a) TGA plots (b) DTA plots of p(m-ABSA-co-Ani) at various concentrations of sodium persulfate P1.6 = 67, P2 = 84, P3 = 126, P4 = 168, P5 = 210 and P6 = 252 mM.

depends upon the porosity of the sample. Larger porosity of the sample means larger absorption of moisture and higher the weight loss. There is very small weight loss variation with oxidant concentration upto  $100^\circ\text{C}$ . Thus, there is no significant change in the porosity of the samples. As all samples have a significant weight loss upto  $100^\circ\text{C}$ , thus these materials are useful for gas sensing application because, the gas sensing behavior of the samples mainly depend upon the porosity of the samples. The second step of weight loss can be attributed to the loss of oligomers and unbounded dopant and finally weight at somewhat higher temperature is due to elimination of bounded dopant and degradation of main Pani chains.<sup>23</sup> The middle, third step of weight loss in temperature range  $150\text{-}310^\circ\text{C}$  of sample P1.6 may be occurred due to presence of larger amount of oligomer and unbounded dopant at lower oxidant concentration due to incomplete polymerization. Beyond  $100^\circ\text{C}$ , the weight loss is increases with increasing the oxidant concentration. However, the sample P2 has a stable structure as compared to other samples throughout temperature range and sample P1.6 have highest weight loss.

It has been illustrated from the figure 4a that about 50-60 % weight is lost by the co-polymer samples upto 600°C. The TGA plots also illustrate that the thermal stability of the samples increases upto 168mM concentration of oxidizing agent and decreases beyond it.

Figure 4b illustrates the DTA plots of p(m-ABSA-co-Ani) co-polymer samples. The DTA plots show the respective exothermic and endothermic peaks for all the weight losses which have occurred confirming the corresponding decomposition temperatures and also the decomposition processes. The intense exothermic peaks for all the samples were observed around 130°C, these peaks mainly correspond to the weight loss due to moisture while another exothermic peaks were observed at 500 and ~580 °C for different samples. Except from other samples, sample P1.6 has an intense endothermic peaks around ~330°C which attributed to the weight lost oligomer and unbounded dopant. Almost, all the samples have two step of weight loss through an exothermic reaction.

### 3.5 Solubility test

The synthesized co-polymer samples were tested for the solubility in chloroform, DMSO and NMP. The solubility of synthesized copolymers of aniline increases with the increase in the bulky substituent proportion in the copolymer. The solubility of the synthesized co-polymers arises mainly due to the steric groups, introduced by the substituted alkyl groups in the polymer matrix. It has been found that the solubility of the prepared co-polymer was around 75% in chloroform, 65 % in DMSO and about 58 % in NMP. The prepared samples are weakly soluble in water only about 20 %. The solubility of the synthesized materials increases with increase of oxidizing agent upto around 5 %.

### CONCLUSION

The p(m-ABSA-co-Ani) co-polymers have been synthesized by the simple chemical oxidation method at various concentrations of oxidizing agent. The prepared samples were tested for chemical bonding and electronic structures by FT-IR, UV-Vis and EPR studies. FT-IR spectra of all the samples contain all the characteristics band of Pani with some other bands related to the sulfonic groups which confirm the doping of Pani chains with sulfonic groups. The FT-IR spectra of the prepared samples confirms the synthesis of p(m-ABSA-co-Ani) co-polymer doped with sulfonic acid. The UV-Vis spectra of the doped Pani illustrate the synthesis of conducting form of Pani (emeraldine salt) with oxidizing agent concentration. The EPR studies of the synthesized samples show that the line width of the EPR signal decreases with oxidizing agent concentration (168mM) and increase beyond this concentration. Whereas, the electrical conductivity of the samples have just a reversal trend to the line width of EPR signal. The thermal stability of the prepared samples was determined from the TGA measurements. TGA thermograms show two-step thermal degradation process of the co-polymer samples. All the samples have a weight lost of ~20% weight upto 100°C which attributed the weight loss

by the absorbed moisture. This is also infer that the samples are highly porous and can be used for gas sensing application. The thermal stability of the samples increases with the oxidant. The co-polymer samples show around 75 % solubility in chloroform, 65% in DMSO and 58 % in NMP.

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