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Research Article

Assessment of Spectral, Electrical and Physical Properties of Polyaniline-dodecylbenzenesulfonic Acid Salts

Salma Gul[1], Anwar-ul-Haq Ali Shah[2] and Salma Bilal[1*]

[1]National Centre of Excellence in Physical Chemistry, University of Peshawar, Peshawar, Pakistan

[2]Institue of Chemical Sciences, University of Peshawar, Peshawar, Pakistan

Abstract: In the present study some results related to various properties polyaniline salt synthesized via inverse emulsion polymerization pathway [1] has been discussed. The synthesized PANI salt was found to be completely soluble in tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), dimethylformamide (DMF), chloroform and in a mixture of toluene and 2-propanol. The synthesized polymer salt was also further characterized with cyclic voltammetry (CV), scanning electron microscope (SEM), X-ray diffraction (XRD), UV-vis spectroscopy and viscosity measurements. Thermogravimetric analysis (TGA) was used to analyze the thermal properties of synthesized polymer. The extent of doping of the PANI salt was determined from UV-vis spectra and TGA analysis. The activation energy for the degradation of the polymer was calculated with the help of TGA.

Keywords: Polyaniline (PANI), Intrinsically conducting polymers, PANI-DBSA salt, common organic solvents, CV, SEM, XRD, UV-Vis spectroscopy

1. INTRODUCTION

Intrinsically conducting polymers (ICPs) have generated a tremendous interest due to interesting electrical and optical properties [2]. Among often studied ICPs like polyacetylene, polyaniline (PANI), polythiphene, polypyrrole, poly(paraphenylene vinylene), polyaniline is particularly attractive because of its ease of synthesis with high yield, the good environmental stability and the ability to reversibly tune its conductivity to any value from the insulating to metallic regime [3]. There are four principal oxidation states of PANI. Among them leucoemeraldine (fully reduced), emeraldine (half reduced and half oxidized), pernigraniline (fully reduced) are insulating while emeraldine salt is the only conducting state of PANI [4, 5]. This polymer can be applied to batteries [6, 7], anion exchanger [8, 9], tissue engineering [10], inhibition of steel corrosion [11], sensors [12, 13] and so on.

PANI can be synthesized through either electrochemical or chemical polymerization [14]. The latter one is of particular importance since this process is the most feasible route for the production of PANI on large scale [15]. However, like other ICPs, PANI also exhibit poor thermal stability and poor processability in common organic solvents which limit its various technological applications. Numerous methods have been developed to overcome these shortcomings. These include the use of substituted aniline as monomer, synthesis of co-polymers and synthesis of PANI by emulsions/ inverse emulsions polymerization [16]. Cao et a.[17] used dodecylbenzene sulfonic acid (DBSA) and dinonylnaphthalinic acid (DNNSA) as dopant for improvement of processability. However, the PANI salts produced were partially soluble in organic solvents [18].

In order to fulfill this goal, we started a systematic

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* Corresponding author: Salma Bilal; Email: anw_sk@yahoo.com

study aimed at establishing effective polymerization pathway for the synthesis of processable polyaniline. Recently, we developed a novel method for synthesis of completely soluble and highly thermally stable polyaniline- dodecylbenzene sulfonic acid (PANI-DBSA) salts [1]. The purpose of present study was to analyze these polymers by various testing techniques to further assess its spectral, electrical and physical properties.

2. MATERIALS AND METHODS

Reagent grade Aniline (Acros, USA) was distilled under vacuum, the resulting colorless liquid was stored under nitrogen. Chloroform (Scharlau, Spain), Benzoyl Peroxide (Merck, Germany), 2-Butanol (Aldrich, Italy), DBSA (Acros, USA), 2-Propanol (Merck, Germany), Toluene (Scharalau, Spain), Tetrahydrofuran (Scharalau, Spain) were used as received.

The polyaniline-dodecylbenzenesulfonic acid salts were synthesized via pathway reported elsewhere [1]. In a typical experiment desired amount of chloroform was taken in a 100 mL round bottom flask. Then benzoyl peroxide was added to it under mechanical stirring. To this solution 2-butanol, DBSA, and aniline were added. The resulting mixture of deionized water (Millipore) was added to form a milky white emulsion. The mixture turned green in 5 hours and polymerization reaction was allowed to proceed for 24 hours. In the end the organic phase containing polyaniline salt was separated and washed four times with 50 mL of acetone. After thorough washing, a dark green highly concentrated polyaniline salt was obtained. Then it was dried at room temperature for 24 hours in a Petri dish. On addition of small amount of acetone to the Petri dish the film broke into flakes. Then PANI-DBSA salt was separated by filtration and dried in a desiccator. Prior to this the experimental conditions were optimized by stepwise changing concentration of oxidants, monomer and surfactant. The polymers obtained with the varying amount of aniline were labeled as sample 1, sample 2, sample 3 and sample 4 where the aniline concentrations were $5.36 \times 10^{-4,}$ 6.52×10^{-4}, and 7.66×10^{-4} and 8.18×10^{-3} mol, respectively. Similarly, the samples with different concentrations of benzoyl peroxide were named as sample 5, sample 6, and sample 7 when the concentrations of benzoyl peroxide were $4.17 \times 10^{-4,}$ 1.25×10^{-3} and 2.08×10^{-3} mol, respectively. Sample 8, 9 and 10 represent polymers with 3.73×10^{-3}, 4.35×10^{-3} and 4.97×10^{-3} mol of DBSA respectively.

2.1 Characterization

Percent yield of PANI-DBSA was calculated by using following formula [19].

$$\text{Percent yield} = \frac{\text{weight of PANI} - \text{DBSA}}{\text{weight of xM aniline} + \text{weight of xM DBSA}} \text{ X } 100$$

Viscosities of PANI-DBSA were determined using capillary viscometer. Intrinsic viscosity [η] was obtained by linearly extrapolating the line of specific viscosity divided by the c (η_{sp}/c) vs c and the line of the natural logarithm of relative viscosity divided by c ($\ln \eta_{rel}/ c$) vs c to the same intercept at zero concentration [20].

CV was recorded in 0.5 M H_2SO_4 in a three electrode cell, using bipotentiostat Model 2323. In this system gold disk electrode was used as working electrode. PANI dissolved in tetrahydrofuran (THF) was dip-coated onto this electrode. Saturated calomel electrode and a platinum coiled wire were used as reference and as counter electrode, respectively. UV-vis spectra were obtained using Perkin Elmer 650 (UK) spectrophotometer. A quartz cell of 1cm path length was used for recording spectra of different samples of PANI-DBSA dissolved in different solvents. The morphology of PANI-DBSA was done by using a JSM5910 (JEOL Japan) scanning electron microscope (SEM). Powder material was deposited on adhesive tape fixed to stub and then coated with gold by sputter coater prior to SEM measurements. X ray diffraction patterns were recorded by using Rigaku (Japan) X-ray diffractometer using Cu Kα radiations of wavelength 1.5405 A°) with a continuous scan speed of 0.05°/s. The diffraction patterns were collected between 2 - 65°.

Thermal analysis of the polymer was carried out by using Perkin Elmer Diamond series TG/ DTA 1300 °C (USA) at a heating rate 10°/min in the presence of N_2 atmosphere.

3. RESULTS

3.1. Yield of PANI-DBSA

The inverse emulsion polymerization reaction of aniline was carried out by varying the amount of

benzoyl peroxide, aniline and surfactant. At first for low concentration of aniline no product was obtained, attained a maximum value at 5.36 x 10^{-4} mol and then decreased with further increasing the monomer concentration. Similar observations were obtained with benzoyl peroxide and surfactant concentration. The results are represented in Table 1.

Table 1. Percent yield of PANI-DBSA.

S. No.	Sample Code	% Yield
1	1	21.2
2	2	9.8
3	3	9.7
4	4	8.6
5	5	0
6	6	21.2
7	7	0
8	8	21.2
9	9	16.3
10	10	17.1

3.2. Solubility

The synthesized PANI-DBSA was completely soluble in mixture of toluene and 2-propanol and chloroform. The polymers were also found to be soluble in THF, DMSO and DMF [1].

3.3. Intrinsic Viscosity

The viscosity plots of polyaniline salts are given in Fig.1. It was observed that intrinsic viscosity of PANI-DBSA decreased with increasing monomer concentration in the order of 33.13 > 23.86 > 22.74 > 20 for sample 1, 2, 3 and 4, respectively.

3.4 Cyclic Voltammetry (CV)

The redox property of the synthesized PANI-DBSA was investigated by cyclic voltammetry. Fig. 2. shows the representative CV of sample 1 showing two redox peaks. The first redox peak around E_{SCE} = 0.2 V was assigned to the transition of leucoemeraldine to emeraldine state and the second peak around E_{SCE} 0.6V was due to the emeraldine to pernigraniline transition. These peaks confirmed the electroactivity of the synthesized polymer [21].

3.5 UV-Vis Spectrum

UV-vis spectrum of PANI-salt was recorded by diluting the sample in tetrahydrofuran. The

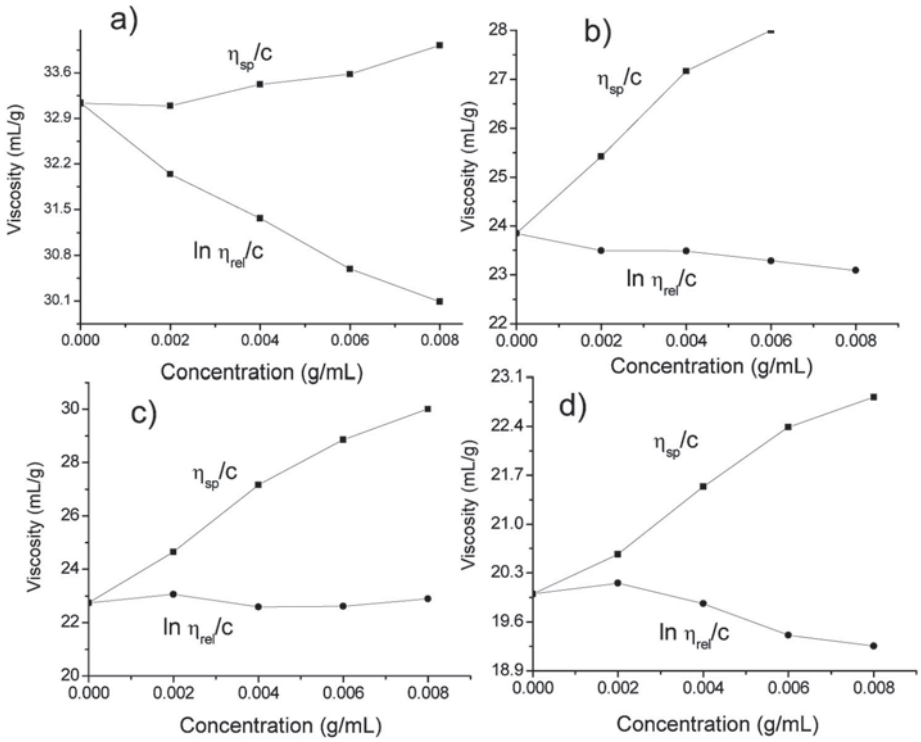


Fig. 1. Viscosity vs concentration plots for determination of intrinsic viscosity of polyaniline salt for a) Sample 1, b) Sample 2, c) Sample, 3 d) Sample 4.

spectrum given in Fig.3 showed three characteristic peaks. The first band was observed at around 338 nm, the second at 428 nm and third peak was observed at 801 nm.

3.5.1 Extent of Doping

The extent of doping can be estimated from the absorption spectra of PANI in which the exiton (π-polaron transition)/ benzenoid (π-π* transition) ratio indicates the doping level [22]. It is seen from the Table 2 that sample 1 has the biggest ratio among all sample which means that doping level of sample 1 is higher than the others.

Table 2. Absorption ratio exiton/benzenoid (E/B) for different concentrations of aniline.

S. No.	Sample Code	E/B
1	1	2.47
2	2	2.36
3	3	2.28
4	4	2.26

3.6 X-ray Diffraction of PANI-DBSA

XRD is extensively used in material identification. It is a non destructive, very simple and rapid technique for powder and other microcrystalline samples. The XRD patterns of PANI-DBSA are shown in Fig. 4 which demonstrates the characteristic peaks at 2θ = 2.5°, 19°, 20° and 25°.

3.7. Thermogravimetry of PANI-DBSA

The results of the TGA of PANI-DBSA are given in Fig.5. The DBSA doped polyaniline salts synthesized at room temperature showed three main weight loss stages. The first step weight loss was of about 5-12%. The second step weight loss being in the range 48-66 %. A slow and somewhat gradual weight loss was observed for these polymers at around 500°C.

3.7.1 Activation Energy for the Degradation of PANI-DBSA

According to Chan et al. [23] a plot of (ln k/w) versus 1/T gives a straight line with the slope equal to –Ea / R

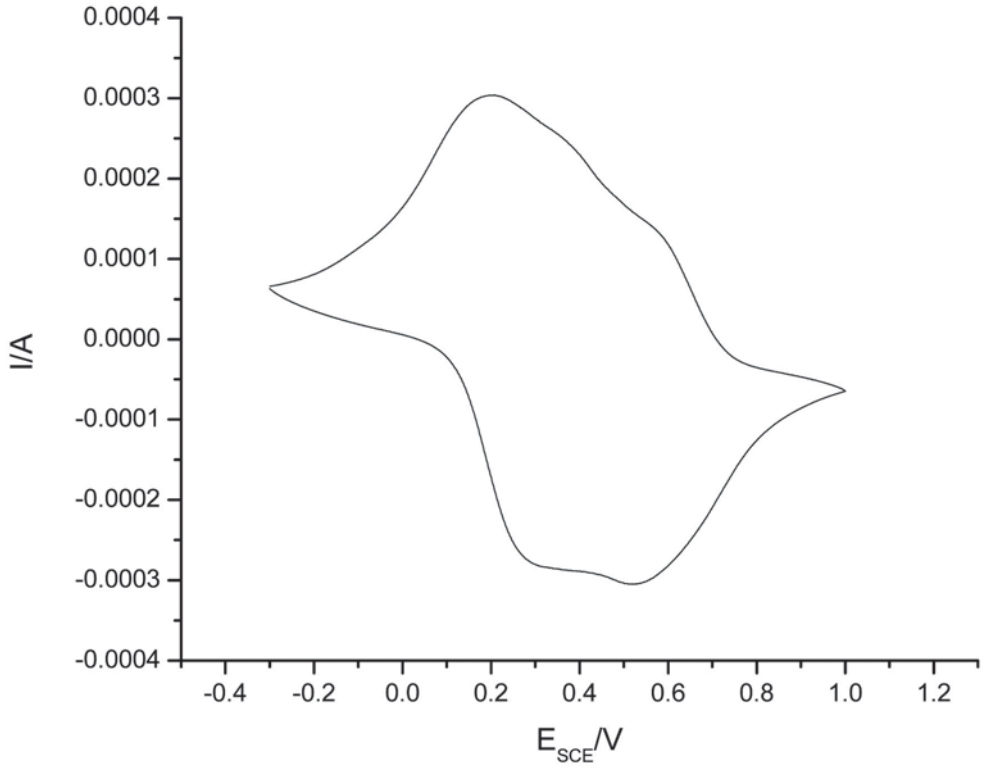


Fig. 2. Cyclic voltammogram of sample 1 on a gold disc electrode (vs SCE) in solution of 0.5 **M** H_2SO_4.

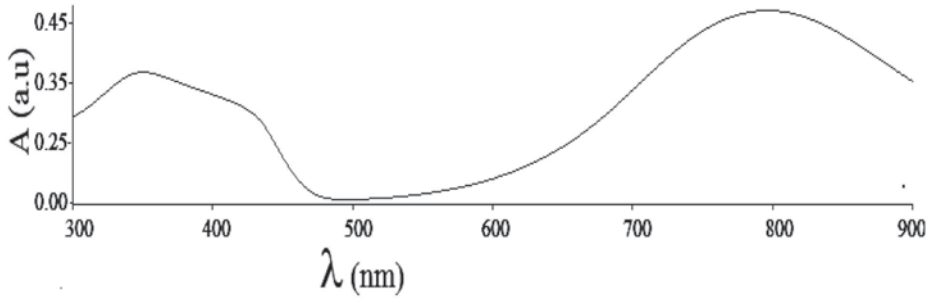


Fig. 3. UV-Vis spectrum of polyaniline salt recorded in tetrahydrofuran.

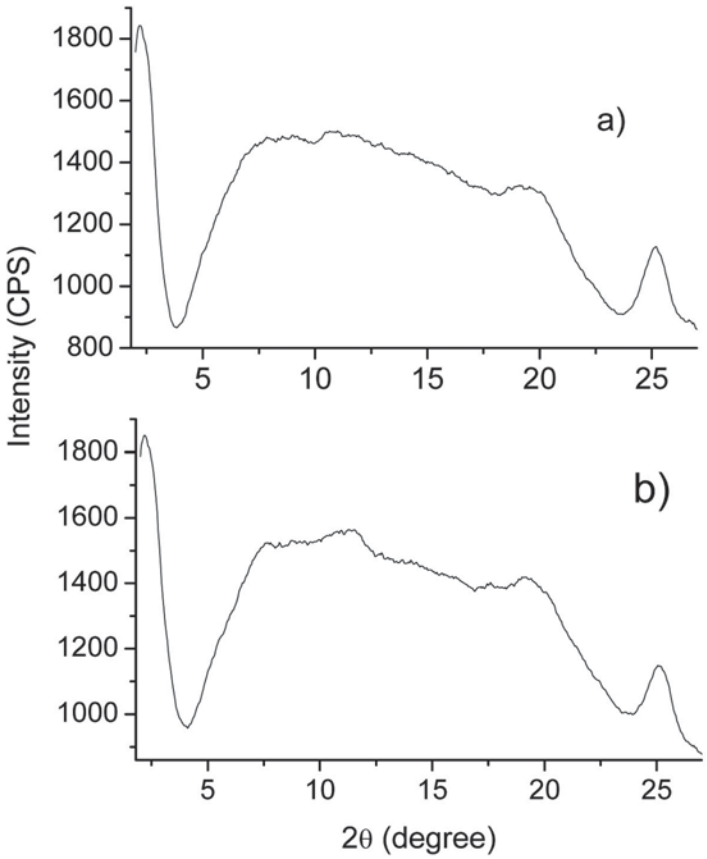


Fig. 4. X-ray diffraction patterns of polyaniline salts (a) Sample 1, (b) Sample 4.

Where

k = rate of weight loss [ln%(orginal wt) min^{-1}) at temperature T

w = corresponding weight [ln% (original wt) of the polymer remaining.

From the slope (-Ea/R) of this plot activation energy for the degradation of polymer can be calculated. Fig. 6 shows the plots obtained from kinetic analysis of TGA data of PANI doped with DBSA and activation energy calculated from these plots is 55.39kJ/mol, 81.67kJ/mol, 92.43kJ/mol and 76.75kJ/mol for sample 1, 2, 3 and 4, respectively.

3.8 Morphology of PANI-DBSA

The morphology of PANI-DBSA was obtained from scanning electron microscope. The result is presented in Fig. 7 showing aggregated granular morphology.

4. DISCUSSION

There have been several reports on the polymerization mechanism of polyaniline [24,

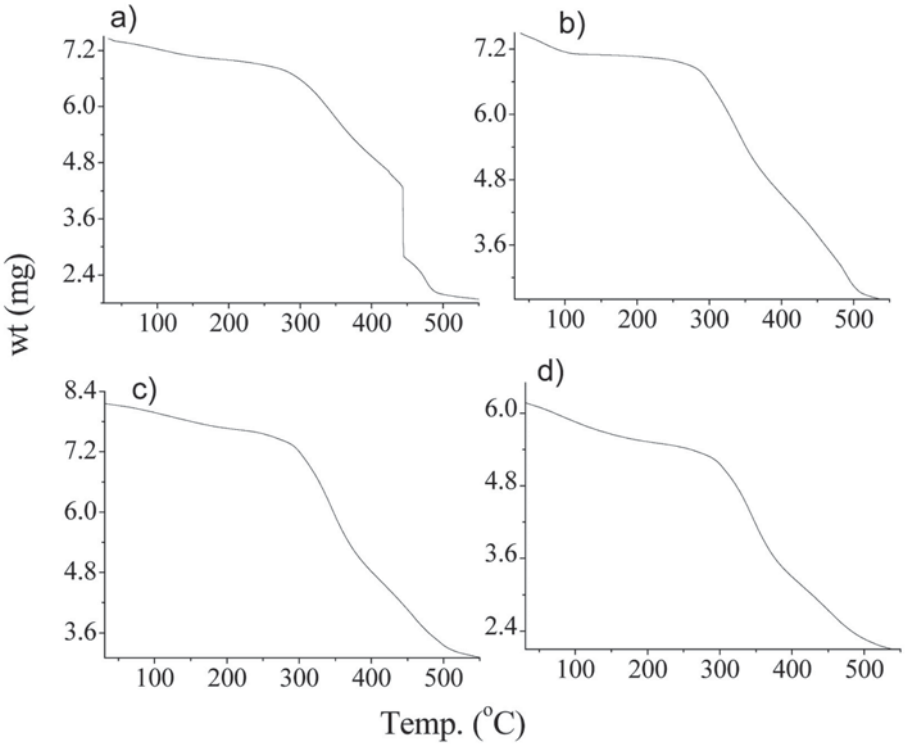


Fig. 5. Thermogravimetric curves for polyaniline salts a) Sample 1, b) Sample 2, c) Sample, 3 d) Sample 4.

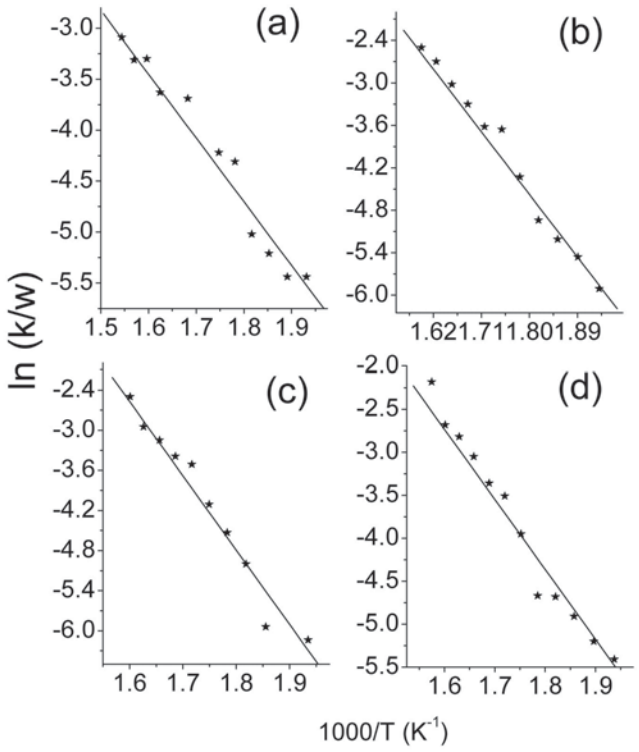


Fig. 6. Calculation of activation energy for polyaniline salts a) Sample 1, b) Sample 2, c) Sample, 3 d) Sample 4.

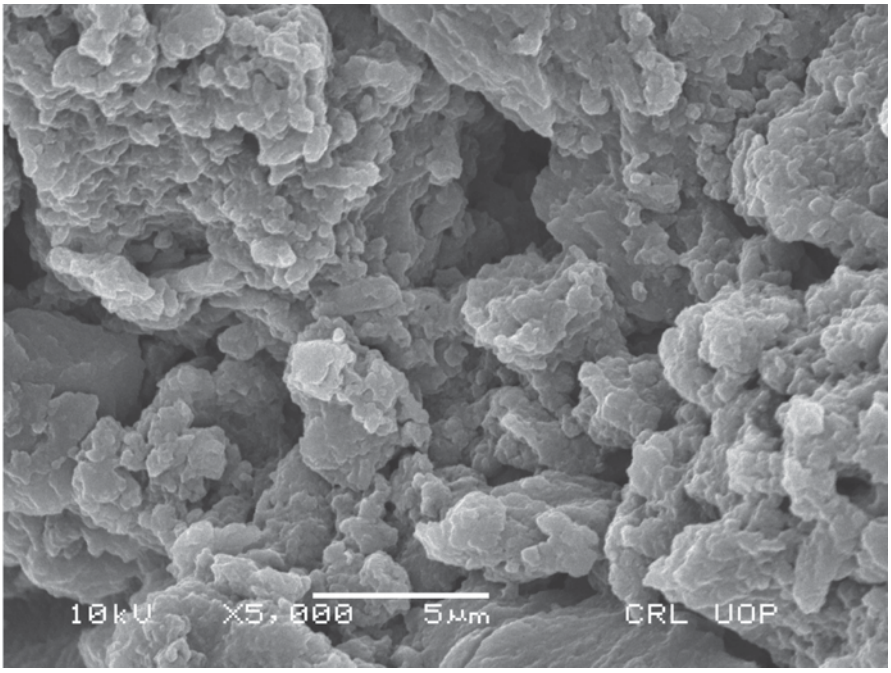
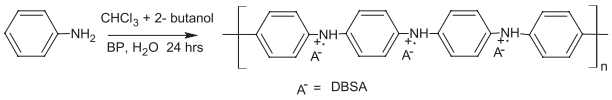


Fig. 7. Scanning electron micrograph of polyaniline salt.

25, 26]. In the first step oxidation of aniline into a radical cation takes place by an oxidant. The second step involves the formation of the intermediately oxidized nitrenium cation by losing one proton. Continuous combination of these intermediates leads to the formation of PANI. In this study aniline is oxidized by benzoyl peroxide which further makes PANI chain as shown in scheme 1.



Scheme 1. PANI-DBSA

After successful synthesis, the reaction parameters were optimized by changing the reactant concentrations in the feed. The observed change in the yield of the product with different parameters may be due to over oxidation process or may be that the kinetic effects were favored in the oxidation of aniline [27]. Generally, soluble PANI exhibits low % yield. Dan and Sengupta [28] prepared soluble polyaniline in formic acid media but they obtained very low yield i.e. 7.8% and 6.9 %. The high % yield results in the present case reveal that the soluble polymers were successfully prepared with quite high yield [1].

All these PANI salts are highly soluble in common organic solvent due to proper incorporation of DBSA moieties in its backbone. Indeed, the large sized organic sulfonic acids (DBSA) have a good solubility and processability in common organic solvents. It is due to enlarge interchain distance, which means weaker interchain reaction and strong interaction between dopant and solvent [29].

These PANI salts were systematically characterized by various techniques to investigate their properties. It is seen that with increasing concentration in the feed the intrinsic viscosity decreases. The results are in accordance with Dan and Sengupta [28]. They concluded that the dropping trend in the intrinsic viscosity is due to the direct consequence of rapid lowering in initiator efficiency.

UV-vis spectrum showed three characteristic peaks. The results are similar to Han et al [22]. They assigned the first absorption band at 338 nm to π-π^* electron transition within benzoid (B) ring. The second and third at around 428 and 801 nm, respectively, is attributed to the polaron-transitin and bipolaron transition respectively. The last two bands relates to the doping level and formation of polaron lattice. The results support the formation of

PANI-DBSA salt. The calculation of doping level demonstrates that the concentration of aniline plays an important role in the synthesis of PANI-DBSA.

The XRD patterns of PANI-DBSA observed in Fig. 4 show the characteristic peaks of PANI-DBSA. The peaks from 20° to 27° are ascribed to the momentum transfer and periodicity and perpendicular to the chain direction [30, 31]. The peaks at $2\Theta \approx 19°$ and another one at $2\Theta \approx 25°$ are characteristics of van der waals distances between aliphatic chain and between stakes of phenylene rings respectively [32, 33]. The peak at 2.5° observed in both sample 1 and 4, showed the well organized layered structure in which stacks of charged aniline backbone are uniformly spaced by the alkyl tails of DBSA [34]. All peaks are observed at lower value of 2Θ indicating the better crystallinity [1, 35]. SEM study revealed the typical granular morphology of these PANI salts [36, 37]. It is seen in the TGA study that the DBSA doped polyaniline salts showed three main weight loss stages. The first step weight loss of about 6-13% is associated with the loss of moisture. PANI always shows high moisture loss because it is highly hygroscopic in nature and some moisture still remains even after vaccume drying [38]. The second step weight loss being in the range 47-65%, is attributed to destroy of the NH^{+}…..SO^{-}_{3} interaction between the PANI chain and the DBSA dopant with degradation of DBSA [39]. A slow and gradual weight loss was observed for these polymers at around 500°C, is due to the structure decomposition of PANI backbone. This is quite high temperature for its degradation compared to the reported literature. Chen [40] found that the degradation temperature of ES form of PANI was lower (around 360-410 °C) than that of the EB form (around 420-450°C). Svelko et al [41] prepared PANI in the presence of non-ionic surfactants which was stable upto 400°C. Jayakkannan et al [42] synthesized azobenzenesulfonic acids doped PANI which was stable upto 300°C. In present study high thermal stability up to about 500°C was achieved which presents effectiveness of polymerization pathway [1]. The PANI-DBSA salts were not completely destroyed because in nitrogen atmosphere carbonization of polymer takes place leaving a marked residue [43]. It was found that among all samples, Ea is highest for sample 3. Therefore it is thermally more stable. These results show that DBSA doped PANI material is highly stable and can be used for various high temperature applications.

5. CONCLUSIONS

In this study, PANI- DBSA salts were successfully prepared from DBSA reversed micelle solution. High yield of PANI was obtained by optimizing reaction conditions. The characterizations of PANI-DBSA revealed comparable or preferable properties i.e. percent yield, solubility, crystallinity, electrochemical activity, thermal stability and intrinsic viscosity with the products obtained from other approaches. Thus this inverse emulsion polymerization is a feasible and attractive approach to prepare processable PANI- DBSA salts with a number of valuable chemical properties which may be used for various technological applications.

6. ACKNOWLEDGEMENTS

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7. REFERENCES

1. Bilal, S, S. Gul, K. Ali & A.A. Shah. Synthesis and characterization of completely soluble and highly thermally stable PANI-DBSA salts. *Synthetic Metals* 162: 2259-2266 (2012).
2. Nabid, M.R., Z. Zamiraei, R. Sedghi & N. Safari. Cationic metaloporphyrins for synthesis of conducting, water-soluble polyaniline. *Reactive and Functional Polymers* 69: 319-324 (2009).
3. Yang, J., Y. Ding, G. Chen, & C. Li. Synthesis of conducting polyaniline using novel anionic gemini surfactant as micellar stabilizer. *European Polymer Journal* 43: 3337-3343 (2007).
4. Gettinger, C.L., A.J. Heeger, D.J. Pin, & Y. Cao. Solution characterization of surfactant solubilized polyaniline. *Synthetic Metals* 74: 81-88 (1995).
5. Hassan, P.A., S.N. Sawant, N.C. Bagkar & J.V. Yakhmi. Polyaniline nanoparticles prepared in rodlike micelles. *Langmuir* 20: 4874-4880 (2004).
6. Xiao, L., Y. Cao, J. Xiao, B. Schwenzer, M.H. Engelhard, L.V. Saraf, Z. Nie, G.J. Exarhos & J. Liu. A Soft Approach to encapsulate sulfur: polyaniline nanotubes for lithium-sulfur batteries with long cycle life. *Advanced Materials* 24: 117-1181 (2012).

7. Ghenaatiana, H.R., M.F. Mousavia, & M.S. Rahmanifar. High performance battery supercapacitor hybrid energy storage system based on self-doped polyaniline nanofibers. *Synthetic Metals* 161: 2017-2023 (2011).
8. Ansari, R. Application of polyaniline and its composites for adsorption/recovery of chromium (VI) from aqueous solutions. *Acta Chimica Slovenica* 53: 88-94 (2006).
9. Ghorbani, M., H. Esfandian, N. Taghipour, & R. Katal. Application of polyaniline and polypyr role composites for paper mill wastewater treatment. *Desalination* 263: 279-284 (2010).
10. Li, M., Y. Guo, Y. Wei, A.G. MacDiarmid, & P.I. Lelkes.Electrospinning polyaniline-contained gelatin nanofibers for tissue engineering applications. *Biomaterials* 27: 2705-2715 (2006).
11. El-Shazly, A.H. & H.A. Al-Turaif. Improving the corrosion resistance of buried steel by using polyaniline coating. *International Journal of Electrochemical Science* 7: 211-221 (2012).
12. Liu, C., K. Hayashi & K. Toko. Au nanoparticles decorated polyaniline nanofiber sensor for detecting volatile sulfur compounds in expired breath. *Sensors and Actuators B: Chemical* 161: 504-509 (2012).
13. Srivastavaa, S., S.S. Sharma, S. Agrawala, S. Kumara, M. Singha & Y.K. Vijay. Study of chemiresistor type CNT doped polyaniline gas sensor. *Synthetic Metals* 160: 529-534 (2010).
14. Palaniappan, S. Benzoyl peroxide oxidation route to polyaniline salts-Part I. *Polymers of Advanced Technologies* 15: 111-117 (2004).
15. Cao, Y., A. Andreatta, A. J. Heeger, & P. Smith. Influence of chemical polymerization conditions on the properties of polyaniline. *Polymer* 30: 2305-2311 (1989).
16. Palaniappan, S. & A. John. Polyaniline materials by emulsion polymerization pathway. *Progress in Polymer Science* 33: 732-758 (2008).
17. Cao, Y., P. Smith & A.J. Heeger. Counter-ion induced processsibility of conducting polyaniline and of conducting polyblends of polyaniline in bulk polymers. *Synthetic Metals* 48: 91-97 (1992).
18. Kinlen, P.J., J. Liu, Y. Ding, C.R. Graham & E.E. Remsen. Emulsion polymerization process for organically soluble and electrically conducting polyaniline. *Macromolecules* 31: 1735-1744 (1998).
19. Shreepathi, S. & R. Holze. Spectroelectro-chemistry and preresonance raman spectroscopy of polyaniline-dodecylbenzenesulfonic acid colloidal dispersions. *Langmuir* 22: 5196-5204 (2006).
20. Yang, J, & B. Weng. Inverse emulsion polymerization for high molecular weight and electrical ly conducting polyanilines. *Synthetic Metals* 159: 22249-2252 (2009).
21. Shreepathi, S. & R. Holze. Spectroelectrochemical investigations of soluble polyaniline synthesized via new inverse emulsion pathway. *Chemistry of Materials* 17: 4078-4085 (2005).
22. Han, Y-G., T. Kusunose & T. Sekino. One-step reverse micelle polymerization of organic dis persible polyaniline nanoparticles *Synthetic Metals* 159: 123-131 (2009).
23. Chan, H.S.O., P.K. H. Ho, E. Khor & M.M. Tan. Preparation of polyaniline doped in mixed protonic acids: their characterization by X-ray photoelectron spectroscopy and thermogravimetry. *Synthetic Metals* 31: 95-108 (1989).
24. Wei, Y., X. Tang, Y. Sun, & W. W. Focke. A study of the mechanism of aniline polymerization. *Journal of Polymer Science Part A: Polymer Chemistry* 27: 138-2396 (1989).
25. Ding, Y., A.B. Padias, H.K. Hall & Jr. Chemical trapping experiments support a cation-radical mechanism for the oxidative polymerization of aniline. *Journal of Polymer Science Part A: Polymer Chemistry* 37: 2569- 2579 (1999).
26. 29. Kim, J., S. Kwon & D.W. Ihm. Synthesis and characterization of organic soluble polyaniline prepared by one-step emulsion polymerization. *Current Applied Physics 7:* 205-210 (2007).
27. Palaniappan, S. & C.A. Amarnath. A novel polyaniline– maleicacid–dodecylhydrogensulfatesalt: Soluble polyaniline powder. *Reactive and Functional Polymers* 66: 1741-1748 (2006).
28. Dan, A. & P.K. Sengupta. Synthesis and characterization of polyaniline prepared in formic acid medium. *Journal of Applied Polymer Science* 91: 991-999 (2004).
29. Huang, J. & M. Wan. Polyaniline doped with different sulfonic acids by in situ doping polymerrization. *Journal of Polymer Science Part A: Polymer Chemistry* 37: 1277-1284 (1999).
30. Chen, J., Y. Xu, Y. Zheng, L. Dai, & H. Wu. The design, synthesis and characterization of po lyaniline nanophase materials. *Comptes. Rendus Chimie* 11: 84-89 (2008).
31. Palaniappan, S. & S. L. Devi. Thermal stability and structure of electroactive polyaniline fluoroboric acid dodecylhydrogensulfate salt. *Polymer Degradation and Stability* 91: 2415- 2422 (2006).
32. Sarvanan, C., S. Palaniappan, & F. Chandezon. Synthesis of nanoporous conducting polyaniline using ternary surfactant. *Materials Letters* 62: 882-885 (2008).
33. Duffour, B., P. Rannon, P. Fedorko, D. Djurado, J.P. Travers & A. Pron. Effect of plasticizing dopants on spectroscopic properties, supramolecular structure, and electrical transport in metallic polyaniline. *Chemistry of Materials* 13**:** 4032-4040 (2001).
34. Han, M.G., S.K. Cho, G.S. Oh, & S.S. Im. Preparation and characterization of polyaniline nanoparticles

synthesis from DBSA micellar solution. *Synthetic Metals* 126: 53-60 (2002).
35. Vijayan, M, & D. C. Trivedi. Studies on polyaniline in methane sulphonic acid (MeSA). *Synthetic Metals* 107: 57-64 (1999).
36. Konyushenko, E.N., M. Trchova, J. Stejskal, & I. Sapurina. The role of acidity profile in the nanotubular growth of polyaniline. *Chemical Papers* 64: 56-64 (2010).
37. Stejskal, J., I. Sapurina, M. Trchova, & E.N. Konyushenko, Oxidation of aniline: polyaniline granules, Nanotubes, and oligoaniline microspheres, *Macromolecules* 41: 3530-3536 (2008).
38. Bhadra, S., S. Chattpadhyay, N.K. Singa, & D. Khastgir. Improvement of conductivity of elec trochemically synthesized polyaniline. *Journal of Applied Polymer Science* 108: 57-64 (2008).
39. Babazadeh, M. Aqueous dispersions of DBSA-doped polyaniline: one-pot preparation, character rization and properties study. *Journal of Applied Polymer Science* 113: 3980-3984 (2009).
40. C. -H. Chen. Thermal and morphological studies of chemically prepared emeraldine-base-form polyaniline powder. *Journal of Applied Polymer Science* 89: 2142-2148 (2003).
41. N. K. Svelko, S. Reynaud. J. Francois, Synthesis and characterization of polyaniline prepared in the presence of nonionic surfactants in an aqueous dispersion, Synth. Met. 150 (2005) 107-114. .
42. M. Jayakannan, P. Anilkumar, A. Sanju, Synthesis and characterization of new azobenzenesulfonic acids doped conducting polyaniline. *European Polymer Journal* 42: 2623-2631 (2006).
43. Brozova, L., P. Holler, J. Kovarova, J. Stejskal, & M. Trchova. The stability of polyaniline in strongly alkaline or acidic aqueous media. *Polymer Degradation and Stability* 93: 592-600 (2008).