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Calculation of Activation Energy of Degradation of Polyaniline-Dodecylbenzene Sulfonic Acid Salts via TGA

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Abstract

This paper presents a study on the determination of thermal stability of highly thermally stable polyaniline-dodecylbenzenesulfonic acid (PANI-DBSA) salts using thermogravimetric analysis. This technique was also used to calculate energy of activation (Ea) for the degradation of polymer using Horwitz & Metzger, Coats & Redfern and Chan et al. methods. The results showed that the synthesized polymer is highly stable even upto 500 C0 (so far highest reported temperature for stability of polyanile). Previ-ously the synthesis of PANI-DBSA was carried out via inverse polymerization following a novel pathway. Further characterization of the synthesized materials was done with the help of UV-Vis spectroscopy and XRD.

Keywords: PANI-DBSA salt, common organic solvents, XRD, UV-Vis spectroscopy. TGA, Activation energy

Introduction

Intrinsically conducting polymers (ICPs) possess interesting electrical and optical properties previously found only in inorganic systems.[1] ICPs have attracted much at-tention because they have the electrical properties like that of metals as well as the fun-damental characteristics of organic polymers such as light weight, resistance to corrosion, flexibility, low cost and that their properties can be tailored to the required applications.[2]

Research interests in these polymers initiated in 1977 with the wonderful discov-ery by Shirakawa *et al.*[3] They demonstrated that the electrical conductivity of polyacetylene can be increased by several orders of magnitude by treatment with an ap-propriate oxidizing agent such as bromine or iodine vapours. Following this study other conducting polymers such as polypyrrole, polythiophene, polyaniline (PANI), polyphenylenevinylene), poly(p-phenylene sulfide) and their derivatives have been syn-thesized.[4] PANI is the most promising candidate among all the available ICPs due to its unique reversible proton dopability, good environmental stability, excellent redox re-cyclability, tunable electrical conductivity and easy synthesis.[5] It can be synthesized electrochemically or chemically by oxidation of aniline. In case of electrochemical polymerization generally a polyaniline film is deposited on the anode while chemical polymerization is the feasible route for the production of PANI in bulk quantity.[6] PANI can be used in batteries[7], electrochromic devices[8], anion exchanger[9, 10] tissue engineering[11], inhibition of steel corrosion[12], sensors[13] and so on.

However, its insolubility and infusibility resulting from the stiffness of backbone and H-bonding interactions between adjacent chains limit not only its commercial appli-cations but also studying its physicochemical properties.[14] In order to improve these shortcomings different strategies were attempted.[15-18] Along with good processability, thermal stability of a polymer is another important factor for its various technological applications. Recently we have reported on the synthesis of polyaniline via a novel route.[19] The synthesized polymer was soluble in so far highest number of or-ganic solvents and showed thermal stability upto 500 C0 which is indeed a good achievement too. The use of conducting polymers in industries is limited due to its unde-sirable properties such as loss of dopant and decomposition at high temperature. Also due to the loss of conductivity at high temperature, their use in electronic devices, solid sate batteries, chemical sensors, electromagnetic shielding, anticorrosion coatings, etc, has been restricted.[20] Therefore, the knowledge of thermal stability and degradation mech-anism is particularly important. Therefore, several investigators have discussed the thermal stability by using TGA technique. Kim et al.[21] synthesized PANI nanoparticles in sodium dodecyl sulfate (SDS) miceller solution. For higher concentration of aniline, they found that the polymer degraded at 450°C while for lower concentration of aniline it de-graded at 438°C. Chen[22] determined thermal property of emeraldine base (EB) and emeraldine salt (ES) form of PANI. He 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.*[23] prepared PANI in water-dispersed medium in the presence of nonionic surfactants. The PANI obtained by this process was stable upto 400°C. Jayakkannan *et al.*[24] synthesized azobenzenesulfonic acids doped PANI which was stable upto 300°C. Chen et al. studied the thermal degradation of co-doped polyaniline. They reported 410~600°C temperature for degradation of the polymer. How-ever, there are only few detailed reports on the thermal degradation of PANI.[19]

In the present study, we have attempted to address these objectives. TGA was used for the study of thermal properties of PANI-BSA. This technique was also used to calculate energy of activation (Ea) for the degradation of the polymer to understand more about the degradation process. The results indicated that PANI-DBSA is thermally stable up to quite high temperature (500°C). The synthesized polymer was also characterized by X-ray diffraction (XRD) and UV-Vis spectroscopy.

Experimental

Materials

Aniline (Acros), Chloroform (Scharlau), Benzoyl Peroxide (Merck), 2-Butanol (Aldrich), DBSA (Acros), 2-Propanol (Merck), Toluene (Scharalau), Water (Milipore).

Methodology

Synthesis of Polyaniline Salt

In a typical experiment 0.29 mol of chloroform was taken in a 100 mL round bot-tom flask. Then 1.25 x 10-3 mol benzoyl peroxide was added to it under mechanical stir-ring. To the above solution 0.13 mol of 2-butanol, 3.73 x 10-3 mol DBSA, and 5.36 x 10-4 mol of aniline were added. To the resulting mixture 0.28 mol of water 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 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.

The experimental conditions were optimized by stepwise changing concentration of oxidant, monomer and surfactant. Polymerization reaction was carried out by varying the amount of benzoyl peroxide, DBSA and aniline.

The polymers obtained with the varying amount of aniline were labeled as ANI 5, ANI 7, ANI 9, and ANI 11 where the aniline concentrations were 5.36 x 10-4 mol, 7.52 x 10-4 mol, 9.66 x 10-4 mol, 1.18 x 10-3 mol, respectively.

Characterizations

UV-Vis spectrum was obtained using Perkin Elmer (UK) Spectrophotometer. A quartz cell of 1cm path length was used for recording spectrum of PANI-DBSA dissolved in chloroform. XRD pattern was recorded using Cu Kα radiations (λ = 1.5405 A°) on a Rigaku (Jappan) X-ray diffractometer. Thermal analysis of the polymer was carried out by using Perkin Elmer (USA) at a heating rate 10°/min in the presence of N2 atmosphere.

Results and Discussions

There have been several reports on the polymerization mechanism of polyaniline.[25-27] In the first step oxidation of aniline into a radical cation place by an oxidant. The second step involves the formation of the intermediately oxidized nitrenium cation by losing one proton. These intermediates combine continuously to form PANI chain, shown in Scheme 1.
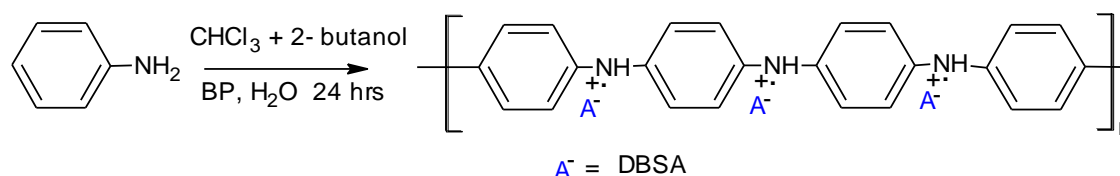
Scheme 1: Synthesis of PANI-DBSA

Solubility

PANI-DBSA synthesized in the present work was completely soluble in DMSO, DMF, and Chloroform and in 2:1 mixture of toluene and 2-propanol, which can be spin, dip or drop coated on metallic and glass substrates.[28]
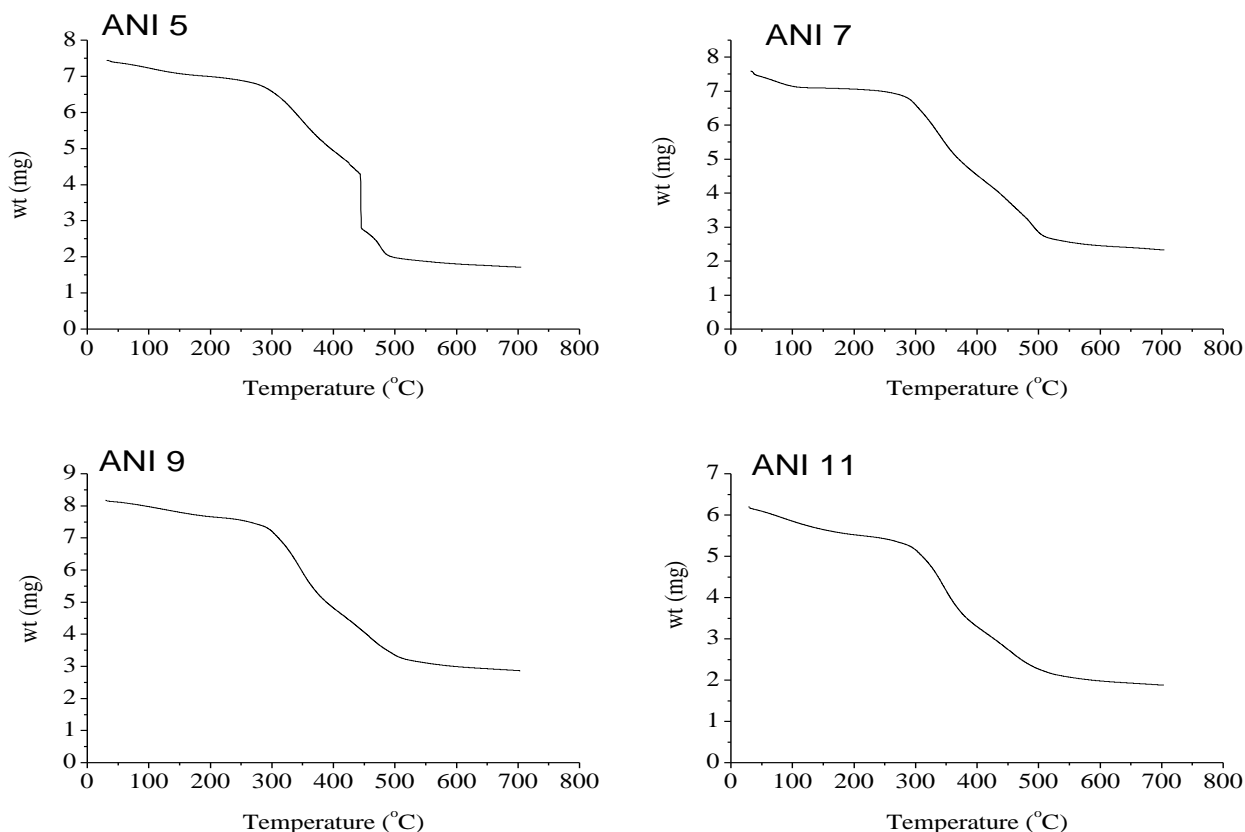
Thermogravimetry Analysis

Knowledge of thermal stability of PANI under various thermal conditions is important for their use in many practical applications. Thermal degradation of PANI is explained by thermogravimetry. Thermogravimetry may be defined as the change in mass of sample as a function of temperature when it is subjected to controlled temperature pro-gram. The resulting mass change Vs temperature curve provides the information concerning the thermal stability and composition of the initial sample, intermediates and the resi-due. This technique provides sufficient information to calculate the amount of dopant present in the PANI backbone and to study the thermal decomposition kinetics of the polymer.

The results of the TGA of the PANI-DBSA samples prepared with various aniline concentrations are tabulated in Table 1 and their thermograms are presented in Fig.1. The DBSA doped polyaniline salts synthesized at room temperature showed three main weight loss stages. The first step weight loss of about 5 - 12% 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 vacuum drying. The second weight loss step being in the range 48 - 66%, is attributed to destroying of the NH^+.......SO^{-3} interaction between the PANI chain and the DBSA dopant with degradation of DBSA. A slow and somewhat gradual weight loss was observed for these polymers at 500°C are due to the structure decomposition of PANI backbone. All PANI-DBSA samples were not completely destroyed because in nitrogen atmosphere carbonization of polymer takes place leaving a marked residue. PANI-DBSA synthesized in the present work show very good thermal stability.[29-32]

Table 1: A comparison of TGA data for PANI-DBSA samples

Sample	Temperature range in °C (% weight loss)		
	1st Step	2nd Step	3rd Step
ANI 5	30-190 (5.4)	197-480 (66.2)	480
ANI 7	30-105 (6.6)	205-490 (60.5)	500
ANI 9	30-285 (10.12)	285-497 (48.78)	500
ANI 11	30-178 (11.29)	206-480 (50)	500

Figure 1: Thermo gravimetric curves for PANI-DBSA salts

Kinetic analysis of TGA data

TGA data can be used to study the kinetic parameters of a thermal decomposition reaction. Knowledge of these parameters such as activation energy, pre-exponential factor and order of reaction, are the keys to determine the reaction mechanisms in solid phases. The observed changes in the mechanisms can lead to a unique thermal behavior and hence a better knowledge of the materials.[33] Several methods have been reported for calculating the kinetic parameters of solid state reactions.[34-36]

The kinetics of the heterogeneous condensed phase reactions occur in non-isothermal conditions is described by following expression.

$$\beta \left(d\alpha/dT \right) = A\, f(\alpha)\, \exp\left(-Ea\,/RT \right) \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$f(\alpha) =$ differential conversion function

$\alpha \quad =$ degree of conversion

$T \quad =$ Temperature

$\beta \quad =$ linear heating rate (constant)

$A \quad =$ pre-exponential factor

$Ea \quad =$ activation energy

$R \quad =$ gas constant

From the above expression it can be concluded that the kinetic triplet (A, E, $f(\alpha)$) gives the kinetic description of a certain reaction. For its determination various procedures were developed classified into three categories: differential, integral and so called other special methods.[32]

In the present study three methods were used to evaluate kinetic parameters for degradation of synthesized PANI-DBSA by assuming first order kinetics.[33]

Horowitz and Metzger method

Horowitz and Metzger derived an approximate integral method to extract pyrolysis parameter using TGA.

According to this method a plot of double logarithm of the reciprocal of the reactant versus temperature gives the activation energy of pyrolysis. For first order reaction they obtained following equation.[38]

$$\ln[\ln\{(Wo-Wf)/(Wt-Wf)\}] = Ea\,\theta/RTs^2 \qquad \text{......... (2)}$$

Where

Wo = initial weight of the sample

Wf = final weight of the sample

Wt = the weight of the sample at temperature t

R = gas constant

$\theta = T - Ts$

Ts is the refernce temperature when

$(Wt-Wf)/(Wo-Wf) = 1/e$

Thus a plot of the double logarithm of the reciprocal of the weight fraction of the reactant versus temperature whose slope ($Ea \times 10^3 / RTs^2$) is related to activation energy.

Coats and Redfern Method

Coats and Refern derived an equation for the determination of activation in which the order of reaction is an important parameter. The equation is given below.[33]

$$\log\,[\,1-(1-\alpha)^{1-n}/T^2\,(1-n)]$$

$$= [\log(AR/\alpha\,Ea)\,\{1-(2RT/Ea)\}] - (Ea/2.303\,RT)$$
$$\text{............ (3)}$$

For first order reaction when n = 1 the equation is

Log $[-\log(1-\alpha)/T^2]$ against 1000/T will result in a straight line having a slop (Ea/2.303R) to calculate activation energy.**Error! Bookmark not defined.. Error! Bookmark not defined.**

Chan *et al.* Method

According to this method Arrhenius plot can be used to calculate activation energy by assuming first order reaction kinetics.

From the Arrhenius plot of (in k/w) versus 1/T, the slope is equal to –Ea / R

Where

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

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

From the slop (-Ea/R) of this plot activation energy can be calculated.

Rao *et al.*[36] calculated activation energy for the degradation of PANI salts doped with different sulfonic acids. The Ea calculated using Horowitz & Metzger method was in the range of 37.6 - 44 kJ/mol and for Coats and Redfern method they obtained values in the range of 39.2 - 49.5 kJ/mol. Chan et al. have reported a comparative study of polyaniline doped with mixture of protonic acids. The Ea for degradation of PANI salts was found to be 32 - 54 kJ/mol.[38, 39]

In the present work, Figs. 2-5 show the plots obtained from kinetic analysis of TGA data of PANI doped with DBSA. The activation energies calculated from these plots are presented in Table 2. Ea for PANI doped with DBSA is

38.91 - 47.94 kJ/mol for Horowitz & Metzger method, 21.77 - 27.56 kJ/mol for Coats & Redfern and 55.39 - 92.43 kJ/mol for Chan et al. method. The Ea for the degradation is the highest for ANI 9, calculated by all the three methods suggesting it to be thermally more stable.

From above discussions it is inferred that DBSA doped PANI salts, synthesized in the present work, are thermally more stable and can be used for various high temperature applications. In addition to thermal properties spectroscopic properties and crystalline nature of PANI-DBSA powder were also studied by using UV-Vis spectroscopy and X-Ray diffraction (XRD) respectively.

**Table 2:** Activation energy (Ea in kJ/mol) for PANI-DBSA as a function of monomer (Aniline) concentration

Sample	Activation Energy (kJ/mol)		
	Horowitz and Metzger method	Coats and Redfern method	Chan et al. method
ANI 5	46.16	21.77	55.39
ANI 7	47.77	25.60	81.67
ANI 9	47.94	27.56	92.43
ANI 11	38.91	26.80	76.75
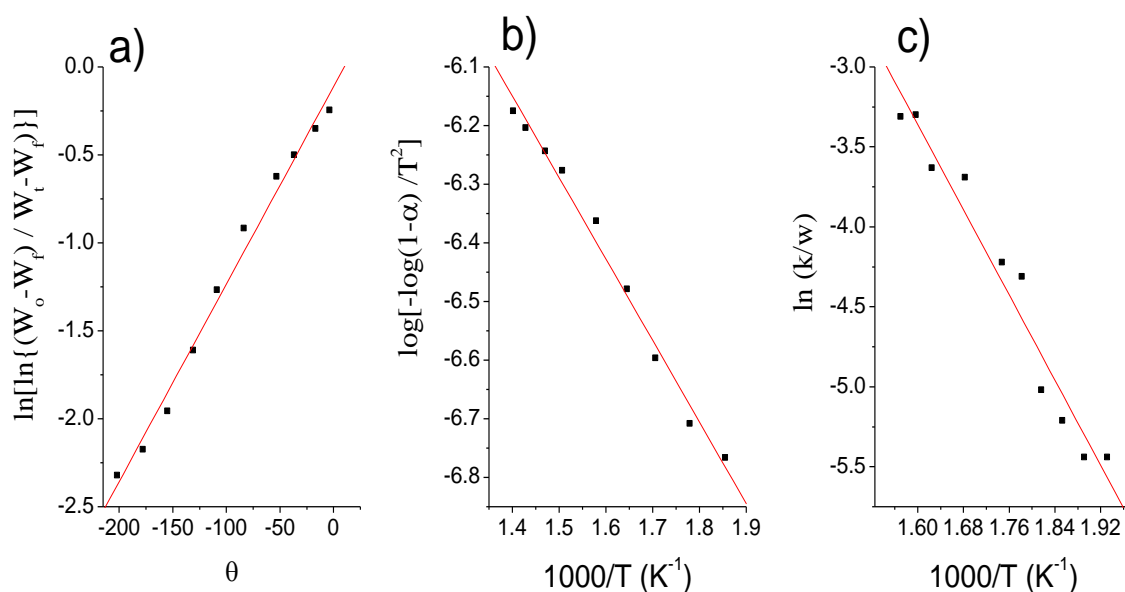
Figure 2: Calculation of activation energy for ANI 5, a) Horowitz and Metzger method b) Coats and Redfern method c) Chan *et al*. method.
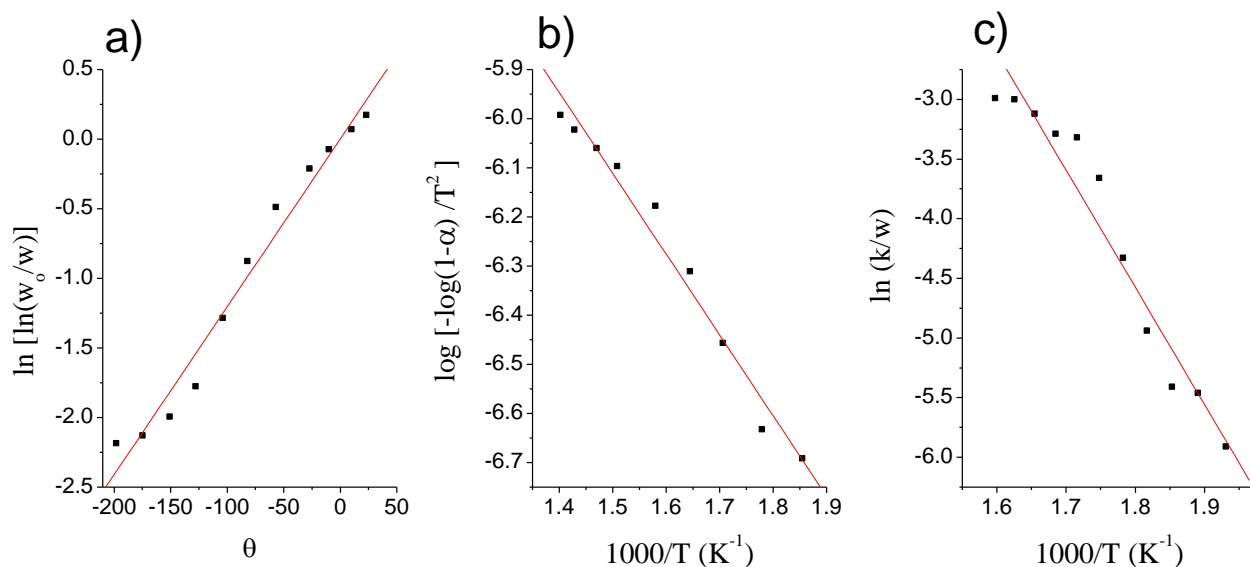
Figure 3: Calculation of activation energy for ANI 7, a) Horowitz and Metzger method b) Coats and Redfern method c) Chan *et al.* method.
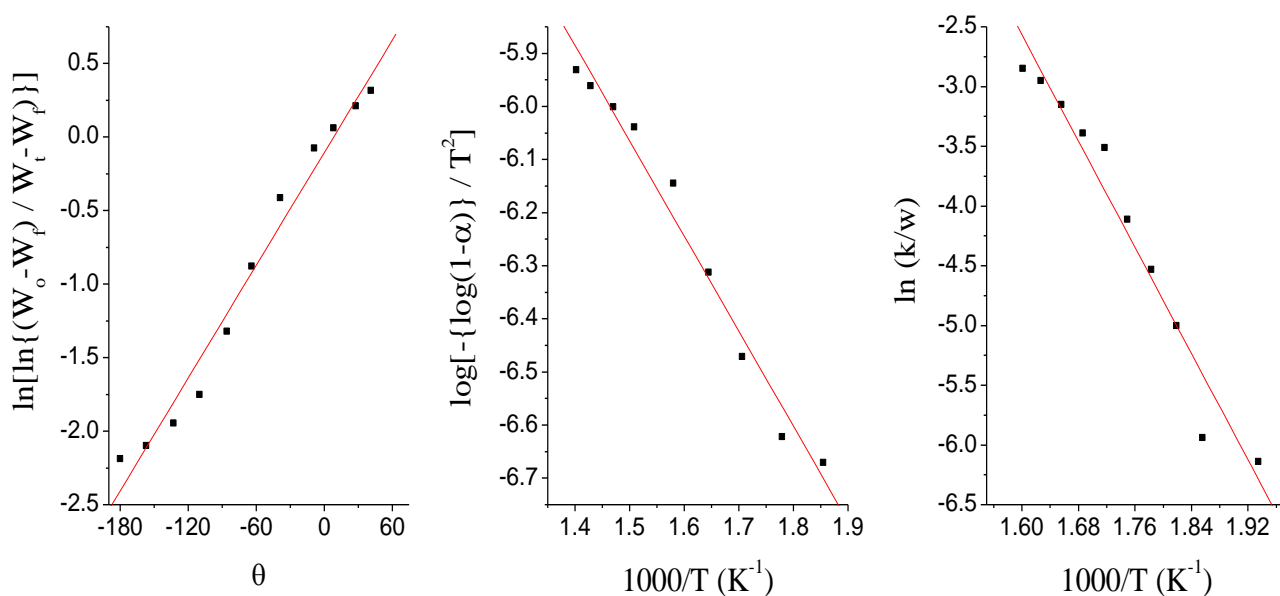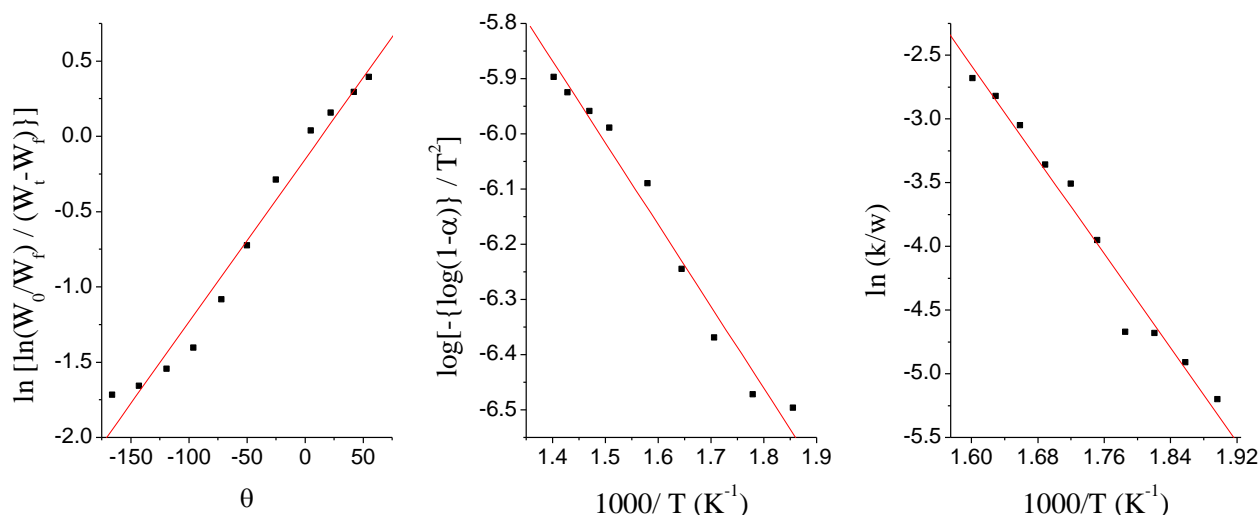

Figure 4: Calculation of activation energy for ANI 9, a) Horowitz and Metzger method b) Coats and Redfern method c) Chan *et al.* method.

Figure 5: Calculation of activation energy for ANI 11, a) Horowitz and Metzger method b) Coats and Redfern method c) Chan *et al*. method.

UV-Vis Spectroscopy of PANI-DBSA

Absorption spectroscopy is a valuable tool to detect the presence of PANI base and its salts. Absorption spectrum of ANI 5 dissolved in chloroform, is shown in Fig. 6. PANI-DBSA shows three peaks at 350, 436 and 795 nm.

The first peak is due to π - π^* transition of benzenoid ring, the second and third peaks are corresponding to the polaron to π^* and π to polaron transition, respectively.[4] These peaks confirmed the conductive emeraldine salt form of PANI.
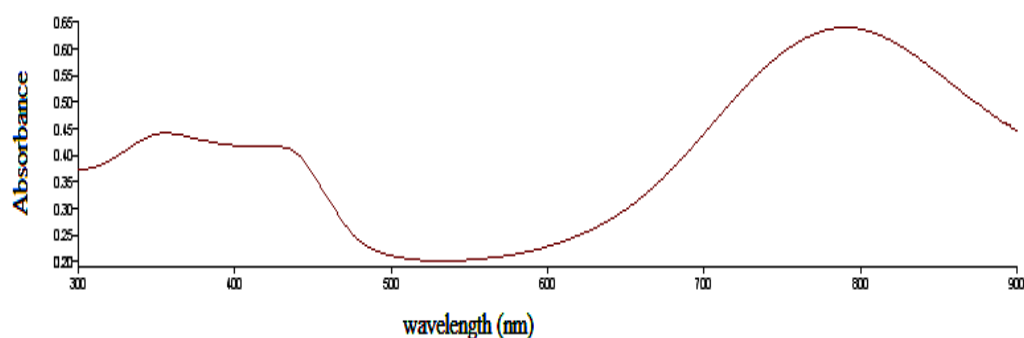
Figure 6: UV-Vis spectrum of PANI-DBSA salts recorded in chloroform

XRD 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 pattern of PANI-DBSA is shown in Fig. 7. The PANI salt

show peaks at 2Θ = 2.5, 19, 20, 25.05 and 27° corresponding to the interface distances d = 34.617, 4.659, 4.425, 3.545 and 3.293 A°, respectively. The peaks from 20 to 27° are attributed to the momentum transfer and periodicity, perpendicular to the chain direction. These

positions are in accordance with the earlier report for polyaniline salts.[40, 41]
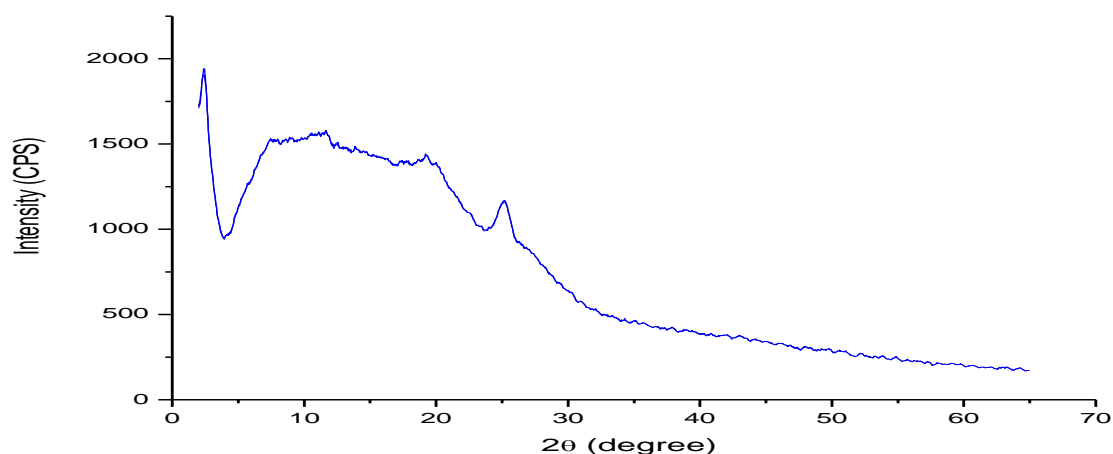

Figure 7: XRD patterns of PANI-DBSA salts

Conclusions

PANI-DBSA salts, soluble in common organic solvents, have been synthesized by inverse emulsion polymerization. The polymerization is carried out in a mixture of chloroform and 2-butanol as a dispersing medium. X-ray diffraction and UV-Vis spectroscopic studies support the formation of PANI-DBSA salt. Detail thermal characterization of the polymer show that it is highly thermally stable and can be used for various high temperature applications.

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