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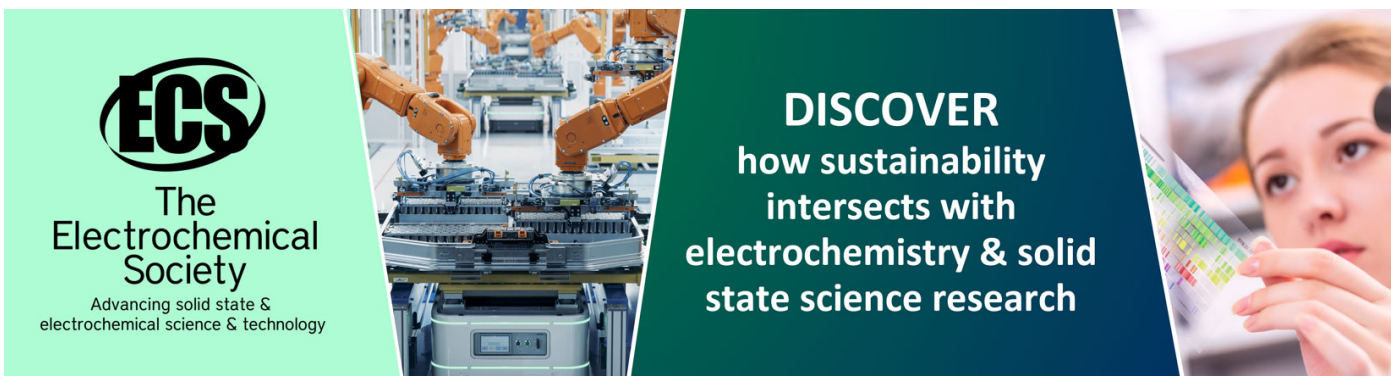
Synthesis and Characterization of Processable Polyaniline Salts

To cite this article: Salma Gul *et al* 2013 *J. Phys.: Conf. Ser.* **439** 012002

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Synthesis and Characterization of Processable Polyaniline Salts

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Abstract

Polyaniline (PANI) is one of the most promising candidates for possible technological applications. PANI has potential applications in batteries, anion exchanger, tissue engineering, inhibition of steel corrosion, fuel cell, sensors and so on. However, its insolubility in common organic solvents limits its range of applications. In the present study an attempt has been made to synthesize soluble polyaniline salt via inverse polymerization pathway using benzoyl peroxide as oxidant and dodecylbenzenesulfonic acid (DBSA) as dopant as well as a surfactant. A mixture of chloroform and 2-butanol was used as dispersion medium for the first time. The influence of synthesis parameters such as concentration of aniline, benzoyl peroxide and DBSA on the yield and other properties of the resulting PANI salt was studied. The synthesized PANI salt was found to be completely soluble in DMSO, DMF, chloroform and in a mixture of toluene and 2-propanol. The synthesized polymer salt was also characterized with cyclic voltammetry, SEM, XRD, UV-Vis spectroscopy and viscosity measurements. 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: PANI-DBSA salt, common organic solvents, SEM, XRD, UV-Vis spectroscopy.

1. Introduction

In 1970s chemists began to prepare a new type of organic polymers which were good electronic conductors [1]. They were called intrinsically conducting polymers (ICPs). Since their discovery a tremendous research has been done in the field because of the interesting properties and numerous application possibilities of these ICPs. Among ICPs, polyaniline (PANI) is found to be the most promising because of its high stability toward air and moisture, high electrical conducting and unique redox properties [2]. It has been widely employed in various areas such as, fuel cells [3], batteries [4], anion exchanger [5], tissue engineering [6], inhibition of steel corrosion [7], sensors [8] and so on. It can be synthesized by oxidizing aniline either electrochemically or chemically. The latter one is of particular importance since this is the most feasible route for the production of PANI on large scale [9].

However, its poor process ability restricts not only its applications but also determination of molecular structure of this polymer. Therefore, several strategies were developed to overcome these shortcomings. These include copolymerization [10-12], use of substituted aniline as monomer [13] and synthesis by emulsion/inverse emulsion polymerization [14]. In first two cases processability increases but conductivity decreases [15]. So the only feasible route is emulsion/inverse emulsion polymerization. In this case aniline (monomer), a protonic acid and an oxidizing agent are combined with a mixture of



water and non polar/ weakly polar solvent such as xylene, chloroform or toluene [16]. But it is seen that at the completion of the reaction the product remains entrain in the emulsion and it is very difficult to collect the PANI in pure form.

In the present work a new inverse emulsion polymerization pathway has been developed to resolve the current limitations of PANI. We introduced a mixture of chloroform and 2-butanol as a novel dispersing medium and polymerization was carried out in the presence of dodecyl benzenesulfonic acid (DBSA) surfactant. This system is unique and simple because after the completion of the reaction, two phases are separated from each other. The organic phase consists of the PANI-DBSA because of its high solubility in chloroform while the aqueous phase consists of byproducts of the reaction such as un-reacted DBSA, 2-butanol and benzoyl peroxide due to their solubility in this phase. The aqueous layer was readily removed from the highly concentrated organic phase. The latter phase was washed several times with acetone for further purification and then it was dried to get highly pure PANI-DBSA in powder form. The synthesized polymers were highly soluble various common organic solvents. The effects of reaction parameters on yield, intrinsic viscosity, morphology, structure, crystallinity of polymers were also investigated. Cyclic voltammetry confirmed the purity and good electroactivity of the polymer. TGA data showed the high thermal stability up to 500 °C.

1. Experimental

1.1. Materials

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

1.2. Methodology

1.2.1. Synthesis of Polyaniline Salt

In a typical experiment 0.29 mol of chloroform was taken in a 100 mL round bottom flask. Then 1.25×10^{-3} mol benzoyl peroxide was added to it under mechanical stirring. To the above solution 0.13 mol of 2-butanol, 3.73×10^{-3} mol DBSA, and 5.36×10^{-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 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 5.36×10^{-4} mol, 7.52×10^{-4} mol, 9.66×10^{-4} mol, 1.18×10^{-3} mol respectively. Similarly, the samples with different amounts of benzoyl peroxide were named as BP 101, BP 303, and BP 505 when the amounts of benzoyl peroxide were 4.17×10^{-4} , 1.25×10^{-3} and 2.08×10^{-3} mol, respectively. DB 12, DB 14 and DB16 represent polymers with 3.73×10^{-3} , 4.35×10^{-3} and 4.97×10^{-3} mol of DBSA respectively.

Percent yield of PANI-DBSA was calculated by using following formula [17].

$$\text{Percent yield} = \frac{\text{weight of PANI - DBSA}}{\text{weight of xM aniline + weight of xM DBSA}} \times 100 \dots \dots \dots (i)$$

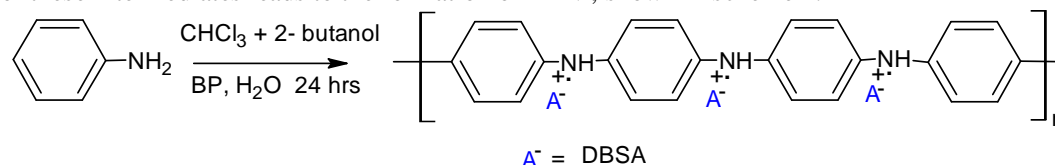
Viscosities of PANI-DBSA were determined using capillary viscometer. Intrinsic viscosity $[\eta]$ was obtained by linearly extrapolating the line of specific viscosity divided by the c (η_{sp}/c) vs c and the line of the natural logarithm of relative viscosity divided by c ($\ln \eta_{rel}/c$) vs c to the same intercept at zero concentration [18].

UV-Vis spectra were obtained using Perkin Elmer 650 (UK) Spectrophotometer. A quartz cell of 1 cm path length was used for recording spectra of different samples of PANI-DBSA dissolved in chloro-

form. Cyclic voltammograms (CVs) were recorded with bipotentiostat 2323 (ALS) in 0.5 M H₂SO₄ at a scan rate of 50 mV/s in a three electrode cell at scan rate of 50 mV/s. PANI-DBSA was dissolved in chloroform and dip coated on gold disc which was used as a working electrode. The reference electrode was saturated calomel electrode and a gold wire was used as counter electrode. CVs were obtained by scanning the potential from $E_{SCE} = -0.3$ V to $E_{SCE} = 1.0$ V. The morphology of PANI-DBSA was investigated by using JSM5910 (JEOL Japan) scanning electron microscope. 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 K radiations of wavelength 1.5405 Å with a continuous scan speed of 0.05°/s. Thermal analysis of the polymer was carried out by using Diamond Series TG/DTA Perkin Elmer (USA) at a heating rate 10°/min in N₂ atmosphere.

2. Results and Discussion

There have been several reports on the polymerization mechanism of polyaniline [19, 20]. 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. Continuous combination of these intermediates leads to the formation of PANI, shown in scheme 1.



Scheme 1. Molecular structure of PANI-DBSA

3.1 . Yield of PANI-BDSA

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 yield obtained, attained a maximum value at 5.36×10^{-4} mol and then decreased with further increasing the monomer concentration. Similar observations were obtained with benzoyl peroxide and surfactant concentration (Table 1). The observed change in the yield of the product with different parameters may be due to overoxidation process or may be that the kinetic effects were favored in the oxidation of aniline [21].

Table 1. % yield of PANI-DBSA

S.No.	Sample	% Yield
1	ANI 3	0
2	ANI 5	21
3	ANI 7	9.91
4	ANI 9	9.7
5	ANI 11	8.58
6	BP 101	0
7	BP 303	21
8	BP 505	0
9	DB 12	21
10	DB 14	15.3
11	DB 16	16.2

3.2. Solubility

It has been demonstrated that PANI doped by large sized organic sulfonic acids, such as DBSA have a good solubility and processibility in common organic solvents. It is due to the enlarge interchain distance, which means weaker interchain reaction, and strong interaction between dopant and solvent [22]. In the present work the synthesized PANI-DBSA is soluble in mixture of toluene and 2-propanol, chloroform, DMSO and DMF.

3.3. Intrinsic Viscosity

The intrinsic viscosities of PANI-DBSA prepared at different aniline concentrations are given in table 2. It was observed that intrinsic viscosity of PANI-DBSA decreased with increasing monomer concentration in the order of ANI 5 > ANI 7 > ANI 9 > ANI 11. The high intrinsic viscosity of PANI-DBSA was 32.09mL/g for ANI 5. The dropping trend in the intrinsic viscosity is viewed as a direct consequence of rapid lowering in initiator efficiency [23].

Table 2: Change of Intrinsic Viscosity with change in monomer concentration

S. No	Sample	Intrinsic viscosity [η] (mL/g)
1	ANI 5	33.43
2	ANI 7	24.96
3	ANI 9	21.77
4	ANI 11	19.31

3.4. UV-Vis Spectroscopy

Absorption spectroscopy is a valuable tool to detect the presence of polyaniline salt (conducting state) and its base (insulating state). Absorption spectra of PANI-DBSA dissolved in chloroform are shown in Fig. 1. All the spectra showed three peaks in the range of 349-360, 433-436, and 782-810 nm. The first absorption bands arises from $\pi - \pi^*$ electron transition within benzenoid (B) ring, the second and third absorption bands are attributed to the polaron transition (quinoid, Q) and bipolaron transition (exciton) respectively. The last two bands relate to the doping level and formation of polaron lattice, which represent the protonation stages of PANI chain. The last bands are usually ascribed to an exciton, located in the quinoid ring, ascribing from charge transfer from adjacent benzenoid rings with each side contributing half an electron on average [24, 25]. All these bands are characteristics of PANI salt.

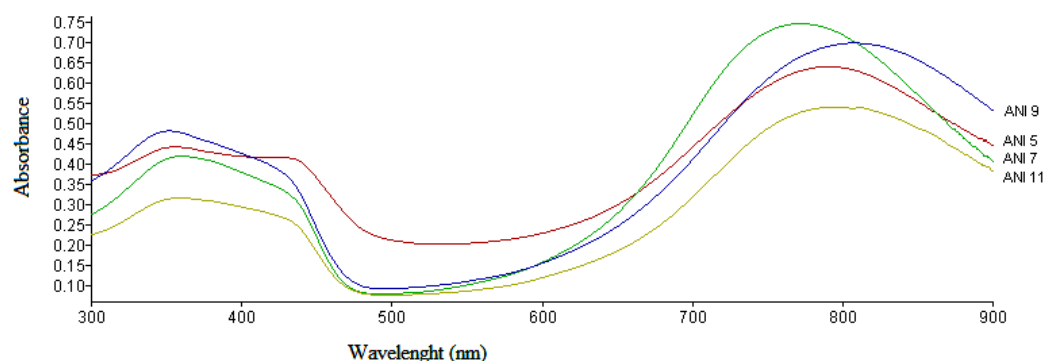


Fig. 1: UV-Vis spectra of PANI-DBSA salts recorded in chloroform solvent

3.4.1. Extent of doping

The extent of doping can be estimated from the absorption spectra of PANI in which the exciton (π -polaron transition)/ benzenoid (π - π^* transition) ratio indicates the doping level [26]. It is seen from table 3 that ANI 5 has the biggest ratio among all sample which means that doping level of ANI 5 is higher as compared to other samples of the synthesized PANI-DBSA. These results show that the concentration of aniline plays an important role in the synthesis of PANI-DBSA.

Table 3: Absorption ratio exciton/benzenoid (E/B) for different samples of PANI-DBSA

1	ANI 5	2.27
2	ANI 7	2.24
3	ANI 9	2.24
4	ANI 11	2.25

3.5. Cyclic Voltammetry

The redox property of the synthesized PANI-DBSA was investigated by cyclic Voltammetry. Fig.2. shows the representative CV of ANI 5. It shows two redox peaks. The first redox peak around $E_{SCE} = 0.2$ V is assigned to the transition of leucoemeraldine to emeraldine state and the second peak around $E_{SCE} 0.6$ V is due to the emeraldine to Pernigraniline transition. These peaks confirmed the electroactivity of the synthesized polymer [27].

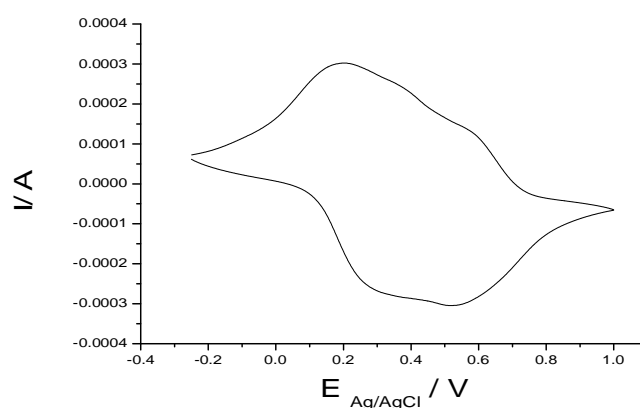


Fig.2. Cyclic voltammogram of ANI 5.

3.6. 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 patterns of ANI5 are shown in Fig. 3 and the value of 2θ and d spaces are given in table 4. The peaks from 20° to 27° are ascribed to the momentum transfer and periodicity and perpendicular to the chain direction [28, 29]. The peaks at $2\theta \approx 19^\circ$ and another one at $2\theta \approx 25^\circ$ are characteristics of van der waals distances between aliphatic chain and between stakes of phenylene rings respectively [30, 31]. The peak at 2.5° showed the well organized layered structure in which stacks of charged aniline backbone are uniformly spaced by the alkyl tails of DBSA [32]. All peaks are observed at lower value of 2θ indicating the better crystallinity [33].

Table 4. A comparison of the major peaks of XRD patterns for PANI-DBSA salts

Peak Number	ANI 5	
	2θ (degree)	d (\AA)
1	2.5	34.617
2	19	4.659
3	20	4.425
4	25.05	3.545
5	27	3.293

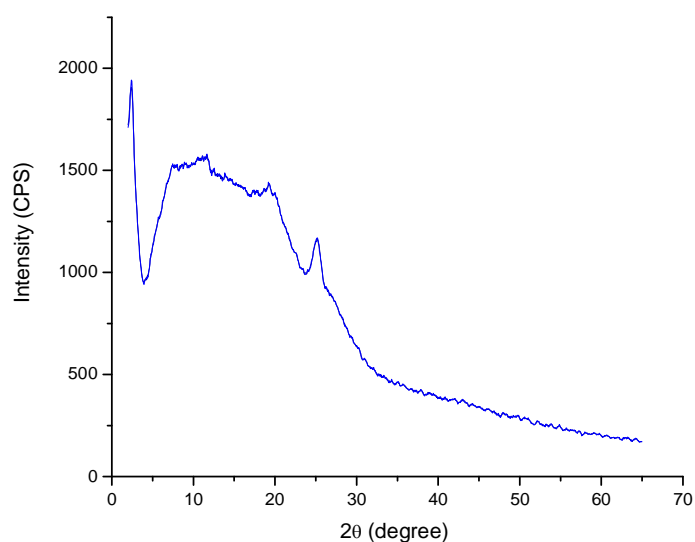


Fig. 3. XRD pattern of ANI 5

3.7. SEM of PANI-DBSA

Fig.4 demonstrates the scanning electron micrographs of PANI-DBSA prepared with different concentrations of aniline. These show granular morphology of the polymers, which is often been reported [34, 35]. It has been assumed that during polymerization phanazine nucleates associate randomly to produced granular structures of PANI. The reasons for such type of associations are high concentration and reduced solubility of these nucleates. Random associations also happen when the conversion rate of phanazine nucleate to initiation centers (to start PANI growth) is very fast and thus PANI chains grow before the organization of phanazine nucleates [36].

All these images show irregular shapes with no significant change in the morphology which indicate that change in concentration of monomer does not have an effect on the morphology, of resulting PANI. However, their porosity increased with increase in aniline concentration and can be used as bi-sensors [37].

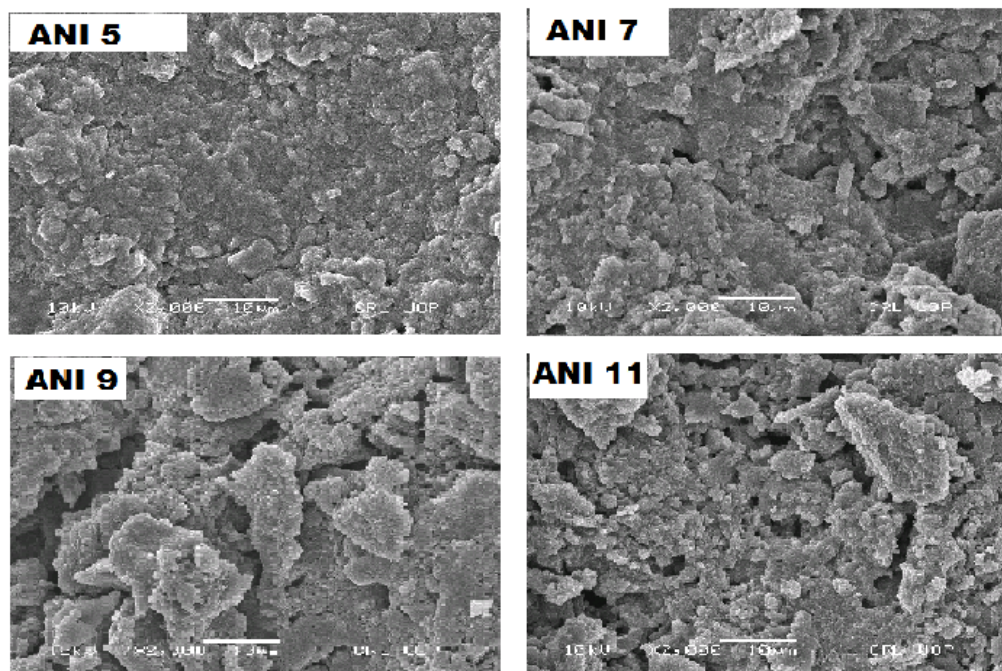


Fig. 4: SEM pictures of PANI-DBSA salts

3.8. 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 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 [38]. The second step weight loss being in the range 48-66%, is attributed to destroy of the $\text{NH}^+ \dots \text{SO}_3^-$ interaction between the PANI chain and the DBSA dopant with degradation of DBSA [39]. A slow and somewhat gradual weight loss was observed for these polymers at around 500 °C is due to the structure decomposition of PANI backbone. The weight loss of DBSA doped polymers are almost proportional to their percentage weight of dopant and attributed mainly to a dopant loss. The PANI-DBSA salts were not completely destroyed because in nitrogen atmosphere carbonization of polymer takes place leaving a marked residue [40]. These results show that DBSA doped PANI material is highly stable and can be used for various high temperature applications.

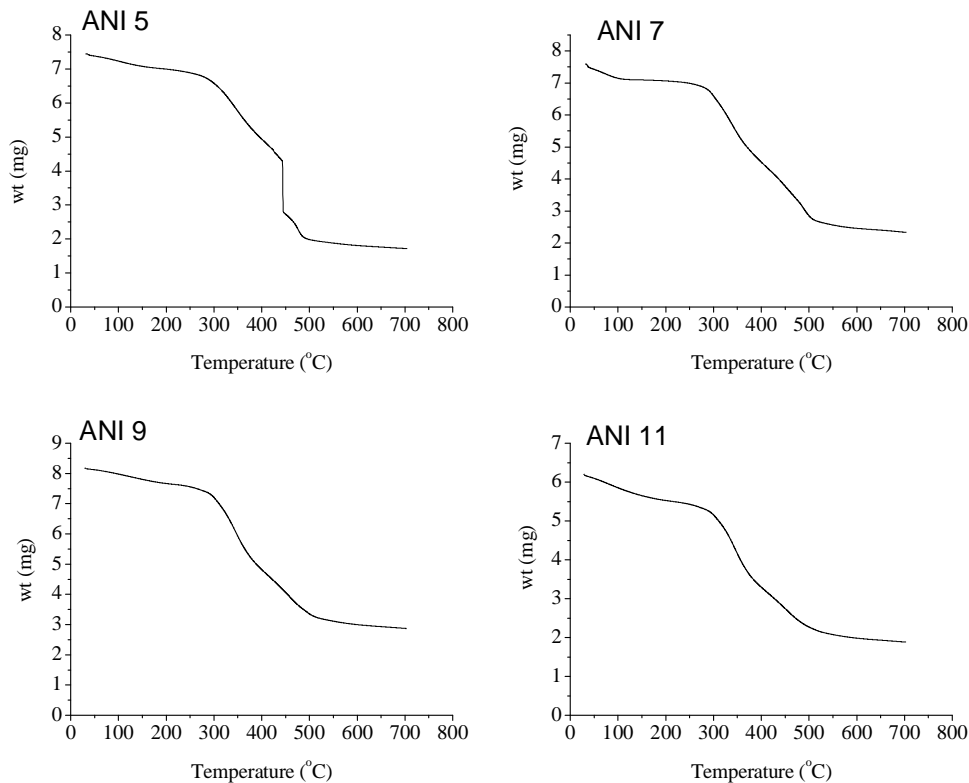


Fig. 5. TGA Thermograms of PANI-DBSA

3.8.1. Activation Energy for the Degradation of PANI-DBSA

The following method was used to evaluate kinetic parameters for degradation of PANI-DBSA by assuming first order kinetics [41].

3.8.1.1. Horowitz and Metzger method

Horowitz and Metzger [42] obtained following equation:

$$\ln[\ln \{(W_o - W_f) / (W_t - W_f)\}] = E_a \theta / RT_s^2 \dots\dots\dots (1)$$

Where

- W_o = initial weight of the sample
- W_f = final weight of the sample
- W_t = the weight of the sample at temperature t
- R = gas constant
- θ = T - T_s
- T_s is the reference temperature

From the slope (-E_a/R) of this plot activation energy 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 tabulated (Table 5). The E_a for the degradation is the highest for ANI 9 and is thermally more stable.

Table 5. Activation energy (E_a in kJ/mol) for PANI-DBSA as a function of monomer (Aniline) concentration

S. No	Sample	Activation energy (kJ/mol)
1	ANI 5	46.16
2	ANI 7	47.77
3	ANI 9	47.94
4	ANI 11	38.91

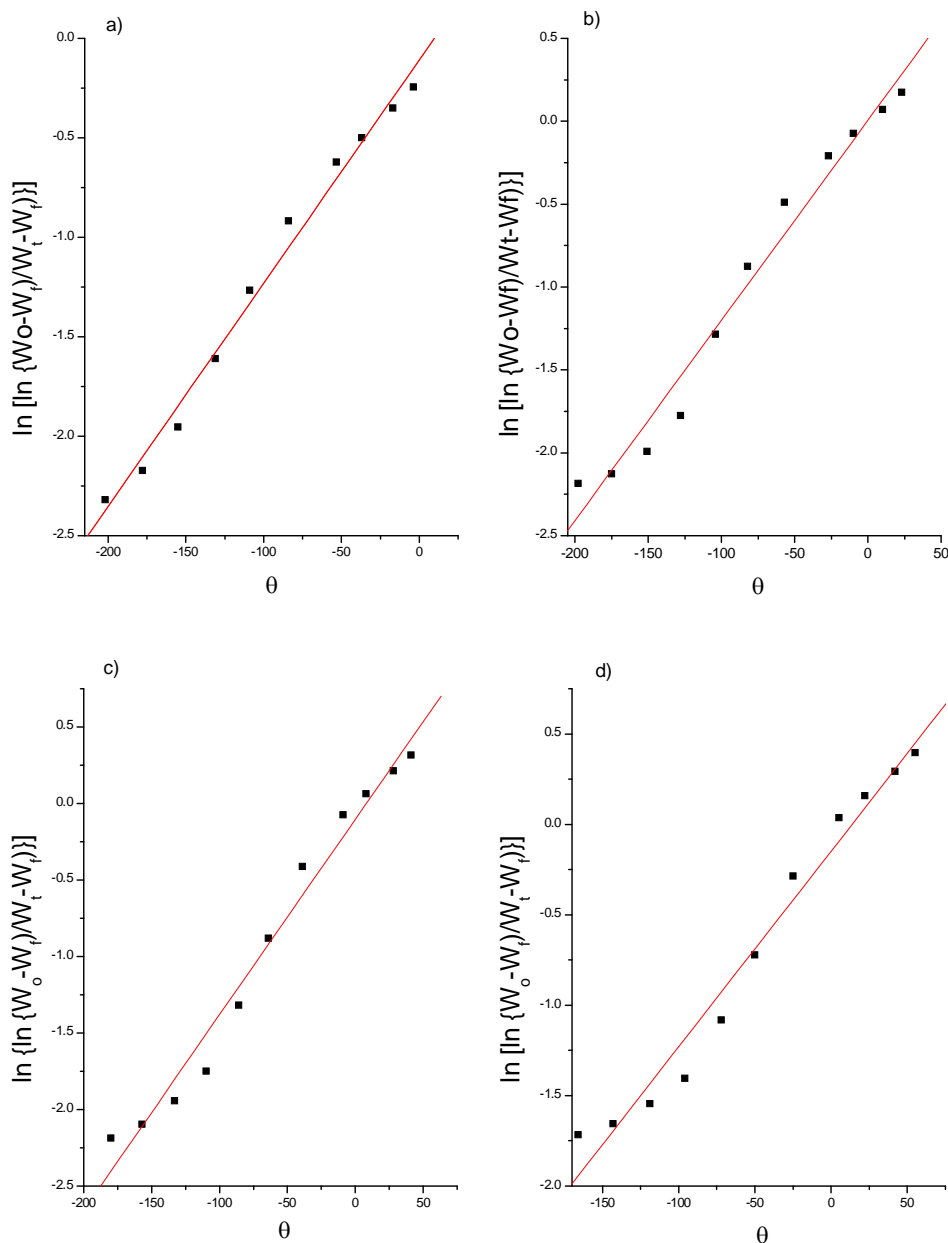


Fig. 6: Calculation of activation energy for a) ANI 5, b) ANI 7, c) ANI 9 d) ANI 11

Conclusions

PANI-DBSA salts were successfully prepared via inverse emulsion polymerization. These salts were soluble in so far highest number of common organic solvents. It was found that intrinsic viscosity decreases with increase in monomer concentration in the feed. The results of TGA reveal that the prepared polymers were thermally stable and can be used in various technologies.

Acknowledgement

National centre of Excellence in Physical Chemistry, University of Peshawar is gratefully acknowledged for research facilities and financial support.

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