Volume : 2 | Issue : 11 | November 2013 • ISSN No 2277 - 8179

Research Paper

Calorimetric and Thermogravimetric Studies in Para Tolune Sulphonic Acid (PTSA) Doped Polyaniline

Physics

KEYWORDS : Polyaniline, PTSA, Thermogravimetric, Differential Scanning Calorimetric

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ABSTRACT

Conducting polyaniline (PANI) has been synthesized using oxidative chemical polymerization method containing para-Toluene Sulphonic Acid (PTSA) as a dopant and ammonium per sulphate as an oxidising agent. The prepared emeraldine salt (conducting) form was investigated by thermogravimetric (TGA) and differential scanning calorimetric (DSC) studies. The TGA studies show that the polymer is thermally stable up to 200^{o}C. Above this temperature the degradation of the sample starts due to the evaporation of the dopant. Above 600oC, the polymer degrades rapidly. The DSC analysis for the three doped samples shows two endothermic peaks at around 75^{o}C can be assigned to the expulsion of moisture from the sample. The second endothermic peak at around 275^{o}C-310^{o}C is due to the thermal degradation of the material.

Introduction

Polyaniline is a typical phenylene based polymer having a chemically flexible –NH– group in the polymer chain flanked either side by phenylene ring ('Handbook of ….'). The protonation, deprotonation and various other pysico-chemical properties of polyaniline are due to the presence of this –NH– group ('Handbook of ….'). Polyaniline is the oxidative polymeric product of aniline under acidic conditions and has been known since 1862 as aniline black (Letheby, 1862). Willstatter and co-workers (Willstatter et al, 1907 and Willstatter et al., 1909) in 1907 and 1909 regarded aniline black as an eight-nucleus chain compound having an indamine structure. However in 1910 Green and Woodhead (Green A.G. et al.,1910) were able to report various constitutional aspects of aniline polymerization and the conclusions of their study were as follows.

1. There are four quinoid stages derived from the parent compound leucoemeraldine.
2. The minimum molecular weights of these primary oxidations of aniline are in accordance with an eight-nucleus structure.
3. The conversion of emeraldine into nigraniline consumes one atom of oxygen.
4. The conversion of emeraldine into perinigraniline consumes two atoms of oxygen.
5. The conversion of nigraniline into perinigraniline consumes one atom of oxygen.
6. The reduction of emeraldine to leucoemeraldine consumes four atoms of hydrogen.
7. The reduction of nigrinaline to leucoemeraldine consumes six atoms of hydrogen.
8. The reduction of perinigraniline to leucoemeraldine consumes eight atoms of hydrogen.

Almost 50 years later, Surville *et al.* (Surville R. et al., 1968) in 1968 reported proton exchange and redox properties with the influence of water on the conductivity of polyaniline. However, interest in polyaniline was generated only after the fundamental discovery in 1977 that iodine-doped polyacetylene has a metallic conductivity (Shirkawa H. et al., 1977) which triggered research interests in new organic materials in the hope that these would provide new and improved electrical, magnetic, optical material or devices. The hope was based on electronic structure and the combination of the metal-like or semiconducting conductivity with the processibility and flexibility of classical polymers and, above all, ease with which structural modification can be carried out via synthetic organic chemistry methodologies ('Handbook of ….').

From the thermo-gravimetric and differential scanning calorimetric studies, it is found that the degradation process of poly-aniline occurs in two or three steps being attributed to the expulsion of water, removal of dopant and also the breakdown of the polymer backbone. Also the TGA/DSC studies give some important information regarding the structure of polyaniline, when subjected to a controlled heating. Thermo-gravimetric (TGA) and Differential scanning calorimetry (DSC) were used in this work to study the behaviour of emeraldine salt of chemically doped polyaniline (PANI-ES).

3. Experimental

2.1. Synthesis of emeraldine salt

9 ml aniline (0.1 M) was taken in a round bottom flask containing 150 ml of distilled water and 10 ml of concentrated hydrochloric acid. 11g (0.05M) of ammonium persulphate was dissolved in 100 ml of distilled water, and then added drop-wise to a stirred solution of 0.1 M of aniline dissolved in hydrochloric acid, pre cooled to 0 – 5^{o}C. Ammonium peroxy disulphate solution is added very slowly with constant stirring. After completion of the addition, stirring is continued for 2-3 hours to ensure completion of the reaction.

The precipitated emeraldine salt is filtered and washed with distilled water until the filtrate is colourless. The precipitate is then washed with methanol to remove oligomeric impurities. Finally it is washed with acetone, to remove water content, and kept overnight for filtering. The precipitate is collected in a beaker and dried under dynamic vacuum at 70^{o}C for 6 hours. The dried precipitate is then crushed into fine powder to get emeraldine salt.

2.2. Preparation of emeraldine base

The prepared emeraldine salt (powder form) was taken in a round-bottomed flask containing 20 ml of ammonia solution and 80 ml of water, and was stirred continuously for 24 hours. The precipitated blue emeraldine base is filtered and washed with distilled water, methanol and finally with acetone. After keeping over night for filtering, the precipitates are collected and dried under dynamic vacuum at 70^{o}C for 6 hours. The dried precipitate is then crusted in to fine powder to get emeraldine base.

2.3 Emeraldine Base Doped With Para Toluene Sulphonic Acid (PTSA)

In the present study, para toluene sulphonic acid (PTSA) was used as dopant. PANI–(PTSA)$_{y}$ was prepared in three different doping levels (y = 0.1, 0.3 and 0.5). PANI–(PTSA)$_{0.5}$ was prepared by a thorough mixing of 0.012 M emeraldine base PANI with 0.006 M paratoluene sulphonic acid (PTSA) using a glass mortar and pestle. PANI–(PTSA)$_{0.3}$ was prepared by mixing of 0.012 M emeraldine base PANI with 0.0036M PTSA, as explained above. For the preparation of PANI–(PTSA)$_{0.1}$, 0.012 M emeraldine base PANI was mixed with 0.0012M PTSA.

4. Result and Discussion

Polyaniline doped with hydrochloric acid (HCl) was prepared by chemical oxidative polymerization of aniline (ANI) in aqueous medium with ammonium peroxy disulphate as an oxidant. In the presence of oxygen, aniline undergoes polymerization rapidly and leads to the formation of scum like product. The deprotonation of the PANI: HCl samples were performed by stirring the PANI: HCl powder (emeraldine salt) in 0.1 M aqueous so-

Volume : 2 | Issue : 11 | November 2013 • ISSN No 2277 - 8179

lution of ammonium hydroxide for 24 hours at room temperature, thus obtaining the polymer in the emeraldine base form. The redoping of the PANI (emeraldine base) with para toluene sulphonic acid was performed by mixing emeraldine base (EB) with Para Toluene Sulphonic Acid (PTSA) using a glass mortar and pestle to obtain the required doping levels (Y = 0.5,Y =0.3,Y =0.1), known as the molar ratio of TSA to phenyl-nitrogen repeat units (S/N).

3.1 Differential Scanning Calorimetry (DSC) Measurements

The thermal behaviour of the PTSA doped PANI at different doping levels (Y = 0.5, Y = 0.3 and Y = 0.1) investigated by DSC are shown in Figs. 1, 2 and 3. Fig. 1 shows the DSC curve for PANI–$(PTSA)_{0.5}$. There are two endothermic peaks at around 75°C and 275°C. The first one can be attributed to the expulsion of moisture from the sample, and the second one is due to the thermal degradation of the material. Fig. 2 shows the DSC curve for PANI – $(PTSA)_{0.3,}$ which shows two endothermic peaks at around 75°C and 290°C, due to expulsion of moisture from the sample, and due to the thermal degradation of the material, respectively. In the case of PANI – $(PTSA)_{0.1}$, these peaks are observed at 75°C and 310°C, respectively, as can be seen from Fig.3. This clearly shows that the thermal stability is better for the PANI – $(PTSA)_{0.1}$.

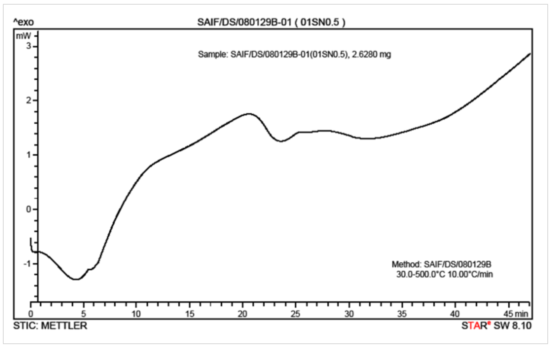

Fig.1 DSC Curve of PANI – $(PTSA)_{0.5}$

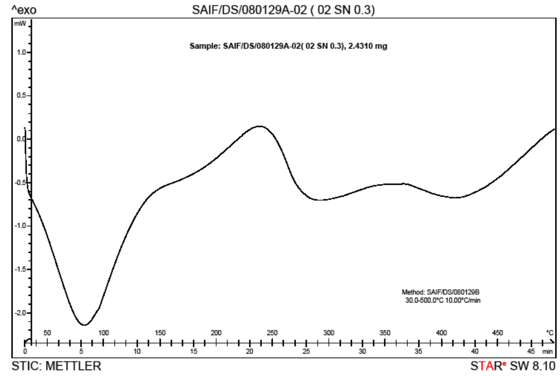

Fig.2 DSC Curve of PANI – $(PTSA)_{0.3}$

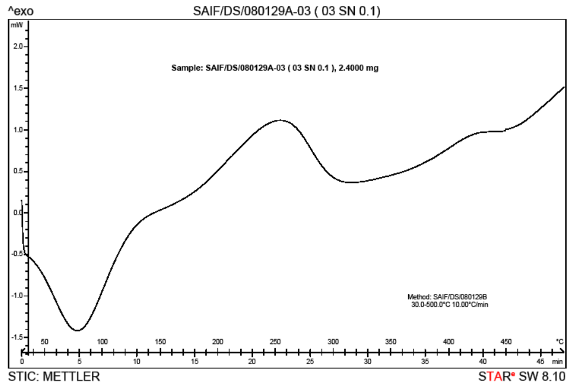

Fig.3 DSC Curve of PANI – $(PTSA)_{0.1}$

4.1 Thermo-Gravimetric (TGA) measurements

The thermal behaviour of the PTSA doped PANI at different doping levels (Y = 0.5, Y = 0.3 and Y = 0.1) investigated by TGA are shown in Figs. 4, 5 and 6. The interaction between the polymers can also be noted from the oxidative degradation curves through thermo gravimetric analysis (TGA) studies. The degradation of PANI occurs in three stages. The first stage is the loss of absorbed moisture and solvent from the room temperature to around 150°C. The second stage, occurring between 150°C and 350°C is due to the loss of acid dopant in PANI salt. The final degradation of the polymer occurs from 350°C to 650°C.

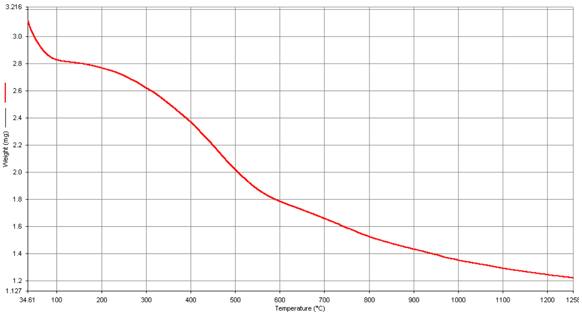

Fig.4 TGA Curve of PANI – $(PTSA)_{0.5}$

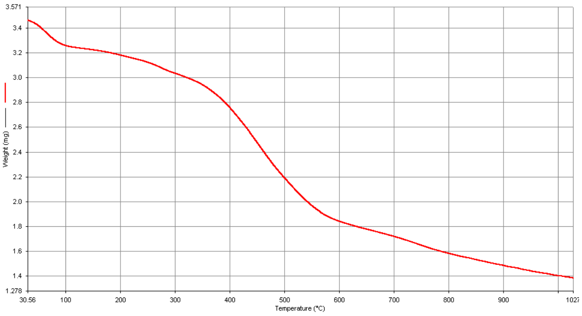

Fig.5 TGA Curve of PANI – $(PTSA)_{0.3}$

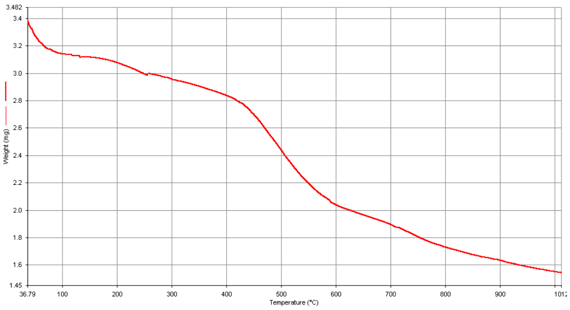

Fig.6 TGA Curve of PANI – $(PTSA)_{0.1}$

The TGA curve (Fig. 4) for PANI – $(PTSA)_{0.5}$ shows an initial weight loss up to 100°C, due to the loss of water or moisture from the polymer. The polymer is thermally stable up to 150°C. The second stage observed within the temperature range of 200°C – 400°C is related to removal of dopant molecules from the polymer structure. The weight loss observed between 500°C and 600°C after the removal of the dopant molecule corresponds to the degradation of the polymer chain. Above 600°C, the polymer degrades rapidly.

The TGA curve (Fig. 5) for PANI – $(PTSA)_{0.3}$ shows an initial weight loss up to 100°C, due to the loss of water or moisture from the polymer. The polymer is thermally stable up to 200°C. The second stage observed within the temperature range of 200°C – 400°C is related to removal of dopant molecules from the polymer structure. The weight loss observed between

450°C and 600°C after the removal of the dopant molecule corresponds to the degradation of the polymer chain. Above 600°C, the polymer degrades rapidly.

The TGA curve (Fig 6) for PANI – $(PTSA)_{0.1}$ shows an initial weight loss up to 100°C, due to the loss of water or moisture from the polymer. The polymer is thermally stable up to 200°C. The second stage observed within the temperature range of 200°C – 400°C is related to removal of dopant molecules from the polymer structure. The weight loss observed between 450°C and 600°C after the removal of the dopant molecule corresponds to the degradation of the polymer chain. Above 600°C, the polymer degrades rapidly.

5. Conclusions

The TGA curve of the three doping levels shows an initial weight loss up to 100°C is due to the loss of water or moisture from the polymer. The polymer is thermally stable up to 200°C. The second stage observed within the temperature range of 200°C – 400°C is related to removal of dopant molecules from the polymer structure. The weight loss observed between 450°C and 600°C after the removal of the dopant molecule corresponds to the degradation of the polymer chain. Above 600°C, the polymer degrades rapidly.

The DSC curve for the three doped samples shows two endothermic peaks at around 75°C can be assigned to the expulsion of moisture from the sample. The second endothermic peak at around 275°C-310°C is due to the thermal degradation of the material.

6. Acknowledgement

We are thankful to the Karpagam University for giving the facilities for the preparation of the samples. Also, we are thankful to Dr. Premnazeer, Principal of Islamiah College, Vaniambadi for his help and fruitful discussions.

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