

Thermal Stability Studies of Electrochemically Prepared Polyaniline Using Thermal Gravimetric Analysis

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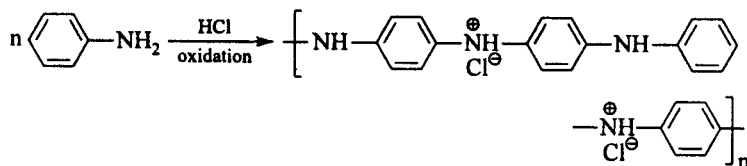
In the current thermal studies, polyaniline (PAn) was prepared electrochemically in the presence of HCl, H₂SO₄ and *p*-toluene sulfonic acids. Thermal stabilities of polymers were then studied using TGA technique. It was found that polymer prepared by cyclic voltammetry method (CV) is more thermally stable than those prepared by constant potential (CP) method. It was also found that the nature of dopant acid has a great effect on thermal stability of the PAn.

Key Words: Thermal Stability, Polyaniline, TGA.

INTRODUCTION

Thermal studies on conducting polymers not only facilitate a fundamental understanding of their properties but also assist in the determination of the limitations and practical applications of these materials. Thermal gravimetric analysis (TGA) has been found one of the most useful techniques for evaluating the onset of thermal decomposition temperature and determining thermal stability of conducting polymers. Among conducting polymers, a great deal of researches have been devoted to polyaniline (PAn) due to its unique electrical, electrochemical properties, good environmental stability, easy polymerization from aqueous solutions (unlike most conducting polymers) and low cost of monomer¹⁻⁴. Polyaniline films can be easily synthesized by chemical oxidants or electrochemical deposition through oxidation of aniline in the presence of non-oxidizing bronsted acids⁵⁻⁷. For many practical applications of polyaniline conducting polymers such as battery applications, the thermal stability of the material is very important⁸.

Polymerization reaction of PAn can be simply shown as:



The oxidation process is accompanied by the insertion of anions of acid electrolyte in order to maintain the charge neutrality of the final polymer. However, PAn in contrast to polypyrrole conducting polymers could not be prepared as free standing film electrochemically. Electrochemically prepared PAn has lower conductivity, a powdery appearance and easily wipes off the electrode surface.

EXPERIMENTAL

A three electrode electrochemical cell was used to prepare PAN conducting polymers used in these studies⁴. Electropolymerization of polyaniline was carried out using 0.4 M of freshly distilled aniline in a solution of 1 M selected acids. A constant potential (0.80 V vs. Ag/AgCl) and potentiodynamic method (scanning the potential between -0.2 and +0.900 V, scan rate 20 mV/sec) was employed. Platinum plate was employed as working electrode, platinum (gauze) was used as the auxiliary electrode and an Ag/AgCl in 3 M NaCl electrode was used as the reference throughout this work. Electropolymerization was carried out at room temperature. Polymer powder was removed from the electrode and washed completely with distilled water. The samples were dried under ambient conditions before thermal gravimetric analysis.

For the potentiodynamic (CV) growth of PAN, electropolymerization was carried out using a BAS CV-27. Alternatively, a Princeton Applied Research (PAR) Potentiostat/Galvanostat (Model 363) was employed for potentiostatic deposition of PAN. Thermal gravimetric analysis (TGA) was carried out using a Rigaku thermal analyzer instrument. The analyses were conducted on 10 mg samples of polymer heated from room temperature to 500°C.

RESULTS AND DISCUSSION

For electrochemical deposition of PAN, the growth potential of polyaniline was first determined using cyclic voltammetry (CV) method (Fig. 1). Polymer samples were prepared employing the potentiostatic or CV methods because of the greater control which can be achieved over the electrode potential. From the CV recorded during electrodeposition, it was found that a suitable potential for potentiostatic (CP) growth of polymer was found 0.8 V (Fig. 1). Below this potential, the rate

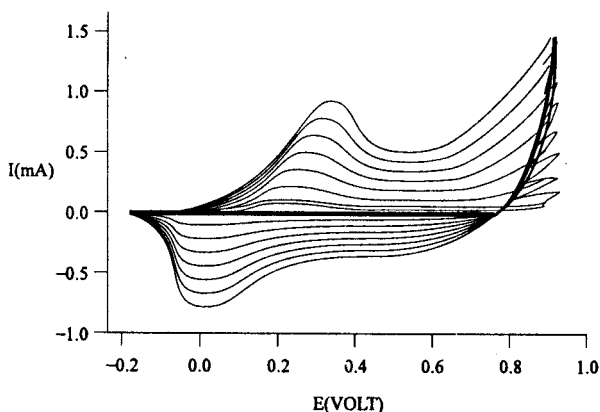


Fig. 1. Cyclic voltammograms (CV) recorded during growth for polyaniline. Scan rate = 20 mV/sec. Electropolymerisation was carried out using a solution of 0.4 M aniline in 1 M HCl.

of oxidation was too low. Anodic polarization at potentials more than 0.85 V causes oxidation leading to gradual degradation of polymer film. Cyclic voltammogram (CV) of polyaniline prepared electrochemically is shown in Fig. 2.

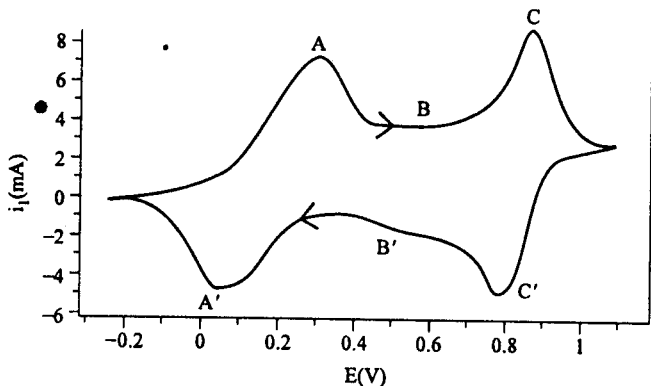
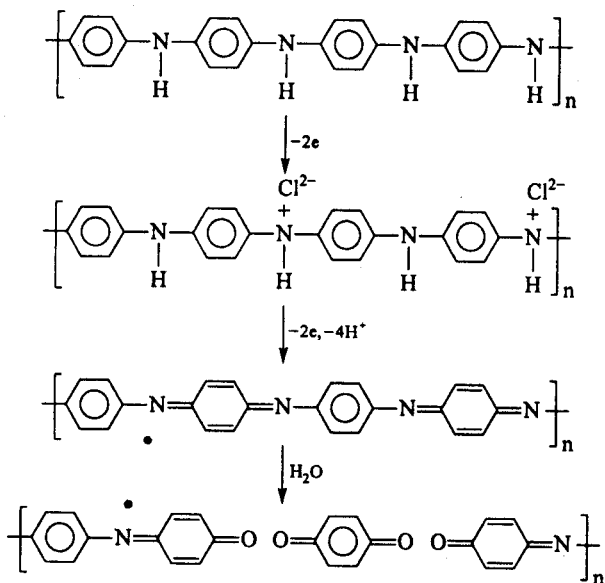
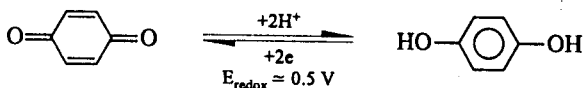


Fig. 2. Typical cyclic voltammogram (CV) of polyaniline synthesized electrochemically ($E_{app} = 0.80$ V vs. Ag/AgCl) from a solution of 0.4 M aniline and 1 M HCl. CV was recorded after growth in 1 M HCl as supporting electrolyte. Glassy carbon was used as the working electrode. Scan rate was 20 mV/s.

The responses observed (A/A') and C/C') are due to the reactions described in the following equations⁹:



The middle peak (B/B') ca. 0.5 V in the cathodic scan can be related to the formation of quinones (mostly benzoquinone) as a consequence of a hydrolysis reaction in water¹⁰.



Upon electrochemical doping, delocalized positive charges form along the PAN chains. Electroneutrality is maintained by the incorporation of anions from solu-

tion¹¹. Initial electrochemical responses occur without loss or gain of protons; however, the second electrochemical response involves protonation and deprotonation. When polyaniline (PAN) is employed as a practical material in applications using its electrochemical redox processes, non-aqueous systems have been found more effective than aqueous systems since hydrolysis can be minimized¹².

Simultaneous measurement of the resistance of polyaniline during cyclic voltammetry analysis showed that PAN is less conductive in the fully reduced and fully oxidized states. It is conductive when it is partially oxidized and is the most conductive state when it is 50% reduced and 50% oxidized.

TGA of polyaniline

The thermograms (a plot of mass vs. temperature) obtained for PAN/HCl prepared by constant potential (CP) and cyclic voltammetry methods (CV) are shown in Figs. 3 and 4. A three step decomposition process for the protonated conducting is observed for both CP and CV produced acid doped polymers, three separate stages of weight loss were observed under N₂. The first continues weight loss that is observed above room temperature may be attributed to loss of moisture, free HCl and unreacted monomer. The second may be attributed to loss of dopants from deeper sites in the material. At more extreme temperatures (the third weight loss) degradation of the polymer backbone occurs.

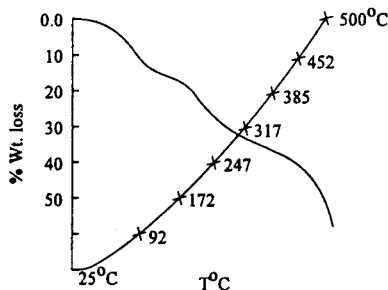


Fig. 3. Thermal gravimetric analysis of PAN prepared potentiostatically (CP) at 0.8 V. A heating rate of 10°C/min was employed throughout this work unless otherwise stated. The experiments were performed under nitrogen atmosphere. The flow rate of N₂ gas over the samples was 80 mL/min.

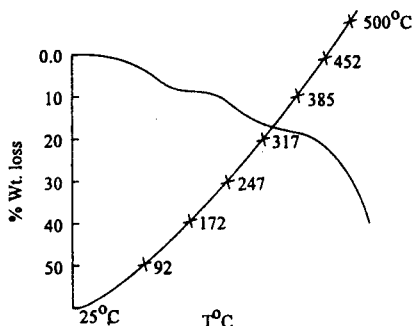


Fig. 4. Thermogram of PAN/HCl prepared by CV method. The TG analysis conditions were the same as used in Fig. 2.

According to our TGA results, the temperatures required for degradation were slightly higher for samples prepared using the CV method. It may be concluded that PAN conducting polymers synthesized by CV method are more thermally stable than those prepared by CP methods. It was also observed that cyclic potential sweep deposition produces more adherent films with higher structural integrity than potentiostatic deposition. The thermograms obtained for PAN/H₂SO₄ and PAN/HPTS are shown in Figs. 5 and 6.

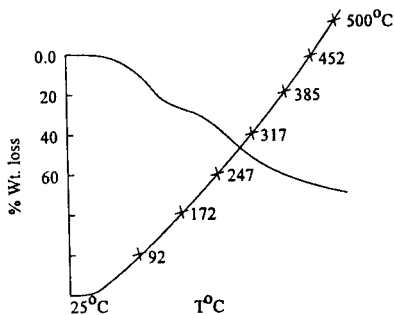


Fig. 5. Thermogram of PAN/H₂SO₄. The TGA conditions were the same as used in Fig. 3.

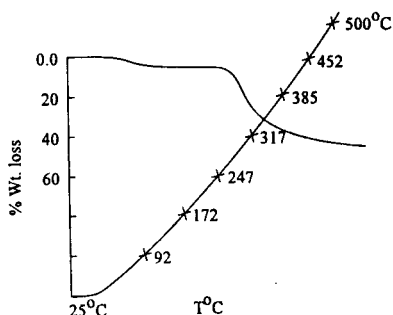


Fig. 6. Thermogram of PAN/HPTS. The TGA conditions were the same as used in Fig. 3.

The initial weight loss observed in TGA of PAN/H₂SO₄ (Fig. 4) from 50° to 100°C can be attributed to loss of moisture. The higher moisture content of this polymer compared to PAN/Cl may be due to the hygroscopic properties of the dopant acid (H₂SO₄). The larger mass loss (compared to PAN/HCl) occurred at temperatures between 200° and 320°C. This is most probably due to the evaporation of acid bound to the polymer chain as protonating dopant. PAN/HPTS showed higher thermal stability than PAN doped with HCl or H₂SO₄ acids (Fig. 5). The major weight loss in PAN/HPTS occurred at temperatures between 250° and 320°C. The initial weight loss observed at 110°C may be attributed to solvent evaporation (water). The second weight loss observed at 250°C is probably due to the evaporation of the dopant. The polymer backbone seems to be thermally stable up to 500°C.

Conclusions

TGA profiles confirmed that the polyanilines grown by a sweep potential (CV) method are more thermally stable than those grown by constant potential (CP) method. Weight losses were greater and more rapid with the latter. This may be due to a lower amount of impurities in the polymer from the CV method. Polyaniline conducting polymers, like as other reactive and conducting organic materials, suffer from their poor thermal stability in air because of the chemical reaction of oxygen with the highly conjugated system of PAN. The thermal stability of the polyaniline is greatly dependent on the type of the dopant acid employed during synthesis. So it may be possible to prepare polyaniline conducting polymers with higher thermal stability by polymerization of PAN in the presence of high thermally stable acids as dopant electrolyte under suitable electrochemical conditions.

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