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Thermogravimetry Analysis of Electrochemically Synthesized Polypyrrole Conducting Polymer Films

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Free standing films of polypyrrole were prepared in the presence of different organic dopants at room temperature electrochemically (galvanostatic method). Thermal stability of polypyrrole films was then investigated using thermogravimetry analysis technique. On investigation of thermal stability of polypyrrole films by using thermogravimetry analysis, it was found that in all cases the polymer (PPy^+/C^-) decomposed at temperatures below the decomposition temperature of their dopant or counterions. It was found that thermal stability of polypyrrole conducting polymers is affected by the nature of its dopant anion which is employed during electropolymerization. Electropolymerization of polypyrrole in the presence of benzene sulfonate dopants with small and non-nucleophilic substitutions under suitable synthesis conditions produces more thermally stable polymer films.

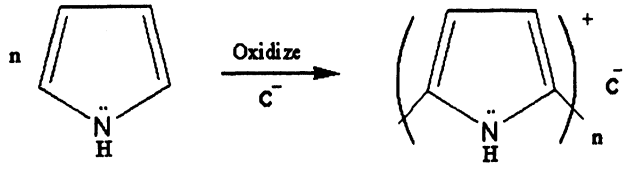
Key Words: Polypyrrole, Dopant, Thermal stability, Thermal gravimetric analysis.

INTRODUCTION

Inherent conductive films of polypyrrole polymer can be generated on electrode surfaces by the oxidation of pyrrole monomer in the presence of appropriate electrolytes ($E_{appl.} \geq 0.70$ V *vs.* Ag/AgCl). It is noticeable that polypyrrole (PPy) is one of the few electronically conducting polymers that can be prepared from aqueous solutions by simple chemical or electrochemical methods[1-4]. The electrochemical approach for making electroactive/conductive films is very versatile and provides a facile way to vary the film properties by simply varying the electrolysis conditions (*e.g.*, electrode potential, current density, solvent and electrolyte) in a controlled way.

Furthermore, the electrosynthesis allows an easy control of the thickness of the polymer films. In chemical polymerization, the polymer is produced as black powder with inferior conductivity than electrochemical polymerization. Chemical polymerization of pyrrole appears to be a general and useful tool for the preparation of conductive composite or blends of PPy with insulating conventional polymers[5]. Preparation of conducting polymers electrochemically is a complex process and the yield and quality of the resulting polymer films is affected by various factors such as pH, electrodes, temperature, nature and

concentration of monomer/counterion, potential of growth and even cell configuration[6–9]. In the electrochemical method, the monomer is first dissolved in a salt solution (where the electrolyte is highly dissociated and slightly acidic) with low nucleophilicity and solution resistance. The overall electropolymerization of polypyrrole can also simply be shown as:



where C^- is the counterion (dopant) incorporated during polymerization. Polymer is deposited as adherent film on the surface of working electrode (anode) in doped, positively charged and conductive form. Anions from polymerization reaction called counterion or dopant are incorporated with polymer in order to maintain charge balance or electroneutrality.

Recognizing that the polymerization reaction proceeds *via* radical cation intermediates, it is clear that the reaction will be sensitive to the nucleophilicity of the environment (*e.g.*, Lewis bases) in the region near the electrode surface. Because of the infusibility and lack of solubility of these new polymer materials in most common solvents, many of the conventional methods of analysis that require solubility cannot be applied to these materials.

Therefore, thermal stability studies on conducting polymers not only assist in the determination of the limitations in practical applications of these materials but also can be considered as an appropriate method for characterization of PPy conducting polymers[9–16]. Moreover, in some commercial applications of PPy such as rechargeable batteries, capacitors and sensors, thermal stability of polymer is of great importance.

EXPERIMENTAL

Princeton Applied Research potentiostat/galvanostat (model 363) was employed for electrosynthesis of PPy membranes. TGA was carried out using a Rigaku Thermal Analyzer instrument. All chemicals used were of analytical reagent (AR) grade and were used as purchased except pyrrole (Sigma), which was used after distillation. All polymerization solutions were prepared in Milli-Q deionized water. The counter ions selected to prepare free standing films were the para-substituted forms of the sodium salts of benzene sulfonate (BS), toluene sulfonate (TS), 1,5-naphthalenedisulfonate (NDS), sodium dodecyl sulfate (SDS), and dodecylbenzene sulfonate (DBS).

Preparation of polypyrrole films: Electropolymerization was carried out galvanostatically using a current density of 2 mA/cm^2. Galvanostatic growth of PPy produces more uniform and reproducible depositions than other methods (*e.g.*, potentiostatic). Polymerization solutions were prepared from 0.2 M pyrrole as monomer in 0.05 M aqueous solutions of the counter ions. A conventional single compartment electrochemical cell was used for electropolymerization. This

cell consisted of a mirror polished stainless steel plate as working electrode, reticulated vitreous carbon as auxiliary electrode and an Ag/AgCl (3 M NaCl) as reference electrode. The electrochemical cell used for preparing polypyrrole membranes has been shown in Fig. 1.

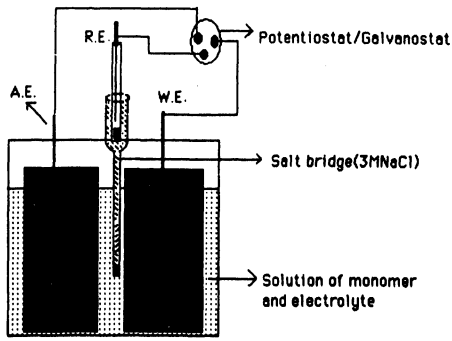


Fig. 1. Electrochemical cell set up used for preparation of free standing films of polypyrroles

The cell solutions were deoxygenated using high purity nitrogen before electropolymerization. PPy films with a thickness of 5–6 μm were obtained by applying current density of 2 mA/cm^2 for 12 min. Polymer films were peeled off the working electrode, with the help of a surgery knife, washed thoroughly with Milli-Q water and finally dried at room temperature before thermal analysis. All the TGA experiments were conducted on 10 mg samples of polymer heated from room temperature to 500°C with rate of heating 10°C per min under high purity nitrogen gas with a flow rate of 80 mL/min.

RESULTS AND DISCUSSION

TGA is a useful technique for rapidly evaluating per cent of volatiles as well as the onset of thermal decomposition temperature of conducting polymers[16]. In this work, thermal stability studies of PPy films using TGA were performed under nitrogen atmosphere in order to eliminate the possible chemical reaction of polymer backbone with oxygen.

(i) TGA of PPy/BS film

Thermogram (TG) obtained for PPy/BS is shown in Fig. 2. Weight loss of polymer occurred in two distinguished steps.

The first weight loss observed from 50–110°C is expected to be mainly due to the evaporation of moisture or solvent and volatile trapped fragments (low MW polymers or oligomers). The second mass loss is presumed to be due to the decomposition of the polymer or dopant. The TGA results show (Fig. 2) that the weight loss observed for temperatures of up to 250°C was less than 10%. This may be attributed to a decrease in moisture content. A greater weight loss was

observed at a temperature of around 260°C. From 250 to 500°C a weight loss of 52–54% was observed, which may be attributed to the breakdown of the polymer backbone. In present case, TGA studies clearly show that thermal degradation of PPy/BS did not occur at the decomposition temperature of its dopant, since NaBS is thermally stable up to 500°C.

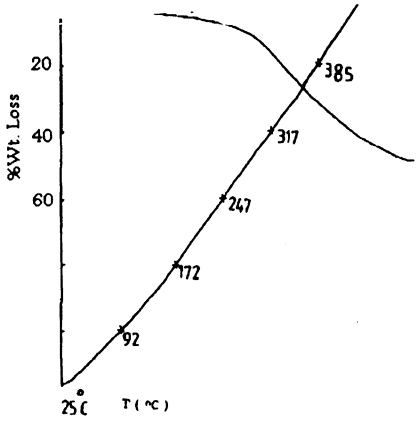


Fig. 2. Thermogravimetric analysis of PPy/BS

(ii) TGA of PPy/PTS

PPy/PTS films did not show significant weight loss until around 250°C (Fig. 3). At 260°C only 10% of the polymer mass was lost. From 260 to 500°C, 25% of the polymer mass was lost which is mostly due to the removal of counter ion.

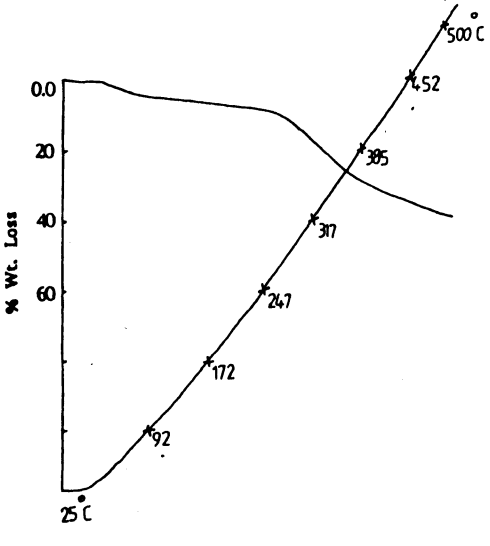


Fig. 3. Thermogravimetric analysis of PPy/PTS

According to this TGA result (Fig. 3), PPy/PTS will not thermally dedope before 250°C. Degradation of PPy/PTS, the same as of PPy/BS, occurs at temperatures lower than the decomposition of the counterion salt that was stable up to 400°C. The thermogram obtained for PPy/PTS (Fig. 3) showed nearly the same thermal stability as PPy/BS. PPy/PTS films obtained in present case, were more conducting, more thermally stable than other investigated polymers. Mechanical properties of PPy/PTS (flexibility and tensile strength) were also superior to other polymer films.

(iii) TGA of PPy/NDS

The thermogram obtained for PPy/NDS has been shown in Fig. 4. PPy/NDS has weaker thermal stability than PPy/BS or PPy/PTS films.

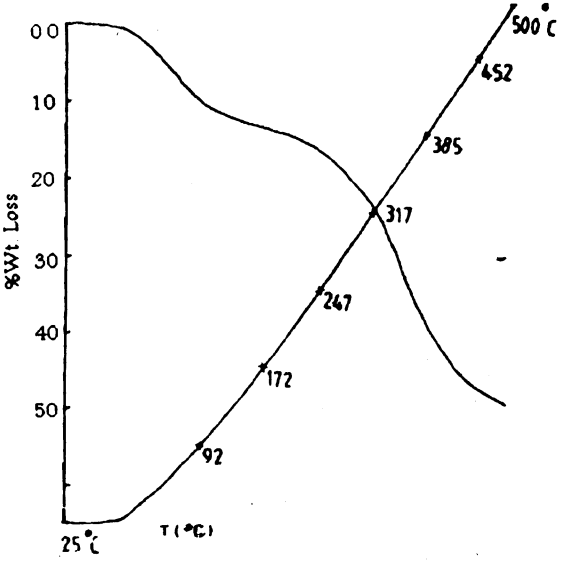


Fig. 4. Thermogravimetric analysis of PPy/NDS

Initial weight loss starting from 50°C, in both PPy/NDS, can be due to elimination of moisture. Higher weight loss of polymer or NDS salt before decomposition, compared to other investigated samples, can be due to the high hydrophilic nature of PPy/NDS. As the TGA results in Fig. 4 show, PPy/NDS was not stable at temperatures of 200°C or higher.

(iv) TGA of PPy/DS

The TGA result obtained for PPy/DS has been shown in Fig. 5. Concluded and that PPy/DS films are stable up to 200°C under inert atmosphere.

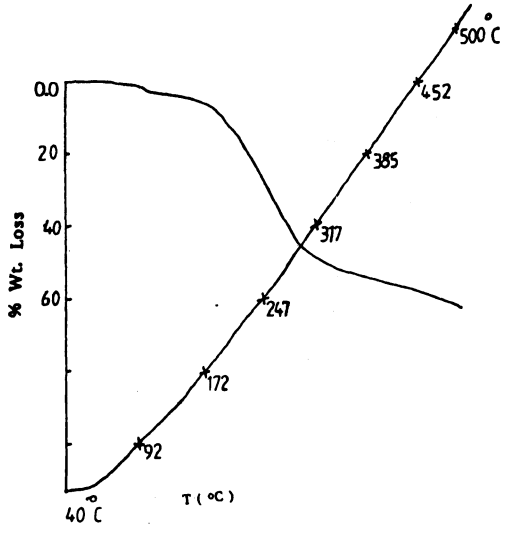


Fig. 5. Thermogravimetric analysis of PPy/DS

The less thermal stability of PPy/DS compared with PPy/PTS is most likely due to the lower thermal stability of DS counterion compared to PTS dopant in PPy/PTS. Higher weight loss of this polymer (compared to PPy/PTS) can be due to the higher weight fraction of DS anions. It may also be concluded that PPy films doped with large size dopants such as surfactants have poorer thermal stability than benzene sulfonate dopants. And thermal degradation of PPy doped with aliphatic surfactants happens at temperature degradation of the dopant surfactant.

(v) TGA of PPy/DBS films

There was no major weight loss for PPy/DBS upon thermal treatment of up to 240°C (Fig. 6). The major weight loss observed at 250°C was due to the

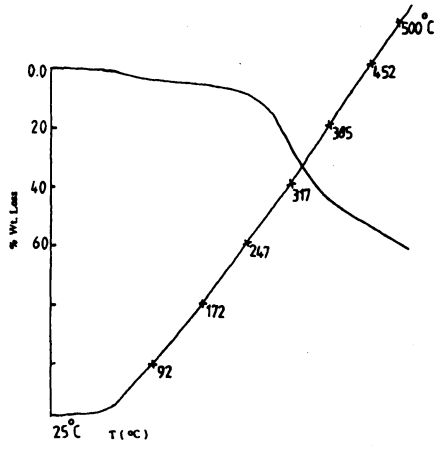


Fig. 6. Thermogravimetric analysis of PPy/DBS

decomposition of the polymer structure. It was also noticed that the weight loss from room temperature to 110°C, which is attributed to the water content, is less for this polymer than other tested polymers. This may be due to the more hydrophobic nature of this polymer. As TGA results in Fig. 5 and 6 show, it may be concluded that thermal stability of PPy doped with aromatic surfactants is higher than those doped or prepared in the presence of aliphatic surfactants. It can be due to the higher thermal stability of aromatic surfactants than aliphatics employed as dopant during synthesis of PPy films.

Final conclusions

TGA was found to be useful to characterize and investigate the thermal stability of the PPy conducting films. The thermal degradation of polypyrrole films was found to be significantly dependent on the nature of dopant anion (*e.g.*, structure, geometry, size and charge) used during synthesis.

On the basis of these investigations, more thermally stable dopants usually produce more thermally stable products. Among the organic dopants, benzene based dopants produce more thermally stable polypyrrole films and with superior conductivity and mechanical properties as well.

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