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Thermal stability and structure of electroactive polyaniline–fluoroboric acid–dodecylhydrogensulfate salt

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Abstract

Oxidation of aniline by emulsion polymerization pathway using benzoyl peroxide oxidant in the presence of fluoroboric acid and sodium lauryl sulfate surfactant leads to incorporation of both acid group as well as surfactant group onto the polyaniline chain as dopants i.e. formation of polyaniline–fluoroboric acid–dodecylhydrogensulfate salt (PANI–HBF_4–DHS). Amount of dopants such as fluoroboric acid (HBF_4), dodecylhydrogensulfate (DHS) and water present in the PANI–HBF_4–DHS was found out for the first time. Electrochemical activity and rheological stability of the polymer were determined. Thermal stability of PANI–HBF_4–DHS was determined by subjecting the polyaniline salt in macroscale at four different temperatures (100, 150, 200 and 250 °C). Structure, composition and thermal stability of polyaniline salt were determined by chemical analysis, conductivity, IR, UV/vis, XRD spectral measurements from the heat treated samples. Polyaniline salt contains 8.3 wt% water, 22.4 wt% HBF_4 and 15.4 wt% DHS at ambient temperature. Upon vacuum, polyaniline salt loses 4.7 wt% water and on heating the sample at 100 °C it loses the remaining 3.6 wt% water. On further heating polyaniline salt loses its dopants and at 250 °C it loses both the dopants almost completely. Polyaniline salt on heating undergoes cross-linking even at 100 °C and however, conductivity (3×10^{-2} S/cm) of polyaniline salt was found to remain almost the same up to 150 °C.

Keywords: Composition of polyaniline salt; Thermal studies; Spectral studies; Emulsion polymerization; Electrode

1. Introduction

Polyaniline is one of the most investigated intrinsically conducting polymers due to its environmental stability, ease in preparation, exciting electrochemical, optical and electrical properties and possible applications in rechargeable batteries, supercapacitors, biosensors, electrochemical displays and chemical sensors [1–5]. Usually these materials are synthesized from monomeric aniline either by chemical polymerization or electrochemical polymerization [6–8]. Chemical polymerization of aniline is important since it is the more feasible route for the production of polymers in large scale. In electrochemical polymerization, polymer is deposited directly on the current collector electrode by electro-oxidation of the monomer. But the thickness of the electrode cannot exceed 100 μm and hence, the fabrication of large electrode is not easy to achieve [9–11]. The oxidant traditionally employed in the polymerization of aniline has been ammonium persulfate, which is unstable on standing and also generally yields an insoluble and infusible polymer. Moreover ammonium persulfate being a strong oxidizing agent and aniline polymerization being exothermic, controlling reaction temperature is rather difficult and consequently polymers with a wide distribution of molecular weight results. To overcome these difficulties, recently our group synthesized polyaniline salt by emulsion polymerization technique using benzoyl peroxide as novel oxidant, wherein polyaniline salts are not soluble in common organic solvents [12]. Very recently, we have prepared soluble polyaniline salt using fluoroboric acid by emulsion polymerization pathway and used it as recyclable catalyst in organic transformations [13]. In recent years, there has been

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improved synthetic procedure by adopting the concept of "dopant engineering" using various surfactants to synthesize material with excellent properties [14].

Polyaniline has been considered as potential candidate for the application of electrode in energy devices because of its many advantages such as fast charge–discharge kinetics, low cost, suitable morphology and fast doping–undoping processes. The electrode material should be stable in different solutions from strongly acidic (or basic) and able to perform in a wide range of temperature.

A knowledge of physical properties and thermal stability of polyaniline under various thermal conditions is important for their use in many practical applications. While the synthesis, structure and redox properties of the electroactive polymers have been reported extensively, there have been only few systematic studies on their aging and thermal degradation behaviour. Most of these investigations on the thermal degradation of the polyaniline are explained by the thermogravimetic and differential scanning calorimetric analyses [15–18].

In this work, the thermal properties of polyaniline salt were determined in quantitative manner by calculating the amount of dopants present in the polyaniline backbone and how the dopants and polymer backbone undergoes degradation during the thermal treatment of polyaniline salt in macroscale. PANI–HBF_4–DHS salt was synthesized via emulsion polymerization pathway. Polyaniline salt contains both acid group (HBF_4) as well as surfactant group (DHS) as dopants. Amount of water present in the polyaniline salt and also the amount of dopants, HBF_4 and DHS present in the polymer were determined by chemical analysis. Electrochemical activity and viscosity of the polymer were determined. Polyaniline salt was subjected to heat treatment at four different temperatures (100, 150, 200 and 250 °C). The heat treatment consists of raising the temperature of the sample (macroscale, i.e. 2 g) in an oven and holding at that temperature for a particular time and then cooling the sample back to room temperature. Composition and thermal stability of polyaniline salt were determined by chemical analysis, conductivity, IR, UV/vis, XRD spectral measurements on the heat treated samples.

2. Experimental

2.1. Materials

Aniline from E. Merck was distilled prior to use. Reagent grade benzoyl peroxide (BDH, India) was recrystallized from chloroform/methanol mixture. Solvents were distilled by appropriate procedure prior to use. Reagent grade sodium lauryl sulfate (SLS), fluoroboric acid (HBF_4) were used without further purification.

2.2. Emulsion polymerization pathway for synthesis of polyaniline salt

In a typical experiment, 3.0 g benzoyl peroxide was dissolved in 30 ml chloroform in 250 ml round bottomed flask. To this solution, 20 ml distilled water containing 1 g sodium lauryl sulfate was added and the reaction mixture was stirred at 40 °C. Aqueous solution (50 ml) containing 5.5 ml fluoroboric acid and 1.0 ml aniline was prepared and added dropwise into the above initiator–surfactant mixture for a duration of 15 min. After addition, the reaction was continued for 8 h. Chloroform layer containing polyaniline salt was separated from aqueous layer and washed thrice with distilled water. Polyaniline salt was precipitated from the chloroform containing polyaniline salt layer with 300 ml acetone. Precipitate of polyaniline salt was separated by filtration, washed with water followed by acetone and dried under vacuum till a constant mass.

2.3. Dedoping of polyaniline salt to polyaniline base

The dark green powder of polyaniline salt (1 g) was treated with 100 ml of 2 N KOH solution. The reaction mixture was kept under stirring for 8 h at ambient temperature. The solution was filtered, washed with 2 N KOH solution followed by distilled water and dried under vacuum at ambient temperature till a constant mass. The dried polyaniline base containing potassium salt of dodecylhydrogensulfate and fluoroboric acid was washed with excess methanol to remove the potassium salts from polyaniline base. Polyaniline base was dried under vacuum at ambient temperature till a constant mass. Methanol solvent containing potassium salts was evaporated to get dry potassium salts. Potassium salts are treated with acetonitrile to separate soluble potassium salt of dodecylhydrogensulfate and insoluble potassium salts of fluoroboric acid. Weight of potassium fluoroborate and potassium dodecyl sulfate was found out and the amount of fluoroboric acid and dodecylhydrogensulfate present in polyaniline salt was calculated.

2.4. Heat treatment

Polyaniline salt (2 g) was subjected to heat treatment at four different temperatures 100, 150, 200 and 250 °C for 1 h as well as 2 h at atmospheric temperature. The heat treatment consists of raising the temperature of the sample in an oven and holding at that temperature for about 1 h then cooling the sample back to room temperature by removing it from the oven. Weight of the sample was considered to find out the weight loss.

Heat treated samples were subjected to dedoping process to find out the amount of potassium salts of fluoroboric acid and dodecylhydrogensulfate.

2.5. Continuous weight loss from macroquantity of sample

In order to know the continuous weight loss of polyaniline salt and its base, 2 g of sample (macroscale) was subjected to heat treatment from 50 to 250 °C. The heat treatment consists of raising the temperature of the sample in an oven and holding at that temperature for about 10 min, then cooling the sample back to room temperature by removing it from the oven and the weight of the sample was taken.