



SYNTHESIS AND PROPERTIES OF CONDUCTING POLYMER

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Abstract

Polyaniline has been synthesized by chemical oxidative polymerization using sodium chlorite (NaClO_2) as an oxidant. This synthesis approach was very easy, inexpensive and environmentally friendly. The process of polymerization took less than 1 h. Polyaniline was characterized by viscosity, UV-Vis.spectra and FTIR spectra. The acid base indicator property is studied.

Keywords: Polyaniline, Sodium Chlorite, Acid-base indicator

Introduction

Over 30 years conjugated polymers were considered as a futuristic new materials that would lead to the next generation of electronic and optical devices. The development of plastics electronics devices based on conjugated polymers has evolved the states of these materials from academic curiosity to the rapidly growing new electronic industry.

Among all conducting polymers, polyaniline (PANI) and its derivatives have attracted much interest in worldwide because of chemical stability, simple polymerization, good conductivity. PANI has been used in various applications like optoelectronics, bio-sensors, gas sensors, microelectronics etc.¹⁻² PANI can be synthesized by either chemically or electrochemically oxidative polymerization as a bulk powder or film. Many papers dealing with the synthesis of have been published.³⁻⁵

In this work PANI has been synthesized by chemical oxidative polymerization using sodium chlorite (NaClO_2) as an oxidant. A synthesis approach had several advantages including (1) the process of polymerization took less than 1 h. (2) the dosage of the oxidant was smaller due to the lower molecular weight of NaClO_2 . (3) a part of the oxidant could be cycled in this polymerization process.

Experimental Materials

Aniline (RFCL limited) was used after distillation. NaClO_2 (Loba Chem.) was used without further purification. Other chemicals were used as purchased.

Preparation

Using NaClO_2 as an oxidant, polyaniline was prepared as follows:⁶

0.4M aniline (3.65ml) was dissolved in 100 ml of 1M HCl. Then 0.9 gm to 1.8 gm (0.1M to 0.2M) was added into solution under constant stirring and the polymerization allowed to proceed for 60 minutes at 0-5°C. The product was filtered and then washed with distilled water. Finally it was dried at 60°C for 24 h in oven to obtain a fine green powder namely doped polyaniline.

Measurements

Viscosity: The intrinsic viscosity $[\eta]$ of base form of sample has been measured in formic acid by a Tuan-Fouss viscometer at 25°C. From the time of flow of solutions and solvent, the intrinsic viscosity was determined by the graphical

extrapolation method proposed by the Huggins equation⁷.

$\eta_{sp}/C = [\eta] + K[\eta]^2C$ for dilute solution.

UV-spectra: The UV-Vis. Absorption spectra was recorded on UV-1800 Shimadzu automatic recording double beam spectrophotometer.

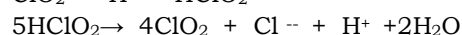
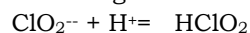
FTIR spectra: The FTIR spectra was recorded on Shimadzu FTIR-8101A spectrophotometer.

Acid-Base Indicator: 20 mg of salt form of sample was transferred in 50 ml DMF and stirred for 1h. The solution was filtered and filtrate solution was used as an acid-base indicator⁸. 10ml of 0.1N HCl was taken in a conical flask, 2-3 drops of the above solution was added. A reddish brown colour was obtained. The mixture was titrated with 0.1N NaOH solution, a blue colour appeared.

Results and Discussions

Oxidative polymerization of aniline using NaClO_2 as an oxidant

In hydrochloric acid, NaClO_2 decomposes according to the following reaction:



Here, the ClO_2 is as an initiator for an polymerization. ClO_2 is the free radical in itself comparing with the polymerization of aniline initiating by $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ⁶.

Viscosity

The viscosity of a polymer solution can yield valuable information about interaction between the polymer and solvent molecule. Viscosity measurement constitutes an extremely valuable tool for the molecular characterization of polymers. The intrinsic viscosity $[\eta]$ of polymer at 25°C is 1.15 dl/g.

UV-Vis. Spectra

Fig.1 shows the UV-Vis. absorption spectra of polyaniline prepared using NaClO_2 as an oxidant had two peaks at 360 nm and 460 nm. The peak at 360 nm arose from electron transition within the benzenoid segments. The absorption peak at 460 nm represented the protonation of polyaniline chains. This implied that the oxidant had an effect on conjugated structure of the conducting polyaniline.

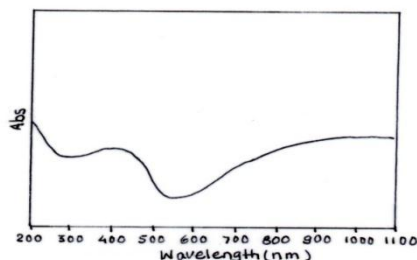


Fig.1. UV-Vis.Spectra of polyaniline prepared using NaClO₂ as an oxidant

FTIR Spectra

FTIR spectra of polyaniline prepared using NaClO₂ as an oxidant is given in Fig.2. FTIR spectra of polyaniline shows that the absorption bands are at about 3462 cm⁻¹, 1571 cm⁻¹, 1485 cm⁻¹, 1302 cm⁻¹, 1244 cm⁻¹, 1145 cm⁻¹ and 809 cm⁻¹. The bands at 1571 cm⁻¹, 1485 cm⁻¹, 1302 cm⁻¹, 1244 cm⁻¹, 1145 cm⁻¹ corresponding to the stretching mode of C=N, C=C for the benzenoid ring. The band at 1145 cm⁻¹, which is assigned to an in-plan bending vibration of C-H⁹.

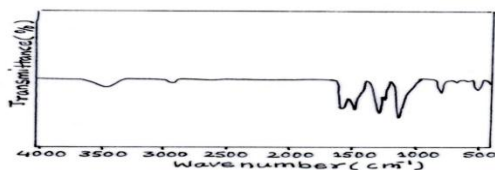


Fig.2. FTIR Spectra of polyaniline prepared using NaClO₂ as an oxidant

Acid-Base Indicator

The end point values are in good agreement with potentiometric and conductometric end point results. The change in colour upon addition/elimination of protons is the basis for the use of polymer as an acid-base indicator. At the end point the emeraldine salt form of polymer is converted into emeraldine base form.

Conclusions

Polyaniline was synthesized by chemically oxidative polymerization using NaClO₂ as an oxidant. This was an easy, inexpensive, environmentally friendly and one step method to produce conducting polyaniline in its conductive state both in bulk and at nanometer level. Sodium chlorite is safer than ammonium persulphate and this an added advantage of using an alternative oxidant. The polyaniline can be used as acid-base indicator which will give additional importance to the exploration of new property of chemically synthesized polymer.

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