Characterization of doped polyaniline by linear mode of MALDI-TOF MS method

M.E.Raja Saravanan* and S.Sivakumar

Department of Physics, Government Arts College (Autonomous), Salem-636 007, Tamilnadu, India.

ABSTRACT

Polymers, the synthetic materials have truly unique properties. The polymers are a very special kind of compounds, which do not behave like small molecules do, but the properties of polymers depend on molecular weight and molecular weight distribution (MMD). The molecular characterization of PANi base synthesized chemically by condensation method is attempted using MALDI-TOF MS technique. Further the study is extended on doped PANi with two different strengths (0.01N, 1 N) of dopant $HClO_4$. The detailed descriptions of the method of TOF (Time of Flight) and the molecular weight determination of the PANi base and its doped form as conducting polymers have been studied quantitatively and strength of the dopant on the molecular characterization is also identified.

Introduction

In recent times the narrow perspective about the carbon based polymers as insulators have been changed to as a new class of polymer called intrinsically conductive polymers or electro active polymers. The potential uses of conductive polymers are quite significant today. Their characterization study in determining the molecular weight is vital part of the present study.

Materials and Method

Aniline is polymerized to polyaniline(PANi) by chemical method with electrical conducting properties. Their conductivity was also enhanced upon doping with an oxidizing or reducing agent (Terje Skotheim, 1986). The molecular weights of the new class of synthetic metals are in the range between thousand to hundreds of thousand with their structural units of monomer recurring structurally (Dinesh Chandra Trivedi, 1994). Dopant induces bond alterations resulting in increased electrical conductivity (Mool et al, 1994) between 10 to 100 S/cm.

The MALDI-TOF MS instrument from Bruker Daltonics(Germany) used the ultraviolet laser(Nitrogen) at the wavelength of 337nm. The Operating pulse rate is 50 Hz and ions accelerated at 20kv. The samples were analyzed by operating in linear mode. Then ions were detected using micro channel plate (MCP). Dihydrobenzoic (DHB) acid was used as matrix and the samples were dissolved in Ethanol.

The molecular weight and molar-mass distribution of a polymer sample is a critical determinant of its material characteristics (Wyatt N. Vreeland et al, 2001). The determination of the molecular weight (MW) and molecular weight distribution (MWD) (Mool et al, 1994) using MALDI-TOF-MS requires only pico moles of samples, comparing with Gel Permeation technique (GPC). Also a time of 10 minute is sufficient to sensitively give the detailed information of the sample. The single monomer resolution of the samples up to ~20kDa in molar mass is also possible in MALDI-TOF-MS (Kazuya Itoda, 2003).

Results and Discussion

Time of flight mass Spectrometry (TOF-MS), a separation-in-time technique, is one in which ions are spatially separated. The time needed by the ions pockets to travel the length of the drift region (the time of flight) can be related to the mass of the ions. The molecules of 1,000,000 amu and greater have been analyzed on this technique (Bush, 1997; Haining Ji et al, 2002). It is found that the molecular weight of the base and its doped polymer as 3645.116 da 3406.886 da and 3479.342 da respectively. The decrease in molecular weight on doping may be attributed to the link breakages or the solubility of monomer in the acid doping.
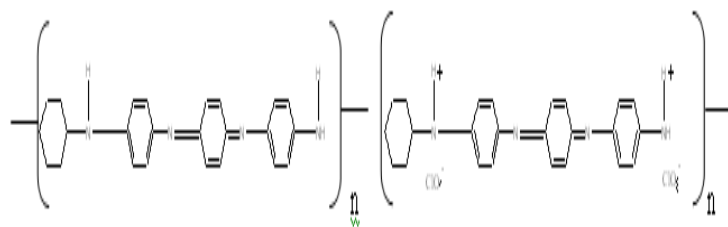
Molecular structure of Polyaniline (Base) Figure 1

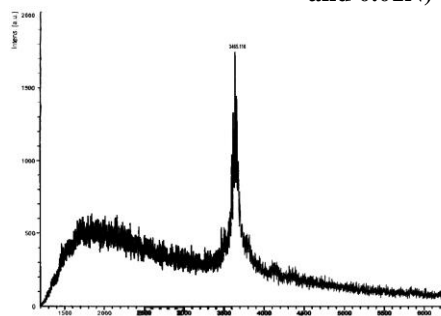**Molecular structure of Polyaniline+ $HClO_4$-(1N and 0.01N) Figure 2**
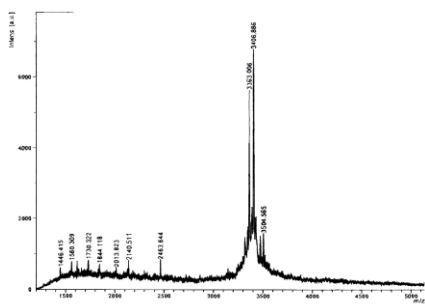

Figure 3 MALDI-TOF MS PANI base

Tele:+91- 94434 28307
E-mail addresses:raja_megs1@yahoo.com

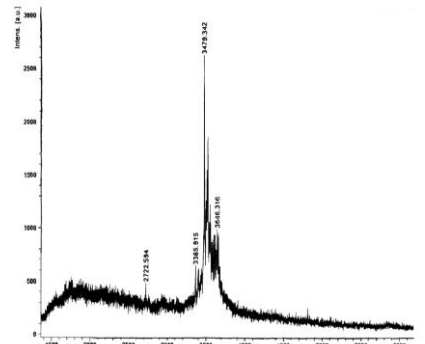**Figure 4 MALDI-TOF MS PANI+ HClO$_4$(1N)**

Figure 5 MALDI-TOF MS PANI+ HClO$_4$(0.01N)

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