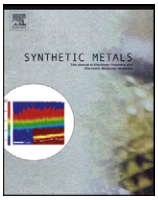
Synthetic Metals 160 (2010) 1627–1630

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet



Spectrophotometric investigation of co-solvent induced doping of PCA-protonated polyaniline solutions

Rama Dubey*, Dhiraj Dutta, Vinay Kumar Yadav, T.C. Shami, K.U. Bhasker Rao

Defence Materials and Stores Research and Development Establishment, DMSRDE P.O., G.T. Road, Kanpur-208013, India

ARTICLE INFO

Article history:
Received 30 December 2009
Accepted 26 May 2010
Available online 22 June 2010

Keywords:
Polyaniline
Dedoping
UV–vis absorption
2-Pyrrolidone-5-carboxylic acid

ABSTRACT

Protonation of polyaniline emeraldine base (PANI EB) was carried out by using different molar concentrations (0.1–0.5 M) of 2-pyrrolidone-5-carboxylic acid (PCA) in dimethylformamide (DMF) solvent. A dedoping effect was observed by UV–vis spectroscopic analysis when doped PANI solutions were diluted with DMF. This effect is due to interaction between the dopant and the solvent which leads to dedoping. It was observed that the dedoping effect was minimized on diluting with methanol. Further on methanol addition a dilution-induced partial doping effect was observed. It is assumed that this may be due to hydrogen bonding interactions between the two solvents.

1. Introduction

Polyaniline (PANI), an inherently conducting polymer, has attracted considerable attention in the past two decades due to its ease of preparation, environmental stability, and potential use in a wide range of applications including electrochromic devices, light emitting diodes, electro-magnetic absorber, electrostatic discharge protection, secondary batteries and corrosion protecting paint [1–6]. Preparation of polyaniline in conducting salt form is generally carried out either by electrochemical or chemical oxidative polymerization [7]. In addition to these methods conducting PANI can alternatively be made via the reprotonation of emeraldine base form of polyaniline with any protonic acid in a solvent medium [8]. This approach of post-protonation is rather flexible as it is utilized for protonation with wide variety of acids including sulphonic, phosphoric, carboxylic or even chiral acids. This sometimes induces novel functional properties such as solution processability and chirality into the resulting polyaniline salts depending on the nature of acid [9,10].

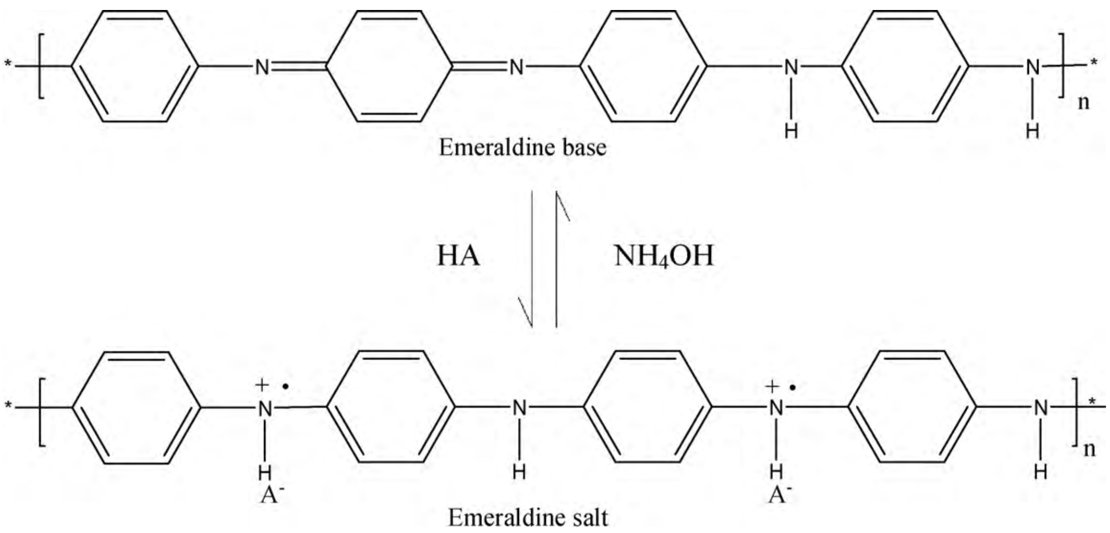
The post-protonation of PANI EB is generally carried out by stirring together 1–2 mg of EB and the respective acid in a high boiling solvent such as dimethylformamide (DMF), dimethylacetamide (DMAc), dimethylsulphoxide (DMSO), N-methyl pyrrolidone (NMP) and m-cresol leading to doped PANI green solutions. It has been reported that stronger sulphonic acids are used in lower concentrations (0.01–0.1 M) whereas weak acids as carboxylic acids are used in higher concentrations (>0.5 M) for protonation [11]. On dilution of PANI salt solutions in DMF, DMAc and NMP with the respective solvents, a dedoping effect has been reported [12], which was confirmed by UV–vis spectroscopy, showing the presence of both a polaron band due to salt at 420 nm and a band at 630 nm due to EB. The presence of both the bands shows partial dedoping. With increasing dilution the peak at 420 nm due to polaron gets totally eliminated and only the peak at 630 nm is present which signifies total dedoping. In addition to dilution, deprotonation is also sensitive towards nature of solvent medium in which protonation is carried out. For e.g. at the same concentration deprotonation is nearly complete in NMP solutions [13]. However the protonated spectra can be regenerated by addition of respective acid (dopant) into the dilute solutions. On the other hand the case with m-cresol is totally different. Its phenolic group acts as a hydrogen bonding donor to the polar linkage (C=O, O=S=O) of organic dopant acids, thus aligning itself above the PANI repeat units by Van der waals interactions [14]. This interaction straightens the polymer chain, increasing conjugation length and thus promoting crystallinity. In this way m-cresol induces specific extended coil conformation into the PANI chains. This phenomenon is known as secondary doping effect [15]. Thus post-protonation process in polyaniline is very much sensitive towards nature of solvent as well as concentration of acid.

The aim of this work is to investigate the effect of pyrrolidone carboxylic acid concentration on doping of PANI EB dissolved in DMF by UV–vis spectroscopic analysis. At the same time the effect of addition of respective solvent or co-solvent such as methanol on doping–dedoping phenomenon has also been studied. The spectroscopic analysis shows that the optical properties of PANI dissolved in DMF, completely change on addition of a co-solvent.

---

* Corresponding author. Tel.: +91 512 2451759 78; fax: +91 512 2404774.
E-mail address: rdubey17@rediffmail.com (R. Dubey).

0379-6779/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.synthmet.2010.05.031



Scheme 1. Chemical structure of undoped (base) and doped (salt) form of polyaniline.

2. Experimental

Aniline (s.d. fine, India) was distilled under reduced pressure and stored in amber bottle at low temperature. Ammonium persulphate (s.d. fine, India) and DMF, HCl, NH_4OH (Merck, India) were used as received. All aqueous solutions were prepared using distilled water.

2.1. Synthesis of polyaniline

The method used to prepare polyaniline was adapted from the literature procedure [16]. Briefly, a solution of 0.5 M of ammonium persulphate was added dropwise to an aqueous solution of 0.5 M of aniline dissolved in 1 M HCl, and the mixture was vigorously stirred at 0–5 °C for 1 day. After that, the precipitate emeraldine salt, was filtered and washed with 1 M of aqueous HCl until the filtrate was clear, to remove low molecular weight and monomeric residue. To obtain the emeraldine base form of polyaniline the product was treated with ammonium hydroxide 1 M for 10 h at room temperature. The polymer was subsequently washed with water and dried under dynamic vacuum at room temperature for 24 h.

2.2. Preparation of stock solution

Stock solution of emeraldine base polymer was prepared by dissolving 0.015 g of EB in 100 ml of DMF. For doping with PCA, 10 ml EB solution was stirred with different concentrations of PCA (0.1–0.5 M), for 5–6 h and left overnight. The spectroscopic analysis was carried out 24 h after addition of PCA.

2.3. Measurement

UV–vis characterization was carried out by a UV 2600 double beam UV–vis spectrophotometer (Chemito). The quartz cuvettes of 1 cm path length and 3 ml volume capacity were used for measurement of PANI solutions. The samples were diluted with respective solvents in some measurements due to scale limit.

3. Results and discussion

The pristine PANI doped with HCl is dedoped by stirring in aqueous ammonia solution to produce the neutral emeraldine base (EB) form of polyaniline. The neutral PANI thus prepared is doped again by reacting with protic acid to produce the doped conductive PANI (Scheme 1). This doping reaction of EB is basically a simple acid–base reaction as the most basic imine nitrogens in EB is protonated first and emeraldine salt (ES), the conductive PANI is produced after internal redox reaction and charge separation process.

Fig. 1 shows the UV–vis spectrum of the stock EB DMF solution. The solution appeared deep blue in colour. The spectrum shows two strong absorption peaks at 355 and 620 nm characteristic of EB form of PANI arising from π–π^* electron transition within benzenoid segment and exciton (n–π^*) transition respectively. When the EB solutions were stirred with different molar concentrations of PCA (0.1–0.5 M) the solutions turned bluish green and green respectively with increasing PCA concentration. Fig. 2 shows the UV–vis spectrum of different solutions. It was observed that when the concentration of PCA was 0.1 M the spectrum was similar to that of EB. When the concentration was 0.2 and 0.3 M the spectrum shows EB peaks at 330 and 620 nm as well as small polaron band at 450 nm (polaron to π^* transition). The intensity of 630 nm peak gets reduced with increasing concentration of dopant, showing the reduced concentration of EB form in the solution with respect to EB solution. Thus at these concentrations the solution is in partially partially doped state. This suggests that these concentrations of PCA are too low for doping to be effective. On further increasing the concentration to 0.4 and 0.5 M it was observed that the intensity of 620 nm peak gets further reduced and the hump at 450 nm gets more intensified.

Thus a molar concentration of >0.4 M is essential for EB solutions with PCA. Although this concentration is also not enough to lead to total or complete doping since a small shallow peak at 620 nm

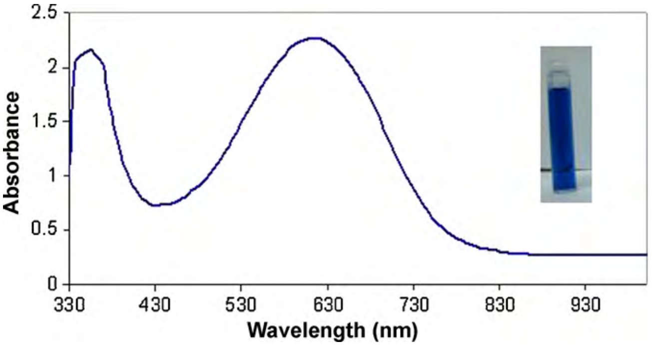


Fig. 1. Electronic absorption spectrum of PANI EB in DMF (inset shows solution).