



# Reprotonated polyanilines: The stability of conductivity at elevated temperature



Jaroslav Stejskal<sup>a,\*</sup>, Jan Prokeš<sup>b</sup>, Miroslava Trchová<sup>a</sup>

<sup>a</sup> Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic

<sup>b</sup> Charles University in Prague, Faculty of Mathematics and Physics, 180 00 Prague 8, Czech Republic

## ARTICLE INFO

### Article history:

Received 12 November 2013

Received in revised form

7 January 2014

Accepted 5 February 2014

Available online 18 February 2014

### Keywords:

Conducting polymer

Conductivity

Hydrogen bonding

Polyaniline

Thermal stability

## ABSTRACT

Reprotonation of polyaniline base with various acids opens a way to conducting materials widely differing in physical properties. The thermal stability of the resulting polyaniline salts was tested by measurements of the conductivity at 125 °C for up to 500 h. Polyaniline sulfate was the most stable and its resistivity increased only by 3.6 times after that time. The stability differed considerably depending on the acid used for reprotonation. The room-temperature conductivity of polyaniline salt is determined by the strength of the acid and its ionic bond with the imine nitrogen in polyaniline. The thermal stability of conductivity, however, is controlled by the ability of the acid to constitute hydrogen bonds with the secondary amine nitrogens in polyaniline. For that reason, oxygen-containing counter-ions, such as sulfates or sulfonates, produce more stable salts with polyaniline, compared with polyaniline protonated with, e.g., hydrochloric acid. The presence of hydroxyl group in the counter-ions also enhances the thermal stability of the polyaniline salt. These conclusions are supported by the analysis of FTIR spectra.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

Polyaniline (PANI), an important conducting polymer [1,2], is usually prepared by the oxidation of aniline hydrochloride with ammonium peroxydisulfate [3]. In this way, PANI is obtained as a salt (Fig. 1). By immersion in ammonia solution the protonating acid is removed, and the conducting PANI salt converts to a non-conducting PANI base. This well-known transition may be reversed (Fig. 1) and PANI base can again be reprotonated with various acids to corresponding PANI salts. Depending on the type of acid, the reprotonation of PANI thus offers the preparation of materials differing in conductivity, hydrophobicity, density, and other physicochemical parameters [4].

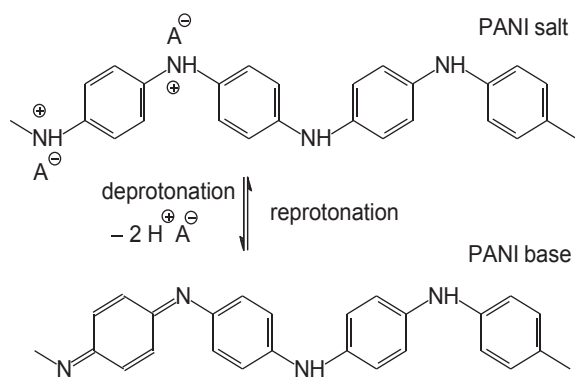
The stability of conducting polymers in general and of PANI in particular, is of importance in many potential applications. Any decrease in conductivity is either due to deprotonation [5], chain degradation [6], or chemical changes in the molecular structure of the PANI [7,8]. The decrease in conductivity during long-term storage of PANI [3] or polypyrrole [9] has not exceeded one order of magnitude. The stability of PANI in strongly alkaline or acidic

media is also good [10]. Polyaniline proved to be surprisingly stable with respect to various oxidants [11] or in electrochemical oxidation [12] despite the fact that the oxidized form of PANI, pernigraniline [13], is regarded as chemically less stable [14]. The stability during UV-irradiation has also been investigated [15,16]. The stability of conductivity with respect to pH changes is another important issue. Common PANI salts convert to the non-conducting base above pH 4–6. The shift of this transition above neutral conditions [17–20], pH > 7, is thus often needed, e.g., in biomedical applications. The electrical and chemical stability with respect to elevated temperature [7,21–23], however, remains to be the most important issue. Photothermal tumor destruction [24] may serve as an example where high thermal stability is required.

Temperature cycling revealed that the conductivity during heating and cooling stages is not reversible [25]. This was explained by assuming that partial deprotonation takes place. The trend was confirmed during long-term aging at 80 °C [8]. When PANI was prepared in solutions of various acids, the stability of the conductivity at 175 °C depended on the acid constituting the medium [5]. For example, while PANI prepared in hydrochloric acid solutions lost most of its conductivity before reaching the target temperature, PANI prepared in a solution of methanesulfonic acid displayed only a moderate decrease in conductivity after exposure to 175 °C for three weeks. The reduction of conductivity is caused at first by the loss of the protonating acid, and later by changes in the molecular

\* Corresponding author. Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic. Tel.: +420 296 809 351; fax: +420 296 809 410.

E-mail address: [stejskal@imc.cas.cz](mailto:stejskal@imc.cas.cz) (J. Stejskal).



**Fig. 1.** Conducting polyaniline salt is deprotonated in alkaline media to a polyaniline base. The base can be again reprotonated with acids (HA) to corresponding salts.

structure, such as oxidative degradation or crosslinking [8,26–28]. It was observed that the aging rate below *ca* 85 °C was much slower than the aging above this limit [29]. The exposure to temperatures above 300 °C leads to the irreversible conversion of PANI to nitrogen-containing carbon [30–34]. The stability of conductivity of reprotonated PANI at elevated temperature is investigated in the present study and offered as a way to stability enhancement.

## 2. Experimental

### 2.1. Preparation and reprotonation of polyaniline

Polyaniline hydrochloride was prepared in the “standard” manner [3,35] by the oxidation of 0.2 M aniline hydrochloride (Fluka, Switzerland) with 0.25 M ammonium peroxydisulfate (Lach:NER, Czech Republic) in an aqueous medium at room temperature. The solids were collected on a paper filter and converted to the PANI base by suspension in 1 M ammonium hydroxide and with subsequent drying in air at room temperature and then over silica gel. Portions of PANI base were reprotonated in aqueous solutions of various acids and the resulting PANI salts were again collected on filter and dried.

For the infrared spectroscopic studies, PANI films were grown on silicon windows 24 mm in diameter [8]. The supports were immersed at room temperature in the reaction mixture during the oxidation of 0.2 M aniline with 0.25 M ammonium peroxydisulfate in the presence of 1 M hydrochloric or sulfuric acid. The protonated PANI was converted to the corresponding base by treatment with an excess of 1 M ammonium hydroxide. The resulting films of PANI base were reprotonated in aqueous solutions of 1 M hydrochloride or 1 M sulfuric acid.

### 2.2. Spectroscopic characterization

Fourier-transform infrared (FTIR) spectra of the films deposited on silicon were recorded by 64 scans per spectrum at  $2 \text{ cm}^{-1}$  resolution with a fully computerized Nicolet IMPACT 400 FTIR spectrometer. The spectra were corrected for the presence of moisture and carbon dioxide in the optical path. An absorption subtraction technique was applied to remove the spectral features of silicon wafers.

### 2.3. Thermal stability of conductivity

For electrical measurements, the PANI powders were compressed with a manual press at 540 MPa into pellets 13 mm in

diameter and 1 mm thick. Their resistivity was measured with a four-point van der Pauw method using a Keithley 238 current source, a Keithley 706 scanner and a Solartron–Schlumberger 7081 precision voltmeter [5]. The temperature of the samples raised from 20 °C to 125 °C, and the samples were kept at the target temperature until the recorded resistivity became too high or for a maximum of 500 h allocated for the experiment.

## 3. Results and discussion

### 3.1. Thermal stability of reprotonated polyanilines

In order to make a relative comparison of the conductivity stability of PANI base reprotonated with various acids, the samples were kept at 125 °C (Table 1) and their resistivity was continuously monitored. The room-temperature resistivity of the reprotonated PANI,  $\rho$ , and the resistivity relative to this value,  $\rho_t/\rho$ , after time  $t = 0$  (i.e. when the target temperature was reached, typically after  $\approx 3$  h), additional 5 h, 25 h ( $\approx 1$  day), 125 h ( $\approx 5$  days), and 500 h ( $\approx 3$  weeks) have been recorded. If these ratios are lower than unity, it means that the resistivity decreased (i.e. the conductivity increased) in the course of heating. The lower are the values listed in Table 1, the better is the thermal stability. If no value is given, it means that the resistivity was more than a thousand times higher than the resistivity of the original sample and the measurement was then terminated. This may have two reasons: (1) PANI was deprotonated or its molecular structure otherwise damaged, and the sample has consequently lost most of its conductivity or (2) the electrical contact of the sample pellets with the probes was reduced or lost, e.g., due to mechanical changes, such as sample shrinkage or the formation of cracks.

Polyaniline salts are ordered in Table 1 from the most unstable to the most stable. The room-temperature resistivity,  $\rho$ , usually reflects the strength of the ionic bond between the PANI base and the protonating acid. The stronger is the acid (the lower is its pK value), the higher conductivity is usually observed. For that reason the resistivity of salts produced with strong inorganic acid is of the order of units  $\Omega \text{ cm}$ , while carboxylic acids yield salts with resistivity of the order of 100  $\Omega \text{ cm}$  [4] (Table 1). The higher room-temperature conductivity does not imply higher stability at elevated temperature. This is demonstrated by the rather random order of values listing the room-temperature conductivity in Table 1. For instance, PANI reprotonated with hydrochloric or sulfuric acid has a comparable room-temperature resistivity; but the thermal stability of the former is poor and for the latter excellent. The same applies to organic acids, when PANI citrate is compared with PANI 5-sulfosalicylate.

The thermal stability of materials in general is improved with the increasing extent and strength of hydrogen bonding [36], in addition to ionic bonding. It is proposed that also in the present case, the hydrogen bonding between secondary amino groups of PANI chains (Fig. 1) and oxygen atoms in various counter-ions is responsible for the improved stability of PANI salts (Fig. 2). This seems to apply especially to sulfates and sulfonates which display the best thermal stability by combining ionic and hydrogen bonding.

The stability of salts with hydrohalogenic acids, on the other hand, is rather poor, due to less strong hydrogen bonding of hydrogen atoms in PANI with halogen atoms in acid. The same applies to PANI salts with carboxylic acids, which may produce hydrogen bonds with PANI but the strength of the ionic bonds is weak. Obviously, the synergistic effect of ionic and hydrogen bonding is needed for high thermal stability.

The present hypothesis is supported by the observation that another oxygen-containing group known for its ability for

Download English Version:

<https://daneshyari.com/en/article/5201965>

Download Persian Version:

<https://daneshyari.com/article/5201965>

[Daneshyari.com](https://daneshyari.com)