Polymer Degradation and Stability 134 (2016) 357–365

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

Interaction of polyaniline film with dibutyl phosphonate *versus* phosphite: Enhanced thermal stability

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ARTICLE INFO

Article history:
Received 4 July 2016
Received in revised form
26 September 2016
Accepted 4 November 2016
Available online 5 November 2016

Keywords:
Polyaniline
Conducting polymer
Dibutyl phosphite
Dibutyl phosphonate
Thermal stability
FTIR spectroscopy
Raman spectroscopy

ABSTRACT

Interaction between blue film of polyaniline base with dibutyl phosphonate yields green polyaniline film. This resembles the classical protonation of polyaniline base with acids but, in the contrast, there is no proton available in prevailing phosphonate tautomeric form. The character of interaction was studied by evolution of the infrared spectra of the film recorded during heating up to 200 °C. The experiments demonstrate that dibutyl phosphite, and not its phosphonate tautomeric form, interacts with polyaniline base. Above 140 °C, the original polyaniline base is recovered in dry air purged environment in spectrometer. The interaction with polyaniline base prevents dibutyl phosphite from the oxidation into dibutyl phosphate which occurs in case of heating of neat dibutyl phosphite, in which phosphonate form predominates. The thermal stability and the changes in molecular structure have been assessed by UV–visible, FTIR and Raman spectra. The model of the interaction based on the quantum-chemical optimization of the idealized structure is proposed.

1. Introduction

Polyaniline (PANI) is an important conducting polymer [1]. Thin PANI films has often been prepared by the technique of *in-situ* surface polymerization [2]. Such films have the thickness of 100–200 nm and many applications, such as sensors [3], hole-injection layers in light-emitting devices [4], dye-sensitized solar cells [5]. In addition, polyaniline is used in antistatic and anticorrosion coatings, in catalysis, noble-metal recovery, and biomedicine [6,7]. The thermal stability of PANI and its films in these applications is of great importance. The thermally induced structural changes in PANI and its deprotonated form, PANI base, has been studied by spectroscopic methods by many authors [8–14]. The structural changes are due to deprotonation, chain degradation, chemical changes in the molecular structure, cross-linking to phenazine-like units, etc.

The room-temperature conductivity of PANI salt is determined by the strength of the acid and its ionic bond with the imine nitrogen in PANI (Fig. 1). It has been shown that the thermal stability of conductivity, however, is controlled by the ability of the acid to constitute hydrogen bonds with the secondary amine nitrogen atoms in PANI [15]. Oxygen-containing counter-ions, such as sulfates or sulfonates, produce considerably more stable salts with PANI compared with, e.g., hydrochloric acid. The presence of hydroxyl group in the counter-ions also enhances the thermal stability of the PANI salt [15] due to its ability to form hydrogen bonds with PANI [16,17]. Improved thermal stability of the material obtained after the exposure of PANI base to ionic liquid up to 200 °C compared with the standard PANI hydrochloride has also been observed [18]. The FTIR spectroscopic analysis suggests that, in this case, hydrogen bonding of amine groups in PANI to oxygen atoms in trifluoromethanesulfonate anion [19] is responsible for the enhanced stability of conductivity.

Some applications of conducting polymers welcome the presence of phosphorus [20], such as corrosion protection of metals [6,21–25], supercapacitor electrodes [26,27] or catalysts electrodes in fuel cells [28]. Composites of PANI with noble metals have been employed in acidic catalysis of organic reactions [29] and inorganic phosphites have also been used for similar purpose [30]. The synergistic effect may be expected for the combination of both components, PANI and phosphites. Also biosciences are the prospective field because organophosphorous compounds play an important role in the biological activity of a wide variety of natural compounds [31]. Modification of surface of PEDOT with a self-assembled monolayer of the corresponding phosphonate has

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http://dx.doi.org/10.1016/j.polymdegradstab.2016.11.005

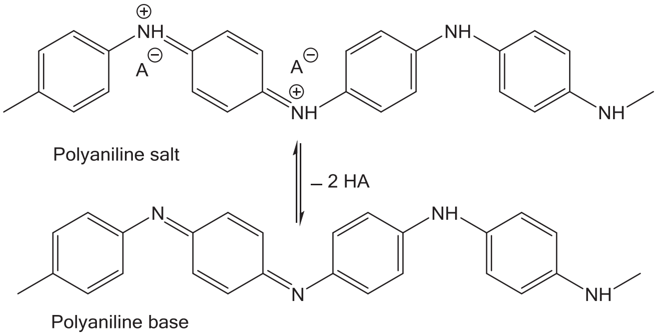

Fig. 1. Conducting polyaniline salt converts under alkaline conditions to a non-conducting polyaniline base. The reaction is reversible. HA is an arbitrary acid.

been applied for efficient tuning of its work function [32] and unexpected interaction between PEDOT and phosphonium ionic liquid has been observed in Ref. [33]. The protonation of PANI with *ortho*-phosphoric acid (H_3PO_4) is the most straightforward way how to introduce phosphorus atom into PANI [21,26,34,35]. Phosphotungstic acid ($H_3PO_4 \cdot 12WO_3$), has also been used for similar purpose [25,35–39].

Phosphorous acid (H_3PO_3) and its tautomeric form, phosphonic acid, have also been considered for the combination with PANI. The substituted derivatives of phosphonic acid, when hydrogen atom is replaced with an organic substituent such as *n*-decyl [24], *tert*-butyl [40] or phenyl [41], have been successfully used for the protonation of polyaniline. Self-protonated poly(2-methoxyaniline-5-phosphonic acid) was also synthesized [42–44].

The phosphites are diesters of phosphorous acid (H_3PO_3) [45]. This acid is dibasic and its diesters exist as tautomers, phosphites and phosphonates (Fig. 2). Depending on the type and conditions, one of the forms usually dominates [45]. In such diesters, however, there is no proton available for the interaction with PANI. Nevertheless their interaction with PANI takes place, it has not yet been reported in the literature, and it is discussed in the present paper. Phosphonates may further be oxidized to phosphates, diesters of phosphoric acid, which are able to protonate PANI via their proton present in their OH group (Fig. 2). The phosphoric acid diesters have indeed been used to improve PANI solubility and processability [46–49].

Conducting form of emeraldine PANI salt can be achieved by doping PANI base with various dopants, such as Brønstead and Lewis acids, ionic salts or transition-metal cations [50–54]. The doping by the ionic liquids is similar to a protonation by protonic acids [19]. No protons appear in transition-metal systems, the doping occurs by pseudo-protonation of imine nitrogens by the metal cations [50]. Lewis acid doping occurs both on amine an imine nitrogens [55,56]. There are compounds that are not classical Brønstead acids but they still interact with non-conducting PANI base in similar manner to produce conducting materials. The interaction with PANI then does not involve directly protons, but acidic hydrogen atoms or hydrogen bonding. The former type is represented by 2,4,6-trinitrophenol (picric acid) [57,58] or 3-nitro-1,2,4-triazol-5-one (NTO) [59], the latter by ionic liquids [18,19]. The present study reports interaction between PANI base with organic phosphites resulting in the formation of conducting materials. The interaction of PANI base with dibutyl phosphite and the thermal stability at elevated temperature of the resulting film are investigated by using FTIR and Raman spectroscopies.

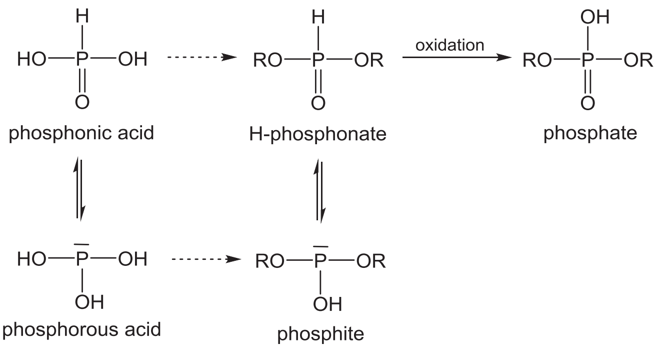

Fig. 2. Tautomeric phosphonic and phosphorous acids and corresponding esters, H-phosphonates and phosphites. H-phosphonates are oxidized to phosphates.

2. Experimental

2.1. Synthesis

Aniline hydrochloride, p.a. (Penta, Prague, Czech Republic) and ammonium peroxydisulfate, 98% (Lach-Ner, Neratovice, Czech Republic) were used as received. Dibutyl phosphite (DBPH; Sigma-Aldrich) was used as received; dibutyl H-phosphonate tautomer (Fig. 2), however, dominates in this commercial product.

Polyaniline films were deposited *in situ* during the oxidation of 0.2 M aniline hydrochloride with 0.25 M ammonium peroxydisulfate [60] on glass or silicon substrates immersed in the reaction mixture [2]. The films were immersed in water for several hours at first and then deprotonated to PANI base in 1 M ammonium hydroxide (Fig. 1), and dried. Supports with blue films of PANI base were then transferred into neat dibutyl phosphite (DBPH) and left there several days until it became green. The green film are further referred to as polyaniline dibutyl phosphite (PANI·DBPH). After rinsing with acetone the films were kept in desiccator over silica gel.

2.2. Characterization

UV–visible spectra of the films on glass were recorded with a Lambda 20 spectrometer (Perkin Elmer, UK). Some films were heated to 100 °C in an oven. Fourier-transform infrared (FTIR) spectra of the PANI films on silicon were recorded in the range of 650–4000 cm^{-1} at 256 scans per spectrum at 4 cm^{-1} resolution using a Thermo Nicolet NEXUS 870 FTIR Spectrometer. The films were heated from 20 to 200 °C in the temperature-controlled cell and the spectra were recorded at 10 °C steps. The spectrometer was purged with dry air. An absorption subtraction technique was used to remove the spectral features of silicon. Spectra of powdered samples dispersed in potassium bromide pellets were taken for comparison in transmission mode.

Raman spectra of PANI films grown on silicon were registered with a Renishaw InVia Reflex Raman microspectrometer using an Ar-ion 514 nm, a HeNe 633 nm, or a diode 785 nm lasers for excitation. A research-grade Leica DM LM microscope with an objective magnification 50× was used to focus the laser beam on the sample. The scattered light was analyzed by the spectrograph with holographic gratings 2400, 1800, and 1200 lines mm^{-1} for the individual lasers, respectively. In order to avoid the damage of the samples by laser beam, the spectra were recorded with the low power obtainable and by gradually increasing the power until the spectrum started to change. The spectrum was then recorded with the highest power that did not alter the sample.

2.3. Calculations

The model calculations were carried out at the density