Materials and Design xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Materials and Design

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

Cyclic temperature dependence of electrical conductivity in polyanilines as a function of the dopant and synthesis method

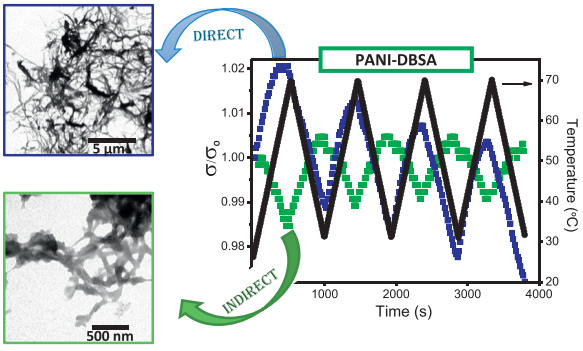
Laura Horta-Romarís [a], María-José Abad [a,*], M. Victoria González-Rodríguez [a], Aurora Lasagabáster [a,b], Pedro Costa [c], Senentxu Lanceros-Méndez [c,d,e]

[a] Universidade da Coruña, Grupo de Polímeros, Centro de Investigacións Tecnolóxicas, Campus de Ferrol, 15471 Ferrol, Spain
[b] Dpto Química Orgánica I, Facultad de Óptica y Optometría, Universidad Complutense de Madrid, Arcos de Jalón 118, Madrid 28037, Spain
[c] Center/Department of Physics, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal
[d] BCMaterials, Parque Científico y Tecnológico de Bizkaia, 48160 Derio, Spain
[e] IKERBASQUE, Basque Foundation for Science, Bilbao, Spain

HIGHLIGHTS

- PANI-DBSA prepared by direct and indirect synthesis scalable to industrial volumes is a promising material as thermal sensor
- PANI-DBSA exhibits electrical linearity and reversibility in heating-cooling cycles
- Direct route leads to higher amplitude of electrical response in cyclic test
- Indirect route reduces moisture dependence of electrical conductivity

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 September 2016
Received in revised form 2 November 2016
Accepted 4 November 2016
Available online xxxx

Keywords:
Polyaniline
NaSIPA
DBSA
Electrical conductivity
Heating-cooling cycles
Ageing

ABSTRACT

Most of the studies dealing with polyanilines (PANIs) are focused on electrochemical polymerization; however, chemical polymerization is more suitable for large–scale production. In order to develop commercially viable, clean, effective materials for thermal sensor devices, temperature dependent electrical response has been studied in PANIs obtained by simple, low-cost synthesis conditions, transferable to industrial processing. PANIs doped with HCl, dodecylbenzene sulfonic acid (DBSA) and sodio-5-sulfoisophtalic acid (NaSIPA) were prepared by chemical oxidative polymerization, through direct and indirect routes of synthesis. TEM images disclosed formation of nanorods and microfibrils. Microstructural analysis confirmed differences in doping level and crystallinity which were related with the PANI conductivity.

Two PANI-DBSA synthesized by direct and indirect methods, exhibit the best conductivity retention up to 150 °C. In cyclic tests, they show excellent performance after 4 heating-cooling cycles up to 70 °C. The amplitude of electrical response for PANI-DBSA obtained by direct synthesis is twice the value of PANI-DBSA prepared by indirect route. Conversely, the latter displays slightly better repeatability due to its lower moisture content. This study suggests that both PANI-DBSA are suitable for use in electronic applications, under ambient conditions below 150 °C, and are promising materials for temperature sensor applications.

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* Corresponding author.
E-mail address: mjabad@udc.es (M.-J. Abad).

http://dx.doi.org/10.1016/j.matdes.2016.11.021
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Please cite this article as: L. Horta-Romarís, et al., Cyclic temperature dependence of electrical conductivity in polyanilines as a function of the dopant and synthesis method, Materials and Design (2016), http://dx.doi.org/10.1016/j.matdes.2016.11.021

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1. Introduction

In recent years, there has been increasing interest in the synthesis and application of conducting polymers [1]. Specifically, polyanilines (PANIs) are the subject of considerable attention owing to their unique electrical behavior, good environmental stability in doped and neutral states and simple synthesis [2].

PANI has a broad application range covering rechargeable batteries [3], data storage [4], corrosion protections [5], solar cell devices [6] and sensors [7–10], among others. Polyaniline is an excellent candidate for fabricating sensor devices due their intrinsic electrical properties. It possesses valuable characteristics such as reversible acid/base doping/dedoping chemistry, enabling control over properties (free volume, conformational changes, solubility, electrical conductivity and optical activity) which result in sensitive and rapid responses to specific analytes and/or environmental factors [9].

In order to develop thermal sensors, it is essential to understand the temperature dependence of the electrical conductivity. Thus, from a theoretical point of view, it is common practice to study the variation of conductivity with temperature in the range of ~50–300 K to comprehend the mechanism of conductivity [11,12]. Notwithstanding, in practice these devices are often applied at room temperate and above. As a result, the thermal stability of conductivity in the latter temperature range is critical. A greater number of factors should be considered as in these conditions different changes are taking place in the system like doping, dedoping (extrinsic), oxidation, chain scission, cross-linking and changes in crystal structure (intrinsic) [13]. In addition, the study of the thermal stability of polyaniline is essential to understand the effect of heat treatment on physical properties. Despite the number of studies focusing on the improvement of the electrical properties of PANI, those analyzing the influence of thermal ageing on these properties are relatively scarce [13–17].

In this context, the main objective of this work is to develop reliable, eco-friendly and scalable synthetic routes for large-scale production of polyaniline intended for the manufacture of sensors, including thermal sensors. As the chemical oxidation of aniline is more suitable than electrochemical polymerization for bulk production [18–20], the first alternative has been investigated. Concerning the synthetic methods, the properties of polyaniline can be tailored through doping with a wide scope of dopants and using direct and indirect approaches.

Regarding direct synthesis, HCl has been chosen as inorganic dopant due to the ease of synthesis and high electrical conductivity [21]. Dodecylbenzene sulfonic acid (DBSA) has been selected among organic dopants owing to the well-known enhancement of processability, as DBSA acts both as dopant (DBSA bonded to PANI backbone) and plasticizer (DBSA in excess or free DBSA) [20].

Another option is to obtain a synergistic combination between the high conductivity of the inorganic dopant and the improvement in processability and thermal stability achieved with the organic dopant by an indirect synthetic route, known as *dedoping-redoping* [11]. In this option, polyaniline doped with HCl (PANI-HCl) is completely dedoped in aqueous NH_4OH solution and, subsequently, redoped with a second organic dopant. As second organic dopants, the bulky counterions DBSA and sodio-5-sulfoisophtalic acid (NaSIPA) have been used [11].

The polymers thus synthesized were characterized using transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), Elemental Analysis, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and Thermogravimetric analysis (TGA). Their room temperature electrical conductivity has been compared by the four probe technique and the effects of various dopants and synthetic routes on DC conductivity are discussed. Finally, thermal stability of the DC electrical conductivity was monitored at different heating conditions and through heating-cooling cycles to analyze the potential of PANIs as thermal sensors.

2. Experimental

2.1. Materials synthesis

Aniline and potassium peroxodisulfate (APS) were purchased from Fluka (Steinheim, Germany). Dodecylbenzensulfonic acid (DBSA) 70 wt.% solution in 2-propanol and 5-sulfoisophtalic acid sodium salt (NaSIPA) 95 wt.% were obtained from Sigma–Aldrich (Steinheim, Germany), acetone was obtained from Scharlau (Sentmenat, Spain), chloroform and methanol were supplied from Merck (Darmstadt, Germany). All the solvents and reagents except DBSA were at least of 99% purity. Water was purified on a Milli-QUltrapure 109 system (Millipore, Molsheim, France).

Table 1 summarizes the main synthesis conditions and the sample nomenclature. The preparation of PANI-HCl (P1) was adapted from the method described by Park et al. [22]. Aniline and APS were dissolved separately in 0.5 M aqueous HCl. The polymerization reaction was initiated by the drop wise addition of the oxidant during approximately 20 min. Afterwards, the reaction was allowed to proceed for 2 h under mechanic stirring (350 rpm) at room temperature. The precipitate was filtered under vacuum and washed with a mixture of 1:1 water:acetone. The PANI-HCl was obtained as a dark green powder after drying at 40 °C in vacuum until constant weight.

The polymerization of polyaniline doped with DBSA (PANI-DBSA direct synthesis) (P2) was prepared according to the method described by Dopico et al. [23].

For the indirect synthesis, PANI-HCl prepared as described in the preceding paragraph, was dedoped with 1 M NH_3 for 2 h in ultrasonic bath, filtered under vacuum and washed with water until neutral pH. The resultant product was redoped with 1 M DBSA in acetone and 0.5 M aqueous NaSIPA during 2 h in ultrasonic bath leading to PANI-DBSA indirect synthesis (P3) and PANI-NaSIPA (P4), respectively. This indirect procedure has the advantage of avoiding chloroform (less environmentally-friendly) which is used in the direct polymerization of PANI-DBSA. The samples were washed with large volumes of acetone to remove excess free acids. Finally, the products were filtered under vacuum and dried in vacuum at 40 °C for 2 days [11].

After polymerization, the polyanilines thus prepared were stored inside an opaque container in a desiccator, to protect them from light and moisture until tests execution.

2.2. Characterization

The transmission electron microscope (TEM, Jeol JEM 1010, 80 KV) was used to investigate the morphology of the powder samples dispersed in isopropanol.

Fourier transformed infrared (FTIR) spectra of the polymers in KBr pellets were recorded on a Bruker Vector 22 spectrometer. The spectra were collected from 4000 to 400 cm^{-1} with a 4 cm^{-1} resolution over 100 scans.

The elemental analysis of C, H, N, S was conducted using ThermoFinnigan FlashEA1112 elemental analyzer.

The XPS spectra were performed with a Thermo Scientific K-Alpha ESCA instrument with Al-Kα monochromatized radiation at 1486.6 eV X-ray source, operated in a constant analyzer energy mode (CAE) with 100 eV and 20 eV pass energy for survey and high resolution spectra,

Table 1
Experimental procedure for the synthesis conditions of doped PANI.

	Sample	Dopant	$M:D_1:O:D_2$	T (°C)	Addition dropwise speed	Stirring speed (rpm)
PANI direct synthesis	P1	HCl	1:5.6:1.25	RT	>1 drop/s	350
	P2	DBSA	1:3:1	0–5	<1 drop/s	150
PANI indirect synthesis	P3	HCl-DBSA	1:5.6:1.25:5.6	RT	>1 drop/s	350
	P4	HCl-NaSIPA	1:5.6:1.25:2.8	RT	>1 drop/s	350

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