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Structural and morphological characterization of Poly(*o*-ethoxyaniline) Emeraldine-salt form using FTIR, XRD, LeBail Method and SEM

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HIGHLIGHTS

- XRD patterns did not show structural differences with increasing polymerization times.
- The presence of the functional group $-OCH_2CH_3$ in the *ortho* position of the carbon rings need to increase cell parameters.
- Polymer morphology showed interconnected vesicular microspheres.

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ABSTRACT

The introduction of polar functional and alkyl groups into the main chain of Polyaniline (PANI) is a mechanism to obtain soluble polymers in a wider variety of organic solvents. Poly(*o*-ethoxyaniline) (POEA) is a derivative of PANI and its structural difference is the presence of the group ($-OC_2H_5$) in the *ortho* position of the carbon rings. Despite the large number of studies performed with PANI and its derivatives, there are few that focus on a structural study of these materials in doped form (ES). Poly(*o*-ethoxyaniline) Emeraldine-salt form (POEA-ES) was synthesized in polymerization times of 3, 24 and 48 h. Through XRD measurements were observed that different polymerization times did not cause structural changes in polymer structures. It were found in XRD patterns peaks at $2\theta = 8°$, 12°, 16°, 24°, 26°, 38°, 44° and 52°. Crystallinity percentage was calculated using the Peak Fitting Module Program and showed that POEA-ES has around 39% of crystallinity. FTIR analysis allowed to identify characteristic absorption bands in the structure of POEA-ES. By Scanning Electron Microscopy (SEM) it was observed micrometric particles of varying sizes, with morphologies similar to interconnected vesicular microspheres. Through LeBail Method, it was observed that crystallites of POEA-ES are present in the order of 26 Å. It was found a conductivity value of 0.3×10^{-7} S/cm for POEA-ES.

Introduction

Within the Intrinsically Conducting Polymers class (ICPs), Polyaniline (PANI) and its derivatives have received great attention due to the low cost of monomer, ease of synthesis and doping and chemical stability under ambient conditions, enabling technological applications that have been developed industrially [1–4].

Despite the prominence of PANI in the class of ICPs, there are some limitations that hinder its use in industrial scale, such as the low solubility in organic solvents, low mechanical flexibility and processability. A widely used mechanism for improve the PANI solubility in organic solvents is the introduction of polar functional and long flexible alkyl groups mainly bonded to the main chain, allowing their characterization and processability [5–7].

PANI and its derivatives can be synthesized in different oxidation states. Their synthesis and derivatives are influenced by a number of parameters, such as pH, reactants concentration, nature of the oxidizing agents and protonic acids, polymerization temperature and time [8], may result in polymers with different structural characteristics and physicochemical properties [9,10].

Poly(*o*-ethoxyaniline) Emeraldine-salt form (POEA-ES) is a derivative of PANI and its structural difference is the presence of the group ($-OCH_2CH_3$) in the *ortho* position of the aniline rings [11,12]. Based on the structural proposals existing in the literature and considering the importance of these materials in technological applications, the goal of this paper is provide greater benefits to a

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better understanding of the structural and morphological characteristics of PANI derivatives. Thus, we proposed a structural and morphological characterization of POEA-ES synthesized at different polymerization times.

Fourier-transformed Infrared Spectroscopy (FTIR) was used for bonds structural information; XRD was used for determination of cell parameters and crystallinity percentage; LeBail Method was performed to refine cell parameters and to obtain crystallite size and shape; SEM was carried out for polymer morphology investigation. Then, these results were correlated with POEA-ES electrical properties.

Experimental

Polymer synthesis

POEA-ES was obtained based on previously published literature synthesis [12], with some modifications [8]. Chemical synthesis was made using hydrochloric acid (HCl) and ammonium peroxydisulfate (APS). After precipitation, aliquots collected at 3, 24 and 48 h were vacuum filtered and washed with acetone to obtain powder polymers.

Fourier-transformed Infrared Spectroscopy (FTIR)

FTIR spectra were measured in *Nanomed Inovação em Nanotecnologia*, São Carlos/SP, Brazil, with a spectrophotometer Bomem-MB Series-Hartmann & Braun in the range of 400–3500 cm^{-1} and 16 scans. Pellets were prepared with KBr in mass ratio of 1:100 using a hydraulic press Perkin–Elmer at a pressure of 15 tons.

X-ray diffraction and crystallinity percentage

XRD data were obtained at the Laboratory of X-ray crystallography of IFSC/USP – São Carlos/SP, using a Rigaku Rotaflex diffractometer equipped with graphite monochromator and rotating anode tube, operating with Cu Kα, 50 kV and 100 mA. Powder diffraction patterns were obtained in stepscanning mode, 2θ = 5–60°, step of 0.02° and 5 s/step. Peak Fitting Module Program [13] was used for the peak decomposition of the semi crystalline pattern and determination of area due to the amorphous phase. Crystallinity percentage was obtained by the ratio between the sums of the peak areas to the area of amorphous broad hallo due to the amorphous phase.

LeBail fit

The use of LeBail Method [14] to obtain structural information from semi crystalline patterns is not very common due to the large overlapped peaks on diffractograms. Nevertheless it has been used to characterize polyaniline and substituted polyanilines [8,15,16]. LeBail Method was performed using the software package Fullprof [17]. All parameters were refined by the least-squares method [18]. The pseudo-Voigt function modified by Thompson–Cox–Hastings was used as peak profile function [19]. Instrumental resolution function parameters were obtained from a lanthanum hexaborate standard, LaB_6. Aniline tetramer single crystal parameters obtained by Evain et al. [20] were used as initial parameters (a = 5.7328 Å, b = 8.8866 Å, c = 22.6889 Å, a = 82.7481°, b = 84.5281° and c = 88.4739°). Particle size was determined from the anisotropic crystallites size using spherical harmonics (SHP) [21].

SEM analysis and conductivity measurements

SEM experiments were performed using a Supra 35, Carl Zeiss, 3.0 kV. Powder samples were deposited on a carbon tape and the surface morphology was obtained at room temperature. Conductivity measurements were performed using the Van Der Pauw method [22]. Samples were processed into pellets with 1.27 cm of diameter and 1.5 mm of thickness which were coated with silver ink on both sides in which were made electrical connections using metal wires. Measurements were performed at room temperature using Keithley Model 2612A from 500 mV to 2 V.

Results and discussion

FTIR analysis

Analysis of POEA-ES FTIR spectra basically showed the absorption bands corresponding to bonds and functional groups by consulting a framework for spectral analysis. Fig. 1 shows the FTIR spectra of POEA-ES obtained to wave numbers between 3500 and 400 cm^{-1}, which is the most useful range for chemical characterization of organic materials [23,24].

It was observed no significant differences between the obtained spectra. The absorption band at 3157 cm^{-1} (peak 1) corresponds to the plane symmetrical stretching of N–H due to secondary amines and imines present in the structure of POEA-ES. The band located at 2358 cm^{-1} (peak 2) is related to the angular deformation of the functional group $-OCH_2CH_3$ located at the *ortho* position of the carbon rings. The absorptions at 1581 (peak 3) and 1491 cm^{-1} (peak 4) are corresponding to the quinoid and benzoid rings, respectively. The plane symmetric stretching related to C–N resulted in absorption bands at 1349 (peak 5) and 1294 cm^{-1} (peak 6). The characteristic absorptions of the aromatic ring *ortho* substituted are present at 1117 (peak 7) and 1027 cm^{-1} (peak 8).

X-ray diffraction and crystallinity percentage

X-ray diffraction techniques examine the long-range order produced as a consequence of very short range interactions. XRD patterns for POEA-ES showed no significant structural differences when the polymerization times increased from 3 to 48 h. Thus, samples exhibited peaks at 2θ = 8°, 12°, 16°, 24°, 26°, 38°, 44° and 52°, as shown in Fig. 2. It was noted that the more defined

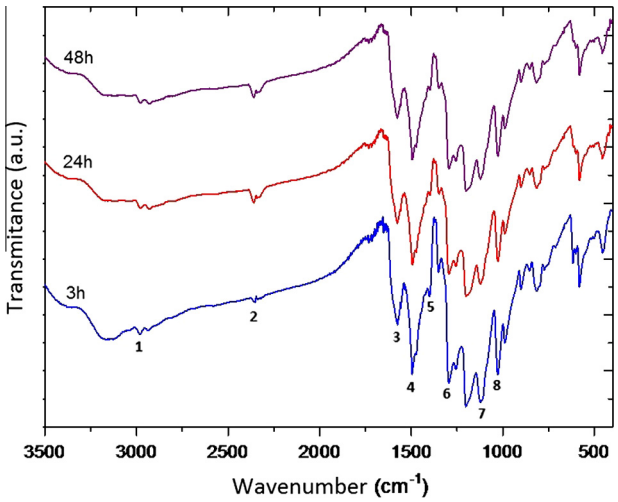

Fig. 1. FTIR spectra of POEA-ES.