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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 –OCH2CH3 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 (–OC2H5) 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 2θ = 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 crystallities 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.

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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 (–OCH2CH3) 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
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 peroxodisulfate (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, LaB₆. 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 2500 and 4000 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 –OCH₂CH₃ located at the ortho position of the carbon rings. The absorptions at 1581 cm⁻¹ (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 cm⁻¹ (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
of crystallinity around 50% [26–28]. Recent studies have shown that for PANI-ES, the percentage of crystallinity obtained was 22% [29] by the ratio of the area of the peaks and the amorphous halo method. Bharda et al. [30] obtained PANI-ES chemically synthesized with percentage of 60.8%. Sanches et al. [16] obtained values of 49% and 51% related to synthesis times of 0.5 and 48 h, respectively. More recently, results ranged from 48% to 63% for POMA-ES related to the time of synthesis of 0.5 and 72 h, respectively [8].

To determine the crystallinity percentage of semi-crystalline polymers, it is assumed that the polymer consists of a well-defined mixture of amorphous and crystalline regions [31,32]. Fig. 3 shows the decomposition peaks of POEA-ES. Through Peak Fitting Module Program the POEA-ES crystallinity percentage was around 39%.

LeBail Method analysis

Structural refinement through LeBail Method started using as input data the symmetry and unit cell parameters of PANI tetramer obtained by Evain et al. [20]. However, it is important to note that the obtained diffraction pattern is from a derivative of PANI, whose structural difference is the presence of the functional group –OCH2CH3 in the ortho position of carbon rings. With the presence of this functional group in POEA-ES chains, it was needed to modify the dimensions in the directions “a” and “b” of the unit cell due to accommodate this functional group.

Fig. 4 shows the obtained refinement for POEA-ES and the respective main plans reflections. It is observed that the XRD patterns showed a good fit after change cell parameters “a” and “b”. After the adjustment, it was possible to visualize the crystallites in the directions [1 0 0], [0 1 0] and [0 0 1] (Fig. 5) using the GFourier Program [33]. It was observed that POEA-ES showed an average crystallite size of 26 Å. Table 1 shows the refined parameters for POEA-ES. The values were compared with Evain et al. [20] and Leite et al. [25]. The cell parameters “a” and “b” obtained here are larger than those proposed by Leite et al. [25] due to the presence of the functional group –OCH2CH3 in ortho position of the carbon rings, resulting in a larger unit cell in these directions to accommodate this functional group.

Using the lattice parameters calculated from XRD data, it was proposed a geometry for POEA-ES and the molecule was computationally parameterized with atom types from the General Amber Force Field (GAFF) [34] and Gasteiger charges [35]. The proposed unit cell for POEA-ES is shown in Fig. 6. A proposed POEA-ES unit cell model was obtained using the refined cell parameters and introducing the chloride ions on the structure voids, near of the nitrogen atoms.
**SEM analysis**

SEM technique was used in order to identify the POEA-ES morphology at room temperature. Fig. 7 shows the SEM images of POEA-ES and it was observed micrometric particles of varying sizes, with morphologies similar to the interconnected vesicular microspheres.

**Conductivity measurements**

The electrical conductivity for POEA-ES was obtained by averaging three samples and the value found was \(0.3 \times 10^{-7}\) S/cm. Studies have shown that the conductivity of PANI and its derivatives depend on the oxidation state and protonation degree. For PANI derivatives, an important factor in the efficiency of the electrical conductivity is the size of the ortho functional group in the polymer main chains. The greater the extent of this group size, the greater the steric hindrance between the chains, and lower the flow of inter-chain charge carriers. Nogueira et al. [36] synthesized POMA thin films and obtained conductivity values in the range of \(10^{-10}\) and \(10^{-3}\) S/cm. Gazotti and De Paoli [37] also synthesized POMA and obtained the value of \(4.5 \times 10^{-2}\) S/cm. Bhadra et al. [30] obtained for chemically synthesized PANI-ES the value of \(6.3 \times 10^{-4}\) S/cm, while for electrochemical synthesis it was obtained \(1.7 \times 10^{-4}\) S/cm. Recent studies in structural characterization of PANI-ES [16], and POMA-ES [8] showed conductivity.

**Table 1**

Comparison between the values found for POEA-ES.

<table>
<thead>
<tr>
<th>Refined parameters</th>
<th>Evain et al. [20]</th>
<th>Leite et al. [25]</th>
<th>POEA-ES (1.0 M HCl, 3 h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) ((\text{Å}))</td>
<td>5.732 (8)</td>
<td>5.412 (2)</td>
<td>7.623 (4)</td>
</tr>
<tr>
<td>(b) ((\text{Å}))</td>
<td>8.886 (6)</td>
<td>8.845 (2)</td>
<td>12.136 (4)</td>
</tr>
<tr>
<td>(c) ((\text{Å}))</td>
<td>22.888 (9)</td>
<td>21.612 (8)</td>
<td>22.547 (2)</td>
</tr>
<tr>
<td>(\alpha) (°)</td>
<td>82.74 (8)</td>
<td>84.15 (2)</td>
<td>82.264 (8)</td>
</tr>
<tr>
<td>(\beta) (°)</td>
<td>84.52 (8)</td>
<td>84.59 (2)</td>
<td>85.811 (9)</td>
</tr>
<tr>
<td>(\gamma) (°)</td>
<td>88.47 (3)</td>
<td>88.38 (1)</td>
<td>89.277 (8)</td>
</tr>
<tr>
<td>(V) ((\text{Å}^3))</td>
<td>1141.2 (9)</td>
<td>1024.4 (5)</td>
<td>2061.5 (8)</td>
</tr>
<tr>
<td>Global average size ((\text{Å}))</td>
<td>–</td>
<td>75</td>
<td>26/10</td>
</tr>
<tr>
<td>Crystallite apparent size(\text{100}) ((\text{Å}))</td>
<td>–</td>
<td>76</td>
<td>22</td>
</tr>
<tr>
<td>Crystallite apparent size(\text{010}) ((\text{Å}))</td>
<td>–</td>
<td>76</td>
<td>32</td>
</tr>
<tr>
<td>Crystallite apparent size(\text{001}) ((\text{Å}))</td>
<td>–</td>
<td>44</td>
<td>22</td>
</tr>
<tr>
<td>(R_{exp})</td>
<td>–</td>
<td>10.2</td>
<td>1.93</td>
</tr>
<tr>
<td>(R_p)</td>
<td>–</td>
<td>8.71</td>
<td>2.60</td>
</tr>
<tr>
<td>(R_{exp})</td>
<td>–</td>
<td>–</td>
<td>1.77</td>
</tr>
<tr>
<td>(\chi^2)</td>
<td>–</td>
<td>6.11</td>
<td>2.16</td>
</tr>
</tbody>
</table>

Fig. 5. Crystallites visualization in [1 0 0], [0 1 0] and [0 0 1] directions using the GFourier Program.

Fig. 6. Proposed unit cell for POEA-ES.
values of $1.8 \times 10^{-4}$ and $5.2 \times 10^{-7}$ S/cm, respectively, for conventional chemical synthesis. Thus, we can see different conductivity values found for PANI and POMA, which are closely related to the methods of synthesis.

Conclusion

We successfully obtained Poly(o-ethoxyaniline) Emeraldine-salt form (POEA-ES) by chemical polymerization. Through FTIR technique it was observed that the spectra showed no differences compared to synthesis times of 3, 24 and 48 h. It was possible to identify characteristic absorption bands of deformation and stretching of chemical bonds and functional groups present in POEA-ES structure, which allowed its organic chemical characterization. XRD patterns did not show structural differences in relation to the increasing of polymerization times, suggesting that the synthesis times do not affect the polymer crystallinity, which was found around 39%. Through LeBail Method it were possible to obtain POEA-ES cell parameters, indicating that the presence of the functional group $\text{OCH}_2\text{CH}_3$ in the ortho position of the carbon rings need to change the values of “a” and “b” to accommodate the orthoethoxy group. Average crystallite size was found around 26 Å. The analysis of the polymer morphology was obtained by SEM, suggesting that POEA-ES consists of interconnected vesicular microspheres. The conductivity value obtained for POEA-ES was lower when compared with values published in the literature for PANI-ES and POMA-ES, as expected. The result means that the size of the orthoethoxy group in the polymer main chain creates an inter-chain difficulty in mobility of charge carriers, which can be verified by comparing the conductivity values for each polymer.

References

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