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Characterization of Poly(o-methoxyaniline) Emeraldine-base form obtained at different time neutralization

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HIGHLIGHTS

- The use of SAXS and XRD provide a systematic study on the structural characterization of polymers.
- LeBail fit represents a recent tool applied in structural researches of polymeric materials.
- EB-POMA has changed slowly its structure under neutralization process.

ABSTRACT

Poly(o-methoxyaniline) Emeraldine-base form (EB-POMA) was obtained thought the neutralization of the Poly(o-methoxyaniline) Emeraldine-salt form (ES-POMA) using NaOH 0.1 M at 3.0, 24.0 and 48.0 h of neutralization. X-ray Diffraction (XRD), LeBail Fit, Small-angle X-ray Diffraction (SAXD), Small-angle X-ray Scattering (SAXS) and Scanning Electron Microscopy (SEM) were used to characterize the obtained EB-POMA. Crystallinity was obtained from XRD patterns and remained around 38% up 24.0 h of neutralization, decreasing to 27% at 48.0 h. Crystal data (for 3.0 h of neutralization, \(a = 6.793\), \(b = 9.529\), \(c = 19.640\), \(\alpha = 83.043\), \(\beta = 84.656\) and \(\gamma = 88.586\)) were obtained from LeBail fit and showed crystallites very small lamellae with an oblate spherical shape and global average size around 20 Å. By SAXS it was obtained the particle Radius of Giration (\(R_g\)) ranging from 200 Å at 3 h of neutralization to 160 Å at 48 h. The maximum particle size (\(D_{max}\)) ranged from 650 to 550 Å was obtained from the Pair-distance Distribution Function (\(g(r)\)). SEM images showed a globular vesicular morphology with micrometric sizes. Electrical conductivity values showed a decrease between 3 and 48 h of neutralization, from \(1.52 \times 10^{-10}\) to \(1.13 \times 10^{-10}\) S/cm.

1. Introduction

The use of the Intrinsically Conducting Polymers (ICPs) has been hampered by the fact that many of these materials are insoluble and infusible because of the delocalized \(\pi\) bonds along their macromolecular chains [1]. Polyaniline (PANI) has always been regarded as an intractable material due to its poor solubility in common organic solvents. To address this, many attempts have been made, such as structural modification by ring or \(N\)-substitution, doping with functionalized protonic acids and blend with conventional polymers [2].

PANI derivatives show an improved solubility, essentially due to the flexible groups incorporated into the polymer chain, that induce torsion in the backbone with departure from planarity effect and the presence of the polar substituent group that increases the overall polarity of the polymer chain [3,4]. Accordingly, one ring-substituted polyaniline derivative, Poly(o-methoxyaniline) (POMA), has attracted considerable attention [5–9]. POMA has a group (–OCH_3) in the ortho position of the carbon rings [10,11]. As in PANI, POMA also can be obtained in different oxidation states and the POMA Emeraldine-form can be found in the basic form (EB-POMA) or salt form (ES-POMA) [12,13].

Structural aspects in polymers continue to be an interesting research topic [14–16,21]. Understanding the regular arrangement of polymer materials is essential for the prediction of processing methods, properties and new applications in technology. The aim
of this paper is to analyze the structure and morphology of the EB-POMA obtained from the neutralized ES-POMA at different times, from 3 to 48 h of neutralization. XRD and SAXD were used for the determination of cell parameters and crystallinity; LeBail fit was used to refine cell parameters and to obtain crystallite size and shape; SAXS was used to determine size and shape of the scattering particles and SEM for the determination of the solid polymer morphology. Then, these results were correlated with EB-POMA electrical properties.

2. Experimental

2.1. Polymer synthesis

EB-POMA was obtained by the neutralization of Emeraldine-salt Poly(α-methoxyaniline) (ES-POMA). The doped form of POMA obtained at 3.0 h of synthesis [9,21] in HCl (1.0 M) was neutralized in NaOH (0.1 M) for 3.0, 24.0 and 48.0 h to obtain its respective Emeraldine-base form.

2.2. XRD analysis and crystallinity percentage

XRD data were obtained at the Laboratory of X-ray Crystallography of IFSC/USP 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 step-scanning mode, 2θ = 5–60°, step of 0.02° and 5 s/step. Peak Fitting Module program [17,18] was used for the peak decomposition of the semi-crystalline pattern and determination of area due to the amorphous phase. The crystallinity percentage was obtained by the ratio between the sums of the peak areas to the area of amorphous broad halo due to the amorphous phase.

2.3. Data analysis

The use of LeBail fit [19] to obtain polymer structural information is not very common due to the large overlapped peaks on diffractograms. Nevertheless it has been used to characterize polyaniline and substituted polyanilines [16,20–22]. This method is used in order to fit the XRD profile, refining cell parameters and the shape of the extracted peaks. LeBail fit was performed using the software package Fullprof [23]. All parameters were refined by the least-squares method [24]. The pseudo-Voigt function modified by Thompson-Cox-Hastings was used as peak profile function [25]. Instrumental resolution function parameters were obtained from a lanthanum hexaborate standard, LaB₆. The aniline tetramer single crystal parameters obtained by Evain et al. [26] were used as initial parameters (a = 5.7328 Å, b = 8.8866 Å, c = 22.6889 Å, α = 82.7481°, β = 84.5281° and γ = 88.4739°). Particle size and shape were determined from the anisotropic crystallites size using spherical harmonics (SHP) [27].

2.4. SAXS measurements

SAXS experiments were performed at the National Synchrotron Light Laboratory (LNLS), Campinas, Brazil, using a monochromatic X-ray beam (λ = 1.488 Å). Powder samples were placed in a parallel window cell and the scattering curves were normalized with respect to the decreasing intensity of the incoming synchrotron beam and to the sample absorption [28]. Two values of the distance between sample and detector were used: 394.2 mm (Small-angle X-ray Diffraction – SAXD, to record Bragg reflections) and 1010.6 mm (Small-angle X-ray Scattering – SAXS, to record the scattering due to the scattering particles). The scattered intensity was measured over the scattering vectors, q = (4π/λ)sinθ, where 2θ is the scattering angle [29–31]. To perform most of the SAXS calculations it was used the GNOM program package [32].

2.5. 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 [33]. 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.
3. Results and discussion

3.1. XRD and SAXD analysis

X-ray Diffraction techniques examine the long-range order produced as a consequence of very short-range interactions. Fig. 1 shows the diffractograms of EB-POMA obtained at 3, 24 and 48 h of neutralization. Three peaks at 2θ = 12°, 17.8°, 23.5° were observed and a broad peak around 2θ = 44.0°. As the neutralization of ES-POMA occurred slowly due to the difficulty of removal of Cl⁻ ions due to the largest group o-methoxy in its structure, it was possible to observe a slower decrease of crystallinity up to 48 h.

To determine the percentage of crystallinity in semi-crystalline polymers, it is assumed that these materials are composed of a mixture of well-defined crystalline and amorphous regions...
In the case of EB-POMA, we observed major changes in XRD patterns after 24 h of neutralization, showing that the neutralization process promoted loss of crystallinity, ranging from 38% at 3 h of neutralization to 27% at 48 h.

The application of SAXD technique was used to verify the presence or absence of possible Bragg reflections at lower angles. SAXD curves obtained for EB-POMA shown in Fig. 2 presented two peaks located respectively at $2\theta = 2.5^\circ$ ($q = 0.18 \text{ Å}^{-1}$, $\lambda = 1.49 \text{ Å}$, $d = 34.1 \text{ Å}$) and a broad peak located at $2\theta = 4.9^\circ$ ($q = 0.36 \text{ Å}^{-1}$, $\lambda = 1.49 \text{ Å}$, $d = 17.4 \text{ Å}$). Due to neutralization process, it is observed a decrease in peak intensity located at $2\theta = 2.5^\circ$, which is attributed to a lamellar arrangement of crystallites. The peak located at $q = 0.36 \text{ Å}^{-1}$ is corresponds to the reflection (001). The peaks located at larger angles (observed in Fig. 1) are formed by many reflections (wider clusters). Thus, with an appropriate scaling it was possible to obtain the EB-POMA full diffractogram using the SAXD/XRD data as a function of $q$. Fig. 3 shows the full diffractogram for EB-POMA obtained at 3.0 h of neutralization.

3.2. LeBail Fit

The observed (Iobs) and calculated (Icalc) diffractograms and the residual line (Iobs–Icalc) as well as indexes for the main reflections for 3 h of neutralization are shown in Fig. 4. The vertical bars are the Bragg reflections. Table 1 shows the refined parameters. Comparing with the input parameters [26], it was observed a decreasing in “c” cell parameter, reduced to around 19 Å, suggesting that the neutralization process contributed to form EB-POMA foldermic chains. Neutralization process showed crystallite average size around 19 Å. Fig. 5 shows the visualization of EB-POMA crystallites in the directions [100] [010] and [001] obtained through the program GFourier [36]. At 48 h of neutralization, there is a smaller apparent size around 16 Å in the [001] direction and almost equivalent along [010] and [100], respectively around 20 and 21 Å. It is important to stress that the standard deviation appearing in the average apparent size is calculated using the reciprocal lattice directions so it is a measure of the degree of anisotropy. Fig. 6 shows a proposed EB-POMA unit cell model obtained using the refined cell parameters and introducing the o-methoxy group on the aniline tetramer chains. The proposed model is just an adequate speculative model of the

![Fig. 6. Proposed EB-POMA unit cell speculative model.](image)

![Fig. 7. p(r) curves for EB-POMA at 3.0, 24.0 and 48.0 h of neutralization.](image)

![Fig. 8. Kratky curves for EB-POMA.](image)

![Fig. 9. SEM images of EB-POMA at (a) 3 and (b) 48 h of neutralization.](image)
Emeraldine-base form of Poly(o-methoxyaniline) (EB-POMA) based on the structure of the aniline tetramer obtained by Evain et al. [26].

3.3. SAXS

3.3.1. Radii of Gyration ($R_g$), Pair-distance Distribution Function $p(r)$ and Kratky curves

Though the SAXS technique is possible to obtain the Radii of Gyration ($R_g$), the Pair-distance Distribution Function $p(r)$ calculation and the Kratky curves. The $R_g$ values of EB-POMA were decreasing as the neutralization time increased, ranging from 200 Å for 3 h of neutralization to 160 Å for 48 h of neutralization. Fig. 7 shows the $p(r)$ curves for the EB-POMA at 3.0, 24.0 and 48.0 h of neutralization, which showed changes in their particle shapes with increasing time neutralization. It was observed that the system tends to form particles with less globular structures, indicating that the particles deviate continuously from the globular shape. For EB-POMA, $D_{max}$ values ranged from 650 to 550 Å. Kratky curves (Fig. 8) show that the time neutralization influences on the organization of the system, indicating that the system at 48 h of neutralization is more disorganized than the system found at 3 h of neutralization.

3.4. SEM and conductivity measurements

Fig. 9(a and b) shows the SEM images of EB-POMA at 3 and 48 h of neutralization. It was noted that the polymeric structures obtained from 3 to 48 h of neutralization indicated loss of globular character, which is more evident for the polymer obtained at 48 h. The conductivity values showed a decrease from $1.52 \times 10^{-10}$ to $1.13 \times 10^{-15}$S/cm during the neutralization process.

4. Conclusions

We successfully obtained Emeraldine-base form of Poly(o-methoxyaniline) (EB-POMA) by neutralization in the presence of sodium hydroxide (NaOH). It was reported a detailed systematic observation of crystalline phases in its undoped forms, which differ in their semi-crystalline structures and morphology. It was observed that the crystallinity decreases very slowly because of the steric hindrances due to the greatest volume of the o-methoxy group. XRD analysis showed different profiles with increasing time neutralization. Thus, with an appropriate scaling it was possible to obtain the full diffractogram using the SAXS/XRD data as a function of $q$. LeBail fit allowed the determination of useful structural information. It was possible to determine the unit cell parameter values, observing a reduction of the $c$ value, suggesting the formation of EB-POMA folded trimmeric chains. Through SAXS it was observed that the system tends to form less globular particle structures, indicating that the particles deviate continuously from the globular shape. SEM analysis showed that increasing time synthesis promotes the reduction of the EB-POMA structures, which lose their globular vesicular character with decreasing crystallinity. It was observed a decrease in EB-POMA conductivity during the neutralization process. Thus, we report here a detailed systematic observation of crystalline phases in Emeraldine-base form of Poly(o-methoxyaniline) obtained at different time neutralization.

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