



INFLUENCE OF REACTION TIME ON THE STRUCTURE OF POLYANILINE SYNTHESIZED ON A PRE-PILOT SCALE

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Abstract – The aim of this work is to follow the structural variations of polyaniline (PAni) obtained by chemical oxidation on a pre-pilot scale, with different reaction times. Synthesis of PAni is well known, but when it is carried out on a pre-pilot scale, several factors can lead to structural changes and understanding these changes is important to improve controls on the synthesis process. The polymers formed were characterized by spectroscopic techniques (Raman spectroscopy, Fourier Transform Infrared - FTIR and UV-Visible). Degree of oxidation and yield were calculated for each reaction time. The analysis by FTIR, the calculated degree of oxidation and the yield showed significant changes in polymer structure at reaction times of 65 and 80 min. This result was attributed to the excessive oxidation of PAni, with the breaking of its polymer chain. The changes observed in the structure of PAni gave subsidies to the optimization of the process of obtaining polyaniline by chemical synthesis.

Keywords: Chemical reactor, spectroscopy, synthesis, conducting polymer.

INTRODUCTION

Intrinsic conducting polymers (ICPs) are among the most successful and important discoveries in modern polymer chemistry and physics. These polymers are successfully used in new advanced materials for photovoltaic, optoelectronics, sensors, antistatic protection, catalysis, corrosion protection and so forth (Ogurtsov et al., 2013). Polyaniline (PAni) is an environmentally stable and tech-

nologically important conductive polymer, whose electronic conductivity can be altered reversibly by both oxidation/reduction and acid/base chemistries (Kolla et al., 2005). The PAni can be used, among other applications, such as secondary batteries, for electromagnetic interference (EMI) shielding, solar cells, bio/chemical sensors, corrosion devices, organic light emitting diodes (OLED), electro-luminescence and chemical membranes. These applications reflect the characteristic properties of this

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material. However, the commercial applications of PANi have been limited due to harsh chemical conditions in the synthesis and purification procedures that often lead to an inflexible polymer (Jaymand, 2013).

The oxidized and reduced states of PANi, and its derivatives, are represented by the index of “y” reduced units (benzenoid ring) and “1 - y” oxidized units (quinoid ring), as indicated in the chemical structure presented in Figure 1, where x is the polymerization degree (Albuquerque et al., 2004).

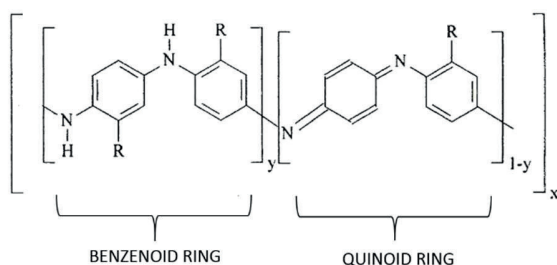


Figure 1. Benzenoid/quinoid rings (based on Albuquerque et al., 2004).

Three different oxidation states of the PANi, in base form, are known: the completely reduced leucoemeraldine (LB) is obtained when $(1 - y) = 0$; the oxidized form pernigraniline (PB) is obtained when $(1 - y) = 1$; and the 50 % oxidized form emeraldine (EB) is obtained when $(1 - y) = 0.5$ (Albuquerque et al., 2004). Each PANi oxidation state exists in two forms, namely protonated and deprotonated (Sapurina and Stejskal, 2010). The reaction parameters, such as acid concentration, temperature, time, oxidant concentration, aniline/oxidant molar ratio, concentration and the nature of protonic acid and of the electrolyte have a great influence on the rate of chemical oxidative polymerization of aniline, as well as on its final properties (Dan and Sengupta, 2004; Chowdhury and Saha, 2005; Genies et al., 1985).

The influence of some reaction parameters on PANi structure is well established. In relation to aniline/oxidant mole ratio, it was reported that yield, color and electrical conductivity were strongly dependent on this ratio (Chowdhury and Saha, 2005). As the oxidant concentration is increased above a mole ratio of 1 (oxidant/aniline mole ratio), the yield and intrinsic viscosity decrease. This may be attributable to over oxidation of radical cations responsible for both the growth rate and the chain length of the polymer (Dan and Sengupta, 2004).

The acidity of the medium can be considered the most important parameter of synthesis and has a decisive effect on the formed polymeric structure. The nature of the ac-

id's anion, the ratio [monomer]: [acid] and the variation of over acidity of the reaction are factors that can induce alterations in the polymerization process, in the morphology and in the properties of the aniline oxidation products (Sapurina and Stejskal, 2010).

There are many papers on optimizing the preparation of PANi with variables like pH (Genies et al., 1985), kind of oxidizer (Fong and Schlenoff, 1995), temperature (Stejskal and Gilbert, 2002), and electrolyte effect (Matto, 1996). However, the results are difficult to compare because different studies have used different conditions of preparation and characterization (Blinova et al., 2007).

In this study, the synthesis of PANi was carried out on a pre-pilot scale, with different times of reaction, keeping the other parameters of synthesis constant. Through spectrometric analysis by Fourier Transform Infrared (FTIR), Raman spectroscopy and UV-Visible, the quantification of the degree of oxidation and yield seeks to determine the changes that occur in the structure of PANi during the chemical synthesis, following the addition of oxidant until 2 h after the end of this addition, aiming at contributing to the optimization of this synthesis process.

MATERIALS AND METHODS

Synthesis of PANi in different reaction times

Aniline solutions (1.0 M/1,8 L) and ammonium peroxydisulfate (1.9 M/0,7 L) solutions have been prepared in aqueous solution containing 1.0 M hydrochloric acid and 1.0 M sodium chloride.

The salt addition was used to prevent freezing when synthesis is carried out at temperatures below 0°C (Sbaitte et al., 2004).

The chemical synthesis was performed in a 5-L glass reactor with glass rods and Teflon naval type propellers, for agitation. A cooling jacket was connected to a constant temperature bath, containing ethylene glycol. The reactor temperature was maintained at $(-5 \pm 1)^\circ\text{C}$.

First, the aniline solution was added to the reactor and kept under constant stirring. Then ammonium peroxydisulfate solution was added drop-wise, through an addition funnel, at a rate of 14 ml per minute. The reaction times were 10, 20, 35 and 50 min, during the addition of the oxidant. After the complete addition of the ammonium peroxydisulfate solution, five other reactions continued stirring for 15, 30, 45, 60 and 120 min, respectively. The time the addition of ammonium peroxydisulfate solution started was considered the initial time of the reaction, so the final reaction times were 65, 80, 95, 110 and 170 min.

The precipitated polyaniline salts were filtered and washed with approximately 10 L of distilled water, until

the washing liquid was colorless and pH was around 6. The polymer, re-suspended in a 1.0 M ammonium hydroxide solution, was kept under agitation for 12 h to perform the deprotonation process. After deprotonation, the material was filtered again, washed with approximately 10 L of distilled water and the powder (dark brown color) was dried in a conventional oven at 60°C until constant weight.

Characterization of PANi

The FTIR spectra of the synthesized polymers were recorded on samples in powder form, without previous preparation, using a FTIR spectrometer Spectrum 2000 (PerkinElmer), in 4000 to 600 cm^{-1} region. The technique used was Attenuated Total Reflectance (ATR), with 120 N of torque.

The Raman spectra were recorded by pressing the powder sample on a glass slide. These analysis were performed on a Raman spectrometer model 2000 (Renishaw) with an Argon laser (0.5 MW) at 514.5 nm.

The UV-Visible spectra were recorded in a UV-Visible spectrometer Lambda 35 (PerkinElmer) using 1-methyl-2-pyrrolidinone (NMP) as a solvent. PANi samples were dissolved in NMP, kept under stirring for 12 h and filtered to remove the undissolved material. The filtrate was diluted at a ratio of 1: 20 (v/v) in NMP and this solution (0.01 g/L) was used to obtain the spectra.

The polymer yield was calculated by the ratio between the amount of PANi formed and the amount of aniline charged, in g (Chowdhury and Saha, 2005).

RESULTS AND DISCUSSION

The synthesis was carried out reproducing the same conditions of temperature, concentration of reactants and additives (HCl and NaCl). The only variable was the reaction time, considered in two distinct steps: PANi obtained during the addition of oxidant (reaction times ≤ 50 min) and PANi obtained after the addition of oxidant (reaction times > 50 min).

Polymerization of aniline

The reaction started immediately when the ammonium peroxydisulfate solution was added. The formation of a dark precipitate in the solution was observed from the beginning of the reaction. Under these synthesis conditions — temperature of -5°C, acidic medium (1 M HCl) and a high concentration of oxidant (1.9 M) —, this reaction is very fast and it is not possible to visually distinguish if the reaction occurs in one or more steps. The

solid material formed remains in suspension throughout the reaction.

Generally, the oxidation of aniline in hydrochloric acid solution by ammonium peroxydisulfate gives PANi, sulfuric acid, hydrochloric acid and ammonium sulfate (Sedenková et al., 2011).

As the polymer was deprotonated with 1 M ammonium hydroxide, the formed PANi must not have conductive structures. In FTIR spectroscopy, the characteristic bands of conductivity are assigned to frequencies between 1237 and 1248 cm^{-1} and also in the region between 1124 cm^{-1} and 1160 cm^{-1} (Dimitrieva and Dunsch, 2011; Trchová et al., 1999; Tang et al., 1988). The Raman frequency related to conductivity, for a 514 nm excitation line, is localized at frequencies between 1335 and 1339 cm^{-1} (Morávková et al., 2012; Lapiński and Dubis, 2012). In the UV-Visible spectra, the protonated form of PANi shows absorption bands at 335 - 340 nm, 440 - 480 nm and 800 - 870 nm (Rao et al., 2000; Kavitha et al., 2012). The frequencies relating to PANi protonated in FTIR spectra bands were found with very low intensities, indicating that these bands can be trace amounts. In the Raman and UV-Visible spectra, bands assigned to conductivity have not been identified.

Yield of PANi

At 10 and 20 min reaction times, the oxidant was 20 and 40% of the total amount, respectively, and the yield was close to 17%. According to Yang and Weng (2009), PANi yield is greatly influenced by the molar ratio of oxidant/aniline. Therefore, this lower value is due to the smaller amount of oxidants present in the reaction. Chowdhury and Saha (2005) demonstrated that the incomplete conversion of aniline to PANi, due to the smaller quantities of oxidant, could lead to smaller yield, when the mole ratio aniline/oxidant is greater than 2.4 soluble oligomers could be produced.

At 35 min reaction time, 70% of the oxidant was added and the yield almost doubled, going to 32.9%. A maximum value of 66.0% was obtained at 50 min reaction time, when ammonium peroxydisulfate addition was complete. In 65 and 80 min reaction time, there was a decrease of the yield (34.5 and 39.9%) and it increased again for 95 min (58.7%), when it began to be stable (50.1 and 53.8% for 110 and 170 min reaction time, respectively).

The yield decrease found at 65 and 80 min reaction can be explained by the oxidative degradation of the polymer, due to the high concentration of oxidant, which promoted the formation of oligomers and yielded a large amount of water-soluble material (Cao et al., 1989). When

there is a high oxidant concentration (molar ratio aniline/oxidant less than 2.0), the formation of oxidation products with low molecular weight occurs, which are also water soluble, reducing the yield (Chowdhury and Saha, 2005). On the other hand, at 95, 110 and 170 min reaction times, the yields were close to 50%, indicating a stabilization. It is likely that the yield does not suffer major changes, even with the increased reaction time. The results obtained are consistent with those found by Cao et al. (1989), who obtained a yield from 36.9% and Rodrigues and Paoli (1991) who obtained a yield lower than 80%.

FTIR spectroscopy

FTIR spectroscopy is a useful tool for various science and engineering fields, due to high sensitivity or selectivity toward trace amounts of sample, as well as low noise to signal ratio; moreover, this method is easy and inexpensive. Apart from those qualitative applications, FTIR spectroscopy is also used in quantitative determinations (Arasi et al., 2009). Figure 2 shows the FTIR spectra of PANi EB for some reaction times.

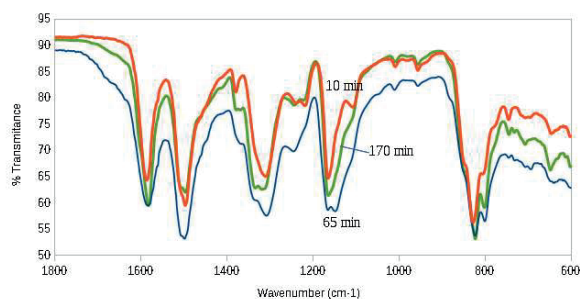


Figure 2. FTIR spectra of PANi EB for 10 min, 65 min and 170 min reaction time.

The assignments of the absorption bands were described in several papers. The frequencies found for PANi samples obtained at different reaction times as well as the tasks set for each region are described next:

1. 1800 - 1450 cm^{-1} region, where the aromatic ring vibrations, N-H bending and C=N stretching are found. The bands attributed to C=C stretching in quinoid and benzenoid rings are found in this region too. These two very strong bands were used to determine the degree of oxidation (R), which is the ratio between the intensity of the band assigned to the quinoid ring (frequency of 1582 to 1587 cm^{-1} , for this experiment) and the intensity of the

band assigned to the benzenoid ring (frequency of 1495 to 1498 cm^{-1} , for this experiment). This variation is related to the oxidation of benzenoid rings, which are transformed into quinoid rings, including the transformation of amino groups into imino groups upon oxidation of the polymer (Kellenberger et al., 2012; Furukawa et al., 1988).

2. 1400 - 1240 cm^{-1} region, where the C-N stretching of aromatic amines is found. A strong band at 1306 - 1315 cm^{-1} appears at all reaction times. The 50 min reaction time begins to show a shoulder around 1330 cm^{-1} , which, at the 170 min reaction time, turns into a doublet. The shoulder and the doublet imply that this band may contain more than a single vibrational mode (Kellenberger et al., 2011). The doublet can be associated with the existence of two different conformations of PANi (Nascimento, 2010). Other bands in this region (1377 - 1379 cm^{-1} , 1239 - 1246 cm^{-1} , 1220 - 1224 cm^{-1}) have low intensity and do not show variations with the reaction time.

3. 1200 - 600 cm^{-1} region, where the bending vibrations in-plane and out-of-plane of C-H are found and two strong bands appear, one at 1160 - 1165 cm^{-1} and the other at 822 - 824 cm^{-1} , with a small band behind it, at 830 cm^{-1} . The 65 and 80 min reaction times feature a doublet at 1160 and 1147 cm^{-1} . This second band can be attributed to the presence of pernigraniline base form (PB). A doublet with a shoulder near 1497 cm^{-1} and a shift to higher frequencies (1500 cm^{-1}), which appears at the 80 min (doublet) and 65 - 95 min (shoulder) reaction times, can also be attributed to the PB form (Quillard et al., 1994). It is well established that, in the polymerization of aniline by strong oxidizers such as ammonium peroxydisulfate, the initially formed product is PB (fully oxidized form), which is reduced to the EB form, due to excess aniline present in the solution (Beadle et al., 1998).

So, the main changes in the FTIR spectra to PANi obtained in different reaction times were found at 65 and 80 min, probably due to over oxidation.

Raman spectroscopy

Raman scattering spectroscopy is useful to study and characterize different oxidation and doping forms of PANi (Nobrega et al., 2014). Raman spectra of PANi and other related polymers are usually rich in bands which correspond to a wide variety of vibrational modes, characteristic for these species (Mažeikienė et al., 2007).

Figure 3 shows the Raman spectra of PANi EB for several reaction times.

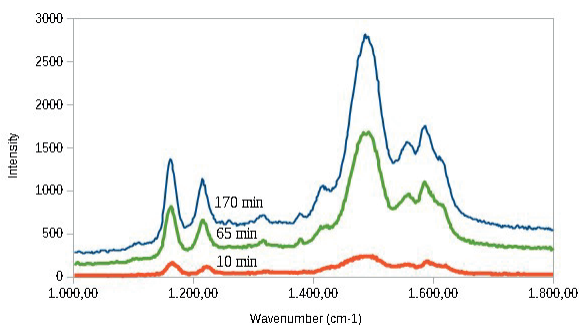


Figure 3. Raman spectra of PANi EB at 10 min, 65 min and 170 min reaction time.

The band frequencies found in the Raman spectra for these polymers are aligned with the values found in the literature for the EB base form (Maser et al., 2003; Berrada et al., 1995).

Generally, there are three regions in Raman spectra of PANi that are sensitive (Mažeikienė et al., 2007):

1. 1100 - 1200 cm^{-1} region, where C-H bending vibrations of benzene or quinoid rings are more prominent. Two medium intensity bands were found in the range of 1162 to 1167 cm^{-1} and 1216 to 1223 cm^{-1} , which were attributed to quinoid and benzenoid rings, respectively.

2. 1210 - 1520 cm^{-1} region, stretching vibrations characteristic of C-N (imine) and C=N. A band with greater intensity was found at 1485 - 1489 cm^{-1} and, besides this band intensity varied with the time of reaction from the shortest time to the biggest one, the frequency did not show significant variation.

3. 1520 - 1650 cm^{-1} region, with the domain of C-C and C=C stretching vibrations of the benzene and quinone rings. Overlapping bands were found at 1557 - 1560, 1586 - 1594 and 1613 - 1619 cm^{-1} , which varied in intensity with the reaction time, that is, the longer the time, the greater the intensity. The variation in frequency was random, not being observed any pattern.

The assignment of frequencies for Raman spectroscopy varies greatly with the laser frequency used, as well as with the polymer form (base or salt). The bands that are ascribed to the C-H bending in quinoid and benzenoid rings are close to 1160 and 1881 cm^{-1} , respectively, giving direct information about the degree of oxidation of PANi (Ogurtsov et al., 2013). In the spectra obtained for different reaction times, the band found at 1216 - 1223 cm^{-1} was assigned to the benzenoid ring due to the intensity and because there is not another band in this region that could be assigned to that.

UV-Vis spectroscopy

The UV-Vis spectra for several reaction times are shown in Figure 4.

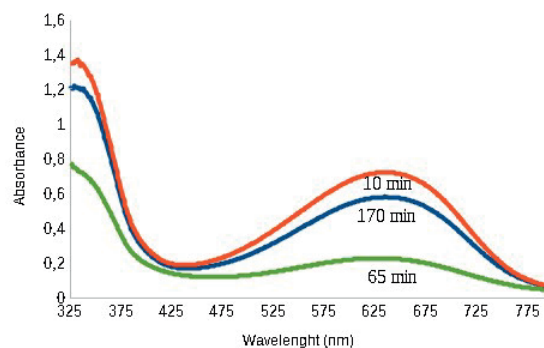


Figure 4. UV-Vis spectra of PANi EB at 10 min, 65 min and 170 min reaction time.

The UV-Visible spectrum of PANi in base form is dominated by two absorption bands, one at 330 nm (IB), assigned to the $\pi-\pi^*$ transition in the benzenoid ring, and the other in the visible region, 630 nm (IQ), attributed to excitation in the quinoid rings (Bairi et al., 2013). The ratio between the intensity of IQ and the intensity of IB indicates the relative amount of quinoid units in PANi molecules, *i.e.* the oxidation state of PANi, which plays a key role in determining the properties of PANi (Wang and Jing, 2005). For the 10 to 170 min reaction times, the bands were found at the frequencies of 325 - 333 and 635 - 645 nm. The variation in frequency was random e not linear with the reaction time.

Measurement of the degree of oxidation (R)

The R value is an indicative of the PANi oxidation level. It is calculated by the ratio $R = IQ/IB$, where I is the intensity of the UV-Visible or FTIR or Raman spectrum band; Q is the band corresponding to the quinoid ring and B is the band corresponding to the benzenoid ring, for each spectroscopic technique. For determining the intensity of the bands corresponding to the absorption of quinoid and benzenoid rings, deconvolutions were carried out for the respective bands, with the aid of the software Origin 8, where the bands were fit using Lorentzian functions, after correction for the baseline. Figure 5 shows the format of the bands for each technique, after deconvolution and fit. The spectra shown in the figure were obtained for the sample with 110 min reaction time.

The procedure used to obtain the intensity of the bands was the same for the three techniques of characterization,

and R values obtained through the bands of FTIR, UV-Visible and Raman spectra are shown in Table 1.

Table 1. R values (IQ/IB) for PANi obtained at different reaction times

Reaction time (min)	UV-Vis	FTIR	RAMAN
	R=I ₆₃₀ /I ₃₃₀	R=I ₁₅₈₅ /I ₁₄₉₆	R=I ₁₅₈₇ /I ₁₆₂₀
10	0.79	0.92	1.65
20	0.79	1.05	1.48
35	0.73	1.04	1.70
50	0.76	1.06	1.97
65	0.60	0.84	1.21
80	0.58	0.91	1.32
95	0.80	1.05	1.85
110	0.77	1.05	1.80
170	0.76	1.14	1.91

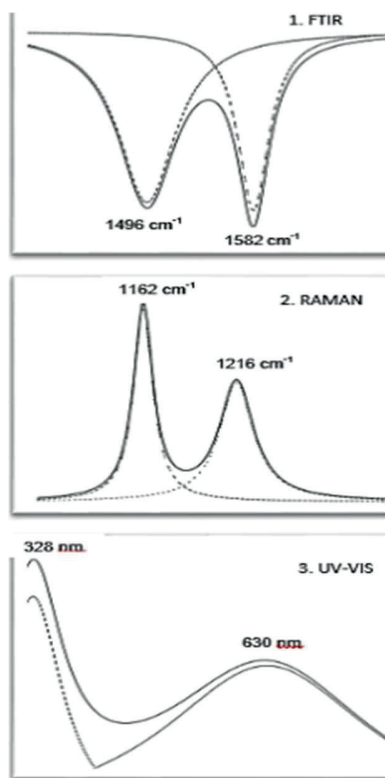


Figure 5. Bands after fitting and deconvolution for 1. FTIR; 2. Raman; 3. UV-Visible. Reaction time of 110 min. Full line: normal bands; dashed line: bands after deconvolution.

The UV-Visible spectra results suffer interference from the solvent and the phase separation, due to the par-

tial solubility of PANi in NMP. The spectra were obtained for the polymer soluble in NMP, unlike the FTIR and Raman spectra, that were obtained with the material in powder form, without previous preparation and, therefore, without interference of the solvent.

The R values obtained from the FTIR spectra are very close to 1, the R values for Raman are above 1 and for UV-Visible, the R values are lower than 1. If the ratio between the two bands is less than 1.0, there are more benzene units within the polymer. A value of 1.0 defines the emeraldine type structure and the polymer can have higher conductivity (Abdiryim et al., 2005) in protonated form.

The material insoluble in NMP contributed to the reduction of the UV-Visible intensity, resulting in lower values. Raman bands presented difficulty for deconvolution, due to the proximity between them and the bands could overlap each other. The FTIR technique appears to be the best for determining the R value.

At 65 and 80 min reaction times, the R value decreases, regardless of the spectroscopic technique (FTIR, UV-Visible or Raman), when compared with other reaction times. As R is indicative of the degree of oxidation of the polymer, there is a reduction of the oxidation in those times. This reduction may be associated with a hydrolysis that occurs in more acidic media and becomes more significant for polymers exhibiting higher oxidation states than that of EB (Pron et al., 1988). The excessive oxidation of PANi, causing degradation of the polymer by hydrolysis, can produce benzoquinone and hydroquinone (Chen et al., 2002).

The breaking of the carbon-nitrogen bonds by hydrolysis may lead to chain breaking or elimination of nitrogen, if a terminal group is involved (Pron et al., 1988). For hydrolysis, a more acidic environment is needed and this condition is achieved due to the presence of hydrochloric acid and sulfuric acid release as a by-product. This hydrolysis may also occur with a polymer having a higher oxidation state than that of EB. The FTIR spectra for 65 and 80 min reaction times have absorption frequencies that can be attributed to PB base, supporting the idea of an over oxidation of the polymer and a process of breaking the polymer chain, in agreement with the literature (Gospodinova and Terlemezyan, 1998; Gao et al., 2011).

CONCLUSIONS

The synthesis of PANi was studied on a pre-pilot scale, seeking improvements in the process of obtaining the polymer. The synthesis conditions (aniline and oxidant, acid and salt concentrations added to the reaction medium

and temperature) were maintained constant for each synthesis, with the time as the single variable. The polymer produced at each reaction time was characterized by spectroscopic techniques (FTIR, Raman and UV-Visible), degree of oxidation and yield.

Differences in yield were found, as a function of reaction time. In the addition step (10, 20, 35 and 50 min), this yield grew in a linear fashion, but it was reduced at times after the end of the addition (65 and 80 min), returning to grow and stabilizing at the longer times (95, 110 and 170 min). This variation in yield is consistent with the possibility of having occurred a hydrolysis at reaction times of 65 and 80 min, and stability indicates that, at 110 min after addition started, it is possible to obtain a constant value for the yield.

At 65 and 80 min reaction times the FTIR spectra show the possibility of PB being present along with EB, while the UV-Visible and Raman spectra show the typical bands of EB base.

These spectra were used to quantify the degree of oxidation and the obtained values show that, during the addition, for 10 to 50 min reaction times, the R values showed little variation. In the 65 and 80 min reaction times, these values decreased. This behavior can be explained by the hypothesis of hydrolysis due to the excess of acid in the reaction medium and over oxidation of the polymer. Hydrolysis leads to the breakdown of the polymer chain and over oxidation produces the more oxidized form of polyaniline, the pernigraniline form.

At 95 to 170 min reaction times, the degree of oxidation increased again, with values very close at these reaction times. Therefore, under the evaluated conditions of synthesis, the appropriate reaction time to obtain the best product was 110 min after the onset of the reaction.

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