X-ray irradiation: A non-conventional route for the synthesis of conducting polymers

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ABSTRACT

A non-conventional methodology for polyaniline (PANI) synthesis using X-ray irradiation is presented in this article, and shows the oxidants normally used in the (chemical or electrochemical) conventional synthesis of PANI are not necessary. The method uses only high energy photons to interact with nitrate ions (NO_3^-) and aniline monomer in an aqueous solution. The polymerization mechanism has also been investigated using radical scavenger (DMSO), and the results suggest that the hydroxyl radical (OH) generated *in situ* during exposure to X-ray could be the main agent responsible for oxidation and subsequent polymerization of the aniline monomer. Characterization of the morphology of the polymer by scanning electron microscopy (SEM) reveals that the PANI obtained by X-ray presents a predominantly fibrillar morphology with an average fiber diameter of 90 nm. Additionally, thermogravimetric analysis (TGA), elemental analysis, gel permeation chromatography (GPC), conductivity measurements, and spectroscopic characterization in the UV–vis and IR regions, showed that the polymer obtained is the polyemeraldine salt (the conducting form of the polymer).

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1. Introduction

In recent years, ionizing radiation has been used as a tool to prepare conventional non-conjugated polymers such as in free radical polymerization to obtain polymers with a narrow distribution of molecular weight. This has attracted considerable interest from both the scientific and technological points of view due to the fact that this presents several advantages over conventional techniques [1–3]. In particular, the approach of exposing a monomer to ionizing radiation can be used for polymer synthesis at room temperature. Additionally the process can be switched on and off upon exposure or removal of radiation instead of using initiating or stopper molecules to start or terminate the polymerization process.

There are very few papers published on the subject of interaction of ionization radiation with non-conventional polymers, and most of them only analyze the influence of ionizing radiation on polymer conductivity [4–7], and not on polymerization. From such analysis, it is found that polymer conductivity could increase or decrease depending on the doping state of the polymer, if the polymer is in the undoped state the result of the interaction of ionization radiation with the polymer is similar to the doping effect

when using acid solutions [8,9], namely an increase in conductivity. However, the response is quite different if the experiment is performed in a solution with dimethyl sulfoxide (DMSO) [10]. In this case, the polymer changes its oxidation state and becomes reduced. In order to profit from the radical produced by ionizing radiation, we developed a route for synthesis in which a solution of the aniline monomer and silver ions was irradiated with gamma radiation from a cobalt source. As a consequence of that interaction the conducting polymer (PANI) and silver nanoparticles were obtained simultaneously [11,12]. The mechanism which explains this result was based on the hydroxyl and hydrogen radicals produced by the radiation, which act as oxidizing agents for the polymerization of the aniline monomer and as a reducing agent for the silver ions, respectively. Since we performed the synthesis of a conducting polymer using low energy ionizing UV light [13] and high energy ionization gamma ray photons [12], in this paper we report for the first time, a non-conventional route for the synthesis of PANI in aqueous medium without traditional oxidants, but using only intermediated energy photons (X-ray). We also propose a mechanism that is able to explain the polymerization process.

2. Experimental

Aniline (Nuclear) was distilled under atmospheric pressure, stored in the dark and at low temperature prior to synthesis.

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Ammonium hydroxide (Merck), nitric acid (Merck), DMSO (Merck), acetonitrile (Aldrich) and all the other reagents were used without further purification. All aqueous solutions were prepared using Ultra-pure water from a Mili-Q system (resistivity 18.2 MΩ cm). Stock solution of the desired concentration of aniline in nitric acid was prepared and stored at low temperature, in a dark place, prior to use. Aniline polymerization synthesis using X-ray radiation was carried out in a plastic cuvette (with a 1 cm optical path), in which a solution of 0.5 M of aniline in 1.0 M of nitric acid, HCl or H_2SO_4 was used. The solution was irradiated using as an X-ray source a Philips model PW 1720 with Cu anode ($\lambda = 0.1541$ nm) with a voltage of 30 kV and a current of 40 mA. The samples were placed 33 mm from the tube with a uniform X-ray beam at a dose rate of 0.570 Gy/s. Afterwards, the solution was centrifuged and the material precipitated was washed with water and acetonitrile, several times, until the remaining solution became clear. Spectroscopic characterization in the UV–vis and infrared region was performed, with an Ocean Optics spectrophotometer model CHEM2000-UV-Vis, and with a FTIR Bruker model IF 66 spectrophotometer, respectively, whereas the morphology of the materials was analyzed with a (FEG-SEM) field emission scanning electron microscope model (FEI, Quanta 200). The TGA measurements were carried out in N_2 atmosphere at a heating rate of $10\,^\circ C\,min^{-1}$ up to a temperature of $900\,^\circ C$, using a Shimadzu analyzer model TGA 50, and the polymer conductivity was measured by the four-point-probe method using a Keithley model 6517A as a current Source and a Mminipa model ET-2500, as a voltmeter. The sample dimensions were 0.6 mm (thickness) × 12.6 mm (diameter). The elemental analysis was determined using a Carlo Erba Instruments equipment model EA 1110. To perform yield measurements, the samples were washed with water and acetonitrile several times (to remove oligomers). Then, they were filtered and dried in a vacuum at room temperature for 48 h. The undoping process was performed by treating the green powder in 1 M NH_4OH solution for 4 h. Finally, the undoped polymer was again dried and then weighed in order to determine the percentage yield. This was determined using the following formulae: yield % = (mass of PANI)/(mass of aniline monomer) × 100. The samples for gel permeation chromatography (GPC) studies were made by dissolving emeraldine base (EB)-form PANI powder in N-methyl-pyrrolidone (NMP) at a concentration of 0.140 mg/ml. The solutions were allowed to stand for 2 h at room temperature and were then filtered through a 0.20 μm filter. The solutions were then injected into the GPC column. The GPC studies were performed using a Viscotec Viscogel column operating at $40\,^\circ C$. Narrow distribution polystyrene was employed as the standard, and the GPC analysis was performed using a Viscotek model TDA 302 triple detector array.

3. Results and discussion

The visual effects of the interaction of X-ray with the aniline nitrate solution are shown in Fig. 1. We observe that prior to irradiation the solution is colorless (Fig. 1(a)) and as the dose increases, Fig. 1(b) 5 kGy and Fig. 1(c) 10 kGy, polymerization starts as small green marks in the cuvette wall, on the X-ray beam pathway. Also, as the dose increases, polymerization increases and more polymer is formed in the beam direction (see selected area, Fig. 1(b) and (c)). Polymerization proceeds while there is available aniline in the solution.

Fig. 2(a) shows the absorption spectra of the polymer material after it has been precipitated by centrifugation, washed with NH_4OH solution, and subsequently dried and dissolved on DMSO for analysis. It can be seen that the absorption spectra present only two absorption bands, one at 300 nm and the other at 650 nm, which are characteristics of the polyemeraldine base [14]. On the
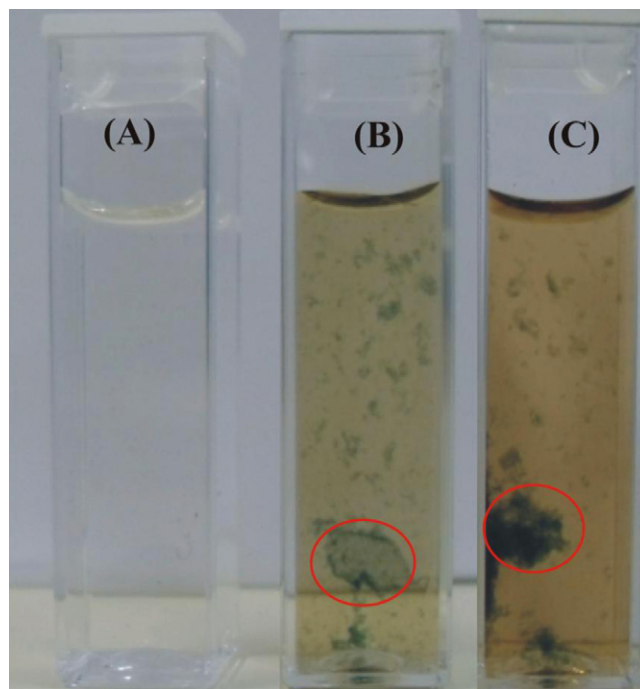

Fig. 1. Images of aqueous solution of aniline nitrate (a) before irradiation, (b) after 5 kGy X-ray irradiation (front view), and (c) after 10 kGy X-ray irradiation at room temperature (side view).

other hand, when the polymer is dissolved in formic acid, two new absorption bands are observed: one at 420 nm and the second at 800 nm. These can be attributed to the polaron–p*, and polaron–p transitions of the polymer PANI in the conducting state. These absorption bands are a strong indication that the PANI has been synthesized [15,16].

Fig. 3 shows the FTIR spectrum of a mixture of KBr pellets and the polymeric material in the 400–4000 cm^{-1} region. From these results, two strong bands at 1575 cm^{-1} and 1493 cm^{-1} can be assigned to the quinoid and benzenoid unit stretching modes; the vibration at 1293 due to the C–N stretch from the benzenoid unit stretching the mode of the PANI; the band at 1160 cm^{-1} assigned to the quinoid unit doped PANI; and the band at 820 cm^{-1} and the bands at 737 and 697 cm^{-1} indicate 1.4-ring substitution and 1.2-ring substitution respectively, all vibration bands – except the strong vibration mode at 1387 cm^{-1} that is assigned to NO_3^- [18]
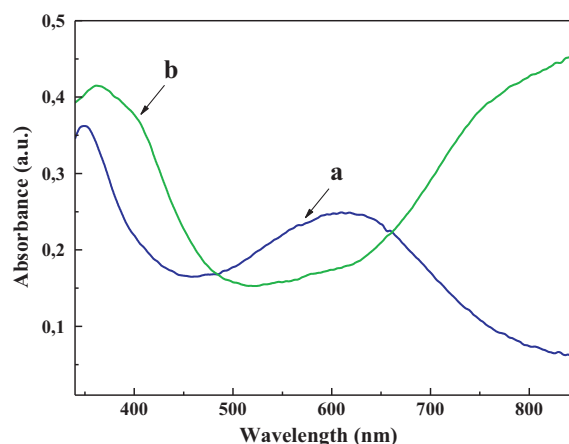

Fig. 2. UV–vis absorption spectra of PANI synthesized by X-ray irradiation (dose of 5 kGy) (a) in DMSO and (b) in formic acid.
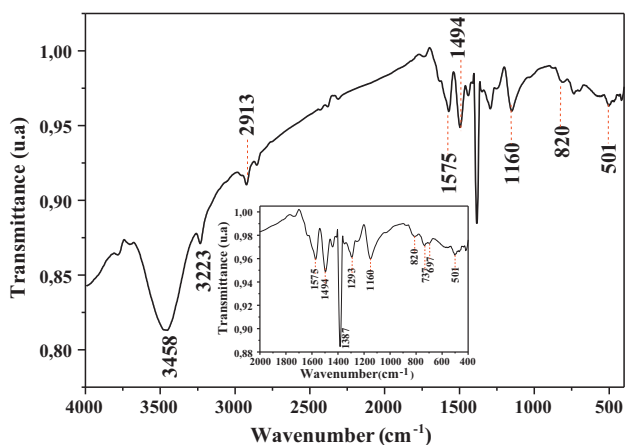
Fig. 3. FTIR spectrum of PANI synthesized by X-ray. The inset shows the same spectra expanded in the 1800–400 cm⁻¹ region.

– confirm the identity of the polymer and this is in agreement with results published in the literature [19,18].

The elemental analysis indicates that significant amounts of water (ca. 10%) are present in the sample. For that reason the theoretical calculations for the percentage of carbon, hydrogen and nitrogen for the undoped PANI, assuming the adsorbed water molecule $C_6H_{4.5}N(H_2O)_{0.62}$, are: %C, 70.83; %H, 5.65; %N, 13.77; whereas the experimental results found are: %C, 70.9; %H, 4.4; %N, 13.9. This is very consistent with the TG analysis which shows a loss of mass that approaches 10% in the temperature range from RT to 120 °C. Furthermore, the C/N ratio is not higher than 6/1, which strongly indicated that the material does not present a structural defect in its polymer chain due to hydrolysis or degradation [20], and again these results indicate that polyaniline has been obtained.

In order to confirm that the conducting polymer polyaniline has been obtained instead of oligomer of low molecular weight, GPC measurements were taken. The result showed a distribution of molecular weights, with a calculated M_w of 13,863 Da, a M_n of 13,500 Da, and the ratio $M_w/M_n = 1.026$ which are quite reasonable molecular weights for polyaniline when compared with results in the literature. Fig. 4 shows the TGA analysis for the doped polyaniline, in the temperature range from room temperature to 900 °C. From these results, we observe that the small fractions of weight loss up to 120 °C are attributed to the loss of moisture in the polyaniline sample, whereas the weight loss between 120 and 300 °C was mainly due to the evolution of the doping acid. On the
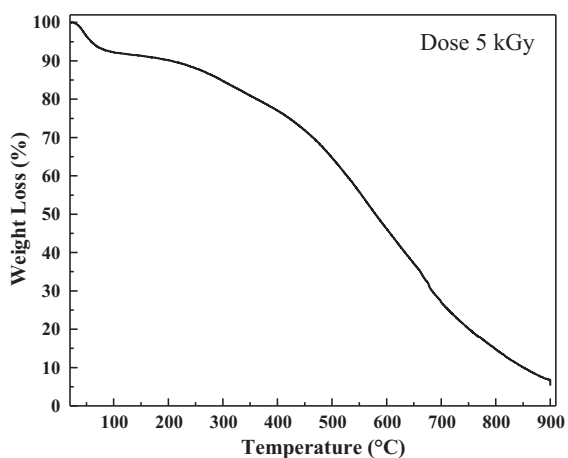

Fig. 4. Thermogravimetric analysis of PANI nanofiber obtained under nitrogen atmosphere at a heating rate of 10 °C min⁻¹.
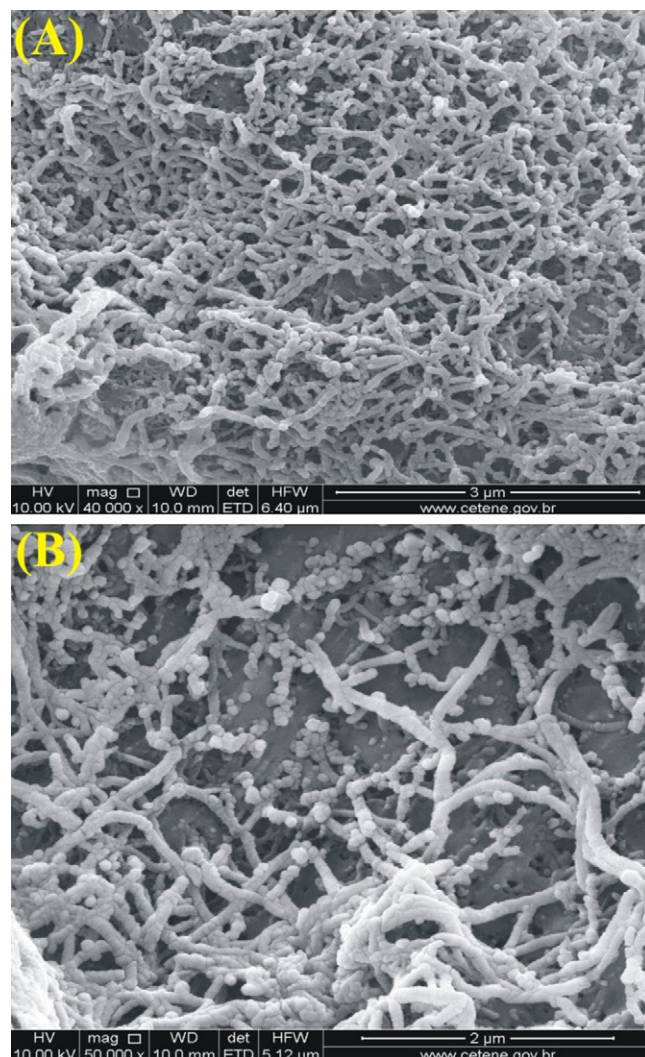

Fig. 5. SEM images of PANI nanofibers synthesized by X-ray irradiation at a dose of 5 kGy (a) low magnification image and (b) higher magnification image.

other hand, we observe that there is very little weight loss for PANI up to 365 °C, indicating that PANI presents good thermal stability. However, a very significant weight loss begins to occur above 365 °C which is attributed to thermal decomposition of the molecular main chains. This thermal behavior seems to be in agreement with the results found for polyaniline synthesized by conventional techniques [21,22].
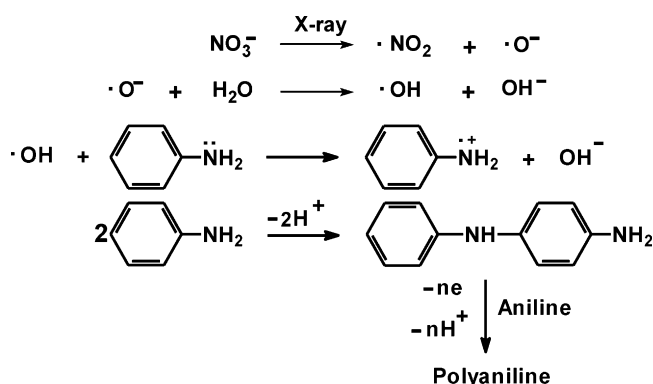

Fig. 6. Proposed polymerization mechanism.

As to the yield (%) and electrical conductivity σ (S cm^{-1}) measurements for PANI obtained by X-ray irradiation to a total dose of 5 kGy, we obtained the values of 5.1 and 0.7×10^{-3}, respectively. The low yield measured for the polymer can be attributed to the characteristics of the experimental set up, such as the small cuvette optical pathway (1 cm) and the X-ray beam convergence on a small point of the cuvette. In addition, Fig. 1 shows that the polymer grows in the direction of the X-ray beam. The reason for these behaviors is still under investigation. However, we observe that if we introduce transition metal ion to the reaction medium the yield increases considerably. On the other hand, the conductivity obtained (σ) of the order of 0.7×10^{-3} S cm^{-1} is low compared with 1–10 S cm^{-1} found in the literature [23,24]. Nevertheless, this is considerably higher when compared with the oligomeric conductivity which presents conductivity of the order of 2.4×10^{-10} S cm^{-1} [25]. This result together with GPC measurement allowed us to conclude that the conducting polymer has been obtained instead of an oligomer [26].

Fig. 5 shows the FEG-SEM image of the dried PANI polymer grown from a solution of aniline nitrate irradiated with X-ray radiation to a total dose of 5 kGy. From this result, we can see that instead of a micro-compact spheroid surface morphology which is usually found for pure PANI obtained by chemical synthesis [17], the SEM image clearly shows fibrillar morphology with an average fiber diameter of 90 nm and a length of several microns. In addition, we noticed that the fiber is highly networked and is probably formed by the fusion of several spheroid structures, induced by the X-ray radiation field along the beam propagation. The reason for this morphology is still under investigation. It is interesting to mention here that when we compare the morphology of the chemically synthesized polyaniline [27], the polyaniline obtained by gamma radiation [11,12] and the results of Fig. 5, we observe that the morphology somehow seems to be correlated with the energy of the ionization radiation. For the chemical synthesis the morphology is globular while for the sample irradiated with gamma radiation, the fiber morphology is more defined. On the other hand, the X-ray synthesis appears to be a half term, and we observed that globules are formed together with fiber that seems to be the fusion of several globules.

Also, it is interesting to mention here that the polymerization only occurs when nitrate ions are used. If we change to H_2SO_4 or some other acids, polymerization does not occur, which once again suggests that the nitrate ions play an important role in the PANI polymerization process. Additionally, if we carry out the experiment in the presence of an ($^\bullet$OH) radical scavenger such as DMSO, polymerization does not occur [10].

A search in the literature reveals that NO_3^- has been extensively used as an oxidizing agent for treating organic contaminants in water [28], and the mechanism suggested is the decomposition of NO_3^- by ionization with UV light which yields hydroxyl radicals ($^\bullet$OH) that turn out to be oxidizing agents. In our case, we irradiate the aniline nitrate solution with an X-ray that is more energetic than UV light. However, the mechanism could be the same since it is only the solution with nitrate ions that is able to polymerize.

The above results strongly suggest that it is again the hydroxyl radicals ($^\bullet$OH) which seem to be responsible for aniline photon polymerization in the first stage. In Fig. 6 we present the most likely mechanism for aniline photo polymerization. In summary, the X-ray radiation interacts with the NO_3^- ions and forms the hydroxyl radicals ($^\bullet$OH), which attack the aniline monomer and form the cation radical, which therefore couples with another cation radical, thus forming the dimmer, tetramer, octamer and finally the polymer.

4. Conclusions

This article showed that only nitrate ions are able to promote the polymerization of the aniline monomers when irradiated with X-ray. The results presented here strongly suggest that the aniline monomer is oxidized by the hydroxyl radicals ($^\bullet$OH) produced by the interaction of X-ray radiation with the nitrate ions NO_3^-. The radicals ($^\bullet$OH), attack the aniline monomer, and the process continues until the polymer is formed. The GPC measurements showed that polyaniline with a molecular weight M_w of the order of 13,863 Da has been obtained and the SEM measurement shows that the polymer presents highly fibrillar morphology with an average fiber diameter of 90 nm and several microns in length. In addition, we noticed that the fibers are highly networked and are probably formed by the fusion of several spheroid structures, induced by the X-ray radiation field along the beam propagation, instead of templates or other organic solvents usually used for that purpose. Further studies are underway to better understand the polymerization process and the physical and chemical properties of the polyaniline fibers and their networked structure.

Acknowledgments

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