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Precipitation and surface polymerizations of aniline at different aniline:oxidizer molar ratios

Lucia Helena Mascaro,[1] *Débora Gonçalves*[2]

[1] Departamento de Química, Universidade Federal de São Carlos, C.P. 676, 13565-905, São Carlos, SP, Brazil; lmascaro@dq.ufscar.br.

[2] Instituto de Física de São Carlos, Universidade de São Paulo, Av. Trabalhador São-carlense 400, CP 369, 13560-970, São Carlos, SP, Brazil; gdebora@if.sc.usp.br.

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Abstract: The oxidative polymerization of aniline was monitored by means of open-circuit potential (OCP) measurements of Pt electrodes immersed in an aqueous acidic medium containing different aniline:oxidizer (ammonium persulfate) molar ratios. Thin polyaniline (PANI) films were formed on the Pt electrode surfaces during the OCP measurements, and they were studied by SEM and cyclic voltammetry in a monomer-free solution at different reaction times. A precipitate also obtained during the polymerization process was analyzed by UV-VIS spectroscopy in 1-methyl-2-pyrrolidinone. It is observed that aniline or short oligomeric species are necessary to initiate the growth of a PANI film, which takes place at the first few minutes of the reaction.

Introduction

Polyaniline (PANI) is one of the most studied conducting polymers mainly justified by its relatively high conductivity after doping, environmental stability, and applicability on devices, sensors, and batteries. PANI can be promptly synthesized by chemical (and also electrochemical) oxidation of aniline in both aqueous and non-aqueous media. However, it is worth noting how different protocols have been reported in the literature for the chemical synthesis of PANI and its derivatives including different concentrations of aniline and oxidizer, temperatures of synthesis, aniline:oxidizer molar ratios, and polymerization-end times. In order to accomplish the progress of chemical polymerization of aniline after varying the synthesis conditions, *in situ* techniques have been employed. Among them, it should be mentioned the open-circuit potential (OCP)-time profile, which appoints as an alternative tool giving information on the oxidation state of products formed throughout the progress of polymerization of aniline [1-5]. The OCP measurements can be done as a function of the reaction time by immersing inert electrodes (commonly Pt) into an aqueous acidic medium containing both aniline and oxidizer. For the particular use of PANI on corrosion protection studies, the OCP-time technique is also of great interest because it gives information on the kinetic and mechanical behaviour of the electrode reactions [6].

Recent studies in the research field of PANIs have been focused on films deposited on solid substrates, such as glass or Au [7-10], and prepared by means of a process called *surface polymerization* that precedes polymerization of PANI as a powder (*precipitation polymerization*). Aniline cation radicals and oligomeric species are primarily formed in the vicinity of a solid surface added into the reaction medium [11, 12]; thus, a process of nucleation and growth of nuclei on the solid surface takes place, and a film is formed on the substrate surface prior to a precipitate in the bulk of the reaction medium. The presence of this substrate in the reaction medium affects the rate of polymerization of aniline, which increases and depends on the type of substrate used, such as a bare substrate or a pre-recovered polymer (PANI) film [13]. So far, among these studies, none had shown a concern on how the measured OCP variations of PANI films that are formed on the electrodes can be characterized and also, how the OCP results may vary in case of using different aniline:oxidizer (A:O) molar ratios, a parameter that characterizes properties such as reaction yield, conductivity and molecular weight of PANI. Our contribution in this paper was directed to monitor the progress of surface polymerization of aniline on Pt electrodes by means of OCP measurements after varying the A:O molar ratio. Cyclic voltammetry was used to verify differences in the redox processes of PANI films deposited on Pt at different reaction times. PANI as a precipitate was also characterized by UV-VIS spectroscopy after isolation and solubilization in 1-methyl-2-pyrrolidinone (NMP).

Results and discussion

Surface polymerization

The Pt electrodes used to monitor the OCP variations were covered with a PANI film as soon as the polymerization of aniline initiates, and they were strongly bound to the Pt surfaces with a uniform and good visual quality.

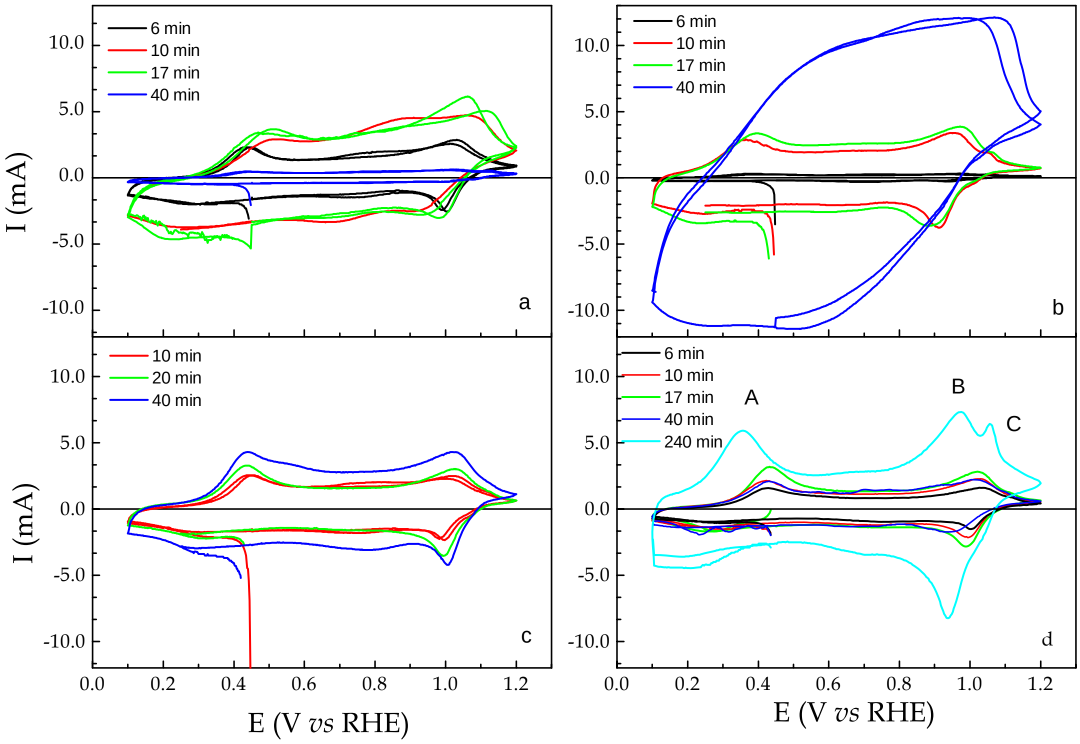

Fig. 1. Cyclic voltammograms of Pt electrodes removed from the polymerization medium of aniline at different reaction times and A:O ratios: 1:1 (a), 1:1.5 (b), 2:1 (c), and 4:1 (d) in an aqueous 1.0 mol L^{-1} HCl solution, v = 50 mv s^{-1}.

Figure 1 shows the cyclic voltammograms of these films obtained at different reaction times and A:O ratios in a monomer-free solution. The films obtained at different A:O ratios showed a typical redox response with the presence in the voltammograms of peaks **A** and **B** due to the interconversion reactions of PANI upon varying the potential (leucoemaldine/emeraldine and emeraldine/ pernigraniline) [14, 15]. These peaks have been assigned to redox reactions involving an overoxidized PANI structure indicating the polymer degradation [16, 17]. The current density for these redox couples increases with the reaction time indicating an enhancement of the film thickness. In general, the voltammograms show a clean response, *i.e.* without the presence of an intermediate process between **A** and **B** which is usually attributed to redox reactions involving an overoxidized PANI structure indicating the polymer degradation [15]. Some voltammogramms show only a distortion for films obtained in an excess of the oxidizer, at a 1:1.5 A:O ratio after 40 min of reaction, and at a 1:1 A:O ratio, after 17 min and 40 min of reaction, thus evidencing that thicker films are obtained under these synthesis conditions, and probably with powdery PANI incorporated into the films.

Another interesting result seen in Figure 1 is the appearance of an unexpected peak at about 1.1V *vs* RHE (**C**), which is even seen after washing the electrodes in an aqueous HCl solution or solvents (acetone and methanol). In this case, raising the modified electrodes only promotes a slight instability of the current, as it can be expected for a small loss of mass of an insoluble film deposited on the electrode surface. The voltammetric response of a Pt electrode immersed for 240 min in the reaction medium (during the whole course of polymerization) also exhibited the peak **C** as it can be verified in Figure 1(d); its total disappearance was only observed for an electrode immersed longer times in the reaction medium, such as about 18 h.

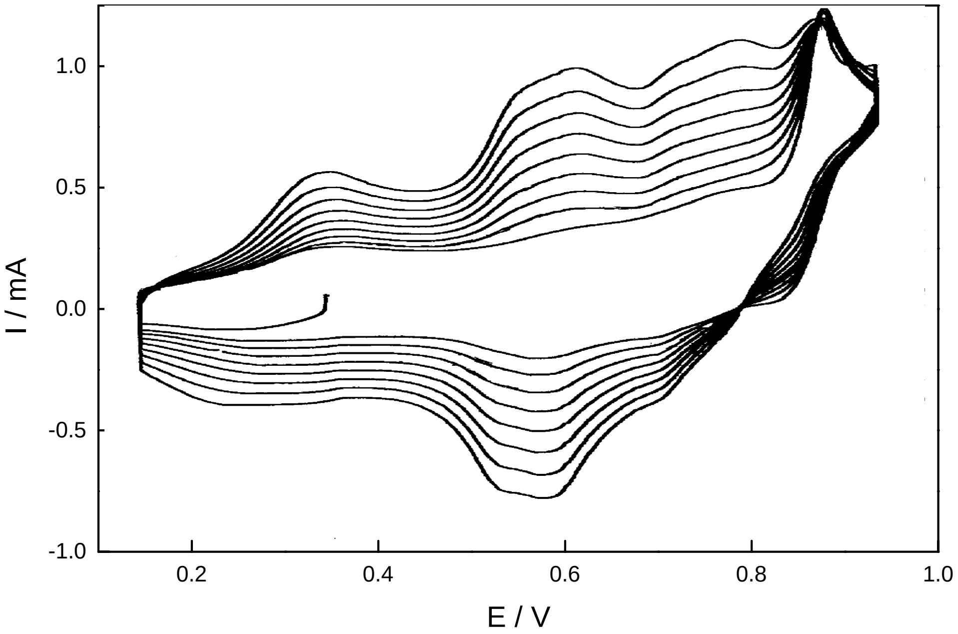

Fig. 2. Cyclic voltammograms of a PANI film on Pt prepared at a 4:1 A:O ratio in an aqueous 1.0 mol L^{-1} HCl solution and 50 mmol L^{-1} aniline, v = 50 mv s^{-1}.

After adding aniline to the electrolyte solution (Figure 2), a considerable increase of the current for peak **C** is noticed with the number of cycles. We assumed that this peak could be attributed to the presence of neutral aniline or short oligomers attached to a pre-existing PANI thin layer. The appearance of a peak similar to peak **C** in the voltammograms of PANI films has been reported in the literature only in a few studies [18, 19], where it has been related to degradation products [18]. Recently, this process was also noticed in the voltammograms of poly-methoxyaniline film on Au electrodes, and it was attributed to oligomeric species incorporated in the film [19]. Our results from Figure 2 clearly elucidate the appearance of the process in the voltammetric response of PANI films as attributed to the redox reactions of neutral aniline or short oligomers incorporated in the PANI film structure.

Precipitation polymerization

Figure 3 shows the evolution of the OCP with the reaction time for Pt electrodes immersed in the polymerization medium of aniline at 4:1, 1:1 and 1:1.5 A:O ratios. The time intervals, $t_{B\text{-}C}$ and $t_{C\text{-}D}$, taken from the OCP curves at different A:O ratios are shown in the insert of Figure 3.

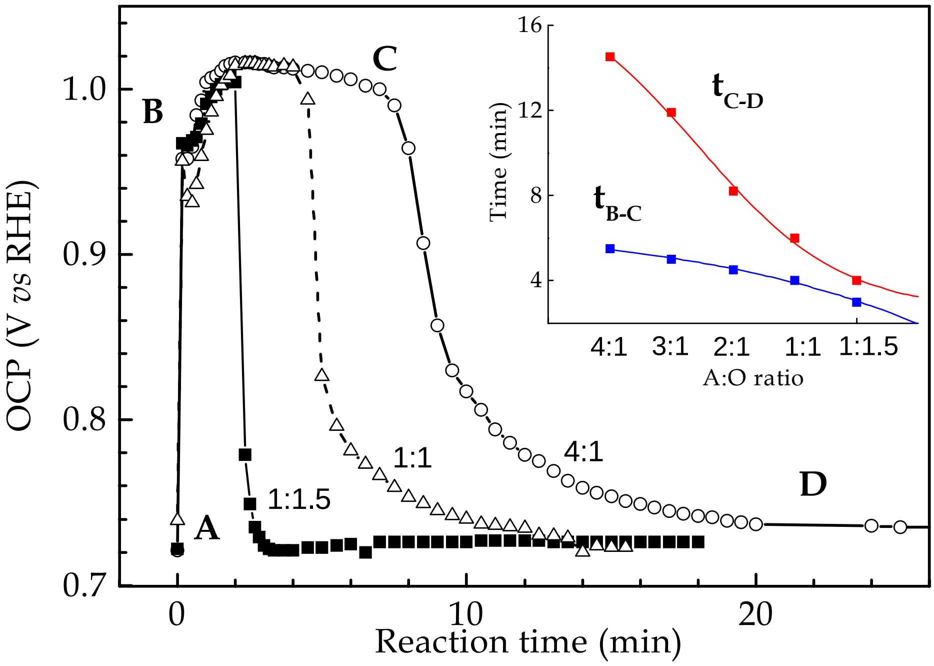

Fig. 3. Open-circuit potential (OCP) *vs* reaction time at different A:O ratios: 4:1; 1:1; and 1:1.5.

The stages **A** to **D** in the OCP curves of Figure 3 can be correlated to the steps of polymerization of aniline: initiation, chain propagation, and termination [20-22]. Initiation involves oxidation of aniline to cation radicals, which after coupling reactions yields reactive dimers (mainly N-phenyl-p-phenylenediamine). Following this mechanism, successive nucleophilic attacks of neutral anilines on oxidized dimers leads to formation of oligomeric intermediates, in particular protonated pernigraniline, at the highest value of the OCP curve (**B**-**C** plateau) ($\mathbf{t_{B\text{-}C}}$) at *ca* 1.01 V *vs* RHE. As a final step, pernigraniline undergoes reduction itself to produce PANI at its emeraldine oxidation state at 0.72 V *vs* RHE (polymerization-end time, $\mathbf{t_D}$). Generally speaking, the potential increases within a few seconds from *ca* 0.72 V (point **A**) to *ca* 0.95 V *vs* RHE (point **B**) (initiation), then reaches a constant value at *ca* 1.01 V (**B**-**C** plateau) (propagation), and decreases asymptotically to an equilibrium value at 0.72 V (point **D**) (termination). These curves are similar to those reported in the literature for PANIs synthesized at a fixed A:O ratio, 4:1 [1, 2]. However, when the A:O ratio is varied, different polymerization rates can be expected and demonstrated by the values of $\mathbf{t_{B-C}}$ and $\mathbf{t_{C-D}}$ seen in the insert of Figure 3.

The polymerization rate of aniline is faster in excess of the oxidizer, with the OCP decaying sharply at a 1:1.5 A:O ratio (t_D = *ca* 3.2 min, and $\mathbf{t_{C-D}}$ = 5.5 min) and exponentially at a 4:1 A:O ratio ($\mathbf{t_D}$ = 20 min, and $\mathbf{t_{C-D}}$ = 14.5 min). For a monomer concentration higher than that of the oxidizer, such as at a 4:1 A:O ratio, it can be expected a large amount of aniline still remaining without reacting at the end of polymerization, with practically all amount of the oxidizer present in the reaction medium being already consumed at 20 min ($\mathbf{t_D}$).

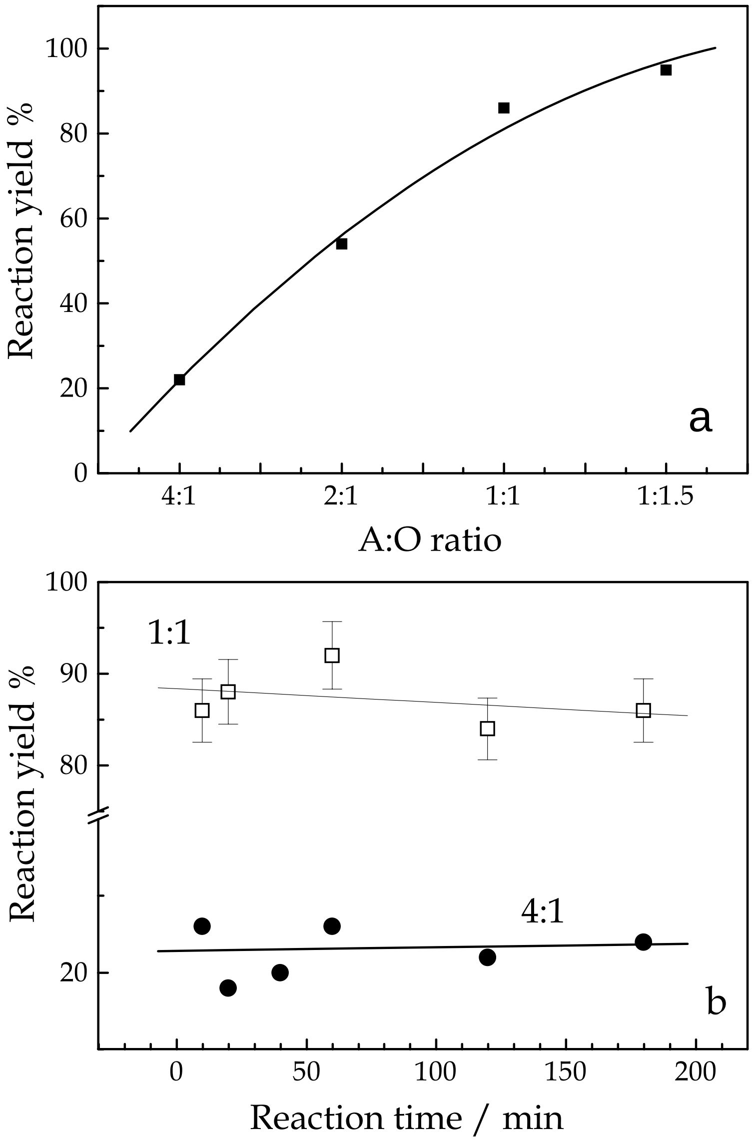

Fig. 4. Reaction yields obtained for the synthesis of PANI: a) calculated after 180 min at different A:O ratios, b) as a function of the reaction time at 4:1 and 1:1 A:O ratios.

No variation on the OCP can be measured if a pre-deposited PANI film on Pt is used instead a bare Pt electrode. Besides, if a bare Pt electrode is immersed in the reaction medium 10 min after initiating the reaction polymerization, no film deposits on the Pt surface. These results corroborate our previous conclusions based on cyclic voltammetry that bound aniline or short oligomeric species are necessary to initiate the growth of a PANI film, which takes place at the first few minutes of the reaction.

PANI as a dark green precipitate was isolated during the progress of polymerization at time intervals varying from 10 min to 4 h, washed, filtrated, and dried. After these steps, the reaction yields were calculated, as shown in Figure 4(a). Figure 4(b) shows how the reaction yields vary at a fixed reaction time (3 h) at 4:1 and 1:1 A:O ratios.

Our results of reaction yield indicated that the highest amount of precipitate formed at the end of polymerization of aniline was for the synthesis carried out in an excess of the oxidizer. The reaction yield for synthesis of PANI at a 1:1.5 A:O ratio was 92%, and at a 4:1 A:O ratio, 22% (Figure 4a). In the literature, there is an agreement that while the use of an excess of aniline for the synthesis of PANI leads to lower reaction yields, favourable properties of PANI can be obtained, such as higher molecular weights and electrical conductivities [23-25], thus justifying why most authors prefer to synthesize PANI at a 4:1 A:O ratio.

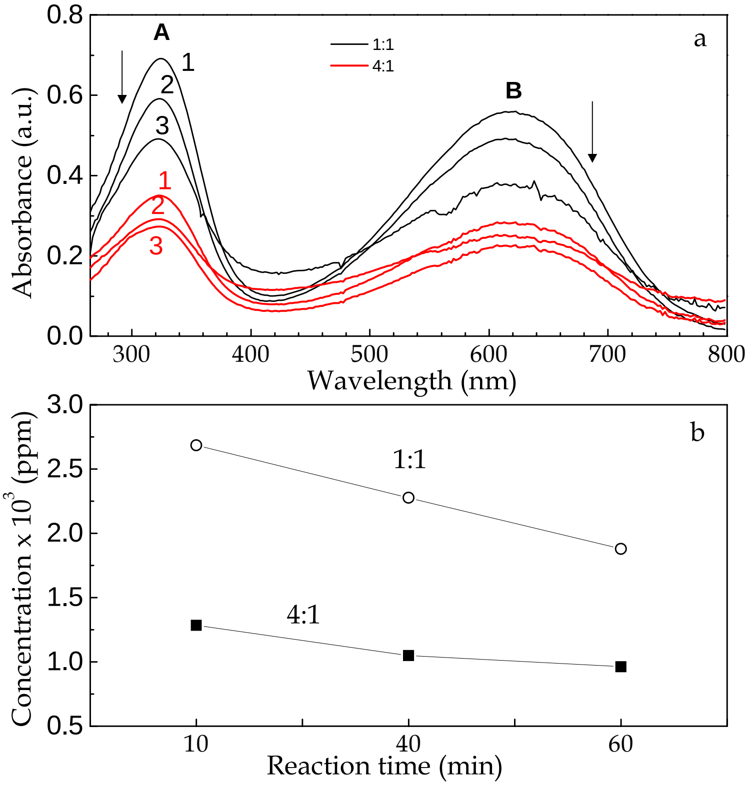

Fig. 5. (a) UV-VIS spectra of PANI as a precipitate in 1-methyl-2-pyrrolidinone (NMP) and isolated from the reaction medium at 10 min (1), 40 min (2), and 60 min (3) at 1:1 and 4:1 A:O ratios; (b) concentration of these solutions in NMP as a function of the reaction time.

From the early stages of polymerization to 180 min of synthesis, an unaltered amount of PANI were practically obtained as a precipitate at both 4:1 and 1:1 A:O ratios (Figure 4b). These results indicate that it is not necessary to keep the polymerization of aniline processing longer than about 10-20 min because the reaction yield will be practically the same. Besides, if the precipitate stays in the reaction medium for longer reaction times, hydrolysis takes place and degradation products can be formed [25].

During the progress of polymerization of aniline, different colours were noted in solution from reddish (soluble products), bluish (pernigraniline base), and dark green (precipitate). In Figure 5(a), we compare the UV-VIS spectra of precipitates isolated from the reaction medium, deprotonated, and solubilized in 1-methyl-2-pyrrolidinone (NMP). Figure 5(b) shows the values of concentration for these solutions in NMP. A calibration curve (absorbance *vs* concentration at a fixed wavelength) was used to estimate the amount of precipitate formed at different reaction times. For clarity, we showed only the spectra from syntheses carried out at 4:1 and 1:1 A:O ratios.

The UV-VIS spectra of PANI solubilized in NMP showed two well-defined bands at *ca* 323 (**A**) and 618 (**B**) nm, which can be related to the typical π-π^* and n-π^* transitions of PANI in its base emeraldine state (undoped form), respectively [24]. The intensity of these bands decreases with the reaction time indicating that the precipitates become more insoluble at longer reaction times. From Figure 3, it is also clearly seen that a less soluble precipitate is formed for synthesis carried out at a 4:1 A:O ratio.

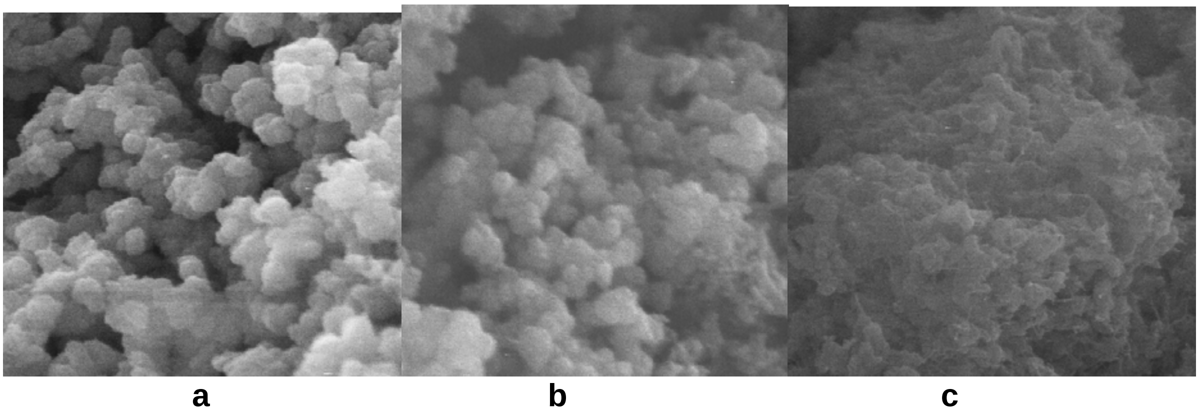

Fig. 6. SEM-micrographs of Pt electrodes removed from the polymerization medium of aniline at different reaction times, and 1:1 A:O ratio after: 10 min (a), 20 min (b) and 40 min (c).

Figure 6 shows the SEM-micrographs of Pt electrodes removed from the polymerization medium of aniline at different reaction times, and at a 1:1 A:O ratio. The PANI films obtained at 10 and 17 min exhibited a globular surface morphology, that is a typical behaviour for PANI films grown on various substrates during the aniline oxidation [9, 26]. However, when the substrate is removed from the polymerization vessel after 40 min, the PANI morphology varies, and a globular structure is not clearly seen anymore. This result is in agreement with the voltammetric behaviour of thicker PANI films obtained at a 1:1 A:O ratio and higher times of immersion of the Pt substrates in the polymerization medium.

Conclusions

Our results demonstrated that the kinetics of polymerization of aniline depends sensitively on the aniline:oxidizer (A:O) ratio molar ratios. The polymerization mechanism involves two slower steps that are related to the formation of oligomeric intermediates, in particular protonated pernigraniline, and a final step, when pernigraniline undergoes reduction itself to produce PANI at its emeraldine oxidation. The polymerization rate of aniline oxidation is faster when reaction is carried out in an excess of the oxidizer.

The reaction yield and UV-vis results indicated that it is not necessary to keep the polymerization of aniline processing longer than about 10-20 min since the reaction yield will be practically the same. Finally, our voltammetric results from Figure 2 clearly indicated that an additional process seen in the voltammogram can be related to redox reactions of neutral aniline or short oligomers incorporated into the PANI film structure.

Experimental part

The oxidative polymerization of aniline was carried out using ammonium persulfate, $(NH_4)_2S_2O_8$, as the oxidizer in an aqueous 1.0 mol L^{-1} HCl solution at aniline:oxidizer (A:O) molar ratios varying from 4:1, 2:1, 3:1, 1:1 to 1:1.5 at a fixed concentration of aniline, 0.74 mol L^{-1}. The oxidizer solution was added into the reaction medium containing aniline for less than 1 min using a burette, and both aniline and oxidizer solutions were kept at 0-5 ^{o}C. During the progress of polymerization, PANI as a black precipitate was formed and extracted from the reaction medium at intervals varying from 10 min to 4 h. Powdery PANI was then was filtrated, rinsed with an aqueous 1.0 mol L^{-1} HCl solution, deprotonated in an aqueous 0.1 mol L^{-1} NH_4OH solution for 24 h, re-filtrated, and dried under vacuum for 48 h. After these steps, the reaction yields were calculated. The solubility tests of powdery PANI were realized after filtration, washing in an aqueous 0.1 mol L^{-1} NH_4OH solution, drying, and then, dissolving in 1-methyl-2-pyrrolidinone (NMP). A final step of filtration guaranteed the absence of insoluble materials.

The open-circuit, potential-time profiles (OCP) were obtained for Pt plates (about 1 cm^2) added into the polymerization medium of aniline against a hydrogen electrode in the same solution (RHE). Before starting the addition of the oxidizer solution into the reaction medium containing aniline, the OCP of a Pt electrode was measured separately for both oxidizer and aniline solutions as 1.25 V and 0.72 V *vs* RHE, respectively. After that, the whole amount of the oxidizer solution was added into the reaction medium for less than 1 min at a constant temperature (0-5 ^{o}C). Five Pt plates and one reference electrode were adapted to the polymerization vessel. This cell configuration allowed us to measure the OCP-time transients from a single Pt electrode meanwhile other electrodes were removed from the reaction medium at different time intervals.

The voltammetric responses of the Pt electrodes used for the OCP measurements were obtained in a monomer-free solution (an aqueous 1.0 mol L^{-1} HCl solution) using an EG&G PAR potentiostat/galvanostat model 273.

The PANI coatings on Pt substrate were characterized by a scanning electron microscope (SEM) Zeiss model DSM 940A.

Acknowledgements

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References

[1] Manohar, S.K.; MacDiarmid, A.G; Epstein A.J. *Synth. Met.* **1991**, 41-43, 711.
[2] MacDiarmid, A.G.; Manohar, S.K.; Masters, J.G.; Sun, Y.; Weiss, H.; Epstein, A.J. *Synth. Met.* **1991**, 41-43, 711.
[3] Wei, Y.; Hsueh, K.F.; Jang, G.W. *Polymer,* **1994**, 35, 3572.
[4] Geng, Y.; Li, J.; Sun, Z.; Jing, X.; Wang, F. *Synth. Met.,* **1998**, 96, 1.
[5] Job, A.E.; Herrmann, P.S.P.; Vaz, D.O.; Mattoso, L.H.C. *J. Appl. Polym. Sci.* **2001**, 79, 1220.
[6] Zhu, H.; Zhong, L.; Xiao, S.; Gan, F. *Electrochim Acta* **2004**, 49, 5161.
[7] Ayad, M.M.; Salahuddin, N.; Sheneshin, M.A. *Synth. Met.* **2003**, 132, 185.
[8] Karpacheva, G.P.; Orlov, A.V.; Kiseleva, S.G.; Ozkan, S.Z.; Yurchenko, O.Y.; Bondarenko, G.N. *Russian J. Electrochem.* **2004**, 40, 305.
[9] Sapurina, I.; Fedorova, S.; Stejskal, J. *Langmuir* **2003**, 19, 7413.
[10] Fedorova, S.; Stejskal, J. *Langmuir* **2002**, 18, 5632.
[11] Riede, A.; Helmstedt, M.; Sapurina, I.; Stejskal J. *J. Colloid Interface Science* **2002**, 248, 413.
[12] Sapurina, I.; Osadchev, A.Y., Volchek, B.Z.; Trchová, M.; Riede, A.; Stejskal J. *Synth. Met.* **2002**, 129, 29.
[13] Tzou, K.; Gregory, R.V. *Synth. Met.* **1992**, 47, 267.
[14] MacDiarmid, A.G.; Yang, L.S.; Huang, W.S.; Humbhrey, B.D. *Synth. Met.* **1987**, 18, 393.
[15] Zhang, A.Q.; Cui, C.Q.; Lee, J.Y. Synth. Met. **1995**, *72*, 217.
[16] Huang, W.S.; Humphrey, B.D.; MacDiarmid, A.G. *J. Chem. Soc., Faraday Trans. 1* **1986**, 82, 2385.
[17] Focke, W.W.; Wnek, G.E.; Wei, Y. *J. Phys. Chem.* **1987**, 91, 5813.
[18] Mazur, M.; Predeep, P. Polymer **2005**, 46, 1774.
[19] Wei, Y. *J. Chem. Education* **2001**, 78, 551.
[20] Stejskal, J.; Kratochvíl, P.; Jenkins, A.D. *Collect Czech Chem. Commun.* **1995**, 60, 1747.
[21] Wei, Y.; Jang, G.W.; Chan, C.C.; Hsueh, K.F.; Hariharan, R.; Patel, S.A.; Whitecar, C.K. *J. Phys. Chem.* **1990**, 94, 7716.
[22] Cao, Y.; Andreatta, A.; Heeger, A.J.; Smith, P. *Polymer* **1989**, 30, 2305.
[23] Rodrigues, M.A.; De Paoli, M.A. *Synth. Met.* **1991**, 41-43, 2957.
[24] Gazotti Jr., W.A.; De Paoli, M.A. *Synth. Met.* **1996**, 80, 263.
[25] Gonçalves, D.; dos Santos Jr., D.S.; Mattoso, L.H.C.; Karasz, F.E.; Akcelrud, L.; Faria, R.M. *Synth. Met.* **1997**, 90, 5.
[26] Sapurina, I.; Riede, A.; Stejskal J. *Synth. Met.* **2001**, 123, 503.