Electro-synthesis and Characterization of Aniline and *o*-Anisidine Oligomers

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Electrochemistry have produced important results as an alternative synthesis route for polymerization because offers several distinct advantages such as process control, cheaper preparation procedures and instrumentation, and also enables an alternative approach for fundamental characterization. The mechanism for conducting polymer electro-synthesis involves, at its early stages, oligomer formation. Therefore, in this work electrochemical techniques are used as an alternative route for the synthesis and characterization of aniline (ANI) and *o*-anisidine (oANS) oligomers. In the present survey synthesis and characterization of ANI and oANS oligomers was successfully accomplished by applying potentiodynamic and potentiostatic techniques to a saturated monomer solution using sulfuric acid as supporting electrolyte. Oligomers characterization was performed by classical means, *e.g*. FT-IR, UV-vis, and NMR spectroscopy, the last one being the most important to establish oligomer chain length. The controlled formation of ANI and oANS oligomers was obtained by simpler methods than those previously reported using chemical synthesis.

1. INTRODUCTION

Since its discovery in 1977[1,2] conducting polymers, *e.g*. polypyrrole, polythiophene and polyaniline, have aroused great interest because they are cheap materials with prospective application in electronic devices, *e.g*., sensors,[3,4] batteries,[5] diodes,[6,7] photovoltaic cells,[8] etc. Polyaniline, PANI, was first synthesized in the 19th century but only became important after its utilization as conducting polymer[9,10]. Among the conducting polymers PANI and its derivatives have been the

most extensively employed[11] due to its stability toward both oxygen and water, unique electrochemical and optical properties, low cost and easy preparation. Among the aniline (ANI) family, o-anisidine (oANS), 2-methoxyaniline, appears as a good candidate for polymerization and characterization, particularly, for data acquisition leading to establish monomer/polymer structure correlations.[12-14] Its synthesis may be accomplished either by chemical or electrochemical[15-17] means, each possessing advantages and disadvantages. As far as the electrochemical approach is concerned, its contribution to the development of conducting polymers has been more relevant and many basic studies related to formation mechanism have been done.[18-24] In 1988 Stilwell and Park determined that during potentiodynamic polyaniline growth, the film presented an autocatalytic behavior, i.e., after the first cycle the aniline oxidation potential became less anodic.[18] Recently others authors have corroborated this finding using different *in situ* modern techniques.[24] This behavior could be ascribed to the effect of more reactive species, such as oligo-anilines, bounded to the surface that might catalyze aniline oxidation. In 1992 Yang and Bard found that the aniline dimer is the predominant intermediate in the early stages of electro-polymerization.[22] It was clear that, for some cases, the electrochemical polymer growth occurs through oligomer formation. Presently this is a widely accepted assumption valid for different monomers or experimental conditions. Consequently, at its early stages electro-polymerization necessarily involves the formation of oligomers of different sizes.[25-26] These oligomers grow until reaching critical chain length allowing their precipitation onto the electrode. The experimental conditions, such as monomer concentration,[18] supporting electrolyte,[27] solvent, type of electrical perturbation,[23] etc., drive the growth and reaction rate of these oligomers.

Therefore, if the effect of each variable on a desired system is known, and the appropriate experimental design is used, electrochemical methods could be used to synthesize oligomers [28] as an alternative to the more expensive and complicate classical methods.[29-30] This is very important since oligomers are useful in different research areas, particularly for the implementation of electronic devices.[31-49]

The aim of the present survey is, by controlling polyaniline (PANI) and poly(o-anisidine) electro-synthesis, the obtention of fragments of known size characterized by NMR and UV-vis techniques. Thus, besides of developing a simpler synthetic method, validation of the previously reported electro-polymerization model was also accomplished.[17]

2. EXPERIMENTAL

2.1. Synthesis

The electrochemical synthesis of ANI and oANS oligomers was conducted in a conventional three-compartment, three-electrode cell using a 4.2 cm^2 stainless steel (AISI 316) sheet as working electrode (SS). In the case of ANI the electrolytic solution was 0.55 mol L^{-1} ANI (monomer) and 0.5 mol L^{-1} H$_2$SO$_4$ (supporting electrolyte). For oANS the working solution was 1 mol L^{-1} oANS (monomer) and 0.5 mol L^{-1} H$_2$SO$_4$ (supporting electrolyte). All the potentials quoted in this work are

referred to a Ag/AgCl electrode in N,N,N-trimethylmethanaminium chloride (TMACI) solution that matches the potential of a saturated calomel electrode (SCE)[50]. The auxiliary electrode was a Pt wire separated from the working electrode by a fine-porosity glass sinter. Prior to each experiment, the working electrode was polished with alumina slurry (particle size 0.3 μm) to a mirror finish, thoroughly rinsed with deionized water, and sonicated for 10 min in water. Before every experiment the working solution was purged with high-purity argon for 10 min.

An Autolab PGSTAT 20 potentiostat was employed for the electrochemical characterization (cyclic voltammetry and j/t transient obtention). A BAS CV-50w connected to a BAS PWR-3 power source, which allows working with higher currents, was used for oligomers synthesis.

The deposit obtained after the first electro-oxidation was removed from the working electrode with methanol followed by solvent vacuum evaporation. Following a procedure similar to that reported elsewhere,[39] the residue was neutralized with $NaHCO_3$, extracted with chloroform, dried with $CaCl_2$, and finally filtered off.

2.2. Characterization

FT-IR spectra were recorded on a Bruker Vector 22 spectrometer using KBr pellets.

UV-vis spectra were taken using different solvents depending on the solubility. Aniline and its oligomers were dissolved in dimethyl sulphoxide, DMSO. On the other hand, anisidine and its oligomers were dissolved in dichloromethane, CH_2Cl_2. These spectra were run on a Shimadzu, type UV 3101 PC spectrometer.

^{1}H NMR samples were prepared in deuterated DMSO. Spectra were obtained on a Bruker, Model ACP 200 MHz spectrometer.

3. RESULTS AND DISCUSSION

3.1. Electro-synthesis of ANI and oANS oligomers

In order to determine the optimum conditions for the electro-synthesis of aniline oligomers, several studies, not worthy to be detailed, employing different composition (monomer, supporting electrolyte, and substrates) were performed. It was found that, according to the previously reported electro-polymerization model,[17,28] the optimal conditions for controlled short oligomer formation is the use of a saturated monomer solution to facilitate early short-chain oligomer precipitation on the electrode rather than growing as soluble long-chain species. Figure 1 depicts the voltammetric profile of aniline obtained using the previously determined optimal experimental conditions for this purpose.

As seen in Fig. 1 the polymer growth starts at *ca.* 0.50 V, therefore a potential step of *ca.* 0.70 V should be appropriate to form the most conducting film. Figure 2 shows the response of a saturated aniline solution, to favor oligomer deposition, when potentials close to 0.70 V were applied for 1 min. The formation mechanism of this process has been reported elsewhere.[17, 28]
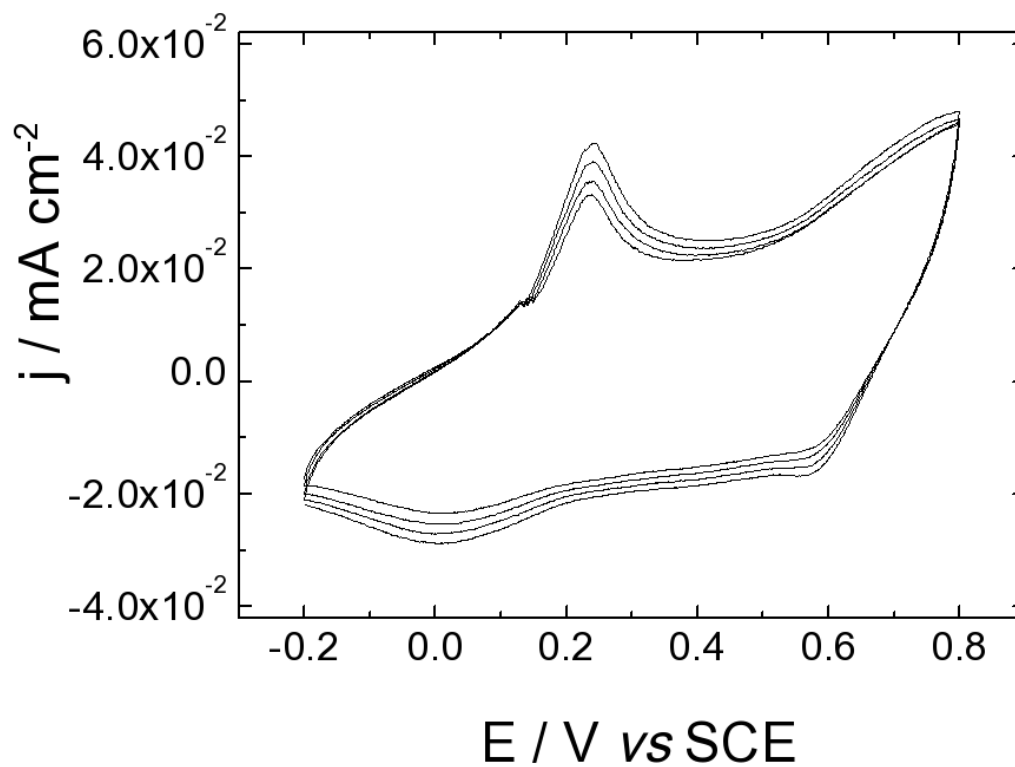
Figure 1. Aniline cyclic voltammogram. Interface: SS|0.55 mol L^{-1} ANI + 0.5 mol L^{-1} H$_2$SO$_4$. Scan rate 100 mV s^{-1}
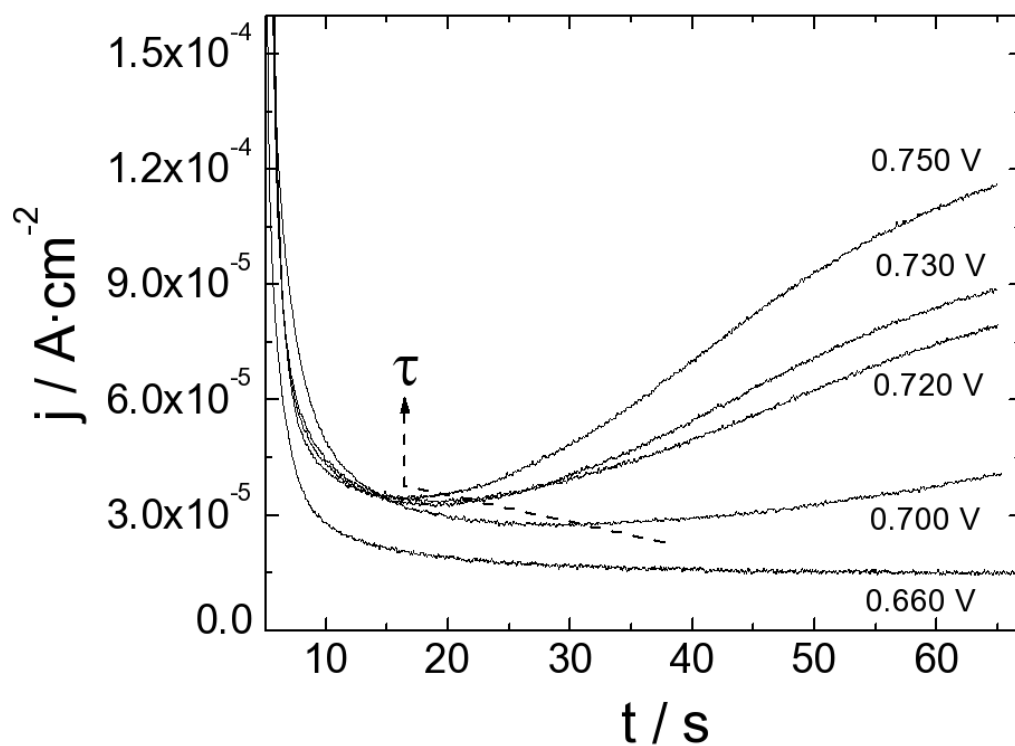

Figure 2. j/t transients of aniline. Interface: SS|0.55 mol L^{-1} ANI + 0.5 mol L^{-1} H$_2$SO$_4$.

From Fig. 2, 0.72 V and 20 s were selected as the most suitable conditions to obtain short-chain aniline oligomers. According to previous model[19, 28] the attainment of shorter oligomers is possible if a suitable potential pulse is applied during short times, so that the oxidation rate and chain growth of the species is directly controlled by the electrochemical setup. The pulse should start at the induction time value, τ, and last no more than 10 s. The τ value determines the beginning of the nucleation process, which will eventually lead to the formation of growth nuclei that determines the deposit morphology.[27, 51, 52] Consequently, the pulse should not be much greater than τ because after this time the deposit is predominantly a polymer and not an oligomers mixture.

Synthesis of oANS oligomers was carried out in a fashion similar to that of aniline. A potentiodynamic study was performed to determine the optimum working conditions using different oANS monomer and supporting electrolyte concentration and electrode substrate were accomplished.

Analysis of oANS voltammetric response (Fig. 3) when several sweeps were applied revealed that poly(oANS) growth starts at *ca*. 0.55 V. Therefore, several potential steps greater than this value were applied to select the most appropriate oxidation potential. The resulting j/t transients are depicted in Fig 4.

Considering the j/t transients in Fig. 4 and the corresponding amount of deposited product, 0.62 V and 35 s were chosen as the optimum parameters to produce short oligomeric chains.

Following electro-oxidation, the products were removed from their respective reaction media, neutralized, purified, and analyzed. The main substances obtained were, respectively, aniline dimer and oANS trimer, Fig. 5.
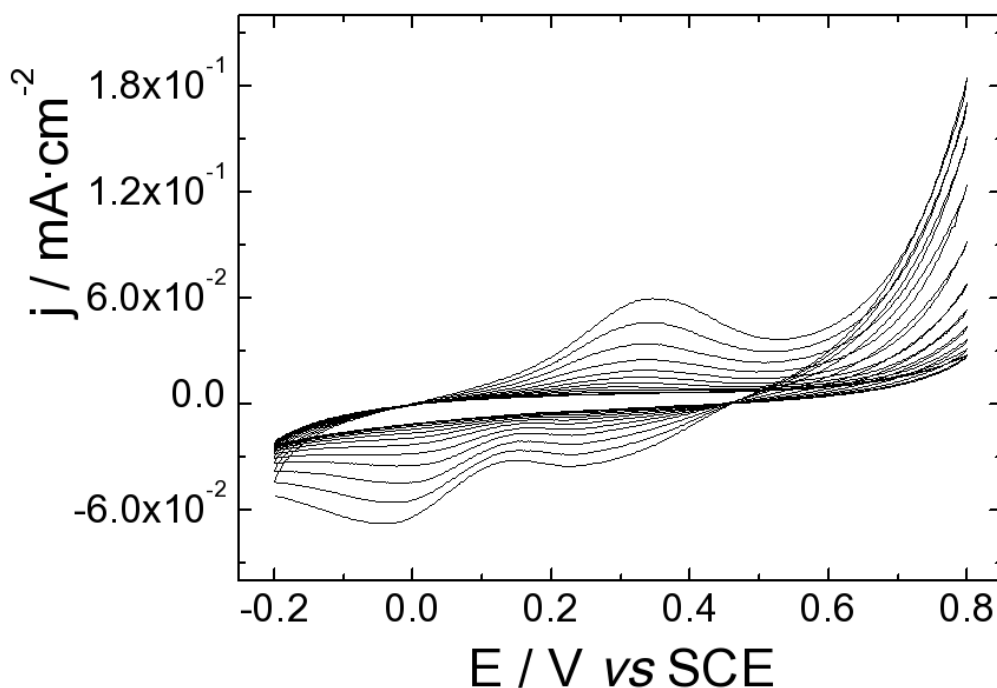

Figure 3. *o*-anisidine cyclic voltammograms. Interface: SS|1 mol L^{-1} oANS + 0.5 mol L^{-1} H$_2$SO$_4$. Scan rate: 100 mV s^{-1}.

Figure 4. oANS j/t transients. Interface: SS|1 mol L^{-1} oANS + 0.5 mol L^{-1} H$_2$SO$_4$.
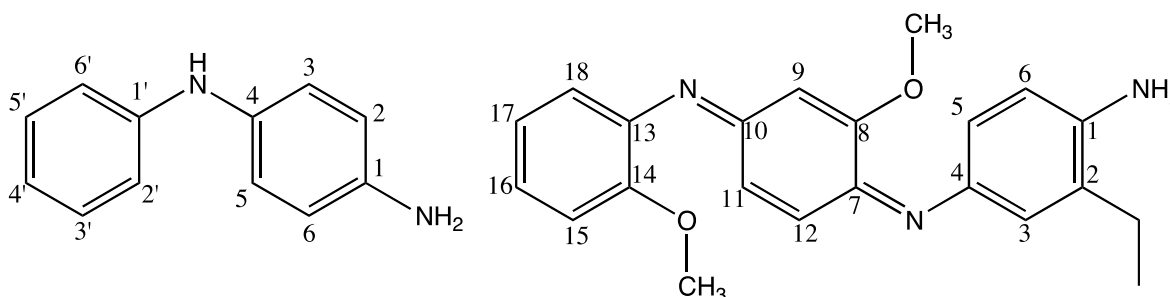

Figure 5. Aniline dimer (di-ANI) and oANS trimer (tri-oANS) structure

3.2. NMR analysis

NMR spectroscopy is a fundamental tool to determine, using integral analysis and the respective signals, the size and oxidation state of the oligomer. The H-NMR spectrum of the obtained aniline dimer presents characteristic signals. The aromatic region (7.05 ppm - 7.55 ppm) showed two coupled doublets at 7.1 ppm and 7.32 ppm, corresponding to protons 2, 6 and 3, 5 respectively (Fig. 5 and Fig. 6 (a)). Each doublet integrates for about two protons, indicating they are attached to a benzene ring substituted in positions 1 and 4. c. A double doublet corresponding to protons 3' and 5' was observed at 7.46 ppm. The signal at 7.2 ppm corresponds to a multiplet due to protons 2', 4', 6'. Integrals addition of this last two signals is *ca.* 5, indicating they are attached to a mono-substituted benzene ring. Integrals addition of the aromatic region is *ca.* 9, i.e. a large proportion of aniline dimers exists. Both rings (mono– and para–substituted) are linked to each other by a sp^3 N-H group, whose signal appears at 6.3 ppm, indicating that none of the benzene rings presented a quinonoid oxidation

state, otherwise the nitrogen would be sp^2 and the signal at 6.3 ppm would not exist. Likewise, the value of the integral is not exactly 1, which is in agreement with the existence of small amounts of oligomers of larger size. Finally, the signal at 3.55 ppm, corresponds to protons of the NH$_2$ group (position 1).

On the other hand, the ratio between aromatic region integrals (7.05 ppm - 7.35 ppm) and remaining integrals (6.3 ppm - 3.55 ppm) is nearly 3:1, which agrees with the structure and corroborates that the molecule is mainly aniline dimer.
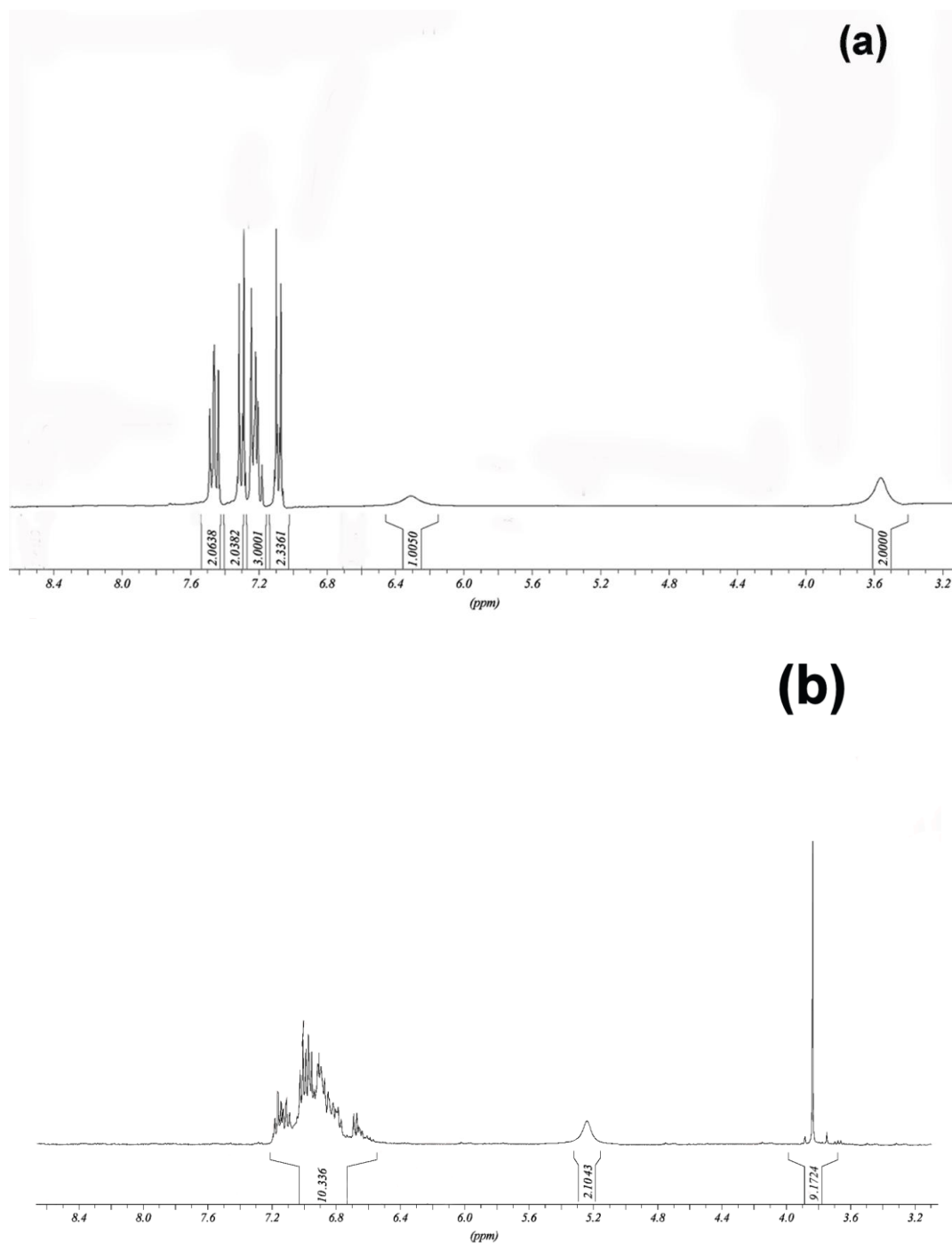
Figure 6. NMR spectrum of (a) aniline dimer and (b) oANS trimer

The NMR spectrum of the tri-oANS presents three signal groups were observed, namely, 6.6-7.2 ppm (aromatic region), 5.25 ppm (proton of NH group), and 3.8 ppm ($-OCH_3$ group protons) Fig. 6 (b).

Contrary to NMR spectrum of aniline dimer, only a signal from protons attached to nitrogen (5.25 ppm) was observed, indicating that the remaining nitrogen atoms present sp^2 hybridization. Consequently, the molecule has a ring with a quinonoid oxidation state, consistent with the UV-vis spectrum further presented.

Integral analysis revealed that the ratio between signals in the aromatic region and protons attached to the nitrogen atom is about $5:1$, indicating that most of the obtained molecules are trimers, because the integral area of the aromatic region is not an exact value, which suggests the presence of small traces of oligomers able to change the exact value of the integral, however the obtained product consists chiefly of trimers. This is probably related to an increase in reactivity of the nitrogen atom due to the electronic donor effect of the $-OCH_3$ group,[53-56] which makes the polymerization process energetically more favorable, forming a radical cation at a lower oxidation starting potential (Fig. 1 and 3), facilitating thus the formation of a trimer at the selected polymerization potential.

It is noteworthy that the NMR spectrum exhibits no signals of oANS head-to-head bonding to afford a phenazine structure (Fig. 7), *i.e.* the ratio of the aromatic region integrals with respect to the aliphatic region integrals for a phenazine structure ought to be 1:1. On the other hand, all phenazine nitrogens exhibit sp^{2-} hybridization, which disagrees with the NMR spectrum of the oANS trimer. This assumption has also been verified by other authors.[57]
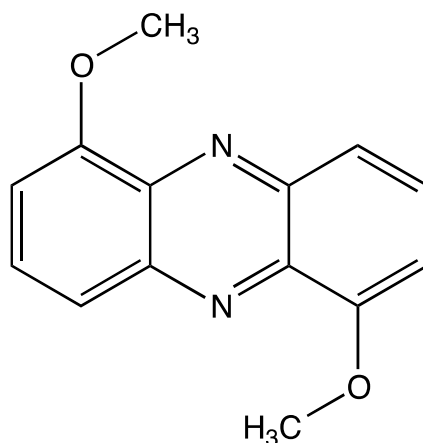

Figure 7. dioAN phenazine structure

The main signals and their assignments of NMR spectra are as follows:

di-ANI: ^{1}H NMR CDCl$_3$, 200 MHz, δ (ppm): 3.5 (s, 2H, NH$_2$), 6.3 (s, 1H, NH), 7.1 (d, *J* 8.02 Hz, 2H, H-2 and H-6), 7.2 (m, 3H, H-2`, H-4`and H-6`), 7.3 (d, *J* 8.02 Hz, 2H, H-3 and H-6), 7.4(dd, *J* 4.03 Hz, *J* 7.03 Hz, 2H, H-3` and H-5`)

tri-oANS:

^{1}H NMR CDCl$_3$, 200 MHz, δ (ppm): 3.8 (s, 3H, H-19), 5.25 (s, 2H, NH), 6.6 – 7.2 (m, 10H, H-3, H-5, H-6, H-9, H-11, H-12, H-15, H-16, H-17 and H-18)

3.3. UV-vis spectroscopic analysis

Figure 8 shows the UV-vis spectra of the monomer and the obtained di-ANI and tri-oANS chains, respectively.
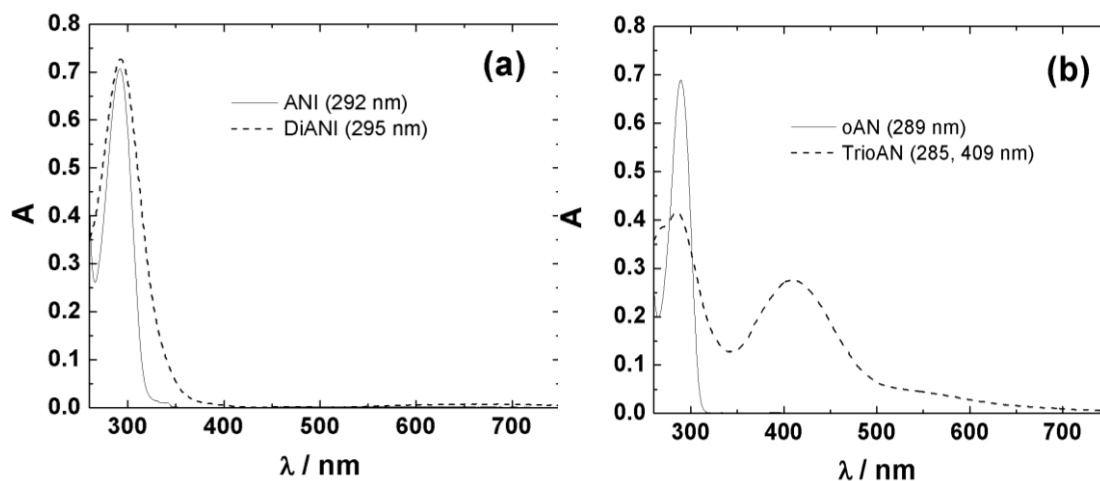

Figure 8. UV-vis spectra of (a) aniline and di-ANI. (b) oANS and tri-oANS

Spectra in Fig. 8, show that ANI and di-ANI share a well defined band at *ca.* 293 nm corresponding to a π→π* transition of the benzenoid structure without appreciable wavelength difference, since both molecules present a similar electronic behavior. This is related to the lack of quinonoid units evidenced by the absence of absorption at *ca.* 600 nm,[58,59] consistent with the signal at 6.3 ppm in the NMR spectrum of the aniline dimer.

On the other hand, oANS UV-vis spectrum, Fig 8 (b), depicts a different electronic behavior with respect to that of aniline dimer: at 300 nm, π → π* benzenoid transitions from monomer and trimer are observed, however, at *ca.* 420 nm, the π → π* transitions of the quinonoid structure of the trimer and the n → π* transitions of the sp^2 nitrogen atoms can be appreciated.[58, 59] The data are consistent with those of NMR spectra. Besides, trimer absorption bands, increase conjugation degree and the presence of quinonoid units, which have the property of reducing the band gap and to shift the signals to higher wavelengths, account for this behavior.[60-63]

It is important to underline that phenazine form, Fig. 7, displays a different electronic behavior than oANS, which has been previously characterized by Ryazanova *et al.*[64] with an absorption maximum near 400 nm, differing from the tri-oANS UV-vis spectrum. Consequently, phenazine structure is not formed during the oligomerization process.
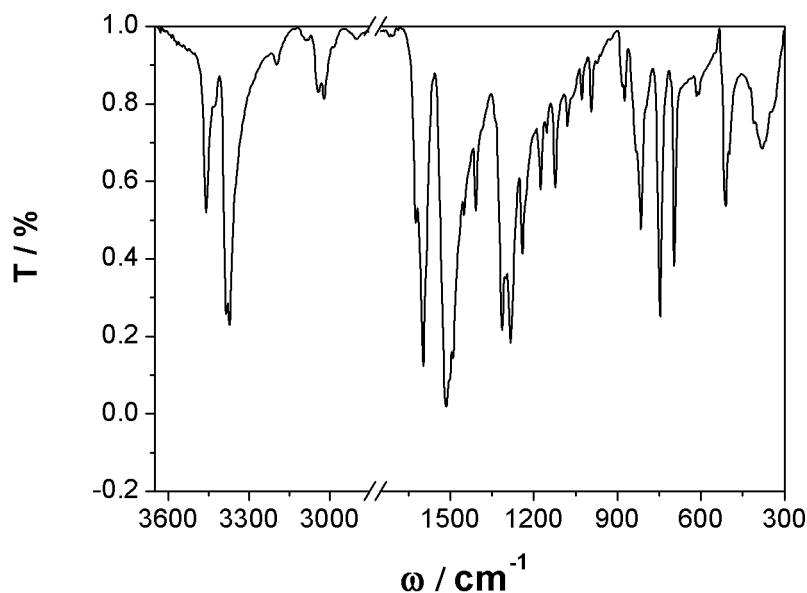
3.4. FT-IR analisys

Figure 9. FT-IR spectrum of di-ANI

The FT-IR spectrum of aniline dimer, Fig. 9, exhibits two bands at 3460 and 3372 cm^{-1}, assigned to symmetric and asymmetric primary amine NH stretching, consistent with data obtained by NRM and UV-vis spectroscopy. The bands at 1597 and 1514 cm^{-1} correspond to C–C benzene stretching. No bands were observed for C–C and C=C stretching at 1650 cm^{-1}, suggesting the absence of quinonoid units and sp^2 type nitrogen, consistent with data from UV-vis spectroscopy and the ratio of integral values from NMR spectra. Furthermore, it is noteworthy that the FT-IR spectrum obtained for aniline dimer has the same characteristic bands as reported by Aldrich for this product[65] in the region above 1000 cm^{-1}. Below this region small transmittance difference with respect to the FT-IR spectrum obtained by Aldrich was observed. This might be ascribed to benzene ring deformation coming from traces of oligomers obtained along with the dimmer. Bands in this frequency range of the FT-IR spectrum are numerous, consequently it is difficult to differentiate between the in-plane and out-of-plane vibrational mode of the benzene ring [67].

The main transmittance bands and their assignments are listed in Table 1.

Table 1. di-ANI FT-IR spectra assignments

ω (cm^{-1})	Band assignments
3460 and 3372	Symmetric and asymmetric primary amine N-H stretching
1597 and 1514	C–C benzenoid stretching
1285 and 1314	Primary and secondary aromatic amine C–N deformation
815	Bi-substituted aromatic ring pattern
745 and 690	Mono-substituted aromatic ring pattern

The 815 cm^{-1} band is characteristic of PANI synthesized in strongly acid media,[66] which normally appears at 829 cm^{-1}.

The tri-oANS FT-IR spectrum, Fig. 10, is very similar to aniline dimer. A band between 3320 and 3423 cm^{-1}, corresponding to NH stretching, exists. However, unlike aniline dimer, two characteristic bands at 2950 and 1250 cm^{-1}, corresponding respectively to the aliphatic C–H stretching of the –OCH$_3$ group and to the "umbrella"-type stretching of the same group, were observed. Quinonoid and benzenoid C=C stretching is observed at *ca.* 1600 and at 1500 cm^{-1}, respectively. These bands are consistent with the results obtained by both UV-vis spectroscopy and NMR spectra integrals.
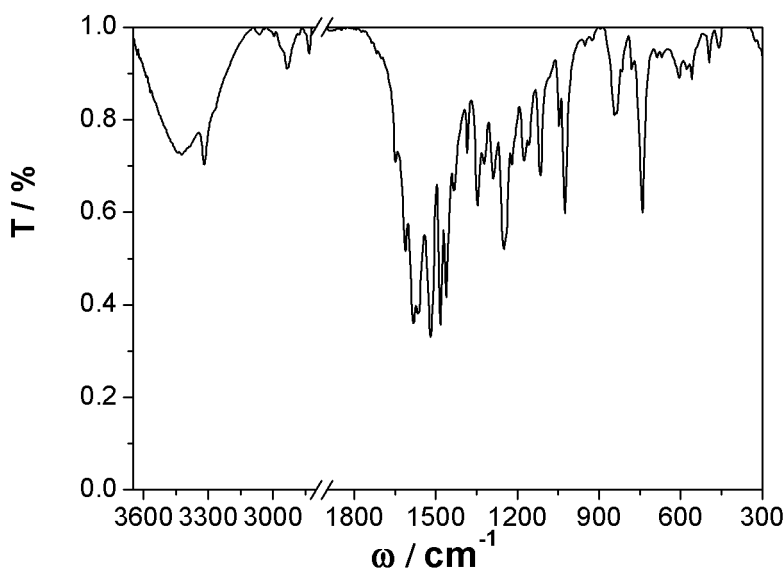

Figure 10. FT-IR spectrum of tri-oANS

The main transmittance bands and their assignments are included in Table 2.

Table 2. Tri-oANI FTIR spectra assignments

ω / cm^{-1}	Band assignments
3423 and 3320	Primary amine N-H stretching
1648	Aromatics amine and conjugated nitrogen compounds C=N stretching
1612	Quinonoid C=C stretching
1582 and 1484	Benzenoid C-C stretching
1347	Tertiary aromatic C-N stretching, specific for aromatic/quinonoid systems
1250	Asymmetric band of R-O-Ar bond "umbrella" like tension
842	C-H signal of 1, 2, 4 tri-substituted benzene
740.6	Ortho di-substituted benzene

Analysis of the results obtained by different spectroscopic techniques employed to characterize the electro-synthesized products, enables establishing that applying a controlled potential during a suitable period of time, ANI or oANS oligomers can be produced utilizing a cheap, simple, and clean general approach.

4. CONCLUSIONS

The electro-synthesis of some short-chain oligomers of aniline and o-anisidine has been accomplished.

The characterization proved that the obtained products correspond to aniline dimer and oANS trimer, along with a non-quantifiable amount of oligomers. The formation of either oligomeric unit depends on the electro-synthesis timing.

Thus, the choice of suitable experimental conditions enables the obtention of oligomers of electroactive species, *e.g.* aniline and oANS.

In conclusion, the methodology herein proposed allows controlling the length of the oligomer chain as a function of the starting unit employed and/or electro-deposition time.

Moreover, these results validate the proposed model evidencing the existence of an Oligomeric High Density Region (OHDR) at the early stages of the potentiostatic electro-polymerization process.

Therefore, a simple and cheap method has been developed for the obtainment of oligomer materials. The proposed approach, using the optimum working conditions, is applicable to any electro-active monomer unit.

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