



*J. Serb. Chem. Soc.* 78 (4) 507–521 (2013)  
JSCS–4434

## Spectroscopic analysis of the structure and stability of two electrochemically synthesized poly(3-alkylthiophene)s

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(Received 27 March, revised 3 September 2012)

**Abstract:** In this work, poly (3-methylthiophene) (P3MT) and poly (3-octylthiophene) (P3OT) films were electrochemically synthesized in non-aqueous media through the oxidation of the monomers, (3-methylthiophene and 3-octylthiophene) using a standard three-electrode cell in acetonitrile with 0.100 mol L<sup>-1</sup> LiClO<sub>4</sub>. The polymeric thin films were deposited on platinum plates for optimal quality control of the process. It was observed that the material as-prepared by anodic electropolymerization undergoes a natural process of deprotonation as a function of time. Moreover, the partial de-doped form obtained in NH<sub>4</sub>OH solution presents a good chemically stable form but becomes unstable again when radiated with blue light. Films obtained by these methods were characterized by cyclic voltammetry, Raman and photoluminescence spectroscopy. Both Raman and photoluminescence (PL) spectra led to the characterization of two structures (pristine and non-pristine forms of the thiophene rings), which formed the P3MT and P3OT polymer chains. These results were associated with the stabilization of pristine chains and mixed chains (non-pristine structures), radical cation and dication forms, in the polymeric film. Their bands in the Raman and PL spectra were broad and asymmetric and their adjustments by Gaussian functions indicated that there were three distinct contributions to the vibration and two to the emission spectra in the formed polymeric material.

**Keywords:** conducting polymers; Raman; photoluminescence; poly(alkylthiophenes).

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doi: 10.2298/JSC120327111R



## INTRODUCTION

Interest in poly(3-methylthiophene) (P3MT) and poly(3-octylthiophene) (P3OT), among the poly(3-alkylthiophene)s (P3ATs), is due mainly to the environmental stability of these materials that usually produces interfaces with metallic electrodes used in electronics.<sup>1-5</sup> In addition, the structural changes that accompany the electrochemical switching reaction, *i.e.*, the reversible cycling between the oxidized conducting state and the neutral insulating state, suggest the applicability of electro-active polymers in passive display devices.<sup>6,7</sup> However, Koizumi *et al.*<sup>8</sup> showed that a natural de-doping of poly(3-octylthiophene) occurs in time. This is caused by the instability of the material due to the presence of the alkyl side chains and other factors, such as the nature of the doping, the length of the alkyl side chain, temperature, humidity and the atmospheric conditions. This chemical stability was recently studied by submitting these materials to a de-doping process after their electrochemical synthesis.<sup>9,10</sup>

Since compounds such as P3ATs have a non-degenerate ground state, they carry the possibility of self-localized excitations, such as polarons (radical cations) and bipolarons (dications).<sup>11</sup> The two possible situations for counter ion-polymer interactions with the studied P3ATs, on simulating the doping of the polymeric chains of P3MT and P3OT, are shown in Fig. 1. The association of the

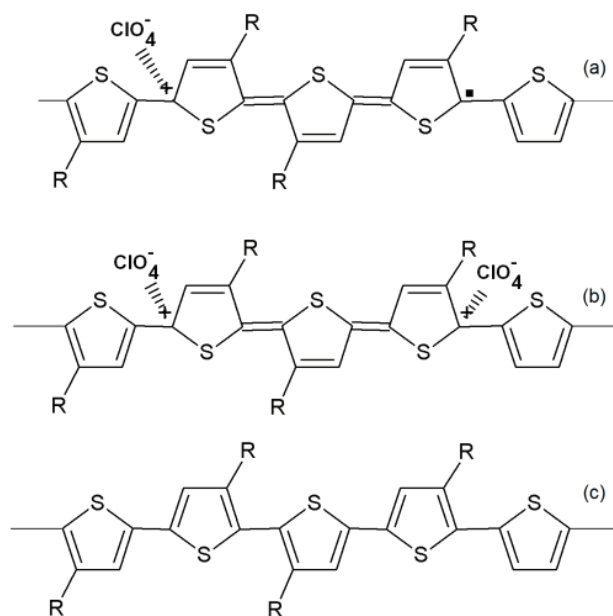


Fig. 1. Probable structures of P3MT and P3OT in the radical cation form (a), dication form (b), both doped with  $\text{ClO}_4^-$  (non-pristine forms) and pristine form (c). R represents the alkyl side chain.

counter ion ( $\text{ClO}_4^-$ ) with the carbon atom in position 2 or 5 of the thiophene ring, which occurs due to coulombic interaction, forms a radical cation in the polymeric chain (Fig. 1a). However, the action of an electrochemical potential enables the formation of structures in the dication form (Fig. 1b). Through doping, the polymeric chain can present two different structures, the pristine and non-pristine forms. The formation of the non-pristine structure will only occur when a doping ion is associated with the polymeric chain. Polymeric chains like this are called mixed chains. In this context, the de-doping consists of removal of anions from the formed polymer; when that transpires, the polymer is called pristine and only pristine thiophene rings are present, Fig. 1c.<sup>12</sup>

In this paper, studies on the formation of P3MT and P3OT thin films on a platinum surface and the typical voltammograms of these systems are reported. Different experimental conditions were considered during the preparation of the samples, such as the electrochemical profile of the polymers, which were characterized by *ex situ* Raman and photoluminescence spectroscopy to verify the pristine and non-pristine forms present in the material. An increase in PL intensity was verified in irradiated partially de-doped P3OT to obtain the PL spectrum, indicating the instability of the sample.

## EXPERIMENTAL

### Chemicals

The 3-methylthiophene ( $\text{C}_5\text{H}_7\text{S}$ ) and the 3-octylthiophene ( $\text{C}_{12}\text{H}_{20}\text{S}$ ) monomers were purchased from Acros-Organics – 99.0 %; lithium perchlorate ( $\text{LiClO}_4$ ) from Acros-Organics – 99.0 % was used as the supporting electrolyte. All these reagents were used without further purification. Acetonitrile ( $\text{CH}_3\text{CN}$ ) of 99.5% purity was obtained from J. T. Baker and used as supplied.

### Electrochemical polymerization and samples

A standard three-electrode cell was used for cyclic voltammetry. A platinum plate ( $25 \times 30 \times 0.5$  mm) acted as the working electrode and a platinum plate ( $10 \times 10 \times 0.5$  mm) was used as the auxiliary electrode. The area of the working electrode covered with the film was maintained constant at  $3.0 \text{ cm}^2$ . All potentials were determined with reference to Ag/AgCl into a Luggin-Haber capillary, using a  $0.100 \text{ mol L}^{-1}$  solution of  $\text{LiClO}_4$  in acetonitrile as the supporting electrolyte. The current *versus* time curve and cyclic voltammograms were obtained with a MQPG-01: Microquímica potentiostat–galvanostat controlled by a personal computer.

The polymerizations of 3-methylthiophene ( $0.035 \text{ mol L}^{-1}$ ) and 3-octylthiophene ( $0.040 \text{ mol L}^{-1}$ ) were realized at a fixed potential. The polymer synthesized on the electrode surface was obtained by taking the working electrode out of the cell and keeping it for some days under ambient conditions (referred to as “as-prepared”). The film was oxidized at 1.70 V for 1 min, using  $0.100 \text{ mol L}^{-1}$   $\text{LiClO}_4$  in acetonitrile as the supporting electrolyte (referred to as “oxidized”). The films labeled “partially de-doped” were obtained by submitting them to a concentrated basic solution (ammonium hydroxide).

### Spectroscopic characterization

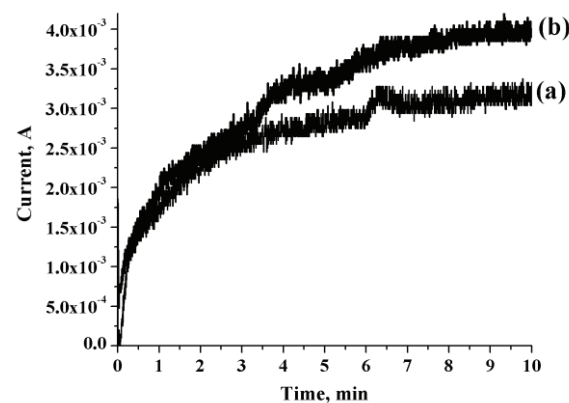
The Raman spectra were obtained from thin film samples using a portable Raman spectrometer DeltaNu with 785 nm laser line and a spectral resolution of  $8\text{ cm}^{-1}$ . DeltaNu software was employed to remove background fluorescence using the baseline features.

### Photoluminescence (PL) analysis

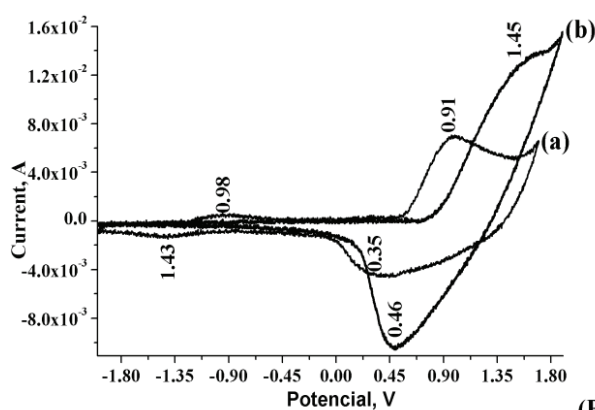
The PL spectra were recorded using a 0.5 m monochromator, a GaAs photomultiplier tube and a conventional lock-in technique for signal processing. The PL spectra were also recorded using a USB4000 Ocean Optics minispectrometer. The excitation source was a diode laser emitting at 405 nm, with a power density of  $0.2\text{ W cm}^{-2}$ .

## RESULTS AND DISCUSSION

The current *versus* oxidation time curves of 3-methylthiophene and 3-octylthiophene on a platinum electrode in a  $0.100\text{ mol L}^{-1}$  solution of  $\text{LiClO}_4$  in acetonitrile are shown in Fig. 2A. The electrochemical syntheses of the respective monomers were accomplished with current densities of  $1.03$  and  $1.11\text{ mA cm}^{-2}$ , as employed by Louarn *et al.*<sup>13</sup> It was observed that during the 3.5 min application of the fixed potential, an abrupt current increase occurred in both systems.



(A) Fig. 2. A) Current *versus* time curves of the oxidation of the monomers, a) 3-methylthiophene,  $0.035\text{ mol L}^{-1}$  and b) 3-octylthiophene,  $0.040\text{ mol L}^{-1}$ , on a platinum electrode in a solution of  $0.100\text{ mol L}^{-1}$   $\text{LiClO}_4$  in acetonitrile, applying fixed potentials of a)  $1.55$  and b)  $1.70\text{ V}$ , respectively; B) cyclic voltammograms of the polymer thin films of a) P3MT and b) P3OT on a platinum electrode in a solution of  $0.100\text{ mol L}^{-1}$   $\text{LiClO}_4$  in acetonitrile, at a scan rate of  $50\text{ mV s}^{-1}$ .



Subsequently, the two systems had individual behavior, due to the different concentrations and potentials applied. Thin films of better morphological quality were obtained at 10.0 min. These behaviors could be explained by the formation of thin films through nucleation and growth mechanisms during the anodic electropolymerization, under charge transfer control.<sup>14</sup>

For the films formed under other synthesis conditions, *i.e.*, under potentials or concentrations below or above those mentioned above, for each different system, they presented low homogeneity and, most of the time, formed a “packed grain” morphology with an substantial amount of empty space on the electrode. It was observed that under these syntheses conditions, the initial abrupt increase in the oxidation current did not occur, as shown previously.

The cyclic voltammograms of the polymer thin films in a 0.100 mol L<sup>-1</sup> solution of LiClO<sub>4</sub> in acetonitrile are shown in Fig. 2B. Peaks at -0.60 and -1.28 V were observed for this electrolytic solution, relative to the oxidation and reduction of the electrolyte, respectively, on a platinum electrode. For surfaces formed by thin films prepared in LiClO<sub>4</sub>, these peaks were shifted to -0.98 and -1.43 V, corresponding to the electrochemical dynamics of the supporting electrolyte in the polymer matrix.<sup>15</sup>

The thin films obtained soon after the electrochemical synthesis under conditions of anodic potentials were not immediately electro-active. Cyclic voltammograms were only obtained after a period of up to three days, demonstrating that, under ambient conditions, spontaneous processes modifying the chemical structure of the material occur with time. The as-prepared films showed oxidation peaks at 0.91 and 1.45 V and of reduction at 0.35 and 0.46 V for the P3MT and P3OT, respectively. However, the bands were well formed, not just shoulders in this potential area, due to an initial sweeping of the potential to -2.00 V, and subsequent acquisition of the voltammograms. This effect could be understood taking into consideration the function of the electrolyte as a dopant, which, after sweeping to negative potentials, reorganizes the chemical structure of the thin film on platinum electrode and the doping, stimulated by the applied potential, probably leads to the formation of structured polymer layers.<sup>16</sup>

The two polymers used are members of the P3AT homologous series, and they differ only by their lateral chain. It could be observed that the displacements in the potentials showed a characteristic electrochemical behavior, under conditions of this study. Bazzaoui *et al.*<sup>17</sup> electrochemically synthesized the same P3ATs as thin films on a gold electrode in a 0.100 mol L<sup>-1</sup> solution of N(Bu)<sub>4</sub>ClO<sub>4</sub> in acetonitrile. For this study, oxidation/reduction peaks were observed at approximately 0.70 and 0.55 V (P3MT) and at 1.00 and 0.70 V (P3OT).

Attempts were made to prepare some extremely thin films under the conditions shown in Fig. 2A, but at shorter times (3 and 5 min) for P3MT and P3OT, respectively. These films showed different behaviors three days after synthesis,

the oxidation and reduction peaks were not obtained as shown in Fig. 2B. The oxidation/reduction peaks were observed at 0.35 and  $-0.45$  V (P3MT) and at 0.37 and  $-0.53$  V (P3OT). Probably, under these conditions, oligomeric structures were formed on the surface of the platinum electrode.

The *ex situ* Raman spectra for P3MT and P3OT, as-prepared and oxidized, are shown in Fig. 3. Bands assigned to the normal vibrations modes of the thiophene ring were observed.<sup>13</sup> Some small frequency displacements in relation to the bands observed in the study of Louarn were also observed, due to differences in the synthesis conditions, the thin thickness of the films and the excitation radiation used for spectra registration. The bands in the P3MT Raman spectra were of larger intensity than those in the P3OT spectra. In the latter spectra, some bands were associated with the presence of the electrolyte creating material doping.

The Raman spectra for the as-prepared samples were compared to the oxidized samples with bands at  $1409$  and  $1423$   $\text{cm}^{-1}$ , related to P3MT and P3OT, and shifted to  $1421$  and  $1428$   $\text{cm}^{-1}$ , respectively. In the P3MT spectrum, the

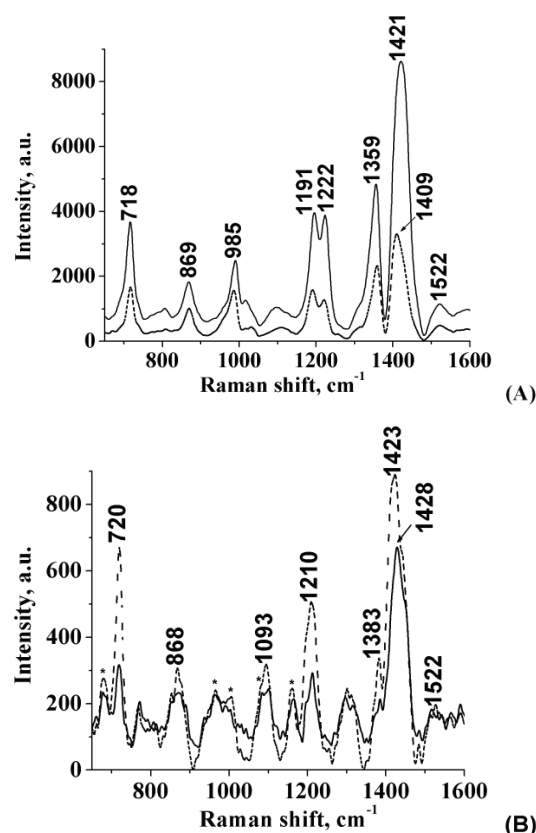


Fig. 3. *Ex situ* Raman spectra of A) P3MT and B) P3OT, obtained as-prepared (---) and oxidized (—). \*) Characteristic  $\text{LiClO}_4$  frequencies.

intensity of the frequency for bands at 1191 and 1222  $\text{cm}^{-1}$  increased after the polymer oxidation, while in the P3OT, there was a broadening of the band centered at 1210  $\text{cm}^{-1}$ . The bands associated with these compositions restrict the discussion of the spectra to these two areas of interest, in other words, at 1140–1250  $\text{cm}^{-1}$  and 1378–1480  $\text{cm}^{-1}$ , due to changes observed in the widths of the bands obtained under different preparation conditions. These bands are due to (C–C) inter-ring stretching and (C=C) aromatic symmetric ring stretching, respectively.<sup>13</sup>

Hernandez *et al.*<sup>18</sup> and López-Elvira *et al.*<sup>19</sup> obtained spectra for P3MT and P3OT in the pristine form and more intense Raman bands at 1450 and 1443  $\text{cm}^{-1}$ , respectively. However, at 1190–1205  $\text{cm}^{-1}$  (P3MT) and 1188  $\text{cm}^{-1}$  (P3OT), these bands presented a certain broadening. López-Elvira *et al.*<sup>19</sup> observed that the (C=C) aromatic symmetric and antisymmetric ring stretching of samples degraded with UV radiation showed band broadening and a 60  $\text{cm}^{-1}$  shift to higher frequencies. It was considered that the broadening observed in the spectra in Fig. 3 was due to structural changes in the thiophene ring during the electropolymerization process. In other words, Raman lines originating from both aromatic and quinoid structured rings could be detected.<sup>17</sup> It was observed that electrochemically synthesized polydiphenylamine showed a band shift at 1609 to 1618  $\text{cm}^{-1}$ , due to the polymeric de-doping.<sup>20</sup> This was the consequence of the presence of different mixed segments that formed in the polydiphenylamine in the reduced state, mainly aromatic and quinoid structures.

The deconvoluted Raman spectra in the range from 1378 to 1480  $\text{cm}^{-1}$  for the as-prepared, oxidized and partially de-doped samples are presented in Fig. 4. The spectra showed three features on deconvolution, probably from the assigned symmetric stretch of aromatic, semi-quinoid and quinoid structures. The presence of semi-quinoid species was considered based on the results obtained previously by EPR spectroscopy.<sup>9,10</sup> For P3OT prepared using a  $\text{LiClO}_4$  containing supporting electrolyte, referred to as doped (oxidized) and partially de-doped samples, a free radical was detected, demonstrating that the polymer was not totally de-doped.

For the as-prepared P3MT, bands were observed at 1403, 1423 and 1457  $\text{cm}^{-1}$ ; the oxidized polymer bands were observed at 1405, 1429 and 1463  $\text{cm}^{-1}$ ; and for partially de-doped polymer at 1405, 1431 and 1460  $\text{cm}^{-1}$ , with relative frequency intensities that varied with the preparation of the materials. For the as-prepared P3OT, bands were observed at 1413, 1428 and 1447  $\text{cm}^{-1}$ ; for the oxidized polymer, bands were observed at 1417, 1432 and 1451  $\text{cm}^{-1}$ ; and for partially de-doped polymer at 1414, 1429 and 1453  $\text{cm}^{-1}$ . The Raman spectrum of the partially de-doped P3OT had a drastic intensity loss, probably due to the fluorescence effect, which will be discussed later. This spectrum variation made a more precise analysis of the intensity variations impossible.



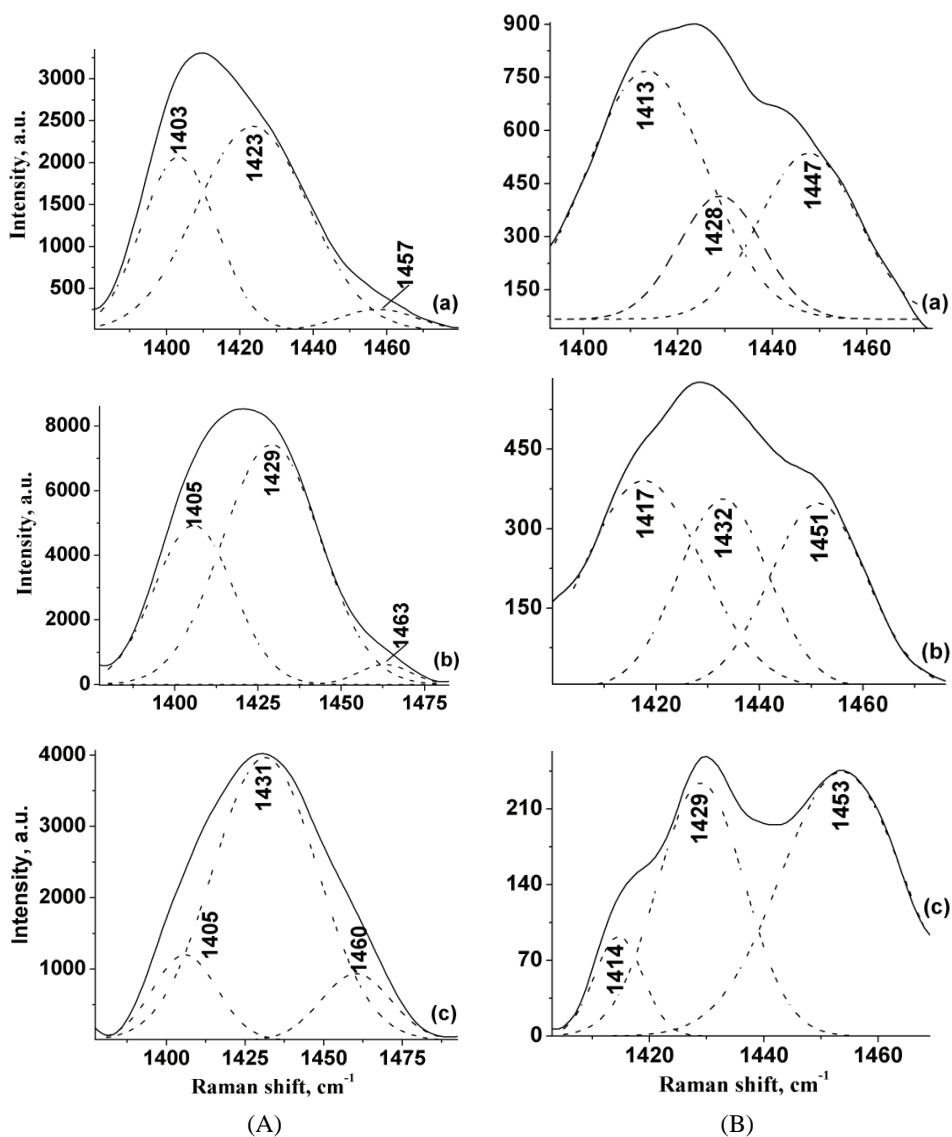


Fig. 4. Deconvoluted Raman spectra from 1378–1480  $\text{cm}^{-1}$  of A) P3MT and B) P3OT; a) as-prepared, b) oxidized and c) partially de-doped.

The bands obtained from the deconvoluted Raman spectra (Fig. 4), at 1403–1405  $\text{cm}^{-1}$  and 1413–1419  $\text{cm}^{-1}$ , were attributed to the aromatic species of P3MT and P3OT, respectively, based on the characteristic frequency of the pristine form.<sup>18,19</sup> The results indicated that there were changes in the aromatic character of thiophene rings to quinone upon electrochemical oxidation, and that the remaining aromatic rings in the polymer chains were slightly disturbed. After



deprotonation of the samples, there was an intensity increase in these bands but, even so, the predominant form was the quinone structure that had the highest intensity in the spectra. The bands obtained in the deconvoluted Raman spectra at  $1423\text{--}1431\text{ cm}^{-1}$  and  $1428\text{--}1435\text{ cm}^{-1}$  were attributed to quinoid species. This assignment was based on the results of Therezio *et al.*<sup>10</sup>, who demonstrated that the polymer chain could exist in quinone and semi-quinone forms that are stabilized by the presence of the electrolyte as a dopant. After removal of the electrolyte in the de-doping process, the quinone form is favored, and radical species destabilize in the chain. The frequencies at  $1457\text{--}1463\text{ cm}^{-1}$  and  $1447\text{--}1453\text{ cm}^{-1}$  were considered characteristics of semi-quinoid segments of representative poly-alkylthiophenes, considering that these species can usually appear at higher frequencies.<sup>21</sup>

The frequencies obtained in the deconvoluted Raman spectra from  $1189\text{--}1195\text{ cm}^{-1}$  and  $1191\text{--}1196\text{ cm}^{-1}$  are shown in Fig. 5, which are attributed to the aromatic species of the P3MT and P3OT, respectively, based on the characteristic frequency of the pristine form.<sup>18,19</sup> Hernandez *et al.*<sup>18</sup> also associated a band at  $1205\text{ cm}^{-1}$  to the aromatic form. However, an increase in the intensity of the bands in the range of  $1211\text{--}1228\text{ cm}^{-1}$  (P3MT) and  $1204\text{--}1227\text{ cm}^{-1}$  (P3OT) was observed. Casado *et al.*<sup>22</sup> observed spectral differences between the pristine and oxidized molecules for oligothiophenes related to the intensity of the bands at  $1217\text{--}1226\text{ cm}^{-1}$ , which were related to the radical cation and dication forms. These authors considered that the assignment of these bands was not straightforward, but it could be expected that the modes have a collective character and are assignable to mixtures of (C–C) inter-ring and (C=C) aromatic symmetric ring vibrations, with the probable involvement of stretching vibrations of the alkyl side chain.

The spectra frequencies for P3MT and P3OT were different from each other, as can be seen in Fig. 5. Considering the assignment of the frequencies to (C=C) of symmetric aromatic ring and their possible collective character, the frequencies at  $1211\text{--}1228\text{ cm}^{-1}$  and  $1204\text{--}1227\text{ cm}^{-1}$ , respectively, could probably be characteristic of the dication form. In the same way, the bands at  $1222\text{--}1228\text{ cm}^{-1}$  and  $1221\text{--}1227\text{ cm}^{-1}$  are characteristic of the radical cation.

The PL spectra of P3MT and P3OT for the as-prepared, oxidized and partially de-doped samples are shown in Fig. 6. It was observed that the PL intensity of the as-prepared and oxidized samples for both films presented the same behavior. In other words, the as-prepared samples exhibited a greater intensity than the oxidized samples, indicating that the species present in the oxidized samples could be causing the loss of luminescence quenching by diminishing the exciton recombination process. Compared to these samples, the PL spectra of the partially de-doped P3MT and P3OT thin films exhibited significantly higher intensities.

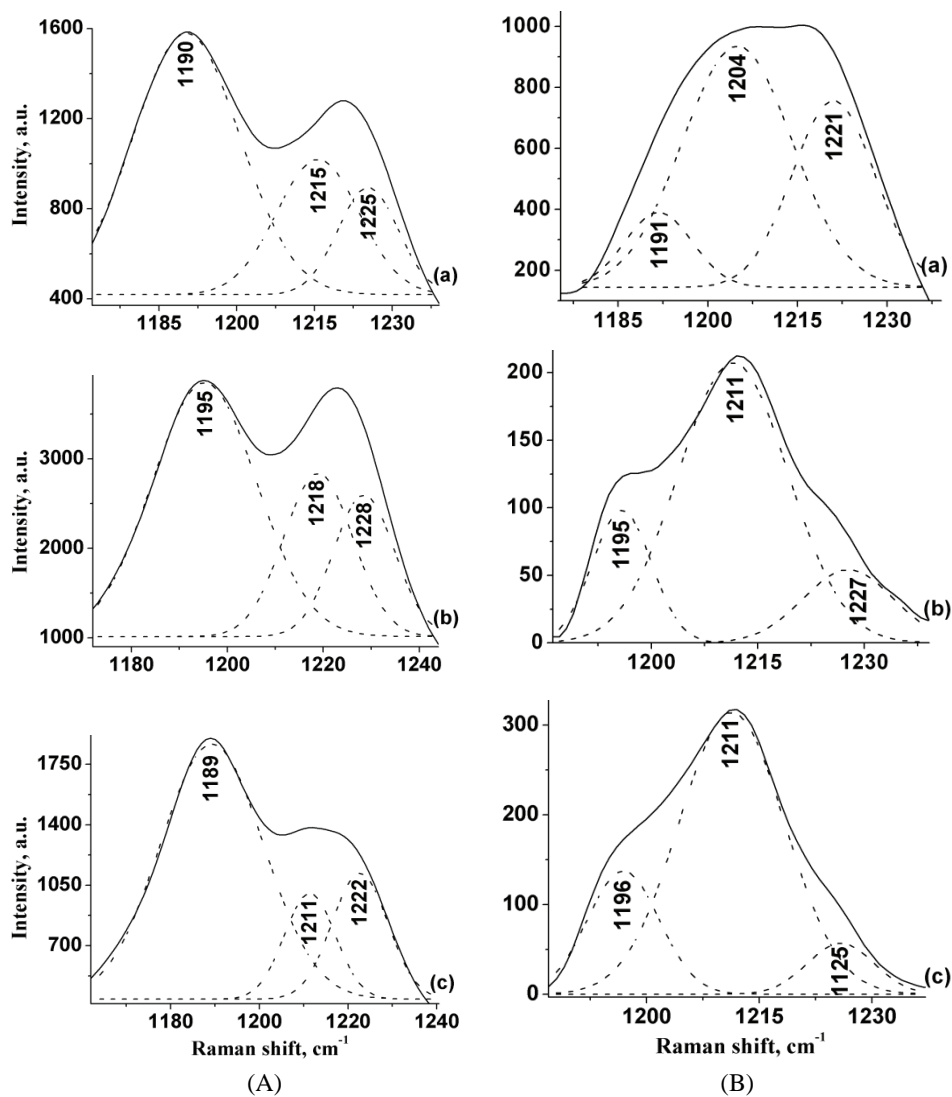
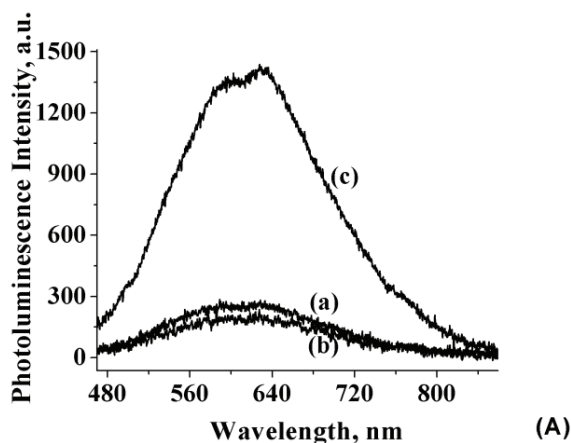
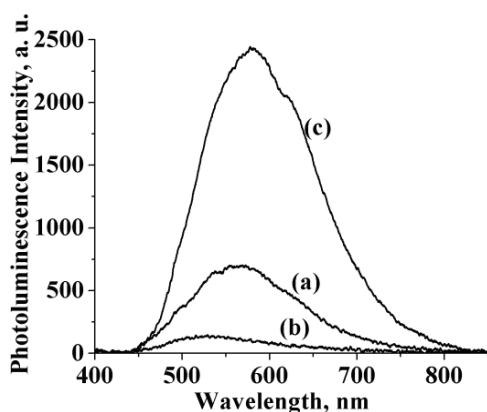


Fig. 5. Deconvoluted Raman spectra from 1140–1250  $\text{cm}^{-1}$  of A) P3MT and B) P3OT; a) as-prepared, b) oxidized and c) partially de-doped.

As verified by Yoshino *et al.*<sup>23</sup> and Ohmori *et al.*<sup>24</sup>, the intensity of the luminescence emission band in P3ATs increases considerably with the nature of the alkyl chain of these materials, being related directly to the increase in the number of carbon atoms. This intensity increase was explained by confinement of the carriers caused by the alkyl chain length,<sup>23,25</sup> which favors carrier recombination in the chain and, consequently, the emission intensity increases.



(A)



(B)

Fig. 6. PL Spectra of A) P3MT and B) P3OT; a) as-prepared; b) oxidized; c) partially de-doped.

The deconvoluted PL spectra for the partially de-doped samples are presented in Fig. 7, from which it can be seen that the fitting of data show two main contributions to the formation of the spectra of the partially de-doped P3MT and P3OT. Deconvoluted PL spectral peaks were observed at 603 and 656 nm for P3MT and 557 and 626 nm for P3OT. Singh *et al.*<sup>26</sup> showed the spectrum of pristine P3OT, *i.e.*, the spectrum of P3OT constituted of pristine chains, presented a band centered at 640 nm, while Wang *et al.*<sup>27</sup> presented a PL spectrum in which, despite having the main band at 642 nm, a small band appeared at 575 nm. Its origin was not explained. The spectra of partially de-doped samples from dos Reis *et al.*<sup>9</sup> and Therezio *et al.*<sup>10</sup> show emission bands centered very close to 599 and 678 nm for P3MT, and 575 and 640 nm for P3OT, similar to the bands discussed in this work. The bands at 599 for P3MT and 575 nm for P3OT were attributed to the formation of mixed chains, composed of pristine and non-pristine structures, in the chains of the polymeric film synthesized by the electrochemical technique.

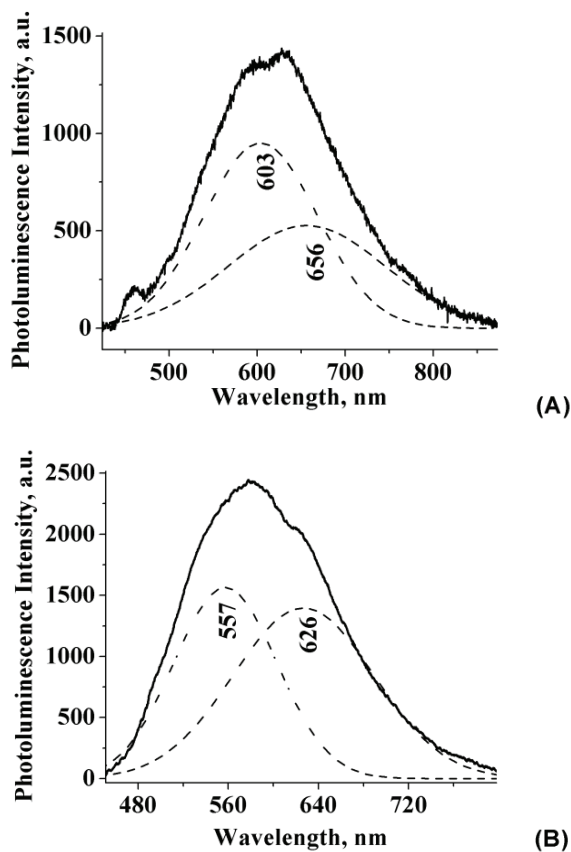


Fig. 7. Deconvoluted PL spectra of A) P3MT and B) P3OT, partially de-doped.

The changes in PL spectra as a function of laser irradiation time for the partially de-doped P3OT sample are shown in Fig 8. An unexpected increase in PL intensity with laser irradiation was observed. It was mentioned previously that the Raman spectrum of partially de-doped P3OT had a drastic intensity loss, probably due to the fluorescence effect. However, this behavior was not observed in P3MT, which presented a quite stable spectrum during the irradiation, and a Raman spectrum with good signal-to-noise ratio.

In general, an increase in polymer fluorescence observed in samples submitted to air photo-irradiation was explained by a model that predicted the creation of an energy profile along the film thickness due to the photodegradation process of the polymer chains.<sup>28</sup> In this case, the excitation was transferred from more conjugated to less conjugated segments, and the transfer process, assisted by a non-uniform distribution of photogenerated defects, led to a higher PL quantum efficiency. López-Elvira *et al.*<sup>19</sup> observed that in P3OT thin films, the polymer degradation was very sensitive to the illumination wavelength, blue light they

found to be more damaging than the UV light. They considered that the degradation induced by the blue light might be intimately related to photo-excitation.

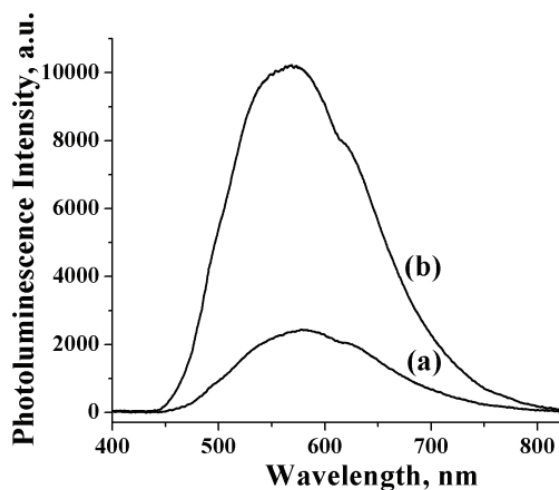


Fig. 8. PL Spectra of P3OT partially de-doped sample; a) 0 and b) 10 min.

Excitation radiation at 405 nm was used to obtain the PL spectrum, a frequency for which there is an increase due to a photochemical process. As it was observed only in P3OT and not in P3MT, it should also involve the participation of the alkyl side chains, destabilizing the chains containing the exciton species. As observed by Yoshino *et al.*<sup>23</sup> and Ohmori *et al.*,<sup>24</sup> the intensity of the luminescence band in P3ATs increased considerably depending on the nature of the alkyl chain, but this might have been influenced by the photochemical process. As discussed by López-Elvira *et al.*,<sup>19</sup> topographic variations were not observed until irradiation exposures of one to two orders of magnitude larger were adopted.

#### CONCLUSIONS

The present article dealt with the electrosynthesis of two P3ATs on platinum electrodes and their characterization by Raman and photoluminescence spectroscopic techniques. It brought some new insights into the procedure that yields thin polymer films and their detailed structural analysis and stability, which is intimately related to photo-excitation.

In order to explain the Raman spectra of P3MT and P3OT thin films, band-fitting was employed, which identified three structures (pristine, quinone and semi-quinone forms) as being the constituents of the polymeric chains. The PL spectra showed two main contributions: the emission of mixed chains (Gaussian of smaller wavelength) and the emission of the chains in the pristine form (Gaussian of larger wavelength).

In addition, this paper provided evidence that the luminescence intensity was inversely related to the conductivity. The luminescence quenching observed in

doped samples was due to the predominant quinone and semi-quinone segments presents in the polymer chains.

*Acknowledgments.* This work was supported by the Araucaria Foundation, Process Nos. 18.575 and 20.380, and CNPq, Process Nos. 470533/2009-9 and 301980/2011-0, and Elaine and Danielly are indebted to CAPES for the grant of a fellowship.

## ИЗВОД

СПЕКТРОСКОПСКА АНАЛИЗА СТРУКТУРЕ И СТАБИЛНОСТИ ДВА  
ЕЛЕКТРОХЕМИЈСКИ СИНТЕТИСАНА ПОЛИ(3-АЛКИЛТИОФЕНА)

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Поли(3-метилтиофен) (РЗМТ) и поли(3-октилтиофен) (РЗОТ) филмови електрохемијски су синтетисани коришћењем стандардне тро-електродне ћелије у ацетонитрилу са 0,100 mol L<sup>-1</sup> LiClO<sub>4</sub>. Полимерни танки филмови су депоновани на плочице од платине ради најбоље контроле квалитета процеса. Опажено је да овако припремљен материјал за анодну електрополимеризацију показује природни процес депротонизације у функцији времена. Такође, врста материјала, добијена у NH<sub>4</sub>OH раствору, показује добру хемијску стабилност али, када је осветљена плавом светлошћу, поново постаје нестабилна. Филмови добијени овим методама су окарактерисани цикличном волтаметријом, раманском и фотолуминисцентном (PL) спектроскопијом. И Рамански и PL спектри омогућавају карактеризацију две структурне форме тиофенских прстенова који граде РЗМТ и РЗОТ полимерне ланце. На добијене резултате утиче стабилизација првобитних ланаца и мешаних ланаца, радикалских катјона и дикатјонских форми у полимерним филмовима. Њихове траке у Раманским и PL спектрима су широке и асиметричне па је њихово дефинисање Гаусовим функцијама било неопходно, што је указало на то да постоје три одвојена доприноса вибрационим и два емисионим спектрима у насталим једињењима.

(Примљено 27. марта, ревидирано 3. септембра 2012)

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