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Spectroscopic study of poly(3-alkylthiophenes) electrochemically synthesized in different conditions

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Abstract In this work, poly(3-alkylthiophenes) films were synthesized electrochemically in acetonitrile with $LiClO_4$ or Et_4NBF_4 at 5 or 18 °C. The films were deposited on platinum plates, and the polymer as-prepared was referred to as-oxidized. The as-reduced polymer was obtained by subjecting the as-oxidized product to -1.70 V for 1 min. These various products were characterized by cyclic voltammetry, reflectance UV–Vis and Raman spectroscopy, and the results were used to estimate the ionization potential (I_P), electron affinity ($E.A.$) and energy gap (E_g) parameters. This study was possible because the Raman spectra demonstrated three structures (aromatic, radical cation and dication segments) which formed the P3MT and P3OT polymer chains.

1 Introduction

Conjugated polymers have been studied intensively because of their optoelectronic properties and other characteristics like flexibility and malleability, making them ideal for producing devices for a wide range of applications: organic light-emitting diodes (OLED), organic solar cells, low-cost integrated circuits and organic field-effect transistors (OFET) [1, 2]. One of the main advantages of using organic polymers in various types of devices lies in the possibility of preparing differentiated chemical structures for forming systems with unique properties, representing an attractive way of producing new, low-cost materials [3].

Among these new materials, the poly(3-alkylthiophenes) stand out for their chemical stability, which means they can be used to produce stable interfaces with metallic electrodes as those used in electronics. The solubility of these materials means that they can be easily deposited on a substrate. They also offer characteristics such as thermochromism, solvatochromism and electrochromism [4]. Organic device characteristics (response time, efficiency, etc.) are not solely dependent on the nature and state (liquid/solid) of the components, but also on a number of other parameters, such as the preparation methods, temperature, mix, solid/liquid interface stability, adherence, etc. [3].

Synthesis conditions (temperature, electrolyte and monomer concentration) influence the stability of the radical cation in the polymer chain. A very stable radical cation can diffuse from the electrode to the bulk of the solution, giving rise to soluble oligomers, whereas a very reactive radical cation may suffer side reactions. Therefore, synthesis conditions must be controlled in order to obtain materials with ideal electrochemical and physicochemical properties [5].

This paper describes the electrochemical synthesis of two poly(3-alkylthiophenes): poly(3-methylthiophene), P3MT, and poly(3-octylthiophene), P3OT. The process consists of depositing the material on platinum plates in different electrolytes ($LiClO_4$ or Et_4NBF_4) at 5 or 18 °C. The materials were synthesized by following anodic current–time curves, and thereby setting up the best conditions for the formation of micrometric films [6] with a high degree of homogeneity over the surface of the substrate.

Although polymer materials are well-covered in the literature [7–11], the aim of this paper was to characterize

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the influence of radical cation and dication segments (quinonic), along with the structure of the thiophenic ring (aromatic), on the properties of the polymer material formed, under different experimental conditions. This involved using cyclic voltammetry (CV), UV–Vis reflectance spectroscopy and Raman spectroscopy. These techniques have made it possible to more accurately define various parameters such as ionization potential (I_P), electron affinity (*E.A.*) and energy gap (E_g), which are important for understanding and controlling electrical and optical properties, as well as the semiconducting polymers doping process [12, 13].

2 Materials and methods

2.1 Reagents

The 3-methylthiophene (C_5H_7S) and 3-octhylthiophene ($C_{12}H_{20}S$) monomers were used as received from Aldrich. The 99.0 % pure lithium perchlorate ($LiClO_4$) and tetraethylammonium tetrafluoroborate (Et_4NBF_4) supplied by Acros Organics were salts used for supporting electrolytes. The 99.5 % pure HPLC grade acetonitrile (CH_3CN), solvent, was obtained from J.T. Baker.

2.2 Electrochemical synthesis

Platinum plates were used for polymer film synthesis and (CV). The area of the working electrode coated with the film was kept constant at 3.0 cm^2. All potentials were determined relative to a Ag/AgC1 reference in a Luggin-Haber capillary. The supporting electrolyte was a 0.100 mol L^{-1} solution of $LiClO_4$ or Et_4NBF_4 in acetonitrile. The current–time curves and the cyclic voltammograms were obtained using a Microquímica MQPG-01 potentiostat coupled to a microcomputer. The CV scanning rate was 100 mV s^{-1}.

Four films of each polymer were synthesized (0.035 mol L^{-1} 3-methylthiophene and 0.040 mol L^{-1} 3-octylthiophene) and the current density was similar to that used for synthesis by Louarn et al. [14]. The polymers were synthesized by applying different fixed potentials at 5 or 18 °C, to 0.100 mol L^{-1} $LiClO_4$ or Et_4NBF_4 in acetonitrile. A potential of 1.65 V was applied to synthesize the P3MT in $LiClO_4$ at 5 °C for 2 min and 1.70 V for 3 min to synthesize the P3OT. At 18 °C, the same potentials were applied for 8 min for each synthesis. This difference in synthesis time at 18 °C was necessary to obtain homogenous films at lower temperature. The P3MT films synthesized in Et_4NBF_4, using the same electrolyte and monomer concentrations and at 5 °C, were obtained by applying a potential of 1.65 V; at 18 °C a potential of 1.75 V was applied for 2 min. To synthesize P3OT at 5 °C, a potential of 1.65 V was applied for 3 min; at 18 °C, a potential of 1.80 V was applied for 2 min. Once deposited, the films were immersed in acetonitrile to remove excess material of low molecular weight and electrolyte salt. The films obtained are referred to as-oxidized films. After reducing the films for 1 min at −1.70 V, they are called as-reduced films. This reduction potential was applied to clear the polymer matrix of the supporting electrolyte that builds up on the platinum at −1.28 V. For the deposition process the solution was at room temperature or cooler utilizing an ice bath (approximately 5 °C) in order to evaluate the effect on the polymer film morphology observed by Nicho et al. [6].

2.3 Determining parameters I_p, E_g and E.A.

The ionization potentials (I_p) were determined considering the oxidation potential onset (E'_{OX}) relative to Ag/AgCl on the cyclic voltammograms and the energy gap (E_g) and electron affinity (*E.A.*) considering the wavelength absorption maximum ($\lambda_{máx}$) and difference $I_P - E_g$, respectively, for the P3MT and P3OT products from different synthesis conditions.

2.4 Spectroscopic characterization

The UV–Vis reflectance spectra of the films were obtained using an Ocean Optics S2000 model fiber optic spectrometer to capture the reflection from the sample of a polychromatic beam of light from a tungsten-halogen lamp (wavelength range 400–950 nm). The equipment was calibrated using the Ocean Optics WS-1 reflectance pattern.

Raman spectra were obtained using a portable Delta Nu Advantage532® Raman spectrometer with a 532 nm laser line and resolution of 8 cm^{-1}. DeltaNu NuSpec software was used with baseline resources to eliminate background florescence.

3 Results and discussion

The cyclic voltammograms of the P3MT and P3OT films in 0.100 mol L^{-1} $LiClO_4$ or Et_4NBF_4, revealed an enlargement and displacement of only one oxidation peak towards more positive potentials (0.73/0.70–1.12/0.95 and 1.18/1.35–1.60/1.44 V respectively), with a variation in synthesis from 5 to 18 °C. Reduction peaks at 0.42 and 0.76 V were observed only on the voltammogram of the P3MT film synthesized at 18 °C, indicating that in this system, two kinds of reduction species are present. Tolstopyatova et al. [7] obtained similar results using CV and Izelt et al. [8] explained that the differences observed are the result of electro-activity of the radical cation and dication species in the case of P3MT. The experimental conditions for the oxidized and reduced films used to obtain the data in this study have been shown to be stable in the analyses conducted, however after a number of cycles there was a tendency to favor the reduced form. This behavior is probably due to natural de-doping, observed by Koizumy et al. [15] for P3OT.

Table 1 shows the results obtained of the I_p estimated from CV, taking into account polymer oxidation potentials. It is important to define the value of I_p since it determines the electrical properties as well as the doping process of the conducting polymer [12, 13, 16].

The values of I_p in Table 1 indicate that P3MT has a higher polymeric chain ionization capacity than P3OT, implying the doping process is favorable. These values correspond to the energy value of the highest occupied molecular orbit (HOMO) and on average P3MT is displaced around 0.5 eV higher based on the I_p value found for P3OT.

Considering the typical electrode/polymer interface of an organic device, it is expected that an electrode (normally with a high work function in relation to the vacuum level, e.g., 4.8–5.0 eV for ITO) [17] will inject holes at the HOMO energy level of both polymer materials, a process that is in part responsible for device efficiency. The values found were considered to be satisfactory for the process at the interface with the p-type polymer (electron donor). Varying experimental conditions should not influence the efficiency of a device formed by these polymers.

With the aim of combining the electrochemical behaviors of the films formed by different segments in the polymer chain, we obtained data on the ex situ reflectance spectra of P3MT and P3OT in $LiClO_4$ or Et_4NBF_4 at 5 and 18 °C.

The enlarged bands of the P3MT and P3OT oxidized films in the spectra exhibited maximum absorption from 600 to 850 nm, displaced according to the nature of the electrolyte and related to the synthesis temperature. For the reduced films of P3MT and P3OT, enlarged bands from 400 to 600 nm were observed and attributed to the gap energy of the polymer. However, the spectra for the P3MT and P3OT reduced in $LiClO_4$ at 5 °C showed a shoulder and a band around 647 (P3MT) and 717 nm (P3OT).

Table 1 Ionization potential (I_p) results obtained from the oxidation potential (E'_{OX}) of the cyclic voltammograms for the P3MT and P3OT from different synthesis conditions

	E'_{OX} (V vs. Ag/AgCl)	I_p (eV)
P3MT in $LiClO_4$ at 5 °C	0.47	4.9
P3MT in $LiClO_4$ at 18 °C	0.34[a]	4.7[a]
P3MT in Et_4NBF_4 at 5 °C	0.18	4.6
P3MT in Et_4NBF_4 at 18 °C	0.38	4.8
P3OT in $LiClO_4$ at 5 °C	0.82	5.2
P3OT in $LiClO_4$ at 18 °C	0.72[a]	5.1[a]
P3OT in Et_4NBF_4 at 5 °C	1.07	5.5
P3OT in Et_4NBF_4 at 18 °C	0.91	5.3

[a] *Source* Ref. [24]

Kondratieve et al. [18] obtained UV–Vis absorption spectra for the P3OT film and concluded that the band at 450 nm corresponded to the gap energy of this polymer, resulting from the π–π* transition and attributed the band at 780 nm to the dication species. Similar results were reported by Sun and Frank [8] for the P3MT film. Working with P3MT and using spectro-electrochemistry, Mazur [19] reported that a band at 520 nm occurs at −0.30 V. After applying 0.50 V, simultaneous bands at 518 and 843 nm were observed, and after applying 0.70 V, a band at 850 nm appeared.

In view of the information we obtained from the literature, we decided to adopt a strategy of deconvoluting the absorption spectra to see whether the enlargements in the bands for the different samples contained characteristics in the spectra that might indicate the presence of radical cation species in the as-oxidized samples.

After deconvolution of the spectra, the P3MT spectrum in Fig. 1 shows a structure at 684 nm, as well as the band at 466 nm. This structure could be related to the radical cation species in the polymer matrix, even after reduction. The P3OT spectrum shows a band at 725 nm associated with this species. Greater persistence of the radical cation was observed by de Santana et al. [20] in diphenylbenzidine. Even applying potentials that are more cathodic than the radical cation reduction potential showed this species stabilizes near the working electrode. Using EPR, Therézio et al. [11] also observed that P3OT exhibited free radicals

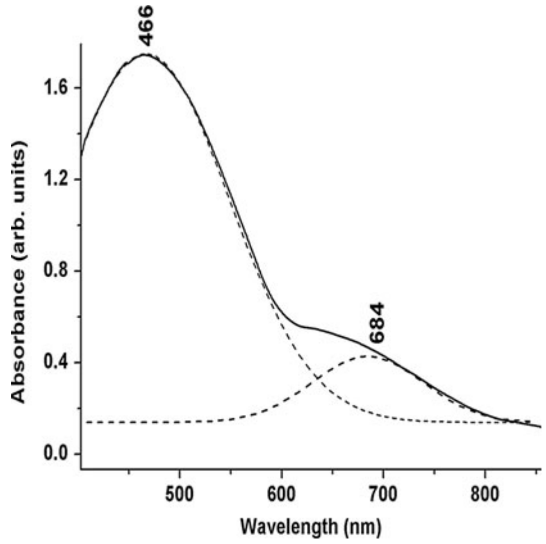

Fig. 1 Deconvolution Reflectance UV–Vis spectrum of the P3MT in 0.100 mol L^{-1} $LiClO_4$/ACN after electrochemical reduction at 5° C

in the partially de-doped sample, indicating that this process is not completed in the P3OT and that a few species still remain in the polymer matrix, even if prepared at 18 °C. Therefore, the 684 and 725 nm bands are characteristic of radical cation species present in larger quantities in samples prepared in $LiClO_4$ at 5 °C, both for P3MT and P3OT. These bands were also observed in the spectra of P3MT prepared in Et_4NBF_4 at 5 °C.

The spectra of the as-oxidized P3MT and P3OT films synthesized in Et_4NBF_4 at 18 °C also showed enlarged bands centered on 747 and 762 nm. These bands were broken down by deconvolution of the spectra at 683 and 886 nm (P3MT) and 708 and 881 nm (P3OT). They may be related to the radical cation and dication species present in the polymer matrix after oxidation.

Table 2 gives the results for E_g (energy gap separating HOMO and LUMO). These values were determined on the basis of the maximum absorption wavelengths ($\lambda_{máx}$) in the reflectance spectra for the polymers after reduction. Using the cutoff wavelength [12, 13, 16] would have resulted in deviations in the observed values, since the bands at the ends of the spectra are enlarged due to radical cation segments in the spectra. It is important to define the E_g parameter because its value indicates the optical properties of the conducting polymer.

The values given in Table 2 show that P3MT has approximately the same E_g as P3OT and the magnitudes are similar to those obtained for derivatives of PPV [21, 22]. These values were used to define *E.A.* by subtracting the data obtained for I_p (Table 1) from the E_g values. In Table 2, the *E.A.* values for P3MT (~2 eV) are lower than those for P3OT (~2.5 eV). This was also the case when P3MT was compared to poly(hexylthiophene) (P3HT) [12, 13]. At the electrode/polymer interface of an organic device, one electrode (normally the low work-function species, e.g. Ca, at 2.9 eV) [17] injects electrons at the polymer material's LUMO energy level, a process partly responsible for device efficiency. The two values of *E.A.* used as examples above mean that the P3OT should favor the electron transfer when in contact with the Ca electrode.

Table 2 The results of the band gap (E_g) and electron affinity (*E.A.*) of the P3MT and P3OT from different synthesis conditions using the wavelengths absorption maximum ($\lambda_{máx}$) and difference I_p–E_g, respectively

	$\lambda_{máx}$ (nm)	E_g (eV)	*E.A.* (eV)
P3MT in $LiClO_4$ at 5 °C	447	2.8	2.1
P3MT in $LiClO_4$ at 18 °C	451[a]	2.8[a]	2.0[a]
P3MT in Et_4NBF_4 at 5 °C	449	2.8	1.8
P3MT in Et_4NBF_4 at 18 °C	449	2.8	2.0
P3OT in $LiClO_4$ at 5 °C	438	2.8	2.4
P3OT in $LiClO_4$ at 18 °C	432[a]	2.8[a]	2.2[a]
P3OT in Et_4NBF_4 at 5 °C	441	2.8	2.7
P3OT in Et_4NBF_4 at 18 °C	441	2.8	2.5

[a] *Source* Ref. [24]

With the aim of confirming the results discussed above, the ex situ Raman spectra (Fig. 2) were obtained for the P3MT and P3OT films initially prepared in Et_4NBF_4 or $LiClO_4$ at 5 °C after electrochemical reduction. The Raman spectra are much more intense than the UV–Vis since at the excitation wavelength absorption occurs in the aromatic segments of the thiophene ring, enhancing resonant Raman spectroscopy. The bands observed were similar to those characterized by Guy et al. [23]. The frequencies observed at 720 and 722, 984 and 1,094, 1,186–1,210 and 1,160–1,210, 1,360 and 1,372, 1,454 and 1,450, 1,520 and 1,522 cm^{-1} were attributed to C–S–C deformation, C–C_{subst} stretching, C–$C_{inter\text{-}rings}$ stretching, C–C_{ring} stretching, C=C_{ring} symmetric stretching and C=C_{ring} asymmetric stretching, respectively.

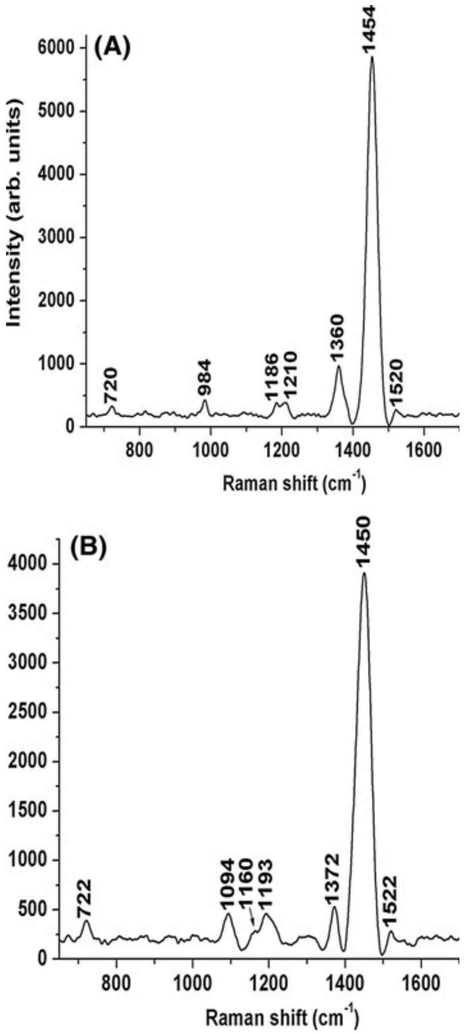

Fig. 2 Ex situ Raman spectra of the (**a**) P3MT and (**b**) P3OT, generated after electrochemical reduction, using 532 nm wavelength excitation

Fig. 3 Ex situ Raman spectra of the (**a**, **b**) P3MT and (**c**, **d**) P3OT, generated in $LiClO_4$ and Et_4NBF_4, respectively, at (***a***) 5 and (***b***) 18° C, using 532 nm wavelength excitation

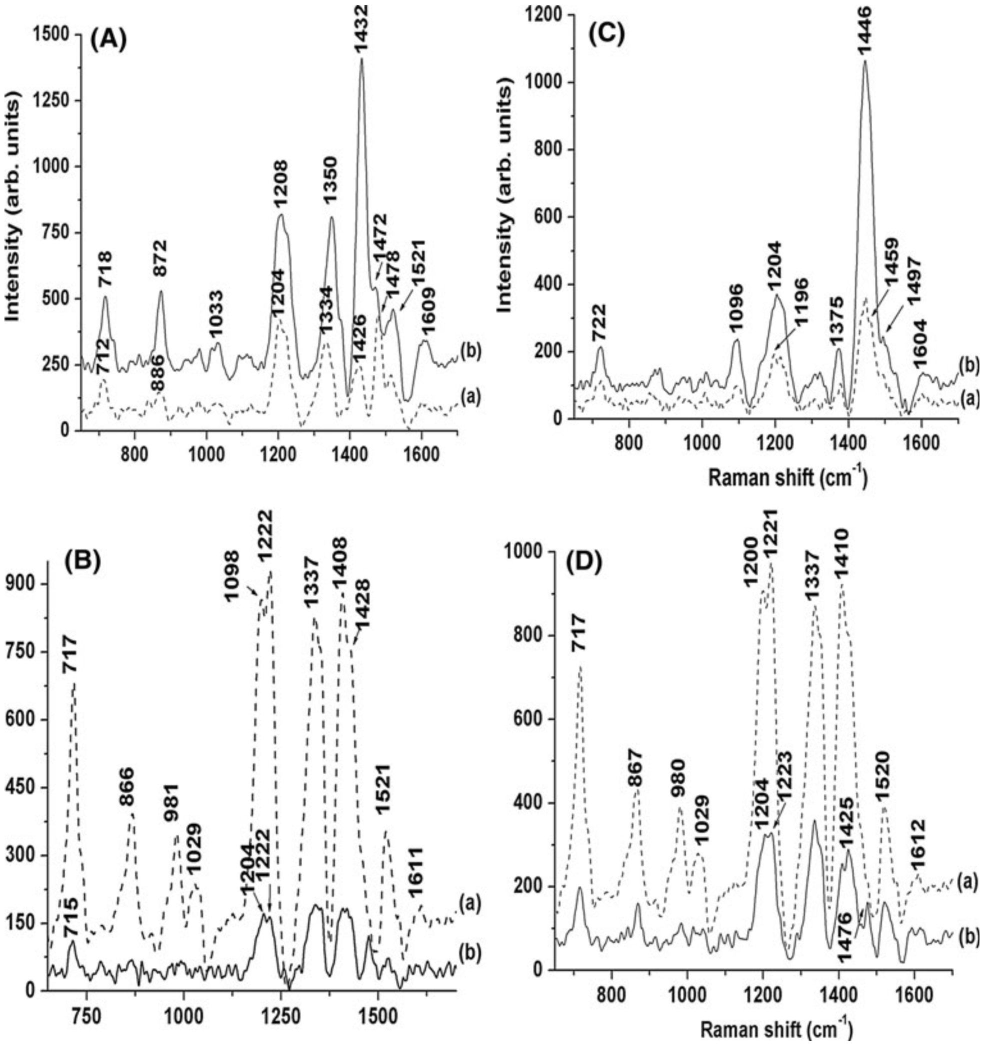

Figure 3 is the ex situ Raman spectra for the P3MT and P3OT films synthesized using anodic potentials in $LiClO_4$ and Et_4NBF_4, respectively, at 5 and 18° C using a 532 nm laser line.

In addition to the frequencies characteristic of the thiophene ring, as mentioned above, the spectra also showed enlargement and displacement of these bands together with new bands. Spectra for the P3MT samples synthesized in $LiClO_4$ at 5° C and in Et_4NBF_4 at 18° C, and P3OT samples synthesized in Et_4NBF_4 at 5° C, showed a band around 1,476 cm^{-1}. In addition, frequencies were observed in the regions of 886–872 and 1,029–1,033 cm^{-1} for P3MT and 867–875 and 1,029–1,096 cm^{-1} for P3OT. The bands for the as-oxidized samples at 1,186, 1,210 and 1,360 cm^{-1} for P3MT and 1,160, 1,193 and 1,372 cm^{-1} for P3OT, were observed to have been displaced in spectra for the as-reduced samples (Fig. 2) to 1,098–1,208, 1,222 and 1,334–1,350 for P3MT, and 1,200–1,204, 1,221–1,223 and 1,337 cm^{-1} for P3OT.

Figure 4 shows the de-convoluted ex situ Raman spectra for P3MT and P3OT synthesized in $LiClO_4$ and Et_4NBF_4, respectively, at 5 and 18 °C.

Deconvolution of the spectra between 1,300 and 1,570 cm^{-1} reveals a number of frequencies with four characteristic structures. This region was chosen because it is ascribed to $C{=}C_{ring}$ symmetric and asymmetric stretching, sensitive to structural alterations of the thiophene ring. One of the bands, close to 1,520 cm^{-1}, relates to C=C asymmetric stretching and underwent only small displacements. It is therefore not sensitive to alterations in the polymer chain structures of the material formed. The intense band around 1,476–1,477 cm^{-1} and other observed bands were considered characteristic of species in the polymer matrix, other than the aromatic thiophene ring.

Frequencies in the regions 1,406–1,431 and 1,401–1,443 cm^{-1} were intense in the majority of the spectra obtained. Considering that the aromatic form of the ring absorbs close to the excitation wavelength of the Raman spectra,

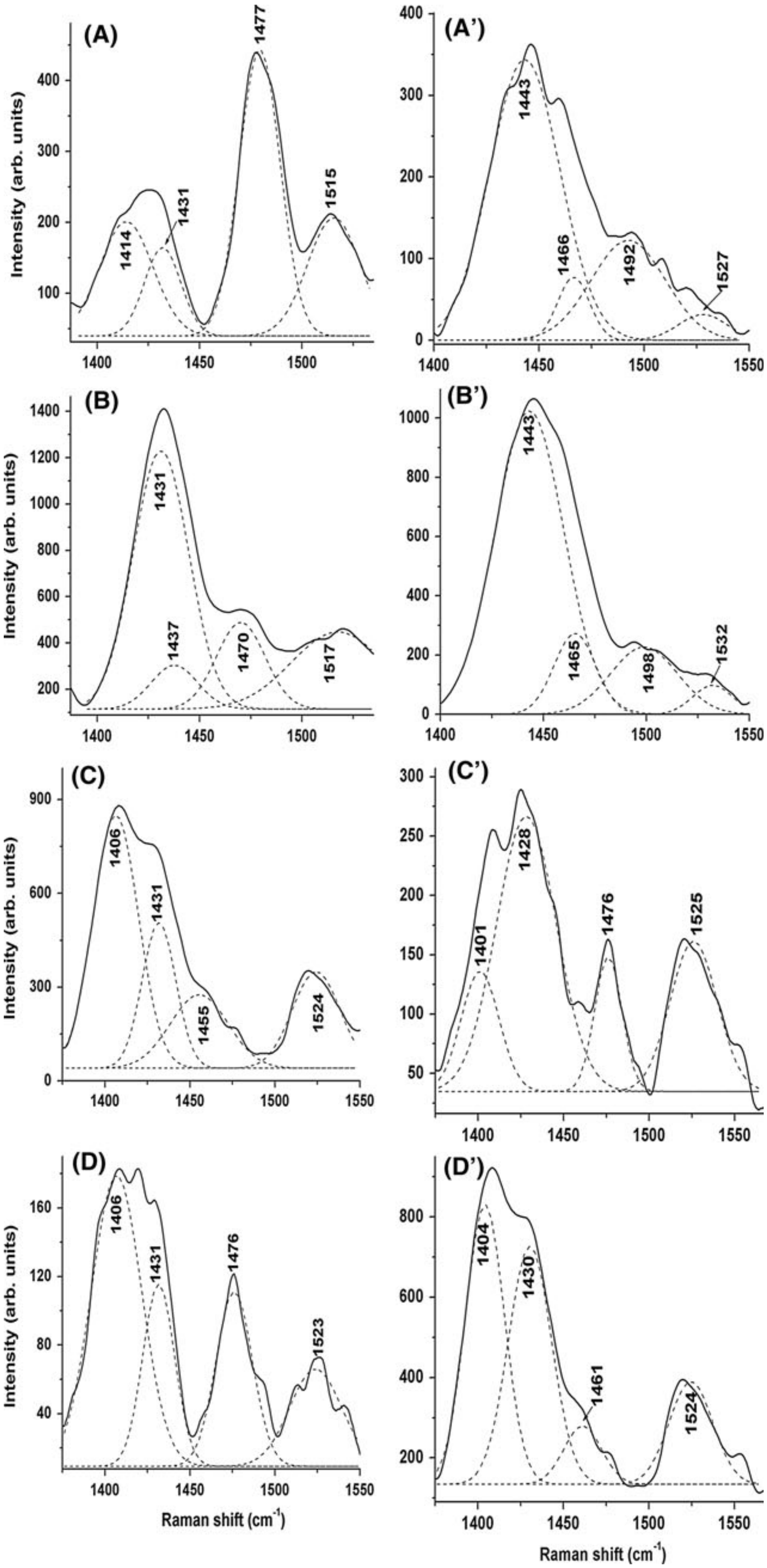

Fig. 4 Deconvolution of ex situ Raman spectra 1,300–1,570 cm^{-1} range: (**a**–**d**) of the P3MT and (**a**′–**d**′) P3OT generated in LiClO$_4$ at 5° C (**a**, **a**′) and 18° C (**b**, **b**′); in Et$_4$NBF$_4$ at 5° C (**c**, **c**′) and 18° C (**d**, **d**′)

this effect should always occur whenever this species is present, and this band has been ascribed to the aromatic segments in the polymer chain. The reflectance results also show that the radical cation form can absorb at around 683–708 nm for the polymers evaluated. This band was considered wide enough and close enough to the excitation wavelength of the Raman spectrum to undergo a pre-resonance intensification when this species is present in the polymer chain. Therefore, the 1,476–1,477 cm^{-1} band could be considered characteristic of this species, and the 1,431–1,437 and 1,428–1,465 cm^{-1} bands characteristic of the dication species [24, 25]. Based on previous results obtained at 785 nm excitation, the frequencies in the 886–872 and 1,029–1,033 cm^{-1} bands (P3MT) and 867–875 and 1,029–1,096 cm^{-1} bands (P3OT) were considered characteristic of the dication segments present in the samples. These segments can coexist with the aromatic structure during film formation and due to the condition of the new material, the bands can be displaced to 1,098–1,208, 1,222 and 1,334–1,350 cm^{-1}(P3MT) and 1,200–1,204, 1,221–1,223 and1337 cm^{-1} (P3OT).

4 Conclusions

The I_p and *E.A.* values found showed that substituting the P3MT thiophene ring for P3OT led to a displacement in the optical and electrical properties of these materials. This was irrespective of the conditions under which the polymers were formed, the doping agent utilized or the species present in the segments forming the polymer matrix.

We were able to come to this conclusion because the Raman spectroscopy results indicated that radical cation and dication segments were present in the polymer matrix. The synthesis temperature and the nature of the electrolyte proved to be important experimental variables for fixing these segments, particularly the segments related to the radical cation species in the structure of the materials.

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