A comparative investigation between poly(1-ethynylpyrene) and poly(1,6-(3-ethynylpyrenylene)): Influence of the structure on the thermal, optical, electrochemical properties and conductivity

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ABSTRACT

A comparative investigation between *trans*-poly(1-ethynylpyrene) (*trans*-PEP) obtained chemically and poly(1,6-(3-ethynylpyrenylene) (E-PEP) prepared electrochemically was carried out. Thermal and optical properties of the polymers were studied by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and absorption spectroscopy. Electrochemical properties were evaluated by cyclic voltamperometry, in a 0.1 M Et_4NClO_4/THF solution at 10 mV/s, using a Pt disc as working electrode and Ag/AgCl as reference electrode. On the other hand, the conductivity of both polymers was measured in pressed pellet. *Trans*-PEP (T_{10} = 369 °C) showed a higher thermal stability than its homologue E-PEP (T_{10} = 256 °C). DSC of the polymers showed that *trans*-PEP exhibits a softening point at 330 °C, whereas E-PEP does it at 117 °C. Absorption spectra of the polymers revealed that *trans*-PEP exhibits two absorption bands at λ = 336 nm and λ = 580 nm due to the pyrene moieties and the highly conjugated polyacetylene main chain, respectively. By contrast, E-PEP showed only an absorption band at λ = 358 nm followed by a tail, which reveals that this polymer possesses a lower degree of conjugation. Molecular modelling performed in short segments of these polymers confirmed this hypothesis. Regarding the electrochemical properties, *trans*-PEP showed an anodic peak at 1500 mV and a conductivity value σ = 2.7 × 10^{-2} S/cm, whereas E-PEP exhibited an anodic oxidation peak at 1670 mV and σ = 8.4 × 10^{-2} S/cm.

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1. Introduction

In the last 30 years, π-conjugated polymers have been considered as promising materials for the development of various opto-electronic devices such as light emitting diodes, photovoltaic cells and non-linear optical systems among others. The opto-electronic properties vary considerably depending on the extent of conjugation length between the consecutive repeat units [1–9]. Previously, we reported the chemical polymerization of 1-ethynylpyrene (EP) and other related monomers under different reaction conditions [10,11]. Catalytic polymerization of EP with WCl_6 resulted in the formation of *trans*-poly(1-ethynylpyrene) (*trans*-PEP) with molecular weights ranging from 24,000 to 470,000 g/mol and polydispersities between 2.9 and 11 [10]. Polymerization of EP was also carried out using the catalytic system (1-Me-Indenyl)(PPh$_3$)Ni–C≡C–Ph and methylaluminoxane (MAO)

[11]. This method provided the formation of soluble *cis*-transoidal poly(1-ethynylpyrene) (*cis*-PEP) with weight-averaged molecular weights (M$_w$) ranging from 2200 to 24,000 g/mol and polydispersities about 2. In both cases, the polymerization takes place exclusively through the triple bond present in the monomer. Furthermore, we reported a comparative investigation between the thermal, optical, electrochemical properties and conductivity of poly(1-ethynylpyrene) in function of the main configuration of the polymer backbone and the internal stacking of the pendant pyrenyl groups [12,13].

We selected pyrene containing monomers to carry out this study, because pyrene is an efficient fluorescent probe, which has been successfully used as molecular label in the study of a huge variety of polymers [14–24]. In this work, we report a comparative study between polypyrenylacetylenes obtained chemically and electrochemically. The chemical and electrochemical polymerization of 1-ethynylpyrene is illustrated in Fig. 1. Thermal, optical, electrochemical properties and conductivity of these polymers were studied in detail, and the results were analyzed, compared and correlated with the optimized geometries predicted by molecular modelling.

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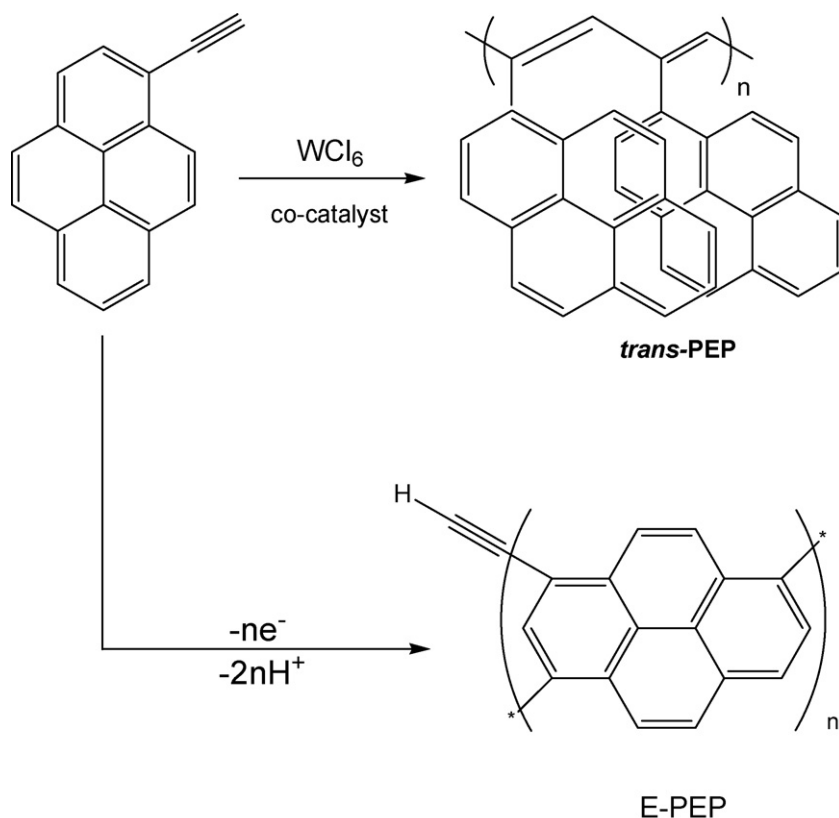*E-mail address:* riverage@iim.unam.mx (E. Rivera).

Fig. 1. Chemical and electrochemical polymerization of 1-ethynylpyrene.

2. Experimental part

2.1. Chemicals and monomers

Acetonitrile (Aldrich, HPLC Grade) was distilled over phosphorous pentoxide (P_2O_5) in order to remove traces of water. Tetraethylammonium tetrafluoroborate (Aldrich) was recrystallized from an acetone–hexane (50:1) solution, and dried overnight under vacuum at 60 °C. Synthesis of 1-ethynylpyrene (EP) and *trans*-poly(1-ethynylpyrene) (*trans*-PEP) was achieved according to the procedures previously reported by us [10].

2.2. Cells, electrodes, and apparatus

All experiments were carried out in a three-electrode undivided cell, using acetonitrile (ACN) as solvent, tetraethylammonium tetrafluoroborate (Et_4NBF_4) as supporting electrolyte and Ag–AgCl as reference electrode. Platinum was used as working and auxiliary electrode in disc, wire and foil shape. In cyclic voltammetry experiments the working electrode was a platinum disc with a surface area of $0.0314 \, cm^2$ and the auxiliary electrode was a platinum wire. For the synthesis of the polymer in an amount enough to enable polymer characterization, a Pt foil of $2 \, cm^2$ surface area was used as working electrode as well as a $4 \, cm^2$ foil was used as an auxiliary electrode. An Autolab PGSTAT100 potentiostat was employed for cyclic voltammetry and a PAR 173 potentiostat/galvanostat for exhaustive electrolysis.

Polymer samples were washed with pure acetonitrile in order to remove the unreacted monomer and then dried at room temperature. FTIR spectra of the polymers were recorded on a PerkinElmer Spectrum 100 FTIR spectrometer with diamond ATR. ^{1}H NMR spectra of the polymers in d_8-THF solution were recorded at room temperature on a Bruker Avance 400 MHz spectrometer. Molecular weights of the polymers, were determined by gel permeation chromatography (GPC), using a Waters 2695 Instrument connected to a Diffraction Index Detector model Waters 2414. Measurements were carried out using tetrahydrofurane (THF) as solvent against a polystyrene standard.

2.2.1. For trans-PEP

IR (KBr): 3035 (=C–H str), 1598 (C=C str), 1583, 1487, 1455.2, 1433, 1414 (C–H bending), 1297, 1242, 1176, 1141, 1080, 839 (C=C–H out of plane), 753, 719, and 681 cm^{-1}. UV–vis (THF): $\lambda_{max} = 336$ and 580 nm. GPC (THF, PS std): $M_w = 20{,}000 \, g/mol$, $M_n = 9100 \, g/mol$, PD = 2.2.

2.2.2. For E-PEP

FTIR: 3195 (≡C-H), 3041 (=C-H, str), 2164 (C≡C), 1592 (C=C, aromatic ring), 1183, 1026, 843 (=C–H out of plane) cm^{-1}. UV–vis (THF): $\lambda_{max} = 348$ nm. GPC (soluble part in THF, PS std): $M_w = 2300 \, g/mol$, $M_n = 1900 \, g/mol$, PD = 1.2.

Thermal properties of the polymers, *trans*-PEP and E-PEP, were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA was conducted on a Hi-Res TGA 2950 Instrument (from 0 to 1000 °C) and DSC was carried out on a DSC 2910 instrument (from 25 to 200 °C), in both cases with a heating rate of 20 °C/min. T_5 (5% weight loss temperature), T_{10} (10% weight loss temperature), and T_m (melting point) were determined for all compounds.

For UV–vis and fluorescence spectroscopies, tetrahydrofuran (THF) was purchased from Aldrich (spectrophotometric grade). Prior to use, the solvent was checked for spurious emission in the region of interest and found to be satisfactory. The absorption spectra in solution were recorded on a Varian Cary 1 Bio UV/vis spectrophotometer (model 8452A) using 1 cm quartz cells and solute concentrations of 1–3×10^{-5} M for the polymers. It has been

verified that the Beer–Lambert law applies for the concentrations used. Fluorescence spectra corrected for the emission detection were recorded on a Spex Fluorolog-2 spectrophotometer with an F2T11 special configuration. Each solution was excited near the absorption wavelength maximum using a 1 cm quartz cell. For the polymers, a concentration of about $1–3 \times 10^{-6}$ M was used, giving absorbances of less than 0.1 in order to avoid any inner filter effect. Molecular modelling was performed in short segments of the polymers with the program Hyperchem 6.0 for Windows. Geometry optimization was estimated by semi-empirical calculations using the PM3 method.

2.3. Procedure

Electrolytic solutions were prepared with 0.1 M Et_4NBF_4 in the following concentration ranges: 0.001–0.02 M of EP. Prior to each experiment, the electrochemical cell was placed inside a Faraday cage and the electrolyte was purged with nitrogen for 40 min, and the reference electrode was immersed in dry acetonitrile for 20 min. Potential sweeps were performed from low (OCP) to high potentials, up to a potential (E_λ) in which the direction of the scan was inversed. Before each measurement, the working electrode was cleaned and polished with 0.05 μm alumina (Buehler), wiped with a tissue and washed with distilled water. In all the experiments reported here, potentials are referred to the ferrocinium/ferrocene (Fc^+/Fc) redox system. To prepare samples to be used for the whole characterization, potential sweeps were stopped at E_λ, and an EP concentration of 20 mM was employed.

3. Results and discussion

3.1. Electropolymerization of EP

The voltammetric behavior of substituted pyrenes depends in a big measure on the nature of the substituents [25,26]. In this case, the cyclic voltammogram of the monomer EP at 100 mV/s (Fig. 2A), shows two irreversible signals: one shoulder located at 0.94 V followed by a broad peak centered at 1.33 V. When the potential scan is switched at the beginning of the broad oxidation peak, the polymerization is inhibited. On the other hand, when it is switched at the oxidation shoulder, a dark polymer film is deposited on the electrode surface. Fig. 2B shows the voltammograms corresponding to the electropolymerization of 5 mM EP in the presence of 0.1 M Et_4NBF_4, employing a scan rate of 20 mV/s. When the potential scan is switched at $E_\lambda = 0.90$ V, current increases with each cycle, which indicates a successful electroactive polymer film growth. During this process two peaks appear, Ic′ and Ia′, which correspond to reduction and oxidation of the formed oligo(1,6-(3-ethynylpyrenylene) (E-PEP), respectively. As the film thickness increases during polymerization, the voltametric wave associated with oxidation of the polymer becomes slightly more positive and reduction becomes more negative with successive scans. This is due to heterogeneous electron transfer jointly with an increase in kinetics. Consequently, an increase in conductivity, counterion mobility and conjugation length is observed [27]. The resulting E-PEP was doped by the incorporation of the supporting electrolyte anions into its framework. The resulting polymer film can be peeled off from the electrode surface, when at least 7.5 mM monomer is used and after a minimum of 12 cycles. After cycle 20, the anode began to be passivated by the electrodeposited product/no more polymer can be electrodeposited on the electrode. Molecular weight of E-PEP was estimated by GPC in THF against a polystyrene standard, obtaining the following values: $M_w = 2300$ g/mol, $M_n = 1900$ g/mol, PD = 1.2. Since E-PEP is fairly soluble in THF, the obtained molecular weights are due to all the polymer chains present in of soluble part
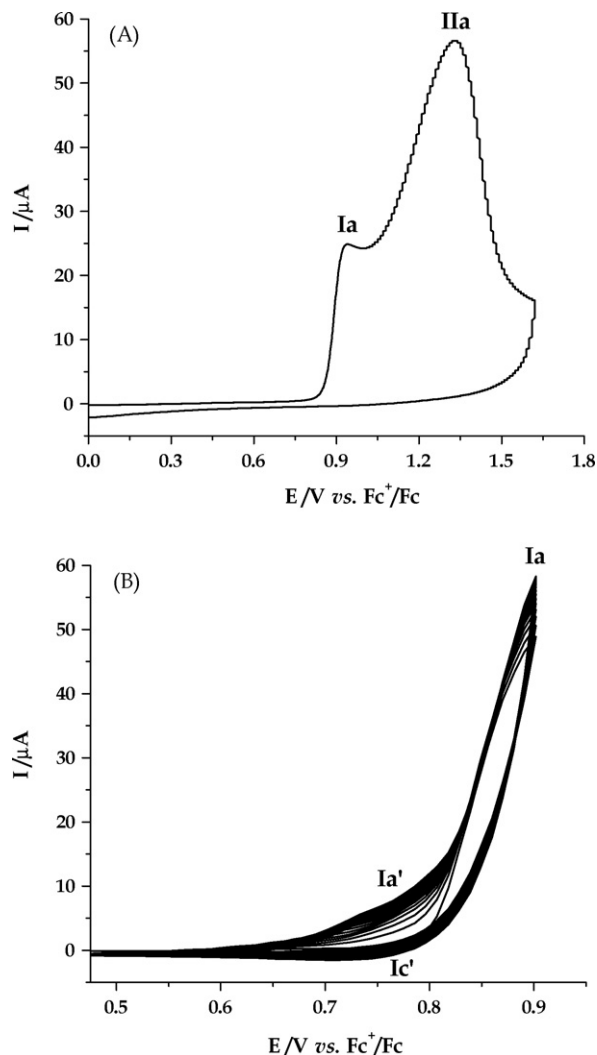

Fig. 2. Cyclic voltammograms obtained from (A) 1 mM EP in 0.1 M Et_4NBF_4/ACN, at 100 mV/s and (B) 5 mM EP in 0.1 M Et_4NBF_4/ACN at 20 mV/s, $E_\lambda = 0.90$ V.

and a single population was observed in the GPC profile. The minimal small insoluble part of the polymer could have been attributed to the formation of a crossed-linked product. However, it is very well known that π-conjugated polymers bearing polycondensed aromatic rings, without alkyl chains in their backbone, become insoluble after a certain number of repeat units [28,29].

3.2. Influence of the polymerization method on the structure of the polymers

Arylacetylenes can be polymerized in the presence of different inorganic or organometallic catalysts to give highly conjugated polymers. The configuration of the polymer backbone totally depends on the catalyst used [28]. Fig. 1 shows the polymerization of 1-ethynylpyrene by chemical and electrochemical means. When this monomer is polymerized in the presence of WCl_6, *trans*-poly(1-ethynylpyrene) (*trans*-PEP) is obtained and the reaction occur via a methatesis mechanism [10]. By contrast, when this monomer is reacted in the presence of the catalytic system (1-Me-Indenyl)(PPh₃)Ni–C≡C–Ph and methylaluminoxane (MAO), *cis*-poly(1-ethynylpyrene) (*cis*-PEP) is formed and the reaction takes place via an insertion mechanism [11,30]. As other substituted aromatic monomers [31], electrolysis of EP in acetonitrile, on a platinum electrode, generates a deposit of an electro-conducting
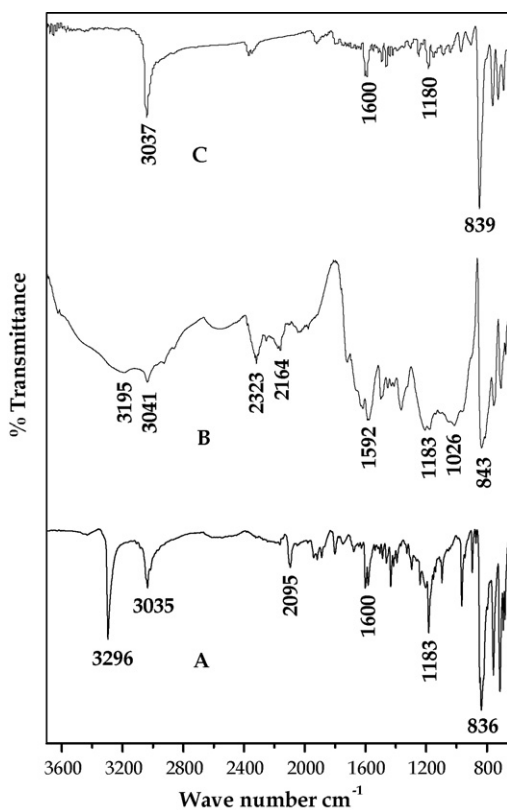
Fig. 3. FTIR spectra (KBr, pressed pellet) of (A) EP, (B) E-PEP and (C) trans-PEP.

Fig. 4. TGA of *trans*-PEP and E-PEP. Heating rate is 20 °C/min.

polymer film on the anode surface, where the polymerization occurs exclusively through the aromatic units. Therefore, a linear conjugated oligomer bearing ethynyl side groups, poly(1,6-(3-ethynylpyrenylene) is obtained.

3.3. FTIR and ^{1}H NMR spectra of the polymers

The structure of E-PEP obtained from the electrolysis of 20 mM EP in the presence of 0.1 M Et_4NBF_4 at 20 mV/s was confirmed by FTIR and ^{1}H NMR spectroscopies. Fig. 3 shows the FTIR spectra of monomer 1-ethynylpyrene (EP) and the corresponding polymers E-PEP and *trans*-PEP. The FTIR spectrum of EP (Fig. 3A) shows a band at 3296 cm^{-1}, due to the terminal alkyne bond ($\equiv$C–H), followed by a second band at 3035 cm^{-1}, which is related to the $=$C–H bond of the pyrene rings. Besides, we can observe a band at 2095 cm^{-1}, due to the C$\equiv$C triple bond [11,32], as well as a band at 1600 cm^{-1}, resulting from the C$=$C stretching vibration of pyrene rings [11,25,31–34].

The FTIR spectrum of polymer E-PEP shows two broad bands at 3195 and 3041 cm^{-1}, due to the terminal alkyne bond ($\equiv$C–H) and the $=$C–H bonds of the pyrene units, respectively. In addition a band a 2164 cm^{-1} reveals the presence of the C$\equiv$C triple bond in the polymer structure. All these bands appear also in the FTIR spectrum of the monomer with slight variations.

If we compare the FTIR spectrum of E-PEP (Fig. 3B) with that of the monomer EP (Fig. 3A), in E-PEP we can observe a decrease in intensity of the band at 755 cm^{-1}, due to the out-of-plane vibrations $=$C–H bonds of pyrene rings, as well as the presence of a band at 1026 cm^{-1} related to the incorporation of BF_4^- counterions [31]. Besides, the band at 843 cm^{-1}, due to the two adjacent bonds of pyrene rings, did not decrease in intensity. This is an indication that the polymerization occurred through an α,α-coupling of the monomers [33,34]. Moreover in E-PEP, the broad band at 3195, which is characteristic of the terminal alkyne group ($\equiv$C–H), confirms that terminal triple bonds are present in the polymer
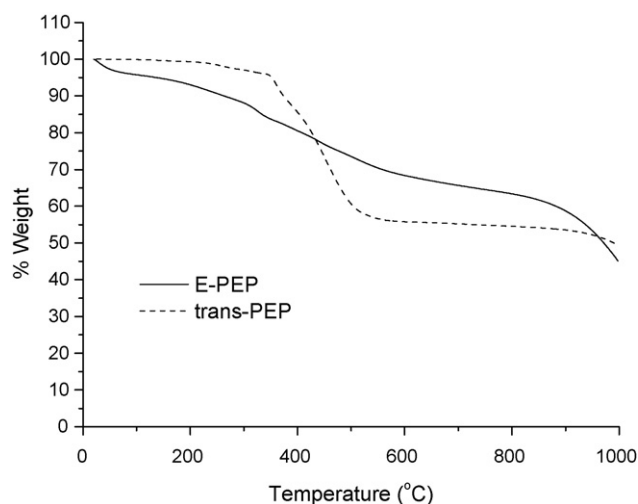
structure, so that the polymerization takes place through the pyrene rings.

By contrast, the FTIR spectrum of *trans*-PEP (Fig. 3C) shows a band at 3037 cm^{-1}, due to the $=$C–H bonds present in the pyrene units and the polymer backbone, followed by two intense bands at 1600 and 839 cm^{-1}, which are related to the C$=$C and $=$C–H bonds present in the pyrene groups, respectively. Unlike EP and E-PEP, this polymer did not exhibit the characteristic bands due to the $\equiv$C–H and C$\equiv$C bonds present in the alkyne group. This is an additional proof that the polymerization in E-PEP occurs exclusively though the aromatic rings and the triple bonds remain intact.

^{1}H NMR spectra of *trans*-PEP and E-PEP were recorded in d8-THF solution (not shown). *Trans*-PEP exhibited a very broad band centered at δ = 7 ppm due to all protons present in the aromatic units and the polymer backbone. On the other hand, the ^{1}H NMR spectrum of E-PEP, which was not totally soluble in this solvent, exhibited two broad bands centered at δ = 7 and 3.6 ppm due to the protons present in the pyrene units and the terminal $\equiv$C–H protons of the acetylene moieties, respectively. In the case of *trans*-PEP, this broadening of the signals can be due to the internal stacking of pyrene pendant groups. However, in the case of E-PEP, since this polymer was not totally soluble in THF, the broadening of the signals could be caused by aggregation.

3.4. Thermal properties of the polymers

Thermal properties of the polymers were evaluated by TGA, from 0 to 1000 °C and DSC from 25 to 200 °C. TGA of *trans*-PEP and E-PEP are shown in Fig. 4. *Trans*-PEP exhibits a T_{10} (10% weight loss temperature) of 381 °C with fast degradation between 334 and 532 °C, reaching 40% of weight loss at 497 °C. Besides, *trans*-PEP exhibits a softening point at 330 °C. According to TGA measurements, E-PEP shows a moderate thermal stability with a T_{10} = 254 °C. However, this polymer exhibits gradual degradation reaching 40% weight loss at 888 °C. DSC measurements (not shown) revealed that this polymer display a softening point at T_s = 117 °C. As we can see, trans-PEP possesses a higher thermal stability than its analogue E-PEP at temperatures below 433 °C, because in the former the presence of a highly conjugated backbone as well as the internal stacking of the pendants groups provide stability to the polymer. Besides in *trans*-PEP, the presence of a softening point indicates the existence of crystalline domains in this polymer. On the other hand, E-PEP is thermally less stable than *trans*-PEP due to the lack of stacking, moderate degree of conjugation and lower molecular weight, which make this polymer more susceptible to degradation. The absorption
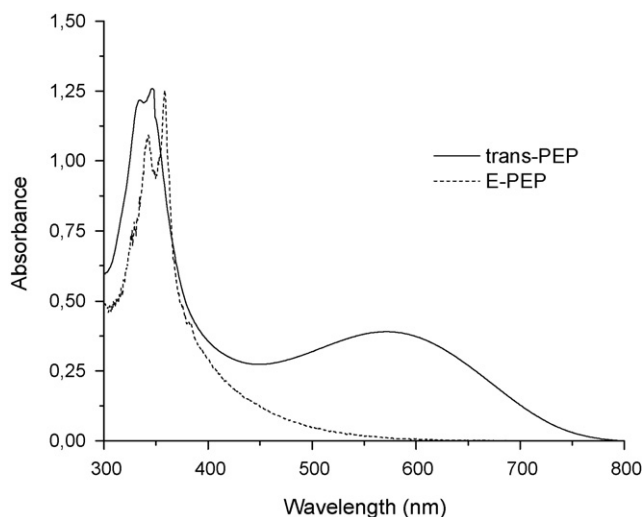
Fig. 5. Absorption spectra of *trans*-PEP and E-PEP in THF solution.

and fluorescence spectra of these polymers support this explanation (*vide infra*).

3.5. Optical properties and molecular modelling of the polymers

Optical properties of the polymers were studied by absorption and fluorescence spectroscopies. Absorption spectra of both polymers in THF solution are shown in Fig. 5. In order to explain better the results obtained by absorption and fluorescence spectroscopies, molecular modelling, by semi-empirical calculations using the PM3 method, was performed in short segments of *trans*-PEP and E-PEP; the optimized geometries for both polymers and unsubstituted polypyrene are shown in Fig. 6.

UV–vis spectra of *trans*-PEP and E-PEP differ considerably. In fact, the absorption spectrum of *trans*-PEP in THF solution shows a band at $\lambda = 336$ nm, which can be attributed to $S_2 \leftarrow S_0$ transition of the pyrenyl groups. Moreover, a band at $\lambda = 580$ nm (cut off at $\lambda = 800$ nm), which is due to the highly conjugated polyacetylene chain is also observed. Molecular modelling confirmed that in *trans*-PEP (Fig. 6A) the polymer backbone is well aligned with the pendant pyrene units arranged perpendicular to the polyacetylene chain plane [11]. Pyrenyl groups adopt an almost parallel orientation, giving rise to a regioregular stacking with pyrene–pyrene distances of about 3.1–4.5 Å. By contrast, the absorption spectra of E-PEP, exhibits a well-defined $S_2 \leftarrow S_0$ band at $\lambda = 348$ nm with cut off at $\lambda = 550$ nm due to pyrene units present in the polymer. According to molecular modelling, in E-PEP (Fig. 6B) the polymer backbone shows a very twisted conformation with dihedral angles between the pyrene units varying from 56 to 65.2°. A similar conformation was predicted for unsubstituted polypyrene (E-PP) (Fig. 6C), where backbone is still more twisted than that of E-PEP, with dihedral angles between aromatic units from 60 to 79°. Therefore, we can conclude that in E-PEP such torsions are not due to the steric effects of the lateral ethynyl side groups. However, the presence of such groups can modify the dihedral angles between pyrene-units in the polymer.

Fluorescence spectra of *trans*-PEP and E-PEP in THF solution, exciting at $\lambda = 350$ nm are shown in Fig. 7. The fluorescence spectrum of *trans*-PEP shows a broad emission band in the 360–465 nm region due to non-associated pyrenyl groups, also named "monomer emission" [12]. Apparently, no excimer emission is observed for this polymer. However, it is worth noting that there is an important emission intensity near 500 nm, a wavelength where pyrene itself does not emit, which reveals the presence
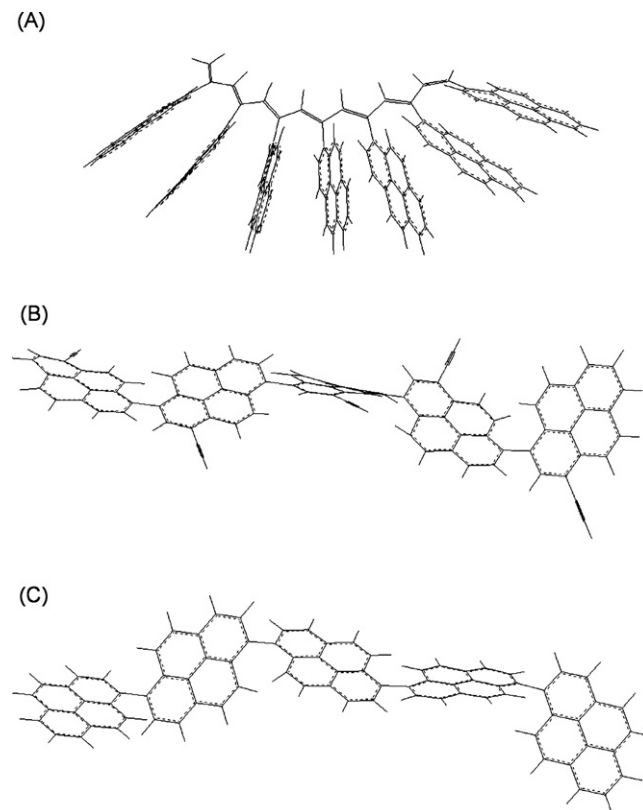

Fig. 6. Optimized geometries for (A) *trans*-PEP, (B) E-PEP and (C) polypyrene, obtained by the semi-empirical method PM3.

of excited pyrene–pyrene complexes in *trans*-PEP [35]. When this polymer is excited at 580 nm, no emission is observed, which confirms that no fluorescence arises from the polyacetylene backbone. On the other hand, the fluorescence spectrum of E-PEP in THF solution (Fig. 7), exhibits an emission band at $\lambda = 388$–408 nm, due to pyrene units in the non-associated state "monomer emission" [34]. Apparently, there is no excimer emission in the fluorescence spectra of this polymer. However, discrete emission beyond 450 nm, a wavelength where pyrene does not emit, makes us suspect the presence of weak pyrene–pyrene interactions in this polymer. Since the fluorescence spectra were recorded in very diluted solutions, such interactions are undoubtedly intramolecular. Pyrene–pyrene
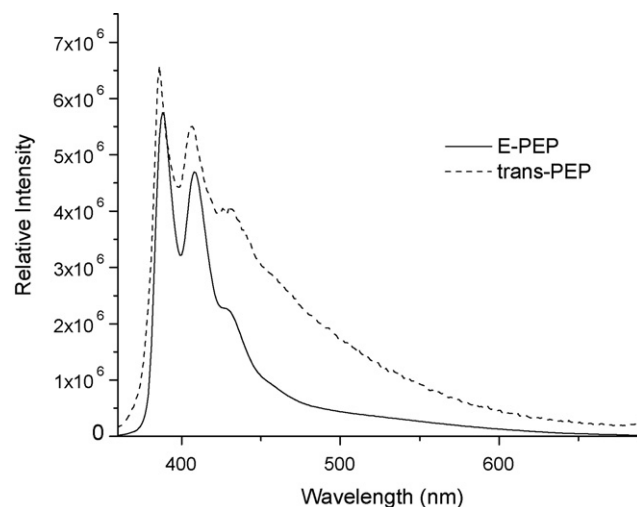

Fig. 7. Fluorescence spectra of *trans*-PEP and E-PEP, exciting at $\lambda = 350$ nm.

interactions are considerably higher in *trans*-PEP than in E-PEP, because in the former there is an internal stacking of the pyrene pendant groups (Fig. 6A). By contrast, in E-PEP pyrene units are linked in a row forming the polymer backbone, so that pyrene–pyrene interactions are more difficult to occur (Fig. 6B). Nevertheless, the twisting of the polymer backbone in E-PEP allows pyrenyl groups to interact in a non-parallel way, giving rise to weak intramolecular interactions.

3.6. Electrochemical properties and conductivity

Conductivity of the polymers were measured in pressed pellet, giving values of $\sigma = 2.7 \times 10^{-2}$ and $\sigma = 8.4 \times 10^{-2}$ S/cm for *trans*-PEP and E-PEP, respectively. According to these results, both polymers are semi-conductors, which can be explained in terms of geometry for *trans*-PEP and doping for E-PEP. *Trans*-PEP was chemically obtained in the non-doped state; in this polymer electrical conduction can occur along the polymer backbone and through the internal stacking of the pendant pyrene groups. By contrast, the polymer backbone of E-PEP adopts a non-planar conformation. Since this polymer was electrochemically synthesized, it was obtained in the doped state, containing BF_4^- counterions in its framework. Therefore, a higher electrical conductivity can be expected.

Cyclic voltammograms of *trans*-PEP (Fig. 8A) and E-PEP (Fig. 8B) show irreversible potential waves at 1500 and 1670 mV, respectively. Molecular modelling jointly with UV–vis spectra of these polymers showed that in *trans*-PEP the polymer backbone is highly conjugated, whereas in E-PEP it adopts a twisted conformation. *Trans*-PEP is oxidized at lower potential than E-PEP, because a higher degree of conjugation in the polymer increases the electronic stability of the resulting cation-radical. By contrast, E-PEP exhibited a higher oxidation potential than *trans*-PEP, because this electro-synthesized polymer has been obtained in the doped state, in other words it has been already partially oxidized.

4. Conclusions

A comparative study of thermal, optical, electrochemical properties and conductivity between *trans*-PEP and E-PEP was carried out. The former possesses a highly conjugated polyacetylene backbone with internal stacking of the pyrenyl pendant groups. By contrast, in E-PEP pyrenyl groups are linked in a row forming the polymer backbone. *Trans*-PEP is thermally more stable than E-PEP at temperatures below 433 °C and according to absorption spectroscopy it is more conjugated and fluorescent than E-PEP. Both polymers showed to be semi-conductors with conductivity values in the order of 10^{-2} S/cm. Concerning the electrochemical properties, *trans*-PEP and E-PEP show irreversible potential waves at 1500 and 1670 mV, respectively. E-PEP exhibited a higher oxidation potential because this polymer has been already obtained in the doped state.

Acknowledgements

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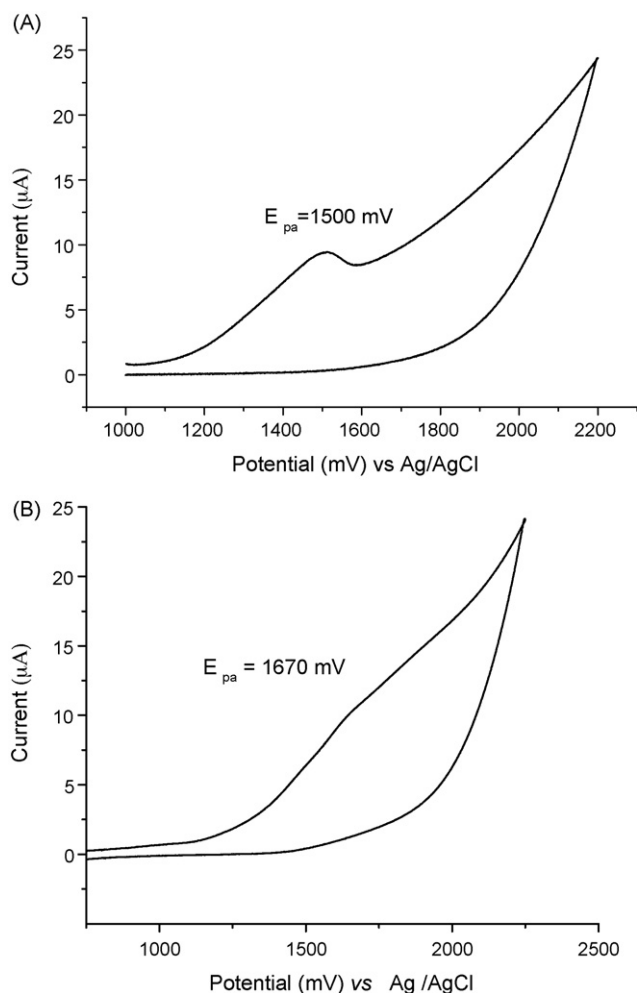[28] T. Masuda, H.J.M.S. Tachimori, Pure Appl. Chem. A31 (1994) 1675.

Fig. 8. Cyclic voltammetry of (A) *trans*-PEP and (B) E-PEP.

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