Polymer Bulletin 61, 461–472 (2008)
DOI 10.1007/s00289-008-0966-y

Polymer Bulletin

# Electrosynthesis, Characterization, Thermal, Optical, Electrochemical Properties and Conductivity of Conjugated Oligomers Bearing Pyrenyl Groups

**Martha Aguilar-Martínez[a], Juan Manuel Reyna-González[b], José Antonio Bautista-Martínez[a], Celso Palomar[a] and Ernesto Rivera[b] (✉)**

(a) División de Estudios de Posgrado, Facultad de Química and (b) Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México. Circuito Exterior Ciudad Universitaria C.P. 04510 México D.F. México
E-mail: riverage@iim.unam.mx; Fax: (5255) 56 16 12 01

Received: 28 February 2008 / Revised version: 25 June 2008 / Accepted: 28 June 2008
Published online: 15 July 2008 – © Springer-Verlag 2008

## Summary

In this paper, we report the electrochemical polymerization of 1-ethynylpyrene (EP), 1-(but-1-yn-3-enyl)pyrene (BP) and 1-(4-trimethylsilanylbuta-1,3-diynyl)pyrene (TMSBDP). The obtained oligomers were characterized by FTIR and NMR spectroscopies. Thermal properties of these compounds were determined by thermogravimetric analysis and differential scanning calorimetry, and their optical properties by absorption and fluorescence spectroscopies. Electrical conductivity of the oligomers was measured in the doped state.

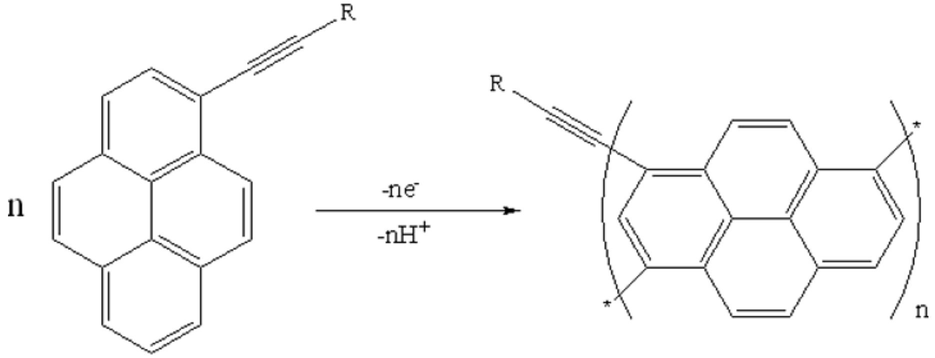
## Introduction

Over the last 30 years, π-conjugated polymers have been considered as promising materials for the development of electronic devices such as light emitting diodes, photovoltaic cells and non-linear optical systems. Opto-electronic properties vary significantly depending on the conjugation length between the consecutive repeat units [1-9]. In previous works, we carried out 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 to 11 [10]. Polymerization of EP was also carried out using the catalytic system (1-methyl-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 molecular weights from $M_w = 2{,}200$ 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 carried out a comparative investigation between the thermal, optical, electrochemical properties and conductivity of poly(1-ethynylpyrene) in function of the configuration of the polyacetylene backbone and the internal stacking of pendant aromatic groups [12-13]. We also performed an in-depth study of the electrochemical behavior of pyrene, 1-ethynylpyrene, 1-(but-1-yn-3-enyl)pyrene and 1-(4-trimethylsilanylbuta-

1,3-diynyl)pyrene by cyclic voltammetry in acetonitrile. It was found that these monomers disclose an irreversible anodic peak around 1260 - 1670 mV *vs* AgCl/ Ag, which is significantly influenced by the electronic and steric effects of the sustituents [14].

In the present work, we report the electrochemical polymerization of three pyrene derivatives: 1-ethynylpyrene (EP), 1-(but-1-yn-3-enyl)pyrene (BP) and 1-(4-trimethylsilanylbuta-1,3-diynyl)pyrene (TMSBDP). Unlike the chemical method, electrochemistry led to the formation of linear oligomers, where the polymerization takes place mainly through the aromatic rings, so that the triple bonds present in the monomers remain intact. We selected pyrene containing monomers in this work, because pyrene is an efficient fluorescent probe, which has been successfully used as a molecular label in the study of a huge variety of polymers [15-25].

The molecular structures of the obtained substituted poly(pyrenylene)s: poly(1-ethynylpyrene) (E-PEP), poly(1-but-1-yn-3-enyl)pyrene (E-PBP) and poly(1-(4-trimethylsilanylbuta-1,3-diynyl)pyrene) (E-PTMSBDP), where E indicates that the oligomer was obtained electrochemically, are shown in Scheme 1.



R = H **EP, E-PEP**
R = $CH{=}CH_2$ **BP, E-PBP**
R = $C{\equiv}CH{-}TMS$ **TMSBDP, E-PTMSBDP**

**Scheme 1.** Electro-synthesis of the oligomers: E-PEP, E-PBP and E-PTMSBDP.

## Experimental

### *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 solution, and dried overnight under vacuum at 60ºC. Synthesis of EP, BP and TMSBDP was achieved according to the procedures previously reported by us [10].

### *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 an Ag-AgCl as reference electrode. Platinum was used as the 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 oligomers in an amount enough to enable characterization, a Pt foil with a 2 $cm^2$ surface area was used as working electrode, as well as a 4 $cm^2$ foil as an auxiliary electrode. An Autolab PGSTAT100 potentiostat was employed for cyclic voltammetry and a PAR 173 potentiostat/galvanostat for exhaustive electrolysis.

FTIR spectra of the oligomers were recorded on a Nicolet FTIR 5 DXB spectrometer using KBr pellets of the samples. $^1$H-NMR spectra of the oligomers in $d_8$-THF solution were recorded at room temperature on a Bruker Avance 400 MHz spectrometer.

Thermal properties of the oligomers, E-PEP, E-PBP, and E-PTMSBDP 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 10°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 $1\text{-}3 \times 10^{-5}$ M for the oligomers. 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 oligomers, a concentration of about $1\text{-}3 \times 10^{-6}$ M was used, giving absorbances of less than 0.1 in order to avoid any inner filter effect. Molecular modeling was performed in model oligomers with the program Hyperchem 6.0 for Windows. Geometry optimization was estimated by semi-empirical calculations using the PM3 method.

## *Procedure*

Electrolytic solutions were prepared with 0.1 M $Et_4NBF_4$ in ACN. 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 ($E_\lambda$) in which the direction of the scan was reversed. Before each measurement, the working electrode was cleaned and polished with 0.05μm 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. In order to investigate the electrochemical behavior of the monomers, a concentration of 1 mM was used. For electropolymerization experiments higher concentrations were utilized. To prepare samples to be used for whole characterization, a concentration of 7.5 mM was employed. Once the oligomer samples were obtained, they were washed with pure ACN in order to remove the unreacted monomer and then dried at room temperature.

## Results and Discussion

### *Electropolymerization of EP, BP and TMSBDP*

The voltammetric behavior of substituted pyrenes depends in a big measure on the nature of the substituents [26, 27]. Figure 1A shows the cyclic voltammogram at 100 mVs$^{-1}$ corresponding to 1 mM pyrene. In the forward scan two anodic signals are observed: one shoulder located at about 0.949 V (Ia), followed by a broad peak centered at 1.270 V (IIa). At the reverse scan it appears a cathodic peak at 0.526 V (Ic). When the potential scan is switched at the beginning of the broad oxidation peak (peak IIa), the polymerization is inhibited. On the other hand, when it is switched at the oxidation shoulder (Ia), a dark oligomer film is deposited on the electrode surface. Figure 1B shows the voltammograms corresponding to the electro-oxidation of 5mM pyrene in the presence of 0.1 M $Et_4NBF_4$, employing a scan rate of 20 mVs$^{-1}$. When the potential scan is switched at $E_\lambda$=0.938 V, current increases with each cycle, which indicates a successful electroactive film growth. During this process two peaks appear, Ic' and Ia', which correspond to the reduction and oxidation of the formed polypyrene film (E-PPy) respectively. As the film grows during the polymerization, the voltammetric wave associated with the oxidation of the oligomer becomes slightly more positive and the reduction wave becomes more negative with successive scans. This is due to the presence of a spherical diffusion regime towards the holes that the film could present or to the resistivity of the film itself, which causes the electron transfer rate to become slower with respect to that of the platinum non modified surface. The resulting polypyrene (E-PPy) was doped by the incorporation of the supporting electrolyte anions into its framework. After cycle 20, the anode began to be passivated by the electrodeposited product; this means that it is not possible to obtain a higher molecular weight polymers. The resulting 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. Figure 2A shows the cyclic voltammograms at 100 mV/s, which correspond to monomers BP, EP, and TMSBDP. By contrast, unlike the voltammogram obtained for pyrene (Figure 1A), these monomers do not show any cathodic signal in the reverse scan. However, in the forward scan, two anodic signals can be seen for pyrene derivatives: a shoulder (Ia) located at about 0.892 V (BP), 0.941 V (EP), and 1.030 V

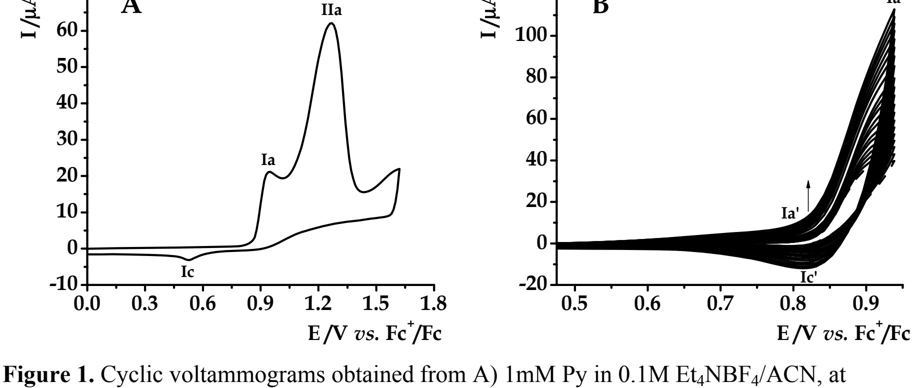


**Figure 1.** Cyclic voltammograms obtained from A) 1mM Py in 0.1M $Et_4NBF_4$/ACN, at 100 mVs$^{-1}$, and B) 5mM Py in 0.1M $Et_4NBF_4$/ACN, at 20 mVs$^{-1}$, $E_\lambda$ = 0.938 V.

(TMSBDP) followed by a broad peak (IIa) centered at 1.252 V (BP), 1.330 V (EP) and 1.358 V (TMSBDP). As in the electrochemical polymerization of pyrene, when the potential scan is switched at the oxidation shoulder (Ia), a dark oligomer film is obtained. Figure 2B shows the voltammograms corresponding to the electrochemical polymerization of 5mM EP in the presence of 0.1 M $Et_4NBF_4$ at 20 $mVs^{-1}$ by the application of successive potential scans. When the potential scan is switched at $E_{\lambda}$=0.900 V current increases with each cycle due to the growth of the E-PEP chain. Molecular weights ($M_w$) of E-PEP, E-PBP, and E-PTMSBDP were estimated by GPC in THF using polystyrene as standard and were found to be 2,300, 2,500, and 2,250 g/mol, respectively. Cyclic voltammetry characterization of the obtained oligomers was performed in acetonitrile solutions containing only supporting electrolyte. All the films present a current decrease with successive scans (not shown) until a typical reproducible voltammetric behavior, after seven scans, is established.

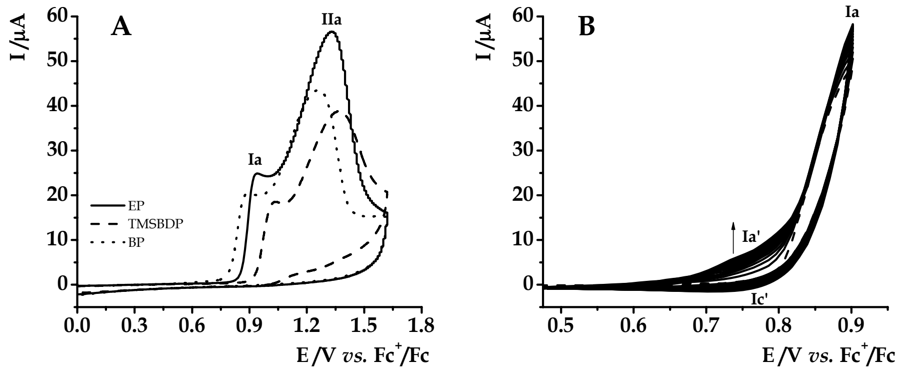


**Figure 2.** Cyclic voltammograms obtained from A) 1mM BP, EP, and TMSBDP in 0.1M $Et_4NBF_4$/ACN, at 100 $mVs^{-1}$, and B) 5mM EP in 0.1M $Et_4NBF_4$/ACN, at 20 $mVs^{-1}$, $E_{\lambda}$ = 0.90 V.

*FTIR Spectra of the oligomers*

Since the $^1H$-NMR spectra of the oligomers (not shown) exhibited very broad bands in the aromatic region between 6-8.5 ppm, which did not provide very much information about the structure of these materials, the structure of the oligomers was supported by FTIR spectroscopy. Figure 3A shows the spectrum of 1-ethynylpyrene (EP). The bands located at 3432 and 3290 $cm^{-1}$ are characteristic vibration bands of the terminal alkyne bond (≡C-H), whereas the bands at 2370 and 2090 $cm^{-1}$, are related to the vibration bands of the alkyne triple bond (C≡C) [11, 28]. The bands at 1640-1620 $cm^{-1}$ are due to the C=C stretching vibrations, while the band at 1600 is related to the C–H bending vibration of the pyrene rings. On the other hand, the stretching band at 3040 $cm^{-1}$ is associated with the C–H of the pyrene rings, whereas the bands at 1180, 841, 750 and 642 $cm^{-1}$ are attributed to the out-of-plane bending vibration of the three adjacent =C–H bonds of pyrene rings [11, 25, 28-31].

It is very well known that positions 1,3,6,8 are the more reactive sites in pyrene [14, 32]. In our monomers, position 1 is occupied so that 3,8 and 3,6-couplings take place (sterically favored), but also traces of 3,3 (sterically unfavored), 6,6 and 6,8-couplings could be present in the oligomers. When comparing of the FTIR spectrum of E-PEP

(Figure 3B) with the corresponding monomer EP (Figure 3A), the oligomers exhibit a much weaker intensity band at 750 cm$^{-1}$, which can be attributed to the out-of-plane vibrations of the three C-H bonds of the pyrene unit. However, the band at 841 cm$^{-1}$, due to the two adjacent bonds of pyrene rings did not decreased in intensity. Such spectral results indicate that the polymerization of pyrene occurred through an α-α coupling of the pyrene rings. These data match well with those previously reported by Shi *et al* for the electrochemically synthesized polypyrene [30, 31]. Taking into account the steric effect of the substituents, we believe that 3,6 coupling and 3,8-coupling (depicted in Scheme 1 and Figure 7) predominate in the polymer backbone.

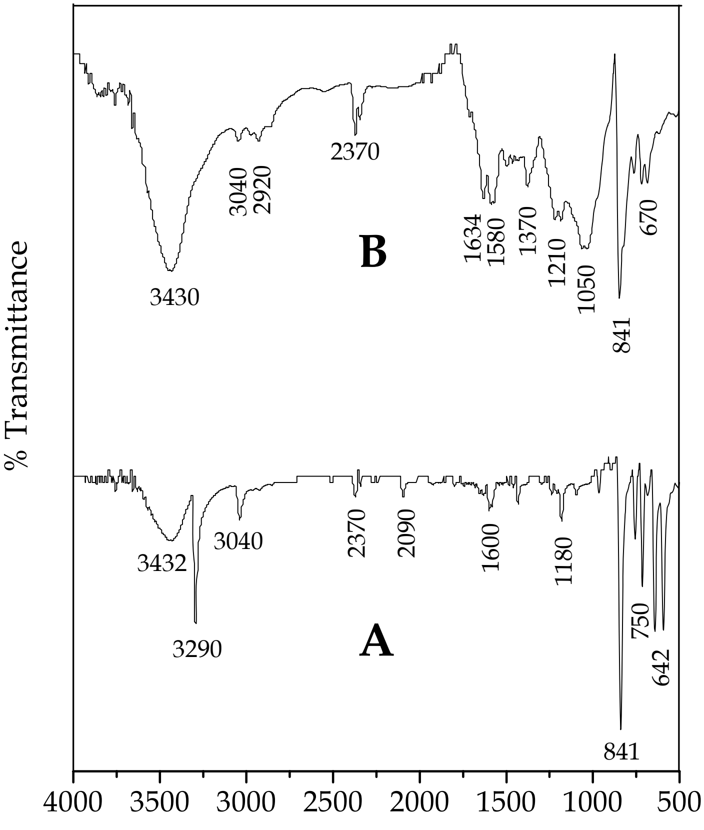


**Figure 3.** FTIR spectra (KBr, pressed pellet) of A) EP and B) E-PEP previously obtained from 20 mM EP in 0.1 M $Et_4NBF_4$/ACN.

The band at 1634 cm$^{-1}$ (Figure 3B) is due to the C=C stretching vibration of pyrene rings and that at 1600 cm$^{-1}$ is related to the C-H bending vibration of these groups; the band at 3040 cm$^{-1}$ is associated with the C-H stretching of the pyrene rings. We observed also a decrease in intensity of the bands at 1180, 750 and 618 cm$^{-1}$, which are associated to the out-of-plane vibration =C–H bonds of pyrene ring, as well as the presence of a band at 1050 $cm^{-1}$ related to the incorporation of $BF_4^-$ counterions [29]. The presence of the bands at 3430 and 2370 $cm^{-1}$, which are characteristic vibration bands of the alkyne group, confirm that the triple bonds present in the monomer remained intact after the reaction, so that the polymerization takes place exclusively through the pyrene units. These bands were not observed in the FTIR spectrum of chemically obtained *trans*-PEP [10]. E-PBP and E-PTMSBDP exhibited very similar FTIR spectra to that obtained for E-PEP.

### *Thermal Properties of the obtained oligomers*

Thermal properties of the oligomers were evaluated by thermogravimetric analysis (TGA), from 0 to 900ºC (Figure 4) and differential scanning calorimetry (DSC) from 20 to 200ºC; the results are summarized in Table 1. According to TGA measurements E-PEP showed a moderate thermal stability with a $T_5$ = 138ºC. This oligomer exhibited degradation in two steps between 250-600ºC and beyond 800ºC. DSC measurements (not shown) revealed that this oligomer displays a softening point at $T_s$ = 117ºC. By contrast, E-PTMSBDP possesses a good thermal stability with a $T_5$ value of 240ºC. This oligomer exhibited gradual degradation leaving 82.5% of remains at 900ºC. Finally, E-PBP showed a very high thermal stability so that its $T_5$ value could not be determined. In particular, this oligomer showed very slight degradation, losing 3.5% weight at 900ºC. According to DSC measurements, E-PBP and E-PTMSBDP exhibited no softening point in the studied range of temperatures. As we can see, the presence of additional triple bonds or double bonds in the monomer increases the thermal stability of the oligomers. The same effect was previuosly reported by us when we compared the thermal properties of poly(1-ethynylpyrene) and poly(1-buta-1,3-diynylpyrene) chemically obtained, using $WCl_6$ as catalyst [10].

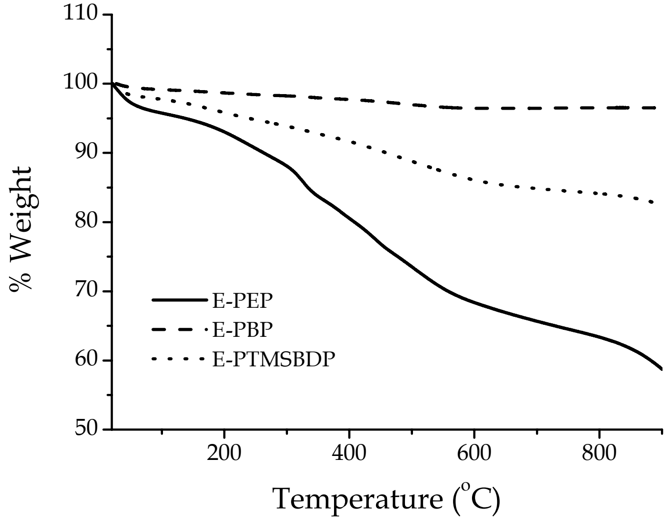


**Figure 4.** TGA of the obtained oligomers: E-PEP, E-PBP and E-PTMSBDP. Scan rate 10ºC/min.

**Table 1.** Thermal, optical properties and conductivity of the obtained oligomers

| Oligomer | $T_5$ (ºC)[a] | $T_s$ (ºC)[a] | $\lambda_{max}$ (nm) | $\lambda_{em}$ (nm) | $\sigma$ (S/cm) |
|---|---|---|---|---|---|
| E-PEP | 138 | 117 | 358 | 387-407 | 8.4 x$10^{-2}$ |
| E-PBP | ND[b] | - | 364 | 387-407 | 2.1 x $10^{-2}$ |
| E-PTMSBDP | 240 | - | 358 | 387-407 | 4.6 x $10^{-2}$ |

[a] Heating rate 10ºC/min; [b] 3.5% weight lost at 900ºC

*Optical Properties of the Oligomers*

Optical properties of the oligomers were studied by absorption and fluorescence spectroscopies and the results are summarized in Table 1. Absorption spectra of the obtained oligomers in THF solution are shown in Figure 5. The absorption spectra of E-PEP exhibited a well defined $S_2 \leftarrow S_0$ band at $\lambda_{max}$ = 358 nm [33] with cut off at $\lambda$ = 550 nm due to pyrene units present in the oligomer. On the other hand, E-PBP exhibited the same band at $\lambda_{max}$ = 364 nm, slightly red shifted compared to that of E-PEP. Plus, we can observe a shoulder at $\lambda$ = 377 nm, which could be due to the presence of slight pyrene-pyrene intramolecular interactions in this oligomer. By contrast, E-PTMSBDP showed a broader absorption band centered at $\lambda_{max}$ = 358 nm followed by a shoulder at $\lambda$ = 389 nm and a tail at $\lambda$ = 430 nm, which reveal the presence of stronger intramolecular interactions between the aromatic units present in the oligomer. It is very well known that non substituted oligopyrene exhibits a twisted conformation of the polymer backbone, because of steric effects between hydrogens

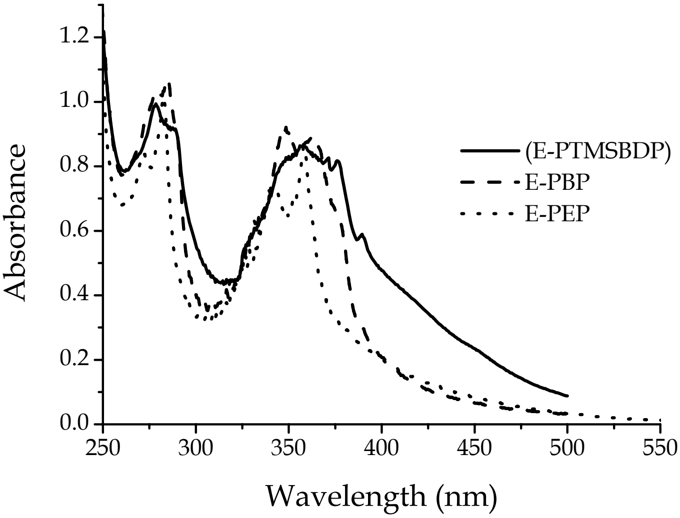


**Figure 5.** Absorption spectra of the obtained oligomers: E-PEP, E-PBP and E-PTMSBDP in THF solution.

belonging to neighbor pyrene units [31]. Although the presence of bulky substituents, in our obtained oligomers, the oligopyrene backbone skews from planarity as oligopyrene itself do, giving rise to intramolecular pyrene-pyrene interactions. The presence of additional triple or double bonds as substituents modify the absorption spectra of the oligomers because of donor electronic effects.

Fluorescence spectra of the obtained oligomers were very similar and exhibited an emission band at $\lambda_F$ = 387-407 nm due to pyrene units in the non-associated state "monomer emission" [33]; the emission spectra of E-PEP is shown in Figure 6. Apparently, there is no excimer emission bands in the fluorescence spectra of these oligomers. Since the fluorescence spectra did not exhibit any broadening of the emission band, as in the case of other chemically obtained polypyrenylacetylenes [10], where the polymerization takes place exclusively through the triple bonds, we can affirm that the oligomers backbone is so twisted that the aromatic rings tend to behave as isolated pyrene units, giving rise mainly to "monomer emission". However, a weak emission beyond 450 nm, a wavelength where pyrene does not emit, reveals the presence of slight pyrene-pyrene interactions. Since the fluorescence spectra were recorded in very diluted solutions such interactions are undoubtedly intramolecular.

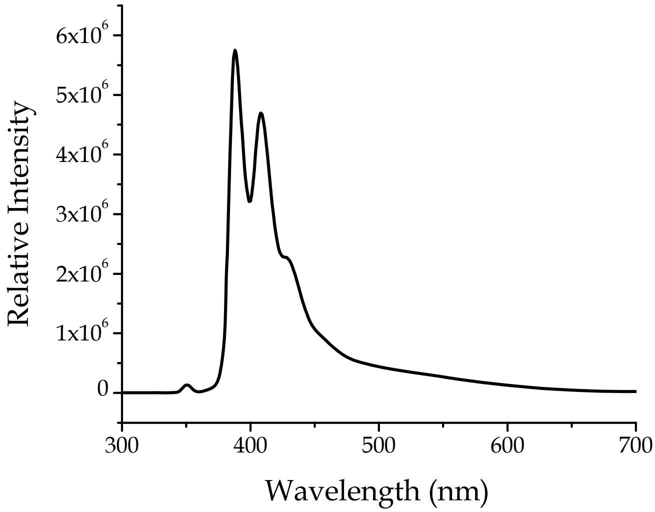
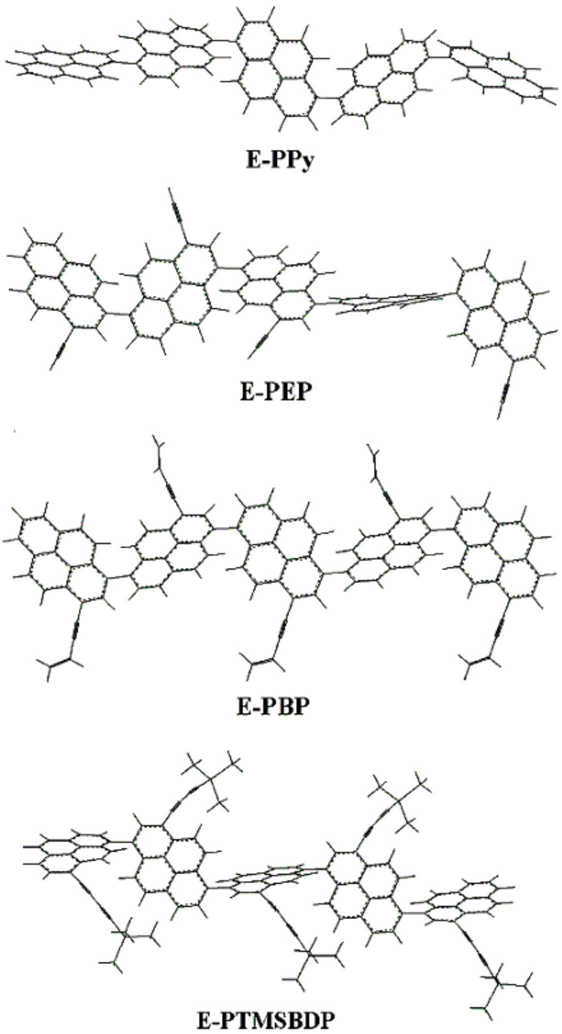


**Figure 6.** Fluorescence Spectra of E-PEP in THF solution ($\lambda_{exc}$ = 350 nm).

### *Molecular Modeling and Conductivity*

In order to support the results obtained by absorption and fluorescence spectroscopies, molecular modeling was performed in model pentamers of E-PPy, E-PEP, E-PBP and E-PTMSBD, by semi-empirical calculations using the PM3 method, and the obtained optimized geometries are shown in Figure 7. As we can see, all oligomers showed a twisted conformation with dihedral angles varying from 55-79º. Therefore, we can conclude that in these substituted oligopyrenes, the oligomer backbone torsions are not increased significantly by the steric effects of the lateral side groups compared to non substituted oligopyrene. However, such torsions prevent the conjugation effect along the polymer backbone so that the emission spectra of oligomers show predominantly “monomer emission” [33].



**E-PPy**

**E-PEP**

**E-PBP**

**E-PTMSBDP**

**Figure 7.** Optimized geometry for E-PPy, E-PEP, E-PBP and E-PTMSBDP calculated by the PM3 method.

Finally, the conductivity of the oligomers was measured in pressed pellet in the doped state giving values of $\sigma = 8.4 \times 10^{-2}$, $2.1 \times 10^{-2}$ and $4.6 \times 10^{-2}$ S/cm for E-PEP, E-PBP and E-PTMSBDP respectively. According to these results, E-PEP seems to be more conducting than E-PBP and E-PTMSBDP. Apparently, oligomers bearing the less bulky substituents reach a better packing in pressed pellet, thereby showing higher conductivity values in the solid state.

## Conclusion

FTIR spectroscopy confirmed that the electrochemical polymerization of EP, BP and TMSBDP takes place predominantly through the aromatic rings, and the triple bonds remain intact. Typically, in the chemical process the polymerization takes place through the triple bonds. All obtained oligomers showed absorption at $\lambda_{max}$ = 358-364 nm and fluorescence at $\lambda_F$ =387-407 nm. Despite the relative absence of excimer bands, slight emission beyond 450 nm, revealed the presence of intramolecular interactions between pyrene units. Such torsions are responsible of the predominance of monomer emission in the fluorescence spectra. Molecular modeling showed that the substituents do not modify significantly the dihedral angles between pyrene units in the oligomers.

*Acknowledgements*. We thank Miguel Angel Canseco, Esteban Fregoso and Gerardo Cedillo for their assistance with thermal analysis, absorption, FTIR and NMR spectroscopies. J.M. Reyna-González is grateful to DGAPA-UNAM for a postdoctoral grant. We thank also CONACYT (Projects J-48933 and 49796-Q) for financial support.

## References

1. Friend RH, Gymer RW, Holmes AB, Burroughes JH, Marks RN, Taliani C, Bradley DDC, Dos Santos DA, Brédas JL, Logdlung M, Salanek WR (1999) Nature 397:121.
2. Heeger AJ (2001) Angew Chem Int Ed Eng 40:2591.
3. Segura JL, Martín NJ (2000) Mater Chem 10:2403.
4. Kraft A, Grimsdale AC, Holmes AB (1998) Angew Chem Int Ed Eng 37:402.
5. Bernius MT, Inbasekaran M, O'Brien J, Wu WS (2000) Adv Mater 12:1737.
6. Bundgaar E, Krebs FC (2007) Solar Energy Mat Solar Cells 91:954.
7. Perepichka IF, Perepichka DF, Meng H (2005) Adv Mat 17:1281.
8. Yamamoto T (2002) Macrom Rapid Comm 23:583.
9. Pron A. Rannou P (2002) Prog Polym Sci 27:135.
10. Rivera E, Belletête M, Zhu XX, Durocher G, Giasson R (2002) Polymer 43:5059.
11. Rivera E, Wang R, Zhu XX, Zargarian D, Giasson R (2003) J Mol Catal A 204-205:325.
12. Belletête M, Rivera E, Giasson R, Zhu XX, Durocher G (2004) Synth Met 143:37.
13. Rivera E, Aguilar-Martínez M, Terán G,. Flores RF, Bautista-Martínez JA (2005) Polymer 46:4789.
14. Aguilar-Martínez M, Bautista-Martínez JA, Rivera E (2008) Designed Monomers and Polymers 11:173.
15. Piçarra S, Relogio P, Alfonso CAM, Martinho JMG, Farinha JPS (2003) Macromolecules 36:8119.
16. Duhamel J, Kanagalingam S, O'Brien TJ, Ingrata MW (2003) J Am Chem Soc 125:12810.
17. Mizayazawa K, Winnik FM (2003) J Phys Chem B 107:10677.
18. Pandey S, Redden RA, Fletcher KA (2003) Macromol Chem Phys 204:425.
19. Berglund KD, Przybycien TM, Tilton RD (2003) Langmuir 19:2705.
20. Beaudoin E, Hiorns RC, Borisov O, François J (2003) Langmuir 19:2058.
21. Gao C, Qian H, Wang SJ, Wei Chen DY, Yu G (2003) Polymer 44:1547.
22. Morimoto H, Hashidzume A, Morishima Y (2003) Polymer 44:943.
23. Yusa S, Sakakibara A, Yamamoto T, Morishima Y (2002) Macromolecules 35: 10182.
24. Ellison CJ, Torkelson JM (2002) J Polym Sci B Polym Phys 40:2745.
25. Duhamel J (2006) Acc Chem Res 39:953.
26. Honeychurch KC, Hart JP, Kirsch N (2004) Electrochim Acta 49:1141.
27. Ferancová A, Bucková M, Korgová E, Korbut O, Gründler P, Wärnmark I, Ŝtepán R, Barek J, Zima J, Labuda J (2005) Bioelectrochemistry 67:191.

28. Şahin Y, Pekmez K, Yildiz A (2002) Synth Met 129:117.
29. Reyna-González JM, Aguilar-Martínez M, Bautista-Martínez JA, Rivera E, González I, Roquero P (2006) Polymer 47:6664.
30. Lu G, Qu L, Shi G (2005) Electrochim Acta 51:340.
31. Lu G, Shi G (2006) J Electroanal Chem 586:154.
32. Heywang G, Roth S (1991) Angew Chem Int Ed Eng 30.176.
33. Winnik FM (1993) Chem Rev 93:587.