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Preparation of *cis*-poly(1-ethynylpyrene) using (1-Me-indenyl)(PPh_3)Ni–C≡C–Ph/methylaluminoxane as catalyst

Ernesto Rivera[1], Ruiping Wang, Xiao Xia Zhu, Davit Zargarian*, Richard Giasson[2]

Département de Chimie, Université de Montréal, C.P. 6128, Succursale Centre-Ville, Montreal, QC, Canada H3C 3J7

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Dedicated to Prof. Renato Ugo on the occasion of his 65th birthday

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Abstract

A combination of the complex (1-Me-indenyl)(PPh_3)Ni–C≡C–Ph and methylaluminoxane (MAO) catalyzes the polymerization of 1-ethynylpyrene to fairly soluble *cis*-poly(1-ethynylpyrene). The polymers have been characterized by IR, solid state ^{13}C and ^{1}H NMR, and UV-Vis (λ_{max} at 346 nm) spectroscopy, and studied by thermogravimetric analysis ($T_{10} \sim 285$–$392\,^{\circ}C$), differential scanning calorimetry, and size exclusion chromatography ($M_w \sim 10^3$–10^4 Da; $M_w/M_n \sim 2$). The thermal and optical properties of these *cis*-polymers have been compared to their *trans*-analogues prepared using different catalysts. The degree of conjugation in the *cis*-polymers was found to be lower than their *trans*-polymers, presumably due to the twisting and coiling of the main chain.

Keywords: Idenyl nickel complex; *cis*-Poly(1-ethynylpyrene); Polyacetylenes; Conjugated polymers; Insertion mechanism

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1. Introduction

Polyacetylene has been the subject of numerous investigations since the discovery by MacDiarmid, Shirakawa and Heeger in 1976 that this polymer becomes highly conducting upon doping [1–3]. In spite of its considerable promise in the area of electronic materials, however, the practical applications of polyacetylene have remained limited due mainly to its low solubility and thermal instability. Fortunately, extensive research in this field has led to the synthesis of a great number of thermally stable and processible polyacetylene derivatives bearing different substituents [4–8]. The latter are highly conjugated polymers which might find applications in the construction of electronic devices such as light emitting diodes, photovoltaic cells, and non-linear optical systems [9–18].

The optoelectronic characteristics of substituted polyacetylenes are highly variable as a function of both the configuration of the main chain and its degree of extended conjugation [19]. These properties are, in turn, determined by the electronic and steric nature of the alkyne substituents and the polymerization method. As a result, a great deal of research effort has been devoted to the development of new methods for the preparation of variously substituted polyacetylenes [20]. Among these, poly(phenylacetylene) (PPA) has been prepared using a variety of catalysts [21] and

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* Corresponding author. Tel.: +1-514-343-2247; fax: +1-514-343-7586.

E-mail addresses: zargarian.davit@umontreal.ca (D. Zargarian), giasson@chimie.umontreal.ca (R. Giasson).

[1] Present address: Instituto de Investigaciones en Materiales UNAM, Circuito Exterior, Ciudad Universitaria, C.P. 04510, Mexico, DF Mexico.

[2] Co-corresponding author.

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used as a model for configurational and conformational analysis [22–24]. For instance, *trans*-rich PPA is obtained via metathesis-type polymerization processes using WCl_6 as catalyst in combination with various cocatalysts [25], while Rh catalysts give *cis*-rich PPA via insertion-type polymerization processes [21]. We have also reported the synthesis of *cis*-PPA by using systems consisting of the complexes (1-Me-indenyl)Ni(PR_3)(X) (R = Ph, Cy; X = Cl, C≡C–Ph) and poly(methylaluminoxane) as cocatalyst; the polymerization reactions promoted by these systems also proceed by an insertion-type mechanism [26].

As part of a research program aimed at the preparation of molecular electronic devices [27,28], we are interested in the synthesis of polymeric materials containing pendant pyrenyl groups. The synthesis of poly(1-ethynylpyrene) (PEP) via the polymerization of 1-ethynylpyrene using W, Mo and Rh catalysts was reported recently by Masuda and co-workers [29]. In our hands, good yields of *trans*-PEP ($M_w \sim 2 \times 10^4$ to 5×10^4; $M_w/M_n \sim 5$–10) were obtained when WCl_6 was used as catalyst, with or without cocatalysts (Fig. 1), while insoluble *cis*-PEP was obtained in low yields with Mo- and Rh-based catalysts [30]. This prompted us to examine the polymerization of 1-ethynylpyrene using the catalytic system (1-Me-indenyl)Ni(PPh_3)(C≡C–Ph)/MAO with a view to obtaining soluble *cis*-PEP. The present report describes the synthesis of moderately soluble *cis*-PEP (Fig. 1) possessing relatively low polydispersities; these polymers have been fully characterized and their properties compared to those of *trans*-PEP reported previously [30].

2. Experimental

The polymerizations were carried out under an inert atmosphere using moisture- and oxygen-free solvents. The preparation of 1-ethynylpyrene [30] and (1-Me-indenyl)Ni(PPh_3)(C≡C–Ph) [26] have been reported previously; all other reagents used in these studies, including MAO, were purchased from Aldrich and used as received.

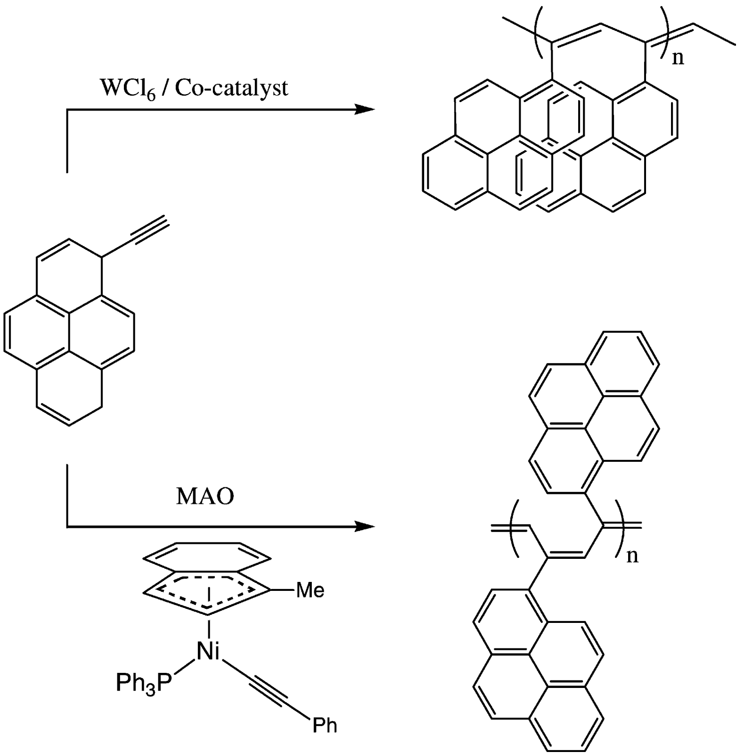

Fig. 1. Polymerization of 1-ethynylpyrene with W- and Ni-based catalytic systems.

Solid state ^{1}H and ^{13}C NMR spectra of the polymers were recorded on a Bruker ARX-700 narrow-bore spectrometer. Fast magic angle spinning (MAS) at 30 kHz was used. The ^{1}H NMR spectra were obtained by the use of a double resonance MAS probe supporting rotors of outer diameter 2.5 mm operating at a ^{1}H Larmor frequency of 700 MHz; the relaxation delays were adjusted to allow complete relaxation of the spins. The IR spectra were recorded on a Nicolet FTIR 5 DXB spectrometer using KBr pellets of the polymer samples.

The molecular weights of the polymers were determined by GPC analysis using a Waters 510 liquid chromatograph equipped with μ-Styragel columns (THF as eluent) and a Waters 410 refractive index detector (relative to polystyrene standards). The thermal properties of the polymers were studied by measuring the following parameters: 10% weight loss temperature (T_{10}), glass transition temperature (T_g), and melting points (T_m). The thermogravimetric analyses were conducted on a Hi-Res TGA 2950 instrument (0–1000 °C) and the differential scanning calorimetry was carried out on a DSC 2910 instrument (−40 to 400 °C) with a heating rate of 20 °C/min.

The absorption spectra of the polymers were recorded using a Varian Cary 1 Bio-UV-Vis spectrophotometer (model 8452A) and 1 cm quartz cells. The sample solutions were kept in the Beer–Lambert concentration regime (1×10^{-5} to 3×10^{-5} M), and the optical transparency of the solvent (THF, Aldrich spectrophotometric grade) in the region of interest was satisfactory.

2.1. Polymerization of 1-ethynylpyrene

The following general procedure was used for the polymerization of 1-ethynylpyrene with the Ni/MAO system; the specific reaction conditions for a selected number of experiments are given in Table 1. A solution of 1-ethynylpyrene in toluene or THF (5 mL) was transferred into a Schlenk tube containing (1-Me-indenyl)Ni(PPh_3)(C≡C–Ph). After complete dissolution, a solution of MAO in the same solvent was added; a 1:10 ratio of Ni:MAO was used throughout. The reaction mixture was stirred under argon at room temperature or at 50 °C for the desired time. The final mixture was treated with acetic acid (five drops) and transferred into methanol (50 mL) in order to precipitate the resulting *cis*-PEP as a dark brown powder. The methanol-insoluble polymer was isolated by filtration, washed with methanol, and dried under vacuum. The following are the analytical data for the polymer sample Ni-9. IR (KBr): ν 3036

Table 1
Conditions for polymerization of 1-ethynylpyrene and properties of the resulting polymers

Run	Polymer	Ratio	Solvent	Time (h)	Temperature (°C)	M_w[a] (10^3 g/mol)	M_w/M_n[a]	T_{10} (°C)	T_m (°C)	T_g (°C)
1	Ni-1	1:10:60[b]	Toluene	2	25	2.2	1.93			
2	Ni-2	1:10:60[b]	Toluene	24	25	5.5	1.93			
3	Ni-3	1:10:60[b]	Toluene	48	25	7.2	2.4	392	–	169
4	Ni-4	1:10:60[b]	Toluene	24	50	5.2	2.09			
5	Ni-5	1:10:60[b]	THF	24	25	19.1	1.74			
6	Ni-6	1:10:60[b]	THF	24	50	14.2	1.25	335	–	–
7	Ni-7	1:10:50[b]	THF	48	25	24	2.15	285	–	–
8	Ni-8	1:10:100[b]	THF	19	25	14.1	2.66			
9	Ni-9	1:10:100[b]	THF	48	25	22.3	1.72			
10	Ni-10	1:10:120[b]	THF	72	25	20.8	1.73			
11	Ni-11	1:10:150[b]	THF	48	25	18.2	2.19			
12	W-1	WCl_6[c]	Toluene	24	25	24.0	2.88	381	330	–
13	W-2	$WCl_6/SnPh_4$[d]	Toluene	24	25	27.6	4.49	383	345	–
14	W-3	$WCl_6/SnBu_4$[d]	Toluene	24	25	277.2	10.67	385	330	–
15	W-4	$WCl_6/BiPh_3$[d]	Toluene	24	25	470.5	1.90	389	327	–

[a] Methanol-insoluble fraction; measured by SEC (THF, polystyrene standard).

[b] Ratio of (1-Me-indenyl)Ni(PPh_3)(C≡C–Ph)/MAO/monomer.

[c] Ratio of WCl_6/monomer = 1:40.

[d] Ratio of WCl_6/cocatalyst/monomer = 1:2:40.

(=C–H stretching), 1598 (C=C stretching), 1582, 1487, 1414 (C–H bending), 1176, 838 (C=C–H out of plane bending), 752, 717 and 679 cm^{-1}. Solid state ^{1}H NMR (700 MHz): δ 7 (broad, aromatic and vinylic protons). Solid state ^{13}C NMR (175 MHz): δ 137 and 125 (broad, all sp^2 carbons). UV (THF) λ_{max}: 346 and 457 nm. Elemental analysis, calculated for $(C_{18}H_{10})_n$: C, 95.54; H, 4.45. Found: C, 95.12; H, 4.33.

3. Results and discussion

The catalytic system consisting of (1-Me-indenyl)-Ni(PPh$_3$)(C≡C–Ph) and MAO as cocatalyst has proven effective for the polymerization of phenylacetylene to *cis*-PPA [26]. This same system reacted with 1-ethynylpyrene to give dark brown powders (20–80% isolated yields) which were identified as *cis*-PEP by comparing their physical properties and spectroscopic characteristics to those of *trans*-PEP obtained from the polymerization of 1-ethynylpyrene using WCl$_6$ as catalyst [29,30]. For instance, the samples of PEP synthesized using the Ni/MAO system are dark brown powders, which are soluble in THF and *o*-dichlorobenzene, partially soluble in chloroform, and sparingly soluble in toluene. For comparison, *trans*-PEP obtained from catalytic systems based on W [30] are dark purple solids, which are totally soluble in *o*-dichorobenzene and THF and only partially soluble in CHCl$_3$ and toluene; in contrast, the PEP samples obtained from polymerizations using $\{Rh(nbd)(\mu\text{-}Cl)\}_2$ are practically insoluble in every organic solvent [29]. Tabata et al. have reported that polymerization of α-ethynylnaphthalene using $\{Rh(nbd)(\mu\text{-}Cl)\}_2$ also gives insoluble polyalkynes; these authors conclude on the basis of Raman studies that these polymers possess a *cis*-cisoidal geometry [31]. On the other hand, polymerization of phenylacetylene with our Ni/MAO system give *cis*-transoidal PPA [26]. On the basis of these precedents, we assign a *cis*-transoidal geometry to the PEP samples obtained from the Ni/MAO system.

Section 3.1 gives a summary of the experiments aimed at optimizing the polymerization of 1-ethynylpyrene with our Ni system; the following section describes the spectroscopic characterization of the polymers, their thermal properties, and a modeling study on their conformations.

3.1. Optimization experiments

The polymeric products resulting from the reaction of 1-ethynylpyrene with the catalytic system (1-Me-indenyl)Ni(PPh$_3$)(C≡C–Ph)/MAO possess molecular weights in the range of 10^3–10^4 depending on the polymerization conditions (Table 1). Longer reaction times (24–48 h) were necessary for attaining higher molecular weights (runs 1–3 in toluene and runs 5 and 7 in THF). The nature of reaction solvent played an even more important role in determining the molecular weight, with THF giving generally higher M_w than toluene. This may be due to the lower solubility of *cis*-PEP in toluene, which would cause the growing polymer to precipitate out of the solution thereby preventing the chain growth process.

The reaction temperature was an important factor for the polymerizations carried out in THF: carrying out the polymerization at ambient temperature for a given reaction time resulted in a diminished monomer conversion (20–50% yields) but gave longer chains; on the other hand, increasing the reaction temperature from 25 to 50 °C resulted in an increase in the yield of the polymer (80%) but gave shorter chains (run 5 versus 6). One possible explanation for this observation is related to the kinetics of the chain transfer step, as follows. It is conceivable that higher temperatures accelerate the transfer of the growing polymer chain from the Ni center to Al centers in MAO, thereby stopping the further growth of the chain; the free Ni centers can then react with more monomers to resume the polymerization. This sequence would result in a higher monomer-to-polymer conversion but shorter polymer chains.

A number of polymerizations were carried out at 25 °C using different catalyst: monomer ratios (runs 7–11) in order to probe the importance of this parameter. The results of these experiments appear to indicate that polymers possessing the highest M_w values are obtained with catalyst: monomer ratios of 1:50 to 1:100.

In summary, polymerization of 1-ethynylpyrene with the catalytic system (1-Me-indenyl)Ni(PPh$_3$)C≡C–Ph/MAO allows the preparation of *cis*-PEP with M_w ranging from 7.2 to 24 × 10^3 g/mol and polydispersities between 1.25 and 2.4. In contrast, polymerization of the same monomer with WCl$_6$ leads to the formation of *trans*-PEP with M_w ranging from 2.4

to 47 × 10^4 g/mol and polydispersities between 1.9 and 10 [30]. A representative sample of the results from the W-catalyzed polymerizations are included in Table 1 for comparison purposes. The physical properties of these materials are discussed in Section 3.2.

3.2. Characterization of PEP

IR, ^{1}H, ^{13}C NMR and UV-Vis spectroscopy were used to characterize the PEP obtained from the present system. The absence in the IR spectra of the characteristic alkyne bands (H–C≡ stretching at 3296 cm^{-1}, ν(C≡C) at 2000 cm^{-1}, and C–H bending at 700 cm^{-1}) confirm the absence of unreacted alkyne moiety in the polymers. The strong bands at 3000 cm^{-1} (=C–H stretching), 1583 cm^{-1} (C=C stretching), and 1414 cm^{-1} (C=C–H bending) are associated with the main chain. The most characteristic absorption of the pyrene substituent is the =C–H out of plane bending at 839 cm^{-1}.

The solid state ^{1}H NMR spectrum of *cis*-PEP displays a broad band centered around 7 ppm; the signals belonging to the vinylic protons present in the polymer backbone are masked by those of the aromatic protons. This broadening of the signals was also observed for *trans*-PEP obtained from the W-based systems [30] and can be attributed to two phenomena: (a) the presence of unpaired radicals arising from the rupture of some C=C bonds; and (b) the slow motion of the rigid polymer chain. The solid state ^{13}C NMR spectrum of *cis*-PEP (Fig. 2) obtained with the Ni/MAO system also exhibits signals at 135 and 125 ppm

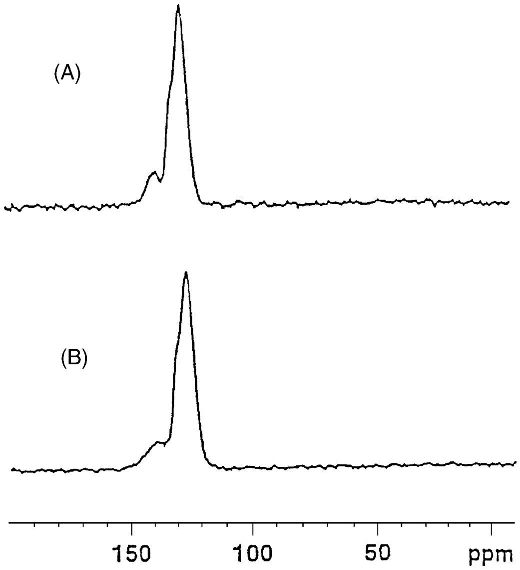

Fig. 2. Solid state CP/MAS ^{13}C NMR 175 MHz spectra of the polymers recorded at a spinning frequency of 30 kHz: (A) *cis*-PEP, (B) *trans*-PEP.

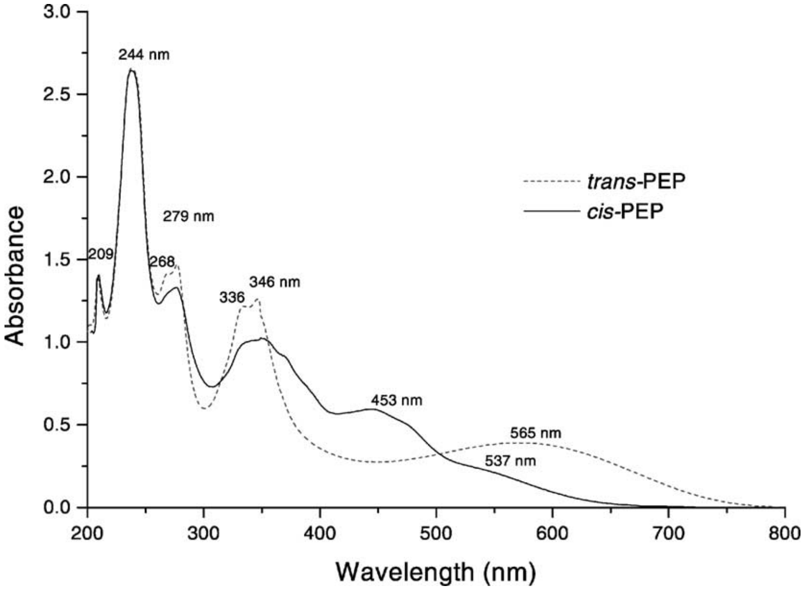

Fig. 3. UV absorption spectra of *cis*- and *trans*-PEP in THF.

corresponding to all sp^2 carbons; these signals are similar to those displayed by the *trans*-polymers.

3.2.1. Thermal and optical properties of the polymers

The thermal properties of *cis*-PEP were measured by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The thermal stability (T_{10}), glass transition temperatures (T_g), and melting points (T_m) of these polymers are compared with those obtained for *trans*-PEP [30] and are shown in Table 1; the following differences in the thermal characteristics of the *cis*- and *trans*-polymers are noteworthy. First, only one sample among the polymers studied showed a glass transition temperature (*cis*-PEP, Ni-3, $T_g = 169\,°C$). Second, all *trans*-PEP samples show a melting or softening point (T_m) between 327 and 345 °C, whereas none of the *cis*-PEP samples melted or softened in the range studied (−40 to 400 °C). Moreover, in almost all cases, the *trans*-polymers are thermally more stable than their *cis*-counterparts. For instance, the samples W-1 and Ni-7 have similar molecular weights (ca. 2.66×10^3 g/mol) but their T_{10} values differ by more than 100 °C.

Another noteworthy difference between the *cis*- and *trans*-PEP polymers is that the thermal stabilities of *trans*-PEP do not seem to vary much with the molecular weight of the sample (T_{10} around 381–389 °C), whereas the *cis*-polymers having longer chains are thermally less stable (e.g. T_{10} for Ni-7 of $M_w = 24 \times 10^3$ g/mol is 285 °C versus 392 °C for Ni-3 of $M_w = 7.2 \times 10^3$ g/mol). We speculate that the underlying

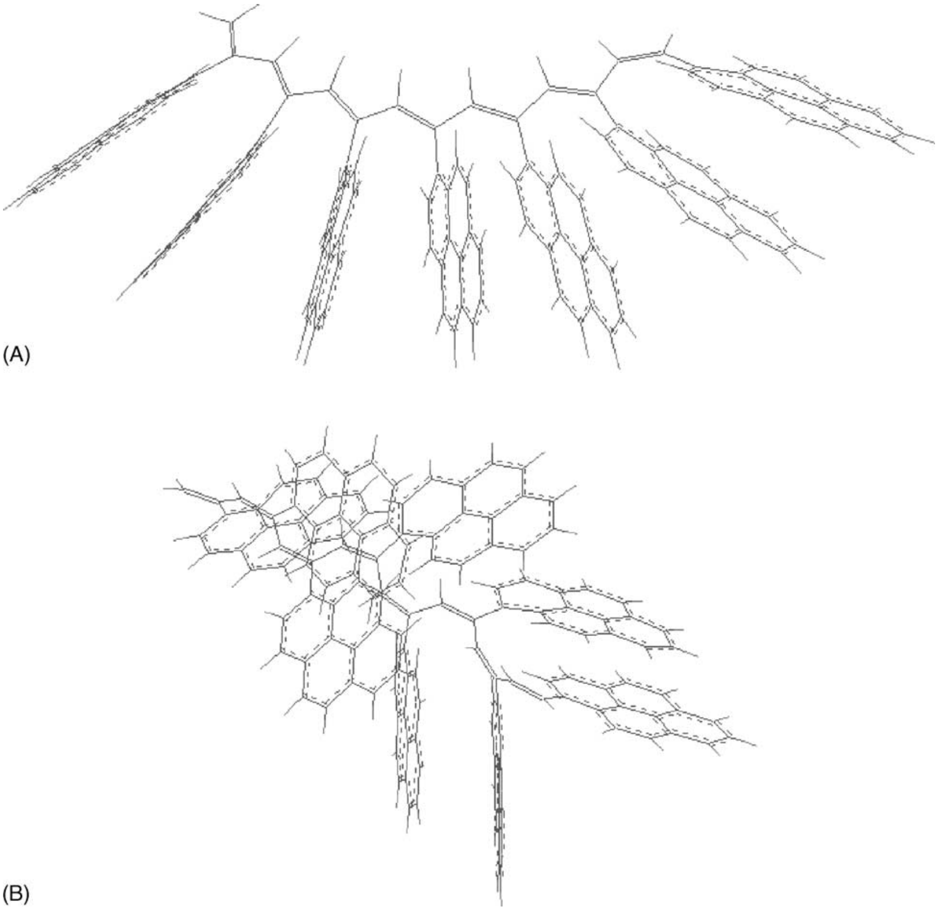

Fig. 4. Conformation of the polymers obtained by molecular modeling: (A) *trans*-PEP, (B) *cis*-PEP.

reason for the lower thermal stability of the *cis*-polymers is that the *cis*-geometry allows a relatively facile extrusion of arylacetylene units from the polymer backbone at elevated temperatures.

The UV-Vis spectra of *cis*- and *trans*-PEP were studied in order to compare the pattern of electronic transitions in these polymers. Fig. 3 displays the spectra obtained for the polymer sample Ni-7 and its *trans*-analogue having similar molecular weight, W-1. Both polymers show an absorption maximum at 346 nm corresponding to the absorption of the pyrene moieties in the non-associated state. The *cis*-PEP also displays a broad shoulder at 453 nm bearing a tail at 537 nm, with a cut-off wavelength reaching 657 nm, whereas the *trans*-PEP shows only one broad band centered at 565 nm with a cut-off wavelength reaching 800 nm. Steady state and time-resolved fluorescence studies have confirmed that the broad band at 453 nm has its origin in a ground state complex resulting from intramolecular interactions between adjacent pyrene units present in the polymer [31]. The tail around 537 nm is likely caused by the short sequences of conjugated *cis*-double bonds present in the backbone of *cis*-PEP, in contrast to the longer sequences of *trans*-double bonds present in *trans*-PEP, which gives a band at a higher wavelength [30].

The above spectroscopic studies were complemented by molecular mechanics calculations (MM2) performed on short segments of *trans*- and *cis*-PEP; the optimized geometries obtained are represented in Fig. 4. According to these modeling studies, the main chain of *trans*-PEP should exist in an almost planar conformation with internal stacking of the pendant pyrenyl groups (Fig. 4A). The distance between two pyrene units varies from 3.1 (near the backbone) to 4.1 Å (far away from it) in this conformation, and the adjacent pyrene units are almost parallel. Thus, the main chain of *trans*-PEP is fully conjugated, consistent with the low energy band at 565 nm in the absorption spectra of this polymer.

The modeling studies also show that it is more difficult for the *cis*-PEP backbone to adopt a planar conformation because of the steric interactions between pendant pyrenyl groups. This causes a twisting of the chain and a coiling of the polymer backbone that may favor intramolecular interactions between pyrene units at long distances and in a non-parallel way (Fig. 4B). Distances between pyrene units vary from 4.4 to 5.3 Å in this conformation. The coiling of the polymer backbone also decreases the degree of conjugation in the main chain, consistent with the low energy band in the absorption spectrum of *cis*-PEP.

4. Conclusions

Cis-poly(1-ethynylpyrene) with molecular weights in the range of 7×10^3 to 24×10^3 g/mol were synthesized using the (1-Me-indenyl)Ni(PPh_3)C≡C–Ph/MAO catalytic system. The *cis*-PEP obtained in this fashion was fairly soluble in THF and *o*-dichlorobenzene, and exhibited lower thermal stability than *trans*-PEP prepared with a catalytic system based on WCl_6. The lowest energy absorption and cut-off wavelengths reached 537 and 657 nm for *cis*-PEP compared to 565 and 800 nm for *trans*-PEP. This is attributed to a lower degree of conjugation in *cis*-PEP due to a coiling of the chain. The band at 457 nm proves the existence of a complex resulting from intramolecular interactions between neighbor pyrene units present in the *cis*-PEP polymer.

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