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# Novel polyacetylenes containing pendant 1-pyrenyl groups: synthesis, characterization, and thermal and optical properties

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## Abstract

We report the synthesis as well as the thermal, optical and photophysical properties of four different polyacetylenes with pendant 1-pyrenyl groups: poly(1-ethynylpyrene) (PEP), poly(1-(trimethylsilanylethynyl)pyrene) (PTMSEP), poly(1-(4-(trimethylsilyl)buta-1,3-dienyl)pyrene) (PTMSBDP) and poly(1-buta-1,3-dienylpyrene) (PBDP). Polymerizations were carried out with W and Ta catalysts, respectively, for mono- and disubstituted monomers. Soluble poly(1-ethynylpyrene) with high molecular weights (up to  $4 \times 10^5$ ) and extended conjugation of the main chain was obtained with good yields. Lower molecular weights (up to  $6 \times 10^3$ ) were obtained with the other polymers. Oligomers and polymers displayed high thermal stability. From the absorption spectra of the various polymers, it is found that PEP possesses a higher degree of conjugation than the other polyacetylenes. Molecular interactions occur between pyrene units present in each polymer giving rise to an emission due to associated pyrenes. These interactions are affected by the steric hindrance present in the polymer backbone. Excitation spectra combined with fluorescence decay profiles show that these interactions occur in the ground state (excited complex). © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* Pyrene; Polyacetylenes; Optical properties

## 1. Introduction

Conjugated polymers are regarded as promising materials for the development of optoelectronic devices such as light emitting diodes, photovoltaic cells, and non-linear optical systems [1–6]. The optoelectronic properties vary significantly depending on the degree of extended  $\pi$ -conjugation between the consecutive repeat units [7,8].

Polyacetylene is an extensively conjugated polymer that shows metallic conductivity upon doping. However, the insolubility and instability of this polymer, as well as its improcessability, limit its practical applications as a functional material [9]. Introduction of some substituents into polyacetylenes, however, can improve remarkably its stability [10–13].

Poly(arylacetylenes) were widely studied by many research groups and were the subject of a review [14]. Arylacetylenes bearing non-polar groups are usually polymerized in the presence of  $WCl_6$ , while disubstituted

acetylenes with  $TaCl_5$ . Masuda and co-workers carried out the polymerization of several arylacetylenes bearing condensed aromatic rings, such as naphthalene, anthracene, phenanthrene, and pyrene, obtaining polymers with good molecular weights ( $M_w$  from 9 to 140  $kg\ mol^{-1}$ ) depending on the structure of the monomer [15–17]. It seems that the position of the acetylene bond on the arene influences significantly the reactivity of the monomer due to steric and electronic effects. While the presence of substituents on polyacetylenes generally reduces the conjugation because of the twist of the main chain caused by the repulsion between the pendant groups, the introduction of condensed aromatic rings tends to give highly conjugated and well-defined polymers, with stacking of the pendant groups [18,19].

As a part of a continuing research effort in the development of new materials for molecular electronics [20,21], we decided to prepare novel polyacetylenes with pendant pyrenyl groups bound directly to the main chain (PEP) or indirectly via an additional acetylene linkage (PBDP). We also decided to study the polymerization of disubstituted acetylenes bearing a trimethylsilyl group on one side and the pyrenyl group on the other (PTMSEP, PTMSBDP). We expected that the presence of either a trimethylsilyl group and/or an additional triple bond could

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influence the physical and optical properties of the resulting polymers by causing a distortion in the main chain due to steric effects. Besides, the trimethylsilyl group can be replaced by other useful functional groups such as Br, OH, OR, etc. that could be useful to graft the polymer backbone [22]. In addition, we synthesized an oligomeric analogue of PEP containing only two repeat units ( $DP = 2$ ), called here DEP, in order to elucidate the influence of the conjugation on the optical properties. These new architectures will serve as models for the development of conducting polymers with extended stacking of aromatic moieties bearing functional groups capable of stabilizing the formation of radical-cations.

In this paper, we report the synthesis of four different monomers, 1-(trimethylsilylethynyl)pyrene (**2**), 1-ethynylpyrene (**3**), 1-(4-trimethylsilylbuta-1,3-diyne)pyrene (**4**) and 1-(buta-1,3-diyne)pyrene (**5**), and their polymerizations using W and Ta catalysts. The synthesis and polymerization of 1-ethynylpyrene (**3**) presented in this paper is more efficient than that previously reported by Masuda et al. [17] Different co-catalysts have been used and the reaction conditions have been optimized to obtain polymers of higher molecular weights. The thermal, optical and photophysical properties of the polymers are also reported. Electronic interactions between adjacent pendant pyrene groups linked to the polyacetylene chains are discussed in terms of the steric effects present along the polymer backbone.

## 2. Experimental section

All the reagents and catalysts used in the synthesis were purchased from Aldrich and used as received. Triethylamine spectroscopic grade purchased from the same company was used as a solvent in Sonogashira's couplings. Toluene used in the polymerizations was dried with metallic sodium prior to use.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the monomers were recorded in solution on a Bruker ARX-400 spectrometer. Solid state  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the polymers were recorded on a Bruker DRX 700 narrow-bore spectrometer. The  $^1\text{H}$  NMR spectra were obtained by the use of a double resonance MAS probe supporting rotors of outer diameter 2.5 mm operating at a  $^1\text{H}$  Larmor frequency of 700 MHz. Fast magic angle spinning (MAS) at 30 kHz was used. The NMR relaxation delay was adjusted to allow the complete relaxation of the NMR signals. IR spectra were recorded on a Nicolet FTIR 5 DXB spectrometer. The molecular weights of the polymers (relative to polystyrene) were determined on a Waters 510 liquid chromatograph equipped with  $\mu$ -styragel columns and a Waters 410 differential refractometer detector. MALDI-TOF spectra were carried out with a Reflex II Bruker spectrometer. Thermal properties of the polymers such as stability, glass transition temperature ( $T_g$ ) and melting point ( $T_m$ ) were determined by thermo-

gravimetric analysis (TGA), from 0 to 1000 °C, and differential scanning calorimetry (DSC), from -40 to 400 °C. The melting points ( $T_m$ ) were determined on a TA Instruments DSC 2910 and thermal stabilities ( $T_{10}$ , 10% weight loss temperature) on a TA Instruments Hi-Res TGA 2950.

Absorption spectra were recorded in tetrahydrofuran (THF) solutions on a Varian Cary 1 Bio UV-visible spectrophotometer (model 8452A) using 1 cm quartz cells and solution concentrations of  $1-3 \times 10^{-5}$  M. It has been verified that the Beer-Lambert law applies for the concentrations used. Fluorescence spectra, corrected for the emission detection, were recorded in THF solutions on a Spex Fluorog-2 spectrophotometer with a F2T11 special configuration. Each solution was excited near the absorption wavelength maximum using a 1 cm quartz cell and the concentration used for each polymer studied was  $1-3 \times 10^{-6}$  M, giving absorbances less than 0.1 to avoid any inner filter effect. Prior to use, the solvent (Aldrich, spectroscopic grade) was checked for spurious emission in the region of interest and found to be satisfactory. Fluorescence lifetimes were measured on a multiplexed time-correlated single photon counting fluorimeter (Edinburgh Instruments, model 299T). Details on the instrument have been published elsewhere [23]. The instrument incorporates an all-metal coaxial hydrogen flashlamp. Reconvolution analysis was performed by fitting over all the fluorescence decay including the rising edge. The kinetic interpretation of the goodness-of-fit was assessed using plots of weighted residuals, reduced  $\chi^2$  value, and Durbin-Watson (DW) parameters. The steady-state fluorescence and lifetime measurements were performed in argon-saturated solutions of the substrates at 298 K.

1-Iodopyrene (**1**). 1-Aminopyrene (**2**) (8.0 g, 37 mmol) was suspended in 100 ml of a HCl/H<sub>2</sub>O (1:2) mixture with vigorous stirring at 0 °C. A solution of NaNO<sub>2</sub> (2.56 g, 37.1 mmol) in water (12 ml) was added in small portions. After 5 min, a solution of KI (6.2 g, 37 mmol) was added to the reaction mixture. The ice bath was removed, the reaction mixture was stirred for 2 h at room temperature and then heated to 60 °C for 1 h. The crude product was separated by filtration, dissolved in ether and washed with a concentrated solution of Na<sub>2</sub>SO<sub>3</sub>. The ether solution was dried with MgSO<sub>4</sub> and concentrated under vacuum. The resulting product was purified by flash column chromatography on silica by eluting with hexanes. 1-Iodopyrene (**1**) was obtained as a white yellowish solid (6.04 g, 50%). Mp 82–83 °C (Lit. 85–87 °C [24]). IR (KBr):  $\nu = 2982$ , 1570, 1425, and 835 cm<sup>-1</sup>.  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 8.45$  (d, 1H, Py-H (*ortho*),  $J = 8.1$  Hz), 8.44–7.95 (m, 7H, Py-H) and 7.79 (d, 1H, Py-H,  $J = 8$  Hz) ppm.  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 136.55$ , 132.32, 131.18, 130.79, 129.18, 127.79, 127.25, 126.89, 126.27, 125.77, 125.63, 125.42, 125.26, 124.81, 123.69, and 96.16 ppm (aromatic carbons). Elemental analysis: Calcd for C<sub>16</sub>H<sub>9</sub>I: C, 58.56%; H, 2.76%. Found: C, 58.60%; H, 2.76%.

1-(Trimethylsilyl)ethynylpyrene (**2**). To a suspension of Pd(PPh<sub>3</sub>)<sub>4</sub> (0.12 g, 0.10 mmol) and CuI (0.2 g, 1 mmol) in triethylamine (50 ml), 1-iodopyrene (**1**) (2.0 g, 6.1 mmol) was added under argon atmosphere. After 10 min, trimethylsilylacetylene (0.6 g, 6 mmol) was added and the reaction mixture was stirred at room temperature for 5 h. The resulting mixture was extracted with ether, washed with a NH<sub>4</sub>Cl saturated solution, dried with MgSO<sub>4</sub> and concentrated under vacuum. The desired product was purified by flash column chromatography on a silica gel column by eluting with hexanes. 1-(Trimethylsilyl)ethynylpyrene (**2**) (1.63 g, 95%) was obtained as a beige solid. Mp 98–99 °C (Lit. 102–103 °C [25]). IR (KBr):  $\nu = 3044, 2956, 2150$  (C≡C), 1598, 1250, 1183, 896, and 846 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 8.58$  (d, 1H, Py-H (*ortho*),  $J = 9$  Hz), 8.24–8.01 (m, 8H, Py-H) and 0.41 (s, 9H, Si (CH<sub>3</sub>)<sub>3</sub>) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 132.12, 131.22, 130.99, 130.82, 129.75, 128.24, 128.04, 127.00, 126.01, 125.50, 125.42, 125.32, 124.22, 124.15, 124.02, 117.43$ , (aromatic carbons), 104.26 (≡C–SiMe<sub>3</sub>), 88.18 (Py–C≡), and 0.08 (Si(CH<sub>3</sub>)<sub>3</sub>) ppm. Elemental analysis: Calcd for C<sub>21</sub>H<sub>18</sub>Si: C, 84.51%; H, 6.08%. Found: C, 84.37%; H, 6.03%.

1-Ethynylpyrene (**3**). A solution of 1-(trimethylsilyl)ethynylpyrene (**2**) (0.5 g, 2 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.5 g, 4 mmol) in a 1:1 methanol/benzene mixture (40 ml) was prepared and heated to reflux for 4 h. The resulting mixture was filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography by eluting with hexanes. 1-Ethynylpyrene (**3**) (0.36 g, 100%) was obtained as a light brown solid. mp 110–112 °C (Lit. 116–117 °C [26]). IR (KBr):  $\nu = 3296$  (≡C–H), 2982, 2198 (C≡C), 1594, 1182, and 836 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 8.60$  (d, 1H, Py-H (*ortho*),  $J = 9$  Hz), 8.24–8.01 (m, 8H, Py-H) and 3.63 (s, 1H, C≡C–H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 132.31, 131.41, 130.98, 130.79, 129.97, 128.37, 128.22, 126.99, 126.10, 125.56, 125.51, 125.12, 124.20, 124.15, 124.00, 116.32$  (aromatic carbons), 82.64 (Py–C≡) and 82.45 (≡C–H) ppm. Elemental analysis: Calcd for C<sub>18</sub>H<sub>10</sub>: C, 95.54%; H, 4.45%. Found: C, 95.39%; H, 4.45%.

1-(4-Trimethylsilylbuta-1,3-diynyl)pyrene (**4**). A suspension of Pd(PPh<sub>3</sub>)<sub>4</sub> (0.51 g, 0.44 mmol) and CuI (0.168 g, 1.17 mmol) in triethylamine (90 ml) was prepared and stirred under argon atmosphere. 1-Iodo-2-trimethylsilylacetylene (2.0 ml, 3.0 g, 13 mmol) and 1-ethynylpyrene (**3**) (3.0 g, 13 mmol) were dissolved in a minimum amount of benzene and the solution was added to the suspension. The reaction mixture was stirred for 24 h at room temperature. The resulting mixture was filtered, extracted with ether and washed with a saturated solution of NH<sub>4</sub>Cl. The organic phase was dried with MgSO<sub>4</sub> and concentrated under reduced pressure. The desired product was purified by flash column chromatography on a silica gel column by eluting with hexanes. 1-(4-Trimethylsilylbuta-1,3-diynyl)pyrene (**4**) (1.7 g, 40%) was obtained as dark yellow solid. mp 130–

131 °C. IR (KBr):  $\nu = 3041, 2954, 2189$  (C≡C), 2088 (C≡C), 1593, 1584, 1246, 850, and 837 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 8.55$  (d, 1H, Py-H (*ortho*),  $J = 8$  Hz), 8.24–8.22 (m, 8H, Py-H) and 0.31 (s, 9H, SiCH<sub>3</sub>) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 133.37, 131.74, 130.94, 130.76, 130.53, 128.69, 128.63, 126.95, 126.21, 125.80, 125.72, 125.07, 124.28, 124.09, 123.87, 115.38$  (aromatic carbons), 92.07 (≡C–SiMe<sub>3</sub>), 88.08 (Py–C≡), 79.36 (Py–≡C); 76.96 (–C≡–TMS) and –0.42 (SiCH<sub>3</sub>) ppm. Elemental analysis: Calcd for C<sub>23</sub>H<sub>18</sub>Si: C, 85.66%; H, 5.62%. Found: C, 85.39%; H, 5.59%.

1-Buta-1,3-diynylpyrene (**5**). A solution of 1-(4-trimethylsilylbuta-1,3-diynyl)pyrene (**4**) (1.7 g, 5.2 mmol) and K<sub>2</sub>CO<sub>3</sub> (1.5 g, 11 mmol) in 100 ml of a 4:1 ether/methanol mixture was prepared and stirred at room temperature for 24 h. Ether was removed under reduced pressure and the desired product precipitated from methanol. The solid was separated by filtration and washed with methanol. 1-Buta-1,3-diynylpyrene (**5**) (1.3 g, 100%) was obtained as a light and air sensitive yellow solid. Mp Decomposes at 91 °C. IR (KBr):  $\nu = 3262$  (≡C–H), 2195 (C≡C), 1596, 1581, 1237, 1187, 844, 821, 757, and 714 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 8.54$  (d, 1H, Py-H (*ortho*),  $J = 9$  Hz), 8.29–8.02 (m, 8H, Py-H) and 2.7 (s, 1H, C≡CH) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 133.44, 131.86, 130.90, 130.70, 130.57, 128.79, 128.71, 126.92, 126.23, 125.86, 125.78, 124.87, 124.24, 124.03, 123.81, 114.89$  (aromatic carbons), 78.60 (Py–C≡), 74.73 (C≡–H), 72.63 (≡C–H) and 68.40 (Py–≡C) ppm. Elemental analysis: Calcd for C<sub>20</sub>H<sub>10</sub> (251.01): C, 95.97%; H, 4.02%. Found: C, 95.89%; H, 4.01%.

*Polymerization of non-silylated monomers.* The catalyst (0.15 mmol) and the co-catalyst (0.3 mmol) were transferred into a Schlenk tube under argon. A solution of non-silylated monomer (6 mmol) in 30 ml of dry toluene was added. The reaction mixture was stirred at room temperature for 24 h. The desired polymer was precipitated from a large excess of methanol, separated by filtration and dried under vacuum.

PEP was obtained as a dark purple polymer, totally soluble in *o*-dichlorobenzene, very soluble in THF, partially soluble in toluene and CHCl<sub>3</sub>, and totally insoluble in DMF. For PEP-3: IR (KBr):  $\nu = 3035.9$  (≡C–H stretching), 1598 (C=C stretching), 1583, 1487, 1455.2, 1433, 1414 (C–H bending), 1297, 1242, 1176, 1141, 1080, 839 (C=C–H out of plane bending), 753, 719, and 681 cm<sup>-1</sup>. <sup>1</sup>H NMR (solid state, 700 MHz):  $\delta = 7$  (aromatic protons) ppm. <sup>13</sup>C NMR (solid state, 175 MHz):  $\delta = 137$  and 125 (sp<sup>2</sup> carbons) ppm. UV (THF):  $\lambda_{\max} = 345$  and 565 nm. Elemental analysis: Calcd for (C<sub>18</sub>H<sub>10</sub>)<sub>*n*</sub>: C, 95.54%; H, 4.45%. Found: C, 94.29%; H, 4.39%.

PBDP was obtained as a dark brown polymer, totally soluble in THF, *o*-dichlorobenzene, toluene, and CHCl<sub>3</sub> and partially soluble in DMF. For PBDP-2: IR (KBr):  $\nu = 3037$  (≡C–H stretching), 2170 (C≡C), 1920, 1596 (C=C stretching), 1582, 1486, 1457, 1434 (C–H bending), 1241,

1187, 967, 842 (C=C–H out of plane bending), 755 and 715  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (solid state, 700 MHz):  $\delta = 7$  (aromatic and vinylic protons) ppm.  $^{13}\text{C}$  NMR (solid state, 175 MHz):  $\delta = 137, 125$  ( $\text{sp}^2$  carbons) ppm. UV (THF):  $\lambda_{\text{max}} = 390$  nm.

**Synthesis of the dimer of 1-ethynylpyrene (DEP), 1,3-di(1-pyrenyl)-1,3-butadiene.**  $\text{WCl}_6$  (0.59 g, 1.5 mmol) was dissolved in the minimum amount of toluene in a Schlenk tube under argon. The solution was cooled to  $-78^\circ\text{C}$  in a dry ice-acetone bath. A solution of 1-ethynylpyrene (0.74 g, 3.3 mmol) in 60 ml of dry toluene was added with vigorous stirring. After 10 min, the ice bath was removed and the reaction mixture was stirred at room temperature for 24 h. The desired product, DEP, was precipitated from methanol, separated by filtration and dried under reduced pressure. Crude DEP (0.52 g, 70%) was obtained as a brown powder which was purified by flash column chromatography on silica gel, using a mixture of hexanes/ethyl acetate (1:4) as the eluent. IR (KBr):  $\nu = 3035$  (=C–H stretching), 1598 (C=C stretching), 1583, 1487, 1455.2, 1433, 1414 (C–H bending), 1297, 1242, 1176, 1141, 1080, 839 (C=C–H out of plane bending), 753, 719, and 681  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.65$ – $7.59$  (m, aromatic and vinylic protons) ppm. UV (THF):  $\lambda_{\text{max}} = 346$  nm. LRMS:  $m/z = 454$  ( $\text{M}^+$ ). Elemental analysis: calcd for  $\text{C}_{36}\text{H}_{22}$ : C, 95.12; H, 4.87. Found: C, 94.83; H, 4.59.

**Polymerization of silylated monomers.** The catalyst (0.3 mmol) and the co-catalyst (0.6 mmol) were transferred into a Schlenk tube under argon. A solution of silylated monomer (7.5 mmol) in 15 ml of dry toluene was added. The reaction mixture was stirred at  $80^\circ\text{C}$  for 24 h. The desired polymer was precipitated from methanol and separated by filtration.

PTMSEP was obtained as a light brown oligomer, totally soluble in THF, *o*-dichlorobenzene, toluene, and  $\text{CHCl}_3$ , and partially soluble in DMF. For PTMSEP-1: IR (KBr):  $\nu = 3039$  (=C–H stretching), 2922 ( $\text{Si}(\text{CH}_3)_3$ ), 2190 (C≡C), 1598 (C=C stretching), 1583, 1487, 1456, 1434 (C–H bending), 1414, 1247, 1179, and 842 (C=C–H out of plane bending)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (solid state, 700 MHz):  $\delta = 7.0$  (aromatic protons), 0.0 ( $\text{Si}(\text{CH}_3)_3$ ) ppm.  $^{13}\text{C}$  NMR (solid state, 175 MHz):  $\delta = 137, 125$  ( $\text{sp}^2$  carbons) and 0 ( $\text{Si}(\text{CH}_3)_3$ ) ppm. UV (THF):  $\lambda_{\text{max}} = 348$  nm.

PTMSBDP was obtained as a yellowish brown oligomer totally soluble in *o*-dichlorobenzene, partially soluble in THF and toluene, almost insoluble in  $\text{CHCl}_3$  and insoluble in DMF. For PTMSBDP-2: IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 3040 (≡C–H stretching), 2953 ( $\text{Si}(\text{CH}_3)_3$ ), 2100 (C≡C), 2093 (C≡C), 1598 (C=C stretching), 1583, 1504, 1486, 1457, 1434 (C–H bending), 1416, 1248 and 843 (C=C–H out of plane bending), 756 and 715.  $^1\text{H}$  NMR (solid state, 700 MHz):  $\delta$  (ppm) = 7.0 (aromatic protons), 0.0 ( $\text{Si}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR (solid state, 175 MHz):  $\delta$  (ppm) = 137, 125 ( $\text{sp}^2$  carbons) and 0 ( $\text{Si}(\text{CH}_3)_3$ ). UV (THF):  $\lambda_{\text{max}} = 384$  nm.

## 3. Results and discussion

### 3.1. Monomer synthesis

The synthesis of the four monomers, 1-ethynylpyrene (**3**), 1-(trimethylsilyl)ethynylpyrene (**2**), 1-(4-trimethylsilylbutyl)pyrene (**4**) and 1-butyl-1,3-diynepyrene (**5**), was accomplished using 1-iodopyrene (**1**) as the starting material (Fig. 1). Iodopyrene (**1**) was synthesized from 1-aminopyrene via a diazotization reaction followed by a nucleophilic substitution with KI. Sonogashira's Pd-catalyzed coupling [25] of **1** with trimethylsilylacetylene gave 1-(trimethylsilyl)ethynylpyrene (**2**) with a 90% yield. The trimethylsilyl group was quantitatively removed with  $\text{K}_2\text{CO}_3$  in methanol to give 1-ethynylpyrene (**3**). The synthesis of the two last monomers was carried out from **3** by Pd-coupling with 1-iodo-2-trimethylsilylacetylene to give 1-(4-trimethylsilylbutyl)pyrene (**4**). The yield of this step was low, about 40%, due to the competitive formation of dimers resulting from the Eglinton and Ullmann couplings. Finally **4** was deprotected in basic medium, under the same reaction conditions as for **2** to afford 1-(butyl-1,3-diyne)pyrene (**5**). All monomers were stable under normal conditions but **5**, which is a photo- and air-sensitive compound that decomposes rapidly. Therefore it must be prepared immediately prior to use.

### 3.2. Polymer synthesis and characterization

The polymerizations of mono- and disubstituted acetylenes can be carried out by the use of W and Ta catalysts, which are both effective in the polymerization of various arylacetylenes. The reaction takes place by a metal carbene mechanism or by insertion depending on the nature of the catalyst [14]. In some cases, a co-catalyst can be added in order to improve the yields and the molecular weights.

Non-silylated monomers **3** and **5** were polymerized in solution at room temperature using  $\text{WCl}_6$  as catalyst and  $\text{Ph}_4\text{Sn}$ ,  $\text{Ph}_3\text{Bi}$ , or  $\text{Bu}_4\text{Sn}$  as co-catalyst. Polymerization of

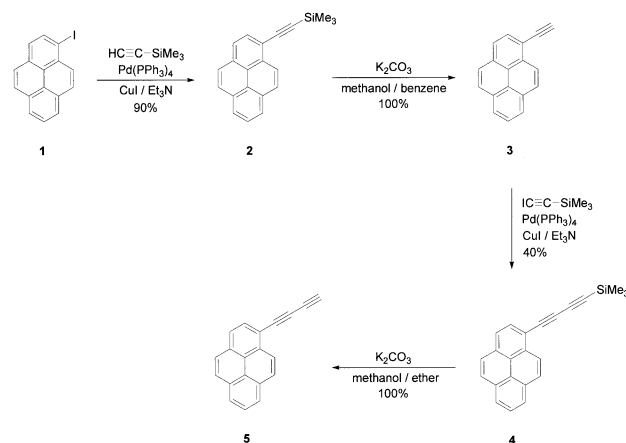


Fig. 1. Synthesis of the monomers.

silylated monomers **2** and **4** was accomplished with  $\text{TaCl}_5$ , sometime in the presence of  $\text{Bu}_4\text{Sn}$ . We prepared four different polymers, poly(1-ethynylpyrene) (PEP), poly(1-(trimethylsilyl-ethynyl)pyrene) (PTMSEP), poly(1-(4-(trimethyl-silyl-but-1,3-diynyl)pyrene) (PTMSBDP) and poly(1-buta-1,3-diynylpyrene) (PBDP). The structures of these polymers are shown in Fig. 2.

The molecular weights of our polymers were determined by size exclusion chromatography (SEC) in THF relative to polystyrene standards. This solvent was more appropriate than  $\text{CHCl}_3$  because all polymers were almost totally soluble in THF. As shown in Table 1, the poly(1-ethynylpyrene) (PEP) obtained in our polymerization possesses low to high molecular weights depending on the conditions used. The best results ( $M_w = 400 \text{ kg mol}^{-1}$ ) were obtained when  $\text{WCl}_6$  was used as catalyst and  $\text{Ph}_3\text{Bi}$  as co-catalyst, with a catalyst/co-catalyst/monomer ratio of 1:2:40 in toluene at room temperature for 24 h. When  $\text{Bu}_4\text{Sn}$  was used as co-catalyst, a high molecular weight was also obtained ( $M_w = 277 \text{ kg mol}^{-1}$ ) together with a larger polydispersity,  $M_w/M_n = 10$ . PEP polymers were partially soluble in  $\text{CHCl}_3$ , very soluble in THF and totally soluble in *o*-dichlorobenzene. Films with good optical properties can be cast from *o*-dichlorobenzene solutions, whereas films cast from THF solutions were opaque and fragile. PEP polymers obtained under these conditions are dark purple. This color is the result of the high conjugation of the *trans*-PEP main chain [17], not a charge transfer complex (vide infra).

The dimer of 1-ethynylpyrene (DEP) was also prepared

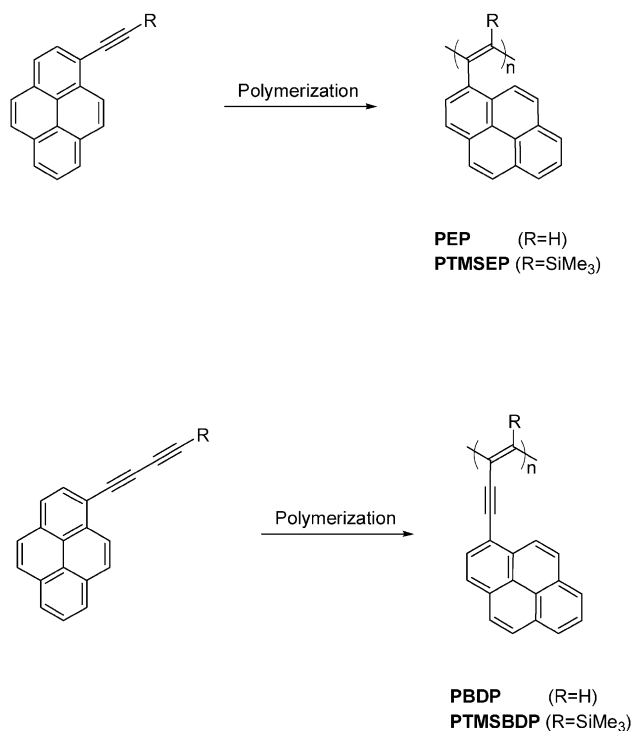


Fig. 2. Structures of synthesized polymers (the geometry of the main chain is not necessarily as depicted).

by the treatment of the monomer **3** with  $\text{WCl}_6$  using a monomer/catalyst ratio of 2.2:1. The dimer was isolated from the reaction mixture by flash chromatography with a 70% yield. DEP was used in spectroscopic studies (vide infra) as a model compound for PEP without the extended conjugation.

By contrast, PEP's analogue poly(1-(buta-1,3-diynyl)pyrene) (PBDP), bearing an additional triple bond, also polymerized with  $\text{WCl}_6$ , displayed lower molecular weights, around  $6 \text{ kg mol}^{-1}$ . This polymer is dark brown and totally soluble in THF,  $\text{CHCl}_3$ , and *o*-dichlorobenzene. This high solubility is an indication that no significant cross-linking took place during or after the polymerization.

The silylated monomers were polymerized using  $\text{TaCl}_5$  with or without  $\text{Bu}_4\text{Sn}$  as a co-catalyst. The molecular weights and yields of poly(1-trimethylsilyl-ethynylpyrene) (PTMSEP) and poly(1-(4-trimethylsilylbuta-1,3-diynyl)pyrene) (PTMSBDP) were quite low. The former was soluble in the same solvents as its non-silylated homologues, while the solubility of the latter in THF,  $\text{CHCl}_3$  and other organic solvents was fairly poor. Silylated polymers were yellowish brown due to the low degree of conjugation. As can be expected, the presence of the TMS group reduces dramatically the reactivity of the monomers towards polymerization because of steric effects.

The polymers were characterized by IR, solid state  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopies and by MALDI-TOF mass spectrometry. Even though most of the polymers were soluble in THF, the signals were difficult to detect by  $^1\text{H}$  NMR spectroscopy in solution. This extreme broadening of the signals in the NMR spectra of polyarylacetylenes is preceded [27]. The phenomena is attributed to the presence of unpaired radicals due to the disruption of some C=C bond and also, to a certain extent, to the slow molecular motion of the polymer chain due to rigid *trans*-conjugated sequences. Better results were obtained with solid state NMR. Therefore, high resolution solid state  $^1\text{H}$  NMR spectra of polymers PEP (PEP-3) and PTMSEP (PTMSEP-1) were recorded on a 700 MHz NMR spectrometer (Fig. 3). Even with fast MAS and ample relaxation delay, the proton signals are seen as relatively broad, but it still represents a major improvement in comparison with the  $^1\text{H}$  solid state NMR signals obtained at lower spinning rates. PEP, a polymer containing only aromatic and vinylic protons, displayed only one large band centered around 7 ppm, while PTMSEP displayed two wide signals centered at 7 and 0.5 ppm corresponding to the aromatic and main chain protons together with the protons of the TMS groups, respectively.

The solid state  $^{13}\text{C}$  NMR spectrum of PEP (Fig. 4) showed broad signals at 125 and 137 ppm, belonging to the  $\text{sp}^2$  carbons of the polymer. The spectrum of PTMSEP exhibited two signals centered at 125 and 0 ppm belonging, respectively, to the  $\text{sp}^2$  carbons and the carbons of the TMS groups. The spectra of PBDP (wide band at 124 ppm) and PTMSBDP (two signals at 125 and  $-2.8$  ppm) were very

Table 1  
Polymerization conditions and results, and thermal properties of the polymers

Polymer	Catalysts	$M_n^a$	$M_w^a$	$M_w/M_n$	DP <sup>b</sup>	Yield (%)	$T_{10}$ (°C) <sup>c</sup>	$T_m$ (°C) <sup>d</sup>
<i>PEP</i> <sup>e</sup>								
PEP-1	WCl <sub>6</sub>	8.3	24	2.9	106	70	381	330
PEP-2	WCl <sub>6</sub> /Ph <sub>4</sub> Sn	6.1	27	4.5	122	71	383	330
PEP-3	WCl <sub>6</sub> /Ph <sub>3</sub> Bi	238	470	1.9	2081	95	385	330
PEP-4	WCl <sub>6</sub> /Bu <sub>4</sub> Sn	26	277	11	1227	60	389	327
<i>PTMSEP</i> <sup>f</sup>								
PTMSEP-1	TaCl <sub>5</sub>	1.1	2.0	1.8	6	5	393	
PTMSEP-2	TaCl <sub>5</sub> /Bu <sub>4</sub> Sn	1.1	1.4	1.3	7	4	294	
<i>PBDP</i> <sup>e</sup>								
PBDP-1	WCl <sub>6</sub>	3.6	5.1	1.4	20	32	533	
PBDP-2	WCl <sub>6</sub> /Ph <sub>3</sub> Bi	4.4	6.3	1.4	26	22	816	
<i>PTMSBDP</i> <sup>f</sup>								
PTMSBDP-1	TaCl <sub>5</sub>	0.5	1.3	2.4	4	7	497	
PTMSBDP-2	TaCl <sub>5</sub> /Bu <sub>4</sub> Sn	0.7	1.9	2.9	6	13	496	

<sup>a</sup> Molecular weights are given in kg mol<sup>-1</sup>. Fraction insoluble in methanol. Obtained by SEC (THF, polystyrene standard).

<sup>b</sup> Degree of polymerization.

<sup>c</sup> 10% weight loss temperature obtained by TGA (heating rate 10 °C min<sup>-1</sup>).

<sup>d</sup> Melting point obtained by DSC (heating rate 20 °C min<sup>-1</sup>).

<sup>e</sup> Toluene, 25 °C, 24 h, [M] = 0.2 M, [Cat] = 5 mM, [Co-cat] = 10 mM.

<sup>f</sup> Toluene, 25 °C, 24 h, [M] = 0.5 M, [Cat] = 20 mM, [Co-cat] = 40 mM.

similar to those of their analogues PEP and PTMSEP. The signals expected from the quaternary carbons of the additional triple bond are too weak to be observed. The presence of this additional triple bond was confirmed by IR spectroscopy. The IR spectrum of PBDP contains a band at 2100 cm<sup>-1</sup>, characteristic of a C=C bond. In the IR spectrum of PBDP, the absence of a band at 3300 cm<sup>-1</sup>, characteristic of terminal alkynes, is also proof that the polymerization took place exclusively at the terminal triple bond. For PTMSEP, the IR spectrum displays two bands at 2190 and 2093 cm<sup>-1</sup> belonging to two different C=C bonds.

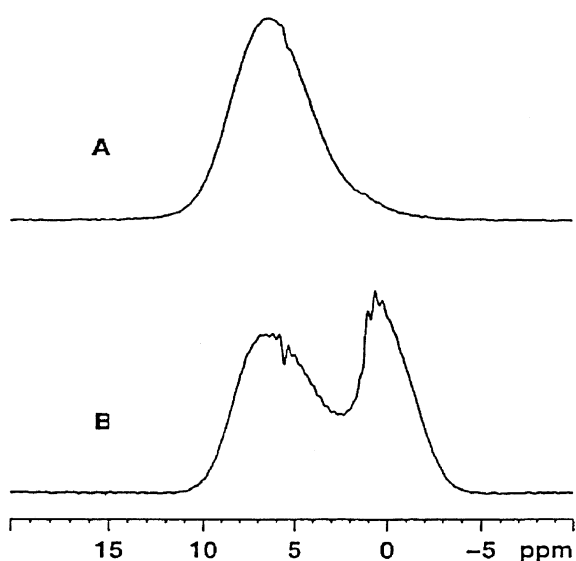


Fig. 3. Solid state <sup>1</sup>H NMR spectra of the synthesized polymers obtained with fast magic angle spinning at 30 kHz: (A) PEP, (B) PTMSEP.

This is an indication that the polymerization occurred at both triple bonds, leading to a polymer which is not regioregular as shown in Fig. 2.

Molecular weight analysis of our rigid polymers by SEC may give overestimated values since polystyrene was used as standard in the absence of more appropriate ones. The polymers were therefore analyzed by MALDI-TOF mass spectrometry [28,29] in an effort to determine the molecular weight distribution more accurately. Unfortunately, only the lower range of molecular weights could be observed with

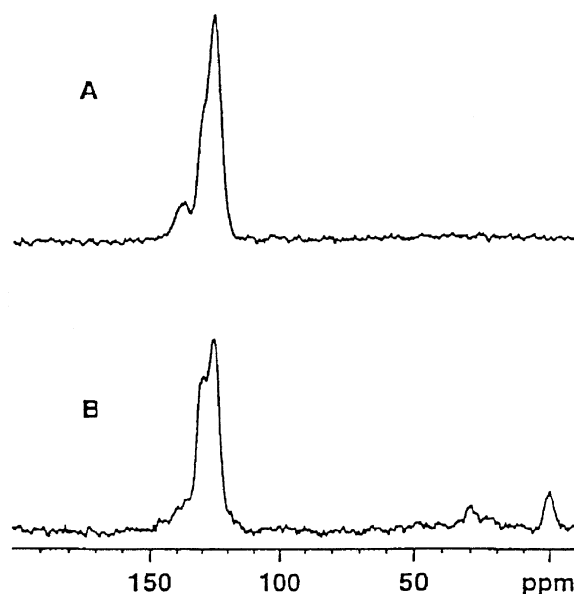


Fig. 4. Solid state <sup>13</sup>C NMR spectra of the synthesized polymers obtained with fast magic angle spinning: (A) PEP, (B) PTMSEP.

this technique. However, the pattern of molecular weights observed confirmed the structure of the polymers. For instance, the MALDI-TOF spectrum of PEP exhibits four peaks ( $m/z = 226, 451, 678, 901$ ) belonging to the monomer, dimer, trimer, and tetramer, respectively. Similarly the mass spectrum of PTMSEP displays a sequence of peaks at multiples of the mass of the monomer,  $(298)_n$ , accompanied in most cases by the loss of TMS. The presence of catalyst as end-group was not detected either for PEP or PTMSEP.

### 3.3. Thermal properties of the polymers

No glass transition was observed with DSC within the temperature range studied, even when the samples were quenched in liquid nitrogen. As shown in Table 1, PEP polymers display a good thermal stability, with a 10% weight loss at 380 °C ( $T_{10}$ ) and almost complete degradation at 800 °C. PEP polymers show an endothermic peak in DSC around 330 °C attributed to the melting or the softening of the polymers. Despite their low molecular weights, PBDP polymers exhibit a higher thermal stability, with a  $T_{10}$  at 533 and 816 °C for PBDP-1 and PBDP-2, respectively. Silylated polymers, PTMSEP and PTMSBDP, are also thermally stable, bearing a  $T_{10}$  of 392 and 496 °C, respectively. For these latter polymers, no  $T_m$  was observed in the range of  $-40$  to 400 °C. This means they could either have a very high melting temperature or be infusible. The addition of another triple bond to both the silylated and non-silylated monomers increases the thermal stability of the resulting polymers (Fig. 5). Indeed, one sample of PBDP studied has lost only 10% of its mass at 816 °C while the other polymers more than 50%.

### 3.4. Optical and photophysical properties of the polymers

The absorption spectrum of PEP in THF is shown in Fig. 6(A). For comparison, Fig. 6(A) also shows the

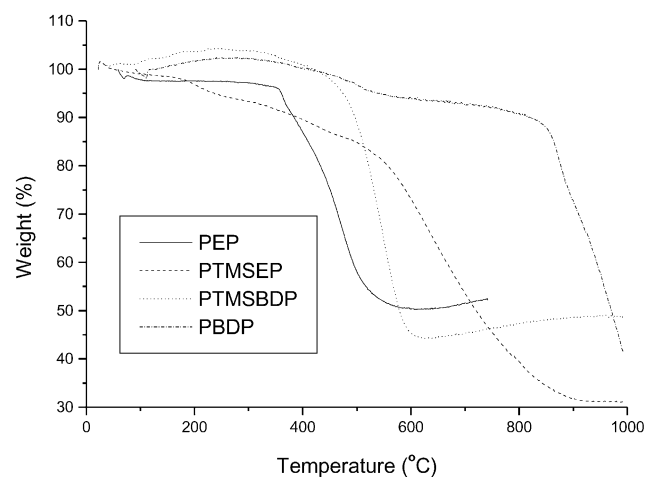


Fig. 5. TGA curves of the synthesized polymers (from 0 to 1000 °C, heating rate 20 °C min<sup>-1</sup>).

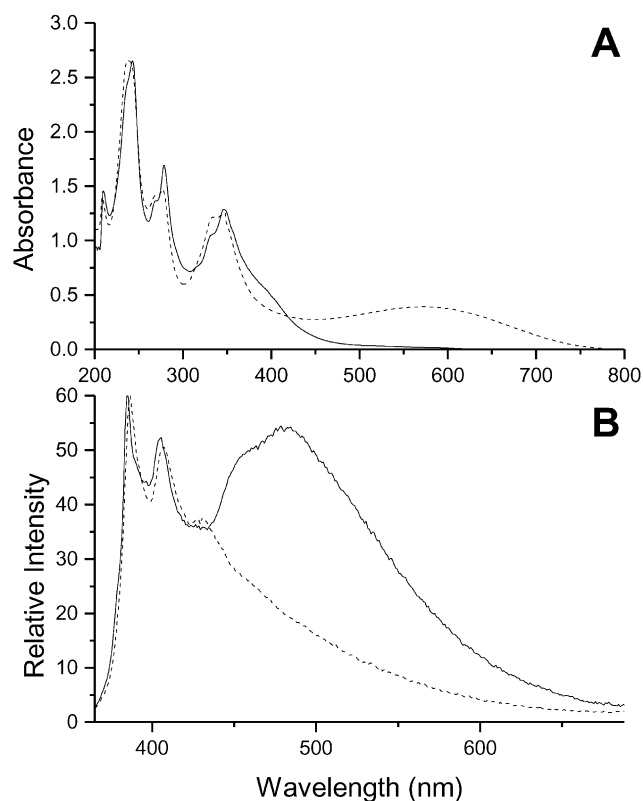


Fig. 6. Absorption (A) and fluorescence spectra (B) of DEP (—) and PEP (---) in THF.

absorption spectrum of the dimer of 1-ethynylpyrene (DEP). The peak at 336 nm in the absorption spectrum of DEP can be attributed to the pyrene moieties [30] whereas the peak at 346 nm and the shoulder around 390 nm should have their origin in intramolecular interactions (complexation) between the two pyrene units present in the dimer. One can see in Fig. 6(A) that the absorption spectrum of PEP is significantly different from that of DEP. Indeed, the shoulder around 390 nm observed in the absorption spectrum of DEP is not observed in the absorption spectrum of PEP. This suggests that intramolecular interactions between adjacent pyrene units in the polymer are weaker than those observed in DEP. Moreover, a broad band is observed around 580 nm, which is not present for DEP. We believe that this band is caused by the polyacetylene chain, which would indicate that the effective electronic conjugation is relatively long for this polymer. Indeed, results obtained from ZINDO/S calculations performed in our laboratory using Zerner's software [31,32] show that 10–12 repetitive units could reproduce the energy of this band. However, charge transfer complexes from pyrene units to the main chain could be also responsible for the long wavelength band. To check this possibility, the absorption spectrum of the polymer has been measured in chloroform, which is a solvent less polar ( $\epsilon = 4.8$ ) than THF ( $\epsilon = 7.58$ ) [33]. The spectra were found to be identical, which is against spectral properties of a charge transfer band. Indeed, a charge transfer band should be red-shifted in more polar

environments [34]. Moreover, iodine has been added to solutions of PEP in THF in order to oxidize this material, without causing any significant spectral changes. A charge transfer band should be much affected by the oxidation of the polymer [35].

The fluorescence spectra of DEP and PEP are shown in Fig. 6(B). Both compounds show a band in the 360–465 nm region, which is due to non-associated pyrene units [30]. DEP also shows a broad band near 480 nm, which should involve molecular interactions between pyrene units present in this molecule [36]. Surprisingly, such a distinct band is not observed in the fluorescence spectrum of PEP. However, the fluorescence intensity of PEP near 480 nm is significant whereas pyrene itself does not emit at this wavelength [30]. This strongly suggests that a complex between pyrene units is also formed in the polymer. We believe that the absence of a distinct band around 480 nm is caused by an inner-filter effect involving the main chain.

In order to distinguish between the formation of an excited dimer or an excimer, the excitation spectra of DEP and PEP have been measured at  $\lambda_F = 404$  nm and 480 nm and are shown in Fig. 7(A) and (B), respectively. One can see that the spectra measured at  $\lambda_F = 480$  nm are much different from those measured at  $\lambda_F = 404$  nm. These results are not in favor of the formation of an excimer, which should have an excitation spectrum identical to that of the non-associated pyrene unit. The fluorescence profiles have also been recorded at these two fluorescence wavelengths and the results of the kinetic analysis are compiled in Table 2. The best fits obtained for these decays are complex and involve a triexponential expression. The fluorescence decays recorded at  $\lambda_F = 480$  nm do not show any rising component, which should be observed for an

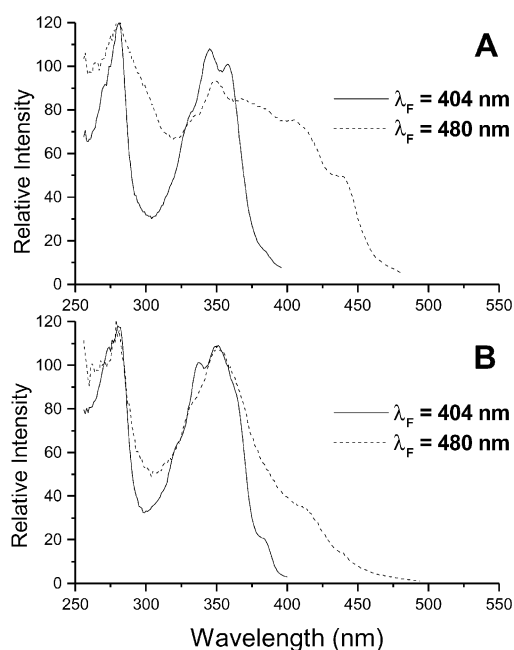


Fig. 7. Excitation spectra of DEP (A) and PEP (B) in THF.

Table 2

Fluorescence decay parameters of DEP and PEP in THF at room temperature (298 K)

Polymer	$\lambda_{exc}$ (nm)	$\lambda_F$ (nm)	$\tau_F$ (ns)	$B^a$	$f^b$	$\chi^2$
DEP	346	404	$\tau_1^c = 1.07$	$B_1 = 0.40$	0.052	1.40
			$\tau_2^c = 7.13$	$B_2 = 0.41$	0.352	
			$\tau_3^c = 26.2$	$B_3 = 0.19$	0.569	
			$\langle \tau_F \rangle^d = 18.2$			
	346	480	$\tau_1^c = 0.41$	$B_1 = 0.54$	0.142	1.02
			$\tau_2^c = 2.29$	$B_2 = 0.40$	0.581	
$\tau_3^c = 6.9$			$B_3 = 0.06$	0.276		
		$\langle \tau_F \rangle^d = 3.3$				
PEP	346	404	$\tau_1^c = 3.0$	$B_1 = 0.24$	0.06	1.40
			$\tau_2^c = 12.9$	$B_2 = 0.73$	0.81	
			$\tau_3^c = 59.8$	$B_3 = 0.03$	0.13	
			$\langle \tau_F \rangle^d = 18.3$			
	346	480	$\tau_1^c = 1.5$	$B_1 = 0.71$	0.31	1.08
			$\tau_2^c = 6.2$	$B_2 = 0.22$	0.38	
$\tau_3^c = 17.8$			$B_3 = 0.07$	0.31		
		$\langle \tau_F \rangle^d = 8.4$				

<sup>a</sup> Normalized preexponential factor.

<sup>b</sup> Fractional contribution to the total fluorescence intensity defined as:  $f_i(\lambda) = B_i \tau_i / \sum_i B_i \tau_i$ .

<sup>c</sup> Obtained from the reconvolution fit:  $A + B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2) + B_3 \exp(-t/\tau_3)$ .

<sup>d</sup> Average lifetime calculated from the expression:  $\langle \tau_F \rangle = \sum_i B_i \tau_i^2 / \sum_i B_i \tau_i$ .

emission originating from an excimer [37]. Moreover, no negative component is calculated from the decay profile analysis. All these data rule out the formation of an excimer between the pyrene units in these derivatives. It is worth pointing out that the average lifetimes measured at  $\lambda_F = 480$  nm are significantly shorter than that measured at  $\lambda_F = 404$  nm.

The absorption spectra of PTMSEP, PTMSBDP, and PBDP are shown in Fig. 8(A). One can see that all the spectra are relatively similar to each other. However, the absorption bands of PTMSBDP and PBDP are broader than that of PTMSEP suggesting that stronger interactions between pyrene units are present in the former polymers. Thus, the distortion of the polymer backbone caused by the presence of a trimethylsilyl group significantly weakens the electronic interactions between pyrene units. On the other hand, the incorporation of triple bonds into the polymeric chain permits better interactions between pyrene moieties. The band observed around 580 nm in the absorption spectrum of PEP is not observed for these polymers (see Fig. 8(A)), which indicates that the effective conjugation is much shorter.

The fluorescence spectra of PTMSEP, PTMSBDP, and PBDP are shown in Fig. 8(B). PTMSBDP and PBDP show two distinct bands similar to the ones observed in the fluorescence spectrum of DEP (see Fig. 6(B)). These results are in agreement with the absorption spectra of these two polymers showing that strong interactions exist between pyrene units in the conjugated chains. On the other hand, the fluorescence intensity around 480 nm is much reduced in



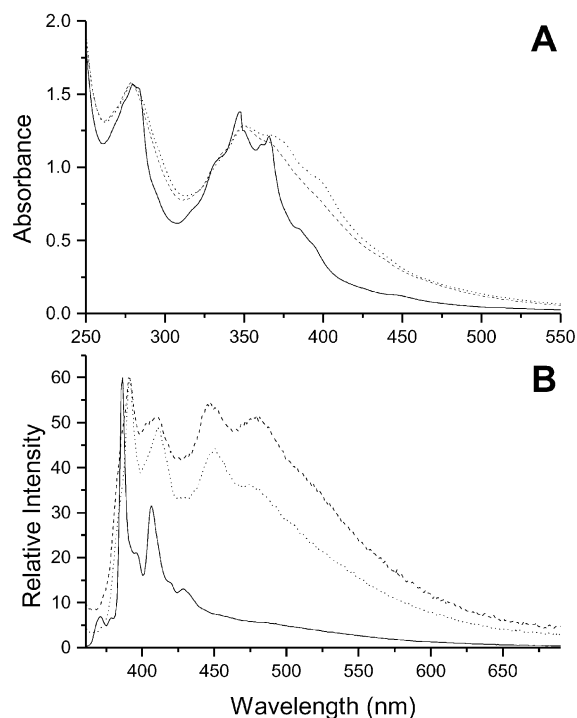


Fig. 8. Absorption (A) and fluorescence spectra (B) of PTMSEP (—), PTMSBDP (---) and PBDP (···) in THF.

the case of PTMSEP, confirming the results above that the incorporation of trimethylsilyl groups along the polymer backbone decreases the interactions between pyrene units. For the three derivatives, we have observed that the excitation spectra monitored at  $\lambda_F = 480$  nm are much different than those measured at  $\lambda_F = 404$  nm (figures not shown). Furthermore, like in the case of DEP, the fluorescence decay profiles do not show any rising component normally observed in the formation of an exciplex. The lifetime parameters are compiled in Table 3. Following the discussion above, we can conclude that the long wavelength band in the fluorescence spectra of all the polymers originates from static interactions (excited complex) between pyrene units. Furthermore, it is clear that a distortion in the polymer backbone greatly affect these interactions as observed in the case of PTMSEP. As a consequence, the photophysical parameters are much affected by the molecular conformation of these systems. Indeed, one can see that the average lifetime monitored at the long wavelength band of PTMSBDP and PBDP is much shorter than that of PTMSEP measured at the same wavelength.

#### 4. Concluding remarks

A series of mono- and di-substituted polyacetylenes with pendant 1-pyrenyl groups was synthesized and characterized. All of the polymers possess high thermal stability. Among these polymers, poly(1-ethynylpyrene) displayed

Table 3  
Fluorescence decay parameters of the polymers in THF at 298 K

Polymer	$\lambda_{exc}$ (nm)	$\lambda_F$ (nm)	$\tau_F$ (ns)	$B^a$	$f^b$	$\chi^2$
PTMSEP	346	404	$\tau_1^c = 1.40$	$B_1 = 0.41$	0.03	1.51
			$\tau_2^c = 9.92$	$B_2 = 0.30$	0.17	
			$\tau_3^c = 49.7$	$B_3 = 0.29$	0.80	
			$\langle \tau_F \rangle^d = 41.6$			
	346	480	$\tau_1^c = 1.30$	$B_1 = 0.68$	0.25	1.30
			$\tau_2^c = 5.01$	$B_2 = 0.28$	0.40	
$\tau_3^c = 28.1$			$B_3 = 0.04$	0.35		
		$\langle \tau_F \rangle^d = 12.2$				
PTMSBDP	346	404	$\tau_1^c = 0.92$	$B_1 = 0.51$	0.09	1.54
			$\tau_2^c = 7.0$	$B_2 = 0.35$	0.46	
			$\tau_3^c = 16.9$	$B_3 = 0.14$	0.45	
			$\langle \tau_F \rangle^d = 10.9$			
	346	480	$\tau_1^c = 1.10$	$B_1 = 0.73$	0.39	1.11
			$\tau_2^c = 3.54$	$B_2 = 0.24$	0.42	
$\tau_3^c = 13.6$			$B_3 = 0.03$	0.19		
		$\langle \tau_F \rangle^d = 4.5$				
PBDP	346	404	$\tau_1^c = 1.6$	$B_1 = 0.38$	0.10	1.16
			$\tau_2^c = 7.5$	$B_2 = 0.48$	0.54	
			$\tau_3^c = 18.0$	$B_3 = 0.14$	0.36	
			$\langle \tau_F \rangle^d = 10.7$			
	346	480	$\tau_1^c = 0.61$	$B_1 = 0.42$	0.14	1.22
			$\tau_2^c = 2.1$	$B_2 = 0.48$	0.52	
$\tau_3^c = 6.8$			$B_3 = 0.10$	0.34		
		$\langle \tau_F \rangle^d = 3.5$				

<sup>a</sup> Normalized preexponential factor.

<sup>b</sup> Fractional contribution to the total fluorescence intensity defined as:  $fi(\lambda) = B_i \tau_i / \sum_i B_i \tau_i$ .

<sup>c</sup> Obtained from the reconvolution fit:  $A + B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2) + B_3 \exp(-t/\tau_3)$ .

<sup>d</sup> Average lifetime calculated from the expression:  $\langle \tau_F \rangle = \sum_i B_i \tau_i^2 / \sum_i B_i \tau_i$ .

high molecular weight and extended conjugation. The presence of a trimethylsilyl group or an additional triple bond on the monomers decreases the degree of conjugation of the resulting polymers. The addition of another triple bond, however, increases significantly the thermal stability of the polymers.

All the polymers involve intramolecular interactions between pyrene units giving rise to non-associated and associated pyrene units emissions. From excitation spectra and fluorescence decay profiles measured at the maximum of both fluorescence bands, it is shown that ground state interactions (static) are responsible for the long wavelength emissions observed. It is also observed that steric effects created by pendant groups along the polymer backbones greatly affect the electronic interactions between pyrene moieties.

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