



Synthesis and optical properties of a poly(2',5'-dioctyloxy-4,4',4''-terphenylenevinylene) with high content of (Z) vinylene units

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ABSTRACT

Poly(2',5'-dioctyloxy-4,4',4''-terphenylenevinylene) with (*E*) configuration of the vinylene double bonds was prepared by Suzuki–Miyaura polymerization of (*E*)-4,4'-dibromostilbene and 2,5-dioctyloxy-1,4-benzenediboronic acid. Attempts to extend this simple procedure to the synthesis of the polymer with (*Z*) configuration, starting from (*Z*)-4,4'-dibromostilbene, were unsuccessful. However, the use of (*Z*)-4,4'-diiodostilbene and a careful choice of Pd catalyst and experimental conditions, lead to a material with a >95/<5 (*Z*)/(*E*) ratio of vinylene units. The investigation of optical properties of both the (*E*) and (*Z*) polymers evidenced that (*Z*) linkages act as defects which reduce the effective conjugation length in the polymer backbone.

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1. Introduction

In the last decade, attractive outlooks in the field of optoelectronic devices have been opened by the discovery of several classes of new organic materials with extended π -conjugation [1], whose electronic structure can be interpreted in terms of valence and conduction bands as in inorganic semiconductors [2]. In the wide class of these materials, particular importance attaches to poly(*p*-phenylenevinylene)s (PPVs) and, in general, to poly(arylenevinylene) derivatives for their potential applications in light-emitting diodes (LEDs) [3] and lasers [4]. In this respect, the possibility of tuning the band gap by structural modifications represents an important feature. Indeed, the modulation of the electroluminescence wavelength can be achieved by electronic and/or steric effects of substituents bonded to the polymeric backbone, by introducing *meta* phenylene linkages [5], and/or by controlling the vinylene units geometry. In particular, the introduction of (*Z*)-olefin linkages in the PPV backbone is reported to reduce the conjugation length and to interfere with the packing in the solid state, thus providing more amorphous materials with blue-shifted emission wavelengths and enhanced electroluminescence efficiencies [6].

Various methodologies have been described for the synthesis of PPV polymers with variable amounts of (*Z*)-vinylene units. An unsubstituted PPV with mixed (*E*), (*Z*) double bond geometry was prepared by thermal elimination of xanthate groups from a non-conjugated precursor polymer [6]. Wittig olefination reaction has been reported to afford PPVs with variable amounts of (*Z*) and (*E*) linkages [7a,7b]. High (*Z*)/(*E*) ratios were achieved in the presence of very bulky substituents on the aromatic rings [7c]. Poly(arylenevinylene) polymers bearing phenyl rings as substituents on both carbon atoms of the vinylene units have been obtained with nearly equal amounts of (*Z*) and (*E*) configuration by McMurry coupling [8]. A control on the (*Z*)/(*E*) ratio in similar polymers could be achieved by the Suzuki–Miyaura cross-coupling or the Yamamoto homocoupling, using suitable mixtures of (*E*) and (*Z*) 4,4'-dibromotetraphenylethylene. The (*E*)/(*Z*) ratio of the polymer obtained reflected the composition of the monomer mixture used in the coupling step [8b]. Poly(arylenevinylene)s with (*Z*)-tetrasubstituted vinylene units have been obtained from monomers with the (*Z*) double bond configuration locked in a small ring, such as the 3-cyclobutene-1,2-dione [9] or the maleimide [10] systems, by means of synthetic protocols based upon Gilch-type condensation or Ni(0) catalyzed homocoupling, respectively. The latter process has been also employed to obtain random copolymers containing 75% of fluorene units and 25% of (*Z*)-1,2-diphenylethene units [11].

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Hiyama palladium-catalyzed cross-coupling has also been exploited to synthesize PPVs with unsubstituted vinylene units with (Z)/(E) ratios up to 66/34 [12].

More recently, the Suzuki–Miyaura-type polycondensation of 2,5-dioctyloxy-1,4-benzenediboronic acid with (Z,Z)-bis(2-bromoethenyl)arenes has been reported to afford geometrically pure all-cis poly(arylenevinylene)s [13]. However, the synthetic process necessary to prepare the bromoethenyl monomers, based upon a (Z)-selective hydrosilylation of suitable diethynylbenzenes in the presence of a specific ruthenium catalyst followed by bromodesilylation of the resulting silyl derivatives, does not appear to be straightforward.

Summing up only a limited range of simple synthetic methodologies leading to PPV polymers with high content of unsubstituted (Z)-vinylene units is presently available. On the other hand, these materials may have a potential interest not only for photoluminescence and electroluminescence studies, in comparison with the corresponding all-(E) counterparts, but also for investigation of their linear and nonlinear optical (NLO) properties. Indeed, our recent studies have highlighted some interesting features in the optical properties of various (E) PPVs [14], prepared by organometallic synthetic processes developed in our laboratories [1b] and, in our opinion, the dependence of these properties on the configuration of the vinyl moiety of the conjugated chain, which had not been reported in the literature before, deserved investigation.

In previous communications, we reported preliminary results on the study of linear [15] and nonlinear [16] optical properties of new poly(2',5'-dioctyloxy-4,4',4''-terphenylenevinylene) **3** (Scheme 1) with moderate to high content of (Z) vinylene units.

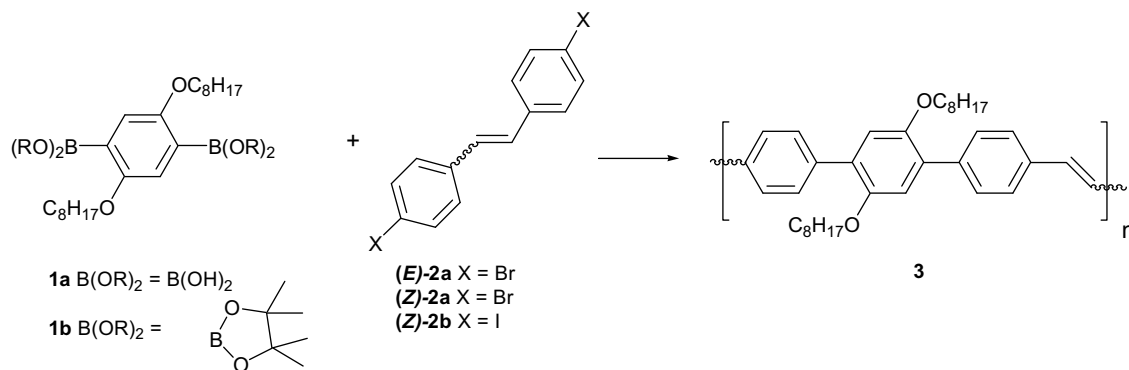
In this paper we wish to present a full account on the synthesis of these materials.

2. Results and discussion

2.1. Synthesis of **3**

The synthesis of the polymer **3** was performed via the palladium-catalyzed Suzuki–Miyaura polycondensation [17] of the boron derivatives **1a,b** with the 4,4'-dihalostilbenes **2** (Scheme 1).

Yields, molecular weights, and the (Z)/(E) ratios of the vinylene units, depending on the catalyst employed and the experimental conditions, are reported in Table 1. In all runs, the polymeric material was recovered from the crude product by a series of sequential extractions in a Soxhlet apparatus with hexane, acetone, diethyl ether and chloroform. Hexane and acetone extracted fractions contained mainly low molecular weight products (the ligands deriving from the decomposition of the catalysts and small amount of starting materials). Polymer **3** with nearly all (E) configuration was obtained in satisfactory yield by coupling reaction of the diboronic acid **1a** with the dibromostilbene (**E**)-**2a** in the presence of tetrakis(triphenylphosphine)palladium(0) Pd(PPh₃)₄ as the catalyst (Table 1, entry 1). The material was well soluble in chloroform but not in diethyl ether, and the ¹H NMR spectrum showed broad singlets at $\delta = 7.05$ ppm and $\delta = 7.25$ ppm, which were assigned to the aromatic protons on the dialkoxy substituted rings and to the vinylic protons, respectively. A broad multiplet in the range 7.55–7.75 ppm is originated by the four aromatic protons on the unsubstituted aromatic rings.



Scheme 1. Synthesis of poly(2',5'-dioctyloxy-4,4',4''-terphenylenevinylene)s **3** with (Z) or (E) vinylene units.

Table 1
Palladium-catalyzed polymerization of **1** with **2**

Entry	1	2	Catalyst	Polymer 3	
				Diethyl ether soluble fraction yield (%); $M_w(M_w/M_n)^d$; (Z)/(E) ^e %	Chloroform soluble fraction yield (%); $M_w(M_w/M_n)^d$; (Z)/(E) ^e %
1	1a	(E)- 2a	Pd(PPh ₃) ₄ ^a	0 ^f	66; 7000 (1.35); <5/>95
2	1a	(Z)- 2a	Pd(PPh ₃) ₄ ^a	11 ^g	11; 7000 (1.32); ~10/90
3	1a	(Z)- 2b	Pd(PPh ₃) ₄ ^a	76; 7800 (1.32); 80/20	0 ^f
4	1a	(Z)- 2b	PdCl ₂ dppf ^b	72; 12600 (1.61); >95/<5 ^d	9; 18500 (2.18); 85/15
5	1b	(Z)- 2b	Pd(PPh ₃) ₄ ^a	0 ^f	40; 11000 (1.75); 20/80
6	1b	(Z)- 2b	Pd(AsPh ₃) ₄ ^c	67; 11900 (1.80); 94/6	25; 19900 (1.64); 94/6

^a Reaction performed in toluene/methanol, aq. Na₂CO₃ (2 M) at reflux.

^b Reaction performed in THF, aq. Na₂CO₃ (2 M), at 35 °C.

^c Reaction performed in toluene/methanol, aq. Na₂CO₃ (2 M) at 35 °C.

^d Determined by GPC based on polystyrene standard.

^e Ratio (E)/(Z) determined by ¹H NMR spectroscopy.

^f No polymer could be extracted with this solvent.

^g M_w and ratio (E)/(Z) not determined (see text).

In principle, this simple protocol could be adopted for the synthesis of polymer **3** with (*Z*) configuration of the double bonds, starting from the dibromostilbene (**Z**)-**2a**. However, the Suzuki–Miyaura polymerization of **1a** with (**Z**)-**2a** afforded poor results (Table 1, entry 2). Sequential Soxhlet extractions with ether and chloroform afforded two different fractions in low yield (11%). The chloroform soluble polymer showed an ¹H NMR spectrum very similar to that of the material obtained from the reaction of (**E**)-**2a** and, therefore, a (*E*) configuration was assigned to the vinylene units. The complex signal pattern in the zone $\delta = 7.30\text{--}7.75$ ppm did not allow to ascertain the effective structure of the diethyl ether extracted fraction. Nevertheless, by replacing the dibromostilbene (**Z**)-**2a** with the diiodo derivative (**Z**)-**2b**, the polymerization occurred in a more clean fashion, and the Soxhlet extraction procedure afforded only a diethyl ether soluble fraction in good yield (Table 1, entry 3).

The ¹H NMR spectrum of the obtained material shows new additional resonances at $\delta = 6.60$ ppm (broad singlet), and at $\delta = 7.38\text{--}7.49$ ppm (two broad doublet-like signals), which are assigned to the vinylic and aromatic protons on the unsubstituted aromatic rings, respectively, of the repeating units with the (*Z*) configuration of the double bonds. These signals are clearly distinct from the resonances ($\delta = 7.55\text{--}7.75$ ppm) of the corresponding protons of the repeating units with the (*E*) double bond geometry, which are also present.

By comparing the integral values of the signals at $\delta = 7.38$ ppm and $\delta = 7.49$ ppm with those of the signals in the $\delta = 7.75\text{--}7.55$ ppm range it was possible to estimate the ratio of (*Z*) to (*E*) vinylene units. It is worth noting that the high content of (*Z*) double bond confers to polymer **3** a higher solubility in diethyl ether with respect to the corresponding (*E*) counterpart, which, in turn, is more soluble in chloroform.

Better results were obtained in terms of yield, stereoselectivity and molecular weight values, by using diphenylphosphinoferrocenepalladium dichloride (PdCl₂dppf) as catalyst (Table 1 entry 4). In this case, a polymer with nearly all (*Z*) double bond configuration was isolated, in good yield, by extraction with diethyl ether. Subsequent extraction of the residue with chloroform gave a small amount (9% yield) of a material with a lower content of (*Z*) vinylene units. Although the (*Z*)/(*E*) ratio of this fraction was still relatively high (85/15), its solubility in diethyl ether was low, if compared with that of the polymer having a slightly lower (*Z*)/(*E*) ratio (80/20 entry 3 of Table 1), reasonably because of its higher molecular weight.

Pinacol boronic esters have been previously employed in polymerization processes based upon the Suzuki–Miyaura cross-coupling reaction, with some advantage with respect to the use of the corresponding boronic acids [18]. However, in our case, polymerization reactions involving **1b** and (**Z**)-**2b** with PdCl₂dppf as catalyst gave no results, whereas Pd(PPh₃)₄ (Table 1, entry 5) afforded the polymer **3** with prevalent (*E*) configuration of vinylene units. A greater stereoselectivity was observed by using tetrakis(triphenylarsine)palladium(0) Pd(AsPh₃)₄, generated in situ from tris(dibenzylideneacetone)dipalladium(0) (Pd₂dba₃) and triphenylarsine (Table 1 entry 6). Both fractions of polymer **3** extracted with diethyl ether and chloroform showed the same (*Z*)/(*E*) ratio of the vinylene units. The higher molecular weight of the chloroform soluble fraction may explain its low solubility in diethyl ether, in spite of the high (*Z*)/(*E*) ratio.

The results of Table 1 show that (*Z*)-(*E*) isomerization of the double bond occurred during the polymerization reaction. The extent of this isomerization appears to be more likely related to the palladium complex used as catalyst, rather than to the temperature or other experimental conditions, although the mechanism of this process is unclear. Indeed, although (*Z*)-poly(arylenevinylene)s appear to be quite thermally [12] and photochemically [13] stable,

some control reaction in order to ascertain the configurational stabilities of the *Z* double bonds in the monomer (**Z**)-**2b** and in the polymer **3** with high content of *Z* linkages were performed. Monomer (**Z**)-**2b** was handled in the more extreme experimental conditions adopted for the polymerization reaction (see entry 3, Table 1), in the presence of the palladium catalyst but without the reaction partner **1a**. After six days the monomer (**Z**)-**2b** was completely dehalogenated, but *Z* to *E* isomerization of the double bond did not occur and the only recoverable product was the (*Z*)-stilbene. In the same way the polymer (**Z**)-**3**, obtained following the experimental conditions of entry 4 in Table 1, was recovered unchanged after handling for six days in the experimental conditions of entry 3 in Table 1. Therefore, the *Z* linkages in the polymer are quite stable and the isomerization process takes place during the growth of the polymer chains in the catalytic cycle of the coupling process.

In conclusion, the Suzuki–Miyaura cross-coupling polymerization of **1a** with (**Z**)-**2b**, using PdCl₂dppf as catalyst afforded in high yield the polymer **3** with near all (*Z*) configuration of the double bonds. The lower stereoselectivity observed when different boron derivatives and/or palladium complexes were used offers the possibility of modulating the (*E*)/(*Z*) ratios in the resulting materials.

2.2. Linear optical properties of polymers **3**

Fig. 1 reports the absorption spectra measured in diluted chloroform solutions for three samples characterized by different (*Z*)/(*E*) ratio of the vinylene units [sample (**E**)-**3**, ((*Z*)/(*E*)) <5/>95; sample (**E,Z**)-**3**, ((*Z*)/(*E*)) 80/20; sample (**Z**)-**3**, ((*Z*)/(*E*)) >95/<5]. For all samples, the main absorption band was attributed to the transition between the highest occupied and the lowest unoccupied π -molecular orbitals ($S_0 \rightarrow S_1$ transition), while the shoulder at higher energies was ascribed to transitions originating from the charge conjugation symmetry breaking [19]. The wavelengths corresponding to the main peak of the absorption spectra are reported in Table 2.

It can be observed that the addition of (*Z*)-vinylene units causes a blue-shift of the absorption spectra, in agreement with the

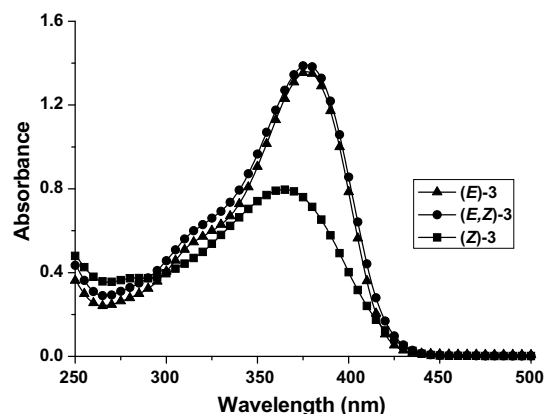


Fig. 1. Absorption spectra of (**E**)-**3**, (**E,Z**)-**3** and (**Z**)-**3** in solution (see text). All experiments were performed at room temperature in chloroform ($c = 0.016$ g/L).

Table 2

Wavelengths of absorption maximum (λ_a), PL maximum in solution ($\lambda_{e,sol}$), zero-phonon emission in film ($\lambda_{e,film}$), and energy difference (ΔE_s) between absorption and PL maxima in solution

Sample	λ_a (nm)	$\lambda_{e,sol}$ (nm)	$\lambda_{e,film}$ (nm)	ΔE_s (eV)
(E)- 3	380	438	447	0.43
(E,Z)- 3	376	444	450	0.51
(Z)- 3	356	441	450	0.67

interpretation that (*Z*) linkages act as defects, thus reducing the effective conjugation length in the polymer backbone [20]. Moreover, the absorption spectra appear broad and structureless due to the distribution of different effective conjugation lengths and to the absorption from many torsionally excited initial states, respectively [15]. Photoluminescence (PL) spectra obtained in solutions and thin films are reported in Figs. 2 and 3, respectively. The wavelengths corresponding to the emission maximum in solutions ($\lambda_{e,sol}$) and zero-phonon emission in films ($\lambda_{e,filim}$) are detailed in Table 2.

The red-shift of film luminescence with respect to solution for sample (*E*)-3 is ascribed to migration of carriers towards longer segment chains. For sample (*E,Z*)-3 and sample (*Z*)-3 the reduction of this red-shift can be justified by inhibition of interchain interactions also in the solid state, which reduces exciton migration. The first emission band is generally ascribed to the transition between the first-excited state and the ground state, while the additional bands/shoulders are attributed to vibronic replica. The latter become better defined in solution measurements upon the introduction of (*Z*) linkages in the polymeric backbone. In the case of film measurements, the increase of (*Z*) bonds concentration causes a variation of the relative amplitude of the zero-phonon and of the first vibronic replica emission bands. The presence of well-defined vibronic structure in luminescence spectra can be explained by considering that, upon relaxation, the geometry of the excited state is less affected by ring torsion as compared to the ground state. Indeed, the excited state is expected to have more quinoidal character than the ground state [21], with a consequent reduction of inter-ring torsion due to the partial double-bond character of the C–C bonds. In Table 2 the energy differences between the position

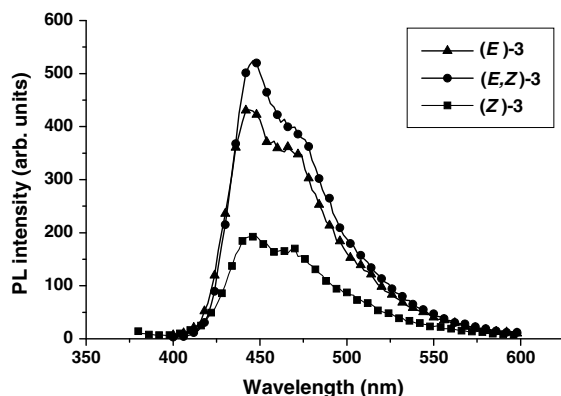


Fig. 2. Photoluminescence spectra of (*E*)-3, (*E,Z*)-3 and (*Z*)-3 in solution (see text). All experiments were performed at room temperature in chloroform ($c = 0.003$ g/L).

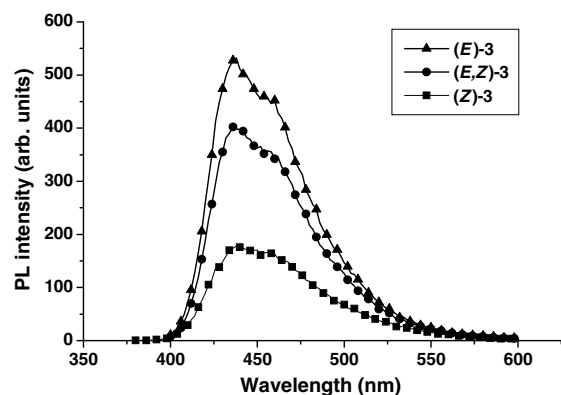


Fig. 3. Photoluminescence spectra of (*E*)-3, (*E,Z*)-3 and (*Z*)-3 in thin films.

of the absorption and PL maxima (ΔE_s) in solution are reported. As expected, ΔE_s increase with the (*Z*) content as for isolated molecules the Stokes shift is proportional to the extent of geometrical relaxation that the molecules undergo upon photo-excitation [22]. It should be noted that we did not measure a significant dependence of PL quantum efficiency on (*E*)/(*Z*) ratio, in apparent contradiction with the reported results by other authors that observed maximum PL efficiency for a (*E*)/(*Z*) ratio of 50/50 [8b]. This can be explained by observing that in our case the (*E*)/(*Z*) ratios (0/100, 20/80, 100/0) are far from 50/50 and justify similar PL efficiencies, in agreement with the reported results [8b] of identical PL efficiencies for (*E*)/(*Z*) = 59/41 and 37/63 polymers obtained using Yamamoto polycondensation and comparable PL efficiencies for (*E*)/(*Z*) = 62/38 and 32/68 polymers obtained using Suzuki reaction.

3. Conclusions

In this paper, we report the synthesis of a poly(arylenevinylene) with high content (>95%) of (*Z*) vinylene units by means of Suzuki–Miyaura cross-coupling reaction of a 2,5-dialkoxy-1,4-benzenediboronic acid with (*Z*)-4,4'-diiodostilbene. The choice of appropriate catalyst and experimental conditions allowed to perform this polymerization process with high retention of the monomer double bond (*Z*) configuration. The optical properties of the materials obtained were compared with those of the same material with all (*E*) configuration of the vinylene units. The blue-shift of the absorption maximum, the greater Stokes shift of the photoluminescence spectrum measured for the (*Z*) polymers with respect to the all (*E*) counterpart evidence that the (*Z*) vinylene units in the polymer chain give origin to a reduced effective conjugation length.

Therefore, the stereochemistry of the double bond represents a further feature that may be employed to tune the optical properties for future specific applications in optoelectronic and photonic fields. Summing up, our procedure compares favourably with the other few synthetic methodologies available for the preparation of poly(arylenevinylene)s with high content of (*Z*) vinylene units, owing to the readily available and inexpensive starting materials, the mild experimental conditions and the high yields.

4. Experimental

GC analyses were performed on a gas chromatograph equipped with a SE-30 (methyl silicone, 30 m \times 0.25 mm id) capillary column. ^1H NMR and ^{13}C NMR spectra were recorded in CDCl_3 at 500 MHz and at 125 MHz, respectively, using the residual CHCl_3 as the standard at 7.24 ppm for ^1H spectra and CDCl_3 signal at 77 ppm for ^{13}C spectra. Molecular weights were determined with a Hewlett-Packard HP 1050 liquid chromatograph instrument using THF as the solvent and a Plgel 5 μ Mixed-D 300 \times 7.5 mm column and are based on monodisperse polystyrene standard. Tetrahydrofuran was distilled from benzophenone ketyl immediately prior to use. $\text{PdCl}_2(\text{dppf})$ [23], 2,5-bis(1-octyloxy)-1,4-dibromobenzene [14a], and (*E*)-4,4'-dibromostilbene (*E*)-2a [24] were prepared as reported in the literature. $\text{Pd}(\text{PPh}_3)_4$, $\text{Pd}_2(\text{dba})_3$, *p*-iodobenzaldehyde, *p*-bromobenzaldehyde, *p*-bromobenzylbromide, *p*-iodobenzylbromide and AsPh_3 were commercial products. Experimental details on the photoluminescence measurements have been reported in the previous communication [15].

4.1. 2,5-Dioctyloxy-1,4-benzenediboronic acid 1a

The diboronic acid 1a was prepared following the procedure reported in the literature for similar 2,5-dialkoxy-1,4-benzenediboronic acids [25].

A solution of 2,5-bis(1-octyloxy)-1,4-dibromobenzene (4.00 g, 8.12 mmol) in anhydrous THF (30 mL) was added dropwise to a suspension of magnesium turnings (0.49 g, 20.16 mmol) in THF (6 mL). When the addition was completed, the solution was refluxed for 3 h. The resulting solution was added dropwise over 2 h to a solution of trimethylborate (5.10 g, 49.08 mmol) in THF (10 mL) at -78°C . The temperature was gradually raised overnight to room temperature and then the mixture was poured in crushed ice (45 g) and concentrated sulfuric acid (1.4 mL). Addition of diethyl ether (10 mL) and water (10 mL) facilitates the separation of the organic and aqueous layers. The latter was extracted with diethyl ether (4×20 mL). The combined organic extracts were dried over anhydrous sodium sulfate and the solvent was removed at reduced pressure. The resulting residue was crystallized from methanol affording a white solid (2.00 g, 58% yield, m.p. 188–190 $^{\circ}\text{C}$). ^1H NMR (DMSO- d_6) δ = 0.86 (t, J = 6.7 Hz, 6H), 1.20–1.31 (m, 20H), 1.73 (quintet, J = 6.5 Hz, 4H), 4.00 (t, J = 6.5 Hz, 4H), 7.20 (s, 2H), 7.64 (bs, 4H) ppm.

Anal. Calc. for $\text{C}_{22}\text{H}_{40}\text{O}_6\text{B}_2$: C, 62.59; H, 9.54. Found: C, 62.89; H, 9.50%.

4.2. 2,5-Dioctyloxy-1,4-phenylenebis[4,4,5,5-tetramethyl-1,3,2-dioxaborolane] **1b**

A solution of 2,5-bis(1-octyloxy)-1,4-dibromobenzene (4.00 g, 8.12 mmol) in anhydrous THF (30 mL) was added dropwise to a suspension of magnesium turnings (0.49 g, 20.16 mmol) in THF (6 mL). When the addition was completed, the solution was refluxed for 3 h. The resulting solution was added dropwise over 2 h to a solution of trimethylborate (5.10 g, 49.08 mmol) in THF (10 mL) at -78°C . The temperature was gradually raised overnight to room temperature, then pinacol (5.80 g, 49.08 mmol) was added. After stirring at room temperature overnight, water (50 mL) addition, extraction with ethyl acetate (3×20 mL) and the usual work-up of the organic phases, crude diester **1b** was obtained. The crude solid was treated with hexane (60 mL), and the insoluble part was filtered off. After evaporation of the solvent at reduced pressure, the residue was crystallized twice from acetonitrile affording a white solid (m.p. 71–72 $^{\circ}\text{C}$, 3.00 g, 63% yield). ^1H NMR (CDCl_3) δ = 0.88 (t like, J = 6.9 Hz, 6H), 1.25–1.35 (m, 16H), 1.34 (s, 24H), 1.45–1.53 (m, 4H), 1.75 (quintet, J = 6.3 Hz, 4H), 3.93 (t, J = 6.3 Hz, 4H), 7.08 (s, 2H) ppm.

Anal. Calc. for $\text{C}_{34}\text{H}_{60}\text{O}_6\text{B}_2$: C, 69.63; H, 10.31. Found: C, 69.80; H, 10.32%.

4.3. (Z)-4,4'-dibromostilbene (**Z**)-**2a**

This product was prepared following a procedure reported in the literature for the synthesis of (Z)-stilbenes [26].

p-Bromobenzaldehyde (0.91 g, 4.92 mmol) and 18-crown-6 (0.13 g, 0.49 mmol) were added to a solution of *p*-bromobenzyltriphenylphosphonium bromide [27] (2.51 g, 4.90 mmol) in CH_2Cl_2 (12 mL). The mixture was cooled to -78°C and freshly powdered potassium hydroxide (0.59 g, 10.52 mmol) was added under stirring. After 3 h at -78°C the mixture was gradually warmed to room temperature and stirred overnight. The reaction mixture was then filtered and the solid was washed with CH_2Cl_2 (20 mL). The organic phases were washed with water (30 mL) and dried over anhydrous sodium sulfate. The residue obtained after removal of the solvent at reduced pressure was dissolved in hexane (10 mL) and triphenylphosphine oxide was filtered off. The hexane was removed at reduced pressure and the crude product was crystallized from methanol, affording a white solid (1.40 g, 84% yield m.p. 54–55 $^{\circ}\text{C}$). ^1H NMR (CDCl_3) δ = 6.54 (s, 2H), 7.09 (d, J = 8.3 Hz, 4H), 7.36 (d, J = 8.3 Hz, 4H) ppm.

4.4. (Z)-4,4'-diiodostilbene (**Z**)-**2b**

This product was prepared following the same procedure described for the synthesis of dibromide (**Z**)-**2a**, starting from *p*-iodobenzaldehyde (1.00 g, 4.31 mmol), 18-crown-6 (0.11 g, 0.43 mmol), *p*-iodobenzyltriphenylphosphonium bromide (2.41 g, 4.31 mmol) and potassium hydroxide (0.52 g, 9.27 mmol). A white solid (1.60 g, 86% yield) with m.p. 84–85 $^{\circ}\text{C}$ (methanol) was obtained. ^1H NMR (CDCl_3) δ = 6.44 (s, 2H), 6.97 (d, J = 7.5 Hz, 4H), 7.25 (d, J = 7.5 Hz, 4H) ppm.

Anal. Calc. for $\text{C}_{14}\text{H}_{10}\text{I}_2$: C, 38.92; H, 2.33. Found: C, 39.46; H, 2.30%.

4.5. Palladium-catalyzed polycondensations. Typical procedure (entries 1 and 3 Table 1)

The diboronic acid **1a** (0.200 g, 0.47 mmol), the dihalostilbene (**E**)-**2a** or (**Z**)-**2b** (0.46 mmol), the catalyst (0.047 mmol of $\text{Pd}(\text{PPh}_3)_4$ or 0.014 mmol of $\text{Pd}(\text{dppf})\text{Cl}_2$) and the solvent (20 mL of a toluene/methanol 1/1 mixture or 10 mL of THF) were introduced in a three necked flask, equipped with a dropping funnel and nitrogen inlet, under an inert nitrogen atmosphere. After 10 min stirring at room temperature, 2 mL of a 2 M aqueous solution of sodium carbonate was added dropwise, and the reaction mixture was refluxed (or warmed at 35 $^{\circ}\text{C}$ in the case of the reaction of (**Z**)-**2b** in THF) for 6 days. After quenching with water, the reaction mixture was extracted with dichloromethane (3×30 mL). The organic phases were dried over anhydrous sodium sulfate and the solvent removed under reduced pressure. The crude polymer was purified by a series of sequential extractions in a Soxhlet apparatus with hexane, acetone, diethyl ether and chloroform.

4.6. Polymer (**Z**)-**3**

The (Z) rich polymer was recovered from the diethyl ether fraction.

Spectral data for the (Z)/(E) > 95/<5 polymer (entry 4, Table 1): IR (KBr) ν 3008, 2926, 2855, 1606, 1523, 1491, 1469, 1386, 1208, 1051, 834, 723 cm^{-1} .

^1H NMR (CDCl_3) δ = 0.72–0.90 (bm, 6H), 1.09–1.41 (bm, 20H), 1.58–1.74 (bm, 4H), 3.84–3.96 (bm, 4H), 6.60 (bs, 2H), 6.96 (bs, 2H), 7.38 (d like, $J \approx 8$ Hz, 4H), 7.49 (d like, $J \approx 8$ Hz, 4H) ppm.

^{13}C NMR (CDCl_3) δ = 14.08, 22.62, 26.00, 29.17, 29.30, 31.72, 69.55, 116.04, 128.47, 129.29, 129.90, 130.35, 135.87, 137.14, 150.43 ppm.

Anal. Calc. for $\text{C}_{36}\text{H}_{46}\text{O}_2$: C, 84.66; H, 9.08. Found: C, 84.08; H, 9.22%.

4.7. Polymer (**E**)-**3**

The (E) rich polymer was recovered from the chloroform fraction.

Spectral data for the (Z)/(E) < 5/>95 polymer (entry 1, Table 1): IR (KBr) ν 3027, 2926, 2855, 1524, 1494, 1470, 1427, 1388, 1210, 1080, 970, 840 cm^{-1} .

^1H NMR (CDCl_3) δ = 0.95 (bt, 6H), 1.15–1.45 (bm, 20H), 1.70 (bm, 4H), 3.90 (bm, 4H), 7.05 (bs, 2H), 7.25 (bs, 2H), 7.55–7.75 (bm, 8H) ppm.

^{13}C NMR (CDCl_3) δ = 14.12, 22.68, 26.11, 29.25, 29.38, 31.79, 69.71, 116.14, 126.11, 126.41, 128.52, 129.62, 136.09, 137.72, 150.44 ppm.

Anal. Calc. for $\text{C}_{36}\text{H}_{46}\text{O}_2$: C, 84.66; H, 9.08. Found: C, 84.71; H, 9.22%.

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