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A convenient *short cut* from aromatic iodides to alkynylstannanes and their use for the straightforward preparation of polyacetylene and polymetallaacetylene polymers

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Abstract

The palladium-catalyzed cross-coupling reaction (Stille coupling) of aromatic iodides Ar–I and tributyl(ethynyl)tin $Bu_3SnC\equiv CH$ form the aromatic acetylides $Ar–C\equiv CH$ and the side product tributyltin iodide Bu_3SnI in equimolar amount. In situ addition of lithium diisopropylamide (LDA) to this crude mixture directly affords the tributyl(ethynyl)tin aromatics $Ar–C\equiv C–SnBu_3$ in high yield. In the case of the bis(iodoaromatic) I–Ar–I (Ar = phenyl, thiophene), this straightforward transformation affords the corresponding bis[tributyl(ethynyl)tin]derivative $Bu_3Sn–C\equiv C–Ar–C\equiv C–SnBu_3$. In the presence of Pd this latter species can be directly reacted with a second bis(iodoaromatic) or a bis(metaliodide) unit to form acetylenic and metallaacetylenic polymers with tailored monomer units inserted in a stereoregular polymer chain. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Stille coupling; Alkynylstannanes; Polyacetylene; Polymetallaacetylene

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1. Introduction

Alkynylstannanes are a class of functionalized alkynes playing an important role in numerous organic and organometallic synthetic designs. They represent the coupling partners that more efficiently perform the palladium catalyzed coupling between organotin reagents and electrophiles [1], namely the Stille reaction; nowadays the most used procedure to form carbon–carbon bond by transition metal catalysis [2]. Moreover, alkynylstannanes are used to prepare alkynyliodonium salts, which are synthons of electrophilic acetylene [3], and to label steroids with metallocarbonyl fragments for their use in immunoessay FTIR tecniques [4]. More recently, material science has also taken advantage of the use of alkynylstannanes for the construction of aromatic polyacetylenes [5], of perethynylated compounds [6], and of linear chain metal-containing polymers [7]. These species constitute a variety of highly ethynylated carbon networks representing the ultimate focus of advanced materials [8].

We have recently found that in the presence of palladium catalysts alkynylstannanes can efficiently couple with metal iodides to form σ-metal acetylides [9], thus adding new usefulness to these intermediates.

All procedures commonly used for the preparation of alkynylstannanes require the previous preparation and isolation of the corresponding pure alkynes, then transformation is accomplished by the use of tin amides, tin oxides, or more often, by treatment with a base and a tin halide [6a,7b,9a,10]. These two steps must be kept separated being the reaction conditions under which the alkyne is formed incompatible with reagents used for the subsequent transformation.

With respect to the preparation of aromatic acetylenes, a wide variety of efficient methods are currently available [11], the most used rely on transition metal

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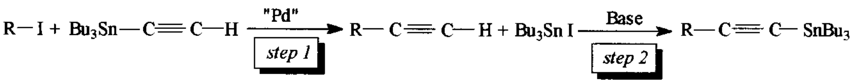
catalyzed couplings of aromatic halides and polyhalides with trimethylsilylacetylene (TMSA) or 2-methyl-3-butyn-2-ol to form the protected aromatic acetylenes, that will be subsequently deprotected just prior to use. Alternatively, the Stille coupling of aromatic halides and tributyl(ethynyl)tin directly affords the aromatic acetylenes. In any case, the free acetylene functionality is a sensitive group that may become very dangerous to handle in the case of aromatic polyacetylenes and peracetylenics [11,12].

Herein, we describe an efficient direct transformation of mono- and bis-iodides into mono- and bis-alkynylstannanes, based on the *one-pot* performance of two steps: (1) the Stille coupling between an aromatic iodide and tributyl(ethynyl)tin to form an aromatic acetylide, and (2) the base promoted recombination of the tributyltiniodide, generated as a side product in the first step, with the acetylide. The basic concept of this transformation is outlined in Scheme 1.

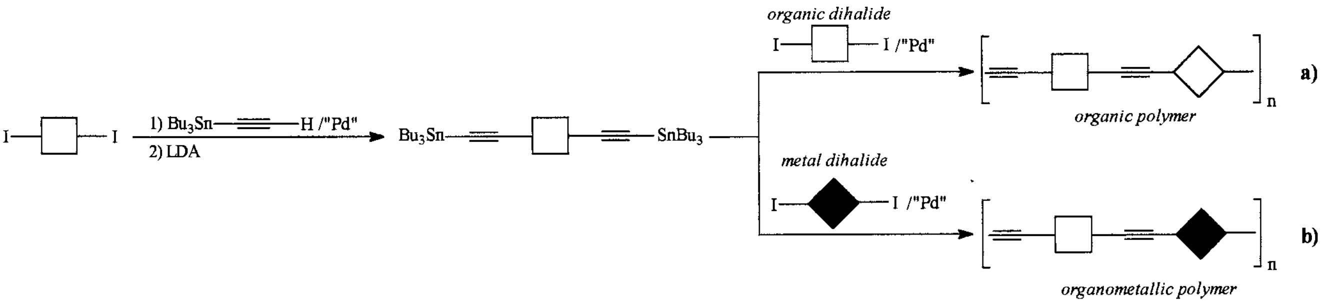
Moreover, by carrying out the same transformation on bis(iodoaromatics) of type I–Ar–I (Ar = phenyl, thienyl) the corresponding bis[tributyl(ethynyl)tin]-derivatives $Bu_3Sn–C≡C–Ar–C≡C–SnBu_3$ (Ar = phenyl, thienyl) were formed and directly reacted with a second bis(iodoaromatic) or a bis(metaliodide) in the presence of Pd to form acetilenic and metallaacetylenic polymers (Scheme 2).

2. Results and discussion

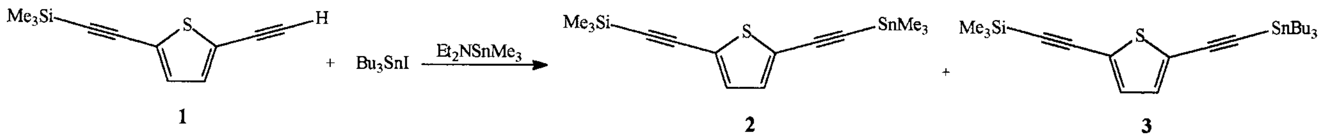
The possibility of achieving direct formation of tin acetylides by the *one pot* sequence of transformation outlined in Scheme 1 was envisaged for the first time by examining the ^1H-NMR spectrum of the product obtained upon reacting a mixture of 2(ethynyl)-5[(trimethylsilyl)ethynyl]tiophene (**1**) and Bu_3SnI with Et_2NSnMe_3 [13] (Scheme 3). ^1H-NMR spectrum showed that along with the expected product 2[(trimethylsilyl)ethynyl]-5(trimethyltinethynyl)tiophene (**2**) a considerable amount of 2[(trimethylsilyl)ethynyl]-5(tributyltinethynyl)tiophene (**3**) was formed. Evidently, while the diethylamino group abstracts the acetylenic proton, reaction with Bu_3SnI occurs and **3** is formed, despite the Me_3Sn functionality is favorite in the replacement of this proton to form **2** (Scheme 4). This



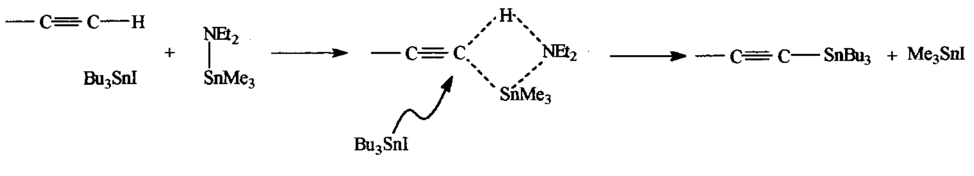
Scheme 1.



Scheme 2.



Scheme 3.



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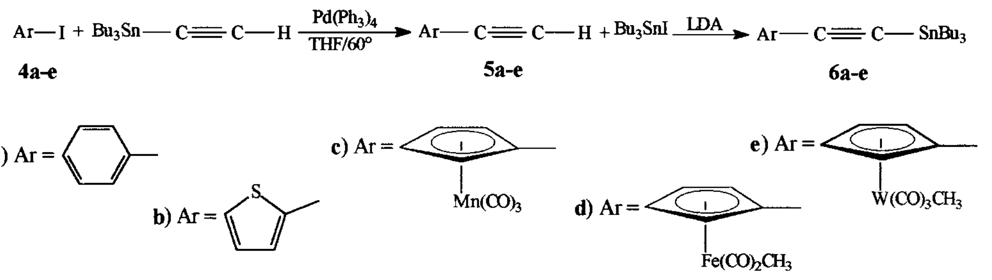


Scheme 5.

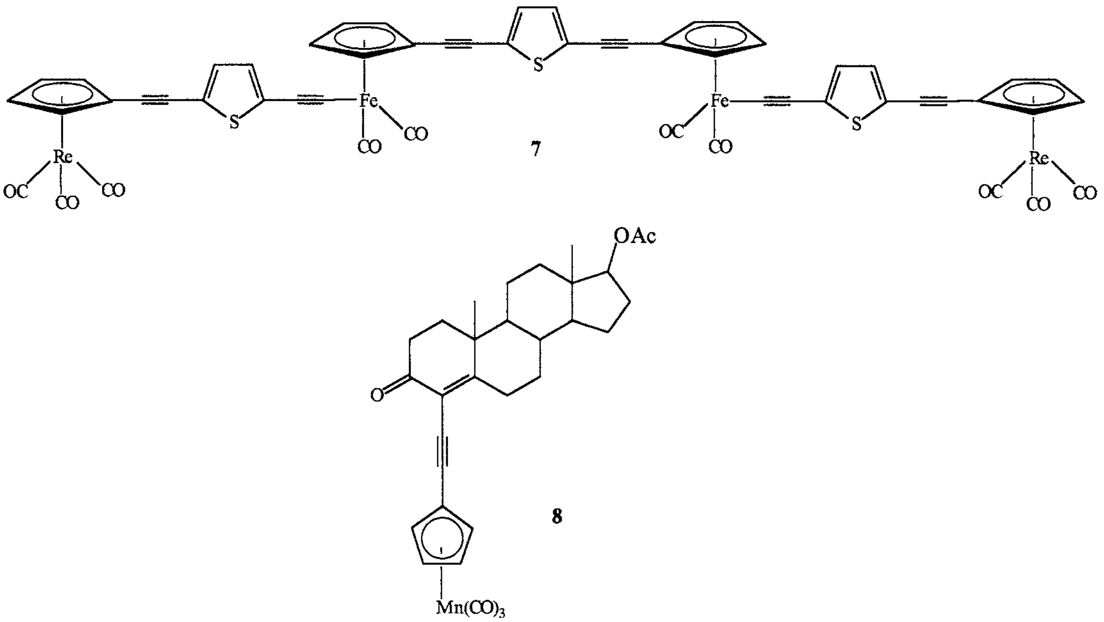


Fig. 1. Organometallic structures of compounds **7** and **8**.

unexpected finding then suggested the possibility of forming tin acetylides directly by recombination of the aromatic acetylide and the tin halide generated during the Stille coupling of aromatic iodides and tributyl(ethynyl)tin (step 2 of Scheme 1).

Iodobenzene (**4a**) was chosen as model in order to verify the feasibility of this transformation and to search the conditions to conveniently carry out the overall process. Since the Stille reaction can be efficiently carried out under a variety of conditions, the use of $Pd(PPh_3)_4$ as catalyst and THF as solvent resulted to be suitable conditions either for the coupling with tributyl(ethynyl)tin and for the subsequent use of LDA as base to allow recombination of phenylacetylene (**5a**) and Bu_3SnI (Scheme 5). Transformations outlined in Scheme 5 were conveniently monitored by GC-MS and/or ^{1}H-NMR. Iodobenzene (**4a**) and tributyl(ethynyl)tin were reacted in the presence of 5 mol.% of $Pd(PPh_3)_4$ catalyst in THF solvent. Following overnight stirring at 70°C, a sample of the reaction mixture analyzed by GC-MS showed only the presence of phenylacetylene (**5a**) and Bu_3SnI. After cooling at 0°C, a stoichiometric amount of LDA was added, and following warm up at room temperature, complete formation of $Bu_3Sn–C≡C–C_6H_5$ (**6a**) was ascertained by GC-MS. Following a simple work-up, the pure product was isolated in 83% yield. By applying the same sequence of transformation to the 2-iodothiophene (**4b**), the 2-ethynylthiophene (**5b**) was first obtained, then after cooling at − 80°C, treatment with LDA afforded the 2-(tributyltin)ethynylthiophene (**6b**) that was isolated in 94% yield. In this case, the treatment with base was carried out at lower temperature in order to prevent a possible attack in position 5 of 2-ethynylthiophene. This straightforward procedure was also tested on (η^5-iodocyclopentadienyl)metallocarbonyl derivatives **4c**–**e** with the expectation of obtaining a convenient access to the corresponding trialkyltinethynyl derivatives, which are important intermediates for assembling a variety of organometallic structures [4b,9e] (Fig. 1).

We performed the Stille coupling to form compounds **5c**–**e** using $(CH_3CN)_2PdCl_2$ as catalyst and DMF solvent [1e,f], which are milder conditions than those used

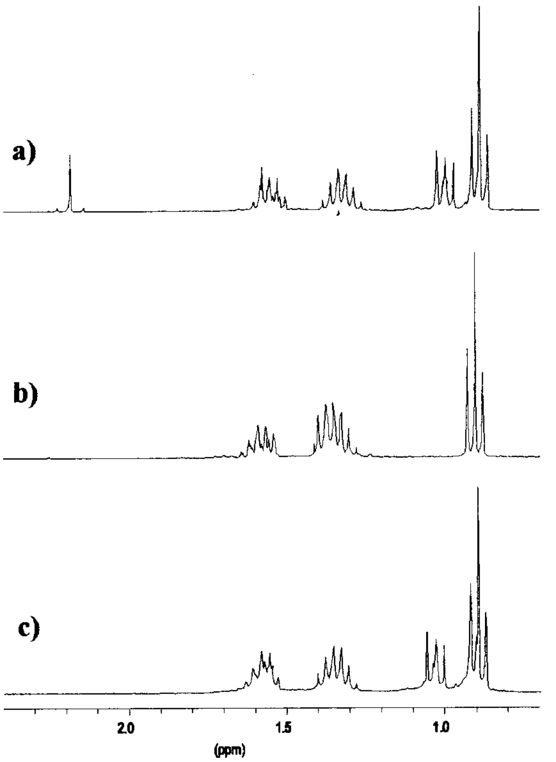


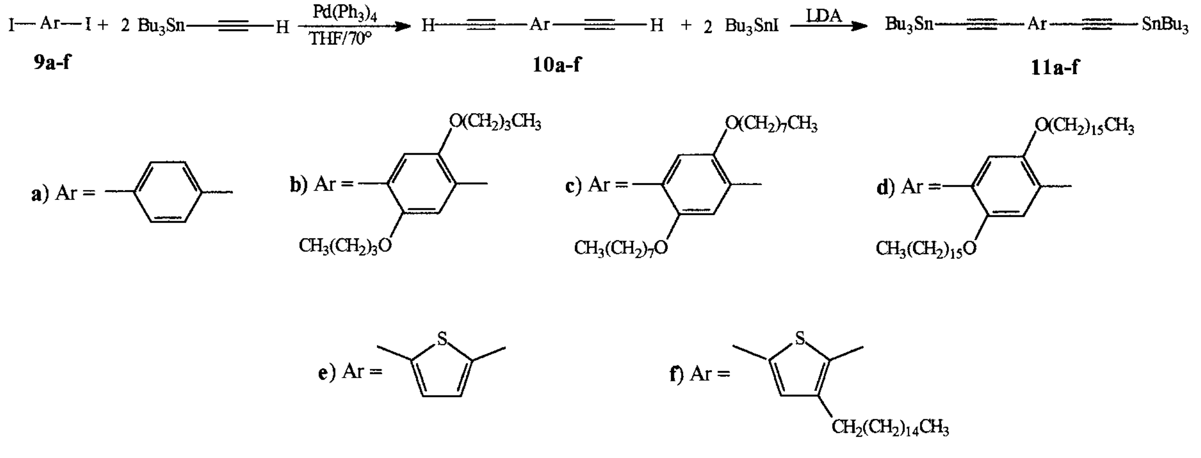
Fig. 2. Portions of ^{1}H-NMR spectra in the range 2.3–0.7 ppm for the transformation **9a**–**11a**. Spectra were recorded on a sample of the reaction mixture evacuated from the solvent and redissolved in $CDCl_3$. Trace (a) **9a** and $Bu_3Sn–C≡CH$ before the addition of the Pd catalyst. Trace (b) complete formation of **10a** and Bu_3SnI. Trace (c) complete formation of **11a**.

on compounds **4a**,**b**, due to the more delicate nature of the intermediate organometallic alkynes. After this first step, LDA was directly added to the cooled reaction mixture, and, trialkyltinethynyl derivatives **6c**–**e** were then isolated in 86–90% yields.

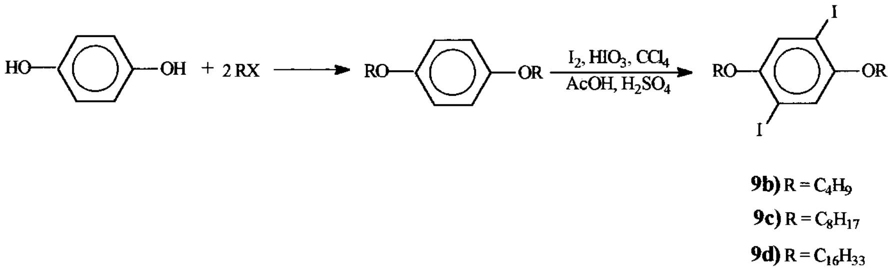
The reactions of compounds **4c**–**e** were monitored by ^{1}H-NMR techniques, which provided a very clear picture of the overall transformation (vide infra Fig. 2). The results obtained in the preparation of compounds **6a**–**e** prompted us to use this *one pot* procedure to form bifunctionalized tin acetylides, in view of the potential of these compounds for the construction of highly ethynylated materials (Scheme 2). The array of diiodo aromatic derivatives **9a**–**f** were then considered (Scheme 6) in the perspective of using combination of them and of the corresponding (bis)stannylethynyl derivatives in the formation of polymeric materials.

All the diiodo compounds **9a**–**f** efficiently undergo the whole transformation outlined in Scheme 6 affording the corresponding (bis)tributyltinacetylides **11a**–**f** in 80–90% isolated yields. As in the case of the monofunctionalized derivatives, the progress of the two steps sequence was conveniently checked by ^{1}H-NMR spectroscopy (Fig. 2). Despite the fact that the side chains on the aromatic rings compounds **9b**–**d** and **f**, can partially overlap with the signals of the butyl groups on tin, a sequence of spectroscopic variations, as those reported in Fig. 2 can be clearly depicted for all substrates.

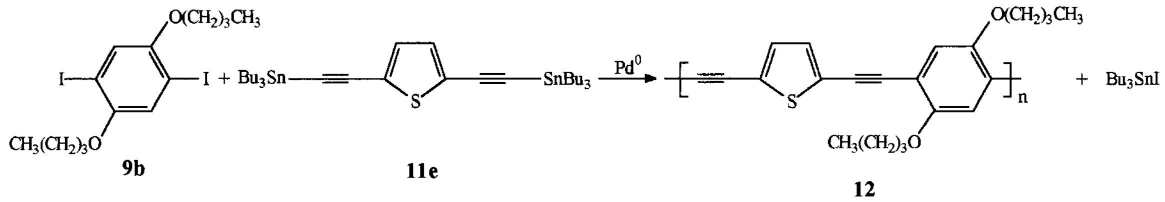
Trace (a) of Fig. 2 represents a portion of the ^{1}H-NMR spectrum of the reaction mixture before addition of the palladium catalyst, thus before the start of the reaction. The spectrum shows the spectroscopic pattern of $Bu_3Sn–C≡CH$ characterized by four distinct multiplets, due to the methyl group and to the three methylene groups, and a singlet due to the acetylenic proton. Trace (b) is the spectrum of the reaction mixture after the completion of the first step. $Bu_3Sn–C≡CH$ has been totally consumed and Bu_3SnI formed displays three multiplets. The methyl and one of the three methylene groups show distinct signals, while signals of the other two methylenes are collapsing in a single multiplet. Trace (c) of Fig. 2 is characteristic of the completion of the overall process. The Bu_3Sn group—bound again to the acetylene moiety—displays the four multiplets pattern as it was in trace (a). This sequence was identically observed for all substrates.



Scheme 6.



Scheme 7.



Scheme 8.

3. Formation of polymers

According to the general design outlined on path (a) of Scheme 2, compounds **9a**–**f** and **11a**–**f** (Scheme 6) represent two arrays of coupling partners suitable to be combined under the Stille protocol to generate π-conjugated poly(arylene ethynylene) type polymers (–Ar–C≡C–Ar′–C≡C–)$_n$ (Ar, Ar′ = phenyl, thienyl). Moreover, by the use of our recently developed Pd-catalyzed procedure for metal–carbon bond formation [9] (path (b) of Scheme 2), coupling of (bis)stannylethynyl derivatives **9a**–**f** with organometallic dihalides should allow formation of polymers incorporating metals into the conjugated backbone of type (–Ar–C≡C–M–C≡C–)$_n$ (Ar = phenyl, M = metal). In this respect, researchers involved in advanced materials sciences are currently devoting a great deal of attention to these two class of polymers in view of their remarkable properties, and new convenient preparative methods are intensely explored [14–22]. With regard to poly(arylene ethynylene) materials, beside the Hay oxidative coupling of terminal alkynes [14], the palladium/copper-mediated couplings of aryl halides and terminal alkynes are the most used methods to obtain these polymers [15–17], while the palladium catalyzed coupling reaction of tinalkynes and aryl halides—the Stille reaction—has only recently received some attention [18,19]. Conversely, preparation of polymers containing σ-bonded metals in the main chain has essentially been developed by the following procedures: (i) dehydroalogenation between bis-ethynyl compounds and transition metal halides, (ii) oxidative coupling of terminal alkyne complexes, (iii) alkynyl ligand exchange reaction [20], and (iv) condensation of transition metal halides with bis(trimethylstannyl) complexes [28].

Compounds **9b**–**d** and **f** of Scheme 6, bearing side chains of variable length on the aromatic ring, were prepared foreseeing that high molecular weight materials would be more easily accessible if good solubility can be assured [19a]. In addition, material properties are strongly influenced by the presence and the size of side chains [21]. It is important to remark that in the preparation of compounds **9b**–**d**, described by Yu [22] and adopted by several other authors [23] (Scheme 7), we experienced that a larger amount of absolutely fresh reagents [24] must be used in order to succeed in the formation of the expected products.

The first attempt of preparing a polymeric material by palladium-catalyzed cross-coupling was carried out by reacting an equivalent amount of 2,5-bis[(tributyltin)ethynyl]thiophene (**11e**) and 1,4-dibutoxy-2,5-diiodobenzene (**9b**) in the presence of 5 mol.% of $Pd(PPh_3)_4$ in THF solvent (Scheme 8). After 24 h at 80°C, a sample of the reaction mixture examined by ^{1}H-NMR showed complete consumption of starting materials and a new set of signals attributable to polymeric material was observed. After filtration on a celite pad precipitation by methanol yielded a red powder. The molecular weight of the polymeric material **12**, evaluated by gel permeation chromatograpy (GPC), is 2100 and corresponds to 6 repeat units (Table 2). Fig. 3 reports the ^{13}C-NMR spectrum of the product obtained; the pattern of the signals indicates the stereoregular structure of the polymer and the estimated 6-term chain length by the ratio of signals of internal and terminal C≡C groups [25].

We then decided to extend the *one pot* procedure, used to form **11e**, to the preparation of the polymer itself. 2,5-Diiodothiophene (**9e**) was thus reacted with tributyl(ethynyl)tin in the presence of $Pd(PPh_3)_4$ and LDA, according to procedure outlined in Scheme 6. Once ascertained complete formation of **11e**, by ^{1}H-NMR, 1,4-dibutoxy-2,5-diiodobenzene (**9b**) and an additional amount of zerovalent palladium catalyst were directly added to *the same* reaction mixture where **11e** had formed. Following 24 h of reflux and work up, a product showing identical characteristics of **12** was isolated. This result shows that not only the two steps needed to transform the diiodide in distannylacetylyde may be carried out *one pot*, but that, once the distannane is formed, a second diiodide may be added directly into the same reaction mixture, thus extending the *one pot* process up to the formation of the polymeric material (path (a) of Scheme 2). It is important to note that while the first coupling only occurs in the presence of $Pd(PPh_3)_4$, the second coupling, leading to the polymer, may be efficiently carried out using either $Pd(PPh_3)_4$ or $Pd(dba)_2$. When $Pd(dba)_2$ is added to perform the second coupling, the reaction mixture contains PPh_3 from the catalyst of the first coupling. Therefore, the effective catalytic specie may be the same in the two different steps [26].

By the use of this *extended one pot* procedure polymeric materials listed in Table 1 were obtained in a straightforward manner. As described for **12** all the polymers were isolated and purified by precipitation with methanol. Polymers **13**–**16** were obtained in good yield as yellow, red or brownish solids and are stable in air, while organometallic polymers **19**–**21**, obtained by Pd-catalyzed coupling of bis(tin)acetylydes **9e**, **b** and **c** with the diiododerivative **17** [9e] (Fig. 4) appear as dark brown solids.

All polymers remained in solution during synthesis, but some of them (vide infra) became insoluble after isolation. Differences in solubility are observed within the set of the organic polymers **12**–**16**. Polymer **12** is more soluble in dicholoromethane than in chloroform, polymer **13** shows a very limited solubility in common organic solvents, while **14**–**16** are well-soluble in chloroform, dichloromethane and THF. These solubility differences are correlated with the length and the number of the side chains on the aromatic moieties [21b,16f]. On the contrary, after precipitation, all the organometallic polymers **19**–**21** remained insoluble. Evidently, the introduction of an aryl spacer bearing two butyloxy (**20**) or octyloxy (**21**) side chains had no effect on solubility with respect to **19**, where a simple thiophene unit is spacing the organometallic blocks. The tetramer **22** is a well-soluble material obtained by our standard procedure. It represents a low oligomer of a polymer obtained by Hagiara by dehydrohalogenation [20]. Although the present method yields only a four chain unit, its formation shows that the platinum–chlorine moiety may also undergo palladium-catalyzed coupling with tributyltin acetylides, thus envisioning a possible expansion of our Pd-catalyzed metal–carbon bond formation procedure [9].

Molecular weights were estimated using GPC. Table 2 reports the weight average molecular weights (M_W), the number average molecular weights (M_n), and the molecular weight distribution (MWD = M_W/M_n) values calculated against polystyrene standards. It is known that, using randomly coiled polystyrene as calibration standards, the molecular weight of rigid rod material may be greatly overestimated. Therefore, we adopted

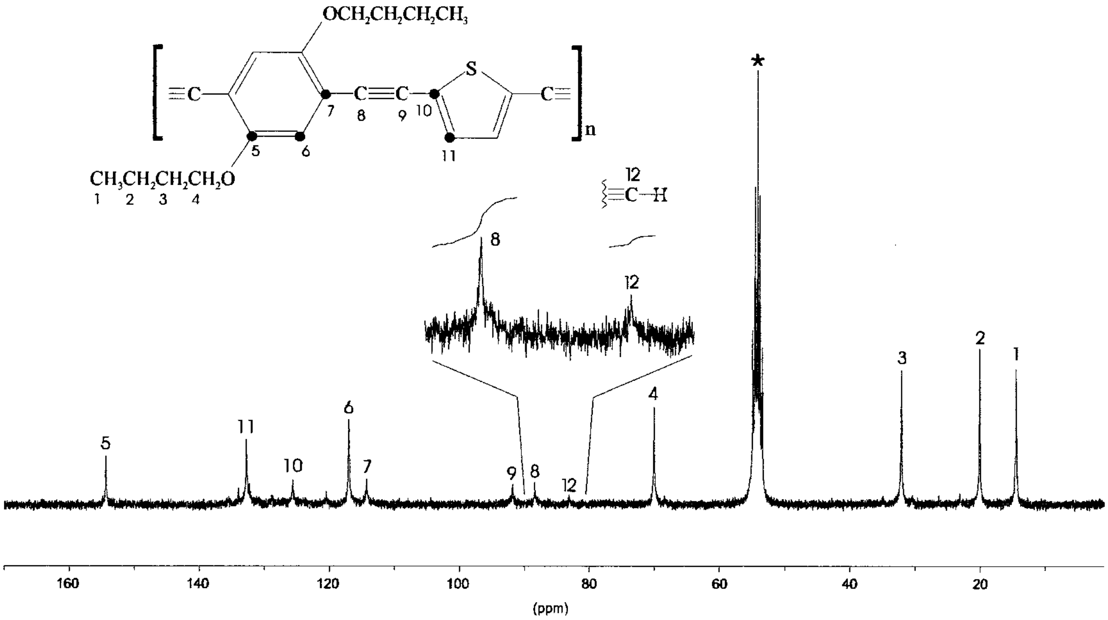
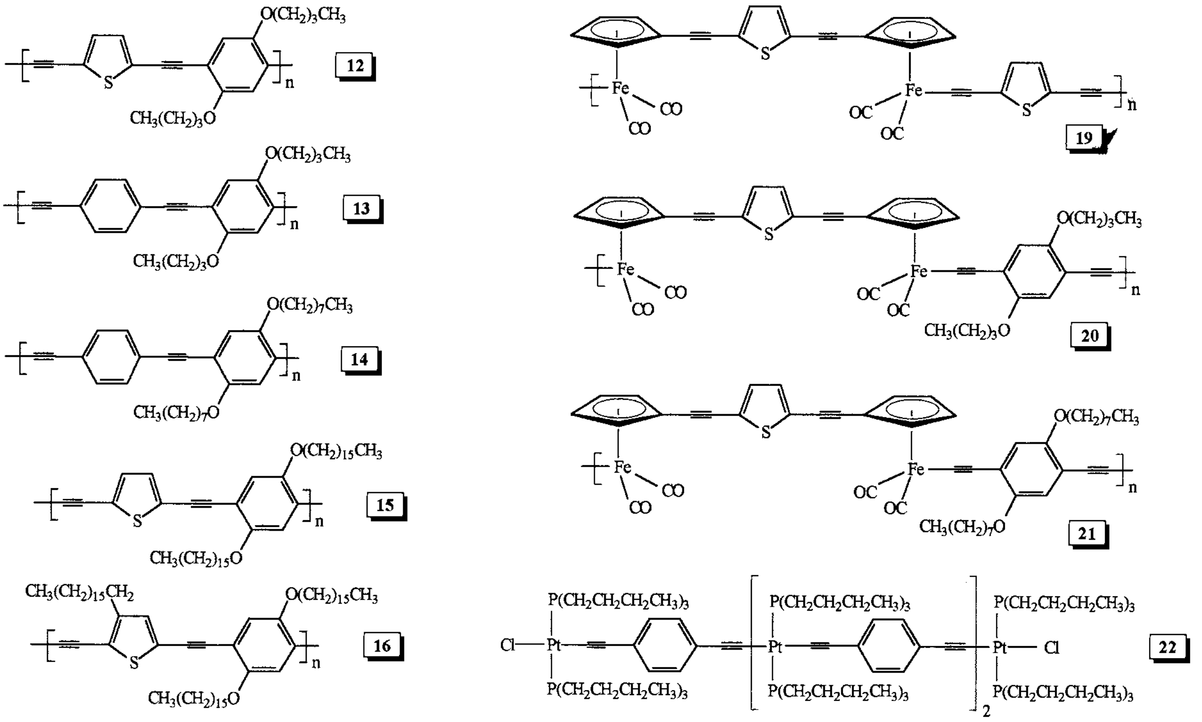


Fig. 3. ^{13}C-NMR spectra of polymer **12**. The multiplet marked with an asterisk is relative to the CD_2Cl_2 solvent.

Table 1



the criteria used by Tour [15b,c], which has demonstrated that the actual molecular weight of rigid rod polymers is better estimated by decreasing of about 20% the M_n value obtained by GPC. In the case of polymers **19**–**21** that are scarcely soluble in THF, the values reported are probably related only to the fractions of lower oligomers. Since the scarce solubility of these polymers did not allow the characterization by NMR, they were characterized only by UV and IR spectroscopy. Two distinct bands in the region 2210–2092 cm^{-1} were observed in the IR spectra of polymers **19**–**21**. The higher frequency was assigned to the stretching of the C≡C spacing the cyclopentadienyl and the thiophene moieties, the second to the C≡C spacing the iron and the other thiophene unit.

Polymers **12**, **14**–**16** and **22** were fully characterized by ^{1}H- and ^{13}C-NMR spectra, whereas only ^{1}H-NMR was recorded for **13**, due to its limited solubility. As in the case of **12** (Fig. 3) the complete carbon skeleton of all the soluble polymers was clearly identified in the ^{13}C-NMR spectra, including the acetylenic carbons that are usually very difficult to detect [16f,19a]. A number average degree of polymerization (DP) of about 5–9 repeated units was obtained for all the soluble polymers by this method. Although these degrees of polymerization are in the lower range of the average values reported for polymers obtained by Pd-catalyzed coupling of bis(trialkyltin) acetylides and dihalides [18,19a,c], we believe that optimization of this procedure can lead to higher order of polymerization. The UV absorption spectra of polymers, recorded in chloroform, show a typical broad absorption with a maximum in the range of $\lambda = 400$–440 nm (Table 2). As an example, Fig. 5 shows the UV spectra of polymer **16** and the corresponding block precursors **11d** and **11f**. The consistent shift with respect of the value of the maximum of the corresponding aromatic diacetylenic units is a rather direct evidence of extensive electronic conjugation, and to some extent it is a direct measure of chain length growing [19b], although to a certain value this effect approaches saturation [15c,17,27].

The *one pot* route to polyacetylene and polymetallaacetylene polymers here described has some resemblance with a *one pot* route to polyacetylenes previously reported by Carpita [28] and others [16,17]. There are however some remarkable differences between the two

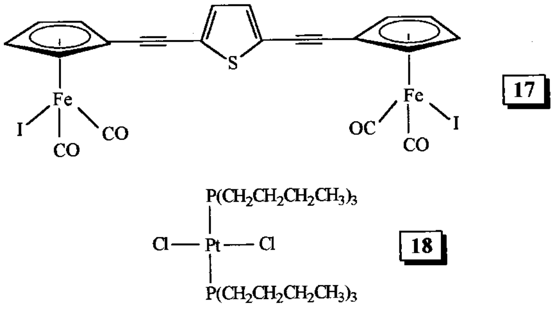


Fig. 4. Organometallic structures of compounds **17** and **18**.

Table 2
Characteristic values of the polymers **12**–**22**

Polymer	Yield (%)	M_W[a]	M_n[b]	MWD[c]	DP[d]	λ_{max} (nm)[e]	ν (C≡C) (cm^{-1})
12	94	8850	2900	3.0	6[i]	437	2206[f]
13	72	10150	3650	2.7	8[i]	394	2209[f]
14	93	6600	3000	2.2	5[i]	404	2208[f]
15	86	7950	4600	1.7	5[i]	412	2196[f]
16	98	25100	10300	2.4	9[i]	443	2194[f]
19	82	3300	2700	1.2	4[j]	339	2210[g] 2091
20	88	2000	1800	1.1	3[j]	365	2192[g] 2101
21	79	3500	3000	1.2	4[j]	356	2204[g] 2105
22	87	2600	1700	1.5	4[j]	380	2102[h]

[a] Weight average molecular weights.
[b] Number average molecular weights.
[c] Molecular weight distribution (M_W/M_n).
[d] Degree of polymerization.
[e] UV–visible spectra recorded in $CHCl_3$.
[f] Recorded in Nujol.
[g] Recorded in KBr.
[h] Recorded in CH_2Cl_2.
[i] Calculated by decreasing the M_n value by 20%.
[j] Calculated on the basis of the M_W value [7b].

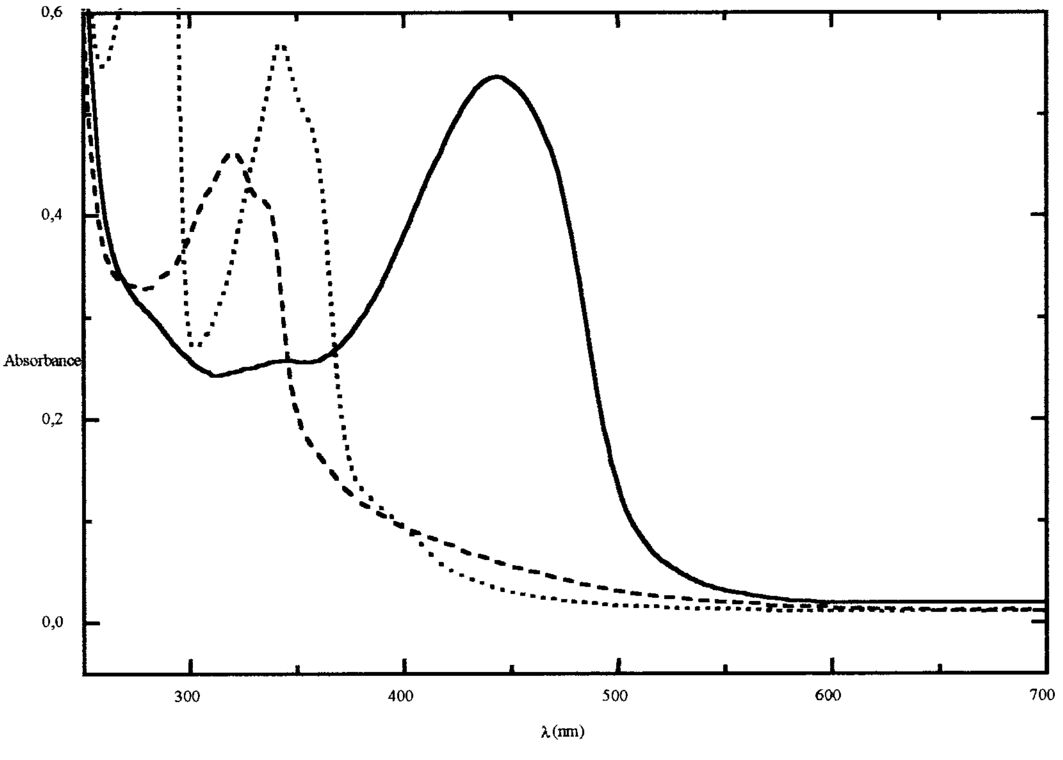
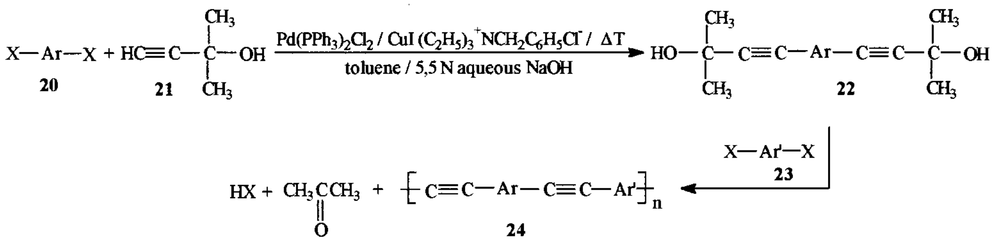


Fig. 5. UV–visible spectra in $CHCl_3$ of **16** (—), **11d** (······) and **11f** (---).

procedures. In that report (Scheme 9), palladium catalysis coupling of a dihaloarene (**20**) with two equivalents of 2-methyl-3-butyn-2-ol (**21**), under basic phase transfer conditions, afforded the arylbisalkynol **22**. Addition of the second dihaloarene (**23**) and warming up of the reaction mixture produced cleavage of the carbinol protecting group and formation of the polymers (**24**).

Although in the reported cases polymers are formed in moderate to good yields, the phase transfer conditions might be restricting conditions for more general



Scheme 9.

uses. Moreover, being deprotection of acetylene groups the rate limiting factor, the second part of the reactions must be run at high temperature (110–130°C) and needs long reaction times (48–72 h), conditions that might be detrimental for the intermediate free diacetylenes. Finally, owing to the more complicate reaction media, isolation of the final product is more laborious.

4. Concluding remarks

With the present work we have disclosed an efficient *one pot* process allowing direct transformation of aromatic iodides and diiodides into the corresponding trialkyltinacetylides and bistrialkyltinacetylides. These products may be either isolated and used for a variety of synthetic purposes or reacted in situ with a proper coupling partner in an *extended one pot* procedure to form polyacetylene or polymetallaacetylene polymers. There are distinct advantages of our straightforward transformation. No isolation of the free alkyne intermediate is necessary. This is a particularly remarkable point, considering the fact that free alkynes are delicate materials which often present uncontrolled reactivity, troublesome preparation, and hazardous handling [11,12], thus discouraging their use. In addition new, expensive or hazardous tin reagents are not required to transform the intermediate free alkyne into tinacetylide, since the side product generated during the first step of the transformation is reutilized. In this respect, authors using the (trimethyltin)ethynyl/halide condensation procedure clearly alert users about the hazardous handling of trimethyltinchloride [29], the most toxic tin reagent [30], whereas tributyltin halides have a very low toxicity and are easier to handle. Finally, the poly(arylene ethynylene) materials prepared by this new and convenient synthetic route show an high degree of stereoregularity, and in most cases of processability, which are important prerequisites for applications in electronic and optical devices. The same procedure was also shown to be very promising for obtaining organometallic polymers. These materials will probably improve their chemical properties by elongation of the side chains on the aromatic moieties.

5. Experimental

5.1. General procedures

Elemental analyses were performed by the Servizio Microanalisi of the Area della Ricerca di Roma (CNR, Montelibretti). IR spectra were recorded on a Nicolet FT 510 instrument in the solvent subtraction mode, using a 0.1 mm CsI cell or polyethylene disk. UV spectra were recorded on a Varian Cary 1 spectrophotometer. ^{1}H-NMR, ^{13}C-NMR and ^{31}P-NMR spectra were recorded on a Bruker AC300P spectrometer at 300, 75 and 121 MHz, respectively. The ^{1}H-NMR chemical shifts (ppm) are relative to Me_4Si, assigning the residual ^{1}H impurity signal in the solvent at 7.24 ppm ($CDCl_3$) and 5.30 ppm (CD_2Cl_2). The ^{13}C-NMR chemical shifts are calibrated to the ^{13}C triplet of $CDCl_3$ at 77.00 ppm and to the ^{13}C multiplet of CD_2Cl_2 at 54.20 ppm. The^{31}P-NMR chemical shifts are relative to 85% H_3PO_4. GC-MS analyses were performed on a HP5890 GC (OV1 capillary column, 12 m × 0.2 mm) coupled with a HP5970 MSD and on a Fisons Instruments VG-Platform Benchtop LC-MS (positive ion electrospray mass spectra, ESP^+) spectrometer. Molecular weights were determined (relative to polystyrene standard) on a Perkin-Elmer gel permeation chromatograpy (GPC) equipped with a set of PL-gel columns and a UV detector. $CHCl_3$ (HPLC grade; Aldrich) was the eluent (flow rate: 1 ml min^{-1}).

Solvents, including those used for NMR and chromatograpy, and liquids were thoroughly degassed before use. Chromatographic separations were performed with 70–230 mesh silica gel (Merck).

All manipulations were carried out with Schlenk-type equipment under an atmosphere of argon on a dual manifold/argon vacuum system. All solvents were dried (sodium–potassium alloy for tetrahydrofuran (THF), CaH_2 for *N*,*N*-dimethylformamide (DMF) and P_2O_5 for CH_2Cl_2) and argon-saturated prior to use. The compounds: (η^5-C_5H_4I)$Fe(CO)_2CH_3$ [6a], (η^5-C_5H_4I)$Re(CO)_3$ [6a], (η^5-C_5H_4I)$W(CO)_3CH_3$ [6a], $(CH_3CN)_2PdCl_2$ [14], $(PPh_3)_4Pd$ [15], *trans*-[$PtCl_2\{$*n*-$C_4H_9)_3P\}_2$] [31] were prepared by known methods. 3-Hexadecylthiophene [32] was prepared from 3-bromothiophene and hexadecylmagnesiumbromide in the presence of Ni(dppp)$_2$Cl$_2$ following a reported procedure [33]. In our hands 1,4-diiodo-2,5-bis(butyloxy)benzene [22], 1,4-diiodo-2,5-bis(octyloxy)benzene [23] and 1,4-diiodo-2,5-bis(hexadecyloxy)benzene [22] were successfully prepared only by using a fourfold excess of freshly received I_2, HIO_3, H_2SO_4 and CH_3COOH [24]. Other chemicals were purchased from Aldrich or Strem and used as received unless otherwise specified.

*5.2. Preparation of 2,5-diiodo-3-hexadecylthiophene (**9f**)*

Finely powdered I_2 (5.205 g, 20 mmol) was added to a stirred solution of 3-hexadecylthiophene (6.368 g, 20 mmol) in CH_2Cl_2 (40 ml) and the resulting mixture was heated to reflux. A solution of HNO_3 (1.7 ml) in H_2O (1.7 ml) was added dropwise with such a rate to maintain a gentle refluxing. After a further 3 h of reflux, the flask was cooled and the organic layer was separated, washed with H_2O (2×50 ml), a saturated solution of $Na_2S_2O_3$ (50 ml), and dried over anhydrous Na_2SO_4. The dried solution was evaporated to a crude product, which was purified by column chromatography (SiO_2) using hexane as eluant. The product (9.37 g; 81%) was isolated as tan solid.

IR (CH_2Cl_2): 3054 (s), 2987 (m), 2928 (m), 2855 (w), 2306 (w), 1422 (m), 1266 (s), 897 (m), 747 (s) cm^{-1}.

^{1}H-NMR ($CDCl_3$): δ 0.85 (t, 3H, $J = 6.6$ Hz, –C*H*$_3$), 1.23 (m, 28H, –C*H*$_2$–)$_{14}$, 2.48 (t, 2H, $J = 7.6$ Hz, –C*H*$_2$–thiop), 6.86 (s, 1H, *H*–thiop). ^{13}C-NMR ($CDCl_3$): δ 14.18 (–*C*H$_3$), 22.73, 29.15, 29.41, 29.74, 29.98, 31.96, (–*C*H$_2$–)$_{15}$, 75.81 (–S–*C*(I)=), 137.80 (–*C*(H)=), 149.56 (–*C*(C$_{16}$)=).

Anal. Calc. for $C_{20}H_{34}I_2S$: C, 42.87; H, 6,12. Found: C, 42.56; H, 6.06.

*5.3. General preparation of bis(ethynyl) derivatives (**10a–f**) and Bis[(tributyltin)ethynyl] derivatives (**11a–f**)*

*5.3.1. 1,4-Bis(ethynyl)benzene (**10a**) and 1,4-bis[(tributyltin)ethynyl]benzene (**11a**)*

The procedure for the preparation of 1,4-bis(ethynyl)benzene (**10a**) and 1,4-bis[(tributyltin)ethynyl]benzene (**11a**) is representative. To a solution of 0.069 g (0.059 mmol) of Pd(PPh$_3$)$_4$ and 0.049 g of (1.49 mmol) of 1,4-diiodobenzene in 15 ml of THF, 0.86 ml (2.98 mmol) of tributyl(ethynyl)tin were added. Following overnight stirring 50°C, GC-MS analysis indicated complete consumption of reactants. After cooling at 0°C, 1.49 ml (2.98 mmol) of a solution of LDA (2.0 M sol. in THF/heptane/ethylbenzene) was added, and the mixture was allowed to warm at room temperature. Water (10 ml) was added to the reaction mixture, which was then by transferred to a separatory funnel along with 50 ml of hexane. The phases were separated, and the organic layer was washed with water (3×50 ml) and dried over sodium sulfate. Filtration and removal of the solvent under reduced pressure provided 1.11 g (90%) of product as a yellow liquid, which was spectroscopically pure. Attempts of obtaining an analytically pure sample by chromatographic separation caused partial removal of tributyltin groups.

In some cases the reaction was interrupted at the formation of the intermediate bisacetylene, and the product was isolated after treatment with an aqueous saturated solution of KF and chromatographic separation [9d,e] (silica gel/hexanes).

*5.3.1.1. **10a**.* ^{1}H-NMR ($CDCl_3$): δ 3.14 (s, 2H, ≡C*H*), 7.42 (s, 2H, Ar–*H*).

MS (EI) *m/e* 126 (M$^+$). Spectroscopic data are consistent with literature reports [34].

*5.3.1.2. **11a**.* IR (neat): 2925 (s), 2854 (s), 2135 (m), 1494 (m), 1461 (m), 1377 (m), 1258 (m), 600 (m), 510 (m) cm^{-1}.

^{1}H-NMR ($CDCl_3$): δ 0.89 (t, 18H, $J = 6.76$ Hz), 1.03 (m, 12H), 1.33 (m, 12H), 1.55 (m, 12H) (SnC*H*$_2$C*H*$_2$C*H*$_2$C*H*$_3$), 7.32 (s, 4H, Ar–*H*).

^{13}C-NMR ($CDCl_3$): δ 10.62, 13.14, 26.42, 28.36 (Sn*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_3$), 122.94, 131.08 (*Ar*), 94.66, 109.22 (–*C*≡*C*–). Spectroscopic data are consistent with literature reports [5].

*5.3.2. 1,4-Bis(ethynyl)-2,5-di(butyloxy)benzene (**10b**) and 1,4-bis[(tributyltin)ethynyl]-2,5-di(butyloxy)benzene (**11b**)*

*5.3.2.1. **10b**.* ^{1}H-NMR ($CDCl_3$): δ 0.94 (t, 6H, $J = 7.41$ Hz, –C*H*$_3$), 1.53 (m, 4H, –C*H*$_2$–), 1.76 (m, 4H, –C*H*$_2$–), 3.95 (t, 4H, $J = 6.51$ Hz, –OC*H*$_2$–), 3.31(s, 2H, ≡C*H*), 6.93, (s, 2H, Ar–*H*).

^{13}C-NMR ($CDCl_3$): δ 13.83 (–*C*H$_3$), 19.12, 31.16, (–*C*H$_2$–)$_2$, 69.24, (–O*C*H$_2$–), 79.75, 117.60, 153.88 (*Ar*), 82.37, 113.14 (–*C*≡*C*–). Spectroscopic data are consistent with literature reports [35].

*5.3.2.2. **11b**.* IR (CH_2Cl_2): 2925 (s), 2854 (s), 2132 (m), 1464 (m), 1377 (m), 1073 (m), 602 (w), 510 (w) cm^{-1}.

^{1}H-NMR ($CDCl_3$): δ 0.89 (t, 18H, $J = 7.17$ Hz), 1.03 (m, 12H), 1.34 (m, 12H), 1.58 (m, 12H) (SnC*H*$_2$C*H*$_2$C*H*$_2$C*H*$_3$), 0.94 (t, 6H, $J = 6.96$ Hz, –C*H*$_3$), 1.53 (m, 4H, –C*H*$_2$–), 1.74 (m, 4H, –C*H*$_2$–), 3.95 (t, 4H, $J = 6.51$ Hz, –OC*H*$_2$–), 6.85 (s, 2H, Ar–*H*).

^{13}C-NMR ($CDCl_3$): δ 11.15, 13.65, 26.95, 28.77 (Sn*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_3$), 13.88 (–*C*H$_3$), 19.21 (–*C*H$_2$–), 31.39 (–*C*H$_2$–), 69.04 (–O*C*H$_2$–), 114.08, 117.46, 153.74 (*Ar*), 99.09, 105.84 (–*C*≡*C*–).

MS (ESP$^+$) *m/e* 887 (M + K)$^+$.

5.3.3. 1,4-Bis(ethynyl)-2,5-di(octyloxy)benzene ***(10c)*** *and 1,4-bis[(tributyltin)ethynyl]-2,5-di(octyloxy)benzene* ***(11c)***

5.3.3.1. ***10c***. ^{1}H-NMR ($CDCl_3$): δ 0.86 (t, 6H, $J = 6.81$ Hz, $-CH_3$), 1.28 (m, 12H, $-CH_2-)_3$, 1.45 (m, 8H, $-CH_2-)_2$, 1.77 (m, 4H, $-CH_2-$), 3.94 (t, 4H, $J = 6.59$ Hz, $-OCH_2-$), 3.31(s, 2H, $\equiv CH$), 6.93, (s, 2H, Ar–H).

^{13}C-NMR ($CDCl_3$): δ 14.08 ($-CH_3$), 22.64 ($-CH_2-$), 25.96 ($-CH_2-$), 29.26 ($(-CH_2-)_2$), 31.83 ($(-CH_2-)_2$), 69.81 ($-OCH_2-$), 79.63, 117.60, 153.78 (*Ar*), 82.37, 113.13 ($-C\equiv C-$). Spectroscopic data are consistent with literature reports [16d].

5.3.3.2. ***11c***. IR (CH_2Cl_2): 2925 (s), 2854 (s), 2130 (m), 1496 (m), 1466 (m), 1377 (m), 1221 (m), 604 (w), 504 (w) cm^{-1}.

^{1}H-NMR ($CDCl_3$): δ 0.89 (t, 18H, $J = 7.41$ Hz), 1.03 (m, 12H), 1.35 (m, 12H), 1.59 (m, 12H) ($SnCH_2CH_2CH_2CH_3$), 0.86 (t, 6H, $J = 6.88$ Hz, $-CH_3$), 1.28 (m, 12H, $-CH_2-)_3$, 1.45 (m, 8H, $-CH_2-)_2$, 1.76 (m, 4H, $-CH_2-$), 3.91 (t, 4H, $J = 6.66$ Hz, $-OCH_2-$), 6.85 (s, 2H, Ar–H).

^{13}C-NMR ($CDCl_3$): δ 11.17, 13.65, 26.72, 28.85 ($SnCH_2CH_2CH_2CH_3$), 14.04 ($-CH_3$), 22.66 ($-CH_2-$), 25.98 ($-CH_2-$), 29.30 ($(-CH_2-)_2$), 31.87 ($(-CH_2-)_2$), 69.41 ($-OCH_2-$), 114.11, 117.52, 153.74 (*Ar*), 99.07, 105.88 ($-C\equiv C-$).

MS (ESP$^+$) m/e 967 $(M + Li)^+$.

5.3.4. 1,4-Bis(ethynyl)-2,5-di(hexadecyloxy)benzene ***(10d)*** *and 1,4-bis[(tributyltin)ethynyl]-2,5-di(hexadecyloxy)benzene* ***(11d)***

5.3.4.1. ***10d***. ^{1}H-NMR ($CDCl_3$): δ 0.86 (t, 6H, $J = 6.67$ Hz, $-CH_3$), 1.23 (m, 52H, $-CH_2-)_{13}$, 1.78 (m, 4H, $-CH_2-$), 3.94 (t, 4H, $J = 6.66$ Hz, $-OCH_2-$), 3.31(s, 2H, $\equiv CH$), 6.92, (s, 2H, Ar–H).

^{13}C-NMR ($CDCl_3$): δ 14.13 ($-CH_3$), 22.69 ($-CH_2-$), 29.35 ($-CH_2-$), 29.69 ($(-CH_2-)_{11}$), 31.92 ($-CH_2-$), 69.60 ($-OCH_2-$), 79.75, 117.62, 153.91 (*Ar*), 82.39, 113.15 ($-C\equiv C-$).

MS (ESP$^+$) m/e 692 $(M + Na)^+$. Spectroscopic data are consistent with literature reports [16c].

5.3.4.2. ***11d***. IR (CH_2Cl_2): 2925 (s), 2854 (s), 2132 (m), 1496 (m), 1466 (m), 1377 (m), 1221 (m), 602 (w), 510 (w) cm^{-1}.

^{1}H-NMR ($CDCl_3$): δ 0.89 (t, 18H, $J = 7.26$ Hz), 1.03 (m, 12H), 1.32 (m, 12H), 1.57 (m, 12H) ($SnCH_2CH_2CH_2CH_3$), 0.86 (t, 6H, $J = 6.82$ Hz, $-CH_3$), 1.23 (m, 52H, $(-CH_2-)_{13}$), 1.76 (m, 4H, $-CH_2-$), 3.91 (t, 4H, $J = 6.51$ Hz, $-OCH_2-$), 6.85 (s, 2H, Ar–H).

^{13}C-NMR ($CDCl_3$): δ 11.18, 13.68, 27.03, 28.87 ($SnCH_2CH_2CH_2CH_3$), 14.12 ($-CH_3$), 22.69 ($-CH_2-$), 29.36 ($-CH_2-$), 29.70 ($(-CH_2-)_{11}$), 31.92 ($-CH_2-$), 69.40 ($-OCH_2-$), 114.06, 117.50, 153.74 (*Ar*), 99.00, 105.86 ($-C\equiv C-$).

MS (ESP$^+$) m/e 1185 $(M + H)^+$.

5.3.5. 2,5-Bis[(ethynyl)thiophene ***(10e)*** *and 2,5-bis[(tributyltin)ethynyl]thiophene* ***(11e)***

5.3.5.1. ***10e***. ^{1}H-NMR ($CDCl_3$): 3.33 (s, 2H, $\equiv CH$), 7.09, (s, 2H, thiop–H).

^{13}C-NMR ($CDCl_3$): δ 76.33, 81.81 ($-C\equiv C-$), 121.87, 131.62 (*thiop*).

MS (EI) m/e 132 (M^+). Spectroscopic data are consistent with literature reports [11a].

5.3.5.2. ***11e***. IR (neat): 2925 (s), 2854 (s), 2122 (s), 1464 (s), 1377 (s), 1165 (s), 1074 (s), 802 (m), 687 (s), 599 (m), 504 (m) cm^{-1}.

^{1}H-NMR ($CDCl_3$): δ 0.88 (t, 18H, $J = 7.20$ Hz), 1.03 (m, 12H), 1.32 (m, 12H), 1.54 (t, 12H, $J = 7.20$ Hz) ($SnCH_2CH_2CH_2CH_3$), 6.94 (s, 2H, thiop–H).

^{13}C-NMR ($CDCl_3$): δ 11.24, 13.64, 26.95, 28.83 ($SnCH_2CH_2CH_2CH_3$), 124.47, 131.26 (*thiop*), 99.54, 101.81 ($-C\equiv C-$). Spectroscopic data are consistent with literature reports [9c].

5.3.6. 2,5-Bis[(ethynyl)-3-(hexadecyl)thiophene ***(10f)*** *and 2,5-bis[(tributyltin)ethynyl]-3-(hexadecyl)thiophene* ***(11f)***

5.3.6.1. ***10f***. IR (neat): 3311 (s), 2924 (s), 2854 (s), 2104 (m), 1640 (m), 1466 (m), 1377 (m), 659 (m) cm^{-1}.

^{1}H-NMR ($CDCl_3$): 0.88 (t, 3H, $J = 6.44$ Hz, $-CH_3$), 1.26 (m, 26H, $(-CH_2-)_{13}$), 1.58 (m, 2H, $-CH_2-$), 2.64 (t, 2H, $J = 7.63$ Hz, thiop–CH_2-), 3.30 (s, 1H, $\equiv CH$), 3.42 (s, 1H, $\equiv CH$), 7.00, (s, 1H, thiop–H).

^{13}C-NMR ($CDCl_3$): δ 14.15 ($-CH_3$), 22.75, 29.19, 29.41, 29.74, 30.04, 30.34, 31.98, ($(-CH_2-)_{15}$), 76.01, 76.69, 81.67, 83.93 ($-C\equiv C-$), ($-C\equiv C-$), 118.89, 122.04, 133.71, 148.65 (*thiop*).

MS (ESP$^+$) m/e 380 $(M + Na)^+$.

5.3.6.2. ***11f***. IR (neat): 2925 (s), 2854 (s), 2135 (m), 1494 (m), 1461 (m), 1377 (m), 1258 (m), 600 (m), 510 (m) cm^{-1}.

^{1}H-NMR ($CDCl_3$): 0.90 (t, 18H, $J = 7.15$ Hz), 1.03 (m, 12H), 1.31 (m, 12H), 1.56 (m, 12H) ($SnCH_2CH_2CH_2CH_3$), 0.89 (t, 3H, $J = 7.16$ Hz, $-CH_3$), 1.23 (m, 26H, $(-CH_2-)_{13}$), 1.57 (m, 2H, $-CH_2-$), 2.59 (t, 2H, $J = 7.78$ Hz, thiop–CH_2-), 6.86, (s, 1H, thiop–H).

^{13}C-NMR ($CDCl_3$): δ 11.20, 13.63, 26.93, 28.88 ($SnCH_2CH_2CH_2CH_3$), 14.08 ($-CH_3$), 22.67, 29.34, 29.67, 31.93 ($(-CH_2-)_{15}$), 98.91, 101.03, 101.67, 102.31 ($-C\equiv C-$), ($-C\equiv C-$), 119.88, 122.67, 132.45, 147.10 (*thiop*).

5.4. General preparation of polymers

The typical polymerization procedure was as follows: the diiodo monomer (1 mmol) and zero valent palladium (2 mol.% equivalent) were directly added to the flask where the distannyl monomer (1 mmol) had just formed according to the *one pot* procedure described as above. The mixture was then refluxed for 24 h and after cooling, was filtered on a glass frit over a celite pad in order to remove the metallic palladium. The filtrate was then concentrate to a minimum volume, and precipitated with methanol. The precipitate was collected by filtration, washed with methanol repeatedly, and dried under vacuum.

5.4.1. Poly{[1,4-bis (ethynyl)-2,5-di(butyloxy)-benzene]-1,4-thiophene} (**12**)

^{1}H-NMR (CD_2Cl_2): δ 0.98 (m, 6H, –CH_3), 1.54 (m, 4H, –CH_2–), 1.81 (m, 4H, –CH_2–), 4.00 (m, 4H, –OCH_2–), 6.96 (s, 2H, thiop–*H*), 7.13, (s, 2H, Ar–*H*).

^{13}C-NMR (CD_2Cl_2): δ 14.46 (–CH_3), 20.08, 32.05, (–CH_2–)$_2$, 70.10, (–OCH_2–), 114.31, 117.05, 154.38 (*Ar*), 125.66, 132.81 (thioph), 88.45, 91.92 (–*C*≡*C*–).

5.4.2. Poly{[1,4-bis (ethynyl)-2,5-di(butyloxy)benzene]-1,4-benzene} (**13**)

^{1}H-NMR ($CDCl_3$): δ 0.99 (m, 6H, –CH_3), 1.57 (m, 4H, –CH_2–), 1.80 (m, 4H, –CH_2–), 4.00 (m, 4H, –OCH_2–), 7.00 (s, 2H, Ar–*H*), 7.48, (s, 4H, Ar–*H*).

5.4.3. Poly{[1,4-bis (ethynyl)-2,5-di(octyloxy)-benzene]-1,4-benzene} (**14**)

^{1}H-NMR ($CDCl_3$): δ 0.86 (m, 6H, –CH_3), 1.26 (m, 20H, –CH_2–)$_4$, 1.54 (m, 4H, –CH_2–), 1.81 (m, 4H, –CH_2–), 3.99 (m, 4H, –OCH_2–), 6.97, (s, 2H, Ar–*H*), 7.47, (br, 4H, Ar–*H*).

^{13}C-NMR ($CDCl_3$): δ 13.94 (–CH_3), 22.86 (–CH_2–), 26.09 (–CH_2–), 27.11 (–CH_2–), 29.42 (–CH_2–)$_2$, 31.99 (–CH_2–), 69.60 (–OCH_2–), 114.96, 117.24, 153.59 (*Ar*), 123.26, 131.37 (*Ar*), 88.47, 93.74 (–*C*≡*C*–).

5.4.4. Poly{[1,4-bis (ethynyl)-2,5-di(hexadecyloxy)-benzene]-1,4-thiophene} (**15**)

^{1}H-NMR ($CDCl_3$): δ 0.85 (br, 6H, –CH_3), 1.23 (br, 52H, (–CH_2–)$_{13}$), 1.79 (br, 4H, –CH_2–), 3.97 (br, 4H, –OCH_2–), 6.95 (s, 2H, thiop–*H*), 7.12, (s, 2H, Ar–*H*).

^{13}C-NMR ($CDCl_3$): δ 14.15 (–CH_3), 22.73 (–CH_2–), 26.05 (–CH_2–), 29.76 (–CH_2–)$_{11}$, 31.97, (–CH_2–), 70.03, (–OCH_2–), 113.71, 116.34, 153.61 (*Ar*), 124.92, 131.70 (thioph), 88.00, 91.01 (–*C*≡*C*–).

5.4.5. Poly{[1,4-bis (ethynyl)-2,5-di(hexadecyloxy)-benzene]-1,4-(3-hexadecyl)thiophene} (**16**)

^{1}H-NMR ($CDCl_3$): δ 0.85 (br, 9H, –CH_3), 1.15–1.45 (br, 78H, –CH_2–), 1.82 (br, 4H, –CH_2–), 3.99 (br, 4H, –OCH_2–), 7.03 (s, 2H, thiop–*H*), 6.93 (s, 2H, Ar–*H*).

^{13}C-NMR ($CDCl_3$): δ 14.13 (–CH_3), 22.72 (–CH_2–), 26.05 (–CH_2–), 29.40 (–CH_2–), 29.74 (–CH_2–)$_{10}$, 31.95, 69.63, ($C_{16}H_{33}$–thioph and $C_{16}H_{33}O_2$–Ar), 113.68, 116.44, 153.52 (*Ar*), 120.39, 123.34, 132.83, 147.76 (thioph), 88.58, 90.80 (–*C*≡*C*–).

5.4.6. Poly{2,5-bis[(η^5-(ethynyl)cyclopentadienyl)-irondicarbonyl]thiophene-2,5-bis(ethynyl)thiophene} (**19**)

IR (KBr): 2210.5, 2091.9, 2041.5, 1997.7 cm^{-1}.

5.4.7. Poly{2,5-bis[(η^5-(ethynyl)cyclopentadienyl)-irondicarbonyl]thiophene-1,4-[2,5-di(butyloxy)benzene]} (**20**)

IR (KBr): 2192.0, 2101.1, 2038.8, 1994.5 cm^{-1}.

5.4.8. Poly{2,5-bis[(η^5-(ethynyl)cyclopentadienyl)-irondicarbonyl]thiophene-1,4-[2,5-di(octyloxy)benzene]} (**21**)

IR (KBr): 2204.4, 2104.8, 2040.1, 1995.7 cm^{-1}.

5.4.9. Poly{2,5-bis[(ethynyl) benzene]-trans-(bistributylphosphine)platinum} (**22**)

IR (CH_2Cl_2): 2959 (s), 2102 (m), 1498 (m), 1436 (m), 1262 (s), 1094 (s), 1019 (s), 904 (w) 801 (s) 367 (w) cm^{-1}.

^{1}H-NMR ($CDCl_3$): δ 0.89 (br, 72H), 1.42–1.53 (br, 96H), 2.11 (br, 48H), 1.56 (m, (P(CH_2CH_2CH_2CH_3)$_3$), 7.08 (s, 12H, *Ar*).

^{13}C-NMR ($CDCl_3$): δ 13.60, 23.95, 26.19 (P($CH_2CH_2CH_2CH_3$)$_3$), 109.44 (–*C*≡*C*–), 127.61, 130.09 (*Ar*).

^{31}P-NMR ($CDCl_3$): δ 0.85 ($J_{P–Pt} = 2302$ Hz), 3.54 ($J_{P–Pt} = 2363$ Hz).

6. Supplementary material

NMR spectra for all new compounds are available on request from the corresponding author.

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