Use of the Pd-Promoted *Extended One-Pot* (*EOP*) Synthetic Protocol for the Modular Construction of Poly-(arylene ethynylene) *co*-Polymers $[-Ar-C\equiv C-Ar'-C\equiv C-]_n$, Opto- and Electro-Responsive Materials for Advanced Technology

Alessandra Micozzi[a], Monica Ottaviani[a], Giorgio Giardina[a], Antonella Ricci[a], Roberto Pizzoferrato[b], Tiffany Ziller[b], Dario Compagnone,[c] Claudio Lo Sterzo[c,]*

[a] Istituto CNR di Metodologie Chimiche (IMC-CNR), Sezione Meccanismi di Reazione Dipartimento di Chimica, Box 34-Roma 62, Università "La Sapienza", Piazzale Aldo Moro 5, 00185 Roma, Italy
[b] Facoltà di Ingegneria, INFM-Dipartimento di Ingegneria Meccanica, Università di Tor Vergata, Via del Politecnico 1, 00133 Roma, Italy
[c] Dipartimento di Scienze degli Alimenti, Facoltà di Agraria, Università degli Studi di Teramo, Via Carlo R. Lerici 1, 64023 Mosciano Sant'Angelo (Teramo), Italy
Fax: (+39)-85-807-1509, e-mail: closterzo@unite.it

Received: July 21, 2004; Accepted: October 29, 2004; Published online: January 11, 2005

Supporting Information for this article is available on the WWW under http://asc.wiley-vch.de/home/.

Abstract: We report on the use of our novel multistep/one-pot/Pd-promoted synthetic strategy, named *extended one-pot* (*EOP*), for the preparation of polymeric conjugated systems characterized by a backbone composed of regularly alternating alkyne and arylene moieties of type $[-C\equiv C-\mathbf{A}-C\equiv C-\mathbf{B}-]_n$. The "**A**" unit (or module) is in charge of impressing mechanical strength, chemical stability and processability to the polymer, while different "**B**" units (or modules) have been selected to obtain polymers with different functional properties. With this "modular approach" concept, a series of *co*-poly(arylene ethynylene)s, of general formula $[-Ar-C\equiv C-Ar'-C\equiv C-]_n$ [Ar = 2,5-bis(octyloxy)benzene; Ar′ = 1,10-phenanthroline, hydroquinone, pyridine, tetrafluorobenzene, dithiophene, benzene, and anthracene] potentially useful for the fabrication of sensory, electroactive and light-emitting materials, have been formed. Investigations of the photophysical properties of these materials, both in solution and in the solid state, have demonstrated a large degree of variation of properties depending on the nature of Ar′ and the extension of the conjugation in the polymeric backbone. This *EOP* synthetic protocol, with its multiple and sequential one-pot Pd-catalyzed processes, is characterized by a very low catalyst charge loading, a consistent cut-down of reaction times, ease of operation and cost with respect to conventional procedures to obtain ethynylated polymers. Moreover, although it is based on the Pd-catalyzed coupling of organostannanes and aromatic halides (Stille reaction), the *EOP* synthetic route optimizes and reduces the use of tin, because during the multi-step one-pot process, tin intermediates are *in situ* formed by complete reconversion of tin by-products generated in the course of the transformation. In addition, after formation and isolation of polymeric materials, tin-containing products are recovered and reused to form new reagents for the delivery of the alkyne moiety into the polymer backbone.

Keywords: C−C coupling; conductive polymers; materials science; palladium; Stille reaction

Introduction

In the last 30 years metal-catalyzed cross-coupling reactions have emerged as the most powerful and useful tool in synthetic organic chemistry, as mainly by means of Cu, Ni, Pd catalysts a wide variety of electrophilic partners (organic triflates, halides and acyl chlorides) and nucleophiles (organo-boron, -aluminium, -copper, -zirconium, -silicon, -tin, etc.), both ranging from simple precursors to highly elaborate structures, can be coupled to form more complex molecules.[1] Among this large family of reactions we intend to focus on a particular class of transformations, promoted by Pd, in which organic electrophiles are coupled with organotin reagents – namely the Stille reaction.[2] Because of its wide versatility due to the mildness of the operating conditions, tolerance

DOI: 10.1002/adsc.200404233

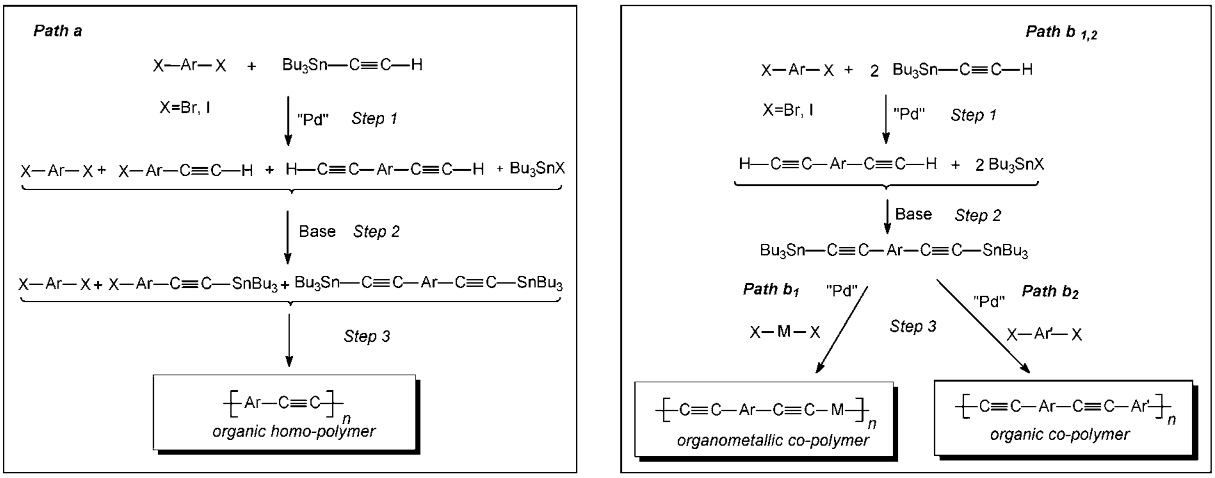


Figure 1. Different uses of the *extended one-pot* (*EOP*) synthetic protocol.

of existing functional groups, very large or complete stereospecificity and the variety of organic residues (alkyl, aryl, vinyl, alkynyl, etc.) both allowed as electrophile and/or organotin partner, the Stille reaction largely is the most highly developed and extensively utilized metal-mediated synthetic organic procedure.[2,3]

One of the most efficient synthetic processes performed by the Stille reaction is the coupling between aromatic electrophiles and alkynyltins,[3a] thus by using bifunctionalized electrophiles and alkynyltins, oligomeric and polymeric conjugated systems characterized by a backbone composed of regularly alternating alkyne and arylene moieties – the polyarylene ethynylenes (PAEs) – might be formed.[4] PAEs are a member of the large family of conjugated polymers, a class of materials that, by virtue of the extended π-conjugated systems spanning throughout the entire polymer backbone, display, to a different degree, a unique combination of narrow band gaps, rigid-rod character and charge-transport capability, both in the solid state and in solution.[5] These properties are of great interest for the realization of optoelectronic devices, like organic light-emitting diodes (OLED), field-effect transistors (FET), molecular wires, sensors, photovoltaic cells and information storage systems, and can be enhanced and/or tuned with the incorporation of heteroatoms and/or metal centers into the conjugated backbone.[4–6] Moreover, properly designed side substitution on aromatic units may address solubility, processability and solid state morphology. Finally, taking advantage of the flexibility of synthetic organic chemistry, the dimension of these molecular materials can be controlled, allowing both the realization of nanosized photo- and electro-active objects, the supramolecularly ordered architectures. For these reasons one of the most intensely explored frontiers in innovative materials science is the replacement of conventional inorganic, silicon-based materials with organic (semi)conductive materials.[7]

Unfortunately, the key to the success of the Stille reaction, the use of organotin reagents as nucleophiles,[2,3,8] because of the toxicity of tin reagents and the consequent related environmental and health concerns, also represents the principal drawback toward the conversion of useful and rationally designed laboratory scale synthetic procedures into industrial applications, since no industrial scale tin-removal procedures are available.

We have been working in this field developing a new palladium-based synthetic protocol, named *extended one-pot* (*EOP*), for the convenient construction of oligomeric and polymeric alkyne-arylene and alkyne-arylene/alkyne-metal skeletons[9] (Figure 1). Although based on the use of tin reagents, the *EOP* processes strongly improve the tin economy by optimization and recycle of tin-containing reagents and by-products. The *EOP* essentially consists in a straightforward, three-step, *one-pot* palladium-promoted cascade of reactions allowing the regular insertion of an alkyne unit between identical or different aromatic moieties and/or organometallic fragments, with formation of highly ethynylated organic and organometallic oligomers and polymers. By varying the stoichiometric ratio between reactants and the different types of aromatic building blocks and/or organometallic fragments introduced in the synthetic route, the *EOP* synthetic protocol can be differently addressed towards the formation of *i*) *homo*-poly(arylene ethynylene)s[9c,9f] $[-\mathrm{Ar}-\mathrm{C}\equiv\mathrm{C}-]_n$ (***Path a***), *ii*) poly(arylene ethynylene-*co*-metallaethynylene)s[9d,9g] $[-\mathrm{Ar}-\mathrm{C}\equiv\mathrm{C}-\mathrm{M}-\mathrm{C}\equiv\mathrm{C}-]_n$ (***Path b$_1$***), and *iii*) *co*-poly(arylene ethynylene)s[9a] $[-\mathrm{Ar}-\mathrm{C}\equiv\mathrm{C}-\mathrm{Ar}'-\mathrm{C}\equiv\mathrm{C}-]_n$ (***Path b$_2$***). Although the different pathways outlined in Figure 1 are affording materials with highly different structural characteristics, the three different processes are essentially consisting of identical key transformations that are; *iv*) a Stille ethynylation reaction (*Step 1*), *v*) the *in situ* formation of ethynyltin derivatives by reuse of a tin by-product formed in the preceding step (*Step 2*), *vi*) the polymerization process (*Step 3*). Since formation of organic *homo*-polymers (***Path a***) and organometallic *co*-polymers (***Path b$_1$***) has already been reported,[9b–g] this paper will focus on key features of the *EOP* route leading to *co*-poly(arylene ethynylene)s $[-Ar-C\equiv C-Ar'-C\equiv C-]_n$ ($Ar \neq Ar'$, ***Path b$_2$***).

In *Step 1* of ***Path b$_2$*** an aromatic dihalide X–Ar–X undergoes a Stille reaction with two equivalents of tributyltin acetylide ($Bu_3Sn-C\equiv C-H$) in the presence of zerovalent palladium to form the corresponding diethynylaromatic species $H-C\equiv C-Ar-C\equiv C-H$ and two equivalents of tributyltin halide (Bu_3SnX) as side product. To this crude mixture LDA is added (*Step 2*), causing deprotonation of both terminal acetylene moieties of the dialkyne and their recombination with Bu_3SnX to form the corresponding bistributyltin species $Bu_3Sn-C\equiv C-Ar-C\equiv C-SnBu_3$. A second aromatic dihalide (X–Ar′–X) is then added to the same reaction mixture (*Step 3*), and because of the active presence of the palladium catalyst remaining from *Step 1*, a second Stille reaction takes place leading to the formation of the polymeric material $[-Ar-C\equiv C-Ar'-C\equiv C-]_n$. Although preliminary investigation of this reaction route has allowed preparation of some representative phenylene-ethynylene-thienyleneethynylene *co*-polymers,[9a] better reaction conditions had to be found for the optimazation of the procedure and widening the scope of this promising synthetic tool.

In the present work we report improvements of the *EOP* synthetic protocol to form *co*-poly(arylene ethynylene)s $[-Ar-C\equiv C-Ar'-C\equiv C-]_n$ ($Ar \neq Ar'$) (*Path b$_2$* of Figure 1), in order to achieve materials of increased molecular weight, better purity and wider variety of different aromatic units (Ar and Ar′) to be combined in the poly(arylene ethynylene) sequences. The photophysical properties of these materials have been also investigated to ascertain their use in optoelectronic devices.

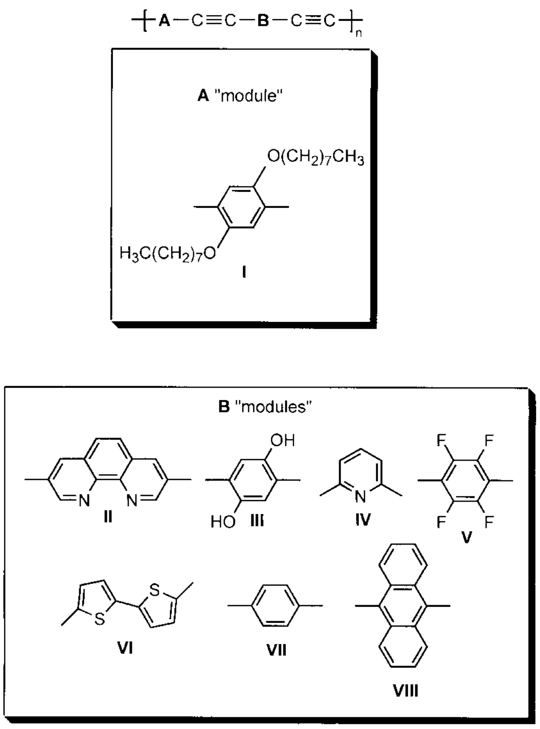


Figure 2. "**A**" and "**B**" modules to be combined in the construction of poly(arylene ethynylene) *co*-polymers according to the "modular approach concept".

Results and Discussion

The synthetic strategy outlined in *Path b$_2$* of Figure 1 is potentially a general route to poly(arylene ethynylene) *co*-polymers with the peculiar possibility of the introduction of a broad variety of different aromatic units ($Ar \neq Ar'$). Thus, in principle, it allows a rational approach for the design of molecular structures useful in advanced technological applications.

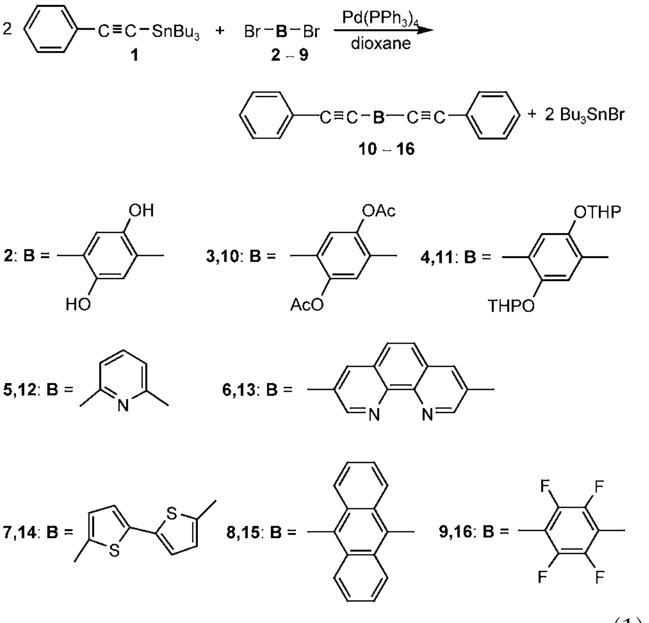
Experimental work was focused on the synthesis of ethynylated **A**–**B** type *co*-polymers $[-C\equiv C-\mathbf{A}-C\equiv C-\mathbf{B}-]_n$, in which the "**A**" unit (or "module") impresses mechanical strength, chemical stability and processability (solubility, fusibility, filmability) to the polymer, while the "**B**" unit (or "module") was selected according to the desired functionality. This concept, which is based on the idea to assign two different but complementary functions to two different "modules", has been called the ***A–B modular approach***.

The 2,5-bis(octyloxy)benzene unit (**I**) was selected as the "**A**" module, considering that the two octyloxy side chains might represent a good compromise for the solubility and tractability of the polymeric material with low effect on functional properties[5d,10,11] (Figure 2).

The "**B**" units were selected in order to have polymeric materials with potentially useful opto- and/or electronic properties. Particularly, we have focused our attention on three different potential applications of poly(arylene ethynylene) materials, as *a*) sensors, *b*) electroactive materials, *c*) light-emitting polymers. The 1,10-phenanthroline unit (**II**) was considered because its coordinating ability toward transition metals is accompanied by a severe quenching of polymer fluorescence, thus highly sensitive chemosensors might be developed.[12] Towards the formation of molecular wires and electroactive materials, the hydroquinone unit (**III**) was selected to introduce a redox-active unit into the polymer backbone[13] and along with pyridine (**IV**), the tetrafluorobenzene (**V**) and dithiophene (**VI**) units are representing building blocks for the formation of polymeric materials displaying different electron-accepting and/or electron-carrying properties. Finally, the benzene (**VII**) and anthracene (**VIII**) modules were selected as representative cases of photoactive components in optical materials[14] (Figure 2).

Preparation of Model Compounds

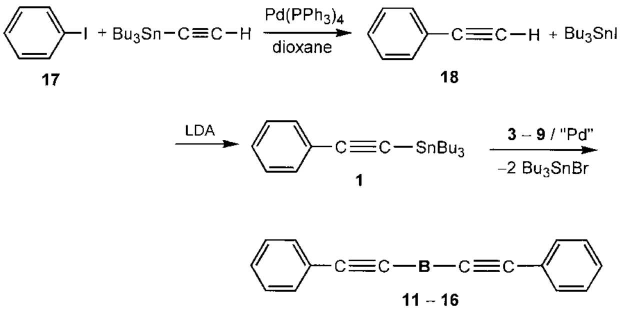
In the formation of *co*-polymers of type $[-Ar-C{\equiv}C-Ar'-C{\equiv}C-]_n$ by means of the *EOP* synthetic protocol (Figure 1), the key point is represented by *Step 3*, the second Pd-promoted coupling process, where the *in situ* formed aromatic bis-tributyltin acetylide species ($Bu_3Sn-C{\equiv}C-Ar-C{\equiv}C-SnBu_3$) must be reacted with the added bis-bromoaromatic Br–Ar–Br, in a quite complex reaction medium containing side products and reactants resulting from the two preceding steps. In a previous work we set optimal conditions to efficiently perform the *EOP* route to poly(phenylene ethynylene) and poly(thienylene ethynylene) *homo*-polymers[9f] (**Path a** of Figure 1). First we decided to investigate the ability of individual dibromides Br-**B**-Br **2**–**9** to undergo coupling with the tributyltin acetylide moiety of the clean $Bu_3Sn-C{\equiv}C-Ph$ (**1**), under the optimized conditions, to form model compounds Ph–C≡C–**B**–C≡C–Ph (**10**–**16**) [Equation (1)]. An additional advantage deriving from this approach is represented by the obtaining of a series of model compounds whose spectroscopic characterization and study of properties might be useful not only to characterize the corresponding polymeric materials (*vide infra*) but also to predict and rationalize their properties.[15]



(1)

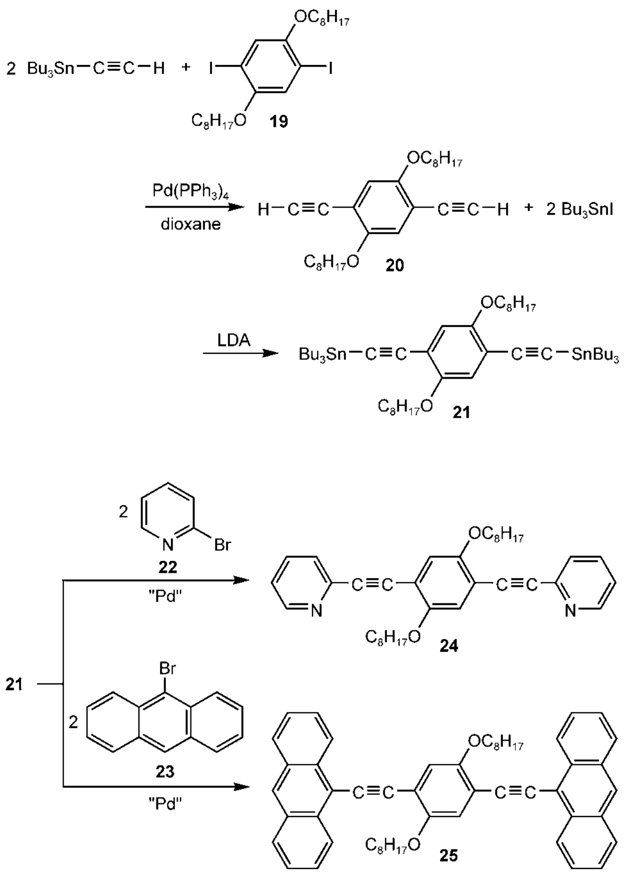
Referring to our previous experience,[9f] the reactivity of the aromatic dibromides **2**–**9** (**2** = 2,5-dibromohydroquinone, **3** = 1,4-dibromo-2,5-diacetoxybenzene, **4** = 1,4-dibromo-2,5-ditetrahydropyranylbenzene, **5** = 2,6-dibromopyridine, **6** = 3,8-dibromo-1,10-phenanthroline, **7** = 5,5′-dibromo-2,2′-dithiophene, **8** = 9,10-dibromoanthracene, **9** = 1,4-dibromo-tetrafluorobenzene), and the commercially available $Ph-C{\equiv}C-SnBu_3$ (**1**) in a 1/2 ratio, using $Pd(PPh_3)_4$ (1%) as catalyst in refluxing dioxane (110 °C), was studied. Under these conditions only the 2,5-dibromohydroquinone (**2**) failed to couple with **1**, while in all the other cases, although different reaction times were required (depending on the nature of the dihalide), coupling reactions smoothly proceeded with complete conversion of starting materials into the corresponding coupled products **10**–**16**. The reluctance of **2** to undergo coupling with **1** was circumvented by transforming **2** into the corresponding bis-acetyl (**3**) and bis-tetrahydropyranyl (THP) (**4**) derivatives, both affording the coupled products **10** and **11** under the same general conditions.

Subsequently, the preparation of model compounds **10**–**16** was repeated under the real *EOP* conditions, by coupling of dihalides **3**–**9** with the *in situ* formed tin acetylide **1** [Equation (2)]. Now these transformations are taking place in a much more complicated system, because of the presence of by-products and the reactants needed to carry out the *in situ* formation of **1**. Moreover, the Pd catalyst only added at the beginning of the first step (formation of **18**), has to withstand the addition of LDA in the second step (formation of **1**), and then must operate again in the third step (formation of **10**–**16**). Under these conditions only the 1,4-dibromo-2,5-diacetoxybenzene (**3**) failed to form the corresponding coupled product **10**,[16] while in all the other cases formation of model compounds **11**–**16** took place with unchanged efficiency.



(2)

Once having assessed the ability of dibromides **4**–**9** to efficiently perform, under *EOP* conditions, coupling with **1** to form model compounds **11**–**16**, formation of complementary models **24** and **25**, more closely resembling the structure of the corresponding polymeric material, was studied [Equation (3)]. In this case, although the intrinsic reactivity of the **B**–Br and $Bu_3Sn-C{\equiv}C-$ moieties are expected not to be much different than that of **5** and **8** *vs.* **1**, the presence of the octyloxy side chains on the central phenyl ring may result in some steric restrictions affecting reaction rate and/or product stability. It has to be noticed that compounds **24** and **25** required only slightly longer reaction times with respect to **12** and **15** to be completely formed and, more importantly, in the case of **25**, this product was safely purified by chromatographic separation.[17] This latter result is quite relevant, because the central unit in models **24** and **25** is the very same "**A**" module that we intend to introduce in the **A/B** type polymer [–C≡C–**A**–C≡C–**B**–]$_n$ and we have attributed to this unit also the role of imparting stability to the polymeric materials.



(3)

Preparation of Poly(arylene ethynylene) *co*-Polymers [–Ar–C≡C–Ar′–C≡C–]$_n$

Scheme 1 represents the general *EOP* route we devised for the preparation of the poly(arylene ethynylene) *co*-polymers [–Ar–C≡C–Ar′–C≡C–]$_n$ **27**–**33**. While the first two steps, consisting of the one-pot straightforward transformation of the 1,4-diiodo-2,5-bis(octyloxy)benzene (**19**) into the 1,4-bis(tributyltin)ethynyl-2,5-bis(octyloxy)benzene (**21**) are obviously identical in all cases, and, were accomplished in 30–40 min, the duration of the third step, the introduction of the "**B**" module into the polymeric chain, reflected the same trend observed in the formation of the corresponding models **11**–**16** and **24**–**25**. Because of the failure of the 1,4-dibromo-2,5-diacetoxybenzene (**3**) to undergo coupling under *EOP* conditions, only the THP-protected derivative **4** was used to introduce the (masked) hydroquinone moiety into the polymer backbone. 1,4-Dibromobenzene (**26**) was added to the array of dihalides **4**–**11** to introduce an unsubstituted benzene moiety as the "**B**" module into the polymer backbone. To a certain degree the molecular weight of polymeric material may be modulated with the duration of the third step (*vide infra*). As experienced in the case of the *EOP* route to form poly(arylene ethynylene) *homo*-polymers[9f] [–Ar–C≡C–]$_n$, transformations occurring in each step of the *EOP* route to *co*-polymers **27**–**33**, are clearly accounted for by ^{1}H NMR spectroscopy.[18] We describe in detail in Figure 3 the formation of the poly-{[(2,5-dioctyloxy)-1,4-phenylene acetylene]-*co*-5,5′-(2,2′-dithiophenylene) acetylene} (**31**) recorded by ^{1}H NMR spectroscopy; this being representative of the general transformations leading to all polymeric materials presented in this work (Figure 3).

In trace **a)** of Figure 3 is reported the ^{1}H NMR spectrum of a specimen of the reaction mixture[18] sampled before starting *Step 1*, thus containing tributyl(ethynyl)tin and 1,4-diiodo-2,5-bis(octyloxy)benzene (**19**) in a 2:1 molar ratio. Although the Pd(PPh$_3$)$_4$ catalyst is present, its ^{1}H NMR signals are not detected because of its low concentration (≅1%). In trace **b)** is reported the spectrum of a sample of the reaction mixture after 20 min of warming at 110 °C (end of *Step 1*). Starting materials are quantitatively converted into 1,4-diethynyl-2,5-bis(octyloxy)benzene (**20**), and tributyltin iodide side-product. After this step is accomplished, the reaction mixture is first allowed to cool at room temperature, then brought to 0 °C, and two equivalents of LDA are added. Under these conditions the base deprotonates both terminal alkyne functionalities of **20** forming the corresponding diethynyl acetylide which reacts with tributyltin iodide, left over from the first step, forming 1,4-bis(tributyltin)ethynyl-2,5-bis(octyloxy)benzene (**21**) (*Step 2*). The NMR spectrum of this step, which requires additional 20 min, is shown in trace **c)** of Figure 1, where only signals of **21** are present. To this reaction mixture solid 5,5′-dibromo-2,2′-dithiophene (**7**) is added (trace **d)**, Figure 3), and the mixture of **21** and **7** is warmed up to 110 °C. The *Step 3* is completed in five hours at 110 °C as reported by the spectrum in trace **e)** of Figure 3, where only signals attributable to the crude polymer **31** and the Bu$_3$SnBr side-product are present. Upon cooling to room temperature a large amount of red-brown precipitate constituted by the higher molecular weights of **31** is formed. This solid material is separated by filtration and washed with dioxane, then redissolved[19] with CHCl$_3$, filtered over Celite, reprecipitated and washed with methanol. In trace **f)** of Figure 3 the spectrum of the purified **31** is reported. The absence of the high field multiplets in trace **f)** with respect to trace **e)** is due to the elimination of the tributyltin bromide side-product which has been achieved by washing the precipitate with methanol. An additional crop of poly-

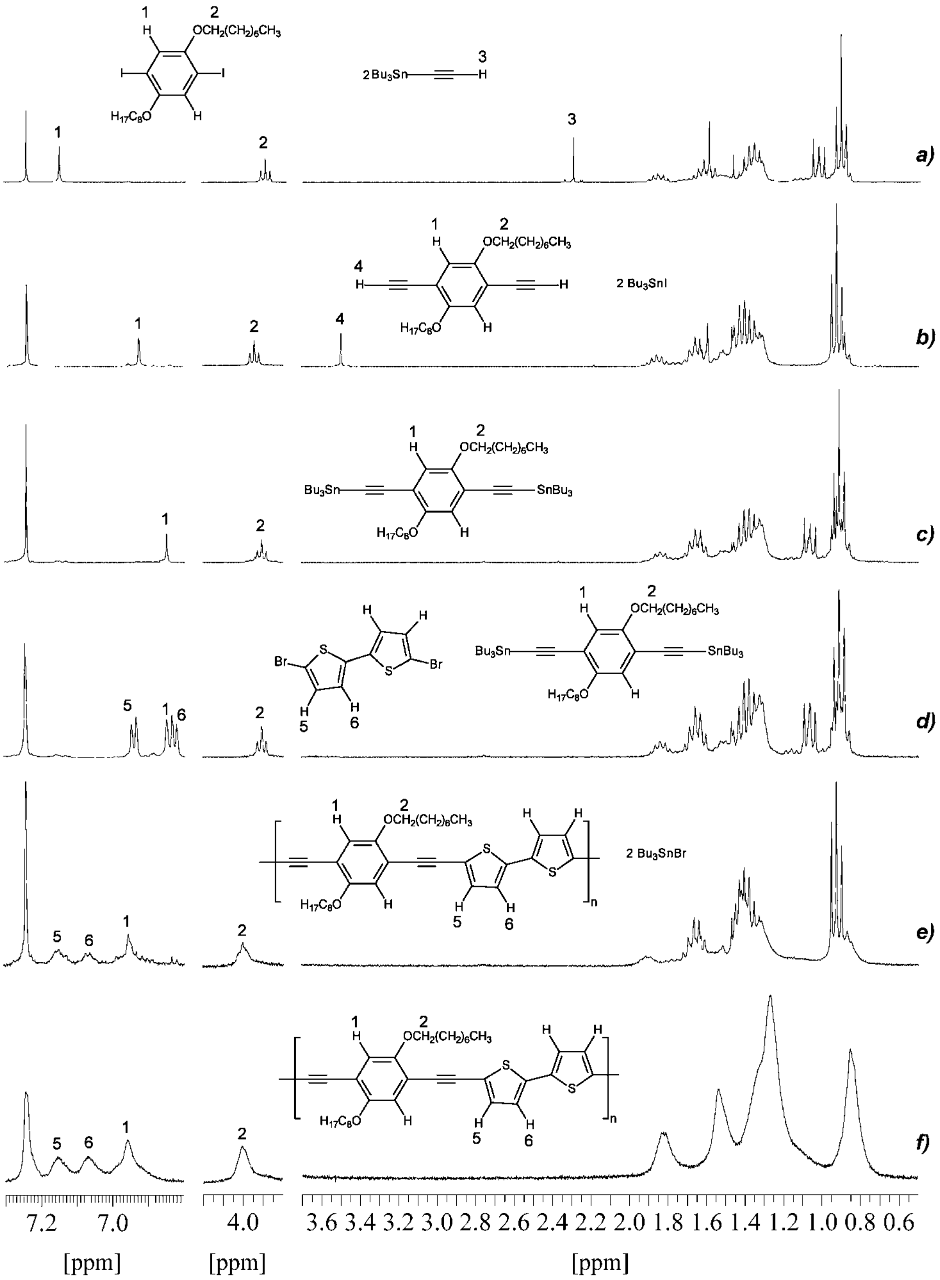


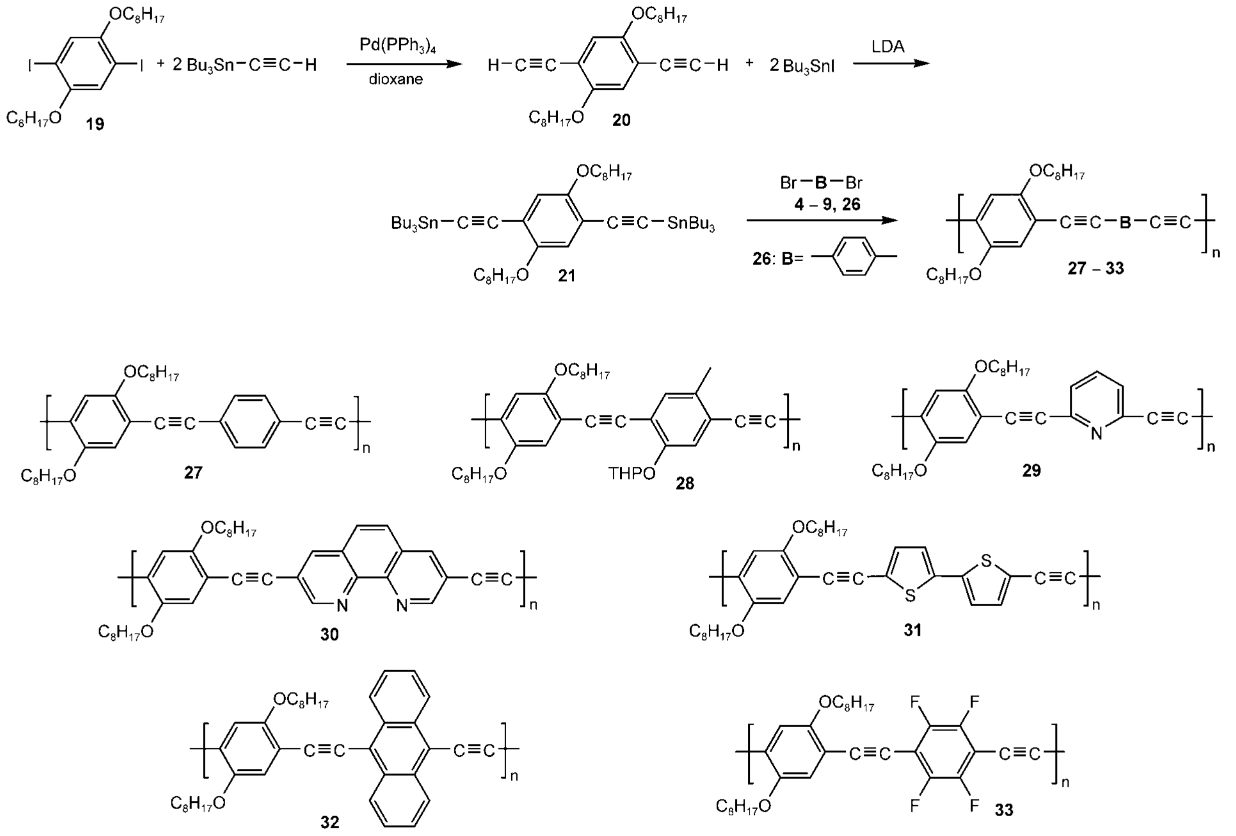
Figure 3. Sections of ^1H NMR spectra for the formation of **31** as outlined in Scheme 1. Spectra were recorded on a sample of the reaction mixture freed from the solvent and redissolved in $CDCl_3$. Trace ***a)*** **19** and $Bu_3Sn{-}C{\equiv}CH$ before starting *Step 1*; trace ***b)*** completion of *Step 1*, mixture of **20** and Bu_3SnI; trace ***c)*** completion of *Step 2*, formation of **21**; trace ***d)*** starting of *Step 3*, mixture of **21** and **7**; trace ***e)*** completion of *Step 3*, mixture of **31** and Bu_3SnBr; trace ***f)*** isolation of **31**.

meric material (consisting of lower molecular weight material – *vide infra*) is recovered upon addition of methanol to the original dioxane solution from which the first crop of precipitate spontaneously formed after cooling of the reaction mixture.

It is important to remark that the two cross-coupling processes, *Step 1* and *Step 3*, are both sustained by the palladium catalyst that is only added once at the beginning of *Step 1*. The overall use of only 1% of Pd catalyst to perform *two* coupling processes, despite the base treatment in *Step 2*, is an example of the high efficiency, and is quite rare even in the case of a *single* coupling process.[2]

Molecular Weight Determination and NMR Characterization

As mentioned before, in all cases (**27**–**33**) the degree of polymerization is directly related to the duration of the



Scheme 1.

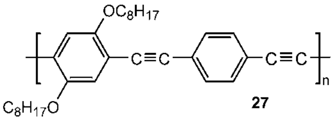
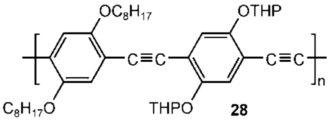
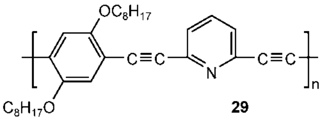
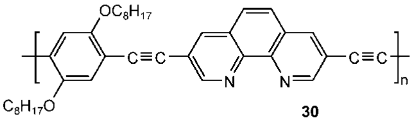
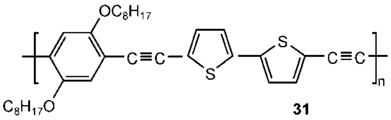
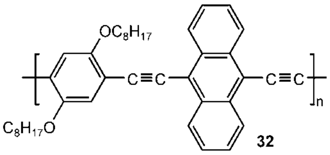
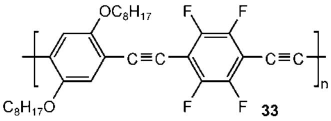
third step. In general, when the polymerization step (*Step 3*) is carried out for more than 2–4 hours, a consistent amount of insoluble polymeric material precipitates upon cooling the reaction mixture at room temperature. Polymers **27** and **32** containing benzene and anthracene as **B** moieties in the main chain, respectively, were not soluble in the hot reaction mixture (110 °C).

The degree of polymerization (*n*), calculated for the polymers **27**–**33** using the M_W values determined by GPC (gel permeation chromatography), is reported in Table 1. In all cases, a low molecular weight material, soluble in the reaction mixture, is always obtained at short reaction times and was precipitated at the end of reaction upon addition of methanol (see Experimental Section). Materials of higher molecular weight are formed at longer reaction times and their yield increases as the reaction time is increased. This fraction spontaneously separates upon cooling of the reaction mixture at room temperature and could be analyzed in THF, chloroform or dichloromethane solution where it proved to be partially or totally soluble (Table 1). On the contrary, polymers **27** and **32**, that precipitate from the hot reaction mixture, remain mostly insoluble in all solvents; in this case data obtained by GPC only refer to the soluble fraction whereas the nature of the high molecular weight polymer was investigated by solid state ^{13}C NMR spectroscopy. In Figure 4 the solution ^{13}C NMR spectra of the model compound **25** (trace **a**) and low molecular weight fraction of the polymer **32** (trace **b**) are compared with the solid state CP MAS ^{13}C NMR spectrum (trace **c**) of the insoluble fraction of **32**. The solution spectra are in fine agreement with the solid state spectrum indicating the structural homogeneity of the material. In the traces **b)** and **c)** the intensity ratio of the ^{13}C NMR signals corresponding to the aliphatic and unsaturated carbons are in the expected 2:1 molar ratio: it is worth noting the presence of two signals for the not equivalent alkynyl carbons 5. The broadness of the ^{13}C NMR signals of trace **c)** suggests the amorphous nature of the polymer and likely the presence of rotamers of the aromatic moieties about the main chain axis. In particular the signals due to carbons 1 and 6, diagnostic of the presence of not equivalent aromatic rings along the macromolecular chain, exhibit a line width broader than that observed for the methyl carbons 8.

Photophysical Properties

The photophysical properties of *co*-polymers **27**, **29**–**33** were investigated in solution and in the solid state. In the case of the pyridine- and anthracene-containing polymers **29** and **32** materials of different chain lengths

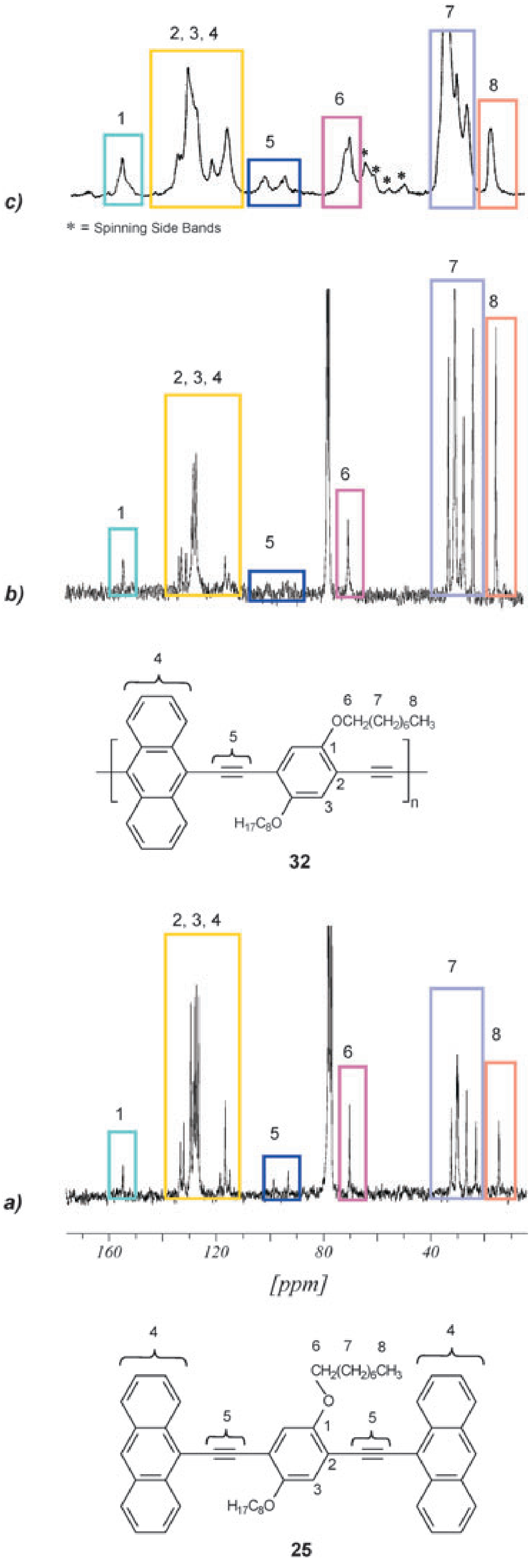
Table 1. Degree of polymerization of polymers **27**–**33**.

Polymer	Time[a]	*n*[b]	% insoluble[c]
 **27**	1 h	44[d]	0
	2 h	45	60
 **28**	6 h	5	0
 **29**	30 min	6	0
	1 h	7[d]	
	2 h	11	
	4 h	20[d]	
 **30**	2 h	5	0
	5 h	9	60
	20 h	11	90
 **31**	2 h	14	0
	5 h	40	50
 **32**	2 h	20[d]	50
	3 h	28[d]	70
 **33**	22 h	12[d]	0

[a] Time of the polymerization step (*Step 3* of *EOP*).
[b] Degree of polymerization, calculated on the basis of the M_w value, determined by GPC (THF, polystyrene).
[c] Polymeric material insoluble in common organic solvents.
[d] The n value is relative to the longest part of the soluble polymer (insoluble in dioxane, soluble in THF).

were examined, and, for comparison optical characteristics of the corresponding model compounds **24** and **25** were reported. The values of the relevant parameters are summarized in Table 2. The UV-VIS optical absorption spectra in dilute $CHCl_3$ solution are reported in Figure 5. The data relative to the *homo*-polymer poly(arylene ethynylene)[9c, f] $[-Ar-C{\equiv}C-]_n$ [Ar = 2,5-bis(octyloxy)benzene] **34** are also shown for comparison. The curves exhibit a certain degree of variety within the typical main features of this class of rigid rod copolymers.[5d,11,12b,14,20] In this regard, the present data confirm that the absorption spectra of *co*-polymers of type $[-Ar-C{\equiv}C-Ar'-C{\equiv}C-]_n$ are derived from and can be easily interpreted in terms of the properties of the Ar and Ar′ constituents (**A** and **B** modules) and the extension of the conjugation of the PAE backbone. Such a behavior allows a large tunability of the optical properties by introducing different arylenic **B** modules and, in some cases, by varying the conjugation length.

We have noticed that, according to theoretical models[21] for poly(arylene ethynylene) PAE and poly(arylene vinylene) PAV polymers, the low-energy absorption band in the range 380–550 nm, depending on the nature of the **B** module, can be attributed to delocalized π–π* transitions, while the relatively weaker structures between 250 nm and 350 nm are related to a combination of delocalized and phenyl-localized π–π* transitions.



◀ **Figure 4.** Trace ***a)*** solution ^{13}C NMR spectrum of the model compound **25**; trace ***b)*** solution ^{13}C NMR spectrum of low molecular weight fraction polymer **32**; trace ***c)*** solid state CP MAS ^{13}C NMR spectrum of the insoluble fraction of **32**.

This attribution is supported by the dependence of the absorption spectra as a function of the degree of polymerization *n* which has been investigated for two systems and is reported in Figure 6. For the case of anthracene-based *co*-polymer **32** (Figure 6a) the effectiveness of π-conjugation gives rise to the progressive red-shift of the low-energy band as the chain length increases from the model compound **25** to the polymer with $n=28$. On the other hand, the position of the high-energy band varies much less with *n* as expected for transitions due to localized states. For pyridine-based **29** (Figure 6b) the same value of the peak wavelength is observed for different values of *n* and this can be explained by the possible interruption of π-conjugation due to the distortion of the planarity of the aromatic rings in the polymer backbone,[22] which localizes the excitation within a few monomeric units.[5d,12b] As matter of facts, the spectrum of **29** exhibits the lowest value of λ_{max} among all the other systems (see Figure 5). Other specific features of PAE *co*-polymers can be verified by comparing the spectra relative to the different **B** modules. For instance, it has been reported[5d] that donor lateral chains can induce a bathochromic shift of the absorption spectra. In the present materials, this effect can be observed by increasing the number of alkoxy-substituted benzene rings passing from the *co*-polymer **27** (with absorption $\lambda_{max}=405$ nm) to *homo*-polymer **34** ($\lambda_{max}=418$ nm). A similar value of bathochromic shift is observed in the cases of polymers **30** and **33** containing 1,10-phenanthroline or tetrafluorobenzene units, respectively, while the larger value measured in **31**

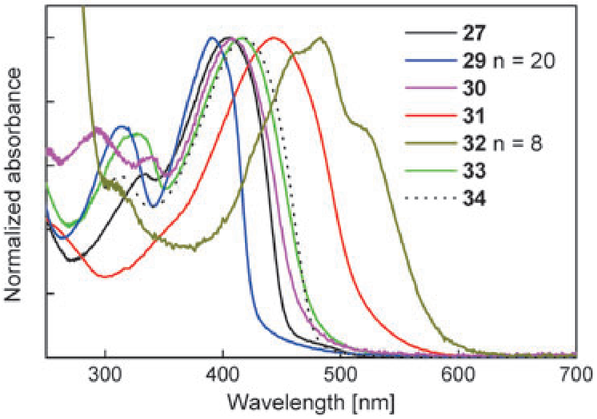


Figure 5. Normalized absorption spectra of the PAEs in $CHCl_3$. For the values of the degree of polymerization *n* not reported in the figure see Table 2.

Table 2. Optical properties of the PAE polymers in solution and solid state.

	n[a]	In $CHCl_3$ solution			In spin-coated films	
		Absorption λ_{max} [nm]	Emission λ_{max} [nm]	Quantum yield	Absorption λ_{max} [nm]	Emission λ_{max} [nm]
34	40	418	470	0.40	420	585
27	45	405	445	0.47	407	555
24	model*	374	420	0.78	–	–
29	11	390	428	0.65	–	–
	17	390	430	0.55	–	–
	20	391	426	0.51	390	545
30	5	410	460	0.57	415	575
31	14	444	500	0.18	438	650
25	model*	470	490	0.60	–	–
32	8*	482	545	0.27	488	622
	28	530	565	0.20	–	–
33	10	417	465	0.44	420	580

[a] Degree of polymerization.
* λ_{max} refers to the low-energy band.

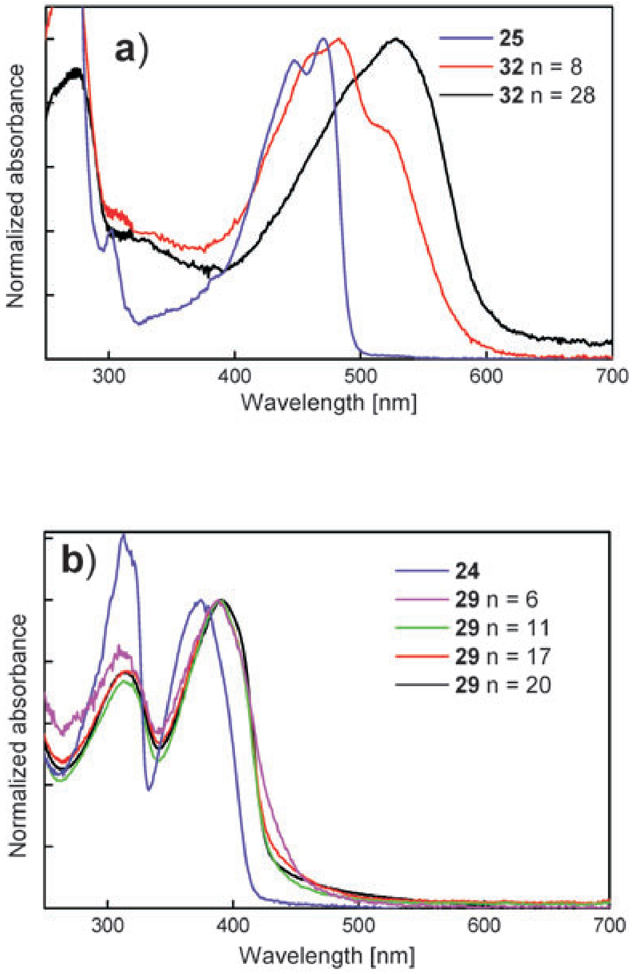


Figure 6. a) Normalized absorption spectra of the model compound **25** and the *co*-polymer **32** in $CHCl_3$ for different values of the degree of polymerization n; **b)** normalized absorption spectra of the model compound **24** and the *co*-polymer **29** in $CHCl_3$ for different values of the degree of polymerization n.

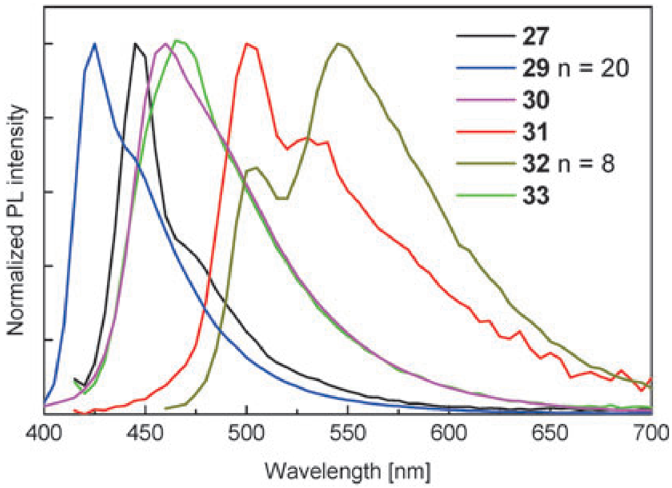


Figure 7. Normalized emission spectra of the PAEs in $CHCl_3$. For the values of the degree of polarization n not reported in the figure see Table 2.

(λ_{max} = 444 nm) confirms the effect of the introduction of thiophene units into conjugated chains.[5d] Accordingly, the very large bathochromic shift observed in **32** (λ_{max} = 482 nm) verifies the tendency of the anthracene unit to an extended conjugation[20a] with a complete loss of its typical absorption structures in the range 300–400 nm. Finally, it should be noted that the absorption spectra measured in concentrated solution (10 mg/mL, not reported here) do not show appreciable differences with respect to dilute ones, which rules out the formation of molecular aggregates.

A similar variability and tunability of the optical properties as a function of the nature of the alternating **B** module can be observed in the photoluminescence (PL) spectra reported in Figure 7. However, as for absorption, all the curves present some characteristic features of PAE polymers[5d,12b,20], i.e., a high-energy peak with a shoulder on the low-energy side, that in some cases become two well-resolved bands, separated by 25–40 nm (15–19 meV). Such structures are attributed to vibronic transitions while the lack of mirror image similarity between absorption and emission spectra suggests a certain degree of vibronic coupling. Moreover, the emission bands are generally slightly narrower than the absorption bands, which is consistent with emission from localized states after migration of the excitations along the polymer main chains.[11] The PL quantum yields of emission in diluted solutions reach reasonably high values in the range 0.2–0.8 (see Table 1), that are comparable with what is reported for similar systems[11,20c] and make these materials quite interesting for electrooptical applications.

As expected, in the two systems investigated at different degrees of polymerization, i.e., **29** and **32**, the values of quantum yield increase with the decrease of n. For the case of anthracene-based **32** the reduction of quantum yield parallels a change of the emission spectral shape so that the low-energy vibronic peak becomes the predominant one (see Figure 8a). These effects can be explained with the migration of the excitations over longer distances along the main chain, which increases the vibronic coupling and the chance of non-radiative de-excitation due to traps and defects. Interestingly, the decrease of quantum yield with n is also found in pyridine-based **29**, even though to a less extent than in **32**, whereas absorption spectra are quite independent of n (see Figure 6b). We can speculate that this suggests a certain degree of delocalization of the *relaxed* excited state.

The solid-state photophysics of PAEs are quite interesting since interchain interactions can occur and influence the emissive properties of thin films deeply. The absorption spectra of spin-coated thin films (not reported here, see values of λ_{max} in Table 1) do not show any appreciable difference with respect to solution. This similarity rules out the formation of aggregates as well as the forced planarization of the π-system in the solid state. On the other hand, PL emissions of pristine films exhibit very large values of red shift, as high as 150 nm in **31**, with respect to solution. Moreover, the bands are broadened and present no vibronic structures (see Figure 9), with the exception of **27** that exhibits also a high-energy peak resembling the solution one. Such a behavior can be interpreted as indicating the formation of excimers, that are complexes between a polymer chain in the excited state and an adjacent one in the ground state. Excimers are very common in other conjugated polymers and have been extensively studied in systems such as poly(p-phenylene)s, poly(p-phenylene vinylene)s and fluorene ladder-type polymer (LPPP)[23] but many questions are still open about their formation. It is a necessary requirement that two chains be parallel over a length of at least several monomers, with a distance between the chains of 0.3 to 0.4 nm.

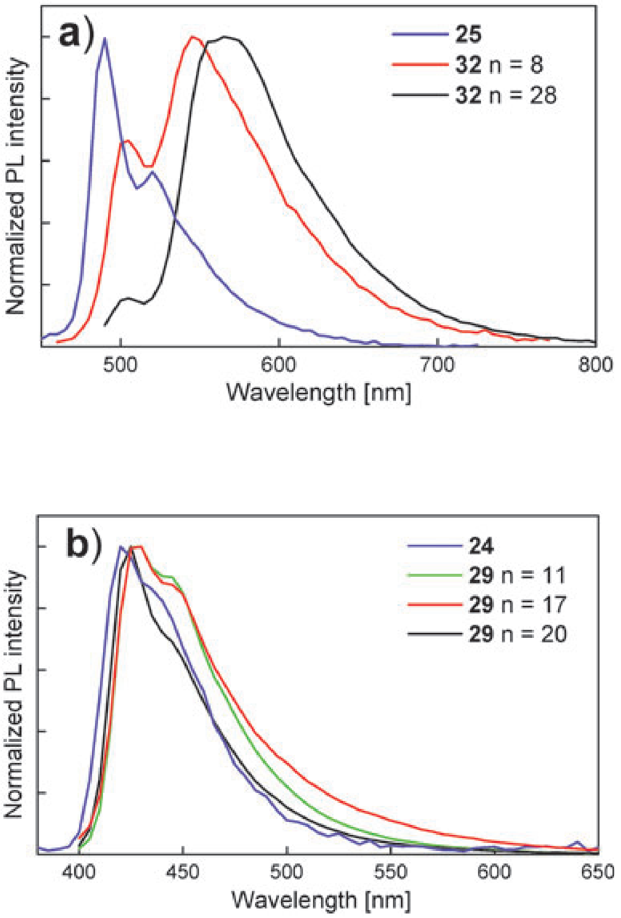


Figure 8. a) Normalized emission spectra of the model compound **25** and the *co*-polymer **32** in $CHCl_3$ for different values of the degree of polarization n; **b)** normalized emission spectra of the model compound **24** and the *co*-polymer **29** in $CHCl_3$ for different values of the degree of polarization n.

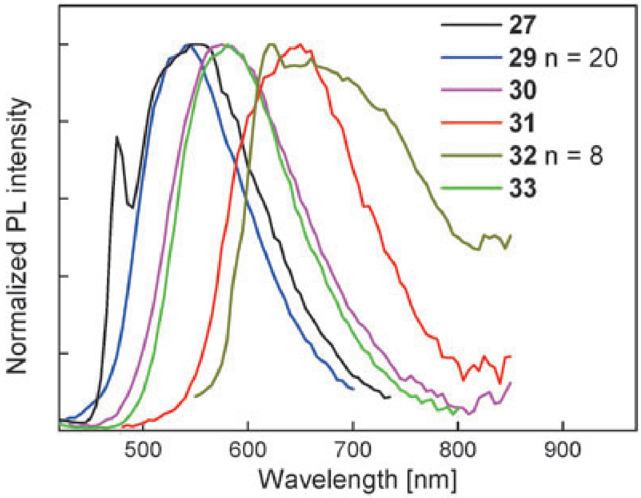


Figure 9. Normalized emission spectra of solid-state films of the PAEs deposited by spin-coating. For the values of the degree of polarization n not reported in the figure see Table 2.

The distance must be small enough for their π orbitals to overlap but not so strongly that the ground state can form a new stable molecule (aggregate). This is consistent with the rigid-rod nature of the present polymers and the trend to form a long-range ordered supramolecular structure in the solid state.[11] Moreover, this hypothesis is supported by the fact that PL spectra of PAEs in solid-state solution with inert polymers,[15] such as polystyrene and poly(methyl methacrylate), show a partial recovery of the characteristic emission bands of the liquid solution; as expected considering the supposed greater separation between PAE chains. Further investigations, however, are needed to clarify this important point.

Comparison of *EOP* Synthetic Protocol and Current Procedures towards Formation of Models and Polymers

Formation of either model compounds **10**–**16** and **24**–**25** as well as polymers **27**–**33**, essentially consist in the coupling of *sp*- and *sp*^{2}-hybridized carbon atoms. In this respect, the milestone for the accomplishment of this transformation is represented by the palladium-catalyzed cross-coupling reaction between vinyl/aryl halides and terminal acetylenes (Sonogashira–Heck–Cassar coupling).[24] In fact, although over the years this reaction has received a number of significant improvement and developments,[25] it still is mostly used according to its original protocol. It is necessary to compare the effectiveness of the *EOP* synthetic protocol with respect to this and other current procedures towards the formation of PAE *co*-polymers (Figure 10).

Route ***a*** represents the traditional and currently most used route[5] composed of three consecutive separate steps consisting in *i*) a Pd-catalyzed TMSA-dihalide coupling to form the TMS-protected bisethynylaromatic intermediate (**36**), *ii*) TMS deprotection to form the free alkyne (**37**) *iii*) Pd-catalyzed coupling of the terminal alkyne (**37**) with a second aromatic dihalide (**38**) to form the polymer (**39**). The major disadvantage in this procedure is that both the TMS intermediate (**36**) and the terminal alkyne intermediate (**37**) need to be isolated and purified before the following step. Nevertheless, it remains the most used because of its great reliability and flexibility, in fact each step can be optimized according to the particular nature of the substrate under transformation.

A one-pot reaction has been carried out by Heitz[27] and other authors,[28] who report an optimization of an efficient *in situ* sequential TMS deprotection-acetylene/aryl halide coupling procedure devised by Haley[26] to form cyclo-oligoacetylenes. After formation and isolation of the trimethylsilyl intermediate (**36**), the removal of the trimethylsilyl group and the polycondensation, under phase-transfer conditions, are simultaneously carried out (*Route* ***b***). Although this procedure presents distinct advantages (no isolation of the alkyne, no butadiyne defects) with respect to the one outlined in Path **a**), to the best of our knowledge it has only received little attention.

The use of the "classical" Stille protocol to form ethynylated *co*-polymers is outlined in *Route* ***c***. Formation of the bis-alkyne **37** can be achieved either by the same TMSA-dihalide coupling used in the first part of *Route* ***a*** or by reaction of **34** with two equivalents of $R_3SnC{\equiv}CH$ in the presence of zerovalent Pd. In both cases the bis-alkyne **37** must be isolated. In addition when **37** is formed by the use of $R_3SnC{\equiv}CH$, two equivalents of R_3SnX are formed (and generally discarded) as by-product. Transformation of **37** into $R_3Sn{-}C{\equiv}C{-}Ar'{-}C{\equiv}C{-}SnR_3$ (**40**) then requires the use of additional tin reagents.[29]

Bunz[30] has recently adapted the acyclic diyne metathesis (ADIMET) approach (*Route* ***e***), originally developed for preparation of *homo*-poly(arylene ethynylene)s, to the formation of *co*-poly-(arylene ethynylene)s. In this synthetic route, two distinct Pd-catalyzed processes are necessary to form the two partners (**41** and **42**) that then need to be isolated and purified before being mixed and reacted under ADIMET conditions to form the corresponding *co*-polymer **43**. The ADIMET itself consists on a very efficient process, promoted by an *in situ* generated/highly reactive Mo catalyst. However high temperatures are required, regiorandom distribution of the two monomers is obtained, and heteroatom-containing monomers display relatively sluggish reactivity.[30,31]

For polymers **30** and **33** it is possible to make a direct comparison between the classical and the *EOP* procedures outlined in *Route* ***a*** and *Route* ***d*** of Figure 10. Starting in both case from 1,4-diiodo-2,5-bis(octyloxy)-benzene [**34**, Ar = 2,5-bis(octyloxy)benzene], Grummt[32] and Weder[20e] first prepared the 1,4-bis(trimethylsilyl)ethynyl-2,5-bis(octyloxy)benzene [**36**, Ar = 2,5-bis(octyloxy)benzene] and then by removal of the TMS protecting groups formed the 1,4-bis(ethynyl)-2,5-bis(octyloxy)benzene [**37**, Ar = 2,5-bis(octyloxy)benzene]. This was subsequently coupled with **6** and **9** to form **30**[32] and **33**,[20e] respectively. In both cases overall yields are acceptable (60–70%), however these procedures require isolation and purification of both the TMS (**36**) and the terminal alkyne (**37**) intermediates. Moreover, in both cases the overall reaction times to carry out the three steps are longer than 24 h.

By the use of the *EOP* synthetic protocol (Route **d**), the 1,4-diiodo-2,5-bis(octyloxy)benzene [**34**, Ar = 2,5-bis(octyloxy)benzene], is straightforwardly converted in 1,4-bis(tributyltin)ethynyl-2,5-bis(octyloxy)benzene [**40**, Ar = 2,5-bis(octyloxy)benzene], and, by direct addition of **6** or **9** into the reaction mixture **30** and **33** are respectively formed. While the characteristics of the obtained products are comparable, using the *EOP* route

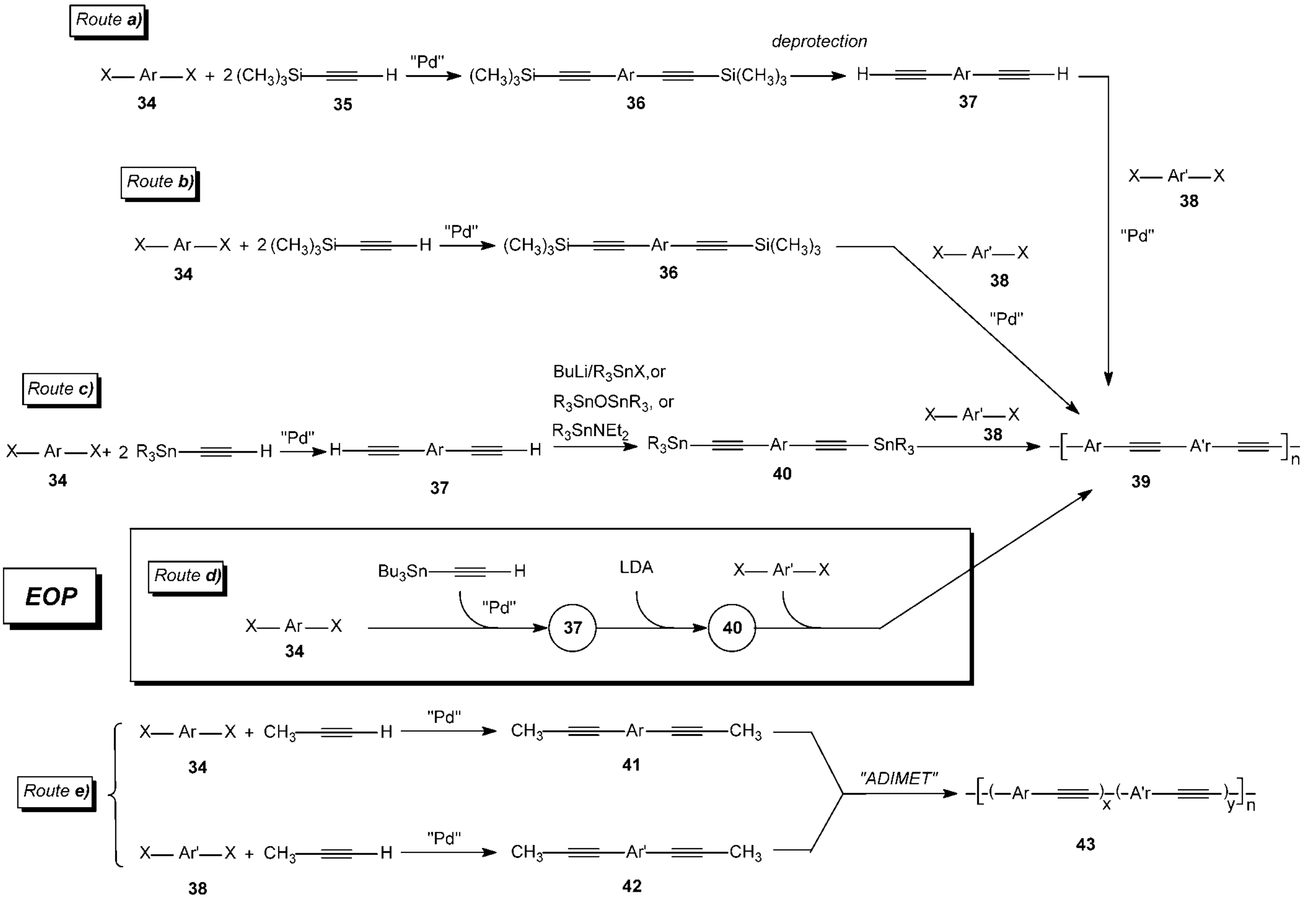


Figure 10. Comparison of the *EOP* synthetic protocol and current procedures towards the formation of PAE *co*-polymers.

no isolation of intermediates is needed, final products are isolated in 60–94% yields, and, in the case of **30** the reaction time is much shorter. Finally, the *EOP* route only requires the use of 1% of Pd catalyst to accomplish the overall formation of **30** and **33**, while *Route **a*** requires two distinct aliquots, each of 3–5%, of catalyst to form the same materials.

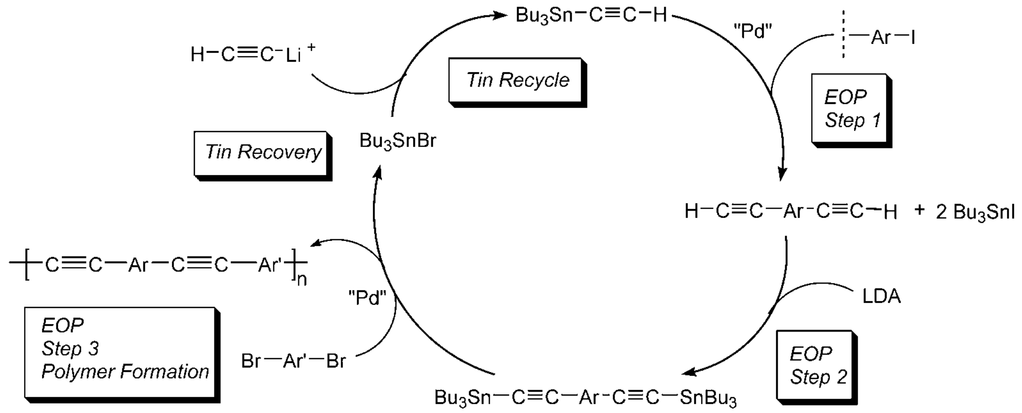
Recovery and Recycle of the Bu$_3$SnBr – The Tin Economy

Upon completion of the third step of the *EOP* synthetic protocol outlined in Scheme 1, higher molecular weight polymeric materials **27–33** spontaneously precipitated, while lower fractions were separated by precipitation with methanol. The crude polymeric material was then purified by redissolution with appropriate solvents and reprecipitation and washing with methanol. The methanolic rinsing solution containing lower oligomers, residual phosphine ligand, and the Bu$_3$SnBr side product, upon evaporation of the volatiles leaves a dark-viscous residue, from which in all cases it was possible to recover more than 90% of pure Bu$_3$SnBr by vacuum distillation. The recovered Bu$_3$SnBr was subsequently utilized in the reaction with the lithium acetylide ethylenediamine complex, to form new Bu$_3$SnC≡CH[33] [Equation (4)], which is the coupling partner of 1,4-diiodo-2,5-bis(octyloxy)benzene (**19**) at the beginning of the *EOP* route outlined in Scheme 1.

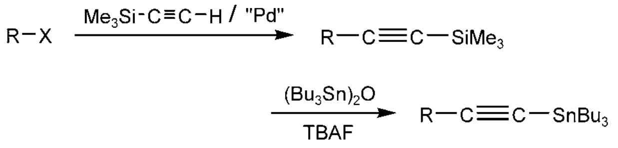
$$\mathrm{Bu_3SnBr} + \mathrm{H{-}C{\equiv}C^-\,Li^+} \longrightarrow \mathrm{Bu_3Sn{-}C{\equiv}C{-}H} \qquad (4)$$

The recovery of the Bu$_3$SnBr at the end of the polymerization process, and its re-conversion into Bu$_3$SnC≡CH allows us to draw a tin cycle (Scheme 2) which further improves the convenience of the *EOP* synthetic protocol to form ethynylated polymers.

To our knowledge, there is only one report in the literature in which alkynylstannanes are formed without the need of forming and isolating the terminal alkyne precursors. Buchwald reported on the use of bis(tributyltin) oxide and tetrabutylammonium fluoride (TBAF) to directly convert alkynylsilanes into alkynylstannanes[34] (Scheme 3). Nevertheless, we believe that our *EOP* procedure (Figure1) is more convenient since *i*) in the for-



Scheme 2.



Scheme 3.

mer method it is necessary to first prepare and isolate the alkynylsilanes, and then to transform them into the alkynylstannanes. We obtain instead the alkynylstannanes directly from the aromatic halide. *ii*) in our procedure, alkynylstannanes are formed by addition of a base and recycling of the tributyltin group of the tributyltin acetylide reagent. In order to achieve the same result, Buchwald needs to introduce bis(tributyltin) oxide and TBAF in the reaction media.

Conclusions

The Pd-driven *EOP* synthetic protocol has the potential of being addressed toward the formation of three different main classes of highly ethynylated materials: *i*) organic *homo*-polymers, *ii*) organic *co*-polymers, and *iii*) organometallic *co*-polymers. Taking advantage of the enormous capability of the palladium catalyst to efficiently perform the coupling of an extremely large variety of organic and organometallic substructures, an alternative and convenient access to innovative materials for advanced technology has been disclosed. In this respect, is worthy of note to underline the concept of a "*modular approach*", which consists in the formation of highly ethynylated material in which one "module" is in charge of impressing mechanical stability and processability to the material and a second "module" is in charge of imparting functional properties to the material. Thus, by combination of appropriate "modules" Ar and Ar′ the opportunity for a systematic and rational tailoring of polymers for certain applications has come within reach.

We have also demonstrated that the physical characteristics of these materials prepared by the *EOP* synthetic protocol are identical to those of materials prepared by more synthetically demanding, conventional procedures. Moreover, the recovery of the Bu_3SnBr at the end of the polymerization process, and its re-conversion into $Bu_3SnC{\equiv}CH$ (which, in turn, is the reagent we use to introduce the ethynyl moiety into the polymer backbone) let us consider the Bu_3Sn- moiety as a recyclable carrier of the ethynyl group into the polymer structure.

In comparison with current procedures to prepare organic and organometallic ethynylated polymers,[5] the key aspects of the process depicted in Figure 1 are: 1) The polymers are accessed without the otherwise mandatory need of purification and handling of aromatic difunctionalized terminal alkynes, materials of a delicate nature whose handling might require special precautions.[35] 2) The multifold and sequential palladium-catalyzed cross-coupling processes takes place with high efficiency, needing only a very low catalyst charge loading. 3) Since tin acetylides are formed by reuse of the Bu_3SnI generated as by-product in *Step 1*, no extra instable and toxic tin reagents are needed to form these key intermediate. 4) The recovery and the recycle of the tin reagent allow us to overcome the major drawback of the Stille reaction, that is the environmental concern related with the use of toxic and costly organostannanes.[29] In this respect, we believe that our *EOP* synthetic protocol is in agreement not only with the desirability for Stille protocols catalytic in tin,[36] but also with the "atom economy" concept recently developed by Trost,[37] and the design of environmentally benign chemical processes.[38]

Experimental Section

General Procedures

Elemental analyses were performed by the Servizio Microanalisi of the Dipartimento di Chimica of Università di Roma "La Sapienza". IR spectra were recorded on a Nicolet FT 510. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC300P spectrometer at 300 and 75 MHz, respectively. Chemical shifts (ppm) are reported in δ values relative to Me_4Si; for ^{1}H NMR, $CHCl_3$ (δ = 7.24) and for ^{13}C NMR, $CDCl_3$ (δ = 77.0) were used as internal standard. Solid state cross polarization magic angle spinning (CP MAS) ^{13}C NMR spectra were recorded on a Bruker Avance 300 operating at a ^{13}C Larmor frequency of 75.47 MHz. Samples were charged in a zirconia rotor (4 mm o.d.) and spun at the magic angle, calibrated with KBr, at 5000 Hz. Spectra were acquired using high power decoupling and a pulse length of 1.93 μs (90° pulse), contact time of 2 μs and a delay of 3 s between the scans. The chemical shifts are referred to tetramethylsilane used as external standard.

Molecular weights were determined (relative to polystyrene standard) on a Perkin-Elmer gel permeation chromatography (GPC) equipped with a set of Waters Styragel columns (HT 6 200K-10M, HT 5 50K-4M, HT 4 5K-600K, HT 3 500K-30K), and a UV detector. THF (HPLC grade; Aldrich) was the eluent (flow rate: 1 mL/min). Mass spectra were performed on an electrospray ionization time of flight (ESI-TOF) Micromass spectrometer.

Solvents, including those used for NMR and chromatography, were thoroughly degassed before use. Dioxane was dried over sodium and argon-saturated prior to 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. Liquids transferred by syringe or cannula.

2,5-Dibromo-hydroquinone (**2**),[39] 1,4-dibromo-2,5-diacetoxybenzene (**3**),[13] 1,4-dibromo-2,5-tetrahydropyranylbenzene (**4**),[40] 3,8-dibromo-1,10-phenanthroline (**6**)[41] were prepared by known methods; 2,5-di(octyloxy)benzene (**19**) was prepared by using our previously described procedure.[9a, c]

Other chemicals were purchased from Aldrich and used as received unless otherwise specified.

Photophysical Characterization

Visible absorption spectra were carried out by using a Perkin-Elmer Lambda 18 spectrophotometer. Photoluminescence spectra were measured on a standard set-up for photoluminescence using a Spectra Physics 2020 Argon Ion Laser, a 411-nm InGaN diode laser or an Oriel Xenon lamp as the excitation sources. The different excitation sources were used so as to excite each *co*-polymer at the wavelength of the main absorption band. Absorption and emission studies in solutions were generally performed in deoxygenated $CHCl_3$ at concentrations in the range 0.01–0.05 mg/mL in a quartz cell with a length either of 1 mm or 10 mm. Quantum efficiencies were determined relative to anthracene and Rhodamine 101 in a 10-mm quartz cell at a concentration of 5×10^{-4} mg/L (absorption less than 0.01). For absorption and fluorescence measurements on film, the polymers were dissolved in $CHCl_3$ at concentrations of 10 mg/mL and were spin-cast on glass substrates. No annealing procedures were generally carried out on pristine films. The thickness of the films as measured with a profilometer was typically 100 nm.

Preparation of Model Compounds 10 – 16 by Coupling of the Dibromides 3–9 with Tributyl(phenylethynyl)tin (1)

The procedure for the preparation of 5,5′-bis(phenylethynyl)-2,2′-dithiophene (**14**) is representative. A Schlenk tube was loaded with 5,5′-dibromo-2,2′-dithiophene (**7**) (0.147 g, 0.45 mmol) and $Pd(PPh_3)_4$ (0.006 g, 0.0051 mmol). After three cycles of vacuum/argon, were added by syringe $Bu_3SnC{\equiv}CPh$ (**1**) (0.371 g, 0.90 mmol) and dioxane (15 mL). The reaction mixture was heated at 110 °C and stirred for 3 h. ^{1}H NMR analysis of a sample showed the complete conversion of starting materials. After cooling to room temperature, ether (20 mL) and an aqueous saturated solution of KF (40 mL) were added, and the resulting solution was stirred for 30 min. After filtration over cotton wadding, the solution was transferred into a separatory funnel. The organic layer was washed with water (3 × 25 mL), dried over sodium sulfate and filtered. Celite (5 g) was added to the filtrate, and the mixture was evaporated to dryness. The residue was chromatographed on a silica gel column (40 × 3 cm) and eluted with hexane-CH_2Cl_2 (6:4). Pure product **14** was obtained as a yellow crystalline solid; yield: 0.160 g (93%).

Preparation of Model Compounds 11 – 16 by *EOP* Synthetic Protocols

The typical procedure was as follows: to a solution of iodobenzene (**17**) (1 mmol) and $Pd(PPh_3)_4$ (0.5 mol % equivalent) in dioxane was added tributyl(ethynyl)tin ($Bu_3SnC{\equiv}CH$) (1 mmol). After 20 minutes of stirring at 110 °C, ^{1}H NMR analysis showed the complete conversion of starting materials. After cooling to 0 °C, LDA (2.0 M solution in THF/heptane/ethylbenzene, 1.1 mmol) was added and the mixture was allowed to warm up to room temperature. ^{1}H NMR analysis of a sample of the reaction mixture indicated complete conversion of phenylacetylene into phenylethynyltin. Subsequently, the dibromide (**4**–**9**; 0.5 mmol) was added to the flask and the mixture was refluxed for 1–3 h (12 h for dibromide **9**). ^{1}H NMR analysis showed the complete conversion of the two coupling partners. After cooling at room temperature, the products **11**–**16** were isolated by the same procedure used for the previously described method.

Preparation of 1,4-Bis(2-pyridylethynyl)-2,5-dioctyloxybenzene (24)

To a solution of 1,4-diiodo-2,5-dioctyloxybenzene (**19**; 0.296 g, 0.505 mmol) and $Pd(PPh_3)_4$ (0.006 g, 0.0051 mmol) in dioxane was added tributyl(ethynyl)tin ($Bu_3SnC{\equiv}CH$) (0.331 g, 1.01 mmol). After 20 minutes of stirring at 110 °C, ^{1}H NMR analysis showed the complete conversion of starting materials. After cooling to 0 °C, LDA (2.0 M solution in THF/heptane/

ethylbenzene; 0.52 mL, 1.03 mmol) was added and the mixture was allowed to warm up to room temperature. ^{1}H NMR analysis of a sample of the reaction mixture indicated the complete formation of 1,4-bis[(tributyltin)ethynyl]-2,5-dioctyloxybenzene (**21**).

2-Bromopyridine (**22**) (0.181 g, 1.11 mmol) was then added to the flask and the mixture was refluxed for 3 h. ^{1}H NMR analysis showed the completion of the reaction. After cooling, the mixture was filtered over a celite pad, concentrated to a small volume and treated with pentane. The precipitate thus formed was collected by filtration and washed repeatedly with pentane to remove Bu_3SnBr. The residue was chromatographed on a short silica gel column (10 × 2.5 cm). Elution with CH_2Cl_2-acetone (9:1) produced a yellow band, which, after removal of the solvent, gave the pure product **24**; yield: 0.162 g (60%). An analytical sample was obtained by sublimation (130 °C/10^{-6} mm Hg).

Preparation of 1,4-Bis(9-anthracenylethynyl)-2,5-dioctyloxybenzene (25)

To a solution of 1,4-diiodo-2,5-dioctyloxybenzene (**19**; 0.298 g, 0.508 mmol) and $Pd(PPh_3)_4$ (0.006 g, 0.0051 mmol) in dioxane was added tributyl(ethynyl)tin ($Bu_3SnC\equiv CH$) (0.337 g, 1.02 mmol). After 20 minutes of stirring at 110 °C, ^{1}H NMR analysis showed the complete conversion of starting materials. After cooling to 0 °C, LDA (2.0 M solution in THF/heptane/ethylbenzene; 0.52 mL, 1.04 mmol) was added and the mixture was allowed to warm up to room temperature. ^{1}H NMR analysis of a sample of the reaction mixture indicated the complete formation of 1,4-bis[(tributyltin)ethynyl]-2,5-dioctyloxybenzene (**21**).

9-Bromoanthracene (**23**; 0.292 g, 1.07 mmol) was then added to the flask and the mixture was refluxed for 3 h. ^{1}H NMR analysis showed the completion of the reaction. After cooling, the mixture was filtered over a celite pad, concentrated to a small volume and treated with pentane. The precipitate thus formed was collected by filtration and washed repeatedly with pentane to remove Bu_3SnBr. The residue was chromatographed on a silica gel column (35 × 2.5 cm). Elution with hexane-CH_2Cl_2 (8:2) produced a first orange band, which, after removal of the solvent, gave the pure product **25**; yield: 0.254 g (68%). An analytical sample was obtained by sublimation (150 °C/10^{-6} mm Hg).

Preparation of *co*-Polymers 27–33

The typical procedure was as follows: to a solution of 1,4-diiodo-2,5-dioctyloxybenzene (**19**; 1 mmol) and $Pd(PPh_3)_4$ (1 mol % equivalent) in dioxane was added tributyl(ethynyl)tin ($Bu_3SnC\equiv CH$) (2 mmol). After 20 minutes of stirring at 110 °C, ^{1}H NMR analysis showed the complete conversion of starting materials. After cooling to 0 °C, LDA (2.0 M solution in THF/heptane/ethylbenzene; 2.1 mmol) was added and the mixture was allowed to warm up to room temperature. ^{1}H NMR analysis of a sample of the reaction mixture indicated the complete formation of 1,4-bis[(tributyltin)ethynyl]-2,5-dioctyloxybenzene (**21**).

Subsequently, the dibromide **4**–**9** (1 mmol) was added to the flask and the mixture was refluxed for 30 min – 6 h, in order to obtain formation of the corresponding *co*-polymers. Materials of different molecular weights are formed depending from the duration of this step (Table 1). Formation of polymer **33** required a longer reaction time (22 h). In general, after cooling to room temperature, insoluble material separated from the dioxane solution. After removal of the solid by filtration, the dioxane solution was filtered over a celite pad, concentrated to a small volume and treated with methanol, until a solid precipitate was obtained, which was washed repeatedly with methanol and dried under vacuum. The original crop of material which spontaneously precipitated upon cooling the reaction mixture was treated with chloroform. In the case of polymers **27**, **30**, **31** and **32**, this material showed to be only partially soluble in THF, chloroform or dichloromethane. This solid was collected by filtration and separately analyzed. From the chloroform solution, polymeric material was obtained by the same procedure adopted for the dioxane solution.

Supporting Information

Characterization data of compounds **10**–**16**, **24**, **25**, and **27**–**33**.

Acknowledgements

This work was partially supported by the Ministero Italiano dell'Università e della Ricerca Scientifica e Tecnologica (M.I.U.R. Roma), with the contract COFIN 2003 "Studio del meccanismo di reazione e applicazione nella sintesi della catalisi da palladio per la formazione di polimeri poli(etinilaromatici) e poli(metalloetinilaromatici), materiali funzionali per applicazioni innovative in optoelettronica". The authors gratefully acknowledge Dott. Patrizia Oliva and Prof. Alfonso Grassi (Università di Salerno) for CP MAS ^{13}C NMR measurements and stimulating discussions.

References and Notes

[1] a) T. N. Mitchell, in: *Metal-catalyzed Cross-coupling Reactions,* (Eds.: F. Diederich, P. J. Stang), Wiley-VCH, Weinheim, Germany, **1998**; b) *J. Organometal. Chem.* **2002**, *653*, Special Issue: 30 Years of the Cross-Coupling Reaction, (Eds.: K. Tamao, T. Hiyama, E-I Negishi).

[2] V. Farina, V. Krishnamurthy, W. J. Scott, *The Stille Reaction*, John Wiley & Sons, Inc., New York, **1998**.

[3] a) J. K. Stille, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 508; b) V. Farina, *Pure Appl. Chem.* **1996**, *68*, 73.

[4] a) M. Bochmann, K. Kelly, *J. Chem. Soc. Chem. Commun.* **1989**, 532; b) R. Giesa, R. C. Schulz, *Makromol. Chem.* **1990**, *191*, 857; c) M. Bochmann, K. Kelly, *J. Polym. Sci., Polym. Chem.* **1992**, *30A*, 2511; d) S. L. Ingham, M. S. Khan, J. Lewis, N. J. Long, P. R. Raithby, *J. Organomet. Chem.* **1994**, *470*, 153; e) L. Yu, Z. Bao, R. Cai, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1345; f) Z. Bao, W. K. Chan, L. Yu, *J. Am. Chem. Soc.* **1995**, *117*, 12426; g) M. E. Wright, M. J. Porsch, C. Buckley, B. B. Cochran, *J. Am. Chem. Soc.* **1997**, *119*, 8393.

[5] a) K. Sanechika, T. Yamamoto, A. Yamamoto, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 752; b) T. J. Skotheim, R. L.

Elsenbaumer, J. R. Reynolds, *Handbook of Conducting Polymers*, 2nd edn., M. Dekker, New York, **1998**; c) P. F. Schwab, M. D. Lewin, J. Michl, *Chem. Rev.* **1999**, *99*, 1863; d) U. F. H. Bunz, *Chem. Rev.* **2000**, 100, 1605; e) J. C. Ellenbogen, J. C. Love, *Proceedings of the IEEE* **2000**, 88 (3).

[6] a) W. J. Blau, P. Lianos, U. Schubert, *Molecular Materials and Functional Polymers*, Springer Verlag, Wien, **2001**; b) N. J. Long, *Angew. Chem. Int. Ed.* **1995**, *34*, 21; c) H. Lang, *Angew. Chem. Int. Ed.* **1994**, *33*, 547; d) T. Yamamoto, *Synlett* **2003**, *4*, 425; e) F. Uckert, Y.-H. Tak, K. Mullen, H. Bassler, *Adv. Mater.* **2000**, *12*, 905; f) E. Breuning, M. Ruben, J.-M. Lehn, F. Renz, Y. Garcia, V. Ksenofontov, P. Gutlich, E. Wegelius, K. Rissanen, *Angew. Chem. Int. Ed.* **2000**, *39*, 2504.

[7] a) J. M. Tour, *Chem. Rev.* **1996**, *96*, 537; b) J. M. Tour, in: *Stimulating Concepts in Chemistry*, (Eds.: F. Vögtle, J. F. Stoddard, M. Shibasaki), Wiley-VCH, Weinheim, **2000**, pp. 237–253.

[8] a) M. Pereyre, J.-P. Quintard, A. Rahm, *Tin in Organic Synthesis*, Butterworths & Co, London, **1987**; b) A. G. Davies, *Organotin Chemistry*, VCH Verlagsgesellschaft, Weinheim (Germany), **1997**.

[9] a) E. Antonelli, P. Rosi, C. Lo Sterzo, E. Viola, *J. Organomet. Chem.* **1999**, *578*, 210; b) C. Lo Sterzo, *Synlett* **1999**, 1704; c) G. Giardina, P. Rosi, A. Ricci, C. Lo Sterzo, *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 2603; d) P. Altamura, G. Giardina, C. Lo Sterzo, M. V. Russo, *Organometallics* **2001**, *20*, 4360; e) A. Ricci, C. Lo Sterzo, *J. Organomet. Chem.* **2002**, *653*, 177; f) R. Pizzoferrato, M. Berliocchi, A. Di Carlo, P. Lugli, M. Venanzi, A. Micozzi, A. Ricci, C. Lo Sterzo, *Macromolecules* **2003**, *36*, 2215; g) A. La Groia, A. Ricci, M. Bassetti, D. Masi, C. Bianchini, C. Lo Sterzo, *J. Organomet. Chem.* **2003**, *683*, 406.

[10] Functionalization of the "**A**" unit must be performed carefully, since regulation of the supramolecular order in rod-like polymers is achieved by controlling the regioregular attachment of substituents of specific size and type at the aromatic units of the polymer backbone. Aggregation and solid-state behavior are in fact essential characteristics in conjugated polymers, since morphology and supramolecular order have a fundamental effect on optical and electrical properties.[11]

[11] C. Weder, M. S. Wrighton, *Macromolecules* **1996**, *29*, 5157 and references cited therein.

[12] a) Q. Zhou, T. M. Swager, *J. Am. Chem. Soc.* **1995**, *117*, 12593; b) Y. Zhang, C. B. Murphy, W. E. Jones, Jr., *Macromolecules* **2002**, *35*, 630.

[13] T. Yamamoto, T. Kimura, K. Shiraishi, *Macromolecules* **1999**, *32*, 8886.

[14] T. M. Swager, C. J. Gil, M. S. Wrighton, *J. Phys. Chem.* **1995**, *99*, 4886.

[15] R. Pizzoferrato, T. Ziller, A. Ricci, A. Micozzi, C. Lo Sterzo, manuscript in preparation.

[16] It is possible that under these reaction conditions the acetyl protecting groups are removed by the action of diisopropylamine.

[17] With the exception of **14** (see Experimental Section), no attempt was made to optimize the amount of isolated products. Having once confirmed by ^{1}H NMR complete conversion of starting materials into products,[18] instead of performing chromatographic separation, analytical samples were isolated simply by precipitation and rinsing with pentane or methanol, followed by sublimation (yields: 30–60%). The anthracene derivative **15** does not withstand chromatographic purification, thus isolation can be only achieved by precipitation and sublimation.

[18] The sequential check of the transformation progresses was typically performed by withdrawing a sample of the reaction mixture (0.1–0.2 mL), stripping off the solvent under reduced pressure (10–15 mmHg/25 °C, 20 min), redissolution with $CDCl_3$, and recording of the ^{1}H NMR spectrum.

[19] The polymeric material spontaneously precipitated upon cooling of the reaction mixture is only partially soluble in THF, chloroform and dichloromethane. The soluble part was characterized by GPC and NMR. The insoluble fraction was only characterized by solid state NMR.

[20] a) M. Moroni, J. Le Moigne, S. Luzzati, *Macromolecules* **1994**, *27*, 562; b) H. Li, D. R. Powell, R. K. Hayashi, R. West, *Macromolecules* **1998**, *31*, 52; c) Y. Pang, J. Li, B. Hu, F. E. Karasz, *Macromolecules* **1998**, *31*, 6730; d) T. Yasuda, T. Yamamoto, *Macromolecules* **2003**, *36*, 7513; e) S. Dellsperger, F. Dötz, P. Smith, C. Weder, *Macromol. Chem. Phys.* **2000**, *201*, 192.

[21] Y. N. Gartstein, M. J. Rice, E. M. Conwell, *Phys. Rev. B* **1995**, *52*, 1683.

[22] Probably the substitution at the 2 and 6 positions of the pyridine ring is causing formation of bent structures (helicate and/or random coiled) in which side-chain interactions are disrupting ring coplanarity with the consequent breakage of conjugation.

[23] E. M. Conwell, *Trends Polym. Sci.* **1997**, *5*, 218.

[24] a) K. Sonogashira, Y. Tohda, N. Hagihara, *Tetrahedron Lett.* **1975**, 4467; b) H. A. Dieck, R. F. Heck, *J. Organometal. Chem.* **1975**, *93*, 259; c) L. Cassar, *J. Organometal. Chem.* **1975**, *93*, 253.

[25] a) M. J. Mio, L. C. Kopel, J. B. Braun, T. L. Gadzikwa, K. L. Hull, G. G. Brisbois, C. J. Markworth, P. A. Grieco, *Org. Lett.* **2002**, *4*, 3199; b) E. Negishi, L. Anastasia, *Chem. Rev.* **2003**, *103*, 1979; c) R. R. Tykwinsky, *Angew. Chem. Int. Ed.* **2003**, *42*, 1566.

[26] a) M. M. Haley, M. L. Bell, J. J. English, C. A. Johnson, T. J. R. Weakley, *J. Am. Chem. Soc.* **1997**, *119*, 2956; b) M. M. Haley, *Synlett* **1998**, 577; c) J. J. Pak, T. J. R. Weakley, M. M. Haley, *J. Am. Chem. Soc.* **1999**, *121*, 8182.

[27] H. Hager, W. Heitz, *Macromol. Chem. Phys.* **1998**, *199*, 1821.

[28] a) A. Kohler, J. S. Wilson, R. H. Friend, M. K. Al-Suti, M. S. Khan, A. Gerhard, H. J. Bassler, *Chem. Phys.* **2002**, *116*, 9457; b) S. Hecht, A. Khan, *Chem. Commun.* **2004**, *3*, 300.

[29] a) U. F. H. Bunz, V. Enkelmann, *Organometallics* **1994**, *13*, 3823; b) J. Lewis, M. S. Khan, S. J. Davis, A. K. Kak-

kar, B. F. G. Johnson, T. B. Marder, H. B. Fyfe, F. Wittmann, R. H. Friend, A. E. Dray, *J. Organomet. Chem.* **1992**, *425*, 165; c) R. Crescenzi, C. Lo Sterzo, *Organometallics* **1992**, *11*, 4301; d) C. Cauletti, C. Furlani, A. Sebald, *Gazz. Chim. Ital.* **1988**, *118*, 1.

[30] U. H. F. Bunz, *Acc. Chem. Res.* **2001**, *34*, 998.

[31] a) N. G. Pschirer, K. Byrd, U. H. F. Bunz, *Macromolecules* **2001**, *34*, 8590; b) G. Brizius, S. Kroth, U. H. F. Bunz, *Macromolecules* **2002**, *35*, 5317.

[32] a) U.-W. Grummt, E. Birckner, M. Al-Higari, D. A. Egbe, E. Klemm, *J. Fluoresc.* **2001**, *11*, 41; b) M. Al-Higari, E. Birckner, B. Heise, E. Klemm, *J. Polym. Sci. Part A: Polym. Chem.* **1999**, *37*, 4442.

[33] a) A. F. Renaldo, J. W. Labadie, J. K. Stille, *Org. Synth.* **1989**, *67*, 86; b) J. C. Bottaro, R. N. Hanson, D. E. Seitz, *J. Org. Chem.* **1981**, *46*, 5221.

[34] B. P. Warner, S. L. Buchwald, *J. Org. Chem.* **1994**, *59*, 5822.

[35] a) T. X. Neenan, G. M. Whitesides, *J. Org. Chem.* **1988**, *53*, 2489 and references cited therein; b) M. Alami, F. Ferri, G. Linstrumelle, *Tetrahedron Lett.* **1993**, *34*, 6403; c) P. Nguyen, S. Todd, D. Van den Biggelaar, N. J. Taylor, T. B. Marder, F. Wittmann, R. H. Friend, *Synlett* **1994**, 299; d) L. Bleicher, N. D. P. Cosford, *Synlett* **1995**, 1115; e) F. Diederich, Y. Rubin, O. L. Chapman, N. S. Goroff, *Helv. Chim. Acta* **1994**, *77*, 1441; f) B. C. Berris, G. H. Hovakeemian, Y.-H. Lai, H. Mestdagh, K. P. C. Vollhardt, *J. Am. Chem. Soc.* **1985**, *107*, 5670; g) R. Giesa, *Rev. Macromol. Chem. Phys.* **1996**, *C36*, 631.

[36] R. E. Maleczka, W. P. Gallagher, I. Terstiege, *J. Am. Chem. Soc.* **2000**, *122*, 384.

[37] a) B. M. Trost, *Science* **1991**, 254, 1471; b) B. M. Trost, M. T. Sorum, C. Chan, A. E. Harms, G. Ruter, *J. Am. Chem. Soc.* **1997**, *119*, 698; c) B. M. Trost, M. J. Krische, *Synlett* **1998**, 1.

[38] P. T. Anastas, J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, Inc., New York, **1998**, pp. 29–55.

[39] T. Vahlenkamp, G. Wegner, *Macromol. Chem. Phys.* **1994**, *195*, 1933.

[40] M. Miyashita, A. Yoshikoshi, P. A. Grieco, *J. Org. Chem.* **1997**, *62*, 3772.

[41] Y. Saitoh, T. Koizumi, K. Osakada, T. Yamamoto, *Can. J. Chem.* **1997**, *75*, 1336.