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Improvement of the Extended One-Pot (EOP) Procedure To Form Poly(aryleneethynylene)s and Investigation of Their Electrical and Optical Properties

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ABSTRACT: A series of π-conjugated homopolymers of type poly(aryleneethynylene) (PAE), $[-\mathrm{Ar}-\mathrm{C}\equiv\mathrm{C}-]_n$, (Ar = 2,5-bis(butoxy)benzene (**7a**), 2,5-bis(octyloxy)benzene (**7b**), 2,5-bis(hexadecyloxy)benzene (**7c**), 3-butylthiophene (**7d**), and 3-hexadecylthiophene (**7e**)) have been prepared by further improvement of the palladium-catalyzed Extended One-Pot (EOP) synthetic protocol. With the use of dioxane as solvent and higher reaction temperature (110 °C), much higher polymerization degree, improved catalytic efficiency, and increased material purity were obtained. Numerical simulations have been performed in a series of different conjugated polymers in order to evaluate the role of the connection between aromatic rings in the maintaining of an effective electronic conjugation through the polymer chain. Experimentally, the conjugation properties have been investigated by means of photophysical measurements in liquid solution and in solid-state films. The electric transport properties have been characterized in view of applications to electronic devices.

Introduction

Organic conductive polymers are fully π-conjugated polymers that are currently attracting increasing attention due to their unique and unconventional physical properties that are interesting for the development of new materials in areas such as microelectronics, optics, sensor technology, and molecular electronics.[1,2]

In the field of organic conductive π-conjugated polymers, three different classes of materials are mostly used: (i) polymers made of aromatic rings directly linked to each other in a linear fashion, the poly(arylene)s[3,4] (PAs) (**I**), (ii) polymers made of alternating aryl and ethylene units, the poly(p-arylenevinylene)s[5] (PAVs) (**II**), and (iii) polymers made of alternating aryl and ethynyl units poly(aryleneethynylene)s[2a,3] (PAEs) (**III**) (Figure 1). In each of these classes, the aromatic unit may be substituted benzenes (and superior polycyclic aromatic hydrocarbons) and heteroaromatics such as thiophenes, pyridines, pyrroles, and thiazoles. Moreover, the main chain of these polymeric materials may be constituted by a sequence of identical moieties or by a combination of different aromatic moieties, forming homo- and copolymers, respectively.

However, for *all* materials presented in Figure 1, the presence of side-chain groups (R) on the aromatic moieties is a *mandatory* requirement in order to obtain soluble and processable materials, but as a consequence of the unavoidable steric interactions occurring between lateral chains on adjacent aromatic rings, the coplanarity of the connected rings—and, thus, conjugation and related phenomenona—is severely affected.

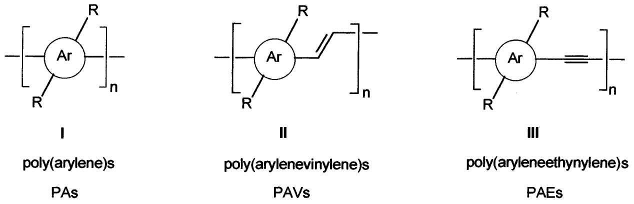

Figure 1. Organic conductive π-conjugated polymers.

Because of the direct ring-to-ring connection, the disturbing of ring coplanarity by side-chain interactions is obviously very heavy on PA polymers (**I**), and in these systems torsion about the aryl−aryl single bond can only be overcome by incorporating the PA backbone into a ladder-type structure,[6] with an additional and demanding synthetic effort. In polymers of type PAVs (**II**), the steric requirements of the R substituents on the Ar unit directly influence the electronic properties of the material by affecting the torsion of the conjugated chain (i.e. the $\pi-\pi^*$ energy gap).[7]

Within this frame we believe that there are a number of reasons by which PAEs (**III**) might offer superior opportunities with respect to the other organic conjugated polymers (**I**−**II**). (i) In PAEs aromatic rings are spaced by straightly aligned acetylene moieties; then the coplanarity of the rings and related conjugation are

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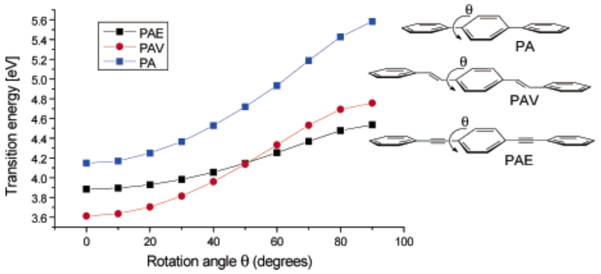


Figure 2. Comparison of the influence of the torsion angle on the effectiveness of the π-conjugation for the three-ring models of PAs, PAVs, and PAEs.

less disturbed by the sterical constraint imposed by side-chain interactions. (ii) Because of the cylindrical symmetry of the π-electron distribution on the triple bonds, an efficient conjugation should be maintained even in the presence of a certain degree of torsion between rings;[9] in other words, in PAEs conjugation is less adversely affected by disturbance of the coplanarity of the rings than in any other conjugated system. Thus, in these systems planarization[6] of aromatic rings is not a severe requirement in order to maintain conjugation. (iii) Since in organic conjugated materials (opto)electronic properties strongly depend on thin film morphology, because electronic overlap between molecules is a consequence of relative molecular orientation,[10,11] in PAEs by the interplay of the rigid rodlike backbone structure and the presence of properly chosen side substituents on the aromatic rings, a control of the supramolecular assembly may be possible,[12] and an ordered control of thin film morphology might be achieved.

The maintaining of a greater extent of conjugation—and related properties—in polymeric materials incorporating an acetylenic linkage between aromatic rings, with respect to other conjugated polymers, is also accounted for by quantum-chemistry calculations. Following the calculation presented by Bunz,[9] in order to evaluate the influence of the torsion angle on the π-conjugation of materials of types **I**−**III**, we have calculated and compared the conjugation properties of a three-ring structure model of compounds of PAs, PAVs, and PAEs as a function of the torsion angle between rings (Figure 2). The geometry of the structure is first relaxed by using standard semiempirical Hartree−Fock methods (PM model[13]), and then the first singlet excited state (fundamental optical transition) is calculated by using a Configuration-Interaction scheme in an INDO context.[14] The energy of the optical transition is calculated for several values of rotational angle of the central ring. Figure 2 shows the calculated transition energy as a function of rotation angle of the central ring for the three systems.

For the planar structure the PAV system presents a smaller transition energy with respect to both PAE and PA. Thus, in the planar case the conjugation property of the PAV system is larger than those of the other two cases. This is confirmed by recent experimental and theoretical results comparing the transport properties of three-ring systems of PAV and PAE.[15] By rotating the central ring, the degree of conjugation reduces for all systems. However, for a rotation angle larger than 50° the PAE system results in a lower transition energy with respect to those for the PAV and PA systems. This clearly shows that, for rotation angles larger than 50°, because of the presence of the acetylenic spacer, PAE materials may perform a more effective conjugation with respect to those of PAV and PA.

Therefore, under real working conditions because of packing interactions between adjacent chains of polymer films, and consequent ring torsion, PAE polymers might display superior performances with respect to PAV and PA materials.

On the basis of these premises, we concluded that PAEs are unique materials in the field of organic conductive polymers.

We have recently entered this field, reporting a new and versatile *one-pot* procedure, named *Extended One Pot* (EOP), based on a cascade of Pd-promoted processes straightforwardly leading from aromatic diiodides to a wide range of ethynylaromatic homopolymers $[-C{\equiv}C-Ar-]_n$ (**IV**), ethynylaromatic copolymers $[-C{\equiv}C-Ar-C{\equiv}C-Ar'-]_n$ (**V**), and ethynylaromatic−ethynylmetallo copolymers $[-C{\equiv}C-Ar-C{\equiv}C-M(L)_m-]_n$ (**VI**) (Scheme 1). The overall EOP routes leading to **IV**−**VI** are essentially constituted by an interplay of Pd-catalyzed processes (steps 1 and 3) and an in-situ base-promoted alkyne/stannane conversion (step 2). The Pd-catalyzed couplings taking place in the formation of **IV** and **V** are Stille[17] couplings, while the formation of the organometallic polymers **VI** in step 3 is achieved by our original Pd-catalyzed metal−carbon bond formation procedure.[18]

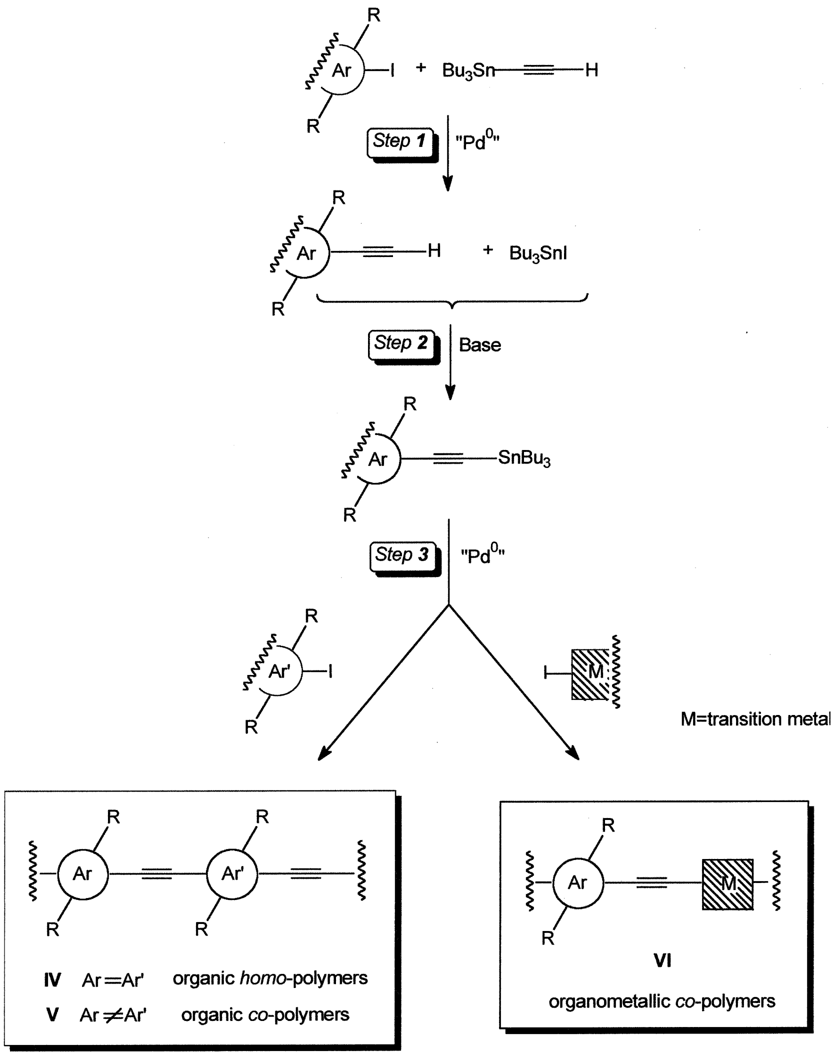
In this paper we report on the further improvement of performances of our EOP synthetic protocol for the preparation of a range of ethynylated homopolymers of type poly(aryleneethynylene)s (PAEs), of general formula $[-Ar-C{\equiv}C-]_n$ (**IV**), and on the investigation of their optical and electrical properties, both in solution and in film, in view of their possible use in device fabrication.

Results and Discussion

Synthesis and Characterization of Polymers. In Scheme 2 is outlined the three-step palladium-promoted EOP synthetic protocol we used to form the poly(aryleneethynylene) homopolymers $[-Ar-C{\equiv}C-]_n$ (Ar = 2,5-bis(butoxy)benzene (**7a**), 2,5-bis(octyloxy)benzene (**7b**), 2,5-bis(hexadecyloxy)benzene (**7c**), 3-butylthiophene (**7d**), and 3-hexadecylthiophene (**7e**)). The aromatic units enter in this synthetic route as 1,4-diodo-2,5-dialkoxybenzenes (**1a**−**c**) and 2,5-diiodo-3-alkylthiophenes (**1d**,**e**), while the acetylenic spacer is conveyed into the polymeric structure by the means of its tributyltin derivative **2**.

In the first step the diiodoaromatic compounds (**1a**−**e**) are reacted with tributylethynyltin ($Bu_3Sn-C{\equiv}C-H$) (**2**) in refluxing dioxane (110 °C), in the presence of 0.5 mol % of $Pd(PPh_3)_4$. In principle, the precise 1:1 stoichiometric ratio between reactants should lead to the exclusive formation of the products of *mono*coupling, the iodo(ethynyl)aromatic compounds ($I-Ar-C{\equiv}C-H$) (**4a**−**e**); however, under these conditions formation of the biscoupled products ($H-C{\equiv}C-Ar-C{\equiv}C-H$) (**3a**−**e**) is unavoidable and, as a consequence, an equivalent amount of unreacted diiodides ($I-Ar-I$) (**1a**−**e**) is remaining. In 20 min step 1 is completed and an equivalent amount of the side product Bu_3SnI (per equivalent of ethynyl group reacted) is formed. Cooling at 0 °C and addition of LDA caused deprotonation of the terminal alkyne moieties of **3a**−**e** and **4a**−**e** and the immediate recombination of the resulting acetylides with Bu_3SnI, to form $Bu_3Sn-C{\equiv}C-Ar-C{\equiv}C-SnBu_3$

Scheme 1



(**5a**−**e**) and I—Ar—C≡C—SnBu$_3$ (**6a**−**e**), respectively, while I—Ar—I (**1a**−**e**) remained unchanged (step 2). This mixture, brought back to 110 °C, led in an additional 2−8 h to the formation of the corresponding homopolymers [—Ar—C≡C—]$_n$ (**7a**−**e**) (step 3). Although both coupling processes taking place in steps 1 and 3 required the presence of zerovalent palladium, the catalyst was only added at once in the first step, with its activity being maintained throughout the whole synthetic route.

Upon cooling at room temperature, the polymeric material separated out from the solution as an orange or orange-brown solid. Precipitation was completed by addition of methanol; then filtration and repeated washing with methanol allowed isolation of the purified material. As experienced before,[16b] by fractional distillation of the methanolic rinsing solution, most of the Bu$_3$SnI formed after completion of step 3 was recovered and then used to form new Bu$_3$Sn—C≡C—H, thus allowing a practically complete recycle of the tin involved in the overall process.

It is important to note that when the same transformations were run in THF solvent, steps 1 and 3 (run at 70 °C) required 16 h and 24 h to be accomplished, respectively.[16] Moreover, under the former conditions in order to avoid secondary transformations, treatment with LDA in step 2 had to be conducted at −20 °C for alkoxybenzenes **3a**−**c** and **4a**−**c** and at −80 °C for alkylthiophenes **3d**,**e** and **4d**,**e**, while in dioxane this step can be safely, and more conveniently, carried out at 0 °C in all cases. The GPC analysis of the polymeric materials **7a**−**e** obtained by operating under these new conditions showed that with respect to reactions performed in THF, in all cases a great increase of polymer molecular weights was obtained, now reaching the 43−94 DP range. Moreover, in refluxing dioxane, yields of **7a**−**c** significantly improved from the 69−76% range to the 86−94% range, while yields of **7d**−**e** are maintained over the range of 90% (Table 1).[19] Upon obtaining materials of higher molecular weights, purification of products became easier. In fact, a crispy solid was obtained by precipitation (with the exception of **7**e), from which a soluble byproduct and lighter oligomeric fractions could be easily washed out. Finally, it is worthy of observation that a remarkable catalytic efficiency (0.5% of Pd^0 for the overall process of Scheme 2) has been maintained also by operating under more severe conditions (110 °C).

With respect to current procedures[2a,3] used to obtain ethynylaromatic homopolymers [—Ar—C≡C—]$_n$, the EOP route outlined in Scheme 2 offers some distinct advantages. In Scheme 3 are reported the two most common strategies used to form (polyaryleneethynylene)s (PAEs): (route a) the AA/BB approach and (route b) the AB approach. In both cases the starting material is the aromatic dihalide ArX$_2$ (**8**) which is reacted with a different amount of trimethylsilylacetylene (TMSA) (**9**)

Scheme 2

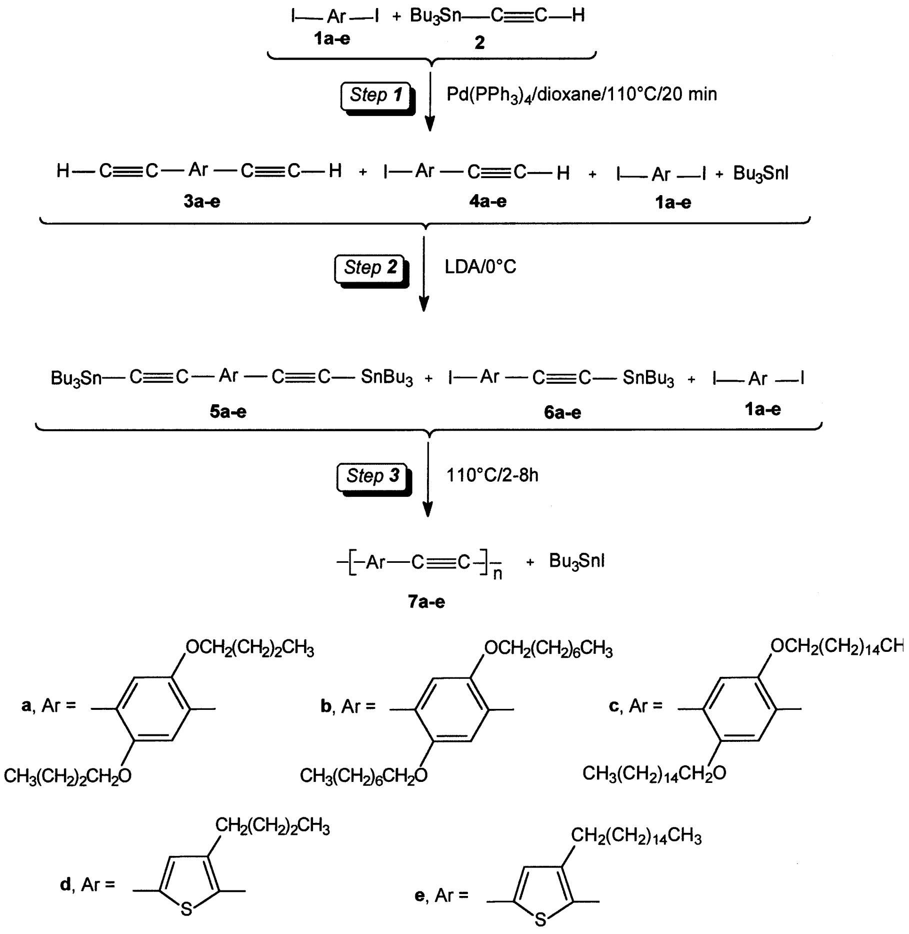
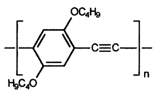
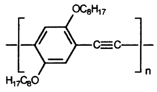
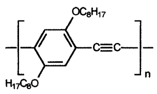
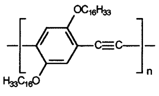
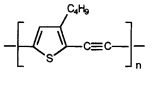
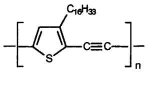


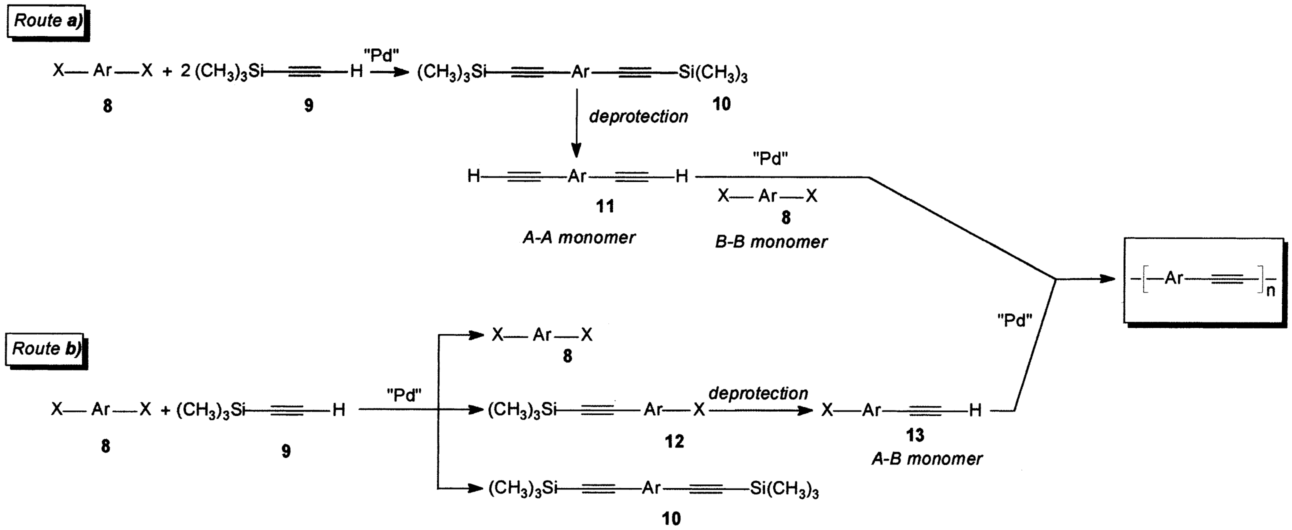
Table 1

		reaction time	Yield (%)	M_w[a]	M_n[a]	MWD[b]	DP[c](M_w)	DP[c](M_n)
7a		2h	86	19410	6170	3.1	79	25
7b$_{\mathrm{I}}$		1h	83	14140	6850	2.1	40	19
7b$_{\mathrm{II}}$		6h	94	31980	12590	2.5	90	35
7c		8h	92	24810	12610	2.0	43	22
7d		2h	97	15310	5420	2.8	94	33
7e		2h	92	27250	10170	2.7	82	31

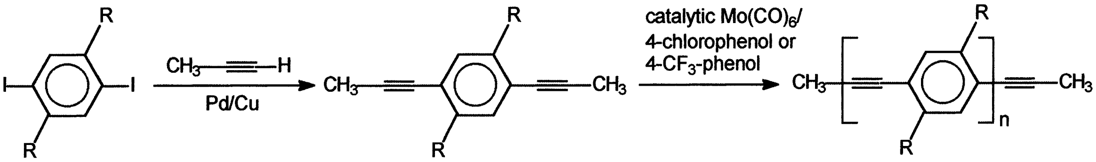
[a] Determined by GPC (THF, polystyrene standard). [b] Molecular weight distribution (M_w/M_n). [c] Degree of polymerization.

in the presence of palladium (Sonogashira[20]–Heck[21]–Cassar[22] coupling). In the first case, the 1:2 ratio between **8** and **9** lead to the formation of **10** while, in the second one, despite the accurate 1:1 stoichiometric ratio between reactants, a mixture of **8**, **10**, and **12** is unavoidably obtained, and as a consequence in order

Scheme 3



Scheme 4



to isolate the only useful precursor **12**, an accurate separation is required. Subsequently, the TMS intermediates **10** and **12** are deprotected, and after isolation,[23] the corresponding acetylide derivatives **11** and **13** are allowed to react with an equivalent amount of the dihalide ArX_2 (route a) or to self-condense (route b). In both cases, to achieve a high polymerization degree, a precise control of the stoichiometric balance is necessary. Since **13** intrinsically offers the precise stoichiometry between the two different functional groups, in principle, the AB approach (route b) is preferable; however, because of the cumbersome separation required to isolate **12** from **10** and **8**, the AA/BB approach is generally preferred.

The EOP synthetic route (Scheme 2) practically offers all the advantages of the AB approach (route b of Scheme 3), without the demanding necessity of dealing with the isolation of pure hetero-difunctionalized species **6a**–**e**. In fact, formation of polymers **7a**–**e** efficiently occurs regardless of the relative ratio of the three coupling partners participating in step 3. The only determining factor to obtain a polymeric material constituted by a regularly alternating alkyne/arene sequence is to have an overall 1:1 iodine/tributyltin acetylyde moieties ratio, independent of the relative ratio of the three different coupling partners bearing these functionalities. Moreover, while intermediates **10** and **11** in route a and **12** and **13** in route b of Scheme 3 need to be isolated and carefully purified prior to the subsequent uses, in the EOP process the polymerization process starts with the reaction of diiodides **1a**–**c** with the tributyltin derivative **2**, and besides the halfway injection of LDA, the transformation straightforwardly proceeds up to the formation of polymers **7a**–**e**. The unnecessary separation and purification of intermediates is a particularly appreciable aspect, especially considering the delicate nature of aromatic alkynes.

Toward this end, Bunz[27] has recently reported the acyclic diyne metathesis (ADIMET) approach (Scheme 4), presenting an alternative route to poly(phenyleneethynylene)s, not relying on Pd-catalyzed processes (Schemes 2 and 3). The ADIMET consists of a very efficient process, promoted by an in-situ generated/highly reactive Mo catalyst. Despite its high reactivity, the active catalyst is conveniently formed in nondried, nonpurified, off-the-shelf solvents, and the process, which is very efficient when hydrocarbon monomers are used, seems to suffer only a few limitations.

Investigation of Photophysical and Electrical Properties

Optical and electrical measurements were carried out in order to characterize the electronic properties of PAEs **7a**–**e** as opto- and electroactive materials. Toward this end, photophysical characteristics were investigated both in solution and in solid-state films, and in the case of **7b**, samples of different degrees of polymerization (**7b**$_{I}$, DP = 40; **7b**$_{II}$, DP = 90) were examined.

Optical Absorption and Photoluminescence of Polymers in Solution. The absorption and emission spectra obtained for diluted $CHCl_3$ solutions are shown in Figure 3, and all the relevant spectral parameters are summarized in Table 2. We note that **7a**, **7b**$_{II}$, and **7c** show almost identical optical properties in solution. The absorption spectra of all polymers consist of a peak at 320 nm and a broad main band centered around 425 nm with a slightly minor blue-shift (417 nm) for the shorter-chain polymer **7b**$_{I}$. The PL emission spectra, which are insensitive to the excitation wavelength in the range from 380 to 460 nm, show a well resolved splitting into a relatively narrow band, centered around 475 nm, and a broader shoulder, peaked in the range from 505 to 515 nm and of slightly different relative intensity depending on the compound. This splitting and the lack of mirror image similarity between absorption and emission spectra suggest the influence of vibronic coupling while the emission bands have been

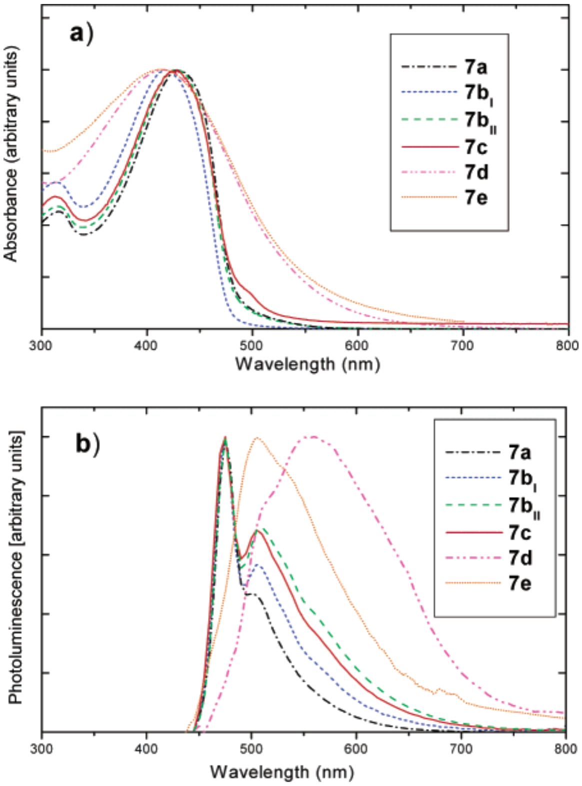


Figure 3. (a) Absorption spectra of the PAEs in $CHCl_3$ at 295 K. (b) Emission spectra of the PAEs in $CHCl_3$ at 295 K. The intensities were arbitrarily chosen in order to optimally fit the graphs.

Table 2. Optical Properties of the Polymers in Solutions[a]

polymer	DP[b]	absorption λ_{max} (nm)	emission λ_{max} (nm)	ϕ_{fl}[c]
7a	79	428	475	0.14
7b$_I$	40	417	475	0.32
7b$_{II}$	90	425	475	0.21
7c	43	424	475	0.21
7d	94	414	550	0.015
7e	82	413	538	0.017

[a] All experiments were performed in $CHCl_3$. [b] Degree of polymerization. [c] Fluorescence quantum yield.

attributed[28] to transitions from localized states after a migration of the excitations along the polymer main chains.

The spectroscopic features of compounds **7a**−**c** are consistent with literature reports for the same polymers prepared by means of conventional methods, even though quite scattered data are presented by other groups. Specifically, for **7a**, synthesized[29] with an average DP of 138, only the PL emission is reported peaked at $\lambda_{max} = 480$ nm; for **7b**[28] with DP = 23 the absorption is peaked at $\lambda_{max} = 449$ nm while the main emission is centered at $\lambda_{max} = 474$ nm; for **7c**[30] only the absorption peak was determined at $\lambda_{max} = 425$ nm. The experimental values of PL quantum yields estimated in the present work are also very similar among the different polymers and lay in the range from 0.14 to 0.32.[31]

Such a striking overall similarity of the optical properties of these polymers in solution seems to confirm that these molecules are predominantly governed by the rigid rod and highly conjugated polymer backbone and are not influenced by the size of the attached side chains. On the contrary, the different sizes of side chains significantly affect the optical properties of the solid state (vide infra), suggesting a different degree of intermolecular interaction or, possibly, the presence of supramolecular ordering. Moreover, the little differences observed for the λ_{max} values for compounds **7b$_I$** and **7b$_{II}$**, as well as for values in the literature for samples of different DPs, further support the evidence that in conjugated polymers optical properties reach saturation for DP values over 30−40 repeating units.[33] The similarity of the optical properties of benzene-based polymers **7a**−**7c** in solution is particularly meaningful in view of the noticeable differences observed with respect to the spectra of thiophene-based polymers. In fact, the absorption spectra of **7d** and **7e** are appreciably broader while the emission bands are not so well resolved in the two structures and are red-shifted by approximately 50 nm. Moreover, the PL quantum efficiencies are 1 order of magnitude lower.

Table 3. Optical Properties of the Polymers in Solid-State Films

polymer	DP[a]	absorption λ_{max} in spin-coated films (nm)	emission λ_{max} in spin-coated films (nm)	emission λ_{max} in spray-coated films (nm)
7a	79	440	540	565
7b$_I$	40	424	585	580
7b$_{II}$	90	447	575	560
7c	43	452	565	575
7d	94	405	630	655
7e	82	413	595	600

[a] Degree of polymerization.

Optical Absorption and Photoluminescence of Solid-State Films. The solid-state photophysics and electrical characteristics of the new PAEs were investigated under ambient conditions and in a vacuum (10^{-4} Torr) on pristine films deposited either by means of casting, with an average thickness in the range 20−40 μm, or by a spin-coating technique (thickness about 0.1 μm). Excitation for photoluminescence spectra was provided by the 457-nm line of the Ar-ion laser with a power flux in the range 50−200 mW/cm^2 or by the monochromatized output from a 300-W Xe lamp. The results regarding spin-coated samples are reported in Figure 4 and summarized in Table 3. Absorption spectra of spin-coated samples are strikingly similar to the ones of liquid solutions apart from a small red-shift of 10−20 nm, for benzene-based polymers, while thiophene ones are not shifted significantly. A more important diversification appears in the PL emission spectra (Figure 4b), and it is even enhanced in casting-deposited films (data in Table 3). The curves, appreciably broadened but still exhibiting vibronic-like features, show noticeable differences from each other even within the class of benzene-based compounds, depending on DP and the size of decorating chains. This is likely due to the intermolecular interaction and to a certain degree of long-range order in the supramolecular structure induced by the attached chains and the rigid-rod length.[28]

Photodegradation Effects on Photoluminescence Intensity. Solid-state samples also provide a way to test the stability of polymers under continuos light excitation, which is a preliminary key point for applications to light-emitting devices (OLEDs). In this respect, the high reactivity of singlet oxygen with double-bond (PAV) polymers has been extensively studied and well understood, while there are few literature reports concerning reaction with triple bonds,[34] such as in the case of the present polymers. We observed that

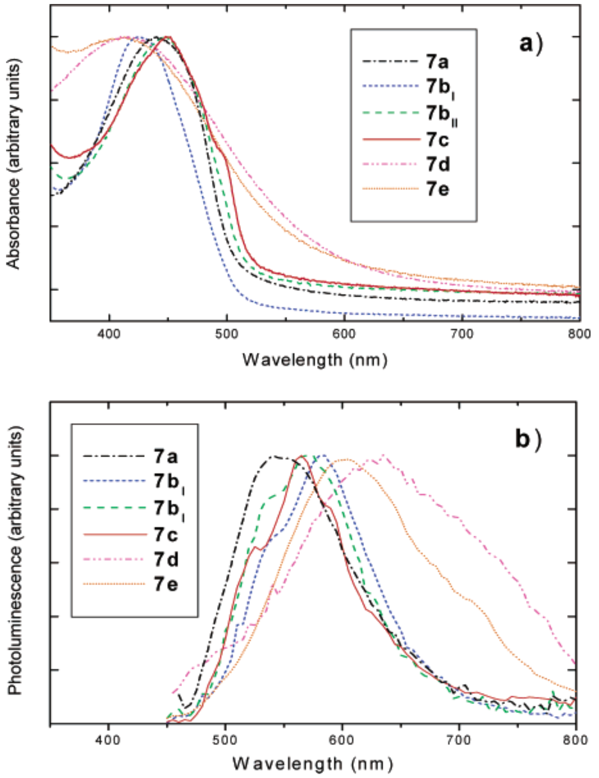


Figure 4. (a) Absorption spectra of solid-state films of the PAEs deposited by spin-coating. (b) Emission spectra of solid-state films of the PAEs deposited by spin-coating. The intensities were arbitrarily chosen in order to optimally fit the graphs.

films of benzene-based compounds **7a**−**c** showed quite a stable photoluminescence signal under a CW laser power density up to 5−10 mW/cm^2 in air while a fast decrease of emission, with a decay time of 600 s approximately, was monitored as the excitation power flux was increased above 30 mW/cm^2 (Figure 5a), resulting in a visible permanent bleaching of the irradiated area. Both these effects were much lower when irradiation was performed in a vacuum (10^{-4} Torr) (Figure 5b). These results, in fact, confirm the hypothesis of PAEs' greater stability toward photooxidation than that of PAV derivatives,[34] even though the range of power density is relatively low. On the other hand, thiophene-based polymers **7d**−**e**, despite the low values of quantum efficiency, did not exhibit any appreciable photooxidation effects.

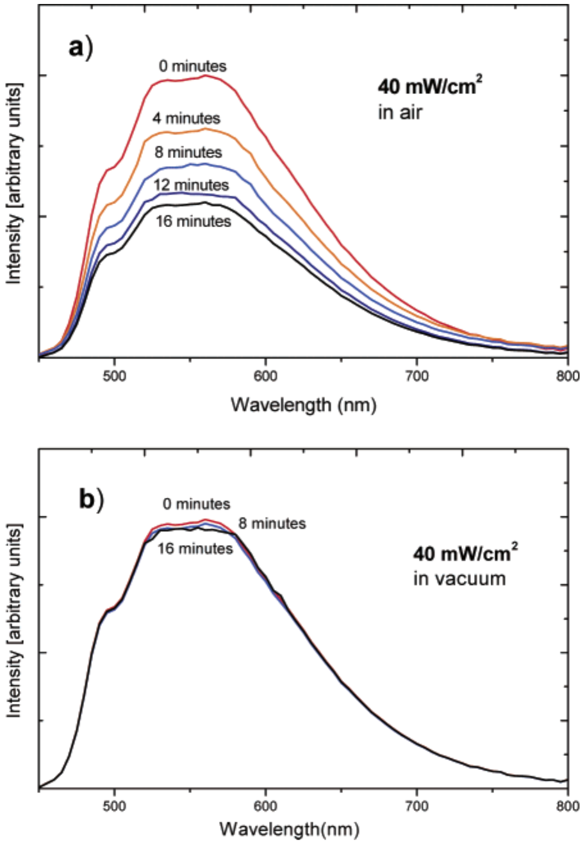


Figure 5. (a) Relative intensity of photoluminescence from a solid-state film of **7b$_I$** during irradiation in air with 40 mW/cm^2 of 457-nm light from an Ar$^+$ laser. (b) The same in a vacuum (10^{-4} Torr).

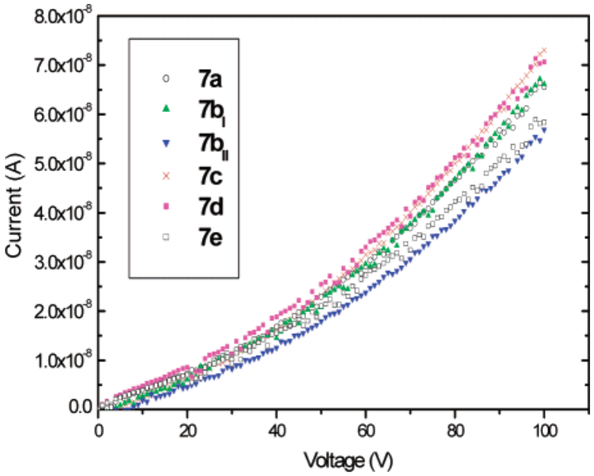


Figure 6. *I*−*V* characteristics at 295 K of the PAE films deposited by casting with aluminum electrodes.

Electrical Conductivity Measurements. Electrical conductivity measurements for each polymer were first carried out at room temperature in solution-cast films deposited onto glass substrates with coplanar gap-separated electrodes (width = 500 μm, length = 1 cm). For measurements at variable temperatures a spray-casting technique with interdigitated coplanar-electrode substrates (width = 60 μm, length = 0.36 cm) was used, to increase the detected current. In the latter case, both aluminum and chromium evaporated electrodes were used. The *I*−*V* curves recorded at room temperature (Figure 6) show a general ohmic behavior, that is, a linear dependence of current on the applied voltage, up to values of the electric field $E = 4 \times 10^4$ V/m, approximately. This allows us to estimate the film conductivity σ to values ranging around 4×10^{-9} S/cm with Al electrodes, in reasonable agreement with results reported in the literature[29] for **7a** prepared with conventional methods. Differently from the fluorescence spectra in the solid state (see Figure 4), the conductivity of films does not exhibit a strong dependence on the degree of polymerization and on the structure of attached chains. This suggests that the presence of possible intermolecular interaction or supramolecular order does not affect the transport behavior, which, on the other hand, is dominated by injection effects (vide infra). For higher fields, a trend to a quadratic dependence appears, which suggests the onset of space-charge limiting effects in the conductive regime. Moreover, Cr electrodes are generally demonstrated to be better charge injectors than Al, allowing values of conductivity up to 3 orders of magnitude higher. Such a large

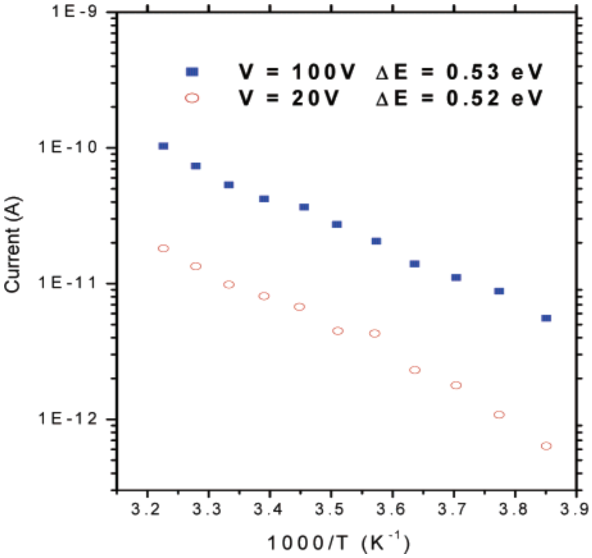


Figure 7. Activation energy for the electrical conductivity of a **7a** film deposited by spray-casting onto a glass substrate interdigitated with aluminum electrodes.

difference suggests that the transport is mainly dominated by injection mechanisms at electrodes rather than by bulk processes in the polymer. Within this model, measurements at variable temperatures indicate that conduction is thermally activated (thermoionic emission) with an energy barrier E_a evaluated in the range 0.3–0.5 eV (Figure 7 for **7a**). Moreover, with respect to the HOMO and LUMO levels reported in the literature for similar polymers,[35] and the Fermi levels of the two metals, these features suggest a hole-transport mechanism for conductivity.

Conclusions

The Pd-promoted Extended One-Pot (EOP) synthetic protocol represents a convenient way to access poly(aryleneethynylene)s (PAEs), a special class of π-conjugated polymers offering unique opportunities as advanced materials for innovative optoelectronic applications. Thanks to the improved performances here presented, by this novel synthetic route, good quality polymeric materials are obtained, whose optoelectronic characteristics are in line with those of similar materials obtained with more demanding conventional procedures. Simplicity and straightforwardness, high yield, safety, and economy are key characteristic of this procedure, whose further exploitation, in parallel with other innovative approaches,[27,36] might lead to a wider use of a very promising class of advanced materials.

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 instrument in the solvent subtraction mode, using a 0.1 mm CsI cell. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC300P spectrometer at 300 and 75 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 ($CDCl_3$). The ^{13}C NMR chemical shifts are calibrated to the ^{13}C triplet of $CDCl_3$ at 77.00 ppm. Molecular weights were determined (relative to polystyrene standard) on a Perkin-Elmer gel permeation chromatograph (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).

All manipulations were carried out with Schlenk type equipment under an atmosphere of argon on a dual manifold/argon–vacuum system. Dioxane was dried over sodium–potassium alloy and argon-saturated prior to use. 1,4-Diiodo-2,5-bis(butoxy)benzene **(1a)**, 1,4-diiodo-2,5-bis(octyloxy)benzene **(1b)**, 1,4-diiodo-2,5-bis(hexadecyloxy)benzene **(1c)**, 2,5-diiodo-3-butylthiophene **(1d)**, and 2,5-diiodo-3-hexadecylthiophene **(1e)** were prepared by using our previously described procedure.[16] Other chemicals were purchased from Aldrich or Strem and used as received unless otherwise specified.

Photophysical Characterization. Visible absorption spectra were carried out by using a Perkin Helmer Lambda 19 spectrophotometer. Photoluminescence spectra were measured on a standard setup for photoluminescence using either a Spectra Physics 2020 argon ion laser or an Oriel xenon lamp as the excitation source. All absorption and emission studies in solutions were performed in deoxygenated $CHCl_3$ at concentrations at absorption between 0.05 and 0.5 (concentrations in the range 0.05–0.5 mg/mL) in a quartz cell with a length of 1 mm. Quantum efficiencies were determined relative to anthracene in a 10-mm quartz cell by means of a Spex-Fluoromax instrument at an absorption of 0.04.

For absorption and fluorescence measurements on film, the polymers were dissolved in $CHCl_3$ at concentrations between 5 and 10 mg/mL and were spin-cast on glass substrates. The polymer films were annealed for 10 min at 100 °C and then slowly cooled to room temperature. The thickness of the films as measured with a profilometer was typically 100 nm.

Electrical characterizations were performed with a 4155B Agilent semiconductor parameter analyzer. Variable-temperature measurements were carried out in an Oxford cryogenic apparatus.

Preparation of the Poly(aryleneethynylene) Homopolymers 7a–e. The procedure for the preparation of poly{ethynyl-[2,5-di(butoxy)]benzene} (**7a**) is representative. To a solution of 0.012 g (0.011 mmol) of $Pd(PPh_3)_4$ and 1.000 g (2.10 mmol) of 1,4-diiodo-2,5-bis(butoxy)benzene in 40 mL of dioxane was added 0.662 g (2.10 mmol) of tributyl(ethynyl)tin. After 20 min of stirring at 110 °C, ^{1}H NMR analysis[16] indicated complete consumption of the tin reagent. After cooling to 0 °C, 1.16 mL (2.31 mmol) of a solution of LDA (2.0 M solution in THF/heptane/ethylbenzene) was added, and the mixture was allowed to warm to room temperature. A sample of the reaction mixture examined by ^{1}H NMR analysis[16b] indicated complete conversion of the alkyne moieties into the corresponding tributyltinalkynyl functionalities. Subsequently, the mixture was refluxed for 2 h and, after cooling, concentrated to a small volume, and treated with methanol. The precipitate thus formed was collected by filtration, washed repeatedly with methanol, and dried under vacuum. 0.568 g (86%) of product was obtained as an orange solid. Evaporation under reduced pressure of the washings afforded a dark oil which was submitted to vacuum distillation (Kugelrohr, 120 °C/10^{-2} mmHg), giving 0.802 g (92%) of tributyltin iodide.

The spectroscopic and analytical features of polymers **7a–e** were in agreement with reported data.[16b]

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References and Notes

(1) *Handbook of Conducting Polymers*; Skotheim, T. J., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998.

(2) (a) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605−1644. (b) Schwab, P. F.; Lewin, M. D.; Michl, J. *Chem. Rev.* **1999**, *99*, 1863−1934. (c) Ellenbogen, J. C.; Love, J. C. *Proc. IEEE* **2000**, *88* (3).

(3) Yamamoto, T. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 621−638 and references therein.

(4) Schluter, A. D. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1533−1556.

(5) (a) Scherf, U. *Top. Curr. Chem.* **1999**, *201*, 163−222. (b) *Synth. Met.* **1997**, *91* (1−3).

(6) (a) Kreyenschmidt, M.; Uckert, F.; Mullen, K. *Macromolecules* **1995**, *28*, 4577−4582. (b) Scherf, U. In *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1996. (c) Tsuda, A.; Osuka, A. *Science* **2001**, *293*, 79−82.

(7) (a) Friend, R. H.; Greenham, N. C. In *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1996. (b) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402−428. (c) A partial relief of the steric hindrance and consequent adverse effect on ring coplanarity may be obtained in PA copolymers made of two regularly alternating different aromatic units, a ring bearing a solubilizing pendant group and an unsubstituted ring, with the latter acting as spacing units.[8]

(8) Ng, S. C.; Xu, J. M.; Chan, S. O. *Macromolecules* **2000**, *33*, 7349−7358.

(9) Levitus, M.; Schmieder, K.; Ricks, H.; Shimizu, K. D.; Bunz, U. H. F.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 4259−4265.

(10) Renack, M. L.; Bartholomew, G. P.; Wang, S.; Ricatto, P. J.; Lachicotte, R. J.; Bazan, G. C. *J. Am. Chem. Soc.* **1999**, *121*, 7787−7786.

(11) Miteva, T.; Palmer, L.; Kloppenburg, L.; Neher, D.; Bunz, U. H. F. *Macromolecules* **2000**, *33*, 652−654.

(12) Bunz, U. H. F.; Enkelmann, V.; Kloppenburg, L.; Jones, D.; Shimizu, K. D.; Claridge, J. B.; zur Loye, H.-C.; Lieser, G. *Chem. Mater.* **1999**, *11*, 1416.

(13) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221−264.

(14) (a) Ridley J. E.; Zerner, M. C. *Theor. Chim. Acta* **1973**, *32*, 111−134. (b) Ridley J. E.; Zerner, M. C. *Theor. Chim. Acta* **1976**, *42*, 223−236.

(15) (a) Kushmerick, J. G.; Holt, D. B.; Pollack, S. K.; Ratner, M. A.; Yang, J. C.; Schull, T. L.; Naciri, J.; Moore, M. H.; Shashidhar, R. *J. Am. Chem. Soc.* **2002**, *124*, 10654−10655. (b) Seminario, J. M.; Derosa, P. A *J. Am. Chem. Soc.* **2001**, *123*, 12418−12419.

(16) (a) Antonelli, E.; Rosi, P.; Lo Sterzo, C.; Viola, E. *J. Organomet. Chem.* **1999**, *578*, 210−222. (b) Giardina, G.; Rosi, P.; Ricci, A.; Lo Sterzo, C. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2603−2621. (c) Altamura, P.; Giardina, G.; Lo Sterzo, C.; Russo, M. V. *Organometallics* **2001**, *20*, 4360−4368.

(17) Farina V.; Krishnamurthy, V.; Scott, W. J. *The Stille Reaction*; John Wiley & Sons: New York, 1998.

(18) (a) Lo Sterzo, C. *Synlett* **1999**, *11*, 1704−1722. (b) Ricci, A.; Lo Sterzo, C. *J. Organomet. Chem.* **2002**, *653*, 177−194.

(19) We found that for this class of polymers GPC measurements are more reliable when THF is used as eluant, than when $CHCl_3$ is used. Our precedent GPC measurement in $CHCl_3$ for samples of polymers **7a**−**c** prepared in THF at 70 °C accounted for quite low DP values. This was sharply contrasting with the NMR data, where no terminal group signals could be detected.[16b]

(20) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467−4470.

(21) Dieck, H. A.; Heck, R. F. *J. Organomet. Chem.* **1975**, 93, 259−263.

(22) Cassar, L. *J. Organomet. Chem.* **1975**, *93*, 253−257.

(23) Recently, Haley[24] has reported an efficient in-situ sequential TMS deprotection−acetylene/aryl iodide coupling procedure in the way to form cyclo oligoacetylenes. To the best of our knowledge, besides formation of short oligomers,[25,26] this procedure has not yet been used to form PAE materials.

(24) (a) Haley, M. M.; Bell, M. L.; English, J. J.; Johnson, C. A.; Weakley, T. J. R. *J. Am. Chem. Soc.* **1997**, *119*, 2956−2957. (b) Pak, J. J.; Weakley, T. J. R.; Haley, M. M. *J. Am. Chem. Soc.* **1999**, *121*, 8182−8192.

(25) Marsella, M. J.; Kim, I. T.; Tham, F. *J. Am. Chem. Soc.* **2000**, *122*, 974−975.

(26) Gallagher, M. E.; Anthony, J. E. *Tetrahedron Lett.* **2001**, *42*, 7533−7536.

(27) Bunz, U. H. F. *Acc. Chem. Res.* **2001**, *34*, 998−1010.

(28) Weder, C.; Wrighton, M. S. *Macromolecules* **1996**, *29*, 5157−5165.

(29) Ni, Q. X.; Swanson, L. S.; Lane, P. A.; Shinar, J.; Ding, Y. W.; Ijadi-Maghsoodi, S.; Barton, T. J. *Synth. Met.* **1992**, *49*−*50*, 447−452.

(30) Davey, A. P.; Elliot, S.; O'Connor, O.; Blau, W. *J. Chem. Soc., Chem. Commun.* **1995**, 1433−1434.

(31) A much higher quantum yield value has been reported for polymer **7b** (0.83).[28] In that case, however, such a high value was obtained after modification of polymer chain terminations with highly emissive phenyl groups. On the contrary, in our cases, the iodine termination may play an opposite role on quantum efficiency.[32]

(32) Moon, J. H.; Swager, T. M. *Macromolecules* **2002**, *35*, 6086−6089.

(33) (a) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537−554. (b) Wautelet, P.; Moroni, M.; Oswald, L.; Le Moigne, J.; Pham, A.; Bigot, J. Y.; Luzzati, S. *Macromolecules* **1996**, *29*, 446−455. (c) Jones, L.; Schumm, J. S.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1388−1410. (d) Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1376−1387. (e) Klaener, G.; Miller, R. D. *Macromolecules* **1998**, *31*, 2007−2009.

(34) Cumpston, B. H.; Jensen, K. F. *J. Appl. Polym. Sci.* **1998**, *69*, 2451−2458.

(35) Montali, A.; Smith, P.; Weder, C. *Synth. Met.* **1998**, *97*, 123−126.

(36) Wilson, J. N.; Waybright, S. N.; McAlpine, K.; Bunz, U. H. F. *Macromolecules* **2002**, *35*, 3799−3800.

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