

Organometallic chemistry directed towards the synthesis of electroactive materials: stereoselective routes to extended polyconjugated systems*

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Abstract: Various synthetic methodologies involving organometallic reagents and leading to conjugated oligomers and polymers are presented. Polyenes and oligomers of poly(*para*-phenylenevinylene) with well-defined length of the conjugated system were prepared by straightforward synthetic procedures based upon organometallic derivatives of silicon or boron. Fluorinated oligo(*para*-phenylenes) containing up to five aromatic rings were easily obtained by homocoupling reaction promoted by copper(I) thiophenecarboxylate. The Stille cross-coupling reaction was applied to the synthesis of poly(*para*-phenylenevinylene) polymers with various substituents on the aromatic rings. Some relevant electro-optical properties of these materials are also discussed.

INTRODUCTION

A novel class of electronic and optoelectronic devices, based upon organic conjugated polymers as active elements, has been recently developed owing to the remarkable semiconductor properties of these new materials. In various categories of photonic and electronic devices, such as diodes [1], light emitting diodes [2], field effect transistors [3], and microcavity lasers [4], the traditional inorganic semiconductors may be replaced by organic conjugated polymers with special advantages related to some features of these devices, i.e. their larger range of emission wavelength and the possibility of fabricating them in various shapes and dimensions.

More recently a great deal of attention has also been devoted to conjugated oligomers with well defined length of the *n*-system. Many optical and electrical features of conjugated polymers may closely correspond to those of oligomers containing only a few repeat units [5]. Moreover, oligomers may serve as well-defined molecular species to establish correlations between structure and properties, acting as a model system to optimize electro-optical properties in the corresponding polymers.

The special interest attached to these classes of conjugated compounds has boosted development of new procedures which permit their synthesis. Now, within the framework of our studies dealing with the application of organometallic reagents to the synthesis of stereodefined conjugated systems [6], we wish to present our recent work concerning the preparation of conjugated polymers and oligomers.

SYNTHESIS OF CONJUGATED OLIGOMERS

Synthesis of conjugated volvenes

Conjugated polyenes represent an interesting class of oligomers acting as a discrete model of

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polyacetylene. Moreover, they are well-known to exhibit nonlinear optical properties [7]. A straightforward stereoselective synthetic route to α,ω -diketopolyenes containing up to eight all-*E* conjugated double bonds was developed [6f] using 1,4-bis(trimethylsilyl)-1,3-butadiene **1** [8], 1,6-bis(trimethylsilyl)-1,3,5-hexatriene **2** [9], and 1,8-bis(trimethylsilyl)-1,3,5,7-octatetraene [6h] **3** as building blocks (Fig. 1).

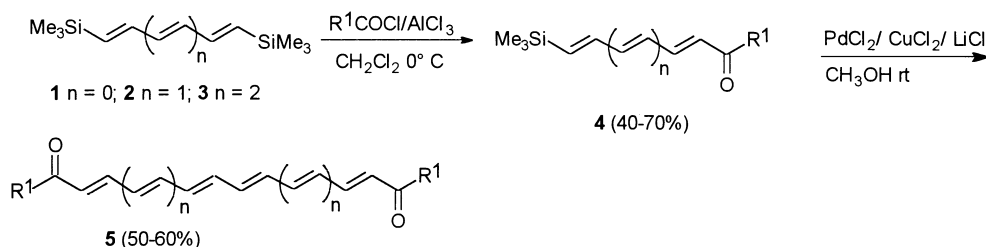
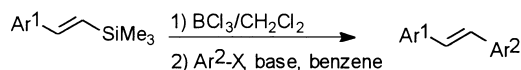


Fig. 1 Synthesis of α,ω -codiketopolyenes.

A chemoselective acylation reaction afforded the silylated ketones **4**. The possibility of doubling the number of conjugated double bonds in one step was offered by a stereoselective homocoupling reaction of polyunsaturated silanes **4**, promoted by the $\text{PdCl}_2/\text{CuCl}_2/\text{LiCl}$ system in methanol. This methodology opens the access to symmetrically substituted polyenes, which are materials with potentially large third-order nonlinear optical coefficient [10].

The versatility of the polyenylsilanes in the construction of longer chains was also shown by our results concerning the use of alkenylsilanes as starting materials into a formal Suzuki–Miyaura cross-coupling reaction. The unsaturated silanes were transformed *in situ* into boron derivatives and these compounds were then coupled with organic halides in the presence of Pd catalysts [6g] (Eqn 1; Scheme 1).



$\text{Ar}^1 = \text{Ph}$, *p*-tolyl; $\text{Ar}^2 = \text{Ph}$, 2-thienyl (50-70%)

The same formal Suzuki–Miyaura cross-coupling process was also performed starting from bis(trimethylsilyl)diene **1** or triene **2** and, due to the chemo selectivity of the silicon-boron substitution, various polyenylsilanes were prepared as shown in Fig. 2 [6h].

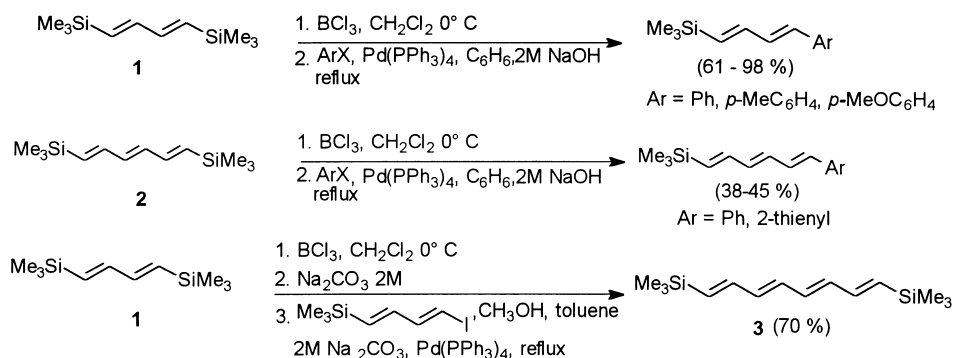


Fig. 2 Synthesis of conjugated polyenes *via* a formal Suzuki–Miyaura cross-coupling reaction.

Synthesis of fluorinated oligo(*para*-phenylenes)

Poly(*para*-phenylenes) (PPP) oligomers and polymers represent a class of conjugated materials with electro-optical properties suitable for light emitting diodes [2]. The introduction of fluorine atoms as substituents on the aromatic rings should increase the HOMO-LUMO energy gap [11], making these

materials potentially appropriate for blue-emitting devices. Moreover, a greater chemical stability is expected by replacing C–H bonds with less reactive C–F bonds.

We developed a simple procedure leading to fluorinated PPP oligomers [6j], by homocoupling reaction of 1,4-diiodo-2,3,5,6-tetrafluorobenzene **6** (Fig. 3).

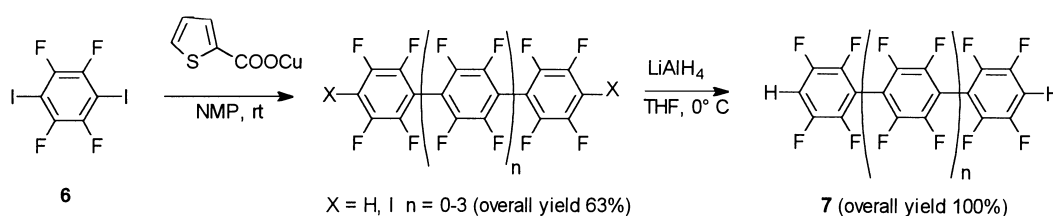


Fig. 3 Synthesis of fluorinated PPP oligomers.

A complex mixture of oligomers containing up to five aromatic rings was obtained. A quantitative dehalogenation reaction with lithium aluminum hydride in THF, led to the four fluorinated PPP with hydrogen atoms as terminal groups **7**, which could be separated by flash chromatography.

The air stable copper(I) thiophene carboxylate [12] was the specific promoter of this homocoupling reaction in N-methylpyrrolidinone as solvent. Other copper(I) salts were ineffective.

Synthesis of oligo(*para*-phenylenevinienes)

An interesting class of polyconjugated compounds is represented by poly(*para*-phenylenevinylene) (PPV) polymers and oligomers, which display semiconductor properties particularly fitted for fabrication of light emitting diodes [2]. Furthermore, amplified stimulated emission under pulsed optical excitation, which is the main factor for obtaining laser action [4,13], has been recently highlighted in thin films of PPV oligomers and polymers.

Some step-growth polycondensation reactions, such as Wittig [14], Wittig–Horner [15], McMurry [15,16], and Knoevenagel [17] reactions have been successfully used for the formation of oligomers, the degree of polymerization being more easily controlled. Transition-metal catalyzed coupling reactions of suitable halogen compounds with olefins (Heck reaction) [18], unsaturated organostannanes (Stille reaction) [6e,19], and organoboranes (Suzuki–Miyaura reaction) [20], have been employed less frequently for both PPV oligomers and polymers.

Our approach to the synthesis of oligomeric PPV structures was based upon the use of unsaturated silyl derivatives and arenediazonium fluoroborates. A useful tool for the coupling of these compounds is represented by a novel cross-coupling reaction starting with alkenyl trimethylsilyl derivatives and arene diazonium salts in the mild conditions used by Genêt and co-workers for the reaction between boronic acids [21] or potassium trifluoroborates [22] with arenediazonium fluoroborates. As in the case of the reaction with aryl or alkenyl halides (Eqn 1 and Fig. 2), the boron derivative necessary in the actual coupling was obtained *in situ* by reaction of silyl derivatives with BCl₃ [23]. Once again, the subsequent cross-coupling reaction involved the use of a vinylosilane (compound **11**) (Fig. 4).

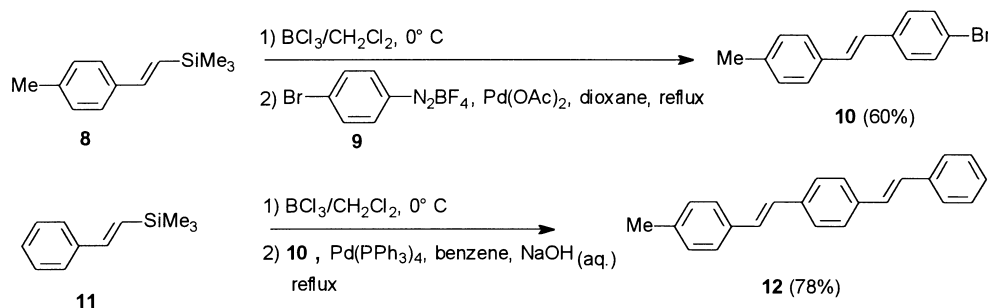


Fig. 4 Synthesis of the conjugated compound **12** via cross-coupling reactions involving alkenyltrimethylsilanes.

Another organometallic approach to the PPV oligomers involved the use of the α -trimethylsilylvinyl benzene derivative **15**, according to the Kikukawa protocol [24], in a Heck type reaction with the arenediazonium fluoroborate **9** (Fig. 5). At variance with the analogous coupling between the P-trimethylsilylvinyl arenes [25] and salts of this type, the reaction was regioselective with respect to the silyl derivative **15**. Furthermore, the process was chemoselective with respect to **9** and stereoselective, affording **16** with all-*E* configuration. The α,α' -bis(trimethylsilyl) derivative **15** was easily obtained by a double cross-coupling reaction of the aromatic Grignard reagent **13** with (bromovinyl)trimethylsilane **14** [23].

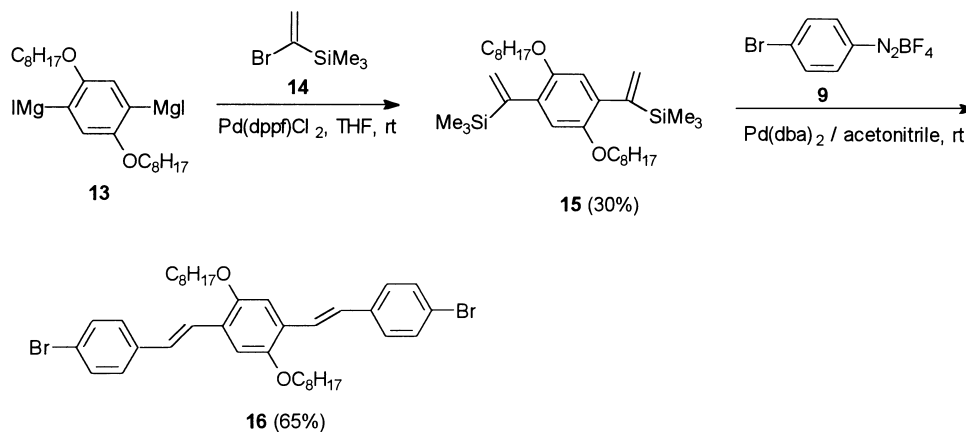


Fig. 5 Synthesis of the PPV oligomer **16**.

A strategy for PPV oligomers synthesis was developed by extending the conjugated system of **16**. The trimethylsilyl derivative **11** (Fig. 6) was converted into boron derivative by applying our BCl_3 procedure. The subsequent cross-coupling reaction with **16** afforded the oligomer **17**. The presence of at least two alkoxy groups is essential to allow solubility in organic solvents [23].

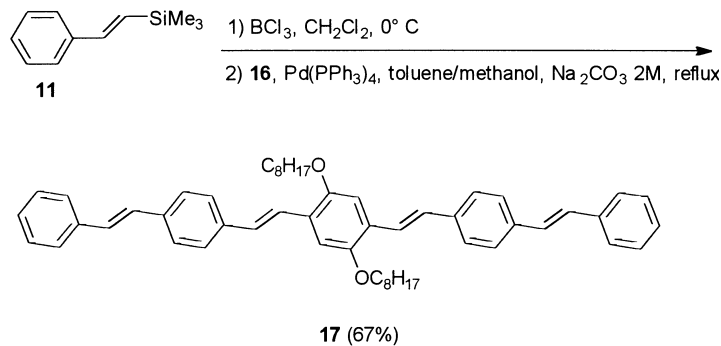
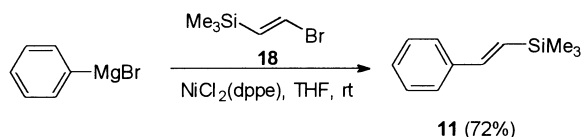


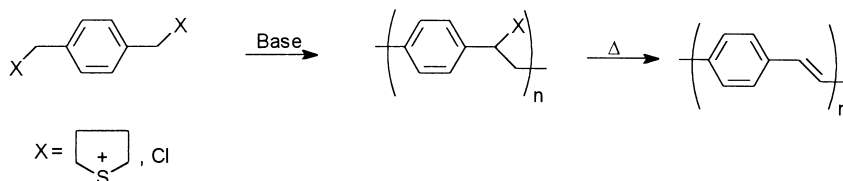
Fig. 6 Synthesis of the PPV oligomer **17**.

The intermediate **11**, necessary for the synthesis of **12** and **17**, was easily prepared by reaction of phenylmagnesium bromide with (bromovinyl)trimethylsilane **18** (Eqn 2; Scheme 2).



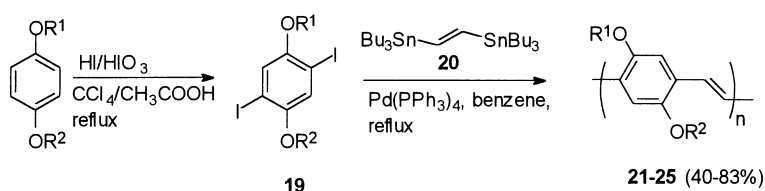
SYNTHESIS OF POLY(PARA-PHENYLENEVINYLENE) POLYMERS

Many synthetic methods for these materials are based upon an elimination reaction from a nonconjugated precursor, prepared by polymerization reaction in which a quinone dimethane active intermediate reacts via a chain-growth process [26] (Eqn 3; Scheme 3).



However, in this procedure a partially conjugated polymer may be obtained with the presence of sp^3 -hybridized carbon atoms due to the incomplete elimination process and to competing side reactions. Among other various synthetic methods proposed for the synthesis of these polymers and for overcoming these drawbacks, palladium-catalyzed cross-coupling reactions with organostannanes [6e,19] or organoboranes [20] have received less attention, although they represent two powerful tools for C–C bond formation.

Our work in this field has been focused on the Stille cross-coupling reaction applied to the synthesis of PPV polymers with various substituents on the aromatic rings [6e,23,27] (Eqn 4; Scheme 4).



The high versatility of this coupling reaction allowed us to prepare a series of materials, including silyloxy substituted PPV **23**, a *para*-crown ether system **24**, and an *ansa*-polymer **25** (Fig. 7), starting from the appropriate dialkyloxy or silyloxy diiodobenzene **19** and 1,2-bis(tributylstannyl)ethene **20** (Eqn 4; Scheme 4).

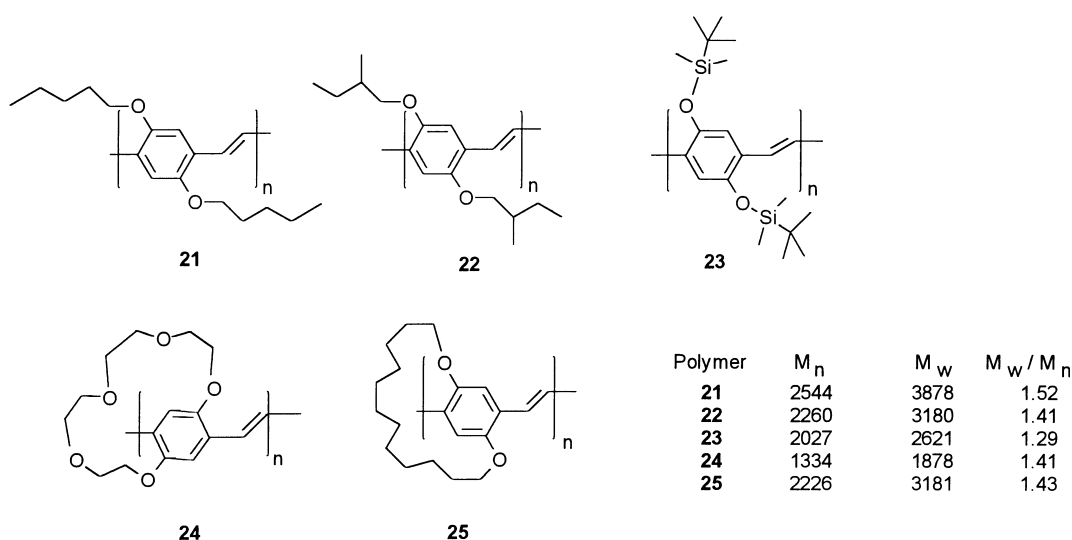


Fig. 7 PPV polymers prepared by Stille cross-coupling reaction.

Taking as a model the PPV derivative **25**, whose higher solubility in most solvents prevents limitation of molecular weight by precipitation of the polymer from the reaction medium, a study of the influence of some combinations of catalyst and solvent on the polymerization reaction was also performed, with reference to literature reports concerning the general conditions in the synthesis of small molecules via the Stille cross-coupling reaction [28]. As a result, the use of a palladium-triphenylarsine complex, generated *in situ* from the weakly coordinated air-stable $\text{Pd}_2(\text{dba})_3$, instead of the air-sensitive $\text{Pd}(\text{PPh}_3)_4$, represented an attractive experimental protocol in consideration of the higher molecular weight obtained ($M_n = 2941$ and $M_w = 4912$).

The substituent groups in the conjugated backbone have a great influence not only on the solubility of the polymers, but also on other physical properties more strictly related to the semiconducting behaviour of these materials [29]. The HOMO-LUMO gap, which is connected with the electro- or photo-emitted radiation wavelength, may be controlled by the electronic and steric effects of substituents. In particular, for silyloxy PPV **23** and *ansa* PPV **25**, the emission spectra show a blue-shift of the absorption wavelength. This result is related to a higher value of the bandgap energy, and may be ascribed to the presence of bulky substituents on the phenyl rings that break the coplanarity of conjugated backbone. In these polymers the photoluminescence emission wavelength is also blue-shifted. All these alkoxy substituted PPVs showed good solubility in organic solvents, and thin films could be obtained by spincoating techniques. Electroluminescence in the yellow region was obtained from a light-emitting diode fabricated with the *ansa* PPV polymer **25** [30]. Moreover, amplified light emission and spectral line narrowing under high pulsed excitation intensity have been also highlighted in solution and thin film for the PPV derivatives **22** and **25** [31].

Stable, highly efficient, and blue-emitting polymers are nowadays a particularly attractive target for research in the field of organic-based devices for multicolor display applications. Blue-shifted emitting polymers were obtained including fluorine atoms [11] or perfluoroalkyl chains [32] as substituent in the conjugate backbone of polymer. Within this framework, we have performed the synthesis of fluoro PPV **27** and perfluoroalkyl PPV **29** polymers, by means of the Stille cross-coupling reaction, starting from the readily available 1,4-diodo-2,3,5,6-tetrafluorobenzene **26**, and from the bis(triflate) **28** (Fig. 8). Both these materials are scarcely soluble in organic solvents. However, thin films with good morphology could be obtained with high vacuum evaporation process and significant blue-shifted values of wavelength in absorption and photoluminescence spectra of these polymers in film, compared with those recorded for alkoxy PPVs, were observed.

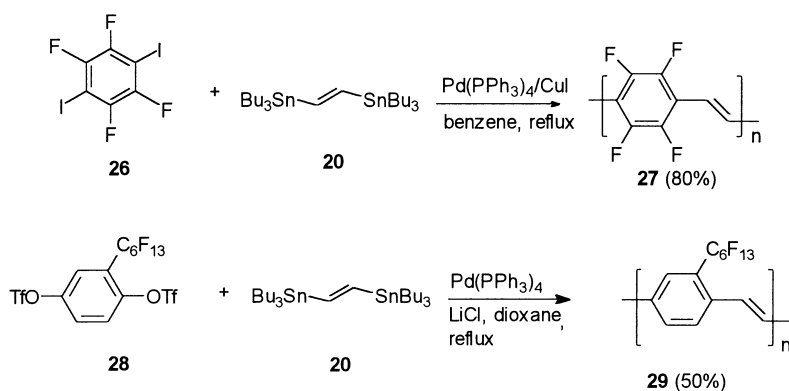


Fig. 8 Synthesis of fluorinated PPV polymers.

Finally, copolymerization of diiodo-dialkoxy-benzene **30** with 1,4-diodo-2,3,5,6-tetrafluorobenzene **26** and 1,2-bis(tributyltin)ethene **20** afforded the more soluble PPV **31** (Fig. 9).

The absorption wavelength of this polymer in thin film is intermediate between the value recorded for the fluoro PPV **27** and dialkoxy PPV **21**, but the photoluminescence wavelength is strongly red-shifted if compared with those typical of alkoxy substituted PPVs.

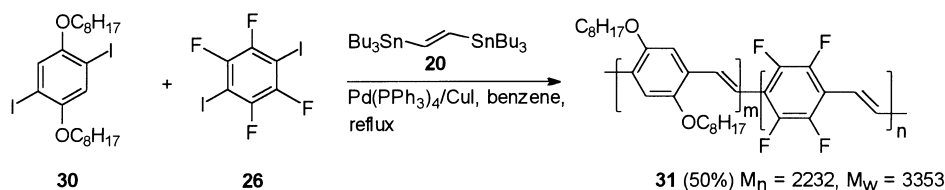


Fig. 9 A PPV copolymer with fluoro and alkoxy substituents.

CONCLUSION

The present work represents a contribution to the development of organometallic synthetic procedures and to their application for the preparation of stereodefined conjugated oligomers and polymers. Silicon, boron, and tin organic reagents offer the possibility of building up an arsenal of new tools for the preparation of conjugated materials, allowing also the introduction of a wide range of substituents in the conjugated systems. A fine control of the electro-optical properties is thus possible, consequently increasing the value of these materials with respect to inorganic semiconductors.

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