Synthesis of Conjugated Polymers by Coupling between Arenediazonium Tetrafluoroborates and Vinyl Silanes

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A new and general methodology for the synthesis of conjugated polymers presenting a variety of structural features is described. The methodology is based upon the palladium-catalyzed coupling reaction of a bis(1-trimethylsilylethenyl)benzene with arenebisdiazonium tetrafluoroborates.

Introduction

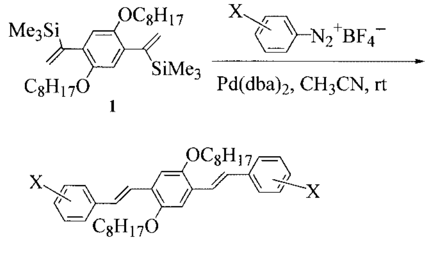
The development of new conducting and semiconducting organic conjugated polymers[1] suitable for replacing the conventional inorganic semiconductors found in various categories of photonic and electronic devices, such as light emitting diodes,[2] field effect transistors,[3] and microcavity lasers,[4] is rapidly growing owing to some distinctive features of these materials. In particular, the possibility of tuning the band gap of these organic semiconductors by modifying their molecular structure and the possibility of fabricating thin films of various shapes and dimensions make this class of polymers potentially competitive with respect to their inorganic counterparts.

The special interest attached to these conjugated compounds has boosted the development of new procedures which permit their synthesis. In this context, organometallic chemistry offers many ways of access to these materials, with the powerful advantage of the control of their stereochemical features, which can strongly affect both electrical and optical properties.

Several polymerization strategies employing organometallic monomers in transition metal catalyzed reactions have been studied. In these[5] and other[6] laboratories aryl and vinyl halides have been cross-coupled with organomagnesium,[5d][6a] organoboron[6b] and organotin[5a–5c,6c] derivatives using Kumada, Suzuki and Stille protocols, respectively.

Unsaturated silicon derivatives have found a more limited use in transition metal mediated cross-coupling reactions with aryl and vinyl halides because of the low polarisation of the silicon-carbon bond.[7] The use of arenediazonium tetrafluoroborates as partners in these coupling reactions with unsaturated silanes can overcome the drawback of this low reactivity. Indeed vinyltrimethylsilanes[8] react easily with arenediazonium tetrafluoroborates, with palladium(0) catalysis, leading to aryldesilylation under mild conditions. In particular, this process is highly stereo- and regioselective in the case of α-trimethylsilylstyrene, affording only the (*E*)-stilbenes.[8d] Furthermore, vinyltriethoxysilane has been employed in polymerisation reactions with arenebisdiazonium salts leading to a series of poly(4,4′-biphenylenevinylene)s.[9]

In recent work[10] dealing with novel methodologies for the synthesis of monodisperse PPV oligomers, we devised a general and useful route to bis(styryl)benzenes bearing either electron-withdrawing or electron-donating groups on the external aromatic rings.[10b] This strategy was based on



X = H, *m*-Br, *p*-Br, *p*-NO$_2$, *p*-OMe, *p*-COOMe

Scheme 1

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the aryldesilylation of 1,4-bis(octyloxy)-2,5-bis(1-trimethylsilylethenyl)benzene (**1**; Scheme 1) with arenediazonium tetrafluoroborates in acetonitrile and in the presence of Pd(dba)$_2$ as catalyst.

We found that the reaction was both regio- and stereoselective, leading only to (*E*,*E*)-bis(styryl)benzenes. Furthermore, this synthetic approach showed many interesting advantages, such as good yields, mild conditions, short reaction times and ease of experimental protocol.

On the basis of these results, we decided to test if the same reaction could be transformed into a tool for the stereoselective synthesis of conjugated polymers.

Results and Discussion

In order to explore the possibility mentioned above, the arenebisdiazonium tetrafluoroborates **2a−e** (Figure 1) were prepared from the corresponding aromatic diamines or arenebisammonium hydrochlorides, according to standard procedures.[11]

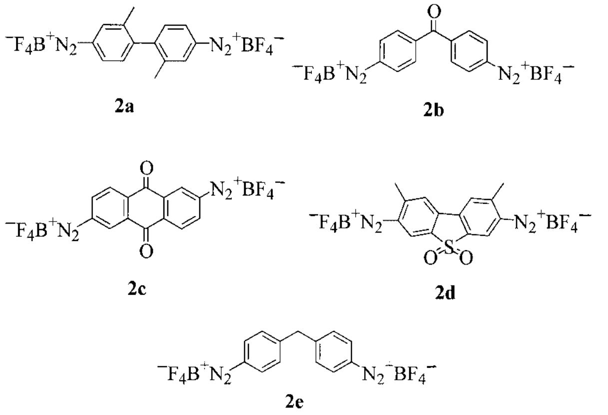
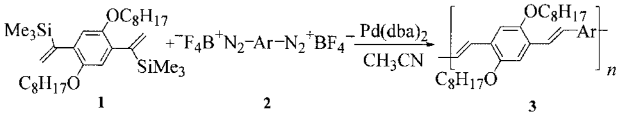


Figure 1. Diazonium tetrafluoroborates **2a−e** used in the polymerisation reaction with **1**

Our work started with a study of the polymerization of **2a** and **1**[10b] in equimolar amounts in the presence of Pd(dba)$_2$ as a catalyst in CH$_3$CN (see Exp. Sect. and Scheme 2).



Scheme 2

After 24 h reaction time, the polymer **3a** (Figure 2) was isolated as described in the Exp. Sect. This first experimental attempt confirmed that the reaction could be very useful as a synthetic route to conjugated polymers.

However, it soon became clear that a problem was faced because of the low yield. Indeed, **3a** was obtained in only a 24% yield. This result was ascribed to the intervention of competing processes, such as solvolysis of the monomer **2a**.[12] Indeed, a substantial amount of unchanged monomer **1** was recovered from the hexane fraction of the Soxhlet extraction. In order to overcome the problem connected with low yields, the experimental conditions were modified by adding a further equimolar amount of **2a** to the reaction mixture 24 hours after the beginning of the polymerization, and then allowing the reaction to reach completion. The yield of the polymer **3a** obtained with this modified protocol (57%) was actually higher than that obtained in the stoichiometric conditions without a substantial alteration of the average molecular masses or the ^{1}H NMR spectrum.

In order to test, to some extent, the scope and limitations of this methodology, we also performed the polymerization of **1** with the tetrafluoroborates **2b−e**, following the same protocol. The yields of the polymers **3b−e** produced (Figure 2) are reported in Table 1 together with their average molecular masses and absorption maxima in the visible region.

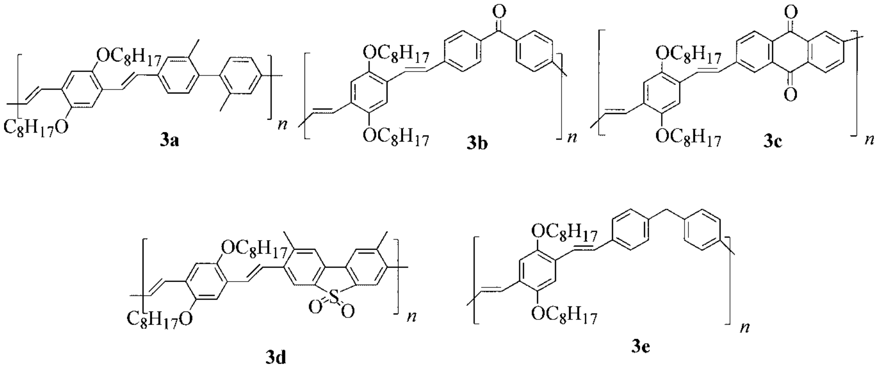


Figure 2. Polymers **3a−e** obtained by reaction of **2a−e** with **1**

Table 1. Yields, molecular masses and absorption maxima of polymers **3a−e**

Polymer	Yield [%]	M_w [a][b]	M_n [a] [c]	M_w/M_n	λ_{max} ($CHCl_3$)[d] [nm]
3a	57	13200	6000	2.2	346, 308
3b	67	8100	5600	1.5	412
3c	57	7800	3900	2.0	307
3d	57	6100	2600	2.3	346, 457
3e	92	12300	4800	2.6	390

[a] Determined by Gel Permeation Chromatography (GPC) with uniform polystyrene standards and THF as solvent. [b] Number average molecular mass. [c] Weight average molecular mass. [d] Absorption maxima in the range 280−600 nm.

A scrutiny of the data reported in Table 1 reveals that this methodology allows access (with yields in the range 57−92%) to various new conjugated materials with interesting structural features. For instance, in the polymers **3b−d** the regular alternation of aromatic systems bearing electron-donating (octyloxy) and electron-withdrawing (carbonyl or sulfonyl) groups may cause a strong electron polarisation in the conjugated system which may lead to enhanced nonlinear optical properties.[13] Furthermore, polymer **3e** may have a special interest in the field of blue-emitting OLEDs.[2] Indeed, the presence of methylene groups in the main chain reduces the conjugation length of the π-system, and a substantial shift of photoluminescence and electroluminescence towards shorter wavelength may be expected.

Conclusion

In summary, the mild experimental conditions and the ready availability of the starting monomers make our synthetic strategy very attractive for the synthesis, in good yields, of a large structural variety of arylenevinylene polymers. In our opinion, this methodology represents a versatile synthetic tool which may lead to new polyconjugated compounds with a wide range of potential applications in the field of semiconducting organic materials.

Experimental Section

General Remarks: ^1H NMR spectra were recorded in $CDCl_3$ at 500 MHz, using the residual $CHCl_3$ resonance as the standard at $\delta = 7.24$ ppm. FTIR spectra were recorded as KBr pellets. Molecular average masses of the polymers were determined using a Plgel 5μ Mixed-D 300 × 7.5 mm column and THF as solvent. Acetonitrile was distilled from 4 Å molecular sieves immediately prior to use. Inert conditions (dry N_2) were maintained throughout all the polymerization reactions. $Pd(dba)_2$ [14] and the monomer **1**[10b] were prepared as reported in the literature. The arenebisdiazonium tetrafluoroborates **2a−e** were prepared from commercial aromatic amines or arylammonium dihydrochlorides, using $NaNO_2$ and HBF_4 (42%), according to reported procedures.[11] If necessary, these monomers were purified by recrystallization from acetone/diethyl ether and could be stored for several weeks at −4 °C.

Typical Polymerization Reaction. Synthesis of the Polymer 3a: Silane **1** (0.300 g, 0.56 mmol), $Pd(dba)_2$ (0.032 g, 0.06 mmol) and arenebisdiazonium tetrafluoroborate **2a** (0.232 g 0.56 mmol) were suspended in dry acetonitrile (9 mL), at room temperature, under a nitrogen atmosphere. After stirring the mixture for 24 h, additional amounts (0.232 g, 0.56 mmol) of **2a** and of $Pd(dba)_2$ (0.016 g, 0.03 mmol) were added. Stirring was continued for 24 h, then the reaction mixture was diluted with water and extracted three times with dichloromethane. The solvent was evaporated at reduced pressure and the crude product extracted in a Soxhlet apparatus, first with hexane and then with methanol, in order to remove low molecular weight fractions and polar impurities, respectively. Finally the polymer **3a** was isolated (0.189 g, 57% yield) by a Soxhlet extraction with $CHCl_3$ and dried under reduced pressure. ^1H NMR (500 MHz, $CDCl_3$ at 45 °C): $\delta = 0.7{-}1.0$ (br. m, 6 H), 1.1−2.5 (m, 30 H), 3.8−4.3 (m, 4 H), 6.6−7.7 (m, 12 H) ppm. FTIR (KBr): $\tilde{\nu} = 2926, 2856, 1669, 1608, 1495, 1202\ cm^{-1}$.

Polymers **3b−e** were prepared by the same procedure.

Polymer 3b: (0.214 g, 67% yield). ^1H NMR (500 MHz, $CDCl_3$ at 45 °C): $\delta = 0.8{-}1.0$ (br. m, 6 H), 1.1−1.9 (m, 24 H), 3.9−4.2 (m, 4 H), 7.0−7.9 (m, 14 H) ppm. FTIR (KBr): $\tilde{\nu} = 2926, 2855, 1652, 1599, 1278, 969\ cm^{-1}$.

Polymer 3c: (0.190 g, 57% yield). ^1H NMR (500 MHz, $CDCl_3$ at 45 °C): $\delta = 0.9{-}2.4$ (m, 30 H), 3.5−4.3 (m, 4 H), 6.5−8.3 (m, 12 H) ppm. FTIR (KBr): $\tilde{\nu} = 2924, 2853, 1673, 1586, 1297\ cm^{-1}$.

Polymer 3d: (0.202 g, 57% yield). ^1H NMR (500 MHz, $CDCl_3$ at 45 °C): $\delta = 0.8{-}1.0$ (br. m, 6 H), 1.1−2.8 (m, 30 H), 3.9−4.6 (m, 4 H), 7.0−8.2 (m, 10 H). FTIR (KBr): $\tilde{\nu} = 2926, 2855, 1603, 1495, 1304, 1262, 1160, 1128, 1085, 1030\ cm^{-1}$.

Polymer 3e: (0.286 g, 92% yield). ^1H NMR (500 MHz, $CDCl_3$ at 45 °C): $\delta = 0.7{-}0.9$ (br. m, 6 H), 1.0−2.2 (m, 24 H), 3.5−4.1 (m, 6 H), 6.6−7.5 (m, 14 H) ppm. FTIR (KBr): $\tilde{\nu} = 2923, 2853, 1667, 1602, 1511, 1202, 1019\ cm^{-1}$.

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

[2] [2a] A. Kraft, A. C. Grimsdale, A. B. Holmes, *Angew. Chem. Int. Ed.* **1998**, *37*, 402−428. [2b] U. Mitschke, P. Bäuerle, *J. Mater. Chem.* **2000**, *10*, 1471−1507.

[3] [3a] F. Garnier, R. Hajlaoui, A. Yassar, P. Srivastava, *Science* **1994**, *265*, 1864−1866. [3b] A. R. Brown, A. Pomp, C. M. Hart, D. M. de Leeuw, *Science* **1995**, *270*, 972−974.

[4] F. Hide, M. A. Diaz-Garcia, B. J. Schwartz, A. J. Heeger, *Acc. Chem. Res.* **1997**, *30*, 430−436.

[5] [5a] F. Babudri, S. R. Cicco, G. M. Farinola, F. Naso, A. Bolognesi, W. Porzio, *Macromol. Rapid Commun.* **1996**, *17*, 905−911. [5b] F. Babudri, S. R. Cicco, L. Chiavarone, G. M. Farinola, L. C. Lopez, F. Naso, G. Scamarcio, *J. Mater. Chem.* **2000**, *10*, 1573−1579. [5c] F. Babudri, A. Cardone, L. Chiavarone, G. Cic-

carella, G. M. Farinola, F. Naso, G. Scamarcio, *Chem. Commun.* **2001**, 1940−1941. [5d] F. Babudri, D. Colangiuli, G. M. Farinola, F. Naso, *Eur. J. Org. Chem.* **2002**, 2785−2791.

[6] [6a] T. Yamamoto, Y. Hayashi, A. Yamamoto, *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2091−2097; M. Rehahn, A.-D. Schlüter, G. Wegner, W. J. Feast, *Polymer* **1989**, *30*, 1054−1059. [6b] M. B. Goldfinger, T. M. Swager, *J. Am. Chem. Soc.* **1994**, *116*, 7895−7896; C. Kowitz, G. Wegner, *Tetrahedron* **1997**, *53*, 15553−15574; F. Koch, W. Heitz, *Macromol. Chem. Phys.* **1997**, *198*, 1531−1544. [6c] R. Galarini, A. Musco, R. Pontellini, A. Bolognesi, S. Destri, M. Catellani, M. Mascherpa, G. Zhuo, *J. Chem. Soc., Chem. Commun.* **1991**, 364−365; Z. Bao, W. K. Chan, L. Yu, *J. Am. Chem. Soc.* **1995**, *117*, 12426−12435.

[7] T. Hiyama, *Organosilicon Compounds in Cross-coupling Reactions*, in *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: F. Diederich, P. J. Stang), Wiley-VCH, Weinheim, 1988 pp. 421−453.

[8] [8a] K. Kikukawa, K. Ikenaga, F. Wada, T. Matsuda, *Chem. Lett.* **1983**, 1337−1340. [8b] K. Kikukawa, K. Ikenaga, K. Kono, K. Toritani, F. Wada, T. Matsuda, *J. Organomet. Chem.* **1984**, *270*, 277−282. [8c] K. Ikenaga, K. Kikukawa, T. Matsuda, *J. Chem. Soc., Perkin Trans. 1* **1986**, 1959−1964. [8d] K. Ikenaga, S. Matsumoto, K. Kikukawa, T. Matsuda, *Chem. Lett.* **1988**, 873−876.

[9] S. Sengupta, S. K. Sadhukhan, *J. Chem. Soc., Perkin Trans. 1* **1999**, 2235−2236.

[10] [10a] F. Babudri, G. M. Farinola, F. Naso, D. Panessa, *J. Org. Chem.* **2000**, *65*, 1554−1557. [10b] F. Babudri, G. M. Farinola, L. C. Lopez, M. G. Martinelli, F. Naso, *J. Org. Chem.* **2001**, *66*, 3878−3885.

[11] A. Roe, *Org. React.* **1949**, *5*, 193−227.

[12] K. Kikukawa, T. Totoki, F. Wada, T. Matsuda, *J. Organomet. Chem.* **1984**, *270*, 283−287.

[13] G. M. Farinola, T. Cassano, R. Tommasi, F. Babudri, A. Cardone, F. Naso, *Proc. SPIE* **2001**, *4461*, 296−303.

[14] Y. Takahashi, T. Ito, S. Sakai, Y. Ishii, *J. Chem. Soc. D.* **1970**, 1065−1066.

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