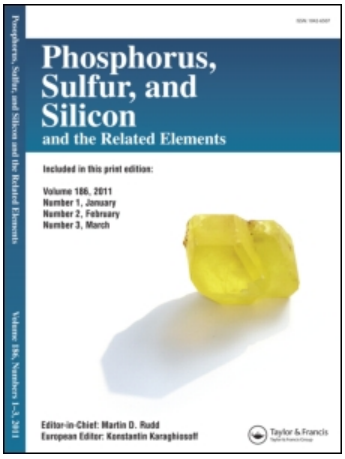

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REACTIVITY OF SILYL MONOMERS FOR THE OXIDATIVE POLYMERIZATION OF PHENYLENE UNITS

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REACTIVITY OF SILYL MONOMERS FOR THE OXIDATIVE POLYMERIZATION OF PHENYLENE UNITS

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Oxidative coupling of silyl monomers containing phenylene units was performed electrochemically and chemically using $FeCl_3$ as oxidant. 2,5-Trimethylsilyl-1,4-dihexoxybenzene led to poly (2,5-dihexoxyparaphenylene) with a degree of polymerization higher than the one obtained upon oxdative coupling of non silyl monomers. The coupling reaction was however moderately improved in the case of 3,6-bis-dimethylsilyl(N-n-butylcarbazole). The role of the silyl substituents during the oxidative polymerization is dicussed.

Keywords: N-n-butylcarbazole; 1,4-dihexoxybenzene; oxidative coupling; activation; trimethylsilyl

INTRODUCTION

Over the last few years, a great deal of attention has been devoted to conjugated polymers owing to their potential applications in electronics, opto-electronics and as non-linear optical materials. Synthetic efforts have been made to improve the conjugation properties and also to prepare new conjugated polymers containing original chain units, from a variety of unsaturated monomers.[1] Silicon-directed reactions, widely used in organic synthesis to improve the selectivity of carbon-carbon bond formation,[2] have also been used in some cases for selective polymerization reactions.[3–6] Improved synthetic routes to polymeric materials are of par-

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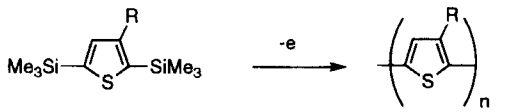
ticular interest in the case of conjugated organic polymers, since the properties of the latter are strongly related to the structural properties of the conjugated chain. The use of silylated monomers for the preparation of polythiophene[4–6] was shown to lead to highly conjugated polymeric materials.[5] On the basis of Raman and photoluminescence criteria, the silyl substituents were shown to activate the 2,5 position of the thiophene ring, the selective α-α′ coupling of thiophene units leading to highly conjugated polymers with improved conjugation properties.[5a] The observed activation also allows for the preparation of high molecular weight of poly-(3-alkyl)thiophene with a low polydispersity[5c] (Eq. 1). The role of silyl substituents, during the oxidative polymerization, was interpreted in terms of an increased stabilisation of an intermediate β-silyl cationic species.[5]



(Eq 1)

The silicon based synthetic methodology seems promising in the field of conjugated polymers. Its extension to the synthesis of other unsaturated polymers may lead to various upgraded conjugated polymeric structures. The polymerization of silylthiophene units was also obtained in the solid state in the case of thienylene bridged silsesquioxane. Its oxidative polymerization gives an organic-inorganic composite consisting in polythiophene chains and in a silicate interpenetrating network.[5b] We were interested in investigating the use of silylated monomers in the polymerization of various unsaturated monomers. A related oxidative polymerizartion was reported in the case of tetraphenylsilane which polymerized to poly(para)phenylene.[7] However, the role of the central silicon atom was not clearly established.

Our interest in exploring the possible activation of phenylene monomers led us to study the oxidative coupling of disilylcarbazole and disilylbenzene derivatives (figure 1) under electrochemical and chemical reaction conditions. We chose these two monomers, because the coupling of related non-silyl monomers only led to dimer or oligomer formation[8,9], and it should allow to probe the effect of silyl substitution in the oxidative polymerization.

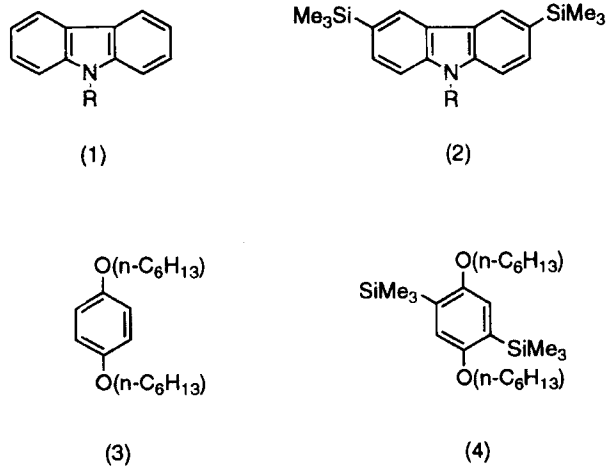
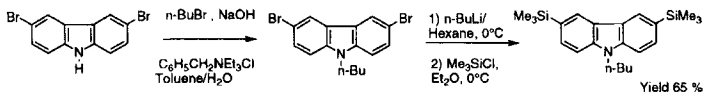


FIGURE 1 Monomers 1–4 used for oxidative coupling

RESULTS AND DISCUSSION

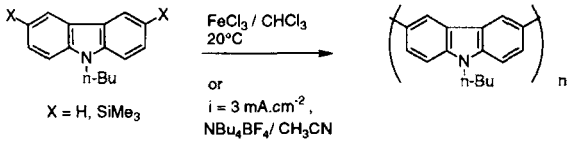
1 – Oxidative coupling of 3,6-disilyl-carbazole (2)

We synthesized derivatives of N-n-butylcarbazole, since the N-alkyl chain was shown to greatly improve the solubility of the poly[3,6-carbazole].[10] The preparation of silyl derivatives was achieved from 3,6-dibromo-carbazole in two steps (Eq. 2). Alkylation at nitrogen was first carried out in the presence of TEBACP as a phase transfer catalyst, then metallation by n-BuLi and treatment with Me_3SiCl gave a good yield of 3,6-bis(trimethylsilyl)-N-n-butylcarbazole.



(Eq. 2)

The oxidative polymerization was then performed using chemical and electrochemical reaction conditions. For comparison, the oxidative polymerization of the non-silylated monomer (N-n-butylcarbazole) was also achieved under identical reaction conditions (Eq. 3).



(Eq. 3)

The cyclic voltamagram of N-n-butylcarbazole and its silyl derivative showed an oxidation peak at 1.0 V (vs Ag-Ag^+ / 10^{-2} mol^{-1}) which can be assigned to the monomer oxidation.[11] The electropolymerization reaction was carried out on a preparative scale under identical galvanostatic conditions for the two monomers (3mA cm^{-2}). The oxidation products were isolated from the electrolytic solution as described (experimental section).

The chemical oxidation was perfomed upon treatment of the monomer with carefully purified $FeCl_3$ at 20°C using $CHCl_3$ as solvent. The analysis and the IR and NMR spectra of the oxidation products are consistent with oligomer formation via 3,6 coupling of the carbazole units. The coupling products were analysed by gel permeation chromatography. The GPC traces revealed 2 to 4 peaks which can be assigned to mixtures containing mainly monomeric to tetrameric compounds. The molecular weight was determined by using a GPC column calibrated with polystyrene standards. The results are shown in Table I. The GPC assignments are supported by the isolation and characterization of pure dimer which mainly formed upon oxidation of non-silyl N-n-butylcarbazole.

TABLE I Oxidative coupling of N-n-Butylcarbazole derivatives

Electrochemical oxidation from monomer	*DPn*[(a)]	%
1	1	40
	2(b)	60
2	1	11
	2	24
	3	54
	4	11
Chemical oxidation from monomer	*DPn*	%
1	1	71
	2	29
2	1	33
	2	20
	3	47

(a) determined by GPC using polystyrene standards.
(b) pure dimer was isolated and characterized from this experiment.

As shown in Table I, the carbazole derivatives exhibited quite low reactivity in oxidative coupling. Only dimer formation with a low conversion was observed upon oxidative coupling of non-silyl N-n-butylcarbazole. This behaviour is probably associated with the high stability of the 9,9′-dialkyl-3,3′-dicarbazyl radical cation.[12] The use of a silyl monomer in the coupling reaction only moderately improved the coupling step; it led to major formation of the trimer together with a few higher oligomers. However, in agreement with observations made with silythiophene derivatives, activation by silicon occurs to some extent. The low reactivity of carbazole radical cation does not allow polymer formation. The polymerization of carbazole units is best achieved using organometallic coupling reactions.[10,13]

2 – Oxidative coupling of 1,4-dihexoxybenzene derivatives (3,4)

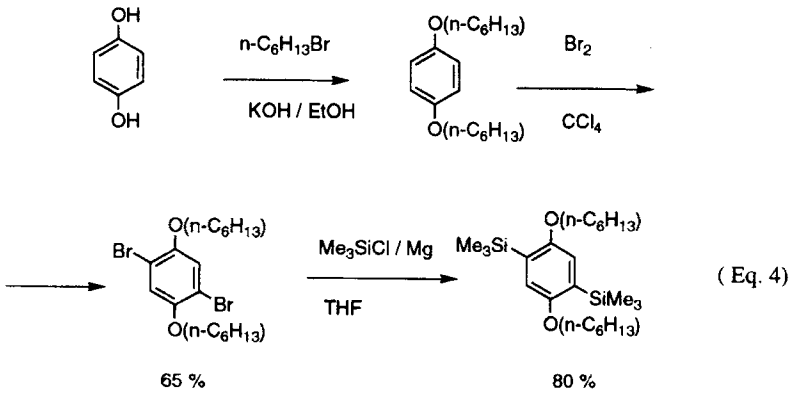
The very low solubility of poly(para)phenylene obtained by dehydro-coupling of aromatic nuclei[14] precluded direct determination of molecular weight. Friedel-Crafts alkylation yielded soluble derivatives but molecular weight determination by vapor-phase osmometry indicated a moderate degree of polymerization.[15] Related observations were made upon electropolymerization of electon-rich dialkoxybenzene monomers. Whereas dimethoxy derivatives proved to be of low solubility,[16] the anodic oxidation of 1-methoxy-4-alkoxybenzene gave polymers soluble in usual organic solvents.[9]

We prepared silyl derivatives of 1,4-dihexoxybenzene according to eq. 4 from hydroquinone using successive alkylation, bromination and silylation reactions.

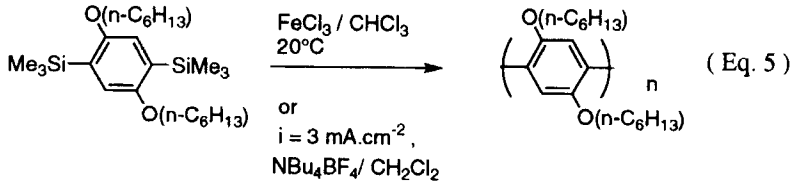
The bis-silyl derivative was then polymerized under chemical and anodic oxidation. The obtained polymers were compared to those arising from oxidative polymerization of non-silylated monomer (eq. 5).

The chemical oxidation was performed at 20°C using purified $FeCl_3$ in $CHCl_3$. The resulting polymers were washed with methanol until complete elimination of iron, and purified by precipitation from their solutions in THF. Polymer yields in the range 65–70 % were obtained.

The anodic oxidation was performed using CH_2Cl_2 as solvent, under galvanostatic conditions (current density of 3 mA cm^{-2}). The soluble polymer which formed was isolated after extraction of the electrolytic solution.



(Eq. 4)



(Eq. 5)

Elemental and EDAX analysis of the polymeric material showed low silicon content (0,5 – 0,05 %) as expected for a desilylative coupling of the monomers. The various polymer samples were also characterised by ^{13}C NMR. The C^{13} NMR spectra exhibited a set of resonance lines which are quite similar in the monomer and in the polymer. This is consistent with extensive 2–5 coupling of the monomeric units (cf. Table II exp. section). The IR spectra are consistent with the polymer structure in eq. 4. It is worth noting that no $\nu_{C\text{-}H}$ vibration appeared in the 3000–3100 cm^{-1} IR region in agreement with the centrosymetric structure of the chain unit.

Electronic absorption spectra were registered for the monomers and for the polymers produced by chemical and anodic oxidation. The λ max values are reported in Table III. The spectra of the monomers showed maxima associated to π-π^* transitions. A bathochromic shift is observed in the case of the bis-silylated monomers. The absorption spectra of the polymers exhibited two maxima ca. 330 nm and 260 nm and are quite similar whatever starting monomer is used and whatever the polymerization method. In particular, no significant difference appeared upon using

silylated monomers. This suggests that there is no increase of the mean length of the conjugated segments. Owing to the dominant steric interactions arising from the presence of alkoxy substituents, the mean conjugation length is quite similar in all cases. Polyparaphenylenes bearing alkyl side-chains have been shown to be poorly conjugated[17]. The UV-Visible spectra of polyparaphenylene derivatives give insights into the average length of conjugation, which is not directly related to the molecular weight.[9,17] In poly(dialkoxyphenylene), bulky substituents at the phenyl ring will lead to torsion around the C-C bond between the phenylene units and can reduce the effective conjugation length. For these compounds the effective conjugation length is shorter than the chain length and independent of the molecular weight.

TABLE II ^{13}C NMR data of dihexoxy monomers (3, 4) and polymers, δppm, $CDCl_3$ solution

Monomer	*Polymer from*	C_1	C_2	C_3	*C(OR)*
3		153.2	115.4	-----	68.6, 31.7, 29.4, 25.8, 22.6, 14.1
4		157.51	116.36	129.75	68.0, 31.8, 29.2, 26.2, 22.3, 14.1
	3	150.41	117.36	127.92	69.9, 32.0, 29.9, 26.1, 23.0, 14.4
	4	150.42	117.39	127.90	69.9, 32.0, 29.9, 26.1, 23.0, 14.4

TABLE III U-V- Visible absorption maximum of dihexoxybenzene monomers and polymers (solvent CH_2Cl_2)

Monomer	*Polymer from*	*λmax (nm)*		
3		238		291
	3[a]	239	262[c]	330
	3[b]	240	269[c]	336
4		238		308
	4[a]	236	265[c]	331
	4[b]	234	263[c]	333

a: produced upon anodic oxidation.
b: produced upon chemical oxidation.
c: shoulder.

Whereas the polymer obtained from silyl and non-silyl monomers exhibited similar analytical and spectroscopic characteristics, differences appeared in the molecular weight distribution. The values determined by gel permeation chromatography using polystyrene standards are presented in Table IV. The polymers which arise from the oxidative coupling of bis-silylated monomers have higher average molecular weight and lower polydispersity (Mw/Mn) values. Although it corresponds to a moderate degree of polymerization (Dp), it is significantly higher than the highest value Dp =10–11 previously reported.[9]

TABLE IV Molecular weight distribution of polymers obtained from monomers (3) and (4) upon anodic oxidation (E) or chemical oxidation (C)

Monomer	*Oxidative coupling*	*Mn*	*Mw/Mn*	*Dpn*
3	E	3321	1.5	12
4	E	5905	1.4	21
3	C	4817	2.3	17
4	C	6242	1.7	25

CONCLUSION

Our results show that the oxidative coupling of N-n-butylcarbazole and that of 1,4-dihexoxybenzene is slightly improved by the presence of two trimethysilyl substituents at the phenyl ring. This is consistent with our previous observation made in the case of the oxidative polymerization of silyl substituted thiophene. In the present case, however, a moderate activation was observed. The coupling of carbazole units only led to trimer and tetramer instead of the dimerisation which was observed in the absence of silyl substituent. The preparation of higher oligomers has been reported recently, by use of nickel catalyzed coupling reactions.[10] The reaction of bis-trimethylsilyl dialkoxybenzene also results in an activation of the oxidative coupling of the phenylene units. Soluble polymers containing 20 to 25 consecutive phenylene units have been obtained. The trimethylsilyl group plays a significant role, although the value of the degree of polymerization appeared much lower than in the thiophene case. It is probably related to the much lower reactivity of the phenylene radical cat-

ion. Similarly to silyl thiophene polymerization,[5] the coupling reaction involves radical cation dimerisation or a monomer / radical cation reaction.[18] In both cases, the presence of trimethylsilyl substituents provided some stabilisation of the electron-deficient cationic coupled intermediate.[5c]

Despite the fact that some activation was observed in the oxidative coupling, leading to material with higher average molecular weight, it does not appear to yield polymer with higher mean conjugated length. This may be related, as noted for poly(disubstitued benzene)[17] to important steric interactions owing to the larger number of alkyl substituents along the polymer chain.

EXPERIMENTAL SECTION

General remarks

All reactions were carried out under nitrogen by use of a vacuum line and Schlenk tube techniques. Solvents were dried and distilled before use. The reported yields refer to pure isolated compounds. Melting points were determined with a Gallenkamp apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrophotometer. ^{1}H NMR spectra were recorded on a BRUKER AW-80 spectrometer, ^{13}C and ^{29}SiNMR spectra on a BRUKER WP 250 SY and FT AM 300 apparatus. Solvents and chemical shifts (δ relative to Me_4Si) are indicated. Elemental analysis were carried out by the "Service Central de Microanalyse du CNRS". Energy Dispersive X-Ray Spectroscopy measurements were carried out using a CAMBRIDGE 515 SEM with a PV 9800 EDAX attachment. The data were acquired by a standard analytical procedure and corrected for ZAF. We checked that the Si/S ratio measured according to this technique were in agreement with those obtained upon elemental analysis of the same sample.

N-n-Butylcarbazole (1)

Carbazole (2 g, 0.015 mole), BuBr (4 ml, 0.015 mole) and triethylbenzyl-ammoniumchloride TEBACl (0.4 g, 1.75×10^{-3} mole) were mixed in

6 ml of toluene and the mixture was stirred and heated at 100°C in the presence of aqueous NaOH for 3 hours. The organic layer was then separated and washed with water up to pH = 7 and dried over $MgSO_4$. After elimination of solvent, the product was isolated upon crystallisation from MeOH. (Yield 80 %). M.p.: 57°C. ^1H NMR ($CDCl_3$, δ, ppm): 8.05 (d, 2H): 7.35 (m, 4H); 7.15 (m, 2H); 4.2 (t, 2H); 1.8 (m, 2H); 1.35 (m, 2H); 0.85 (t, 3H). ^{13}C NMR ($CDCl_3$, δ, ppm): 141.8, 127.2, 124.7, 122.2, 120.4, 110.1, 41.2, 31.2, 20.4, 13.8. Analysis calcd. for $C_{14}H_{12}N$: C, 86.59 %; H, 6.18 %. N, 7.21 %. found: C, 86.63 %; H, 6.15 %; N, 7.18 %.

3,6-dibromo-(N-n-butyl)carbazole

As above, 3,6-dibromocarbazole (1g, 0.003 mole), BuBr (2ml, 0.003 mole) and TEBACl (0.17 g, 7×10^{-4} mole) in 20 ml of toluene were stirred with aq. NaOH (10^{-2}M) for 2 hours at 100°C. After washing and drying over $MgSO_4$, the organic layer was collected and the solvent was evaporated. The crude product was crystallized from methanol and then recrystallized in hexane (yield 75 %). M.p.: 74–75°C. ^1H NMR ($CDCl_3$, δ, ppm): 7.98 (d, 2H); 7.46 (m, 2H); 7.15 (m, 2H); 4.25 (t, 2H); 1.75 (m, 2H); 1.35 (m, 2H): 0.85 (t, 3H). ^{13}C NMR ($CDCl_3$, δ, ppm): 140.9, 112.8, 125.0, 129.2, 125.2, 110.2, 42.3, 32.0, 20.3, 14.2. Analysis calcd. for $C_{14}H_{10}NBr_2$: C, 47,72 %; H, 2.84 %; N, 3.97: Br, 45.45. found: C, 47.8 %, H, 2.82 %; N, 3.92 %, Br, 45.41 %.

3,6-bis(trimethylsilyl)(N-n-butyl)carbazole (2)

To a solution of 3,6-dibromocarbazole (1 g, 2.6×10^{-3} mole) in 10 ml of ether was added slowly at –40°C a hexane solution of n-BuLi (2.08 ml, 5.2×10^{-3} mole). The mixture was then warmed to room temperature and stirred for 3 hours. It was then cooled again to –40°C and a solution of $ClSiMe_3$ (0.72 ml, 5.7×10^{-3} mole) in 10 ml of ether was added and stirred for 3 hours. The reaction mixture was treated with 10 % aqueous HCl, extracted with ether. The organic layer was washed with water, dried over $MgSO_4$. The solvent was distilled and the residue was crystallized in hexane (yield 70 %). M.p.: 93°C. ^1H NMR ($CDCl_3$, δ, ppm): 8.15 (s, 2H); 7.45 (d, 2H); 7.25 (d, 2H); 4.15 (t, 3H); 1.75 (m, 2H): 1.37 (m, 2H); 0.82 (t, 3H); 0.25 (s, 18H). Analysis calcd. for $C_{20}H_{28}NSi_2$: C, 71 %; H, 8.28 %; N, 4.14 %; found: C, 69.88 %; H, 8.31 % N, 4.12 %.

1,4-dihexoxybenzene (3)[19]

To a solution containing KOH (5.09 g, 0.091 mole) in 50 ml of ethanol was added slowly a hydroquinone (10 g, 0.091 mole) solution in 75 ml of ethanol. The mixture was stirred at 20°C for 60 min., then a solution containing 1-bromohexane (30 g, 0.182 mole) in 20 ml of ethanol was introduced slowly. The reaction mixture was refluxed for 24 hours. The crude mixture was washed with H_2O and extracted with CH_2Cl_2. Unreacted hydroquinone was removed upon washing with aqueous K_2CO_3. The organic layer was dried over magnesium sulfate and filtered. The product was crystallized from methanol. (Yield 60 %). M.p. 43–45°C. ^1H NMR ($CDCl_3$, δ, ppm): 6.83 (4H, s); 3,91 4H, t): 1.73 (4H, m); 1.34 (12H, m); 0.92 (6H, t). ^{13}C NMR ($CDCl_3$, δ, ppm): 153.23; 115.40; 68.66; 31.66; 29.41; 22.65; 14.06. Analysis calcd. for $C_{18}H_{30}O_2$: C, 77.69 %; H, 10.79 %. Found: C, 77.89 %; H, 10.81 %.

1,4-dibromo-2,5-dihexoxybenzene

To a solution of 1,5-dihexoxybenzene (4.36 g, 0.0157 mole) in 50 ml of CCl_4 was added slowly at 20°C a solution of Br_2 (1.89 g, 0.037 mol) in 25 ml of CCl_4. The mixture was stirred at room temperature for 20 hours. Then, it was washed with 20 % aqueous solution of KOH until disappearance of the red color, then with H_2O and the organic layer was dried over $MgSO_4$. After distillation of the solvent, the product was isolated upon crystallisation from EtOH. (Yield 65 %). M.p.: 63–64°C. ^1H NMR ($CDCl_3$, δ, ppm): 7.07 (2H, s); 3.93 (4H, t); 1.79 (4H, m); 1.29 (12H, m); 0.88 (6H, t) ^{13}C NMR ($CDCl_3$, δ, ppm): 150.06; 118.44; 111.11; 70.30; 31.80; 29.26; 25.93; 22.67; 14.12. Analysis calcd. for $C_{18}H_{28}O_2Br_2$: C, 49.54 %; H, 6.42 found: C, 49.57 %; H, 6.48 %.

1,4-bis(trimethylsilyl)-2,5-dihexoxybenzene (4)

Chlorotrimethylsilane (0.9 g, 0.087 mole) and magnesium (0.21 g, 0.087 mole) with 10 ml of THF were stirred under nitrogen, while a small portion of THF (10ml) solution of 1,4-dibromo-2,5-dihexoxybenzene (2 g, 0.043 mole) was added. The mixture was heated gently until the reaction started. Then it was cooled to 0°C and the rest of the 1,4-dibromo-2,5-dihexoxybenzene was slowly added. After stirring over-

night at room temperature, the mixture was treated with 2 M aqueous HCL and extracted with ether. The organic layer was dried over $MgSO_4$, filtered and after elimination of the solvent, the product was crystallized from EtOH. (Yield 80 %). M.p.: 98–100°C, ^1H NMR ($CDCl_3$, δ, ppm): 6.82 (2H, s); 3.93 (4H, t); 1.74 (4H, m); 1.29 (12H, m); 0.9 (6H, t); 0.26 (18H. s). ^{13}C NMR ($CDCl_3$, δ, ppm); 157.51; 129.75; 116.36; 68.03; 31.81; 29.24; 26.24; 22.26; 14.10; 0.38. ^{29}Si NMR ($CDCl_3$, δ, ppm): – 4.98. Analysis calcd. for $C_{24}H_{46}Si_2O_2$: C, 68.24; H, 10.90. found: C, 68.34; H, 10.93 %.

Oxidation of N-n-butylcarbazole (1) and (bis)silyl-N-n-butylcarbazole (2)

Chemical oxidation

In a schlenck tube was placed freshly sublimed $FeCl_3$ (7.7 g, 0.048 mole) and 200 ml of dried $CHCl_3$. The mixture was stirred for 15 min and the carbazole monomer (0.012 mole) in 100 ml $CHCl_3$ was added. After stirring for 3 days at 20°C, 400ml of MeOH were added. The mixture was filtered and the solid was collected and washed with MeOH several times. It was then dissolved in CH_2Cl_2 and treated with aqueous $Na_2S_2O_4$. The organic layer was separated, washed and dried over $MgSO_4$. The solvent was eliminated, and the product was dried in vacuo (NMR, UV-Visible, and GPC). Oxidation of **(1)** GPC (THF): $DPn_1 = 1$ (71 %), $DPn_2 = 2$ (29 %) $\lambda_1$max (THF) = 243 nm, $\lambda_2$max = 246 nm, $\lambda_3$max = 300 nm. Oxidation of **(2)** GPC (THF): $DPn_1 = 1$ (32.9 %), $DPn_2 = 2$ (19.7 %), $DPn_3 = 3$ (47.2 %), $\lambda_1$max (THF) = 244 nm, $\lambda_2$max = 246 nm, $\lambda_3$max = 300 nm.

Electrochemical oxidation

The electrochemical synthesis was performed galvanostatically (3mA cm^{-2}) at T = 5°C in a one compartment cell using an "EG & G" potentiostat 363 model under computer control. The working and counter electrodes were platinum (Pt) sheets (2 × 2.5 mm) at a distance of 18 mm and the anodic potential was measured versus an $Ag/AgNO_3$ (10^{-2} M) electrode. The Pt electrodes were carefully polished with Al_2O_3 before each electrochemical synthesis. Oxygen was excluded from the electrochemical cell by using a nitrogen flow. The electrolytic medium was prepared by dissolving the monomer (0.1 mol.L^{-1}) in acetonitrile containing NBu_4BF_4 (0.1 mol L^{-1}).

The products were isolated from the electrolytic solution. After removal of the solvent, the residue was dissolved in CH_2Cl_2 and washed with aqueous $Na_2S_2O_4$, and water. After drying, the crude oligomers were obtained upon elimination of the solvent. Oxidation of **(1)** GPC (THF): $Dpn_1 = 1$ (40 %), $Dpn_2 = 2$ (60 %), $\lambda_1$max (THF) = 244 nm, $\lambda_2$max = 246 nm, $\lambda_3$max = 300 nm. Isolated dimer: (H^1NMR, δ, ppm) 8,45 (S, 2H): 8,2 (d, 2H); 7,8 (d, 2H); 7,49 (m, 6H); 7,28 (t, 2H). Oxidation of **(2)** GPC (THF): $Dpn_1 = 1$ (10.8 %), $Dpn_2 = 2$ (24.3 %), $Dpn_3 = 3$ (54 %), $\lambda_1$max (THF) = 244 nm, $\lambda_2$max = 246 nm, $\lambda_3$max = 300 nm.

Synthesis of poly(1,4-dihexoxybenzene)s

Chemical oxidation

The procedure was similar to the one described for carbazole. The use of $FeCl_3$ (7.7 g, 0.048 mole) and of monomer (0.012 mole) dissolved in 100 ml of $CHCl_3$ led rapidly to a black mixture which was stirred for 17 hours. 400 ml of CH_3OH were then added and the reaction mixture was filtered. The solid collected was washed with MeOH (soxhlet extractor 10 hours) and dried in vacuo. It was then dissolved in 200 ml of THF and precipitated by addition of 500 ml of CH_3OH. After filtration and washing with MeOH, the purified polymer was dried in vacuo.

Electrochemical polymerization

The electrochemical oxidation was performed as above in the case of carbazole derivatives. The electrolytic solution was prepared by dissolving 3.29 g of NBu_4BF_4 in 100 ml of CH_2Cl_2. The solution, 15 ml was placed in the electrolytic cell and then 1.5×10^{-3} mole of monomer was introduced. Preparative electrolysis was performed galvanostatically (3mA cm^{-2}) as previously. After electrolysis, CH_2Cl_2 was distilled off, the residue was washed with methanol and pentane and dissolved in THF. The polymer precipitated upon addition of methanol.

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