

Electroactive poly(3,6-carbazolediyl) with lateral aminoalkyldisiloxane groups

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Summary

Poly[N-(9-dimethylamino 4,4,6,6-tetramethyl 5-oxa 4,6-disilanonyl) 3,6-carbazolediyl] was prepared by electrochemical synthesis. The solubility of this polymer in many organic solvents allows its characterization by GPC and ^{13}C NMR. \overline{DP}_n 's are relatively low (≈ 6), probably due to a reaction of debromination which occurs during the synthesis of the monomer and leads to monofunctional reactants limiting the polymer growth. Electro-oxidation of solution-cast films gives rise to two reversible color changes : yellowish to green and green to blue. Films display a relatively good electrochemical stability in the blue state (up to 1.4 V vs SCE).

Introduction

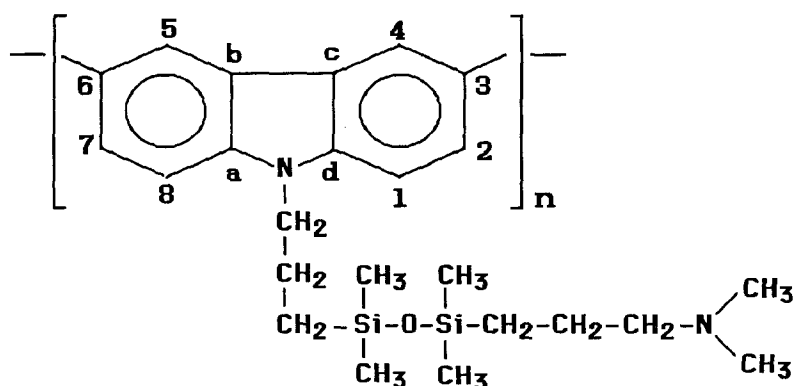
Polymers with lateral carbazolyl groups such as polyvinylcarbazole have been widely studied and an extensive literature has been published concerning their photoconductive properties (1).

Recently, several attempts to prepare electronic conductive materials from polyvinylcarbazole (2) and carbazole-substituted polysiloxanes (3,4) have been reported. In the latter case, electrochromic films have been prepared via anodic oxidation, but cross-linking due to coupling of carbazolyl units occur during electrochemical process. Moreover, it is assumed that the electrochemical response of the remaining monomer carbazole units overlap that of dicarbazolyl units (3).

We recently described a new route for the synthesis of poly(N-alkyl 3,6-carbazolediyl) by electroreduction of the corresponding 3,6-dibromocarbazoles. Linear and well-defined polymers have been obtained (5,6). In this research program, we have been interested in the preparation of polymers exhibiting an extended solubility together with improved transport properties. We focused our attention on anchoring flexible and functional side chains bearing terminal amines or quaternary ammonium salts onto a carbazolic structure.

The present work is devoted to the synthesis, characterization and electrochemical features of poly(3,6-carbazolediyl) N-substituted by an aminoalkyldisiloxane group (hereafter named PCz-Si).

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PCz-Si: Poly[N-(9-dimethylamino 4,4,6,6-tetramethyl 5 oxa 4,6-disilanonyl) 3,6-carbazolediyl].

Experimental

Monomer synthesis

The synthesis of 3,6-dibromo N-(9-dimethylamino 4,4,6,6-tetramethyl 5-oxa 4,6-disilanyl) carbazole (Br_2CzSi) was carried out in three steps:

- 3,6-dibromo N-allylcarbazole was synthesized and purified according to the method previously described for N-ethyl derivative (5). A white product was obtained (melting point: 103°C) and characterized by ^1H NMR (CDCl_3): $\delta = 8.00$ ppm (2H, $\text{H}_{4,5}$); $\delta = 7.48$ ppm (2H, $\text{H}_{2,7}$, d, $J = 8$ Hz); $\delta = 7.10$ ppm (2H, $\text{H}_{1,8}$, d, $J = 8$ Hz); $\delta = 5.86$ ppm (1H, $-\text{CH}=\text{}$, m); $\delta = 4.69$ ppm (2H, $>\text{N}-\text{CH}_2$), $\text{CH}_2=\text{}$: two doublets at $\delta = 5.13$ ppm ($J = 10$ Hz) and $\delta = 4.93$ ppm ($J = 17$ Hz).

- N,N-dimethylaminopropyltetramethyldisiloxane (DMAPS) was prepared by hydrosilylation of N,N-dimethylallylamine with tetramethyldisiloxane according to a method described elsewhere (7). Distillation gives a product of purity higher than 99% determined by capillary GC (Perkin-Elmer model 8500).

- Br_2CzSi was obtained by hydrosilylation reaction of 3,6-dibromo N-allylcarbazole with DMAPS in equimolar ratio (10 mmol), catalyzed by hexachloroplatinic acid (0.02 mmol). The reaction was carried out in toluene under reflux until complete disappearance of the silane functions (4 h). The silane consumption was followed by IR at 2120 cm^{-1} using a Perkin-Elmer model 580 IR spectrometer.

Characterization

Molar masses of PCzSi were measured by GPC in tetrahydrofuran with a Waters GPC apparatus calibrated with standard polystyrene samples.

^{13}C NMR spectra of monomers and polymers were performed with a Bruker ACE 200 spectrometer at 200 MHz.

DSC measurements were carried out with a Perkin Elmer DSC-4 apparatus calibrated with indium, at a heating rate of $20^\circ\text{C} \cdot \text{mn}^{-1}$.

Electrochemical measurements

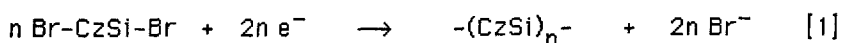
All electrochemical studies were performed with a Solea-Tacussel apparatus (PJT 35-2 potentiostat, GSTP 4 generator, IGSN coulometer). Electrosynthesis conditions have been described previously (5).

Electrochemical characterization of PCzSi thin films casted onto ITO coated glass electrode was made in acetonitrile containing 0.3 mol. l⁻¹ of LiClO₄ as supporting electrolyte. The counter-electrode was a platinum wire and a saturated calomel electrode (SCE) was used as reference electrode.

Results and discussion

Polymer synthesis

The electrochemical process used to synthesize PCzSi involves the cathodic reduction of NiBr₂, 2,2'-bipyridine complex (NiBr₂,B) yielding a Ni(0) based catalytic system which, in the presence of Br₂CzSi, gives rise to the formation of the polymer (eq. [1]):



The yield is higher than 90%. Electrochemical features of the system is similar to that previously described for the 3,6-dibromo N-ethylcarbazole (5). The cathodic reduction of the Ni(II) complex leads to the formation of Ni(0) which is instantaneously inserted into a C-Br bond of the monomer (eq. [2]).



The oxidative insertion of the transition metal generates a C-NiBr* active species which reacts preferentially with monomer at low conversion and with oligomers at higher conversion. Polymer is formed through a step polymerization mechanism (8).

Physico-chemical characterization of PCzSi

PCz-Si are soluble at room temperature in most organic solvents such as tetrahydrofuran, diethyl ether, chloroform, ethanol, benzene, toluene, 1,2,4-trichlorobenzene, nitrobenzene or hexane. It is noteworthy that ethanol and hexane are non-solvents of poly(N-alkyl 3,6-carbazolediyl). As expected, strong polymer-solvent interactions are induced by the aminopropyl-disiloxane side-groups.

This remarkable solubility allows the determination of macromolecular and structural features by classical techniques such as GPC and NMR.

GPC chromatograms of PCz-Si disclose a molar mass distribution \bar{M}_p/\bar{M}_n of roughly 2 with \bar{M}_n values of 2500 g. mol⁻¹ (PS calibration) corresponding approximately to six carbazoly units. This low value which is about one half of that obtained for poly(3,6 N-butylcarbazolediyl) in the same experimental conditions (6).

Structure elucidation

The macromolecular structure of PCz-Si was established by high resolution ^{13}C NMR. Assignments of the resonance signals were made by comparison with the results of a two-dimensional ^{13}C NMR analysis of Br_2CzSi monomer and various poly (N-alkyl 3,6-carbazolediy) (9).

At first, we analyzed the region corresponding to the chemical shifts of aromatic carbon atoms (Table 1). NMR spectrum of PCzSi showed seven sets of signals in the aromatic region. Five of them are also observed in the spectrum of the monomer and correspond to 1,8, 4,5, 2,7, a,d and b,c positions of the carbazole nucleus. It is noteworthy that the chemical shifts of homologous carbon atoms in the polymer and in the monomer are slightly different owing to modifications of the electronic repartition.

A sixth signal at 133.1 ppm was assigned to 3,6 carbon atoms in agreement with the value of 133.4 ppm obtained for poly(N-butyl 3,6-carbazolediy) (6). The strong downfield shift with respect to the monomer (111.6 ppm) is consistent with an extension of conjugation through dicarbazolediy) dyads.

Carbon atom	chemical shift (ppm from TMS)	
	Br_2CzSi	PCz-Si
a,d	138.9	139.9
3,6	111.6	133.1
b,c	125.0	123.5
4,5	122.9	118.8
2,7	128.7	120.3
1,8	110.1	108.6

Table 1 : ^{13}C assignments in the aromatic region of PCz-Si and the corresponding dibromo monomer (solvent : CDCl_3).

The seventh signal at 125.4 ppm corresponds probably to debrominated 3 or 6 positions of the chain ends (equivalent positions in N-ethylcarbazole were found at 127.2 ppm; see ref. 6). This would explain the splitting observed for the other six peaks. As this signal also appears at 127.9 ppm in the monomer spectrum, it should be concluded that debromination occurs during the synthesis of the monomer by hydrosilylation. The presence of a substantial amount of monobrominated derivative may also explain the low molecular weight of the polymer ($\overline{\text{DP}}_n=6$).

Nevertheless the increased intensity of the signal at 125.4 ppm in the polymer spectrum points to the fact that further debromination occurs during electrosynthesis. The absence of signal near to 111.6 ppm indicates that the loss of terminal bromine atoms is probably complete or almost complete, as previously found from elemental analysis of poly(N-alkyl 3,6-carbazolediy) (5,6).

In addition, the presence of two small peaks at 116.7 ppm and 132.3 ppm is observed in the spectrum of the polymer. These signals which are also

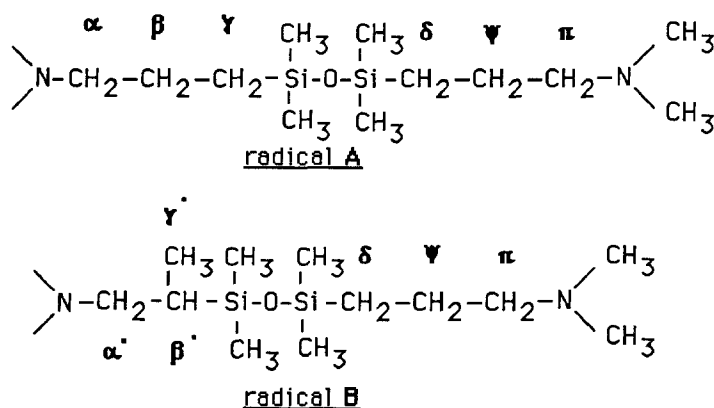
present in the ^{13}C NMR spectrum of 3,6-dibromo N-allylcarbazole are respectively assigned to secondary and tertiary ethylenic carbons of allyl groups. From the ^1H NMR spectrum, the amount of 3,6 dibromo N-allylcarbazole in Br_2CzSi was estimated to about 15 %. The presence of unreacted allylcarbazole (when the silane groups are completely consumed during hydrosilylation) is probably due to the side-reaction of debromination which consumes a part of the silane.

In the region of aliphatic carbon atoms (Table 2), it is worth noting the splitting of the signal of the methyl groups linked to silicon atoms (chemical shifts of 0.2 and 1.1 ppm).

reference of carbon atoms	radical A (ppm/TMS)	radical B (ppm/TMS)
α, α'	44.6	44.6
β	21.2	-
β'	-	22.3
ψ	22.8	22.8
δ, δ	15.7	15.7
δ'	-	11.7
π	62.9	62.9
N-CH_3	45.3	45.3
Si-CH_3	0.2	1.1

Table 2 : ^{13}C NMR assignments of the side chain linked to the poly(N-substituted carbazole) (solvent : CDCl_3).

This indicates that isomers are formed during the addition of DMAPS onto the 3,6-dibromo N-allylcarbazole as reported in the literature for various hydrosilylation reactions (10). Depending on the mode of addition of the silane onto the double bond, the chain linked to the 3,6-dibromo N-carbazole or polycarbazole may be represented as follows :



Small peaks observed at 1.1, 11.7, 22.3 and 44.6 ppm may be assigned respectively to carbon atoms Si-CH₃, δ' CH₃, β' CH and α' CH₂ in structure B, as shown in Table 2.

Electrochemical behavior

Thin films of PCzSi casted from CHCl₃ or THF solutions onto an ITO coated glass electrode (in 0.3 M LiClO₄/acetonitrile solution) were studied by cyclic voltammetry between 0 and 1.4 V versus SCE (Figure 1). Starting from neutral PCzSi at 0.0 V, two oxydation peaks were observed at 0.78 V and 1.15 V by increasing the applied potential. These anodic waves are associated with two cathodic waves appearing successively at 0.96 V and 0.58 V when the potential is reversed.

Electrochemical analysis on glassy carbon electrode (Table 3) shows that PCzSi films are more easily oxidizable than those of poly(N-butyl 3,6-carbazolediy) (PBuC).

Film	First system		Second system	
	E _{pa1}	E _{pc1}	E _{pa2}	E _{pc2}
PCzSi	0.72	0.58	1.1	1.0
PBuC	0.82	0.48	1.25	0.92

Table 3. Peak potentials (V/SCE) for films deposit on a glassy carbon electrode in acetonitrile containing 0.3 mol. l⁻¹ of LiClO₄ (scan rate : 0.1 V. s⁻¹).

Moreover the difference between cathodic (E_{pc}) and anodic (E_{pa}) peak potentials of each system is much lower for PCzSi than for PBuC, which suggests a better stability of the former. Furthermore, as in the case of poly(N-alkyl 3,6-carbazolediy), peak anodic and cathodic currents of PCzSi are proportional to the square root of the scan rate, which indicates a diffusion-controlled process (11).

PCzSi exhibits two reversible color changes accompanying the redox processes : yellowish to green (0.6 V < E < 1.0 V), then green to blue (1.0 V < E < 1.4 V). Such a behavior has been observed in the case of poly(N-alkyl 3,6-carbazolediy) (12) and has been ascribed to the formation of radical cations of carbazolic dyads during the first oxidation step (green state) followed by their oxidation into dications through the second step (blue state).

Furthermore these films exhibit a better stability in the blue state than that of PBuC. For instance, PBuC loses 40 % of the electrochemical response at the maximum of the second oxidation potential after 80 cycles at 0.1 V. s⁻¹, whereas the loss is only 12 % for PCzSi, in the same conditions. This relatively good stability in the blue state is not in agreement with its attribution to an isolated carbazole radical cation proposed by Tieke et

Chard (3) in the case of a carbazole-substituted polysiloxane, because homologous radical cations are known to be very unstable (13).

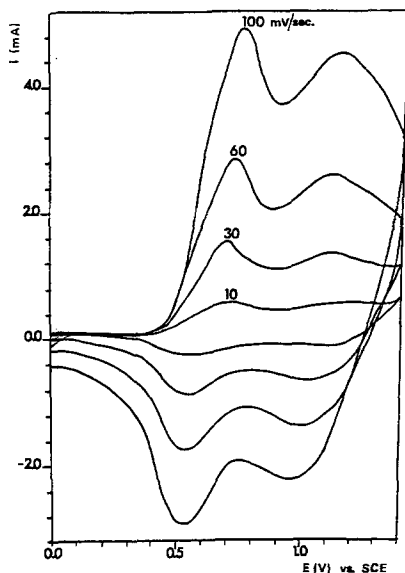


Figure 1. Cyclic voltammograms of a solution-cast PCzSi film onto ITO glass at different scanning rates. Solvent : $\text{CH}_3\text{CN}/0.3 \text{ M LiClO}_4$; SCE reference.

The improved electrochemical stability of the PCzSi films is probably due to a solvation of the dications corresponding to fully oxidized dicarbazolediyl units, by the electron pairs of the heteroatoms of the aminoalkylsiloxane groups ($-\text{O}-$, >N).

After dedoping, PCzSi can be resolubilized in THF or CHCl_3 which indicates that no crosslinking occurred during the electrochemical oxidation of the material.

Properties of neutral and chemically doped polymer

PCzSi in the neutral state is a ductile material exhibiting a wide glass transition centered at 20°C .

Exposed to iodine vapor, PCzSi becomes deep green and the conductivity was in the range $10^{-5} < \sigma < 10^{-4} \text{ S. cm}^{-1}$ (four-point probe). The doped material remains stable exposed to air and presents an increased ductility with respect to undoped material.

Conclusion

Poly(3,6-carbazolediyl) with lateral aminoalkylsiloxane groups was prepared in the neutral state by electroreductive synthesis. This flexible side group bearing electron donor heteroatoms is responsible for the improved physico-chemical and electrochemical properties of the material. Solubility of the polymer in most organic solvents allows the determination of its macromolecular and structural features. Electro-oxidation of

solution-cast films induces two quasi-reversible electrochromic transitions up to 1.4 V vs SCE.

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