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Synthesis of poly(ferrocenyldialkoxysilane) polymers and their introduction into oxide matrices

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Abstract

The synthesis of 1,1′-ferrocenediyldialkoxysilanes $Fe(\eta\text{-}C_5H_4)_2Si(OR)_2$ **M2**–**M5** (R = *i*-Pr, *t*-Bu, $PhCH_2$, Me), consisting of the reaction between 1,1′-ferrocenediyldichlorosilane with the selected alcohols, is described. The thermal ring opening polymerisation of **M2**–**M5** yielded the corresponding poly(ferrocenylsilane) polymers **P2**–**P5**. These linear polymers were soluble in polar solvents and exhibited high molecular weights. The monomers **M2** and **M4** were introduced into a silica matrix by a non-hydrolytic sol–gel process. However, Si–C bond breaking was observed due to the electrophilic ipso substitution. Polymers **P3** and **P4** were easily condensed with $SiBr_4$. When **P3** was condensed with $TiCl_4$ and $AlCl_3$, degradation of the polymer occurred. Interestingly, the hydrolytic sol–gel polycondensation of polymers **P2**, **P4** and **P5** yielded a completely polycondensed hybrid solid, without significant specific surface area and with conservation of the electrochemical properties.

Keywords: 1,1′-Ferrocenediyldialkoxysilanes; Poly(ferrocenylsilanes); Non-hydrolytic sol–gel condensation; Sol–gel process

1. Introduction

In recent decades, polymers containing transition metals in the main chain have attracted considerable attention owing to their physical (redox, magnetic, electrical, etc.) and chemical properties [1].

In the field of nanostructured organic inorganic materials obtained by sol–gel routes, it is possible to introduce organic [2–5] or organometallic [6–8] moieties into a silica matrix. In these solids the organic or organometallic units are covalently bound to each other through covalent Si–C bonds. In such materials the properties of the molecular organic or organometallic moiety are generally preserved in the material [9–15]. In order to verify the generality of this observation, we have been particularly interested by the recently described class of organometallic polymers that contain ferrocene units in the chain [1]. They are very attractive, since a very specific redox cooperation between the iron centres along the polymer backbone, showing a highly characteristic two-wave cyclic voltammogram, has been reported [16–21]. Thus we have studied the presence and the possible evolution of this specific property in the solid. In a preliminary communication we have described the possibility of introducing poly(ferrocenyldialkoxysilanes) into silica matrices by a non-hydrolytic sol–gel process [22]. This route [23,24] permits access to oxides other than SiO_2 and corresponds to a condensation reaction between a metal halide and a metal alkoxide (Scheme 1).

We report here the synthesis of new poly(ferrocenyldialkoxysilane) polymers containing polycondensable alkoxide groups and the attempts at their inclusion in oxides. These polymers were obtained by ring-opening polymerisation (ROP) from the corresponding monomers. Until now, substituents introduced at the silicon in strained ferrocenophanes were limited to alkyl and aryl groups [1,25–27]. Only recently has the synthesis of new ferrocenyldialkoxysilanes been achieved [22,28]. The selected alkoxide groups allowed polycondensation via non-hydrolytic and hydrolytic sol–gel processes, thus enabling their introduction into various inorganic matrices, such as SiO_2, TiO_2 and Al_2O_3.

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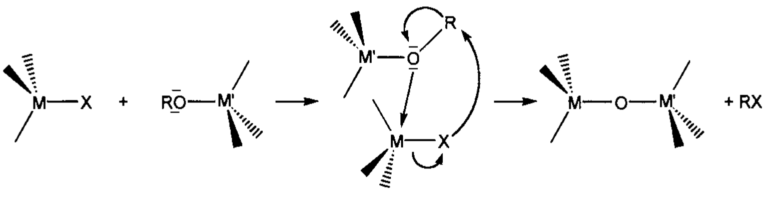


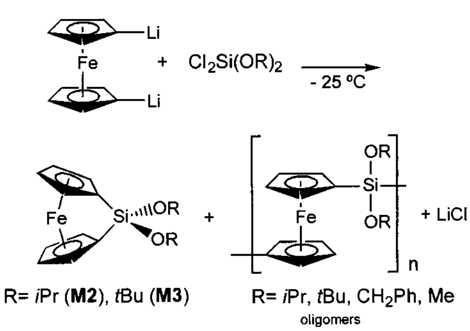
Scheme 1. Non-hydrolytic sol–gel process.

2. Results and discussion

2.1. Synthesis and characterisation of 1,1′-ferrocenediyldialkoxysilanes M2–M5

The preparation of monomers **M2**–**M5** (Scheme 2) was studied. Two routes were investigated to prepare **M2**–**M5**.

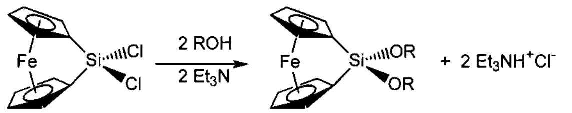
Route 1, previously described in the literature [16,29] for the synthesis of the alkyl and aryl analogues, consists of the reaction between 1,1′-dilithioferrocene and the selected dichlorodialkoxysilanes, and results in a mixture of monomers and small oligomers in the case of **M2** and **M3** (reaction in Eq. (1)).



(1)

Pure **M2** and **M3** were isolated in 30% and 40% yields respectively. The monomers **M4** and **M5** could not be obtained by this route: only small oligomers with a high polydispersity index, identified by size exclusion chromatography (SEC) in THF, were isolated. This was revealed to be independent of the order of addition of the two reactants, as well as of the reaction temperature. Moreover, the required dialkoxydichlorosilanes were not easily available.

The monomers **M2**–**M5** were obtained by route 2, which consists of the reaction between 1,1′-ferrocenediyldichlorosilane **M1** and the selected alcohol (reaction in Eq.(2)).

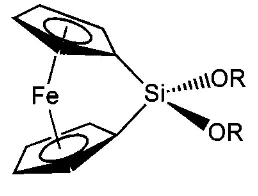


M1 R = iPr (**M2**), tBu (**M3**), $PhCH_2$ (**M4**), Me (**M5**)

(2)

M1 was prepared according to the route originally reported by Wrighton et al. [30]: a reaction between 1,1′-dilithioferrocene/TMDA and $SiCl_4$. The treatment of **M1** with various alcohols in the presence of triethylamine in pentane or THF at room temperature resulted in a nucleophilic substitution of chlorine at silicon, leading to **M2**–**M5** without cleavage of the bridge. The new compounds were isolated in good yields (66–87%) as orange–red solids by recrystallisation of the crude products. **M2** was a liquid at room temperature (m.p. 5–10°C). Compounds **M2**–**M5** were characterised by ^{1}H-, ^{13}C- and ^{29}Si-NMR spectroscopy. In each case the ^{1}H-NMR spectra exhibited the signals corresponding to the hydrogen of the cyclopentadienyl ring in the range between 4 and 5 ppm and the signals normally expected for the hydrogen of alkoxide groups attached to silicon. The ^{13}C-NMR spectra showed the cyclopentadienyl carbon atoms in the regions 40–43 ppm and 75–78 ppm. The signal at ~41 ppm was characteristic of the ipso-cyclopentadienyl carbon atom bound to the bridging silicon atom. The high-field shift observed was directly related to the strained cyclic structure of the 1,1′-ferrocenediyldialkoxysilanes, and is in agreement with the previously reported results described in the case of the alkyl and aryl analogues [17]. The signals corresponding to the carbon atoms from the alkoxide groups were easily identified in the spectra. The ^{29}Si-NMR spectra showed a single signal in all cases. The chemical shifts observed depended strongly on the nature of the substituent and ranged between −31.4 ppm for **M5** and −52.7 ppm in the case of **M3**. Elemental analysis gave satisfactory values in all cases. Spectroscopic data for **M2**–**M5** are listed in Table 1.

The differential scanning calorimetry (DSC) analysis of compounds **M2**–**M5** was performed at a heating rate of 5°C min^{-1} in air. A sharp endothermic signal followed by a broad exothermic band characterised the spectra in all cases. The endothermic peak corresponded to the melting of the monomer and the exotherm was attributed to the ROP. In the case of **M3**,



R = iPr (**M2**), tBu (**M3**), $PhCH_2$ (**M4**), Me (**M5**)

Scheme 2. Monomers **M2**–**M5**.

Table 1
Physical and NMR data for monomers **M2**–**M5**

Compound	Yield[a]	M.p. (°C)	Exotherm (°C)	NMR spectroscopy[b] ^{1}H	^{13}C	^{29}Si
M2	30% (route 1) 70% (route 2)	5–10	190–210	d 1.4 (6H, CH_3) t 4.2 (4H, Cp) t 4.6 (4H, Cp) h 4.7 (1H, CH)	25.9 ($(CH_3)_2CH$) 41.3 (*Cipso* Cp) 65.5 ($(CH_3)_2CH$) 75.4, 77.6 (Cp)	−39.2
M3	40% (route 1) 66% (route 2)	91–93	230–270	s 1.6 (18H, tBu) t 4.3 (4H, Cp) t 4.6 (4H, Cp)	32.4 ($(CH_3)_3C$) 43.8 (*Cipso* Cp) 74.3 ($(CH_3)_3C$) 75.3, 76.9 (Cp)	−52.7
M4	68% (route 2)	48–50	180–200	t 4.2 (4H, Cp) t 4.6 (4H, Cp) s 5.2 (4H, CH_2) m 7.4 (10H, Ph)	40.1 (*Cipso* Cp) 64.8 ($C_6H_5CH_2$) 75.6, 78.2 (Cp) 127.3, 127.8, 128.8, 140.6 ($C_6H_5CH_2$)	−32.9
M5	70% (route 2)	45	130–150	s 3.8 (6H, CH_3) t 4.2 (4H, Cp) t 4.6 (4H, Cp)	40.4 (*Cipso* Cp) 50.5 (CH_3) 75.7, 78.3 (Cp)	−31.1

[a] Overall yield (from dilithioferrocene).

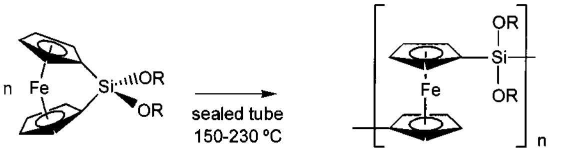
[b] Chemical shifts (ppm) relative to Me_4Si in CD_2Cl_2 (Cp = cyclopentadienyl).

which contains bulky *tert*-butoxide groups, the ROP temperature was higher (230–270°C) than in the other cases. The melting points and ROP temperatures are reported in Table 1. The DSC thermogram of **M4** is presented in Fig. 1.

The molecular structure of **M3**, studied by single-crystal X-ray diffraction [22], shows the expected strained [26,27,31] structure with a tilt angle between the planes of the cyclopentadienyl ligands of 20.3°.

2.2. Synthesis and characterisation of poly(ferrocenylsilanes) *P2–P5*

The ROP process (reaction in Eq. (3)) of **M2**–**M5** has been evidenced by DSC experiments.



M2-M5

R = *i*Pr (**P2**), *t*Bu (**P3**), CH_2Ph (**P4**), Me (**P5**)

(3)

The corresponding new polymers **P2**–**P5** were obtained thermally according to the method already described [16,32,33]. The polymerisation temperatures were deduced from the DSC analysis in each case and are given in Table 2.

The polymers **P2**–**P5** were obtained as orange–red solids. They were soluble in polar solvents such as THF and dichloromethane. The molecular weights M_w were determined by SEC in THF using polystyrene standards. The values reported for M_w in Table 2 were very high and ranged from 206 000 to 360 000 (the detection limit). In the case of **P3** and **P4** the polydispersity indexes were low, which is indicative of a narrow distribution of molecular weights.

The ^{1}H-, ^{13}C- and ^{29}Si-NMR data of polymers **P2**–**P5** were in agreement with the expected spectra. In each case the ^{1}H-NMR spectra exhibited the hydrogen atoms of the cyclopentadienyl rings at 4.2 and 4.4 ppm and the signals corresponding to the hydrogen of the alkoxide groups. The ^{13}C-NMR spectra exhibited the cyclopentadienyl carbon atom signals in the region 66–73 ppm. It is interesting to note that the ipso-cyclopentadienyl carbon atom bound to silicon shifts downfield (~66–69 ppm) compared with the corresponding strained monomers (~40–44 ppm).

The ^{29}Si-NMR resonances for polymers **P2**–**P5** were shifted downfield compared with the corresponding strained monomers. The values are reported in Table 2.

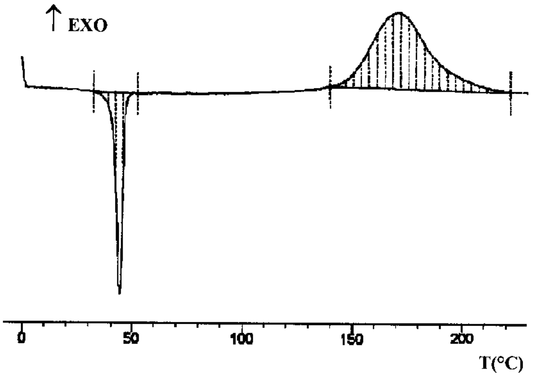


Fig. 1. DSC thermogram of **M4**.

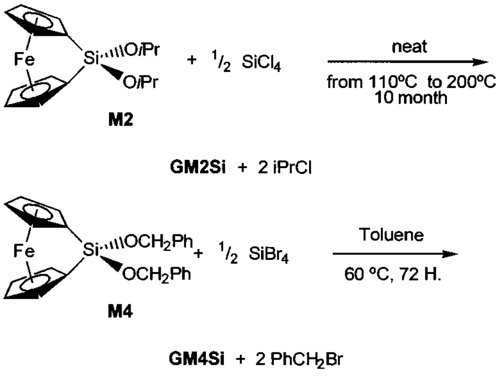
Table 2
Physical and NMR data for polymers **P2**–**P5**

Compound	Polym. temp. (°C)	M_w [a]	NMR spectroscopy[c]		
			^1H	^{13}C	^{29}Si
P2	190	>360 000[b]	d 1.3 (6H, CH_3) t 4.2 (4H, Cp) h 4.3 (1H, CH) t 4.4 (4H, Cp)	26.1 ($(CH_3)_2CH$) 67.5 (C*ipso* Cp) 65.4 ($(CH_3)_2CH$) 72.7, (Cp)	−24.8
P3	230	280 000 Ip = 1.6	s 1.4 (18H, tBu) t 4.2 (4H, Cp) t 4.4 (4H, Cp)	32.4 ($(CH_3)_3C$) 71.2 (C*ipso* Cp) 72.7 ($(CH_3)_3C$) 72.9, 74.6 (Cp)	−36.5
P4	180	290 000 Ip = 2.0	t 4.3 (4H, Cp) t 4.5 (4H, Cp) s 5.0 (4H, CH_2) m 7.4 (10H, Ph)	65.4 ($C_6H_5CH_2$) 65.9 (C*ipso* Cp) 72.9, 74.4 (Cp) 126.8, 127.4, 128.6, 141.4 ($C_6H_5CH_2$)	−18.5
P5	130	206 000 Ip = 17	s 3.7 (6H, CH_3) t 4.2 (4H, Cp) t 4.4 (4H, Cp)	51.4 (CH_3) 68.6 (C*ipso* Cp) 72.2, 73.9 (Cp)	−15

[a] Determined by SEC in THF versus polystyrene standards.
[b] Upper limit detection surpassed, Ip value not avalaible.
[c] Chemical shifts (ppm) relative to Me_4Si in $CDCl_2$ (Cp = cyclopentadienyl).

2.3. Introduction of monomers M2 and M4 into SiO_2 by a non-hydrolytic sol–gel process

This method consists of the condensation between alkoxide and halide functions as outlined in Scheme 1. In this context, we investigated the condensation of 1,1′-ferrocenedialkoxysilanes **M2** and **M4** with silicon halides according to the reaction in Eq. (4).



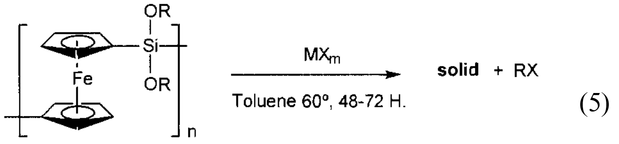
(4)

The solids **GM2Si** and **GM4Si** were isolated as brown powders, which were filtered off and washed before characterisation. The formation of alkyl halide was evidenced by ^1H-NMR spectroscopy analysis of the filtrate. This phase and the washing solutions were very coloured, due to the presence of ferrocene derivatives. A loss of iron was evidenced by elemental analysis of **GM2Si** and **GM4Si**. The ^{13}C-CPMAS-NMR spectra exhibited the cyclopentadienyl carbon atoms signals in the region 65–80 ppm in both cases, as well as small signals corresponding to residual alkoxide groups, at 20–40 ppm for **GM2Si** (isopropyl carbon atoms) and 129 and 141 ppm for **GM4Si** (aromatic carbon atoms). An unexpected signal at 138 ppm was also detected in the case of **GM2Si**, which has been attributed to the possible presence of cyclopentadienyl units arising from the degradation of the ferrocenyl moieties. The ^{29}Si-CP-MAS-NMR spectra exhibited the two signals normally expected at −25 ppm and −100 ppm, corresponding respectively to the D (C_2–$Si(OX)_2$, X = *i*-Pr, CH_2Ph, Si) [34,35] and Q ($Si(OX)_4$) substructures [36]. An additional broad signal centred at −60 ppm was observed and could be assigned to the T units (C–$Si(OX)_3$) already reported in the case of 1,1′-ferrocenylsilsesquioxanes [6]. The formation of T substructures could be provided by the Cp–SiCp bridge breaking that occurs during the condensation process. The silicon–ferrocene bond cleavage may be explained by a Friedel and Crafts type of electrophilic substitution reaction at the ipso position, the alkylating agent being the alkyl halide formed during the condensation reaction and the catalyst the silicon halide ($SiBr_4$ or $SiCl_4$). Such reactions would lead to the silicon–carbon bond cleavage and to the formation of an alkylferrocenylsilane precursor in a T-type configuration with release of alkyl halide (Scheme 3a). Another possibility might involve a concerted process (Scheme 3b). Similar reactions have already been reported in the case of aryl precursors [37].

The solids **GM2Si** and **GM4Si** presented no significant specific surface area ($S_{BET} < 10\ m^2\ g^{-1}$).

2.4. Introduction of polymers into inorganic matrices

Polymers **P3** and **P4** were condensed with $SiBr_4$ according to the reaction shown in Eq. (5).



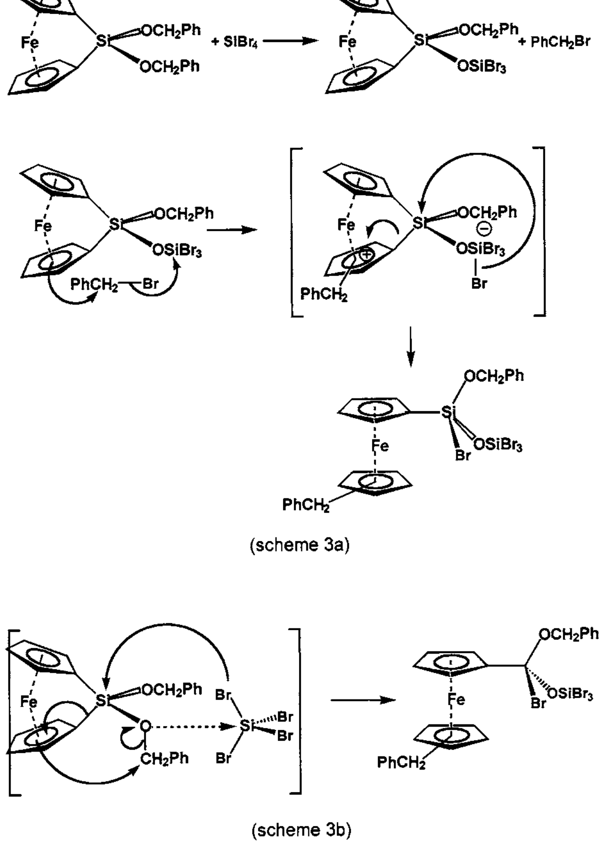
P3-P4

(5)

MX_m	R	solid
$SiCl_4$	tBu	GP3Si
$SiCl_4$	CH_2Ph	GP4Si
$TiCl_4$	tBu	GP3Ti
$AlCl_3$	tBu	GP3Al

The corresponding solids **GP3Si** and **GP4Si** were isolated as brown powders.

In the case of **GP3Si**, the ^{13}C-CPMAS-NMR spectrum exhibited a weak signal at 31 ppm attributed to carbon atoms of the remaining *tert*-butoxide groups and another one at 73 ppm due to the expected cyclopentadienyl carbon atoms. Three resonances were observed for **GP4Si** in the range 60–80 ppm (benzylic and cyclopentadienyl carbon atoms), 129 ppm and 139 ppm (aromatic carbon atoms).



Scheme 3. Formation of T substructures in the solid: (a) with release of alkyl halide; (b) concerted process.

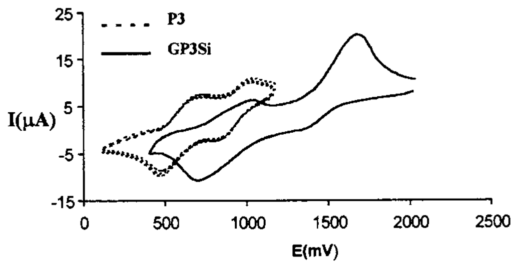


Fig. 2. Cyclic voltammograms in 0.1 M $(NBu_4)BF_4/CH_2Cl_2$ of **P3** and **GP3Si**.

The ^{29}Si-CPMAS-NMR spectra of **GP3Si** and **GP4Si** were very similar. They presented three broad resonances in the ranges -20 to -40 ppm, -65 to -80 ppm and -90 to -100 ppm assigned respectively to D, T and Q silicon substructures. The presence of T units might arise from the cleavage of silicon–carbon bonds involving the rupture of the polymeric chain, according to a mechanism similar to that described in Scheme 3. The elemental analysis was consistent with the loss of ferrocene moieties.

These solids presented no significant specific surface area ($S_{BET} < 10\ m^2\ g^{-1}$).

Preliminary results concerning the electrochemical behaviour of the polymer **P3** and the hybrid solid **GP3Si** showed that, as previously observed [9,10,13–15], the hybrid gel maintained the properties of the incorporated organometallic units despite the high sensitivity of the electrochemical interactions between the ferrocenyl units to the distance (Fig. 2).

Attempts to introduce **P3** in titanium oxide and aluminium oxide matrices were performed by co-condensing the polymer with $TiCl_4$ and $AlCl_3$ respectively (Eq. (5)). **GP3Ti** was isolated as a brown solid, whereas **GP3Al** was a grey powder. The elemental analysis of both samples indicated that the polymer was destroyed and iron was eliminated partially (**GP3Ti**) or totally (**GP3Al**) from the solids. Such a result was attributed to the strong Lewis acidity of the titanium or aluminium halides. The ^{29}Si-CPMAS-NMR analyses were in agreement with the degradation of the organometallic moiety, since only a broad signal in the range -85 to -110 ppm was observed, which corresponded to Q units of $SiO_{4/2}$. The ^{13}C-CPMAS-NMR spectra showed very low resolution. In the case of **GP3Al**, the ^{27}Al-MAS-NMR spectrum (Fig. 3) revealed three resonances which could be attributed to ^{27}Al sites in coordination numbers 6, 5 and 4, as already observed in the preparation of alumina and aluminosilicates by non-hydrolytic sol–gel methods [38,39].

GP3Ti presented no significant specific surface area, whereas **GP3Al** exhibited a surface of $87\ m^2\ g^{-1}$; this could be related to the presence of silica in the solid.

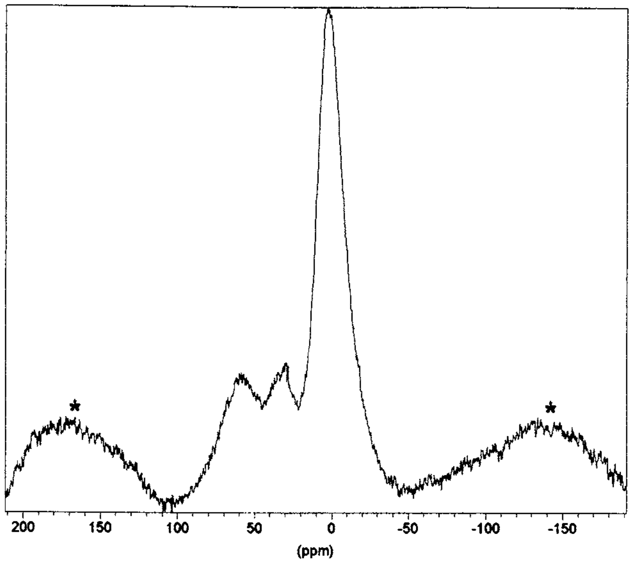


Fig. 3. ^{27}Al-MAS-NMR spectrum of **GP3Al**.

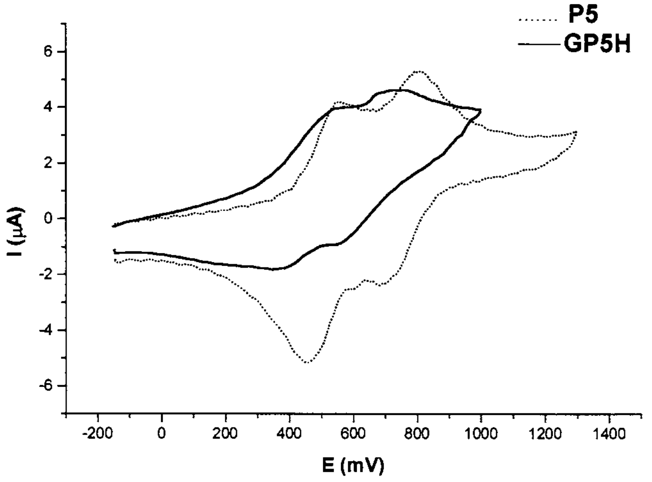
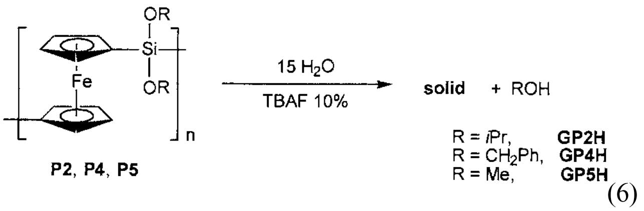


Fig. 4. Cyclic voltammograms in 0.1 M $(NBu_4)BF_4/CH_2Cl_2$ of **P5** and **GP5H**.

*2.5. Hydrolytic sol–gel processing of polymers **P2–P5***

The hydrolysis polycondensation of polymers **P2**–**P5** was performed under nucleophilic catalysis conditions using fluoride ions (reaction in Eq. (6)).



(6)

Orange insoluble solids were obtained in all cases except for **P3**, which did not react because of the steric hindrance of the *tert*-butoxide group. After filtration they were washed with ethanol, acetone and ether (traces of remaining unreacted polymer in the solids were avoided by further Soxhlet extraction with THF). The resulting orange powders were analysed by spectroscopic techniques. **GP2H**, **GP4H** and **GP5H** exhibited the same spectra: a single signal at 68–72 ppm was detected in the ^{13}C-CPMAS-NMR spectra. Remarkably, no signals corresponding to the carbon atoms from residual alkoxide groups were observed, indicating a total polycondensation of the hybrid solids.

The ^{29}Si-CPMAS-NMR analysis corroborated this assumption; only one thin resonance at -30 ppm was detected, which can be assigned to D^2 substructures $(C_2Si(OSi)_2)$ [34,35]. These solids exhibited no significant specific surface areas. It is interesting to note that the solids **GP2H**, **GP4H** and **GP5H** appeared to be very similar, in that they presented the same polycondensation at silicon and the same textural properties with conservation of the ferrocenyl units even though the precursors contained different hydrolysable alkoxide groups. Such behaviour is very different from that observed during the hydrolysis of trialkoxysilyl precursors: the kinetic parameters, and particularly the nature of the leaving group at silicon, have a major influence on the properties of the resulting solids [5,35]. Apparently, the hydrolytic sol–gel route allowed a single highly polycondensed organic inorganic hybrid material to be obtained whatever the alkoxide group at silicon.

A comparison between the cyclic voltammograms of **P5** and **GP5H** showed the conservation of the electrochemical properties of the polymer in the hybrid solid (Fig. 4).

3. Conclusion

We have reported here a convenient synthetic route to new 1,1′-ferrocenediyldialkoxysilanes via a chlorine substitution reaction at the bridging silicon atom of 1,1′-ferrocenediyldichlorosilane with different alcohols in the presence of triethylamine. Thermal ROP of these species provided access to new poly(ferrocenylsilanes) polymers. The incorporation of these monomers into inorganic oxide matrices by a non-hydrolytic sol–gel process was only possible in the case of SiO_2. However, Si–C bonds were cleaved during a side reaction, which consisted in an electrophilic substitution at the ipso position of the alkyl halide formed during the condensation reaction. A similar result was obtained in the case of the polymers. A significant degradation of the polymers occurred when $TiCl_4$ and $AlCl_3$ were employed. In contrast, the hydrolytic sol–gel polycondensation of the polymers led to highly polycondensed hybrid materials without any cleavage of Si–C bonds. In the case of SiO_2 as matrix, the electrochemical properties of the ferrocenyl moieties were preserved in the hybrid solids. Work is currently in progress in order to study the electrochemical properties of the different hybrid solids.

4. Experimental

All reactions were carried out under argon using a vacuum line and Schlenk techniques. Solvents were dried and distilled just before use. Melting points were determined with a Gallenkamp apparatus and are uncorrected. IR data were obtained on a Perkin–Elmer 1600FTIR spectrophotometer. The solution ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker DPX-200 spectrometer and the solution ^{29}Si-NMR spectra were recorded on a Bruker WP-200 SY spectrometer. Solid-state CPMAS-NMR spectra were obtained with a Bruker FT AM 300 spectrometer: ^{13}C-CPMAS-NMR at 75.47 MHz, recycling delay 5 s and contact time 5 ms; ^{29}Si-CPMAS-NMR at 59.62 MHz, recycling delay 10 s and contact time 2 ms. The spinning rate was 5000 Hz in all cases. Chemical shifts are given relative to tetramethylsilane. ^{27}Al-MAS-NMR spectra were obtained with a Bruker FT AM 400 spectrometer at 104.25 MHz, pulse angle $\pi/12$ and recycling delay 1 s. The spinning rate was 10 000 Hz. Chemical shifts were referenced to $Al(H_2O)_6^{3+}$. Specific surface areas were determined using a Micromeritics Gemini III 2375 apparatus. The DSC analyses were carried out on a Micromeritics Accupyc 1330 apparatus. The size-exclusion chromatographs were recorded on a Millipore Waters model 510, equipped with a Waters 441, UV detector. Elemental analyses were carried out by the 'Service Central de Micro-Analyse du CNRS'.

*4.1. Synthesis of monomers **M2** to **M5***

Monomers **M2** to **M5** were readily obtained from the reaction of 1,1′-ferrocenediyldichlorosilane [30] and the corresponding alcohols. In the case of **M3**, the commercially available sodium *tert*-butoxide was preferred.

A typical procedure is given in the case of **M4**: 9.55 g. (0.034 mol) of 1,1′-ferrocenediyldichlorosilane were dissolved in 500 ml of THF and 6.816 g. (0.0675 mol) of triethylamine were added to the solution. The reaction mixture was cooled to 0°C in an ice bath and a solution of 7.29 g. (0.0675 mol) of benzyl alcohol in 50 ml of THF was added dropwise over a period of 2 h. The reaction mixture was allowed to stir for 7 h at ambient temperature and the solvent was evaporated off at the vacuum line. The residue was dissolved in pentane and triethylammonium chloride precipitated off. The pentane solution was filtered and the filtrate was concentrated at the vacuum line until a dense phase was observed in the flask. The solution was then gently warmed to homogeneity and the flask was stored at −18°C allowing **M4** to crystallise as deep-red plates (12.5 g, 86%); m.p. 48–50°C. Anal. Found: C, 67.50; H, 5.05; Fe, 12.60; Si, 6.70. Calc. for $C_{24}H_{22}Fe_1O_2Si_1$: C, 67.61; H, 5.16; Fe, 13.15; Si, 6.57%. ^{1}H-NMR (δ, CD_2Cl_2): 4.2 (4H, t, Cp), 4.6 (4H, t, Cp), 5.2 (4H, s, CH_2), 7.4 (10H, m, Ph). ^{13}C-NMR (δ, CD_2Cl_2): 40.1 (C*ipso* on Cp), 64.8 ($C_6H_5\mathit{C}H_2$), 75.6, 78.2 (Cp), 127.3, 127.8, 128.8, 140.6 ($\mathit{C}_6H_5CH_2$). ^{29}Si-NMR (δ, CD_2Cl_2): −32.9.

M2. Dark-red liquid, (88%), m.p. 5–10°C. Anal. Found: C, 57.02; H, 6.72; Fe, 14.95; Si, 8.30. Calc. for $C_{16}H_{22}Fe_1O_2Si_1$: C, 58.18; H, 6.67; Fe, 16.97; Si, 8.48%. ^{1}H-NMR (δ, CD_2Cl_2): 1.4 (6H, d, CH_3), 4.2 (4H, t, Cp), 4.6 (4H, t, Cp), 4.7 (1H, h, CH).^{13}C-NMR (δ, CD_2Cl_2): 25.9 ($(\mathit{C}H_3)_2CH$), 41.3 (C*ipso* on Cp), 65.5 ($(CH_3)_2\mathit{C}H$), 75.4, 77.6 (Cp). ^{29}Si-NMR (δ, CD_2Cl_2): −39.2.

M3. Deep-red solid, (95%), m.p. 92–93°C. Anal. Found: C, 60.05; H, 7.26; Fe, 15.40; Si, 7.95. Calc. for $C_{18}H_{26}Fe_1O_2Si_1$: C, 60.34; H, 7.26; Fe, 15.64; Si, 7.82%. ^{1}H-NMR (δ, CD_2Cl_2): 1.6 (18H, s, tBu), 4.3 (4H, t, Cp), 4.6 (4H, t, Cp). ^{13}C-NMR (δ, CD_2Cl_2): 32.4 ($(\mathit{C}H_3)_3C$), 43.8 (C*ipso* on Cp), 74.3 ($(CH_3)_3\mathit{C}$), 75.3, 76.9 (Cp). ^{29}Si-NMR (δ, CD_2Cl_2): −52.7.

M5. Deep-red solid, (95%), m.p. 45°C. Anal. Found: C, 52.52; H, 5.24; Fe, 17.80; Si, 9.60. Calc. for $C_{12}H_{14}Fe_1O_2Si_1$: C, 52.55; H, 5.11; Fe, 20.44; Si, 10.22%. ^{1}H-NMR (δ, CD_2Cl_2): 3.8 (6H, s, CH_3), 4.2 (4H, t, Cp), 4.6 (4H, t, Cp). ^{13}C-NMR (δ, CD_2Cl_2): 40.4 (C*ipso* on Cp), 50.5 (CH_3), 75.7, 78.3 (Cp). ^{29}Si-NMR (δ, CD_2Cl_2): −31.4

*4.2. Synthesis of polymers **P2** to **P5***

Polymerisation was performed by thermal ROP of the monomers in vacuum-sealed Pyrex tubes. Polymerisation was complete after approximately 1 h. Soxhlet extraction of the dark-red residues using pentane allowed isolation of pure polymers **P2** to **P5** as red–orange powders soluble in polar organic solvents such as THF or methylene chloride.

P2. Polym. temp.: 190°C, $M_w > 360\,000$. Anal. Found: C, 57.51; H, 6.80; Fe, 16.00; Si, 8.70. Calc. for $C_{16}H_{22}Fe_1O_2Si_1$: C, 58.18; H, 6.67; Fe, 16.97; Si, 8.48%. ^{1}H-NMR (δ, CD_2Cl_2): 1.3 (6H, d, CH_3), 4.2 (4H, t, Cp), 4.4 (4H, t, Cp), 4.3 (1H, h, CH). ^{13}C-NMR (δ, CD_2Cl_2): 26.1 ($(\mathit{C}H_3)_2CH$), 65.4 ($(CH_3)_2\mathit{C}H$), 67.5 (C*ipso* on Cp), 72.7, 74.3 (Cp). ^{29}Si-NMR (δ, CD_2Cl_2): −24.8.

P3. Polym. temp.: 230°C, $M_w = 280\,000$; Ip = 1.6. Anal. Found: C, 62.25; H, 7.82; Fe, 15.65; Si, 7.04. Calc. for $C_{18}H_{26}Fe_1O_2Si_1$: C, 60.34; H, 7.26; Fe, 15.64; Si, 7.82%. ^{1}H-NMR (δ, CD_2Cl_2): 1.4 (18H, s, tBu), 4.2 (4H, t, Cp) 4.4 (4H, t, Cp). ^{13}C-NMR (δ, CD_2Cl_2): 32.4 ($(\mathit{C}H_3)_3C$), 71.2 (C*ipso* on Cp), 72.7 ($(CH_3)_3\mathit{C}$), 72.9, 74.6 (Cp). ^{29}Si-NMR (δ, CD_2Cl_2): −36.5.

P4. Polym. temp.: 180°C, $M_w = 290\,000$; Ip = 2.0. Anal. Found: C, 63.47; H, 5.51; Fe, 12.30; Si, 9.70. Calc. for $C_{24}H_{22}Fe_1O_2Si_1$: C, 67.61; H, 5.16; Fe, 13.15; Si, 6.57%. ^{1}H-NMR (δ, CD_2Cl_2): 4.3 (4H, t, Cp), 4.5 (4H, t, Cp), 5.0 (4H, s, CH_2), 7.4 (10H, m, Ph).

^{13}C-NMR (δ, CD_2Cl_2): 65.4 ($C_6H_5CH_2$), 65.9 (C*ipso* on Cp), 72.9, 74.4 (Cp), 126.8, 127.4, 128.6, 141.4 ($C_6H_5CH_2$). ^{29}Si-NMR (δ, CD_2Cl_2): -18.5.

P5. Polym. temp.: 130°C, $M_w = 206\,000$; Ip = 17. Anal. Found: C, 52.52; H, 5.24; Fe, 17.80; Si, 9.60. Calc. for $C_{12}H_{14}Fe_1O_2Si_1$: C, 52.55; H, 5.11; Fe, 20.44; Si, 10.22%. ^{1}H-NMR (δ, CD_2Cl_2): 3.7 (6H, s, CH_3), 4.2 (4H, t, Cp), 4.4 (4H, t, Cp). ^{13}C-NMR (δ, CD_2Cl_2): 51.4 (CH_3), 69.1 (C*ipso* on Cp), 72.2, 73.9 (Cp). ^{29}Si-NMR (δ, CD_2Cl_2): -15.0.

4.3. Non-hydrolytic polycondensation reactions

A typical procedure is described for the case of **GP3Ti**: 0.85 g (2.4×10^{-3} mol) of **P3** and 8 ml of toluene were introduced in a Pyrex tube in an argon atmosphere. A solution of 0.225 g (1.2×10^{-3} mol) of $TiCl_4$ in 2 ml of toluene was rapidly added at 0°C. The reaction mixture was then frozen in liquid nitrogen and the tube sealed under vacuum. The mixture was allowed to melt at room temperature and the tube introduced to an oven at 60°C for 72 h. A solid precipitate formed and was filtered from the mixture. Repeated washing with pentane, acetone and THF allowed isolation of **GP3Ti** as an insoluble dark-brown solid (0.48 g). Anal. Found: C, 34.74; H, 3.97; Fe, 9.85; Si, 10.05; Ti, 9.30 which corresponds to $C_{8.1}H_{11}Fe_{0.5}O_{4.6}Si_1Ti_{0.54}$. Calc. for $C_{10}H_8Fe_1O_2Si_1Ti_{0.5}$: C, 44.78; H, 2.99; Fe, 20.89; Si, 10.45; Ti, 8.95%. ^{13}C-MAS-NMR (δ): 20 to 40; 60 to 80. ^{29}Si-MAS-NMR (δ): -90 to -110. No significant specific surface area.

GM2Si. Reactant:$SiCl_4$ (ratio 2:1). Oven temperature: 110 to 200°C for 10 months. Colour: brown. Anal. Found: C, 44.8; H, 2.07; Fe, 10.25; Si, 17.10; which corresponds to $C_{9.2}H_{5.1}Fe_{0.45}O_{3.9}Si_{1.5}$. Calc. for $C_{10}H_8Fe_1O_2Si_{1.5}$: C, 46.51; H, 3.10; Fe, 21.71; Si, 16.28%. ^{13}C-MAS-NMR (δ): 20 to 40; 60 to 80; 138. ^{29}Si-MAS-NMR (δ): -23; -50 to -70; -85 to -105. No significant specific surface area.

GM4Si. Reactant:$SiBr_4$ (ratio 2:1). Oven temperature: 60°C for 72 h. Colour: brown. Anal. Found: C, 49.21; H, 4.09; Fe, 12.25; Si, 14.70; which corresponds to $C_{11.7}H_{11.7}Fe_{0.6}O_{3.5}Si_{1.5}$. Calc. for $C_{10}H_8Fe_1O_2Si_{1.5}$: C, 46.51; H, 3.10; Fe, 21.71; Si, 16.28%. ^{13}C-MAS-NMR (δ): 60 to 80; 129; 141. ^{29}Si-MAS-NMR (δ): -17 to -29; -50 to -65; -90 to -105. No significant specific surface.

GP3Si. Reactant:$SiBr_4$ (ratio 2:1). Oven temperature: 25°C for 7 h. Colour: brown. Anal. Found: C, 39.04; H, 3.51; Fe: 16.05; Si, 15.15; which corresponds to $C_9H_{9.7}Fe_{0.8}O_{4.6}Si_{1.5}$. Calc. for $C_{10}H_8Fe_1O_2Si_{1.5}$: C, 46.51; H, 3.10; Fe, 21.71; Si, 16.28%. ^{13}C-MAS-NMR (δ): 31. ^{29}Si-MAS-NMR (δ): -65 to -80. No significant specific surface area.

GP3Al. Reactant:$AlCl_3$ (ratio 3:2). Oven temperature: 60°C for 48 h. Colour: grey. Anal. Found: C, 15.95; H, 3.83; Al, 8.70; Fe, 3.20; Si, 20.80; which corresponds to $C_{1.8}H_{5.15}Al_{0.4}Cl_{0.3}Fe_{0.08}Si_1O_4$. Calc. for $C_{10}H_8Al_{0.66}Fe_1O_2Si_1$: C, 45.80; H, 3.05; Al, 6.87; Fe, 21.38; Si, 10.69%. ^{13}C-MAS-NMR (δ): 30; 73. ^{29}Si-MAS-NMR (δ): -85 to -110. ^{27}Al-MAS-NMR (δ): 60; 30; 2. Specific surface area: 87 $m^2\,g^{-1}$.

GP4Si. Reactant:$SiBr_4$ (ratio 2:1). Oven temperature: 25°C for 15 days. Colour: dark brown. Anal. Found: C, 46.31; H, 3.63; Fe, 12.70; Si, 16.80; which corresponds to $C_{10}H_{9.4}Fe_{0.6}O_3Si_{1.5}$. Calc. for $C_{10}H_8Fe_1O_2Si_{1.5}$: C, 46.51; H, 3.10; Fe, 21.71; Si, 16.28%. ^{13}C-MAS-NMR (δ): 60 to 80; 129; 139. ^{29}Si-MAS-NMR (δ): -20 to -30; -55 to -65; -90 to -105. Specific surface area: 20 $m^2\,g^{-1}$.

4.4. Hydrolytic polycondensation reactions

In a classic procedure, a 0.5 M THF solution of polymer was prepared and the catalyst and water added rapidly. The reaction mixture was stirred for some minutes for homogeneity and the solution was then allowed to stand until an insoluble precipitate was observed and the initial red solution faded. The solid was recovered by simple filtration and was cleaned by repeated washing with water, ethanol, acetone and ether. Any remaining starting material was removed by Soxhlet extraction using THF, although no coloration of the solvent was usually observed.

GP2H. Catalyst:TBAF 3%. **P2**:H_2O ratio, 1:15. Time: 5 days. Colour: orange. Anal. Found: C, 50.75; H, 3.51; Fe, 24.10; Si, 14.20; which corresponds to $C_{8.3}H_{6.9}Fe_{0.85}O_{0.9}Si_1$. Calc. for $C_{10}H_8Fe_1OSi_1$: C, 52.63; H, 3.51; Fe, 24.56; Si, 12.28%. ^{13}C-MAS-NMR (δ): 73. ^{29}Si-MAS-NMR (δ): -31.

GP4H. Catalyst:TBAF 10%. **P4**:H_2O ratio, 1:15. Time: 1 week. Colour: orange. Anal. Found: C, 50.61; H, 3.83; Fe, 23.40; Si, 14.70; which corresponds to $C_8H_{7.3}Fe_{0.8}O_{0.9}Si_1$. Calc. for $C_{10}H_8Fe_1OSi_1$: C, 52.63; H, 3.51; Fe, 24.56; Si, 12.28%. ^{13}C-MAS-NMR (δ): 68 to 72. ^{29}Si-MAS-NMR (δ): -30.

GP5H. Catalyst:TBAF 10%. **P5**:H_2O ratio, 1:1. Time: 1 h. Colour: orange. Anal. Found: C, 52.34; H, 3.74; Fe, 22.00; Si, 13.5; which corresponds to $C_{9.05}H_{8.75}Fe_{0.8}O_{1.1}Si_1$. Calc. for $C_{10}H_8Fe_1OSi_1$: C, 52.63; H, 3.51; Fe, 24.56; Si, 12.28%. ^{13}C-MAS-NMR (δ): 65 to 80. ^{29}Si-MAS-NMR (δ): -30.

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