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Factors influencing the electroreductive polymerization of di-*n*-hexyldichlorosilane

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This paper reports the study of the effects of solvent, support electrolyte and the nature of the electrodes on the electroreduction of di-*n*-hexyldichlorosilane. The work performed involved the use of different types of sacrificial anode (magnesium, aluminium and zinc) and cathode (magnesium, aluminium, zinc, stainless steel, nickel, carbon and palladium) in tetrahydrofuran containing lithium perchlorate ($LiClO_4$). Monomodal poly(di-*n*-hexyldichlorosilane) was obtained with Al/Al and Mg/Mg electrode pairs, but the polymer yield was about ten times higher with Al/Al (11%) than with Mg/Mg (1%). From the solvents and co-solvents used (tetrahydrofuran, hexamethylphosphorotriamide, acetone, hexane, toluene, 1,1,3,3-tetramethylurea, tris(3,6-dioxaheptyl)amine, 1,2-dimethoxyethane, *N,N*-dimethylacetamide and dimethylformamide) with $LiClO_4$, only the system tetrahydrofuran + hexamethylphosphorotriamide, tetrahydrofuran + *N,N*-dimethylacetamide and tetrahydrofuran + toluene have given monomodal poly(di-*n*-hexyldichlorosilane) using an aluminium anode and stainless-steel cathode. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: electroreduction; di-*n*-hexyldichlorosilane; poly(di-*n*-hexyldichlorosilane); sacrificial anode; organic media

Polyorganosilanes are polymers whose structures are characterized by having silicon atoms connected by covalent bonds. Interest in them by the scientific community is related to the particular properties proceeding from σ-electron displacement in the polymer backbone.[1–3] So, technological applications of these polymers in electronics,[1,2,4] photocondutive systems[5] and non-linear optics[6] have been developed. Moreover, in the case of polysilenes several applications have been found, in particular as precursors for Si–C ceramics[7,8] and as photoinitiators for radical polymerization.[1,9]

Polyorganosilanes may be synthesized by four methods: (1) reductive coupling of the Würtz-type;[1,2] (2) dehydrogenative coupling;[10–16] (3) anionic polymerization of disylenes;[17] (4) polymerization of strained cyclic compounds.[18] The Würtz-type condensation of organodichlorosilanes is still the most commonly used chemical pathway for the preparation of high-molecular-weight polymers, but, unfortunately, polymodal molecular weight distributions and low yields are obtained.[1–3,5–7] In spite of some improvements in the Würtz coupling,[17,19–21] this process is limited: reactions involving the use of alkali metals are dangerous at high temperatures; the molecular weight distributions of the polymers obtained are often polymodal and the yield and reproducibility of the synthesis are poor.

Electroreductive synthesis for the formation of C–C,[22] Si–Si[6,23–27] and Ge–Ge[28–30] bonds using sacrificial anodes at room temperature has been proposed as an alternative polymerization pathway. Some researchers have successfully applied this technique to obtain polyorganosilanes[6,23–27] and also polyorganogermanes.[29,30] In the case of di-*n*-hexyldichlorogermane a relatively high-molecular-weight polymer distribution with monomodal molecular weight is obtained in good yield in a tetrahydrofuran (THF)/hexamethylphosphorotriamide (HMPA) mixture with stainless steel as cathode and aluminium as anode.[30]

The goal of this work is to study the effects of different factors that could influence the electropolymerization of di-*n*-hexyldichlorosilane (DHDCS): *viz*. the nature of the metal

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electrodes (sacrificial anode and cathode), the solvent/co-solvent combination and the electrolytic media on the coupling process. The choice of di-*n*-hexyldichlorosilane as monomer also seeks to analyse the effect of the presence of the hexyl group on the polymerization reaction, since previous work done with other silanes yields reticulated polymers and or polymers of small chain length.[26,31]

EXPERIMENTAL

Reagents and solvents

DHDCS monomer (ABCR society, >96%) was distilled under reduced pressure (0.5 mmHg) with magnesium and alumina to eliminate HCl and it was kept under argon with magnesium and alumina, for water elimination. THF (Prolabo Rectapur) was treated with potassium hydroxide (KOH) for 24 h, and then distilled over calcium hydroxide (CaH_2) under dry argon prior to use. HMPA was purchased from Prolabo and distilled over neutral alumina under argon. The co-solvents used were: *N,N*-dimethylacetamide (DMA; Aldrich, >99%), 1,1,3,3-tetramethylurea (TMU; Aldrich, >99%), dimethylformamide (DMF; Ventron, >99%), tris(3,6-dioxaheptyl)amine (TDA-1; Acros, >98%); all them were dried over neutral alumina. 1,2-Dimethoxyethane (DME) was bought in a sealed glass bulb under argon (Fluka, >99.5%). Lithium perchlorate ($LiClO_4$, Acros, >99%) and the tetrabutylammonium bromide (Bu_4NBr; Janssen, >99%) were dried under dynamic vacuum at 60 °C for 24 h.

Electrochemical apparatus and instrumental analyses

A single-compartment closed cell equipped with two electrodes was used to carry out the electropolymerization reaction. Electrolysis at constant current was performed with a PAR Model 273 potentiostat/galvanostat. Different types of electrode were used, such as a stainless-steel grid (Weber), a zinc rod 1 cm in diameter (Prolabo Rectapur), a magnesium rod 6 mm in diameter (Aldrich, >99%), an aluminium rod 12.7 mm in diameter (Alfa, >99%), a palladium sheet 0.127 mm in thickness by $50 \times 50\ mm^2$ (Aldrich, >99.9%), Lorraine carbon fibres with diameter of the order of micrometres (RVC, 94–97%), and nickel sheet 0.125 mm in thickness by $150 \times 150\ mm^2$ (Aldrich, >99.9%). All these electrodes were cleaned with 0.6 M hydrochloric acid, rinsed in water several times, then in THF, and dried at about 100 °C. Aluminium was polished mechanically with a wire brush and rinsed in the same way. The chemical yield R_c is defined as the ratio of the number of reacted moles of monomer to the number of initial moles of monomer, whereas the current yield R_e is defined as the ratio of the expended quantity of electricity to the charge equivalent to the number of initial moles of monomer.

Cyclic voltammograms were obtained in THF containing 0.3 M $LiClO_4$. The small electrodes ($2.5 \leq d \leq 5$ mm) used for the measurements were systematically polished with 3 μm diamond paste before every run. A stainless-steel grid was used as counter electrode and a silver wire previously oxidized by electrolysis to silver chloride (AgCl) in hydrochloric acid was used as a reference electrode. The scan rates used in the cyclic voltammetry were chosen to show the reduction waves of DHDCS and of eventual impurities in solution.

Electronic absorption spectra were recorded in THF solution with a Varian DMS 200 UV–Vis spectrometer. Raman spectra were recorded in the backscattering configuration with a Dilor XY double-monochromatic spectrometer in the subtractive mode equipped with multichannel detection (1024 diodes cooled by Peltier effect) and working with an excitation wavelength of 514.53 nm. IR spectra were registered with a Nicolet 605 X FTIR spectrometer in the transmission mode with the polyorganosilane between two NaCl plates. X-ray photoelectron spectroscopy (XPS) analysis was carried out with a VG Escalab MKI spectrometer (Mg Kα source, 50 eV pass energy, pressure *ca* 10^{-9} mbar). Molecular weights were measured by gel permeation chromatography (GPC) in THF using a Waters 746 GPC equipped with a Chrompack high-performance liquid chromatography column (microgel 5 mixed) with refractive index and Model 486 UV detectors. Molecular weights were determined by comparison with polystyrene standards. Fluorescence spectra were registered with a Perkin–Elmer model LS 50 spectrofluorimeter equipped with a xenon lamp.

Electropolymerization procedure

The monomer DHDCS (0.15 M) was added to different solutions in the presence of 0.3 M $LiClO_4$ in undivided cells. Each solution was purged with dry argon for 30 min before electrolysis and then the cell was kept under a small pressure of dry argon. Polymerization was performed in galvanostatic mode, and the solution was magnetically stirred during electrolysis. After completion of the reaction, the resulting solution was filtered and the filtrate poured into a 500 ml water–ethanol mixture (50:50, v/v) to obtain the polymer; in order to eliminate impurities the polymer was dissolved twice in THF and precipitated; the solid was then dried under vacuum at room temperature for 24 h before analysis.

RESULTS AND DISCUSSION

Reductive cleavage of the silicon–halogen bond

The voltammograms, obtained with a potential sweep range of 0 to −4 V versus Ag/AgCl on cathodes of platinum, aluminium and vitreous carbon in THF containing 0.3 M $LiClO_4$, are shown in Figs 1–3. Results on the first two electrodes show that there is a discharge from −3.2 V versus Ag/AgCl that is attributed to the reduction of the Li^+ cation on the cathode. On the reverse sweep the voltammograms of these electrodes show the following: on platinum, an oxidation peak near −2.4 V versus Ag/AgCl related to the

Figure

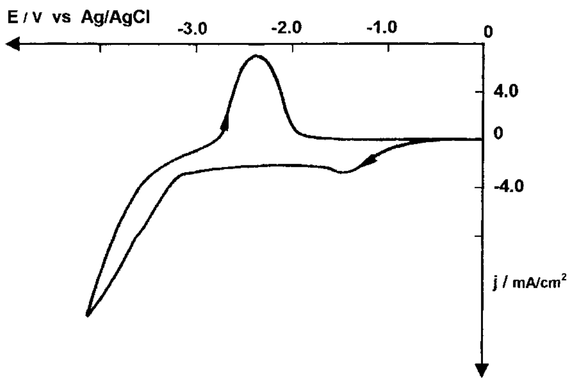

Figure 1. Cyclic voltammogram at a platinum electrode ($d = 2.5$ mm) in THF + 0.3 M $LiClO_4$ versus Ag/AgCl with a scan rate of 70 mV s^{-1}.

oxidation of the lithium: on aluminium, a progressive oxidation wave with a small inflection connected to the reduction of the lithium ion and a peak with a potential of −1.45 V versus Ag/AgCl due to the oxidation of the aluminium. In the case of a vitreous carbon cathode the voltammogram is quite different. Only a reduction wave is observed from −2.5 V versus Ag/AgCl, probably linked with the formation of LiH ($E^{\circ}_{\mathrm{LiH/Li^+}} = -2.33$V versus NHE). The source of the hydrogen is probably traces of water or HCl present in the electrolyte or monomer. Voltammograms of the DHDCS achieved without distillation of monomer (Fig. 4) show two successive reduction waves, which are not recorded using distilled material (see Fig. 3b). In this case there is only the one peak observed at −2.6 V versus Ag/AgCl and related to the reduction of the monomer.

The whole of the electrochemical trials show that it is possible to achieve a macroelectrolysis of DHDCS by using a renewable alkali-metal electrode, such as lithium in the presence of the corresponding lithium salt. In this case the process has several advantages. Firstly, the chemical electron transfer that occurs between the metal and the Si—Cl bond is kinetically controlled and is electrochemically assisted by the high negative reduction potential of lithium. Secondly, by using an alkali metal as cathode an anhydrous medium must be used. Since $LiClO_4$ is highly soluble in ethers, THF was chosen as solvent.

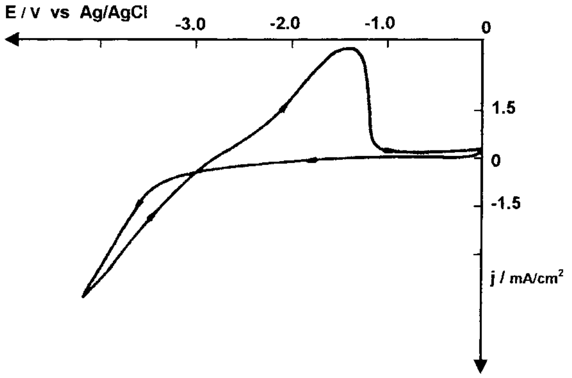

Figure 2. Cyclic voltammogram at an aluminium electrode ($d = 5$ mm) in THF + 0.3 M $LiClO_4$ versus Ag/AgCl with a scan rate of 70 mV s^{-1}.

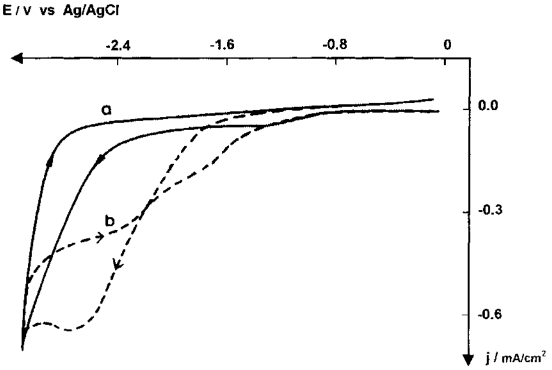

Figure 3. Cyclic voltammogram at a vitreous carbon electrode ($d = 3$ mm) versus Ag/AgCl with a scan rate of 100 mV s^{-1}: (a) THF + 0.3 M $LiClO_4$; (b) THF + 0.3 M $LiClO_4$ + DHDCS (10^{-3} M).

Solvent and co-solvent effect on electropolymerization

The study in polar solvents was performed with an anode of aluminium and a cathode of stainless steel using $LiClO_4$ (0.3 M) as support electrolyte, aiming to determine the effect of solvent polarity on the degree of electropolymerization.

The results of the electroreduction of DHDCS in different organic media are summarized in the Table 1. The data depicted show that the use of THF as solvent results in the formation of a polymer of relatively low molecular weight

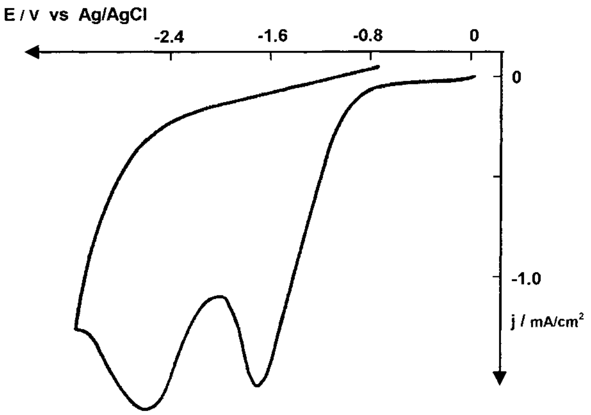

Figure 4. Cyclic voltammogram at a vitreous carbon electrode ($d = 3$ mm) in THF + 0.3 M $LiClO_4$ + DHDCS (3.6×10^{-3} M) versus Ag/AgCl with a scan rate of 500 mV s^{-1} in the presence of traces of HCl.

Table 1. Electroreductive polymerization of DHDCS (0.15 M) using an aluminium anode and a stainless-steel cathode (18 cm^2) in several solvent mixtures in the presence of $LiClO_4$ (0.3 M)

Solvent	j (mA cm^{-2})	Q (C)	λ_{max} (nm)	M_w	M_n	M_w/M_n	DP	R_e (%)	R_c (%)
THF	2.7	1224	308	3250	–	–	16	56	48
				1100			6		
THF + HMPA	3.8	881	308	1752	701	2.5	9	34	21
THF + acetone	5.5	2310	–	–	–	–	–	–	–
THF + DMA	5.5	2222	308	4870	1624	3	25	22	34
			363						
THF + hexane	5.5	1886	241	–	–	–	–	–	–
			316/364						
THF + toluene	5.5	1875	312	1117	692	1.6	6	7	9
THF + TMU	5.5	1860	275	–	–	–	–	–	–
THF + TDA-1	2.7	1170	312	3250	–	–	16	34	28
				2350			12		
				1000			5		
THF + DME	2.2	779	311	–	–	–	–	–	–
			364						
THF + DMF	3.3–1.4	961	315	–	–	–	–	–	–
			364						

with bimodal distribution (M_w = 3250 and 1100), exhibiting an absorption band at around 308 nm. The chemical (R_c) and current (R_e) yields are respectively 48% and 56%. In the case of mixtures composed essentially of THF (80% by volume) and of a co-solvent less basic than THF (in agreement with the scale of Gutmann[32]), the electropolymerization is strongly inhibited. Conversely, co-solvents more basic than THF, such as mixtures of THF + HMPA, THF + DMA or THF + TDA-1, lead to results similar to those obtained in pure THF.

The electroreduction of DHDCS in pure THF results in the production, from time to time, of small amounts of polytetrahydrofuran (PTHF) as an impurity. In this case, the electrolytic solution becomes quite viscous and the formation of large amounts of salts is observed near the electrodes. Therefore, the precipitate product of the solution has a viscous aspect, or that of a foam, and it stays strongly adhered to the walls of the reactor. This side-product could be the result of a cationic polymerization of THF due to the presence of intermediate electrophilic species, such as $AlCl_2^+$,arising from the ionization of $AlCl_3$ according to the following equilibrium:[26,33–36]

$$2AlCl_3 \rightleftharpoons AlCl_2{}^+ + AlCl_4{}^- \tag{1}$$

or caused by the action of the protons formed by hydrolysis of $AlCl_3$ according to:

$$H_2O + AlCl_3 \rightleftharpoons AlCl_3OH^- + H^+ \tag{2}$$

It should be noted that the use of co-solvents such as HMPA or DMA prevents the formation of PTHF. HMPA and DMA are basic and strongly polar solvents, which explains their capacity to neutralize the acidic species formed from the reaction shown by Equation (2).

Effect of the support electrolyte on electropolymerization

The electropolymerization of DHDCS has been carried out in THF or THF + HMPA (80:20 v/v), on a cathode of stainless steel with an anode of aluminium, using $LiClO_4$ (0.3 M) or Bu_4NBr (0.2 M) as support electrolytes, as indicated in Table 2. In a THF medium the $LiClO_4$ has a better performance compared with Bu_4NBr, in spite of the bimodal distribution of the polymer. Conversely, in THF + HMPA media the best support electrolyte is Bu_4NBr. Here, the polymer has a high molecular weight (M_w = 8500), with a monomodal distribution (M_w/M_n = 1.5). On the other hand, when the electrolyte is $LiClO_4$ there is the production of oligomers (M_w = 1752). For both electrolytic media R_e and R_c are identical.

The use of $LiClO_4$ as electrolyte in an organic solvent leads to unusual electrochemical behaviour. Indeed, any electroactive compound with a thermodynamic redox potential more positive than that of Li^+ will be reduced at the same potential as Li^+. This is due to the fact that the surface of the cathode is first passivated by a thin adherent insulating Li_2O layer, which forms at about -1.5 V versus Ag/$AgNO_3$ (10^{-2} M), and at moderate negative potentials prevents electron transfer from occurring.[37,38] Electron transfer happens (probably by tunnelling through the insulating layer) only at very negative potentials, and both Li^+ and the electroactive compounds are reduced at the same time. This explains why the voltammetric reduction curves of DHDCS in a solution of 0.3 M $LiClO_4$ in THF on metal cathodes (Figs 1

Table 2. Electroreductive polymerization of DHDCS (0.15 M) using an aluminium anode and a stainless-steel cathode (18 cm^2) in an organic medium with two different support electrolytes

Solvent	Support electrolyte	j (mA cm^{-2})	Q (C)	λ_{max} (nm)	M_w	M_w/M_n	DP	R_e (%)	R_c (%)
THF	$LiClO_4$	2.7	1224	308	3250	–	16	56	48
					1100		6		
THF + HMPA	$LiClO_4$	3.8	881	308	1752	2.5	9	34	21
THF	Bu_4NBr	2.7	1125	308	1300	–	7	36	28
THF + HMPA	Bu_4NBr	2.7	1095	312	8500	1.5	43	21	16

and 2) do not exhibit a well-defined reduction wave between 0 and −3.2 V versus Ag/AgCl, but only a discharge curve corresponding to a mixed reduction of Li^+ and DHDCS. Consequently, the silicon compound can be chemically reduced by lithium metal according to the reaction:

$$Li + SiCl_2Hex_2 \rightarrow Li^+ + [SiCl_2Hex_2]^{\bullet -} \quad (3)$$

or it can be electrochemically reduced on the lithium electrode, considered as an inert metal, following the electrochemical step:

$$SiCl_2Hex_2 + e^- \rightarrow [SiCl_2Hex_2]^{\bullet -} \quad (4)$$

In both cases the current yield would be the same, and probably a mixed mechanism would occur.

The use of Bu_4NBr as support electrolyte with THF + HMPA is not advisable, despite the fact that it favours the electropolymerization of DHDCS to give a polymer of high molecular weight with a monomodal distribution. Effectively, a little time after the beginning of the electropolymerization the cathode passivates and the process stops. We think that this phenomenon is related to the adsorption and consequent interaction of the support electrolyte with the cathode surface. So, the yields in Table 2 have been calculated until the onset of passivity.

Effect of the nature of the metal electrode on electropolymerization

THF, a good solvent for anionic polymerization, was chosen as a standard to evaluate the feasibility of the polymerization of DHDCS with 0.3 M $LiClO_4$ at different metal electrodes. Magnesium, aluminium and zinc were used as the sacrificial anode and stainless steel, magnesium, palladium, aluminium, carbon, nickel and zinc as the cathode (see Table 3). From the various metal combinations used as electrodes, it seems that a sacrificial aluminium anode associated with a palladium cathode leads to a poly(di-*n*-hexyldichlorosilane) (PDHDS) with the highest molecular weight and the highest yield ($R_c = 96\%$) but with a trimodal distribution (M_w = 11500, 3200, 1200). This behaviour may be related to the catalytic properties of palladium. By maintaining the alu-

Table 3. Electroreductive polymerization of DHDCS (0.15 M) in THF containing $LiClO_4$ (0.3 M) using several electrodes

Cathode	Anode	j (mA cm^{-2})	Q (C)	λ_{max} (nm)	M_w	DP	M_w/M_n	R_e (%)	R_c (%)
Al	Al	4.9	2340	312	8410	42	3	11	7
					11 500	58			
					3200	16			
Pd	Al	2.3	1119	312	1200	6	–	75	96
Mg	Mg	3.2	513	316	9320	47	1.5	1	3
					5700	29			
					1510	8			
Stainless steel	Mg	2.7	1115	320	780	4	–	3	4
Stainless steel	Zn	2.7	1210	277	–	–	–	–	–
					3250	16			
Stainless steel	Al	2.7	1224	308	1100	6	–	48	56
					3200	16			
C	Al	5.6	1170	306	1000	5	–	34	42
					3250	16			
Ni	Al	2.7	1266	309	1100	6	–	48	54
					6000	30			
Zn	Al	4.8	1125	314	1200	6	–	25	32

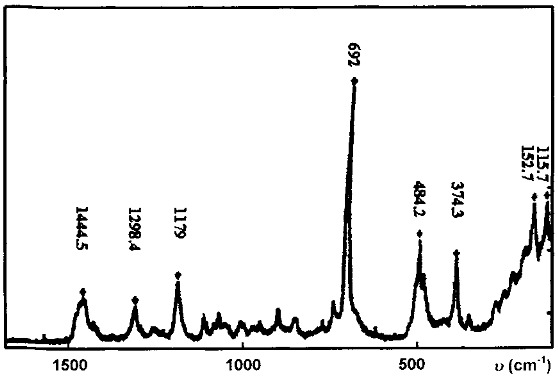

Figure 5. Raman spectrum of PDHDCS in THF at room temperature.

minium as anode and changing the cathode, the molecular weight is substantially reduced and has a bimodal distribution, and the cathodic yield decreased to about half. With the Al/Al or Mg/Mg electrode pairs, high-molecular-weight polymers were obtained, being respectively 8410 Da and 9320 Da, but the cathodic yields were smaller. In the case of the Mg/Mg electrode pair the low yield is probably due to passivating layers that form on either the cathode or the anode. Recently, ultrasonic activation was used in conjunction with magnesium electrodes and was found to give polyorganosilanes with good yields.[39] Since no passivity effects were marked, it is reasonable to consider that ultrasonic stirring cleans the electrode surface and, consequently, allows electrolysis to run smoothly. However, the ultrasonic vibrations have an adverse effect on the polymerization steps and, consequently, the final polymers do not have high molecular weights. It seems that Al/Al is the best electrode combination, yielding a polymer with a single absorption band at about 312 nm and a low polydispersity ($M_w/M_n = 3$).

From the mechanism expressed by Equations (3) and (4) it might be thought that the reduction of DHDCS would not depend on the nature of the metal when using $LiClO_4$ as support electrolyte. This is not true, as is shown by the marked differences in the polymer yield observed with various metallic cathodes for the same anode metal. So, it is reasonable to accept that, depending on the nature of the underlying metal, different lithium–metal alloys can be formed[40] on the cathode and distinct catalytic effects can be expected. In particular, the steps taking place after the formation of $[SiCl_2Hex_2]^{\cdot-}$, which lead to different transient species $[SiClHex_2]^{\cdot}$ and $[SiClHex_2]^-$ could be distinctly favoured.

Structure and electronic properties of the polyorganosilanes

IR, Raman, UV, GPC and XPS were used to characterize the products of the electropolymerization of DHDCS.

Using GPC, the number-average molecular weight M_n was determined and was found to range from 780 to 11500 (Tables 1–3), corresponding to a degree of polymerization (DP) of 4 to 58 dihexylsilane units.

IR analyses showed several absorption bands between 3000 and 600 cm^{-1} corresponding to vibration bands of CH_3 (2960 and 1379 cm^{-1}), CH_2 (2920 and 1470 cm^{-1}), and Si–C (under 700 cm^{-1}). These results are very similar to those of Würtz coupling polymerization.[1,40]

The Raman spectrum of the poly(di-*n*-hexylsilane) (PDHDS) (Fig. 5) is very similar to that of PDHDS obtained by Würtz coupling polymerization at low temperature.[39] Several sharp, strong bands in the low-frequency region (below 700 cm^{-1}), characteristic of the vibrations of Si–Si and Si–C bonds, confirm the presence of a highly ordered structure corresponding to the planar zigzag conformation.

UV spectroscopy of the polymer carried out in THF at room temperature shows a symmetrical weak absorption band at 328 nm (Fig. 6), in agreement with the literature data for the same polymer also supporting a planar zigzag conformation.[2,6,40]

Using fluorescence spectroscopy of the polymer in THF, the excitation spectra (Fig. 7) show a thin band at about 328 nm similar to that obtained by UV spectrocospy, whereas the emission spectra has a band at about 356 nm (Fig. 6). The intensity of the peaks of the two spectra have a difference of the order of 15%, which is attributed to the degradation of the polymer by the radiation.[41–43] The evaluation of the intensity of the peak ($\lambda = 356$ nm) with time (Fig. 8), in emission spectra using a solution of PDHDS (0.9×10^{-5} M), shows an exponential decrease that confirms the last hypothesis. This behaviour has already been observed in the case of polymethylphenylsilanes.[43]

The polymer structures were also characterized by XPS. No traces of oxygen or chlorine were detected, only signals of carbon and silicon were observed. As shown in Figure 9b, the C 1s peak at 285 eV is symmetrical and corresponds to

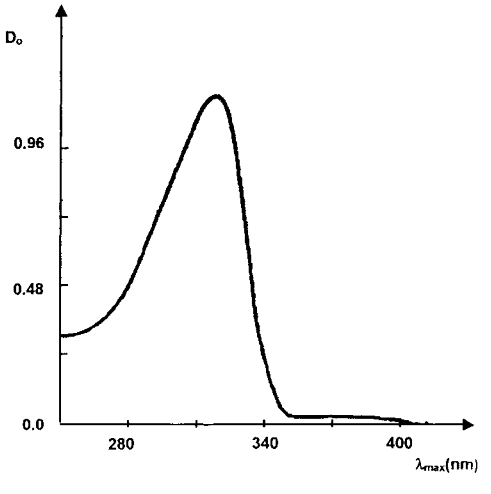

Figure 6. UV absorption spectrum of PDHDCS in THF at room temperature.

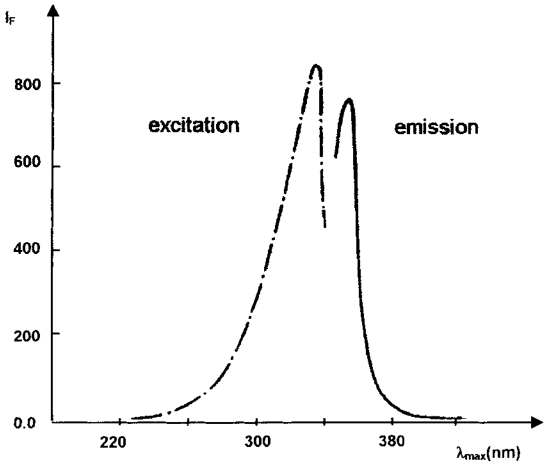

Figure 7. Excitation and emission of fluorescence spectra of PDHDCS in THF at room temperature.

C—C and C—H groups of the side chain (hexyl). The Si 3d symmetrical signal at 102 eV corresponds to an Si—Si bond (Fig. 9a). The absence of chlorine shows that the Si—Cl bonds have been broken to give the desired Si—Si bonds.

CONCLUSIONS

Electroreductive polymerization of DHDCS is achieved by constant-current electrolysis, but the yields and the polymodal distribution are strongly dependent on the solvent, on the electrolytic media and also on the nature of the cathode and the sacrificial anode. The reaction is particularly sensitive to the presence of traces of water, since that permits the production of HCl from the hydrolysis of DHDCS. That compound contributes to secondary reactions, an example being the formation of PTHF in THF + $LiClO_4$ medium, that hinder the propagation of the polymerization reaction. HMPA or DMA, being strong basic solvents, avoid this parasitic reaction, since they neutralize the acid species developed in the system that is responsible for the production of PTHF.

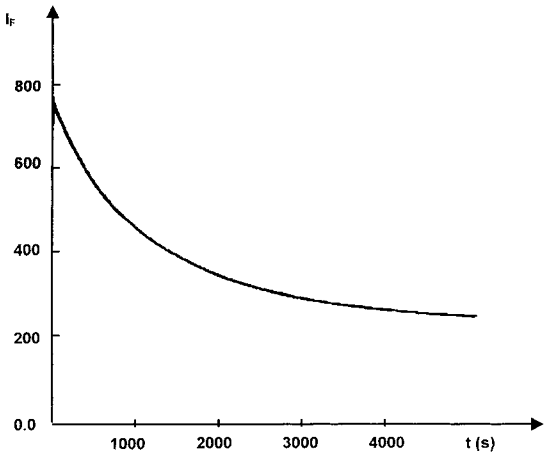

Figure 8. Evolution of the intensity of the peak (λ = 356 nm) with the time in an emission fluorescence spectrum of PDHDCS in THF at room temperature.

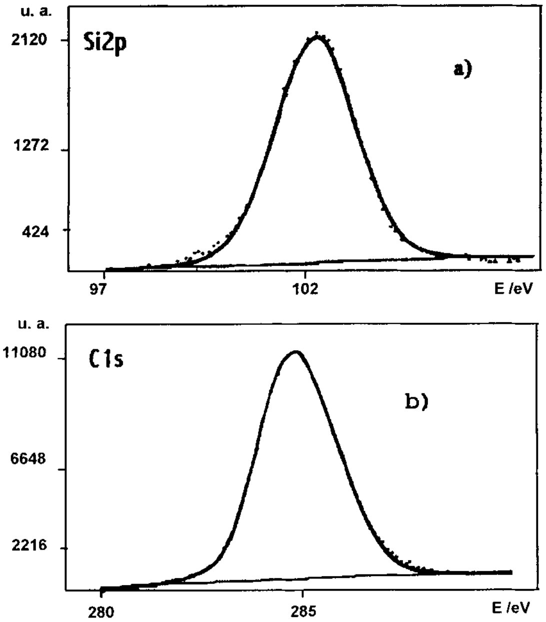

Figure 9. XPS spectra of PDHDCS in THF at room temperature: (a) Si 2p region; (b) C 1s region.

The deposition of lithium on the cathode can have a catalytic effect equivalent to an increase in the current density, contributing also to the production of anionic species of silicon, which supports an anionic polymerization.

The hexyl group allows the production of linear polymers of high molecular weight, which can be attributed to the greater flexibility of the intermediate radical.

From the results achieved it becomes clear that a new pathway to research is opened: the polymerization of DHDCS with an Al/Al pair of electrodes using THF as solvent and DMA as co-solvent and $LiClO_4$ as a supporting electrolyte.

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