APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 11, 583–589 (1997)

Factors Influencing the Synthesis of Polyorganogermanes by Electroreductive Coupling of Di-n-hexyldichlorogermane

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The effects of the nature of the electrodes (sacrificial anode and cathode) and of the solvent on the electroreduction of di-n-hexyldichlorogermane have been investigated. Several sacrificial anodes (magnesium, zinc and aluminium) and cathodes, including stainless steel, magnesium and aluminium, have been used in THF containing $LiClO_4$. Monomodal and polymodal poly(di-n-hexylgermanes) were obtained with Al/Al and Mg/Mg electrode pairs, but the polymer yield was about twice as high with Al/Al (64%) as with Mg/Mg (30%). Various solvents (tetrahydrofuran, hexamethylphosphorotriamide, *N*,*N*-dimethylacetamide, acetonitrile and dimethylformamide) with $LiClO_4$ have been used as electrolytic media. Monomodal PDHG with a relatively narrow molecular weight distribution ($[M]_w/[M]_n = 1.6$) was obtained only in THF/HMPA with Al/stainless steel electrodes. © 1997 by John Wiley & Sons, Ltd.

Appl. Organometal. Chem. **11**, 583–589, (1997)

No. of Figures: 3 No. of Tables: 2 No. of Refs: 38

Keywords: electroreduction; di-n-hexyldichlorogermane; poly(di-n-hexylgermane); sacrificial anode; organic media

Received 4 July 1996; accepted 13 November 1996

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INTRODUCTION

In recent years a considerable effort has been directed towards the study of the chemical and physical properties of polysilanes and polygermanes,[1–8] and the search for high-yield synthetic pathways[9–23] for obtaining high-molecular-weight polymers with well-defined structure (monomodal molecular weight distributions).

Owing to the σ-electron delocalization in the polymer backbone these polymers have interesting properties which could lead to technological applications in electronics,[24, 25] photoconductive systems[26] and non-linear optics.[6, 8, 27, 28] In the case of polysilylenes, which were more extensively studied, several practical applications have been found, in particular as precursors for Si–C ceramics,[29, 30] and initiators for radical polymerization.[31]

Polyorganosilanes and polyorganogermanes are generally synthesized by Wurtz-type condensation of organodichlorosilanes and organodichlorogermanes. The reaction is carried out in the presence of an alkali-metal dispersion in toluene at reflux temperature.[1–5] This synthetic method is still the most convenient chemical pathway for the preparation of high-molecular-weight polymers but, unfortunately, polymodal molecular weight distributions and low yields are obtained.[1–5]

Recently, a modification of the Wurtz coupling reaction was reported.[9, 14, 16, 17, 21] The reductive coupling of methylphenyldichlorosilane with a sodium dispersion at low temperature in toluene, either in the presence of dipolar additives such as diglyme, crown ethers, etc.[9,14,17] or using high-intensity ultrasonic activation,[21] was found to lead to improved polydispersity of the polymers.

In spite of these new developments in the Wurtz coupling the method of polymerization is

 CCC 0268–2605/97/070583–07 $17.50

still limited by the drastic reaction conditions involving the use of alkali metals which are relatively dangerous to handle at high temperatures. Moreover, the molecular weight distributions of the polymers obtained in this way are often polymodal, and the yield and the reproducibility of the synthesis are still poor.

Electroreductive synthesis for the formation of C–C,[32] Si–Si[10, 11, 19, 20, 33, 34] and Ge–Ge bonds[11, 12] using sacrificial anodes at room temperature has been proposed as an alternative polymerization pathway. We[12] and others[10, 11, 33] have successfully applied this technique to obtain polyorganosilanes[10, 11, 33] and polyorganogermanes.[12] We found in the case of di-n-butyldichlorogermane that the polymers usually had a monomodal molecular weight distribution but were obtained in moderate yields.[12]

It is the purpose of this work to study the effects of different factors which could influence the electropolymerization process. The nature of the metal electrodes (sacrificial anode and cathode) and of the solvent are the most important parameters in the coupling process.

EXPERIMENTAL

Reagents and solvents

Di-n-hexyldichlorogermane monomer was prepared as described previously[34] and kept under argon in a sealed glass bulb (2 ml). Tetrahydrofuran (THF; Prolabo Rectapur) was treated with KOH for 24 h, and then distilled over CaH_2 under dry argon prior to use. Hexamethylphosphorotriamide (HMPA) was purchased from Prolabo and distilled over neutral Al_2O_3 under argon. *N*,*N*-Dimethylacetamide (DMA) and 1,1,3,3-tetramethylurea (TMU) were obtained from Aldrich (>99%) and dried over neutral Al_2O_3. Lithium perchlorate (Acros, >99%) was dried under dynamic vacuum at 60 °C for 24 h.

Electrochemical apparatus and instrumental analyses

An undivided closed cell equipped with two electrodes was used to carry out the electropolymerization reaction. Electrolysis at constant current was performed with a PAR Potentiostat/Galvanostat Model 273. Several electrodes were used, including a stainless steel grid (Weber), a zinc rod 1 cm in diameter (Prolabo Rectapur), a magnesium rod 6 mm in diameter (Aldrich, >99%), and an aluminium rod 12.7 mm in diameter (Alfa, >99%).

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.

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-monochromator spectrometer in the subtractive mode equipped with multichannel detection (1024 diodes cooled by the Peltier effect) and working with an excitation wave-

Table 1 Electroreductive polymerization of di-n-hexyldichlorogermanes in 50 ml THF containing $LiClO_4$ (0.3 M) using various electrodes

Cathode	Anode	I (mA)	Q (C)	λ_{max} (nm)	$[\bar{M}_w]$	$[\bar{M}_n]$	DP	Yield (%)	$\frac{[\bar{M}_w]}{[\bar{M}_n]}$	A[a] (cm^2)
Stainless steel	Mg	50	1403	—	713	391	3	—	1.8	18.0
Stainless steel	Zn	50	1170	—	580	—	—	—	—	18.0
Stainless steel	Al	50	1080	328	7700	1250	32	60	6	18.0
Mg	Mg	50–30	634	310	11000	—	45	30	—	15.4
Mg	Al	40–11	534	—	—	—	—	—	—	15.4
Al	Mg	50–25	630	—	—	—	—	—	—	10.2
Al	Al	50	1125	329	11814	3231	49	64	3.6	10.2

[a] Apparent area of cathode.

length of 514.53 nm. IR spectra were registered with a Nicolet 605 X FTIR spectrometer in the transmission mode with the polyorganogermane between two NaCl plates. XPS analysis was carried out with a VG Escalab MKI spectrometer (MgKα 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 HPLC column (microgel 5 mixed) with refractive index and Model 486 UV detectors. Molecular weights were determined by comparison with polystyrene standards.

Electropolymerization procedure

In general, di-n-hexyldichlorogermane (DHCG) (2 ml, 6.4 mmol) was added to the different solutions (see Table 2) in the presence of 0.3 M $LiClO_4$ in an undivided cell. Each solution was bubbled 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 the galvanostatic mode, and the solution was magnetically stirred during electrolysis. After reaction, the resulting solution was poured into 500 ml of a water–ethanol mixture (50:50, v/v); the precipitated polymer was dried under vacuum at room temperature for 24 h before analysis.

RESULTS AND DISCUSSION

Problems encountered in the electropolymerization procedure

Since germanium is more electropositive than carbon it might be thought that electroreduction of a Ge–Cl bond would be easier than that of the C–Cl bond. Consequently, the electroreductive breaking of the Ge–Cl bond would occur on a solid cathode polarized at a fixed potential. Unfortunately, except in the case of the mercury-drop electrode, for which the surface is renewable,[35] all the voltammograms obtained on different solid metal electrodes with different salts were irreversible. In particular, with $LiClO_4$ as electrolyte, strong passivation of the surface occurred which excluded any possibility of achieving a macroelectrolysis of organodichlorogermanes at fixed potentials between 0 and -3.5 V.

One way to overcome this difficulty consists in using a renewable alkaline-metal electrode such as sodium or lithium in the presence of the corresponding sodium or lithium salt and to carry out the electrolysis at constant current. It is well known that applying a cathodic current or a very negative reducing potential in an organic solvent containing $LiClO_4$ or $NaClO_4$ would lead to a fresh lithium or sodium layer on the lectrode.[36, 37] The process in this case will have several advantages. Firstly, the chemical electron transfer which occurs between the metal and the Ge–Cl bond is kinetically controlled and is assisted electrochemically by a high negative potential ($E^{\circ}_{Li/Li^+} = -3.05$ V/NHE) and, secondly, having an alkaline metal as the electrode will necessitate an anhydrous medium. Lithium perchlorate, which is highly soluble in ethers, particularly in THF, was found to be quite suitable for this purpose since thin lithium layers can be deposited on the metal electrode by reduction of Li^+.[36, 37]

Consequently, it might be thought that the influence of the underlying metal would be negligible, and that the reduction of the organodichlorogermane would not depend on the nature

Table 2 Electroreductive polymerization of di-n-hexyldichlorogermane ($1.28.10^{-1}$n) using an aluminium anode and a stainless steel (18.0 cm^2) cathode in different solvent mixtures in the presence of $LiClO_4$ (0.3 M)

Solvent	I (mA)	Q (C)	λ_{max} (nm)	$[\bar{M}]_w$	$[\bar{M}]_n$	DP	Yield (%)	$\frac{[\bar{M}]_w}{[\bar{M}]_n}$
THF	50	1080	328	7700	1250	32	60	6.2
THF + DMA	50	626	329	6330	1810	26	33	3.5
THF + TMU	50	1290	326	3500	1376	14	57	2.5
THF + HMPA	60	1243	328	8000	4900	33	56	1.6
DMA	60	1296	266	—	—	—	—	—
DMF	60	1240	262	—	—	—	—	—
ACN	50	620	—	—	—	—	—	—

of the metal. This is not true, and we shall see that marked differences in the polymer yield are observed with various metallic cathodes for the same anode metal.

In fact, 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^+. That is due to the fact that the surface of the metal is first passivated by a thin adhering insulating Li_2O layer, which forms at about -1.5 V vs $Ag/AgNO_3$ (10^{-2} M) and which at moderate negative potentials prevents electron transfer from occurring.[36, 37]

Electron transfer occurs (probably by tunnelling through the insulating layer) only at very negative potentials and both Li^+ and the electroactive compounds are reduced simultaneously.

This explains why the reduction voltammetric curves of DHCG in the presence of 0.3 M $LiClO_4$ in THF do not exhibit well-defined reduction waves between 0 and -3.05 V, but only a discharge curve at about -3.5 V corresponding to a mixed reduction of Li^+ and DHCG. Consequently, two mechanisms for the first electron transfer are possible. Either the germanium compound is chemically reduced by lithium metal according to Eqn [1]:

$$Li + GeCl_2Hex_2 \rightarrow Li^+ + [GeCl_2Hex_2]\cdot^- \quad [1]$$

or it is electrochemically reduced on the lithium electrode, considered as an inert metal, following the electrochemical step (Eqn [2]):

$$GeCl_2Hex_2 + e^- \rightarrow [GeCl_2Hex_2]^{\bullet -} \quad [2]$$

In both cases the electrical yield would be the same, and probably a mixed mechanism would occur. However, depending on the nature of the underlying metal, different lithium-metal alloys can be formed,[37] and different catalytic effects can be expected. In particular, the following steps occurring after the formation of $[GeCl_2Hex_2]\cdot^-$, which lead to different transient species $GeClHex_2^{\cdot}$ and $GeClHex_2^-$, could be favoured differently.

Effect of the nature of the metal electrode on electropolymerization

THF, which is well known to be a good solvent for anionic polymerization, was chosen as a standard to evaluate the feasibility of the polymerization of DHCG with 0.3 M $LiClO_4$ and with different metal electrodes. Magnesium, zinc and aluminium were used as the sacrificial anode and stainless steel, magnesium and aluminium as the cathode (Table 1).

Of the various metal combinations, it appears that a sacrificial aluminium anode associated with a stainless steel cathode leads to a poly(di-n-hexylgermane) (PDHG) with the highest molecular weight and the highest yield but with wide polydispersity ($[M]_w/[M]_n = 6.2$) (Table 1). When magnesium or zinc was used as a sacrifical anode with stainless steel as the cathode, the molecular weight ($[M]_n$) decreased dramatically to 713 or 580, respectively, and the products of the reaction were attributed to cyclic oligomers which formed in low yield (Table 1).

A high-molecular-weight-polymer was obtained when the same metal was used for anode and cathode. With an Al/Al or Mg/Mg electrode pair the polymer yields were high, about twice as high with Al/Al as with Mg/Mg. In the latter case, several absorption maxima were found at 260, 280 and 310 nm, indicating that the polymer has a polymodal distribution. In contrast, with Al/Al electrodes a single absorption band at 329 nm and a low polydispersity ($[M]_w/[M]_n = 3.4$) were found, corresponding to a monomodal distribution. Another difficulty was encountered with Mg/Mg electrodes. Contrary to what happens with an aluminium cathode, the resistance of the electrochemical cell increased markedly during electrolysis, and it was necessary to reduce the intensity of the current from 50 to 30 mA in order to lower the overvoltage. Although this problem is not yet elucidated, it is probable that this ohmic drop is due to passivating layers which form on either the cathode or the anode. In this latter case one way to improve the electrolysis would be to prevent the passivation from occurring. Recently ultrasonic activation was used in conjunction with magnesium electrodes and was found to give polyorganogermanes, polyorganosilanes and germane–silane copolymers[11] in good yields. Since no passivation effects were indicated, it is probable that ultrasonic stirring cleans the electrode surface and, consequently, allows electrolysis to run smoothly.

Solvent effect on electropolymerization

It was demonstrated that the electrochemical synthesis of Si–Si bonds such as in disilanes

and trisilanes is possible only in basic solvents like dimethoxyethane (DME) and THF. We investigated the electroreduction of organodichlorogermanes in polar solvents in order to test the effect of polarity on electropolymerization using a stainless steel cathode and a sacrificial aluminium anode.

The results, summarized in Table 2, indicate that in media such as DMA, HMPA, CH_3CN and DMF with $LiClO_4$ only cyclic and linear polyorganogermanes with low molecular weights ($[M]_n$) are obtained.

On the contrary, the electroreductive coupling of di n-hexyldichlorogermane in THF or THF/co-solvent (DMA, TMU and HMPA) mixtures (Table 2) leads to a poly(di-n-hexylgermane) with a relatively high molecular weight, in good yield. The best results were obtained in THF/HMPA (80:20, v/v). The polydispersity of the polymer was good ($[M]_w/[M]_n = 1.6$), but its molecular weight was about two times lower than that produced by the Wurtz-type condensation of di-n-hexyldichlorogermane. However, the chemical polymer yields (Table 2) were about three times higher than those obtained from the chemical route.[1, 4, 15] The electronic properties of the polymer products were similar to those of the chemically synthesized polymer, with a UV absorption ranging between 326 and 329 nm.

The electroreduction of organodichlorogermanes in pure THF in the presence of $LiClO_4$ using aluminium as a sacrificial anode produced polyorganogermanes with, from time to time, small amounts of polytetrahydrofuran (PTHF) as an impurity. This side-product probably results from a cationic polymerization of THF due to the presence of intermediate electrophilic species such as $AlCl_2^+$,[38] arising from the ionization of $AlCl_3$ according to the equilibrium shown in Eqn [3]:

$$AlCl_3 \rightleftharpoons AlCl_2^+ + Cl^- \qquad [3]$$

It should be noted that the polymerization rate of THF is fortunately much lower than the electropolymerization rate of organodichlorogermanes, and moreover, the use of co-solvents prevents the formation of PTHF, as is shown in the case of THF/HMPA.

Structure and electronic properties

IR, Raman, UV and ^1H NMR spectroscopy, GPC and X-ray photoelectron spectroscopy (XPS) were used to characterize the products of the electropolymerization of di-n-hexyldichlorogermane.

By GPC, the number-average molecular weight ($[M]_n$) was determined and was found to range from 3500 to 11 800 (Tables 1 and 2), corresponding to a degree of polymerization (DP) of 14 to 49 dihexylgermane units.

^1H NMR spectroscopy of the polymer (in $CDCl_3$) led to three distinct peaks centred at 0.89 (triplet), 1.07 (quadruplet) and 1.47 ppm (multiplet) attributed to the CH_3, CH_2–Ge and $(CH_2)_4$ groups of the hexyl side-chains.[1, 4, 5, 15] It is worth noting that similar results have been found for chemically prepared PDHG.[1, 4, 5, 15]

IR analysis 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 Ge–C (667 cm^{1}).

Interestingly, the Raman spectrum of our polymer (Fig. 1) was found to be very similar to that of the PDHG obtained by Wurtz coupling polymerization at low temperature.[5] Several sharp, strong bands in the low-frequency region (below 300 cm^{-1}), characteristic of the vibrations of Ge–Ge and Ge–C bonds, indicate that the PDHG has a highly ordered structure corresponding to the planar zigzag conformation.[5] Moreover, the sharp band found at 628 cm^{-1}, due to the Ge–C stretching vibration, confirms the planar zigzag structure of the germanium backbone.[5]

UV spectroscopy of the polymer carried out in THF at room temperature exhibits a symmetrical weak absorption band at 328 nm (Fig. 2), in agreement with the literature data for the same polymer,[5] and this too supports a planar zigzag

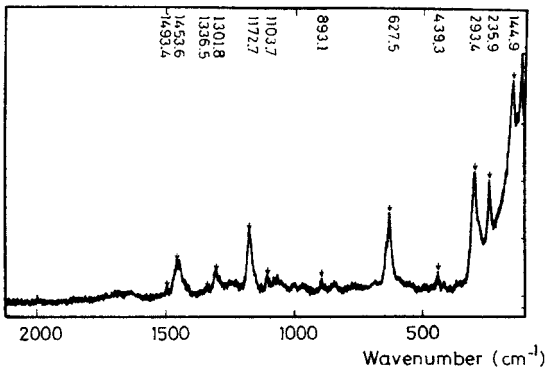

Figure 1 Raman spectrum of poly(di-n-hexylgermane) film obtained with excitation at 514.5 nm at room temperature.

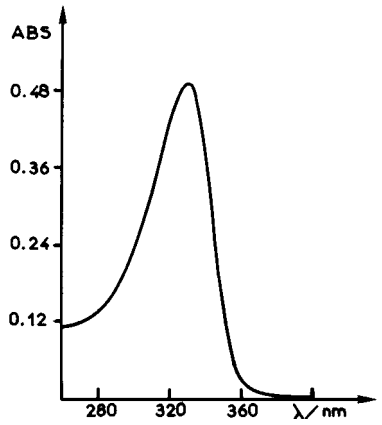

Figure 2 UV absorption spectrum of poly(di-n-hexylgermane) in hexane.

conformation.

The polymer structures were also characterized by XPS. No trace of oxygen or chlorine was detected, only carbon and germanium signals being observed (Fig. 3). As shown in Figure 3(a), the C 1*s* peak at 285 eV is symmetrical and corresponds to C-C and C-H groups of the side-chain (hexyl). The Ge 3*d* signal is slightly asymmetrical and can be deconvoluted into a strong main peak at 31.6 eV, probably due to the Ge-C bond, accompanied by a weaker peak at 30 eV corresponding to a Ge-Ge bond (Fig. 3b).

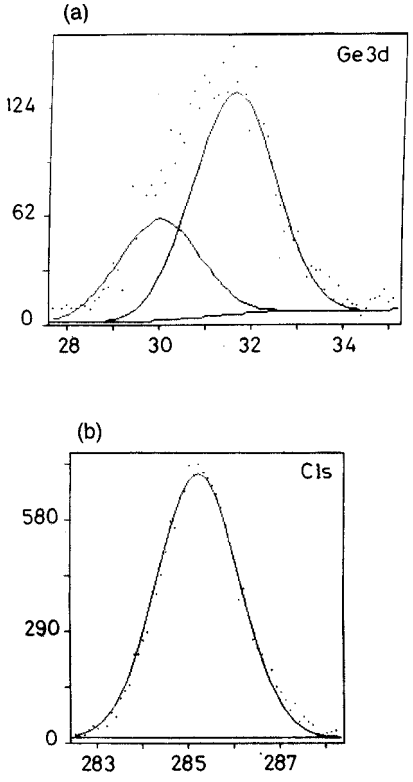

Figure 3 XPS spectra of poly(di-n-hexylgermane): (a) Ge 3*d* region; (b) C 1*s* region.

CONCLUSION

Electroreductive polymerization of di-n-hexyldichlorogermane is achieved by constant-current electrolysis, but the yields of polymer are markedly dependent on the nature of the cathode and the sacrificial anode, and also on the solvent. A relatively high-molecular-weight PDHG distribution, with monomodal molecular weight is obtained in good yield in a THF/HMPA mixture with stainless steel as cathode and aluminium as anode. The reason for these different yields is not yet clear, but could be related to the fact that the Al/Li alloy, which is formed during electrolysis, catalyses the polymerization process.

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