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Electrosynthesis of Linear and Branched Methylene-Bridged Oligo- and Polycarbosilanes

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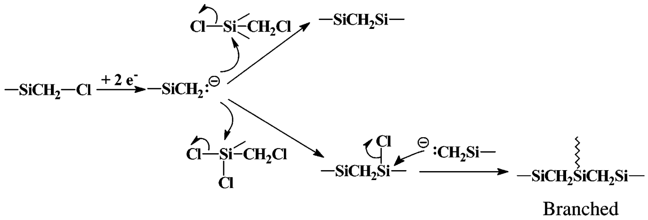
ABSTRACT: Electrosynthesis methods have been employed as a mild and facile alternative for the syntheses of polycarbosilanes. Electropolymerization was conducted on chloromethylchlorosilanes, [$ClCH_2Si(CH_3)_{3-m}Cl_m$ ($m = 1, 2$)], taking advantage of the fact that these compounds contain two types of functional groups, CH_2-Cl and $Si-Cl$, both of which are electrochemically active with different reduction potentials. Under a constant current, $-CH_2Cl$ is preferentially reduced to a carbanion, $-SiCH_2:^-$, that can nucleophilically attack a $Si-Cl$ bond to form a CH_2-Si linkage; branching should occur when more than one Cl atom resides on the silicon atom since each group is capable of reacting with the nucleophilic carbanion. Thus, the condition for polymerization of highly branched polycarbosilanes is $m > 1$. Detailed spectroscopic characterizations of the oligomers and polymers with GPC, NMR, IR, and GC-MS are given. The formation of diverse structures, molecular weights, and reaction yields is strongly dependent on the electrosynthesis conditions, such as electrode composition and supporting electrolyte (SE). Thus, high molecular weight ($M_n \approx 57\,000$) of highly branched but soluble poly[methylsilylenemethylene] is obtained by electropolymerization of $ClCH_2Si(CH_3)Cl_2$ with the Al/nickel (anode/cathode) pair and $Bu_4N^+BF_4$ (SE). GC-MS analysis confirms that a number of oligomeric structures can be produced by electrosynthesis, and diverse structural irregularities (i.e., cross-linking, loop, and fused rings) can be incorporated into the branched skeleton of polycarbosilanes. Cyclic voltammetric analysis suggests that electroreduction of chlorocarbosilanes undergoes an ECE mechanism to initiate polymerization, as well as a myriad of side reactions.

Introduction

Methylene-bridged polycarbosilanes have received growing interest in recent years as a unique organic/inorganic hybrid polymer. These polymers have a backbone with silicon and carbon atoms arranged alternatively, with carbon atoms locked between silicon atoms. Polycarbosilanes, and in particular the highly branched derivative species, are considered superior precursors in processing high-strength, high-modulus silicon carbide composites.[1,2] Highly branched polycarbosilanes also show potential for medical and biological applications due to the chemical inertness of the backbone.

Polycarbosilanes can be synthesized via pyrolysis of polydimethylsilanes,[3] ring-opening polymerization of substituted 1,3-disilacyclobutanes,[4,5] and Grignard coupling of $ClCH_2SiCl_3$ and $ClCH_2Si(CH_3)Cl_2$.[1,2] However, little attention has been directed to the electropolymerization of carbosilanes, which is the objective of the current study. Electrosynthesis methods have been employed as mild and facile alternatives for syntheses of small organosilicon compounds[6−15] as well as polysilanes.[16] Thus, we recently reported on a “clean” electropolymerization of dichlorosilanes to oligo- and polysilanes using a modified gas-diffusion hydrogen anode.[17] These syntheses are based on the electrochemical oxidation/reduction processes of hydrogen, where the transfer of electrons can be controlled accurately and readily. Hence, reactions that traditionally require extreme measures can proceed under mild conditions. The interest in electrosynthesis of carbosilanes stems, in part, from the fact that it is a one-pot approach utilizing common starting materials. Such synthesis exploits the fact that the electrochemical reduction of organohalide species in the presence of chlorosilanes produces silylated compounds bearing Si−C bonds, as reported by Yoshida et al.[6] and others.[7−14] While most of the work focused on the electrosynthesis of small organosilane molecules, a few reported on the production of carbosilane oligomers.[9,14,18] Bordeau et al.[9] reported on the electrosynthesis of oligocarbosilane (up to 4 monomer units) from $ClCH_2Si(CH_3)_2Cl$; a residue of “heavy” uncharacterized carbosilane products was obtained in this reaction using a Mg anode and a stainless steel cathode. The patent literature reports on linear and cyclic oligomers $[CH_2Si(CH_3)_2]_n$ ($n \leq 6$) using the same monomer and Al or Mg anodes.[18]

Scheme 1



These prompted us to examine the possibility of electrosynthesizing polycarbosilanes with monomeric compounds such as $ClCH_2Si(CH_3)_{3-m}Cl_m$ ($m = 1, 2$) that contain two types of functional groups, CH_2-Cl and $Si-Cl$, both of which are electrochemically active with different reduction potentials.[8,9,15] (For example, Jouikov et al.[15] reported that $ClCH_2Si(CH_3)_2Cl$ shows an irreversible reduction potential of $E_p \approx -1.48$ V for $-CH_2Cl$ and a reduction potential of ca. -1.73 V vs SCE for $-SiCl$ in DMF/Bu_4NClO_4.) Under a constant current, $-CH_2Cl$ is preferentially reduced to the carbanion $-SiCH_2:^-$, which can nucleophilically attack a $Si-Cl$ bond to form a CH_2-Si linkage (Scheme 1).[5,15] Therefore, it can be concluded that if more than

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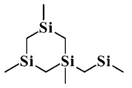
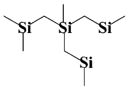
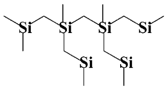
Table 1. Mass Spectral Data of Major Carbosilane Oligomers

n[a]	Carbosilane oligomers	MW (Dalton)	Major MS fragments
2	$[SiH(CH_3)CH_2]_2$	116	M^+ (115,100%), $(CH_3)_2SiH$– (59, 21%) M-$SiH(CH_3)_3$ (43, 25%)
3	$H—[SiH(CH_3)\ CH_2]_3—H$	176	$[M\text{-}H]^+$ (175 16%), M-CH_3 (161, 100%), M-$CH_2SiH_2CH_3$ (117, 75%), M-$SiH(CH_3)_3$ (101, 31%), $(CH_3)_2SiHCH_2$– (73, 37%), $(CH_3)_2SiH$– (59, 16%)
3c	$[SiH(CH_3)\ CH_2]_3$	174	M^+ (174, 23%), M-CH_3 (159, 100%), M-$CH_2SiH_2CH_3$ (115, 12%), M-$SiH(CH_3)_3$ (99, 11%), $(CH_3)_2SiHCH_2$– (73, 11%), $(CH_3)_2SiH$– (59, 10%)
4	$H—[SiH(CH_3)\ CH_2]_4—H$	234	$[M\text{-}H]^+$ (233, 5%), M-CH_3 (219, 90%), M-$CH_2SiH_2CH_3$ (175, 100%), $[M\text{-}H]$-$SiH(CH_3)_3$ (159, 76%), $H[CH_2SiHCH_3]_2$– (117, 38%), $(CH_3)_2SiHCH_2$– (73, 26%), $(CH_3)_2SiH$– (59, 14%)
4c		232	$[M\text{-}H]^+$ (231,10%), M-CH_3 (217, 66%), M-$CH_2SiH_2CH_3$ (173, 100%), M-2$CH_2SiH_2CH_3$ (115, 16%), $(CH_3)_2SiHCH_2$– (73, 34%), $(CH_3)_2SiH$– (59, 29%)
4i		234	$[M\text{-}H]^+$ (233,3%), M-CH_3 (219, 23%), M-$CH_2SiH_2CH_3$ (175, 40%), $[M\text{-}H]$-$SiH(CH_3)_3$ (159, 70%), $H[CH_2SiHCH_3]_2$– (117, 57%), $(CH_3)_2SiHCH_2$– (73, 100%), $(CH_3)_2SiH$– (59, 95%)
5	$H—[SiH(CH_3)\ CH_2]_5—H$	292	$[M\text{-}H]^+$ (291).
6	$H—[SiH(CH_3)\ CH_2]_6—H$	350	$[M\text{-}H]^+$ (349, 22%), M-SiH_2CH_3 (305,22%), $[M\text{-}H]$-$SiH_2(CH_3)_2$ (289, 6%), (231, 35%), (229, 27%), (174, 77%), (159, 42%), $H[CH_3SiHCH_2]_2$– (117, 52%), $(CH_3)_2SiHCH_2$– (73, 100%), $(CH_3)_2SiH$– (59, 61%)
6i		350	$[M\text{-}H]^+$ (349, 22%), M-SiH_2CH_3 (305,22%), $[M\text{-}H]$-$SiH_2(CH_3)_2$ (289, 6%), (231, 35%), (229, 27%), (174, 77%), (159, 42%), $H[CH_3SiHCH_2]_2$– (117, 52%), $(CH_3)_2SiHCH_2$– (73, 100%), $(CH_3)_2SiH$– (59, 61%)

[a] *n*, number of monomer units in oligomers.

one Cl atom resides on the silicon, branching would occur since each group is capable of reacting with the nucleophilic carbanion. Additionally, we should be able to show that the formation of −Si−Si− as a result of Si−Cl electroreduction is also a possibility[19] (introducing Si−Si cross-linking into the polycarbosilane skeleton is desired as a matrix precursor to silicon carbide).

The electrosynthesis using $ClCH_2Si(CH_3)_{3-m}Cl_m$ should lead to linear or multidimensional macromolecular structures. For chain extension (rather than cyclization) to proceed by the nucleophilic attack of carbanion $-CH_2{:}^-$ on a Cl−Si group, the trifunctional $ClCH_2Si(CH_3)Cl_2$ is the preferred candidate rather than the bifunctional $ClCH_2Si(CH_3)_2Cl$, since the former contains twice the amount of electrophiles (Si−Cl).

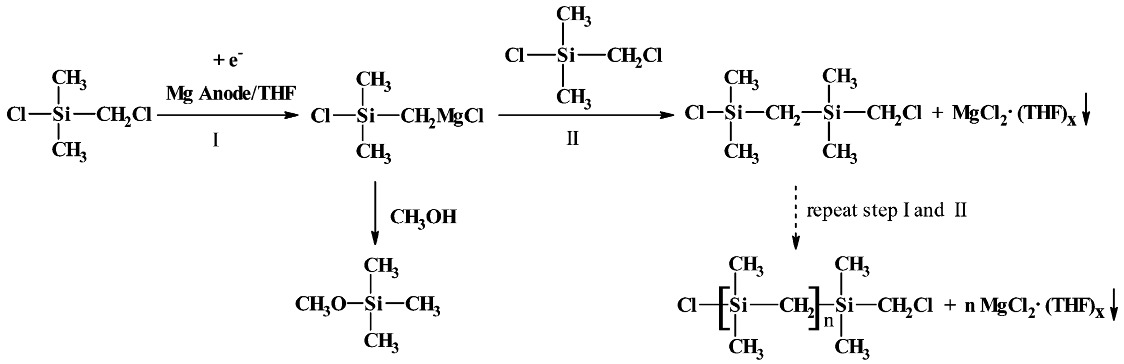
Following these considerations the present work investigates the various aspects of electropolymerization of high molecular weight branched polycarbosilanes and a variety of oligomeric structures. The electrosyntheses of a series of new methylene-bridged carbosilane oligomers and polymers using chloromethylchlorosilanes of the type $ClCH_2Si(CH_3)_{3-m}Cl_m$ ($m = 1, 2$) are reported. Characterization of the structures of the polymeric products and the reaction mechanism are discussed in this article. The electroreduction of the chloromethylchlorosilane monomers has been investigated by cyclic voltammetric measurements, which indicate an electron transfer−chemical reaction−electron transfer (ECE) mechanism.

Experimental Section

Materials. $ClSi(CH_3)_3$, $(CH_3)_3SiCH_2Cl$, $ClCH_2Si(CH_3)_2Cl$, and $ClCH_2Si(CH_3)Cl_2$ (Gelest) were used as received. For cyclic voltammetric (CV) measurements, chlorosilanes were freshly distilled prior to use. Supporting electrolytes Et_4NClO_4 (TEAP), $(n\text{-}Bu)_4N^+BF_4^-$ (TBAF), $n\text{-}Bu_4N^+ClO_4^-$ (TBAP), $n\text{-}Bu_4N^+BPh_4^-$ (TBAPh), and $n\text{-}Bu_4N^+$*p*-Tol-SO_3^- (TBAT) (Aldrich) were dried and stored at 80 °C under vacuum. $AgClO_4$ (Aldrich) was dried and stored at room temperature under vacuum (10^{-3} mmHg). Solvents were freshly distilled from appropriate drying agents, tetrahydrofuran (THF) over Na/benzophenone, tris(3,6-dioxaheptyl)-amine (TDA-1), hexamethylphosphoramide (HMPA) over CaH_2 at 4 mmHg vacuum, and acetonitrile (CH_3CN) over P_2O_5.

Instrumental. ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker AMX 600 MHz using $CDCl_3$. Infrared spectra (IR) of the soluble samples cast on a NaCl window were collected on a Nicolet FT-IR spectrometer (Model 750) at a resolution of 2 cm^{-1} and 100 scans. UV measurements were performed on a Beckman D640 spectrometer, in hexane at room temperature. Polymer molecular weight was determined with a Waters gel-permeation chromatography (GPC) system. GPC conditions: THF eluent, 1 mL/min flow rate, 25 °C; polystyrene standards were used to determine the molecular weights. GC-MS analysis was performed on a HP GC (Model 5890) connected to a mass detector (Model 5989B). GC conditions: low-polarity DB1 capillary column, carrier gas helium, injection temperature 220 °C, starting temperature 35 °C, held for 5 min then ramped to 220 °C at 8 °C/min. MS conditions: fragmentation voltage 70 V, mass scan range 0−600 Da. Thermogravimetric analysis (TGA) was carried on a TGA 2950

Scheme 2



GC-MS: $[M-1]^+$ (103), $(CH_3)_3Si^+$ (73).

(TA Instruments). The samples were dried in a vacuum oven (75 °C) overnight before use. Sample weight was in the range 10−20 mg, analyzed at a constant heating rate of 10 °C/min in argon gas. CV measurements were performed on an EG&G potentiostat/galvanostat (Model 273A) with an EG&G lock-in amplifier (Model 5210) and were processed with PAR-M398 software. An $Ag/AgClO_4$ (0.001 mol/L) reference electrode (+0.238 V vs SCE[20]) calibrated with $Fe(Cp)_2{}^0/Fe(Cp)_2{}^+$ (0.37 V vs SCE) in 0.1 mol/L Et_4NClO_4/CH_3CN was used. Rigorous exclusion of oxygen and water was attained by employing the technique reported by Mills et al.[21] CV measurements were recorded with solutions of 4−5 mM chlorosilanes in THF (containing 0.1 mol/L TBAP) with a stationary Pt microelectrode relative to a $Ag/AgClO_4$ reference electrode.

General Electrolysis Procedures. Electropolymerization was preferentially carried out in an undivided cylindrical cell current control device. A metal rod (Ni, Cu, Al, or Mg) as anode (22 mm in diameter, surface area 30 cm^2, polished with 500-grit sandpaper) was concentrically placed into a nickel net sheet cathode (32 mm in diameter, surface area of 40 cm^2) with a distance of 5 mm. Both electrodes were treated with 0.1 N HCl solution, deionized water, and acetone and then were placed into a 25 mL single-compartment glass cell (35 mm diameter). The whole cell was subsequently dried in a vacuum oven at 120 °C for 12 h and then purged with nitrogen.

A supporting electrolyte solution consisting of 20 mL of 0.02 and 0.4−2.5 mol/L monomer was injected into the electrolysis cell under a dry nitrogen blanket. Electrolysis was conducted at a constant current of 40 mA (current density = 1.0 mA/cm^2). During electrolysis, the mixture was stirred by continuous sonication (45−50 kHz) and was maintained at 25 ± 1 °C.

General Procedure of Electrosynthesis of Linear Poly[dimethylsilylenemethylene] (PDMSM). Electropolymerization of $ClCH_2Si(CH_3)_2Cl$ (0.8 and 2.5 mol/L) was terminated after accomplishing 2.2 F/(mol silane) of charge, which is a 10% excess of theoretical value (2.0 F/mol for conversion of 1.0 mol of silane monomer). Thus, conversion of monomer was controlled by means of total amount of charges consumed during electropolymerization. Subsequently, 1.5 g (0.04 mol) of $LiAlH_4$ (in 30 mL of THF) was added via a syringe to convert the remaining Si−Cl into Si−H. The resulting suspension was transferred to a 250 mL flask and was refluxed overnight under N_2. A dilute HCl solution was then added slowly to the reaction mixture. Intermittent heat was applied to expedite the de-emulsification and dissolution of the lithium and aluminum salts generated in the process. The slightly yellow solution was then extracted with pentane (3 × 30 mL), and the combined extract was back-washed with brine and dried over anhydrous Na_2SO_4. Solvent was removed in a rotary evaporator at 60 °C. A transparent, pale yellowish oil was obtained in 36−46% yield based on $ClCH_2Si(CH_3)_2Cl$. The IR and NMR analyses of polymers gave the following. IR (KBr cm^{-1}): 2956(s), 2902(m), 2875(m), 2120(s), 1412(w), 1357(w), 1255(s), 1134(w), 1057(s), 894(s), 835(s), 804(s), 775(m), 683.9(w). ^1H NMR (δ ppm): 4.1, 3.4, 2.75, 0.5 to −0.3 (br). ^{13}C NMR (δ ppm): 33.2−27.4 (br), 9.51 (complex), 5.2 to −5.0 (br). ^{29}Si NMR (δ ppm): 8.7−6.3 (br), 3.7 - −0.6 (br), −10.0 (minor), −16.6 (complex).

For oligomer analysis, a small portion of pentane extract was purified with silica gel (Scientific Selecto, particle size 32−63) and analyzed by GC-MS. Mass spectral features of principal oligomers are summarized in Table 1.

General Procedure of Electrosynthesis of Branched Poly[methylsilylenemethylene] (PMSM). Electropolymerization was conducted with a known quantity (0.4−2.5 mol/L) of $ClCH_2Si(CH_3)Cl_2$. The reaction was terminated after the completion of 2.2 F/(mol silane) of electricity. The electrolyte solution was treated with $LiAlH_4$ and then neutralized with dilute HCl by the same procedure employed in purifying linear PDMSM. The resulting mixture was settled and was separated into filtrate and solid. The filtrate was extracted with pentane (3 × 30 mL). The combined extract was back-washed with brine to remove trace inorganic salts and dried over anhydrous Na_2SO_4. Solvent was removed in a rotary evaporator at 60 °C. A pale yellow, viscous oil was obtained at 25−35% yield based on $ClCH_2Si(CH_3)Cl_2$. This product is stable in air, and no apparent change was recorded on the IR spectra after exposure for several days. All the viscous, oily products showed the following. IR (KBr cm^{-1}): 2961(m), 2910(w), 2877(vw), 2123(m), 1422(w), 1353(w), 1252(s), 1050(s), 955(m), 940(m), 892(s), 850(s), 835(s), 796(s). ^1H NMR (δ ppm): 4.2−3.9, 3.7, 2.8, 0.4 to −0.3 (v br). ^{13}C NMR(δ ppm): 33.2−30.0 (br), 29.8−28.3 (br), 12.6 to −6.8 (br). ^{29}Si NMR (δ ppm): 11.0−4.2 (br), −13.1 to −21.5 (br), −29.8 to −34.8 (br), −39.1 to −41.0 (triplet). A small portion of pentane extract was purified with silica gel and analyzed by GC-MS. The mass spectral data are presented in Table 1.

A white or gray polymer (floating on the top) was separated from the solution. This polymer was filtered, washed with dilute HCl, water, and methanol, and vacuum-dried at 50 °C. A white or pale yellow polymer was collected in 20−30% yield. The product was not soluble in most common solvents and appeared to be of high molecular weight and partially cross-linked. IR (neat cm^{-1}): 2958(s), 2904(m), 2877(w), 2121(s), 1415(w), 1358(w), 1254(s), 1082(m, shoulder), 1057(s), 960(m), 889(s), 852(s), 787(s). CP-MAS ^{13}C NMR (δ ppm): 29.1−27.3 (br), 16.0 to −10.0 (v br). CP-MAS ^{29}Si NMR(δ ppm): 25.0−16.1 (br), 9.8, 3.1 to −18.5 (v br), −28.4 to −33.2 (br).

Results and Discussion

The electropolymerization of organosilicon halides was carried out using a Ni cathode and several metallic anodes. The anodes (Ni, Cu, Al, and Mg) were selected according to the standard state reduction potentials of the corresponding metal cation/metal couples, i.e., +0.34 > −0.23 > −1.66 > −2.37 V for Ni^{2+}/Ni, Cu^{2+}/Cu, Al^{3+}/Al, and Mg^{2+}/Mg, respectively. The less negative the standard state reduction potential, the easier

Table 2. FT-IR Characteristic Bands of Poly(methylsilylenemethylene] (PMSM) and Poly[dimethylsilylenemethylene] (PDMSM)

PMSM, $-\!\!\left[CH_2-\underset{\wr}{Si}CH_3\right]_n$		*PDMSM*, $-\!\!\left[CH_2-Si(CH_3)_2\right]_n$	
Group	Band (cm^{-1})	Group	Band (cm^{-1})
CH_3	2961.2(m, ν_{as}), 2910.1(w, ν_s), 2887.9(m, ν_s), 1422.2(w, δ_s), 892.3(s, ω), 850.4(s, ω)	CH_3	2956.4(m, ν_{as}), 2902.3(m, ν_s), 2875.3(w, ν_s), 1411.6(w, δ_s), 893.8(s, ω)
Si-CH_2-Si	1352.7(w, δ_s), 1050.6(s, δ_s)	Si-CH_2-Si	1356.7(w, δ_s), 1056.8(vs, δ_s)
Si-CH_3	1252.0(s, ν_{as}), 796.4(s, ρ)	Si-CH_3	1254.5(s, ν_{as}), 775.2(m, ρ)
Si-H	2123.2(m, ν_{as}), 834.8(s, ω), 803.2(s, ω)	Si-H	2120.4(m, ν_{as}), 835.0(vs, ω), 804.1(s, ω)
H-Si-H	954.7(m, ω), 940.3(m, ω)	Si-CH_2-CH_2-Si	1133.9(vw, ν_{as})

the corresponding metal cation is reduced to metal. When Cu or Ni was used as anode, the anodically generated metal ions (Cu^{2+} and Ni^{2+}) were easily reduced back to zero-valence metals on the Ni cathode surface, thus decreasing the current efficiency of the process and producing only small-chain oligomers. With sacrificial anodes, e.g., Mg or Al, the reduction of metal ions (Mg^{2+} and Al^{3+}) was avoided, yielding long-chain macromolecules, as discussed below.

Electrosynthesis with $ClCH_2Si(CH_3)_{3-m}Cl_m$ ($m = 1$). With $m = 1$, the bifunctional monomer $ClCH_2Si(CH_3)_2Cl$ is polymerized to yield linear polycarbosilanes (Scheme 1). On electropolymerization using an aluminum anode, the colorless electrolyte solution slowly turned to a gray suspension as the reaction proceeded and short-chain oligomers (mostly 4−6 units) were isolated as a pale yellowish oil with $M_n \approx 360$ and $M_w/M_n \approx 1.3-1.5$. Electropolymerization with the Mg anode had been characterized by vigorous exotherm at the early stage. At this step, the reaction could not be controlled by electrochemical means. GC-MS analysis of the methanol-quenched electrolyte solution detected the $(CH_3)_3SiOCH_3$ product. These observations suggest that the anodically activated magnesium may facilitate the formation of Grignard $ClMgCH_2Si(CH_3)_2Cl$ (Scheme 2). The Grignard promptly attacked chlorosilane, forming $-Si-CH_2-Si-$ bonds. Due to $MgCl_2$ precipitation, additional THF had to be added to dilute the suspension and to decrease the electrical resistance of the solution in order to continue the electropolymerization. A polycarbosilane with ∼30% yield, M_n of ∼920, and M_w/M_n of ∼1.6 was obtained.

A large quantity of oligomers (∼70%) were also produced during the electrosynthesis with Al and Mg anodes. The GC-MS analysis revealed that the majority of oligomers were linear $HSi(CH_3)_2-CH_{2n}-H$ ($n = 2, 3, 4, 5$), and less than 5% were cyclic carbosilanes ($n = 2, 3$). The results are consistent with a stepwise polycondensation mechanism, where incomplete conversion of functional groups leads to a low molecular weight polymer.

Spectral Characterization of Linear Poly[dimethylsilylenemethylene] (PDMSM). The assignments of the IR vibrations are summarized in Table 2. The main features are the $Si-CH_2-Si$ vibration (strong band at 1056.8 cm^{-1} and a weak deformation at 1350.5 cm^{-1})[22] and the Si−H vibration band at 2120.4 cm^{-1}. The ^1H NMR spectrum (Figure 1a) consists of three groups of peaks, 0.5 to −0.3 ppm ($Si-CH_2-Si$ and CH_3Si-), 4.0 ppm (Si−H), and the unreduced CH_2Cl (2.7 ppm), which is also shown in the ^{13}C NMR at 32.3 to 29.7 ppm (Figure 1b). The estimated molecular weights of PDMSM, measured on the basis of peak integration ratios, were 920 (∼13 silicon units) and 320 (∼4.5 silicon units), for the products of Mg and Al anodes, respectively. These are close to values obtained by the GPC. Three major silicon environments, $ClCH_2Si(CH_3)_2-CH_2-$ (7.8 to 6.3 ppm), $-CH_2Si(CH_3)_2CH_2-$ (3.7 to −0.6 ppm), and terminal $-CH_2-SiH(CH_3)_2$ (−16.3 to −16.6 ppm), were observed in the ^{29}Si NMR (Figure 1c). These features agree with the anticipated linear structure of poly(dimethylsilylenemethylene) as reported by Bacque et al.[23]

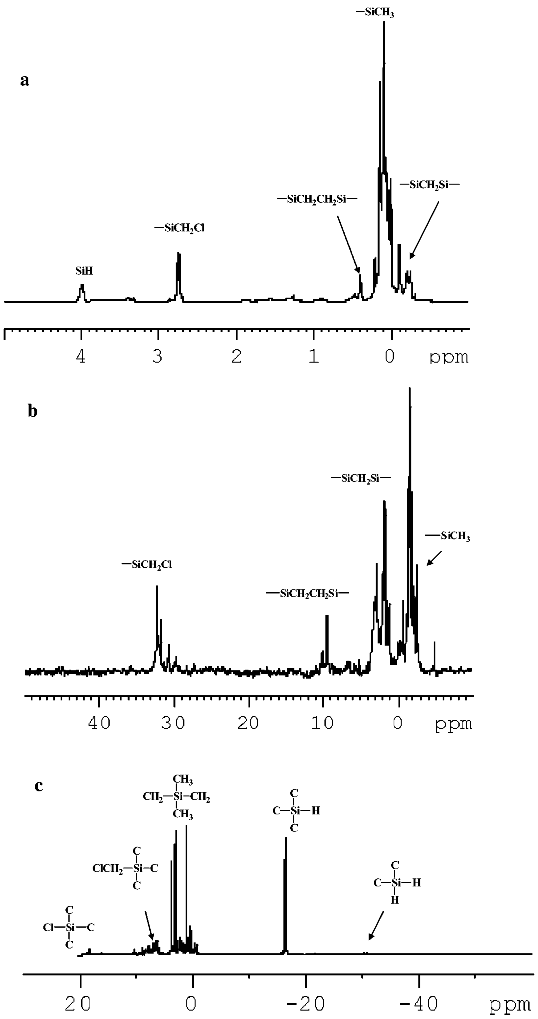


Figure 1. (a) ^1H, (b) ^{13}C, and (c) ^{29}Si NMR spectra of PDMSM.

PDMSM appears to contain a small portion of $Si-CH_2-CH_2-Si$ structure, which is shown in the IR as a weak band at 1135.9 cm^{-1} and a shoulder peak at 1065 cm^{-1},[24] and in ^{13}C NMR at 9.8 ppm (Figure 1b).[25] The presence of this structure suggests that during electrosynthesis of polycarbosilanes a small amount of the "head−head" termination-coupling is taking place (i.e., $-SiCH_2{:}^- + Cl-CH_2Si- \rightarrow -SiCH_2CH_2Si-$).

Some low-fraction oligomers containing $-SiH_2$ and $-Si(CH_3)_3$ terminals were produced when an Al anode was used. This is also observed in the ^{29}Si NMR of PDMSM (Figure 1c). It is probably due to the chlorination process in which $Si-CH_3$ is converted to Si−Cl in the presence of $AlCl_3$, which is a byproduct of the electrolysis. Ishikawa et al.[26] and Bacque et al.[22] had reported the chlorination of silicon compounds by the interchange of methyl and halogen on silicon by the catalysis of $AlCl_3$. To confirm this anodic effect of Al, equimolar amounts of $(CH_3)_3SiCH_2Cl$ and $ClSi(CH_3)_3$ were electrolyzed using an Al anode (Scheme 3). In this electrosynthesis, only ∼5% yield was recorded for 2,2,4,4-tetramethyl-2,4-disilapentane, whereas 1,1,3,3,5,5-hexamethyl-1,3,5-trisilahexane and 1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane were present at 52% and 34% yield, respectively. The latter two were conceivably produced by the electroreduction polymerization of $Cl(CH_3)_2$-

Scheme 3

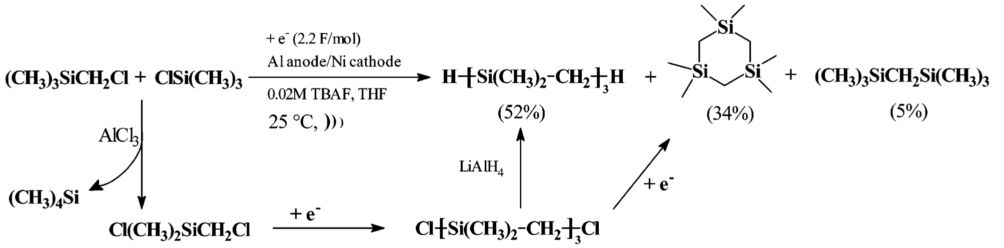


Table 3. Impact of Anode Material, Solvent, and Supporting Electrolyte on the Electropolymerization of $ClCH_2Si(CH_3)Cl_2$[a]

electropolymerization conditions			soluble polymer				
			HMW[b]		LMW[b]		
anode	solvent (v/v)	supporting electrolyte	M_n[c]	M_w/M_n	M_n[c]	M_w/M_n	total polymer yield (%)[d]
Al	THF	$[Bu_4N]^+[BF_4]^-$	11 600	1.3	210	1.2	36.4 (9.5)
Al	THF/HMPA (5/5)	$[Bu_4N]^+[BF_4]^-$	57 600	3.0	430	1.9	59.0 (29.5)
Al	THF/TDA-1 (8/2)	$[Bu_4N]^+[BF_4]^-$	33 000	1.8	270	1.6	46.0 (11.5)
Mg	THF/TDA-1 (8/2)	$[Bu_4N]^+[BF_4]^-$	1060	4.9			53.0 (21.0)
Al	THF/TDA-1 (8/2)	$[Bu_4N]^+[ClO_4]^-$	1970	2.5	280	1.5	32.0 (4.0)
Al	THF/TDA-1 (8/2)	$[Bu_4N]^+[BPh_4]^-$	26 900	1.6	290	1.4	41.0 (16.3)
Al	THF/TDA-1 (8/2)	$[Bu_4N]^+[p\text{-Tosyl}]^-$	34 500	1.6	290	2.1	44.0 (10.4)

[a] Electropolymerization conditions: nickel cathode; $[ClCH_2Si(CH_3)Cl_2]$ 1.0 mol/L; [supporting electrolyte] 0.02 mol/L; current 40 mA; electricity 2.2 F/mol; 45 kHz sonication bath, 25 °C. [b] HMW, LMW: high and low molecular weight fractions, respectively. [c] Determined with GPC, 1.0 mL/min THF eluent, relative to polystyrene standards. [d] Insoluble polymer yield in parentheses.

Table 4. Effect of $ClCH_2Si(CH_3)Cl_2$ Concentration on Electrosynthesis of PMSM[a]

	soluble polymer				
	HMW		LMW		
[M] (mol/L)	M_n[b]	M_w/M_n[b]	M_n[b]	M_w/M_n[b]	total polymer yield (%)[c]
0.4			280	3.3	14.0 (6.7)
0.8	10 500	1.6	420	1.4	52.0 (11.2)
1.2	33 500	1.6	860	1.6	53.6 (12.4)
1.6	38 000	1.8	1010	1.7	67.0 (13.9)
2.5	42 600	1.9	1750	2.0	74.5 (19.4)

[a] Electropolymerization conditions: electrodes nickel cathode/aluminum anode; solvent THF/TDA-1 (80:20); supporting electrolyte 0.02 mol/L $[Bu_4N]^+[BF_4]^-$; current 40 mA; electricity 2.2 F/mol; 45 kHz sonication bath, 25 °C. [b] Determined with GPC, 1.0 mL/min THF eluent, relative to polystyrene standards. [c] Insoluble polymer yield in parentheses.

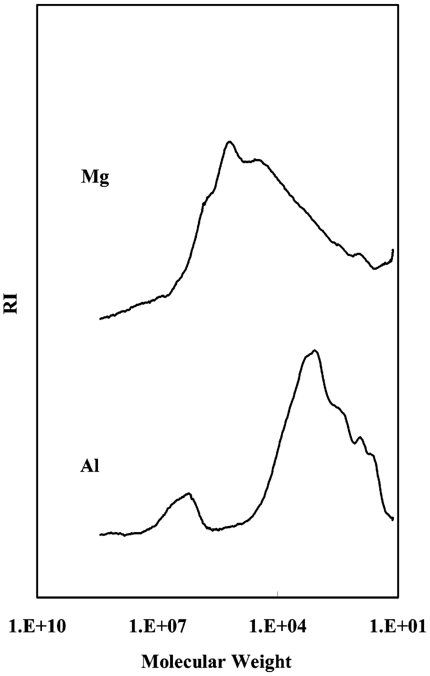


Figure 2. Molecular weight distribution of PMSM prepared using Mg and Al anodes.

$SiCH_2Cl$, which was generated by *in situ* chlorination of $(CH_3)_3SiCH_2Cl$.

Electropolymerization of $ClCH_2Si(CH_3)_{3-m}Cl_m$ ($m = 2$). With $m = 2$, the trifunctional $ClCH_2Si(CH_3)Cl_2$ (one CH_2-Cl and two $Si-Cl$ bonds) is polymerized, and as mentioned above, this silane monomer can lead to branched polycarbosilanes (Scheme 1). The impact of anode materials on the electropolymerization of $ClCH_2Si(CH_3)Cl_2$ is shown in Table 3. Three types of anodes, Zn, Mg, and Al, were examined. When Zn was used as the anode, the major products were $H-[CH_2SiH(CH_3)-]_n-H$ oligomers ($n = 2, 3, 4$). Electropolymerization of $ClCH_2Si(CH_3)Cl_2$ using Mg as the anode resembles the conventional Grignard coupling of $ClCH_2Si(CH_3)Cl_2$,[1,27] which gives rise to branched polycarbosilane of a broad molecular weight distribution and a wide range of linear and cyclic oligomers. The reaction is strongly exothermic, accompanied with rapid coagulation of the electrolyte solution to the extent of disrupting the electropolymerization. A soluble polycarbosilane with $M_n \approx 1060$ and monomodal distribution ($M_w/M_n \approx 4.9$) was isolated in ~32% yield. A mild electropolymerization in which coagulation of the electrolyte solution is avoided was achieved by using an Al anode. A high yield of polycarbosilanes, and oligomers, that are partially soluble and partially insoluble/cross-linked was typically obtained. The soluble polycarbosilane exhibited a bimodal molecular weight distribution with a high molecular weight (HMW) portion of $M_n \approx 33\,000$ and $M_w/M_n \approx 1.8$ and a low molecular weight (LMW) fraction of $M_n \approx 270$ and $M_w/M_n \approx 1.6$ (Figure 2). A bimodal molecular weight distribution was observed with Al, but not with Mg, as the anode. It appears that some $Si-CH_2-Si$ linkages in the polycarbosilane chain were cleaved by a similar chlorination mechanism described in Scheme 3, with $Cl_2Si(CH_3)CH_2Cl$ being the chlorine source. This chain degradation phenomenon was observed previously during the chlorination of PDMSM in the presence of $AlCl_3$ catalyst.[23] The resulting short carbosilane chains contain additional $Si-Cl$ sites that could couple with other polymer chains, producing polymers of longer chains that otherwise could not be produced by a stepwise condensation at

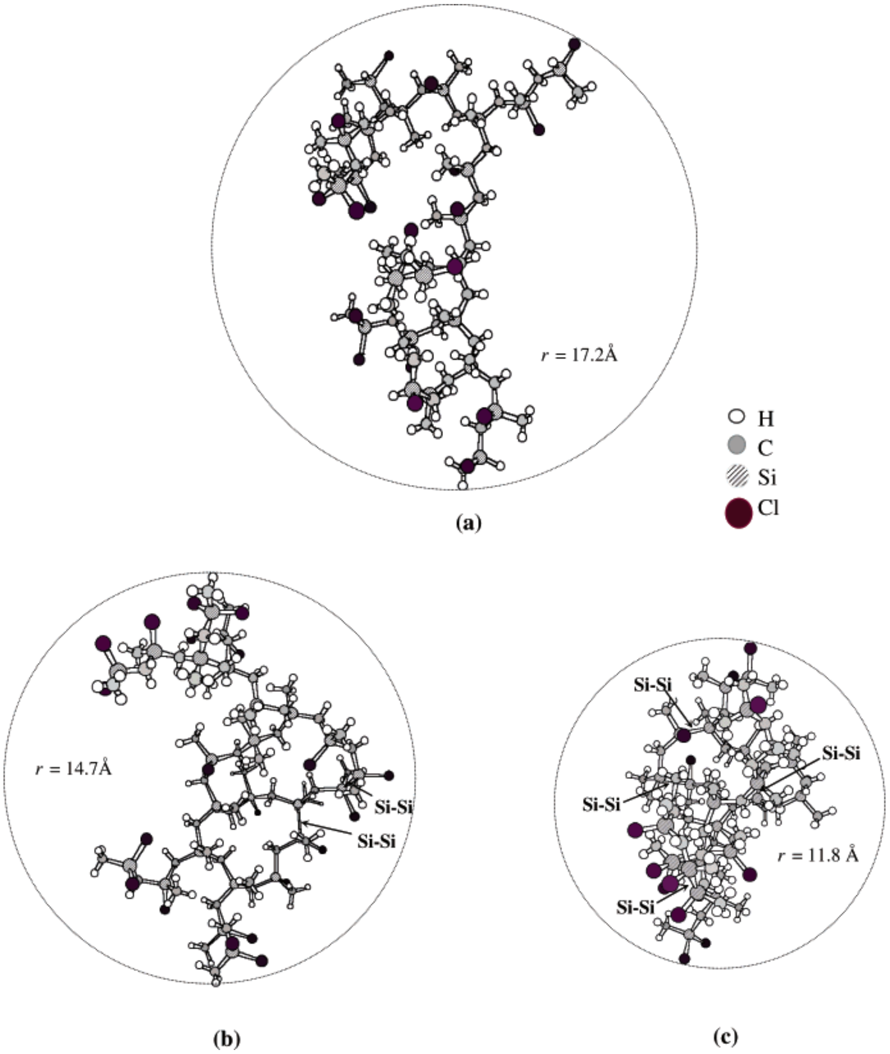
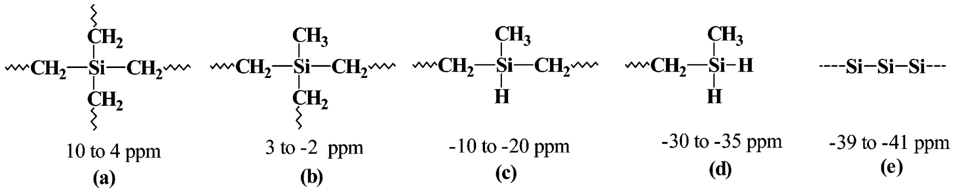


Figure 3. MM2 force field molecular modeling of highly branched PMSM containing 24 $-Si-CH_2-$ repeating units ($M_n \approx 2000$) (a) with no cross-linking, (b) with two cross-links, and (c) with four cross-links.

the same functional group conversion. Since $MgCl_2$ generated by the Mg anode does not have a similar catalytic effect, only a monomodal molecular weight distribution and an average molecular weight of ~1060 were attained.

Table 3 also shows the effect of the supporting electrolyte anion BF_4^-, ClO_4^-, BPh_4^-, and *p*-tosyl$^-$ on electropolymerization of $ClCH_2Si(CH_3)Cl_2$. Tetrabutylammonium, n-Bu_4N^+, was chosen as the supporting electrolyte cation because it is known to enhance the selective reduction of $Cl-CH_2-$ groups over $(CH_3)_3SiCl$.[15] The data indicate that BF_4^-, BPh_4^-, and *p*-tosyl$^-$ anions gave comparable polymerization results. All led to a 10−16% yield of insoluble product and 25−35% yield of soluble polycarbosilane fraction that exhibits a bimodal molecular weight distribution, with HMW of $M_n \approx$ 26 900−34 500. For the perchlorate ClO_4^- anion, however, a HMW with $M_n \approx$ 1970 was obtained. For this anion the insoluble product yield was also low (4.0%), suggesting that cross-linking by forming silicon−silicon bonds is not the dominant path. This result corresponds with the observation by Kunai et al.,[28] who reported that Si−Si bond formation is not particularly favorable in the presence of ClO_4^- supporting electrolyte anion. Thus, unlike BF_4^-, BPh_4^-, and *p*-tosyl$^-$ anions, ClO_4^- is able to minimize cross-linking by hindering the Si−Si bond formation.

The solvent has a great impact on the electron-transfer process and the reactivity of electrogenerated anionic species. Comparison of the electrosynthesis of carbosilanes, with $ClCH_2Si(CH_3)Cl_2$ and Al anode, in three solvent compositions (THF, THF/HMPA, and THF/TDA-1) is shown in Table 3. For each solvent system, a total of 36−60% polycarbosilane was produced, and the soluble fractions exhibit a bimodal molecular weight distribution. THF/TDA-1 and THF/HMPA yielded the highest molecular weight fraction of soluble polymer. TDA-1, a cation complexing agent, and HMPA ($O{=}P[N(CH_3)_2]_3$), which is a highly polar aprotic solvent (dielectric constant $\epsilon \approx 30$) that can strongly solvate counter cations in organic solution, decrease the ion pairing significantly more than the weakly polar THF ($\epsilon \approx 7.8$). The higher conductivity of the solution and the decrease in ion pairing render the process more reactive and confer greater freedom to active anions (e.g., carbanions) in an electrolyte solution.[29,30] Thus, when the synthesis was conducted in THF (Al anode, $[Bu_4N]^+[BF_4]$), the total carbosilane product obtained was ~36.4% (HMW with $M_n = 11\,600$). In comparison, electrosynthesis with the addition of 20 parts of TDA-1 produced a total yield of 46%, with increased molecular weight (HMW with $M_n \approx 33\,000$), and that with THF/HMPA (1:1) yielded ~65% carbosilane (HMW with $M_n \approx 57\,600$). The changes in yields and molecular weights, shown here, suggest significant differences in the kinetics of the synthesis process with the solvent polarity and the weakening of the $CH_2:^-/Al^{3+}$ ion pairing. Substantial increase in the production of insoluble polycarbosilane is directly associated with the increase in the molecular weight of the soluble product (Tables 3 and 4). This



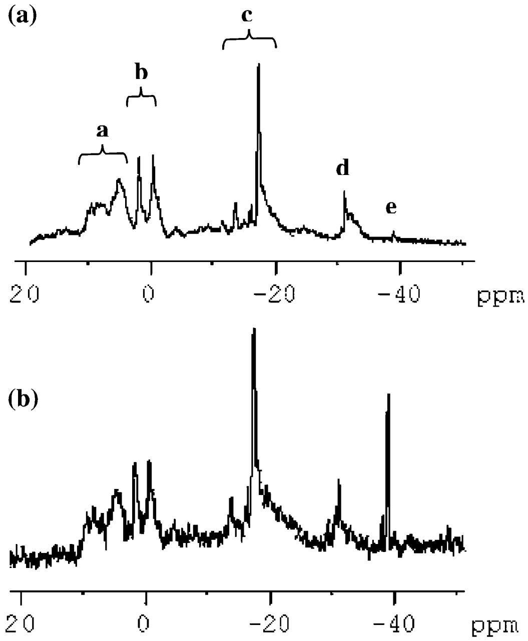


Figure 4. ^{29}Si NMR of PMSM prepared in (a) THF/TDA-1 (8/2) and (b) THF/HMPA (5/5).

is to be expected from a monomer that has multifunctional active groups such as $ClCH_2Si(CH_3)Cl_2$, where inter- and intramolecular linking of the growing chains forms three-dimensional structures. The effects of inter- and intramolecular reactions are considerably higher as the molecular weight increases. At a critical stage, the ability of the solvent to swell the entangled three-dimensional structures is greatly impeded. An MM2 force field modeling of highly branched carbosilane macromolecules containing 24 silicon units (Figure 3) shows that some Si−Cl groups, residing on different branches, are spatially arranged in such a close proximity (Figure 3a) that they could form Si−Si interlinks via electroreduction (Figure 3b). With more branches being interconnected, the originally fully expanded highly branched structure shrinks to a compact three-dimensional configuration (Figure 3c). The sizes of the branched carbosilanes, measured by the radius of the maximum molecular cross section area, r, are 17.2, 14.7, and 11.8 Å, for those with no cross-links, two cross-links, and four cross-links, respectively.

The total yield and the molecular weight of the product are directly related to the monomer concentration, as shown in Table 4 for the electropolymerization of $ClCH_2Si(CH_3)Cl_2$ in THF/TDA-1 (8:2, v/v). At a very low monomer concentration (≤ 0.4 mol/L), only oligomers were obtained. This is due to the extensive cyclization of growing oligomers, which is a known phenomenon that was employed in the synthesis of cyclic carbosilanes in the conventional Grignard reaction.[12] Increasing the monomer concentration of 0.8 mol/L to 2.5 mol/L results in substantial augmentation in the molecular weight M_n (quadruples from 10 500 to 42 600), and the polymer yield increases from 14.0% to 74.5%. However, high monomer concentrations produced high yields of insoluble polymers.

Characterization of Branched Poly[methylsilylenemethylene] (PMSM). Electropolymerization of $ClCH_2Si(CH_3)Cl_2$ formed a branched PMSM having a $-[Si-CH_2-]_n-$ backbone that, in some cases, incorporates Si−Si or $Si-CH_2CH_2-Si$ in the structures. The IR spectrum of PMSM shows a strong vibration around the 1050 cm^{-1} region and a weak deformation at 1353 cm^{-1}, which is due to the $Si-CH_2-Si$ vibration.[22] The Si−H stretching appears as a strong and sharp band at 2120 cm^{-1}, and the H−Si−H scissor mode gives a peak at 950 cm^{-1}. The assignments of all the IR bands are summarized in Table 2. Quantitative ^{29}Si NMR of PMSM (Figure 4) shows four major silicon environments: tri-branching unit "**a**" (10−4 ppm), bi-branching unit "**b**" (2.16 to −0.17 ppm), linear unit "**c**" (−13.2 to −21.2 ppm), and terminal silicon unit "**d**" (−30 to −35 ppm). Integration gives a ratio of 10.0:7.2:4.5:2.2 (**a**:**b**:**c**:**d**). The relatively low content of "**c**" and high content of branching units "**a**" and "**b**" indicate that PMSM is highly branched. The presence of "**a**" reveals that interchange of $Si-CH_3$ and Si−Cl, by a similar process described in Scheme 3, occurred when Al was used as the anode. Additionally, a trace amount of oligosilane structure "**e**" (−39 to −41 ppm), which originated from the tacticity of the silicon chain,[31] was observed. The formation of silicon−silicon bonds suggests that silyl anion can also be formed during electropolymerization. The content of Si−Si linkages increases when PMSM is prepared in the presence of HMPA (Figure 4), indicating that the cosolvent promoted the formation of silyl anions.

The structural information of cross-linking by $SiCH_2-CH_2$-Si and Si−Si can be revealed by IR and UV techniques. The $SiCH_2-CH_2Si$ vibration (1170−1130 cm^{-1}) was not observed in IR spectra of branched polycarbosilanes (Table 2), but was found in linear polycarbosilane. Whitmarsh et al.[25] had reported

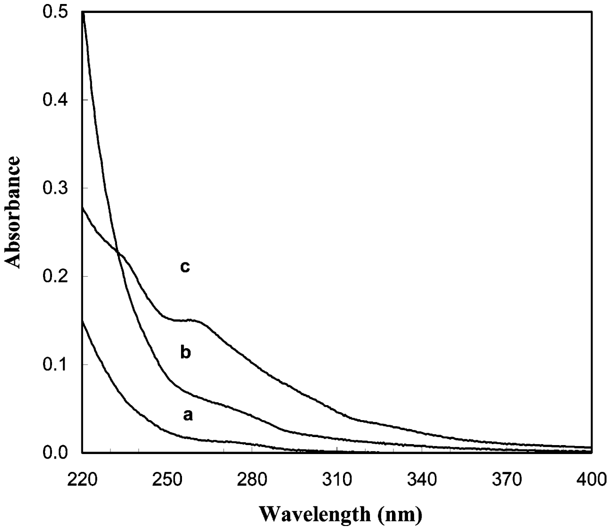


Figure 5. UV spectrum of branched PMSM synthesized in different solvents: (a) THF, (b) THF/TDA-1 (8/2), and (c) THF/HMPA (5/5). Hexane solution, 1.05×10^{-5} mol/L; 25 ± 1 °C.

that nucleophilic reaction of a CH_2-Cl bond with a nucleophile, such as Grignard $(CH_3)_3SiCH_2MgCl$, is much slower than that of a Si−Cl bond. The $SiCH_2-CH_2Si$ structure is even less likely to form for the trifunctional $ClCH_2Si(CH_3)Cl_2$, since the ratios of $[Si-Cl]/[CH_2-Cl]$ in $ClCH_2Si(CH_3)Cl_2$ and its polymer are higher than in the bifunctional $ClCH_2Si(CH_3)_2Cl$ and its polymer.

Polycarbosilane with a $-Si-CH_2-$ backbone does not exhibit absorption in the 200−400 nm region in the UV spectra. However, polymers prepared in THF/HMPA and THF/TDA-1 show a UV absorption extending from 220 to 300 nm, without a defined absorption maximum, which is a characteristic of Si−Si−Si segments (Figure 5). When the electrosynthesis was conducted in THF, the products exhibited very weak UV absorption. These results are consistent with the ^{29}Si NMR analysis that shows increased amounts of silicon units "**e**" at −39 to −41 ppm (Figure 4).

The cross-linking that is caused by formation of Si−Si linkages can be further analyzed by deconvoluting the $Si-CH_2-Si$ IR vibration region 1100−1000 cm^{-1} (Figure 6). The $Si-CH_2-Si$ structure, cross-linked by the silicon−silicon linkage, possesses a large mass when compared to a cross-linked structure that is bridged by $-CH_2-$. It follows that the large mass cross-linking should shift the wavenumber ($\tilde{\nu}$) of the vibration to a lower value according to the simple model of vibrators, $\tilde{\nu} \approx (k/m_{\text{cross-link}})^{1/2}$, where k is the force constant and $m_{\text{cross-link}}$ is the increased mass. The following assumption was made: the 1060−1040 cm^{-1} sub-band is related to linear polycarbosilanes and the 1030−1000 cm^{-1} sub-band is related to cross-linked polycarbosilanes. This definition is useful to qualitatively describe the degree of branching of polycarbosilanes induced by Si−Si linkages. The deconvoluted $Si-CH_2-Si$ vibration band results, shown in Figure 6 and Table 5, reveal that electrosynthesis of polycarbosilanes in the THF/HMPA system consists of a high percentage (∼16%) of cross-linked structures compared to those prepared in the other solvent systems. In comparison, PDMSM contains only ∼5% of cross-linked moieties. This observation confirms that the solvent HMPA promoted Si−Si formation and increased the degree of cross-linking for polycarbosilanes.

Introduction of Si−Si linkages into polycarbosilanes leads to cross-linking, thus increasing the dimensional stability.[2] This can be of significant value to minimize the structural shrinkage,[32] when polycarbosilane is used as a ceramic precursor, as a matrix in a composite, or as a binder of ceramic powders. Figure 7 illustrates the TG analysis of branched PMSMs of different degrees of cross-linking. For the highly cross-linked PMSMs (insoluble products), a ceramic yield up to 90 wt % was obtained (curves a and b). Decreasing the degree of cross-linking (soluble products) leads to a lower ceramic yield (80−30 wt %). For comparison, linear polydimethylsilane gives almost no ceramic products. This high dimensional stability of cross-linked PMSM provides an important feature in developing ceramic material with structural integrity.

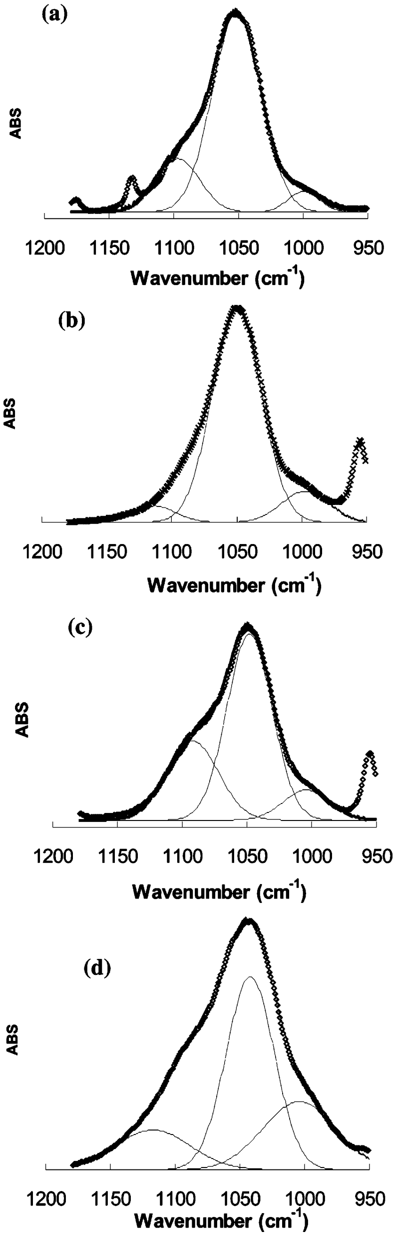


Figure 6. Deconvolution of the $Si-CH_2-Si$ vibration band in the IR region 1120−1000 cm^{-1}. (a) PDMSM; (b) PMSM prepared in THF; (c) PMSM prepared in THF/TDA-1 (8/2); and (d) PMSM prepared in THF/HMPA (5/5).

Carbosilane Oligomers. In the present work on the electrosynthesis using $ClCH_2Si(CH_3)_{3-m}Cl_m$ ($m = 2$), the product composition contained 20−35% soluble polycarbosilane PMSM, 10−30% insoluble/cross-linked polycarbosilane, and 30−45% carbosilane oligomers. These oligomers are indicative of structural irregularity (i.e., cross-linking, loop, fused rings, and other structures) that might be incorporated into the branched

Table 5. Impact of Solvents on Branching in the Electropolymerization of Polycarbosilanes[a]

polycarbosilane	solvent (v/v)	terminal $>1090\ cm^{-1}$ (area %)	linear $1080-1050\ cm^{-1}$ (area %)	cross-linked $<1040\ cm^{-1}$ (area %)
linear PDMSM	THF/TDA-1 (8/2)	14.6	80.4	5.0
branched PMSM	THF	13.4	75.9	10.7
	THF/TDA-1 (8/2)	14.3	75.3	11.4
	THF/HMPA/TDA-1 (8/1/1)	19.1	64.5	16.4
	THF/HMPA (5/5)	38.5	39.8	20.7

[a] The $Si-CH_2-Si$ vibrational band in the IR region $1120-1000\ cm^{-1}$ (Figure 6) was deconvoluted into three sub-bands. The whole $Si-CH_2-Si$ vibrational band was normalized to 100 area %.

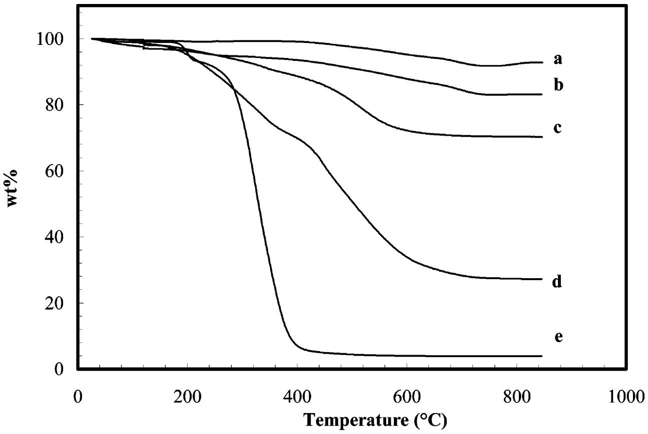


Figure 7. Thermogravimetric analyses of insoluble (**a** and **b**) and soluble (**c** and **d**) cross-linked branched polycarbosilanes and linear polydimethylsilane (**e**). Heating rate is 10 °C/min in argon.

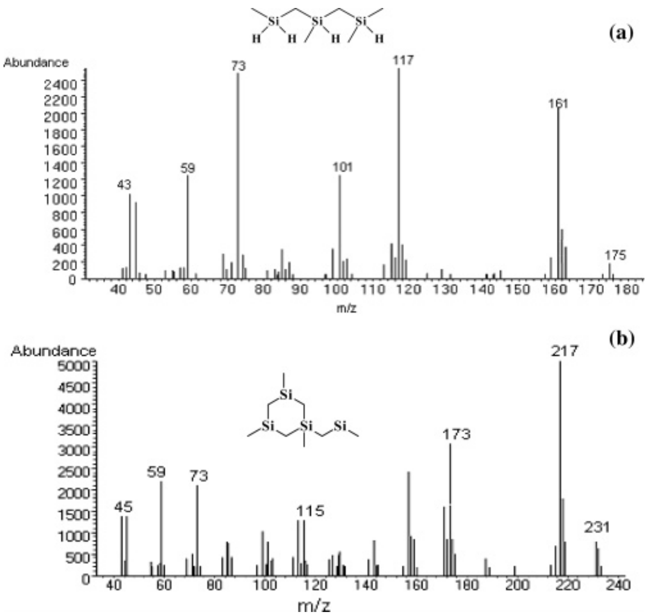


Figure 8. Mass spectra of (a) 2,4-dimethyl-2,4,6-trisilaheptane (*m*/*z*, abundance): $[M - H]^+$ (175, 16%), $M - CH_3$ (161, 100%), $M - CH_2SiH_2CH_3$ (117, 75%), $M - SiH(CH_3)_3$ (101, 31%), $(CH_3)_2SiHCH_2-$ (73, 37%), $(CH_3)_2SiH-$ (59, 16%); (b) 1-(2-silapropyl)-1,3,5-trimethyl-1,3,5-trisilacyclohexane (*m*/*z*, abundance): $[M - H]^+$ (231,10%), $M - CH_3$ (217, 66%), $M - CH_2SiH_2CH_3$ (173, 100%), $M - 2CH_2SiH_2CH_3$ (115, 16%), $(CH_3)_2SiHCH_2-$ (73, 34%), $(CH_3)_2SiH-$ (59, 29%).

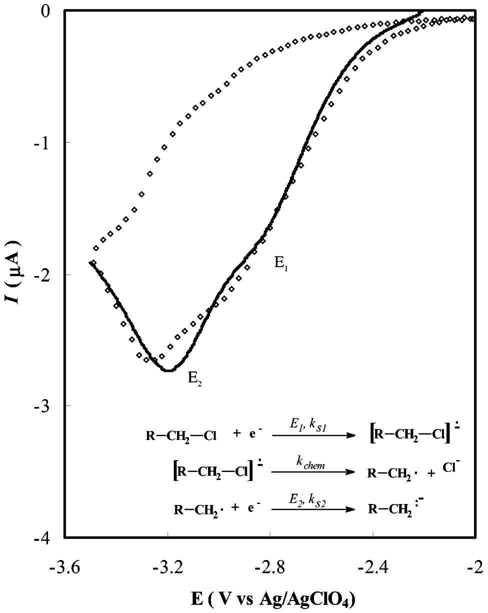


Figure 9. Experimental (◇) and simulated (—) voltammograms of $(CH_3)_3SiCH_2Cl$ at 20 °C. Scan rate is 20 mV s^{-1}.

skeleton of PMSM. These are also useful in unraveling the polymerization mechanism. The typical mass spectra of carbosilane oligomers are shown in Figure 8. On the basis of GC-MS analyses, a large number of linear, branched, and cyclic carbosilane oligomers were identified. Some of them bear the Si−Si bond. The major mass fragments of these compounds are summarized in Table 1. [Note that a minute quantity of the oligomers, presented in Table 1, might have been produced during GC-MS measurements since the injection temperature is 220 °C. The TGA measurements show the soluble PMSM has <5% degradation at 220 °C (curves c and d in Figure 7). A more detailed study is currently underway.] The formation of these diverse structures is strongly dependent on electrosynthesis conditions, such as the anode material, solvent, and supporting electrolyte (Table 6). The results can be summarized as follows: (1) the formation of branched structures is favorable with an Al anode, whereas a Mg anode leads to mostly linear oligomers; (2) less than 1% cyclic carbosilanes were formed when Mg was used as the anode. However, an Al anode generally led to high concentrations (7−16%) of cyclic carbosilanes, regardless of the solvent or the supporting electrolyte (most of these cyclic carbosilanes contained four- and six-membered rings, which are thermodynamically the most stable configuration); (3) a Mg anode impedes the formation of Si−Si linkage. With Al as the anode, supporting electrolyte Bu_4NClO_4 showed similar inhibiting effects, as did Mg. However, other supporting electrolytes generally allowed Si−Si bond formation. Cosolvents such as TDA-1 and, in particular, HMPA facilitated Si−Si bond formation. For example, electroreaction in THF/HMPA (5/5 volume ratio) produced 12.9% carbosilanes that contained Si−Si bonds, compared to only 2.6% with THF. This is probably due to the strong solvation of cations by HMPA, which generates solvated electrons that can reduce Si−Cl bonds into silyl anions, and/or due to the formation of a $[-Si^+HMPA\ Cl^-]$ adduct.[33]

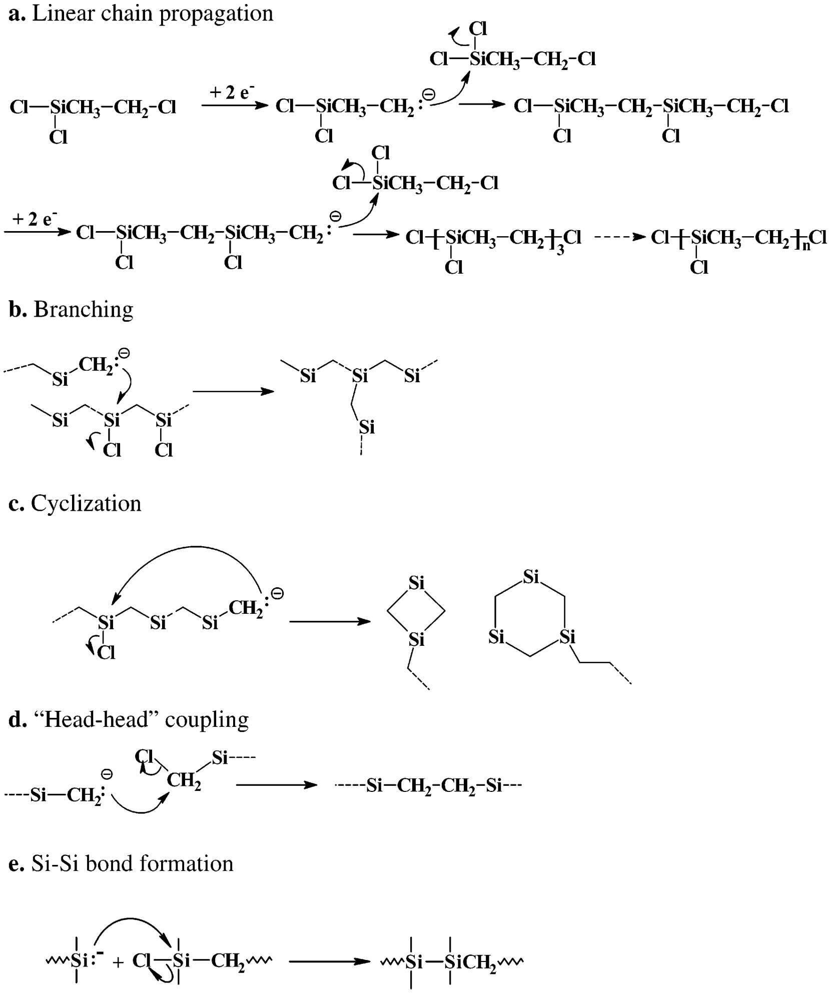
The formation of linear, cyclic, and branched carbosilane oligomers suggests that the structure of branched PMSM is quite complex. The branched PMSM is likely to incorporate intercon-

Table 6. Formation of Carbosilane Oligomers from $ClCH_2Si(CH_3)Cl_2$ under Various Electrosynthesis Conditions[a]

electrosynthesis conditions			
anode	solvent (v/v)	supporting electrolyte	oligomers (GC yield, %)
Mg	THF/TDA-1 (8/2)	$[Bu_4N]^+[BF_4]^-$	**3** (2.0), **3c** (2.4), **4i** (0.2), **5** (20.1), **6** (70.6).
Al	THF/TDA-1 (8/2)	$[Bu_4N]^+[BF_4]^-$	**3** (36.9), **3c** (17.5), **4c** (4.3), **4i** (11.0), **5** (30.2).
Al	THF	$[Bu_4N]^+[BF_4]^-$	**3** (29.1), **3c** (17.2), **4c** (3.1), **4i** (8.3), **5** (34.6), **6** (7.7).
Al	THF/HMPA (5/5)	$[Bu_4N]^+[BF_4]^-$	**3** (5.0), **3c** (7.2), **4c** (3.3), **4i** (16.7), **5** (4.6), **6** (10.1), **6i** (49.9).
Al	THF/TDA-1 (8/2)	$[Bu_4N]^+[ClO_4]^-$	**4c**(5.8), **4i**(29.9), **5**(44.7), **6**(19.6).
Al	THF/TDA-1 (8/2)	$[Bu_4N]^+[BPh_4]^-$	**4c** (8.0), **4i** (14.8), **5** (47.9), **6** (12.1), **6i** (17.1).
Al	THF/TDA-1 (8/2)	$[Bu_4N]^+[p\text{-Tol-}SO_3]^-$	**3** (45.1), **3c** (27.7), **4c** (4.9), **4i** (15.4), **5** (3.1), **6** (2.1), **6i** (1.6).

[a] Electropolymerization conditions: nickel cathode; [$ClCH_2Si(CH_3)Cl_2$] 1.0 mol/L; [supporting electrolyte] 0.02 mol/L; current 40 mA; electricity 2.2 F/mol; 45 kHz sonication bath, 25 °C.

Scheme 4. Electropolymerization of $ClCH_2SiCH_3Cl_2$



nected branches and ring closures. Such diverse structural characteristics are apparently attributed to the complex and broad peaks shown in the ^{29}Si NMR spectra of branched PMSM (Figure 4).

In order to elucidate the reaction intermediate, cyclic voltammetric measurements of $(CH_3)_3SiCH_2Cl$ and $(CH_3)_3SiCl$ were investigated. Figure 9 displays the representative voltammogram of $(CH_3)_3SiCH_2Cl$ at 20 °C and a scan rate of 20 mV s^{-1}. The voltammogram exhibits two irreversible cathodic peaks with cathodic peak potentials $E_{p1} = -2.98$ V vs Ag/AgClO$_4$ and $E_{p2} = -3.29$ V vs Ag/AgClO$_4$. The reduction mechanism has been analyzed by fitting experimental CV data with Gosser's CVFIT program based on the Butler−Volmer equation.[20] From the simulation plot that has been constructed accordingly (solid line in Figure 9), we concluded that the reduction of $(CH_3)_3SiCH_2Cl$ undergoes an ECE mechanism[34,35] that involves reaction sequences outlined in Figure 9. A single electron transfer to neutral R−CH$_2$−Cl at the potential E_1 is followed by the cleavage of the C−Cl bond, producing a carbon-centered radical. The radical is immediately reduced to a carbanion at the potential E_2. The fitting results give electron-transfer rate constants $k_{s1} = 2.0 \times 10^{-4}$ cm s^{-1} and $k_{s2} = 1.1 \times 10^{-4}$ cm s^{-1}, decomposition rate constant $k_{chem} = 8900$ s^{-1}, and the reduction potentials $E_1 = -2.42$ V and $E_2 = -2.79$ V vs Ag/AgClO$_4$. The large reduction potential difference ($\Delta E = E_1 - E_2 = 370$ mV) is comparable to those of *tert*-butyl bromide and *tert*-butyl iodide,[35] indicating a strong stabilization contribution of the substituent $(CH_3)_3Si-$ on the hypothetical carbanion radical $[-CH_2Cl]^{\bullet -}$ and the carbanion $[-CH_2]^-$. The electron transfer to the carbon−Cl bond and to the carbon-centered radical are both extremely slow processes, as evidenced by their low heterogeneous electron-transfer rate constants k_{s1} and k_{s2} (~10^{-4} s^{-1}). This results in a significant shift of the cathodic peak to the more negative potential.[36]

Therefore, the electropolymerization mechanism of $ClCH_2Si(CH_3)_{3-m}Cl_m$ can be understood by the initial electrogeneration of carbanions and the subsequent carbanion attack on a Cl−Si bond of a second monomer, via a nucleophilic displacement, which forms a Cl $(CH_3)_{3-m}Cl_{m-1}SiCH_{22}Cl$ dimer (Scheme 4). The resulting dimer also carries a CH_2Cl "head", which is equally electroactive to that of the monomer and can be electrochemically reduced to dimeric carbanion Cl $(CH_3)_{3-m}Cl_{m-1}SiCH_{22}:^-$, which can then react with either monomer or dimer. The dominant "head" $[-CH_2]^-$ to "tail" [Cl−Si] coupling process (Scheme 4a) repeats progressively to form a long chain of high molecular weight polycarbosilanes, which is comprised primarily of $Si-CH_2-Si$ linkages (Table 3 and Figure 4).

However, branching occurs with the use of $ClCH_2SiCH_3Cl_2$, since multiple Cl−Si "tails" can react with the "head" $-SiCH_2:^-$ (Scheme 4b). With the addition of each monomer, an additional $SiCl_2$ site is introduced, leading to cascading processes that result in a highly branched polycarbosilane molecule, whose size is constrained mainly by kinetic conditions and solubility.

Several side reactions were also observed. For example, cyclization occurs for the $-[CH_2Si-]_n$ chain with $n \geq 2$ through intramolecular attacks of the $-SiCH_2:^-$ "head" on the Si−Cl "tail" (Scheme 4c) to form products containing four- to six-membered-ring structures (Tables 1 and 6). A "head" $[-CH_2]^-$ to "head" $[-CH_2Cl]$ coupling is also possible (Scheme 4d), but proved insignificant. Because the electron transfer to the Si−Cl bond can result in a silyl anion,[16,19] some silicon−silicon linkages can be introduced by nucleophilic displacement of silyl anions with Si−Cl groups (Scheme 4e), as evidenced by a UV absorption band in the 220−400 nm region (Figure 5). This process is apparently accelerated by HMPA, which is known to be a good electron-transfer agent. The intermolecular silicon−silicon bond formation is chiefly responsible for the cross-linking of polycarbosilanes.

Conclusion

This study shows that electrosynthesis methods can be employed as a mild and facile alternative for the syntheses of polycarbosilanes. As such, the electrosynthesis considerations developed in recent times have been extended in this paper to the synthesis of macromolecules. The investigation reported herein shows that electropolymerization using chloromethylchlorosilanes, $ClCH_2Si(CH_3)_{3-m}Cl_m$, leads to the formation of linear ($m = 1$) and branched ($m = 2$) methylene-bridged carbosilane oligomers and polymers. Therefore it can be reasoned that a controlled electro-copolymerization with a mixture of these co-monomers (or even chlorosilane monomers) could be put into practice.

This research reveals that electropolymerization of carbosilane mechanisms consists primarily of iterative stepwise reaction sequences. This sequence involves electroreduction of the CH_2-Cl bond {a single electron transfer−chemical reaction−single electron transfer (i.e., ECE mechanism)} to a carbanion that is stabilized by the α-silyl hyperconjugation effect, followed by S_N2 nucleophilic displacement of a carbanion with a Cl−Si group, where Cl− is a good leaving group. Although this research represents only a preliminary exploration of this new synthetic approach, it points to the possibility of a more general electrosynthetic approach to carbon−heteroatom backbone hybrid polymers, starting from a monomer constituting a highly electroreductive "head" and an electrophilic "tail". The moiety for the "head" could be $X-CH_2-Ar$, $X-CH_2-Si$, $X-CH_2-Ge$, etc., where the X−C bond is highly electroreductive due to the introduction of, for example, aromatic[10] or α-hyperconjugating resonance effects,[37−39] and the electrophilic "tail" should possess a good leaving group, e.g., Ge−Cl, Sn−Cl, or P−Cl. An additional implication of this research relates to the fact that Si−Cl bonds could also be electrochemically reduced through a slow two-electron transfer−chemical reaction (EC) mechanism,[19] to form silyl anions. This observation opens a door to the electrochemical syntheses of carbosilane−silane copolymers utilizing simple halosilane monomers (e.g., $ClCH_2SiMeCl_2$ with Ph_2SiCl_2).

The study proves that electropolymerization of $ClCH_2Si(CH_3)Cl_2$ can yield high molecular weight soluble PMSM ($M_n \approx 57\,000$). However, this should be considered a preliminary (introductory) result since the molecular weight, yield, and the structure of the resulting polycarbosilanes are strongly affected by electropolymerization conditions, such as electrode material, solvents, supporting electrolytes, and monomer concentration. Supporting electrolytes such as TBAT and TBAF and cosolvent HMPA and TDA-1 can generally facilitate polymerization by enhancing the reactivity of the carbanion. All these should be a subject of a thorough investigation for a specific focus of interests in the field.

A thorough analysis of the oligocarbosilanes by GC-MS indicates that a variety of structures, such as interconnected branches, rings, and fused rings, are likely to be incorporated into the polymer chains (Figure 3). A number of side reactions that produce $-CH_2-CH_2-$ and −Si−Si− linkages can be harnessed and be favorably introduced to the carbosilane chain $[Si-CH_2]_n-$, which may be used as a ceramic precursor. The TGA results (>90 wt % ceramic yield) suggest that these polycarbosilanes could be used as a promising matrix for processing SiC/SiC composites, where low mass loss during pyrolysis is critical to maintain the structural integrity.

Control of these side reactions is affected by the electrosynthesis conditions. The cosolvents, such as TDA-1, increase the probability of silyl anion and Si−Si interlinkage formation.

The cross-linking nature of the solid composition and structure need to be quantitatively analyzed. A more detailed study on the effect of solvent, as related to the reactivity of anions, in particular the polarity as well as the nucleophilicity, is currently underway.

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