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Electrosynthesis of new polysilynes: poly(methylsilyne) and poly(cyclohexylsilyne-*co*-methylsilyne)

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Abstract

The electrochemical synthesis and optical properties of poly(methylsilyne) and a series of poly(cyclohexylsilyne-*co*-methylsilyne) network copolymers are described. The new polymers, which are not accessible via the Wurtz coupling reaction, are prepared by electrochemical reduction of methyltrichlorosilane, or mixtures of the monomers methyltrichlorosilane and cyclohexyltrichlorosilane, utilizing copper electrodes in a one-compartment cell. The polymers have optical properties expected for polymers in this class of materials. The poly(methylsilyne) is proposed as a potential soluble precursor for SiC. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polysilynes; Network polysilane; Electrochemical synthesis

1. Introduction

The network polysilanes $(SiR)_n$, where R = alkyl or aryl, also referred to as the polysilynes, have interesting electronic and optical properties due to the nature of the extensive σ delocalization of the Si backbone electrons [1–5]. These polymers are related to the linear polysilanes $(SiR_1R_2)_n$ which have received a great deal of attention due to their potential applications as photoresists, conducting polymers, and nonlinear optical materials [6]. Unlike the polysilanes, the polyalkylsilynes exhibit a broad band edge in the visible region, extending their potential applications to encompass those that require visible light-emitting properties. This shift in the band gap has been attributed to an increase in the σ delocalization due to the increased dimensionality of the silicon backbone compared to the linear polysilanes.

The typical method of synthesis for the polysilanes and related polysilynes is by reductive coupling of dichloro- and trichloro-silanes via the Wurtz method, using an alkali metal reducing agent in high-boiling solvents [1–6]. Due to the severe conditions, the polymer side chains are normally limited to only robust aryl and alkyl groups. In addition, the heterogeneity of the reaction and rapid rate result in the formation of polymers that are typically polydisperse. Alternative methods of synthesis are required to address these issues. For the synthesis of the polysilynes, alternatives that have been reported are the use of graphite–potassium reducing agent [7] and electrolysis [8]. In a recent paper, it was reported that an electrolytic method can be employed to prepare a new silicon network polymer with the more sensitive pentafluorophenyl side chain [9]. In addition, we have reported the synthesis of a series of silicon and silicon–germanium network copolymers by electrolysis which have a much lower polydispersity compared to polymers prepared by the thermal Wurtz coupling method [10].

In the present study, we describe the synthesis of poly(methylsilyne), $(SiCH_3)_n$, and a series of poly(cyclohexylsilyne-*co*-methylsilyne) network copolymers, $(SiC_6H_{11})_x(SiCH_3)_y$, by an electrochemical reduction method (Eq. (1)). We demonstrate that the electrolytic method is a feasible method for the preparation of polysilynes containing the methyl side group, which are inaccessible by the Wurtz coupling method, and that these polymers exhibit spectroscopic and optical properties that are typical for this class of materials.

2. Experimental

Cyclohexyltrichlorosilane and methyltrichlorosilane were distilled prior to use. 1,2-Dimethoxyethane (DME) was stirred with metallic sodium and distilled in the presence of benzophenone radical anion sodium salt in a stream of nitrogen. Tetrabutylammonium perchlorate (TBAP) was dried in vacuo at 50°C overnight.

Gel permeation chromatography (GPC) was performed in

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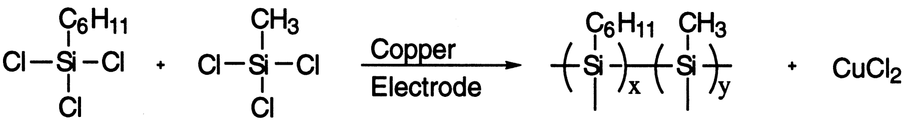

$$Cl-\underset{Cl}{\overset{C_6H_{11}}{Si}}-Cl + Cl-\underset{Cl}{\overset{CH_3}{Si}}-Cl \xrightarrow[\text{Electrode}]{\text{Copper}} -\!\left(\overset{C_6H_{11}}{Si}\right)_x\!\!-\!\left(\overset{CH_3}{Si}\right)_y\!- + CuCl_2 \qquad (1)$$

THF solution using Ultrastyragel columns in series, a Beckman model 110B HPLC pump, and an ISCO UA-5 absorbance/fluorescence detector. The molecular weights obtained were determined by reference to polystyrene standards. NMR spectra were recorded at room temperature in $CDCl_3$ solutions with a Varian VXR-SERIES NMR spectrometer at 300 MHz for ^1H NMR, 75 MHz for ^{13}C NMR, and 60 MHz for ^{29}Si NMR. IR spectra were recorded utilizing a Perkin–Elmer 1605 FTIR Spectrometer. UV–Visible spectra were executed with a Shimadzu UV 160-U UV–Visible recording spectrophotometer. Photoemission spectra were measured on the PTI LS-100™ luminescence spectrophotometer in THF solutions.

Electrochemical reduction of a DME solution of a trichlorosilane (or a mixture of monomers) was carried out in an 80 ml undivided cell equipped with coiled copper wire 1 mm in diameter for both the cathode (4 cm^2) and anode (34 cm^2). In the cell was placed 1.0 g of TBAP and the cell was dried at 50°C in vacuo overnight. 5 mmol of a trichlorosilane (or a mixture of monomers) and fresh, dry DME (30 ml) were added to the cell under a dry argon atmosphere. A voltage (−6.0 V) was applied to provide a current of 50 mA. The electrolysis was carried out within an ultrasonic bath. The use of the bath assists in keeping the surface of the electrode clean and active. The progress of the reaction was monitored by GPC, and the electrolysis was continued until the chromatogram no longer changed. Methanol (20 ml) was then added to the electrolyzed solution to quench the reaction. The mixture was stirred for 2 h. Toluene was added and the organic layer was separated, washed with water and then evaporated. The residue was dissolved in fresh toluene and the yellow polymers were precipitated by adding methanol.

The synthesis of these polymers was also attempted by the thermal reduction method using typical Wurtz conditions. A trichlorosilane (or a mixture of monomers) was added slowly to a refluxing sodium dispersion in toluene under an atmosphere of argon. The reaction was carried out at reflux for 5 h. The reaction was quenched by adding methanol and water. The organic layer was separated and washed with water to remove the traces of sodium salts. The polymers were obtained by precipitation from the solution with methanol. All operations were carried out under an argon atmosphere and light was excluded from the reaction mixture.

2.1. Spectroscopic data

$Si(C_6H_{11})_n$ ^1H NMR δ: 0.8–2.0 (Si–CH_6H_{11}), 3.7 (Si–OCH_3); ^{13}C NMR δ 23.75, 26.4, 27.3, 30.0 (Si–C_6H_{11}); IR 2920(s), 2849(s), 1720(w), 1444(s), 1443(s), 1349(w), 1290(w), 1267(w), 1191(w), 1073(m), 885(s),774(w), 732(w), 515(s).

$[(Si(C_6H_{11})_{0.7}(SiCH_3)_{0.3}]_n$ ^1H NMR δ: 0.7–2.0 (Si–C_6H_{11}); 0.0–0.4 (Si–CH_3); 3.7 (Si–OCH_3); ^{13}C NMR δ: 26.0, 27.5, 28.1 (Si–C_6H_{11}); −4.0 (Si–CH_3); IR, 2931(vs), 2860(vs), 1596(w), 1481(s), 1372(s), 1267(w), 1149(w), 1032(m), 850(w), 779(s), 714(s), 514(w), 451(s).

$[(Si(C_6H_{11})_{0.5}(SiCH_3)_{0.5}]_n$ ^1H NMR δ: 0.0–0.4 (Si–CH_3); 0.6–1.9 (Si–C_6H_{11}); 3.7 (Si–OCH_3); ^{13}C NMR δ: 23.8, 26.4, 27.3, 30.0 (Si–C_6H_5); −4.0 (Si–CH_3); IR 2931(s), 2849 (s), 1715(s), 1448(s), 1377(s), 1290(w), 1267(w), 1167(w), 1078(m), 994(w), 909(w), 885(s), 850(s), 779(m), 720(vs), 509(s).

$[(Si(C_6H_{11})_{0.3}(SiCH_3)_{0.7}]_n$ ^1H NMR δ: 0.0–0.4 (Si–CH_3), 0.6–1.9 (Si–C_6H_{11}); 3.7 (Si–OCH_3); ^{13}C NMR δ: 23.8, 26.4, 27.4, 30.0 (Si–C_6H_{11}); −4.0 (Si–CH_3); IR 2931(s), 2891(s), 1462(s), 1377(s), 1267(w), 1167(w), 1068(m), 994(m), 886(s), 844(w), 774(m), 720(w), 668(vs), 515(m).

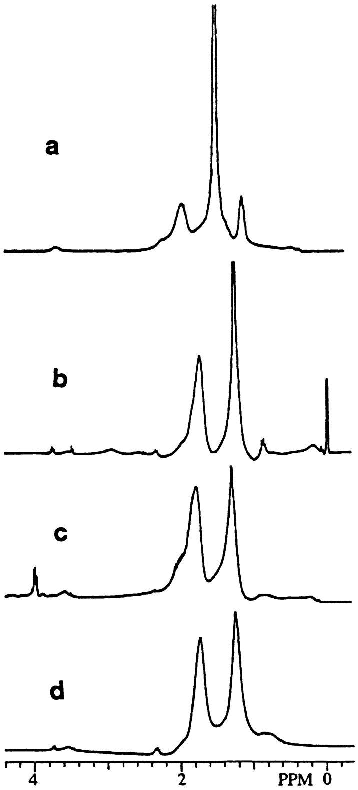

Fig. 1. ^1H NMR Spectra of polymers isolated from the polymerization of mixtures of methyltrichlorosilane and cyclohexyltrichlorosilane under Wurtz coupling conditions. Monomer Feed Ratio, Cyclohexyl:Methyl, (a) 1:3, (b) 1:1, (c) 1:0.5, (d) 1:0.

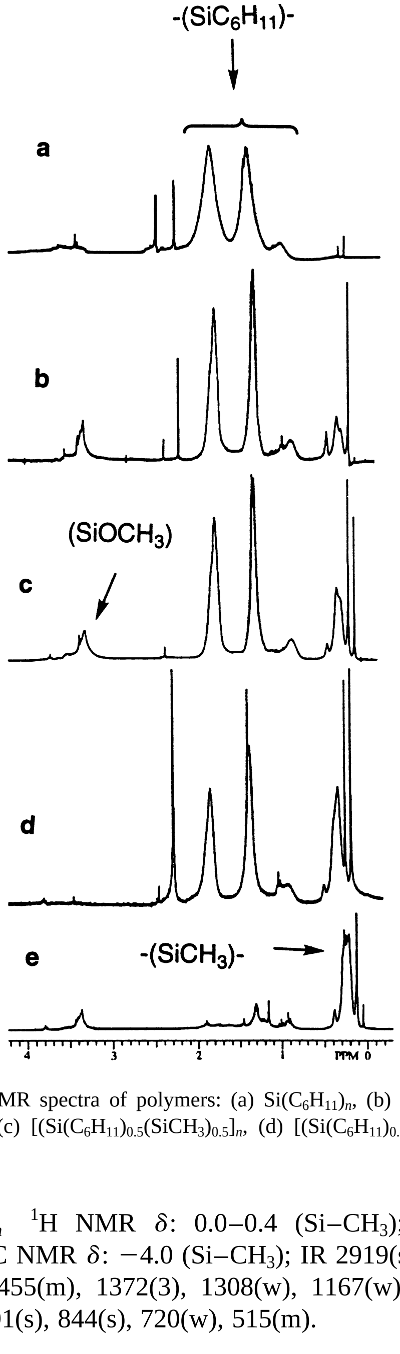

Fig. 2. ^{1}H NMR spectra of polymers: (a) Si(C$_6$H$_{11}$)$_n$, (b) [(Si(C$_6$H$_{11}$)$_{0.7}$-(SiCH$_3$)$_{0.3}$]$_n$, (c) [(Si(C$_6$H$_{11}$)$_{0.5}$(SiCH$_3$)$_{0.5}$]$_n$, (d) [(Si(C$_6$H$_{11}$)$_{0.3}$(SiCH$_3$)0.7]$_n$, (e)Si(CH$_3$)$_n$.

Si(CH$_3$)$_n$ ^{1}H NMR δ: 0.0–0.4 (Si–CH$_3$); 3.7 (Si–OCH$_3$); ^{13}C NMR δ: −4.0 (Si–CH$_3$); IR 2919(s), 2860(s), 1713(s), 1455(m), 1372(3), 1308(w), 1167(w), 1087(m), 957(m), 891(s), 844(s), 720(w), 515(m).

3. Results and discussion

It has been previously reported that Wurtz coupling of methyltrichlorosilane in the presence of sodium yields a white intractable solid [11,12]. A network polymer which would be expected to be yellow is not formed. This occurred in our hands as well. We thought that perhaps copolymers could be prepared by Wurtz coupling and these copolymers would have enhanced solubility. However, alkali metal reduction of the mixtures of the monomers CH$_3$SiCl$_3$ and C$_6$H$_5$SiCl$_3$ yielded only polymers that contain predominantly the cyclohexyl side chain as is seen in the ^{1}H NMR spectra of the obtained products (Fig. 1).

In contrast to the Wurtz coupling method, electrolysis affords the poly(methylsilyne) and copolymers containing both the methyl and cyclohexyl side groups. The relative amount of methyl and cyclohexyl groups present in the polymers closely follows the feed ratio of the monomers as shown in the ^{1}H NMR spectra in Fig. 2 and tabulated in Table 1. The presence of the methoxy side group in the ^{1}H NMR spectrum results from quenching the reaction with methanol and provides a measure of the Si–Cl bonds left unreacted at the end of the electrolysis. Under these conditions, there are about 0.2 chlorines per Si atom remaining at the end of the reaction that react with methanol. The ^{29}Si NMR shows that no Si–Cl bonds remain in the isolated products.

Physical and spectroscopic data for the obtained polymers are provided in Table 1. Molecular weight distributions are monomodal with polydispersities less than 2. The ^{29}Si NMR spectra exhibit broad peaks in the −50 to −70 region which is typical for Si atoms present in trifunctional units [13]. Evidence for linear segments resulting from the quenching with methanol were only observed in polymer (4) with one resonance appearing at greater than −40 ppm.

These network polymers have optical properties which are typical for this class of materials, exhibiting both a broad absorption band edge that tails into the visible region and a broad emission band [1–5]. Emission from [(Si(C$_6$H$_{11}$)$_{0.3}$(SiCH$_3$)$_{0.7}$]$_n$ is blue-shifted compared to the other polymers. This shift is attributed to the existence of some linear components in the chain (–SiOMeR–) which result from quenching the reaction with methanol.

We know of no other report where methyltrichlorosilane was used as a monomer in the Wurtz synthesis to prepare co-polysilynes. However, for the synthesis of variably cross-linked methylsilanes (SiCH$_3$)(SiCH$_3$H), Wurtz coupling of a mixture of CH$_3$SiCl$_3$ and CH$_3$HSiCl$_2$ was utilized [14]. It was reported that copolymers can be obtained by this method; however, as the ratio of SiCH$_3$Cl$_3$ to SiCH$_3$HCl$_2$ is increased, the yield of soluble product decreases significantly. Thus, it is apparent that Wurtz coupling is not a suitable method for the synthesis of soluble highly-crosslinked poly(methylsilyne) or network copolymers prepared from the methyltrichlorosilane monomer.

Soluble silicon backbone polymers with a 1:1 Si:C ratio are of interest due to their potential conversion to silicon carbide [15]. However, highly cross-linked polymers are needed to minimize yield loss due to the extrusion of low molecular weight fragments. One of the most promising precursors reported are the polymethylsilanes with general formula (SiMeH$_x$)$_n$ because they posses both of these important features and also have latent reactivity from the reactive Si–H bonds which can be used to further crosslink the polymer during processing [16,17]. These polymers have been prepared by Wurtz dehalocoupling of SiHMeCl$_2$. However,

Table 1
Physical and optical properties of polymers $[(SiC_6H_5)_x(SiCH_3)_y]_n$

Polymer	Monomer feed ratio (mole fraction) $C_6H_{11}SiCl_3/CH_3SiCl_3$	Polymer composition (mole fraction)[a] $C_6H_{11}Si/CH_3Si$	Methoxy composition (mole fraction)[a] CH_3O/Si	M_n[b]	M_w/M_n	^{29}Si, δ	λ_{em}[c] (nm)
$Si(C_6H_{11})_n$	1.0/0	1.0/0	0.2/0.8	2901	1.30	− 65 (br)	450
$[(Si(C_6H_{11})_{0.7}(SiCH_3)_{0.3}]_n$	0.67/0.33	0.65/0.35	0.2/0.8	2371	1.67	− 48, −58, −61, −68 (br)	453
$[(Si(C_6H_{11})_{0.5}(SiCH_3)_{0.5}]_n$	0.50/0.50	0.51/0.49	0.2/0.8	2781	1.89	− 48, −55, −62, −71 (br)	452
$[(Si(C_6H_{11})_{0.3}(SiCH_3)_{0.7}]_n$	0.33/0.67	0.29/0.71	0.0/1.0	2262	2.00	− 38, −60 (br)	417
$Si(CH_3)_n$	0/1.0	0/1.0	0.2/0.8	3299	1.70	− 50, −60, −66 (br)	448

[a] Composition determined by ^1H NMR.
[b] Molecular weight determined by GPC vs. polystyrene.
[c] Excitation $\lambda = 300$ nm.

polymers prepared in this manner often have low solubility and therefore have processing problems. An alternative synthetic method that has been reported is dehydrocoupling of $MeSiH_3$ via Cp_2MMe_2 where M = Ti, Zr, and Hf or simple derivatives of these complexes [18–20]. A simple modification of our electrochemical procedure and quenching the reaction mixture with lithium aluminum hydride results in the formation of soluble materials with the general formula $(SiCH_3H_x)_n$ [21]. This modification provides an attractive alternative to the synthesis of these polymers and is described in more detail in a forthcoming paper.

4. Conclusion

Poly(methylsilyne) and a series of poly(methylsilyne)-*co*-(cyclohexylsilyne) polymers with variable composition were prepared for the first time by electrochemical reduction. The polymers have optical properties similar to others in this class. A simple modification of the procedure is likely to produce a series of polymers that may be useful as soluble precursors for SiC.

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