First electrochemical synthesis of network silane and silane–germane copolymers: $(C_6H_{11}Si)_x(PhSi)_y$ and $(C_6H_{11}Si)_x(PhGe)_y$

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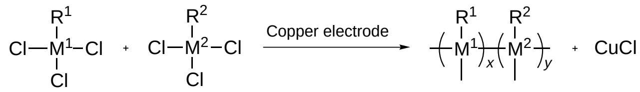
An electrochemical technique is demonstrated for the synthesis of Si–Si and Si–Ge network copolymers poly(cyclohexylsilyne-*co*-phenylsilyne) and poly(cyclohexylsilyne-*co*-phenylgermyne); the molecular mass distributions of the electrochemically prepared polymers are more narrow in comparison to similar polymers prepared by the Wurtz coupling reaction.

Silicon-based polymers have attracted considerable attention owing to their interesting optical and electronic properties, which are strongly related to the dimensionality of the silicon backbone.[1] Polysilanes $(SiR^1R^2)_n$ which consist of a one-dimensional backbone structure exhibit intense near-UV absorption bands and sharp UV emission attributed to the Si backbone σ–σ* transition.[2] The network or crosslinked polysilynes $(SiR)_n$ in which each silicon atom is bonded to three other silicon atoms and one organic side group R are typically yellow materials that photoluminesce in the visible region of the spectrum.[3] It has been proposed that the structure of the network polysilynes consists of rings of different sizes and shapes that are fused together in a random arrangement. The optical features are attributed to the decrease in the Si σ–σ* bandgap compared to the linear polymers, which is caused by increasing the dimensionality of the silicon backbone from a 1D linear structure to a 2D cross-linked structure. Furthermore, it has been reported that Ge three-coordinate polymers (polygermynes)[4] as well as some silicon and germanium copolymers[5] can also be synthesized. The ability to tune the optical properties of these polymers by manipulation of the backbone architecture and composition is an intriguing challenge for the development of these polymers as optoelectronic materials.

The most general synthetic method for the preparation of these metallic backbone polymers is the Wurtz coupling reaction of organo-dichloro- or trichloro-silanes (or germanes) with a sodium dispersion in toluene at refluxing temperature.[2] However, there are several problems with the Wurtz coupling method, most notably the extreme difficulty in controlling the rate of the reaction and thereby obtaining polymers with reproducibly narrow molecular mass distributions. In particular, the network polysilynes that have been prepared by the Wurtz coupling reaction exhibit very broad electronic absorption and NMR spectra. These observations are attributed to the wide variety of macrostructures that are obtained in the Wurtz coupling reaction. Thus, alternative methods of synthesis are desirable for the preparation of materials with structural and optical properties that can be more precisely controlled. To this end, there have been several reports of employing electrochemical techniques for the synthesis of linear polysilanes and germane–silane copolymers.[6]



1 $M^1 = M^2 = Si$; $R^1 = Ph$, $R^2 = C_6H_{11}$

2 $M^1 = Si$, $M^2 = Ge$; $R^1 = C_6H_{11}$, $R^2 = Ph$

Scheme 1†

In the present study, we describe the synthesis and optical properties of two new network copolymers poly(cyclohexylsilyne-*co*-phenylsilyne) $(C_6H_{11}Si)_x(PhSi)_y$ **1** and poly(cyclohexylsilyne-*co*-phenylgermyne) $(C_6H_{11}Si)_x(PhGe)_y$ **2** by an electrochemical reduction utilizing copper electrodes and constant applied potential.† The network polymers were synthesized by the electrochemical reduction of 1,2-dimethoxyethane (DME) solution of a 1 : 1 mixture of the trifunctional monomers as depicted in Scheme 1.

Molecular mass, yield, NMR data, and optical properties of **1** and **2** are provided in Table 1. Notably, the ^{29}Si NMR spectrum

Table 1 Physical and optical properties of **1** and **2**

	x/y^a	Yield^b (%)	$M_n{}^c$	M_w/M_n	^{29}Si, δ	$\lambda_{em}{}^d$/nm	λ_{ex}/nm
1	1.25	49	5839	1.4	−55, −65, −76(br)	470	350
2	1.04	23	3147	2.0	−50 to −80(br)	490	350

[a] Monomer ratio determined by ^1H NMR. [b] Isolated yield obtained by precipitation from toluene–methanol (1 : 8). [c] M_w determined by GPC *vs.* polystyrene. [d] Excitation λ = 300 nm.

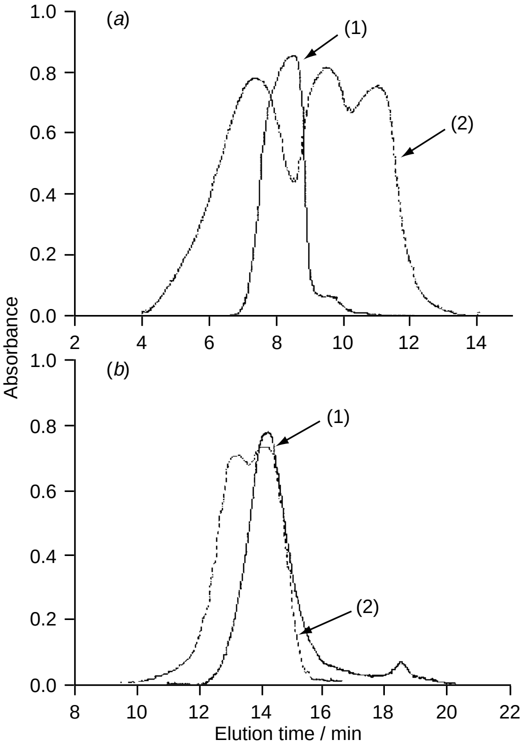


Fig. 1 GPC chromatogram for (*a*) poly(cyclohexylsilyne-*co*-phenylsilyne) (1) electrochemical product, (2) Wurtz product; (*b*) poly(cyclohexylsilyne-*co*-phenylgermyne) (1) electrochemical product, (2) Wurtz product. [Different columns were used for (*a*) and (*b*) and time scales are therefore different]

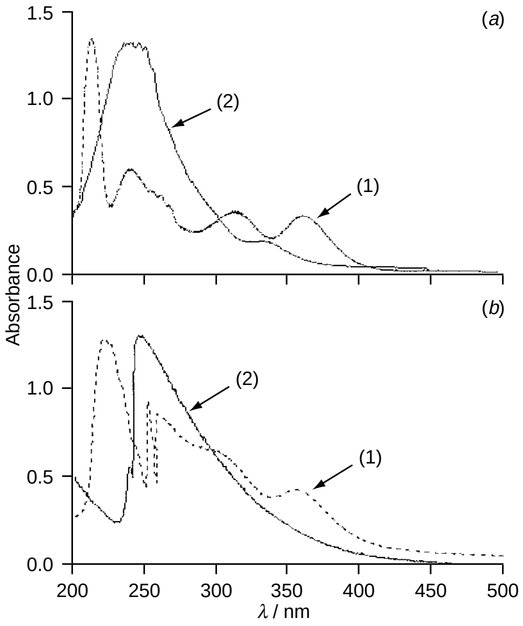


Fig. 2 Absorption spectra of (*a*) poly(cyclohexylsilyne-*co*-phenylsilyne) reaction mixture (1) immediately after quenching with methanol, (2) after ageing in the dark; (*b*) poly(cyclohexylsilyne-*co*-phenylgermyne) reaction mixture (1) immediately after quenching with methanol; (2) after ageing in the dark

of **1** exhibits three broad resolvable peaks in the region typical for tertiary Si atoms (Si bonded to three other Si atoms). Thermally prepared network polymers typically exhibit an extremely broad resonance in this region (δ −20 to −80, with no resolvable peaks).[3] The broad resonance typically observed is attributed to overlapping peaks corresponding to the wide variety of ways that the Si atoms can be bonded together in a random network arrangement. There are no resonances observed which would be typical for linear polysilylene segments.

For comparison, these two copolymers, which are not reported in the literature, were also prepared by the thermal reduction method under typical Wurtz conditions.[2]‡ The molecular mass distributions of all four polymers are shown in Fig. 1. As can be seen, the GPC for the same products obtained by the thermal Wurtz coupling reaction are broader and polymodal compared to those prepared electrochemically.

These network copolymers 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. The Ge–Si backbone polymer exhibits a broader emission which is slightly red-shifted compared to the Si backbone polymer, as expected.[4]

Because of the mild reaction conditions, we were able to observe precursors to the isolated products spectroscopically, which can not be observed from the Wurtz product mixture. Discrete peaks are observed in the absorption spectra of the two electrochemically prepared copolymers prior to work-up as shown in Fig. 2. Both samples were quenched with methanol and stored in the dark and the absorption spectrum was rechecked periodically. Over a period of two weeks, the discrete peaks gradually disappear and the spectrum begins to resemble that of the isolated polymer. The slow conversion to products provides an opportunity to more easily study the reaction mechanism, which is not readily accomplished with the thermal Wurtz reaction. The origin of the discrete peaks in the electronic spectra and a study of the reaction pathway are currently being investigated.

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Footnotes and References

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† *Conditions*: undivided electrolytic cell equipped with coiled copper wire 1 mm in diameter for both the cathode (14 cm^2) and anode (34 cm^2), constant applied potential (−3.0 V), ultrasound, TBAP supporting electrolyte (1.0 g), dry DME solvent (30 ml), cyclohexyltrichlorosilane (0.45 ml), phenyltrichlorosilane (0.40 ml). Reaction was continued until GPC no longer changed and then quenched with methanol. After removal of volatiles and electrolyte, product was purified by precipitation with methanol. Similar procedure was used for the preparation of **2**.

‡ A mixture of monomers in toluene was added slowly to a refluxing sodium dispersion under an atmosphere of Ar. 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 and the isolated polymers were obtained by precipitation from the solution with methanol.

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