

# Zirconocene-catalyzed dehydrogenative coupling of phenylgermane and properties of the resulting partially network polyphenylgermanes

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## Abstract

Dehydrogenative coupling of phenylgermane catalyzed by  $\text{Cp}_2\text{ZrCl}_2$  or  $\text{Cp}^*\text{CpZrCl}_2$  used in conjunction with  $n\text{BuLi}$  (two equivalents) gives partially network polyphenylgermanes of high molecular weights ( $M_w = 4.0\text{--}7.0 \times 10^4$ ) in moderate yields. Resulting polyphenylgermanes are soluble in common solvents and a typical sample displays  $\lambda_{\text{max}}$  at 329 nm in UV absorption and shows  $T_{\text{d}5}$  of 275°C in the thermogravimetric analysis. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* Zirconium; Polygermane; Dehydrocoupling

## 1. Introduction

The chemistry of polysilanes have been widely investigated in the view of unique properties derived from  $\sigma$ -conjugation [1–4], which have a great potential in applications to advanced materials such as photoconductors, photoresists, photoinitiators, and nonlinear optical materials. Although polygermanes also possess similar properties, relatively few attention has been paid to them and related materials [5–13]. Preparation of linear polygermanes by the Wurtz-type coupling of halogermanes [14–16] or by the reactions of germanium diiodide with Grignard [17] or lithium reagents [18,19] has been reported. Bianconi and coworkers prepared polygermynes (network polygermanes) by the Wurtz-type coupling of trichlorogermanes with Na/K [20]. As for catalytic polymerization, Berry and coworkers have demonstrated ruthenium-catalyzed demethanative coupling of  $\text{HGeMe}_3$  as a new approach to polygermanes [21]. Dehydrocoupling polymerization

of primary silanes has been extensively studied and a subject of several review articles [22,23]. However, similar polymerization of primary germanes has been examined only in one case by Harrod's group [24], using phenylgermane, where spectral characterization of the polymer structure and the molecular weight data are missing.<sup>2</sup> We report herein the synthesis of high molecular weight polyphenylgermane with a partial network structure by dehydrogenative coupling of phenylgermane catalyzed by  $\text{Cp}_2\text{ZrCl}_2$  or  $\text{CpCp}^*\text{ZrCl}_2$  used in conjunction with two equivalents of  $n\text{BuLi}$ .

## 2. Results and discussion

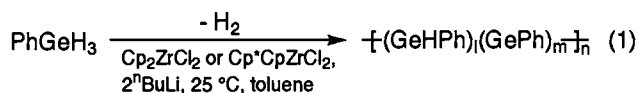
In a typical experiment, toluene (0.5 ml) and  $n\text{BuLi}$  (two equivalents relative to Zr) in hexane were added to  $\text{Cp}_2\text{ZrCl}_2$  (0.023 mmol) placed in a Schlenk tube under nitrogen at  $-78^\circ\text{C}$  and the mixture was stirred first at the temperature for 1 h and then at  $0^\circ\text{C}$  for additional

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<sup>2</sup> A difficulty we have with Ref. [24] is the authors' conclusion about the titanium-catalyzed dehydrogenative coupling of phenylgermane that 'the degree of polymerization are still lower than the values obtained with primary silanes', despite the gelation they experienced.

1 h. Phenylgermane (0.5 ml, 3.27 mmol) was added to the resulting mixture, which was stirred at room temperature. There was observed a long induction period of ca. 30 min, after which the polymerization commenced as visualized by the onset of gas evolution and by the color change of the solution from pale yellow to yellow. The resulting mixture became too viscous in 5 days to stir. The mixture, after dissolved by an addition of THF (3 ml), was analyzed by gel permeation chromatography (eluent; THF, polystyrene standards) to display a trimodal molecular weight distribution with  $M_w$  ( $M_w/M_n$ );  $4.4 \times 10^4$  (2.2),  $3.4 \times 10^3$  (1.3) and  $6.7 \times 10^2$  (1.1) in 57/36/8 ratio. Removal of the catalyst by passing the solution through a short Florisil column and purification by precipitation from THF with pentane gave polyphenylgermane **1** as pale yellow powders in 67% yield.



Results of other reactions using  $\text{Cp}^*\text{CpZrCl}_2$  and/or run under different conditions are summarized in Table 1. In the reaction where a larger amount of catalyst (1.0 mol%) was used (run 1), the mixture solidified in 1 day and the molecular weight of the resulting polymer was higher.  $\text{Cp}^*\text{CpZrCl}_2$  appeared less active in chain

Table 1  
Dehydrogenative coupling of phenylgermanes catalyzed by zirconocene-based catalysts<sup>a</sup>

Run	Catalyst (mol%)	Reaction time (day)	$M_w$ distribution	
			$M_w \times 10^4$ (%)	$M_w/M_n$
1	$\text{Cp}_2\text{ZrCl}_2$ (1.0)	1	7.3 (62)	3.7
			0.31 (32)	1.3
			0.063 (6)	1.0
2	$\text{Cp}_2\text{ZrCl}_2$ (0.7)	1	3.5 (48)	1.8
			0.36 (44)	1.4
			0.062 (8)	1.1
3	$\text{Cp}_2\text{ZrCl}_2$ (0.7)	3	4.1 (55)	2.4
			0.31 (37)	1.3
			0.065 (8)	1.1
4	$\text{Cp}_2\text{ZrCl}_2$ (0.7)	5	4.4 (57)	2.2
			0.34 (36)	1.3
			0.067 (8)	1.1
5	$\text{Cp}^*\text{CpZrCl}_2$ (1.0)	1	3.72 (45)	2.2
			0.32 (43)	1.4
			0.60 (12)	1.1
6	$\text{Cp}^*\text{CpZrCl}_2$ (1.0)	3	4.3 (50)	2.2
			0.34 (37)	1.3
			0.065 (13)	1.1

<sup>a</sup> Procedure: mole ratio of a Zr complex/<sup>n</sup>BuLi = 1/2,  $\text{PhGeH}_3/\text{toluene} = 1/1$  (vol/vol), room temperature.

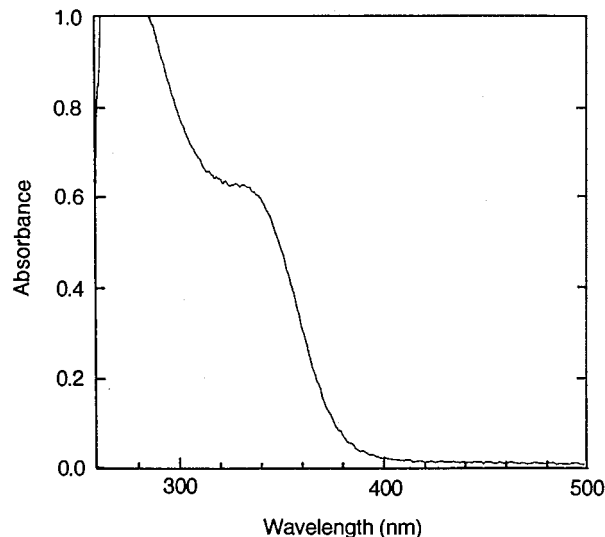


Fig. 1. Ultraviolet absorption spectrum of polygermane **1** obtained from run 4 (highest molecular weight fraction).

growth than  $\text{Cp}_2\text{ZrCl}_2$  (run 1 vs runs 5 and 6); the solidification was evident only after 3 days.

<sup>1</sup>H-NMR of these polymers displayed complex signals at  $\delta$  4.5–5.5 (Ge–H) and 6.3–7.8 (aromatic), the integral ratio (Ge–H/GePh) being 1/15. This result and the observed solidification suggest that **1** comprises partially network structures rather than simple linear chains. The analytical data that conforms to a composition of  $[(\text{PhGeH})_{1/3}(\text{PhGe})_{2/3}]_n$  also support the network structures.

Polygermane **1** resembles, in solubility, the polygermynes obtained by the Wurtz coupling of trichlorogermanes [20] and is soluble in common solvents such as benzene, toluene and THF. However, polygermane **1**, which is illustrated in Fig. 1, is very different from the polyphenylgermyne in UV absorption; **1** obtained from run 4 shows  $\lambda_{\text{max}}$  at 329 nm ( $\epsilon = 470$  for a monomer unit) that tails to ca. 400 nm. The  $\lambda_{\text{max}}$  is only 30–40 nm red shifted as compared to linear polyphenylsilanes ( $M_w = 6.5\text{--}7.0 \times 10^3$ ) [14]. On the other hand, the polyphenylgermyne  $(\text{PhGe})_n$  ( $M_w = 3.2 \times 10^3$ ) shows an onset of absorption at 800 nm, which increases gradually in intensity with decreasing wavelength down to 200 nm. UV absorption of linear polygermanes is reported to be 20–40 nm red shifted as compared to their polysilane analogs [14]. Accordingly, polygermane **1**, despite its partial network structure as suggested by NMR and elemental analysis, still retains a similarity in the UV absorption to linear polygermanes rather than to polygermynes.

Thermogravimetric analysis (TGA) of the same polygermane sample isolated from run 4 under nitrogen did not show substantial weight loss up to 250°C but a gradual weight loss (17%) occurred between 250 and 370°C,  $T_{d5}$  (temperature for 5% weight loss) being

275°C. TG-MS suggested the weight loss arose from extrusions of PhGeH ( $m/z$  152), Ph<sub>2</sub>Ge ( $m/z$  228) and Ph<sub>3</sub>Ge ( $m/z$  305) fragments. A second weight loss (43%) was observed between 420 and 580°C to leave a black material. This precipitous weight loss corresponds to extrusion of benzene ( $m/z$  78, M<sup>+</sup>) from the more developed (extended) network structure resulting from the first weight loss between 250 and 370°C.

In summary, dehydrogenative coupling of phenylgermane by zirconocene-based catalysts gives high molecular weight polyphenylgermanes of partial network structures in acceptable yields.

### 3. Experimental

All experiments were carried out under nitrogen in Schlenk tubes, using standard inert-atmosphere techniques. Dried solvents were freshly distilled and degassed immediately before use. Phenylgermane was prepared by reduction of phenyltrichlorogermane with lithium aluminum hydride as previously described [25]. Bis(cyclopentadienyl)zirconium dichloride was purchased from Strem and used as supplied. Cyclopentadienyl(pentamethylcyclopentadienyl)zirconium dichloride was prepared according to the literature [26]. <sup>n</sup>BuLi (1.6 M hexane solution) was purchased from Aldrich and used as received or after dilution with hexane. Florisil (6–100 mesh) was purchased from Nakarai Tesque. <sup>1</sup>H NMR spectra were obtained on a Bruker ARX-300 (300 MHz) in C<sub>6</sub>D<sub>6</sub>. Infrared and UV-vis spectra were recorded on JASCO FT/IR-5000 and Shimadzu UV-3100 spectrometers. Molecular weights of polymers were determined by GPC using a Shimadzu LC-6A high-pressure pump equipped with Shodex KF-801 and KF-802 columns and a GL Science Model 504R RI detector, using THF as the eluent at 40°C and calibrated with polystyrene standards. TGA was carried out in a range from 30 to 900°C at the heating rate of 10°C min<sup>-1</sup> under He gas at the flow rate of 50 ml min<sup>-1</sup> on a Shimadzu Thermal Analyzer DT-30 system.

#### 3.1. Catalytic polymerization reactions

A typical procedure was as follows. A sample of Cp<sub>2</sub>ZrCl<sub>2</sub> (6.7 mg; 0.023 mmol) was placed in a Schlenk tube equipped with a Teflon stopper and a magnetic stirrer. After the Schlenk tube was purged with nitrogen, toluene (0.5 ml) and <sup>n</sup>BuLi (46 μl of a 1.0 M solution in hexane; 0.046 mmol) were added at -78°C and stirred for 1 h at this temperature. The solution was further stirred for an additional 1 h at

0°C, and then phenylgermane (0.5 ml; 3.27 mmol) was added. After removal of a cooling bath, it was warmed to room temperature and stirred. After 30 min, the color of the solution turned from pale yellow to yellow and vigorous evolution of hydrogen commenced. The mixture was becoming deep reddish brown in color over 5 h and viscous over 5 days to give a gel, which was dissolved in THF (3 ml) and filtered through a short Florisil column. The polymer was sequentially precipitated from THF solution with pentane, which gave 333 mg (67.0%) of polyphenylgermane as pale yellow powders. Spectral data for 1: <sup>1</sup>H-NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) δ 4.5–5.5 (1H, Ge–H), 6.3–7.8 (15H, Ph); IR (KBr, cm<sup>-1</sup>) 3046 (s), 1992 (s), 1578 (m), 1481 (s), 1431 (vs), 1330 (w), 1299 (m), 1185 (w), 1081 (m), 1023 (m), 998 (m), 847 (w), 729 (vs), 694 (vs), 607 (s), 453 (vs); UV-vis (THF): 329 nm. Anal. Calcd. for (C<sub>18</sub>H<sub>16</sub>Ge<sub>3</sub>)<sub>n</sub>: C, 48.03; H, 3.58. Found: C, 48.21; H, 3.76. GPC (THF, polystyrene standard) 4.5 × 10<sup>4</sup>, M<sub>w</sub>/M<sub>n</sub> = 2.1.

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