Organometallic Polysilylenes. First Organometallic Route to Fe−SiC Composites

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Although the study of polyorganosilylenes has aroused considerable interest in recent years, we are not aware of any synthesis of a polyorganometallic silylene.

Theoretically, a quite large number of metal-containing moieties attached to a polysilylene chain may be imagined. Actually, several experimental limitations are evident. First, the Wurtz-type coupling of dichlorsilane derivatives as the most effective general route for the preparation of polysilylenes rules out the use of metal-containing dichlorosilane monomers. Second, the chemical sensitivity of the polysilylene chain imposes again severe limitations in employing a strategy involving metal−organic functionalizations.

In this paper, we present the syntheses of the first organometallic polysilylenes to undergo successful pyrolysis to metal−β-SiC composites. The synthetic strategies for the preparation of polysilylenes with pendant 1,3-diene-Fe(CO)$_3$ groups are outlined in Schemes 1 and 2.

The general procedure applied for the synthesis of poly(methylsilylene) and poly(methylsilylene-*co*-phenyl(methyl)silylene)s was the Wurtz-type condensation of dichlorosilane derivatives with sodium in toluene, as described for soluble polymers by Qui and Du.[1]

Copolymers **1a**−**c** and **4a**−**c** were prepared by hydrosilylation of 1,3,5-hexatriene with polysilylene and copolymers **3a**−**c** in the presence of platinum tetramethyldisiloxane (Pt-DVTMS), respectively. Copolymers **Ib** and **IVa** were synthesized by hydrosilylation of 1,3,5-heptatriene with polysilylene and copolymer **3a**, respectively. The resultant polymers were extracted with THF and precipitated with methanol. Since the polymers containing SiH can be cross-linked by reaction with the difunctional 1,3,5-hexatriene, the soluble polymers **1a**−**c** and **4a**−**c** were obtained in quite low yields. Hydrosilylated copolymers **Ib** and **IVa** have been obtained in very high yields by hydrosilylation of 1,3,5-heptatriene.

Iron tricarbonyl functionalization of polymers **1a**−**c** and **4a**−**c** was accomplished by adding triiron dodecacarbonyl (10 mmol) to a solution of polymer containing 11 mmol of Si diene units in 100 mL of benzene and refluxing under stirring for 8 h in the absence of light. The IR spectra of tricarbonyl(diene)iron-functionalized polymers **2a**−**c** and **5a**−**c** exhibit bands at 2040−2043, 1975−1979, and 1967−1970 cm^{-1} characteristic for the $C\equiv O$ stretching frequencies of tricarbonyl(iron)diene complexes.

The copolymer compositions were determined by integrating H-Si, Ph-Si, H_a−H_e for free, and H_f anf H_i for complexed diene moities in the ^{1}H-NMR spectra and were represented by *x*, *y*, *z*, and *w* in polymers **1**,**2** and **3**−**5**, respectively. ^{1}H-NMR: (CDCl$_3$) δ 3.32−4.65 (H_a−H_e), 4.20 (Hg), 4.50−4.86 (Hh), 7.73−8.34 (H_f and H_i), 9.38 (H_j), 2.75 (Ph-Si), 6.54 (H-Si). The typical proton spectra of polymers **3**, **4**, and **5** are shown in Figure 1.

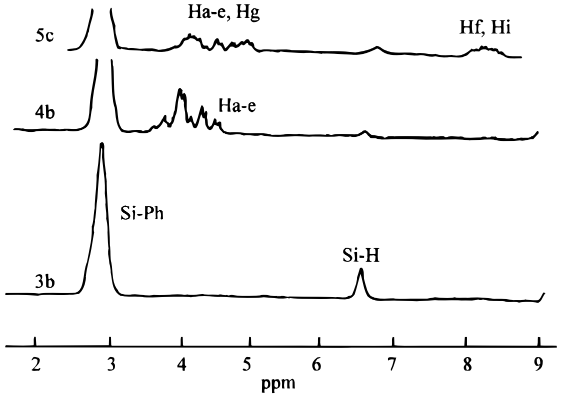
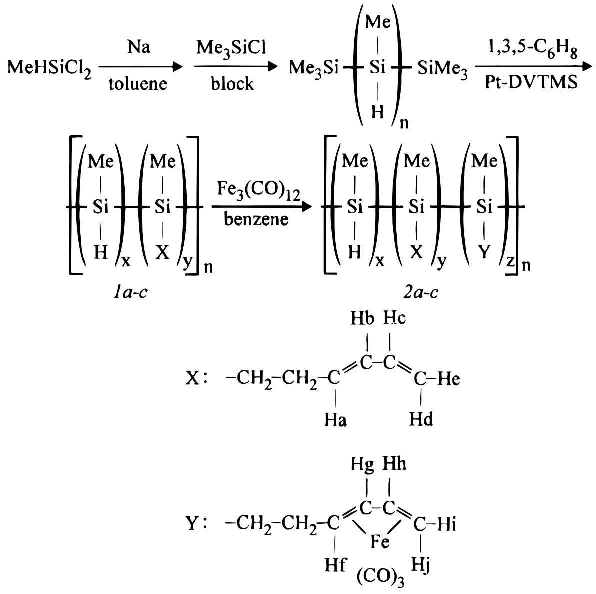
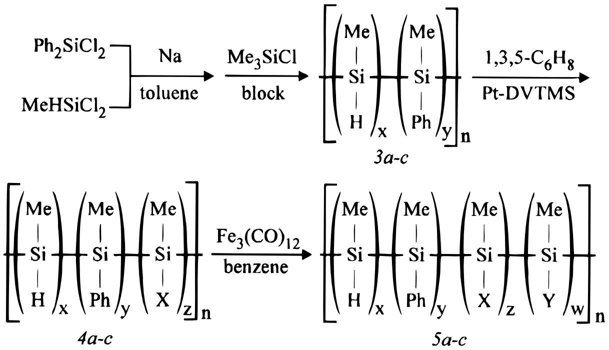


Figure 1. ^{1}H-NMR spectra of polymers **3b**, **4b**, and **5b**.

Scheme 1



Scheme 2



Yields, compositions, and molecular weights of polymers are listed in Tables 1 and 2. All polymers are soluble in common solvents and can be formed into films or drawn into fibers. They are sensitive to both moisture and light.

Since the polymers containing (MeSiH)[2] and (PhSiMe)[3,4] units proved to be useful precursors to β-SiC ceramics, and poly(2,4-hexadienyl-Fe(CO)$_3$ acrylate)[5] was reported to yield, upon controlled pyrolysis, a metal−carbon composite with ultrafine and air-stable iron particles, it seemed practicable to study the pyrolysis of polymers **2a**−**c** and **5a**−**c**. The polymer samples were heated to 1000 °C at a rate of 0.3−0.5

Table 1. Yields, Compositions (*y* and *z* Normalized for *x* = 1 in Formulas 1a–c and 2a–c) and Molecular Weights from GPC Elution Volumes Relative to Polystyrene Standards for Polymers 1 and 2

copolymer[a]	yield (%)	*y*	*z*	$\bar{M}_w{}^b$ (max)
1a	15	0.333		2600
1b	12	0.860		3350
1c	8	4.860		4500
Ib	87	0.750		3700
2a	90	0.206	0.126	3250
2b	85	0.533	0.326	4400
2c	92	2.985	1.897	6300
IIb	95	0.450	0.389	4600

[a] Hydrosilylation times of 45, 90, and 180 min are denoted by **a**, **b**, and **c**, respectively. [b] Polysilylene $(MeSiH)_n$ with $M = 1850$ has been used as precursor for copolymers **1** and **2**.

Table 2. Yields, Compositions (*x*, *y*, and *w* Normalized for *x* = 1 in Formulas 3a–c, 4a–c, and 5a–c) and Molecular Weights from GPC Elution Volumes Relative to Polystyrene Standards for Copolymers 3, 4, and 5

copolymer[a]	yield (%)	*y*	*z*[b]	*w*	$\bar{M}_w$ (max)
3a	45	0.750			2680
3b	48	3.851			7900
3c	35	7.522			12030
4a	7	4.761	5.349		3750
4b	9	26.110	5.444		8825
4c	13	48.205	5.410		12530
IVa	88	5.100	5.355		4200
5a	84	4.760	2.780	2.567	6680
5b	91	26.130	2.654	2.776	9600
5c	89	48.207	2.543	2.866	13500
Va	92	4.925	2.355	3.015	7300

[a] $PhMeSiCl_2/MeHSiCl_2$ molar ratios of 1.5, 5, and 10 used in the syntheses of copolymers **3**, **4**, and **5** are denoted by **a**, **b**, and **c**, respectively. [b] Hydrosilylation time, 8 h.

°C/min under argon, then to 1350 °C at a rate of 1 °C/min, and finally kept at this temperature for 4 h.

With the exception of polymer **2c**, which produced a pyrophoric mixture, all diene-$Fe(CO)_3$-functionalized polysilylenes provided air-stable α-Fe–SiC composites, as proved by XRD measurements (Figure 2). (XRD 2: 35.4 (111), 61.1 (220), 73.1 (311) –SiC; 44.8 (110), 65.4 (200), 82.4 (211) –Fe). However, blending **2c** with **1a**–**c** or **3a**–**c** in appropriate proportions gave precursors which produced the desired Fe–SiC composites in two-stage heating to 1000 and 1350 °C. Neither iron carbide nor iron silicide were detected by XRD measurements, as shown in Figure 2.

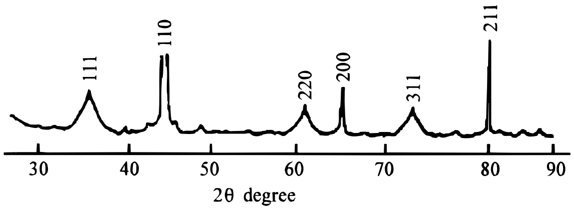


Figure 2. XRD profile of the Fe–SiC composite prepared by pyrolysis of polymer **5b**.

Table 3. Pyrolysis of Copolymers 2a–c and 5a–c

copolymer	theor SiC yield (%)	actual ceramic yield (%)	% yield normalized for SiC theor yield	Fe content of ceramic SiC (%)
2a	51.95	30.25	58.25	17.23
2b	38.14	20.26	53.33	30.52
2c	25.88	8.21	31.72	pyrophoric
5a	21.40	9.77	45.64	39.77
5b	30.73	18.24	59.35	21.76
5c	31.68	19.08	59.97	10.85

As shown in Table 3, the normalized ceramic yields are high and typical for those previously reported for $(PhSiMe)_n$ and (MeSiH) precursors.[2]

The composites derived from polymers **2a**–**c** and **5a**–**c** exhibit fairly good magnetic properties (saturation magnetization $I_m = 17–19$ emu/g; coercive force $H_e = 100–200$ Oe) and may be of practical interest as electromagnetic shielding devices or absorbers.

References and Notes

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