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Neodymium-Catalyzed Dehydrogenative Condensation of Methylsilane and Ceramization of the Resulting Polymer

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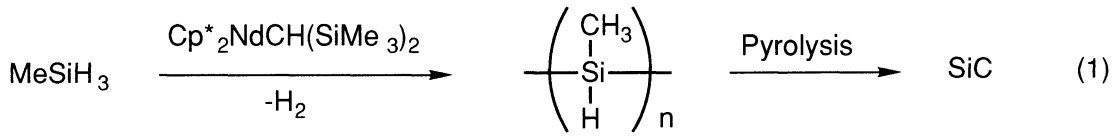
High molecular weight poly(methylsilylene) is obtained in a good yield through dehydrogenative condensation of methylsilane catalyzed by $(C_5Me_5)_2NdCH(SiMe_3)_2$. At a high temperature, polymerization process involves cross-linking *via* the loss of methane. Pyrolysis of the resulting polymer gives β-SiC in a high yield. Blend with a carbon-rich polymer like poly(phenylsilylene) is effective to prevent the formation of contaminative metallic silicon during ceramization.

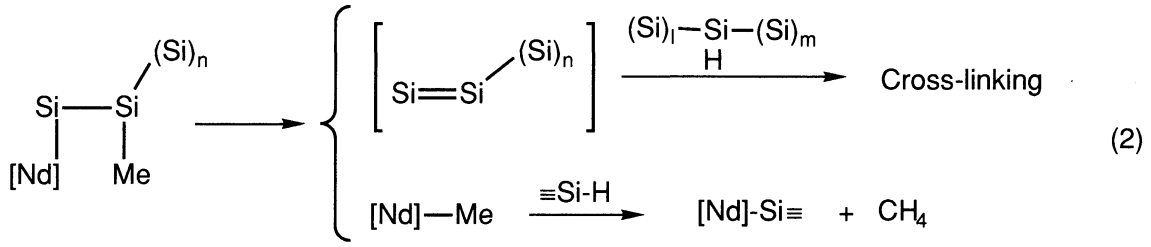
Among many applications of polysilanes,[1] the preparation of continuous SiC fiber (Nicalon®) from poly(dimethylsilylene) is already industrialized.[2] However, the current process has several drawbacks:[1b] i) low ceramic yield after the two step-process *via* polycarbosilane, ii) rigorous reaction conditions in the Wurtz-type coupling of dichlorodimethylsilane, and iii) impurities in the products. In order to circumvent these problems, West et al. proposed polysilastyrene as a new preceramics.[1b] Nevertheless, this route wastes most of the carbon in the polymer because the silicon to carbon ratio is 1 to 9. Hence, efficient new preceramics containing equal numbers of Si and C is strongly desired to produce SiC in a high yield and in a pure form. Poly(methylsilylene) is a promising candidate for this purpose. Since we have recently developed the Nd-catalyzed dehydrogenative condensation of organotrihydrosilanes,[3] we applied the methodology to the preparation of SiC *via* poly(methylsilylene) (Eq. 1).[4]



(1)

In a typical experiment, $MeSiH_3$ (8 kg/cm^2, 22 mmol) was introduced to a glass-lined stainless steel autoclave containing a benzene solution (2 cm^3) of $Cp^*_2NdCH(SiMe_3)_2$ (0.05 mmol). The autoclave was heated at 90 °C for 48 h. The gas phase was collected in a plastic bag and analyzed by GC. The liquid phase was concentrated to dryness under vacuum to give powder (662 mg, 68%). The resulting polymer was characterized by GPC and TGA.

The results at various reaction temperatures are summarized in Table 1. The reaction mixtures kept initial green color of the catalyst after polymerization. The polymeric products did not contain siloxane bonds as proved by the absence of IR band around 1100 cm^{-1}. Up to 70 °C of the reaction temperature, the products were oily and in range of oligomers (Mw < 600). On the other hand, the polymerization was dramatically promoted at 90 °C to give a solid after removal of the solvent; the molecular weight exceeded 7000. The reaction at 100 °C resulted in the formation of a high polymer that was insoluble in usual organic solvents. The extensive polymerization above 90 °C is partly ascribed to cross-linking *via* the loss of methane because a considerable amount of methane (10-15 mol% of dihydrogen) was detected in the gas phase of the reaction above 90 °C. At lower temperatures, gaseous product was overwhelmingly hydrogen. Although the Si-Me bond scission may occur through various routes, a possible mechanism is β-alkyl abstraction (Eq. 2), which is a typical reaction of organolanthanoid complexes.[5] The resulting methylneodymium complex would react with Si-H species to evolve CH_4. This hypothesis is consistent with the fact that the CH_3/SiH ratio (^{1}H NMR) is not affected by the evolution of CH_4.



(2)

Table 1. Dehydrogenative condensation of methylsilane[a]

Temp / °C	Time / d	Gases / mmol		Polymer yield / mg	Mw[b]	Mw/Mn	CH_3/SiH[c]	Residue of TGA[d] / %
		H_2	CH_4					
100	2	15.0	2.0	> 604	e)	e)	e)	72
90	2	13.5	1.6	662	7340	5.0	1.00	74
70	2	5.5	< 0.1	317	530	1.6	1.04	10
50	2	4.6	< 0.1	267	480	1.3	1.06	--
r.t.	3.5	5.7	<0.1	281	540	1.3	1.00	--

a) Reaction conditions: $Cp^*_2NdCH(SiMe_3)_2$ 0.05 mmol, $MeSiH_3$ 22 mmol, benzene 2 cm^3. b) Determined by GPC. Based on polystyrene standards. c) Measured by ^{1}H NMR with relaxation delay 10 s. d) Residue after pyrolysis of the polymers up to 900 °C. e) Not measured because of the low solubility of the polymer.

Although 90% of the weight of the oligomers prepared at 70 °C was lost upon heating up to 900 °C (TGA), pyrolysis of the polymers prepared at 90 °C or higher gave black and powdery ceramics in good yields. Hence, cross-linking *via* the demethanation during the polymerization seems advantageous to achieve a high ceramic yield. The analysis of the gaseous products during the ceramization of the polymer is shown in Fig. 1. Below 400 °C, the major gaseous product was methylsilane. Above 400 °C, a small amount of methane and a large amount of hydrogen were evolved. A possible scenario of the ceramics formation is illustrated in Scheme 1: a) cross-linking through the loss of methylsilane, b) transformation to polycarbosilane,[6] and c) ceramization with the loss of methane and hydrogen.

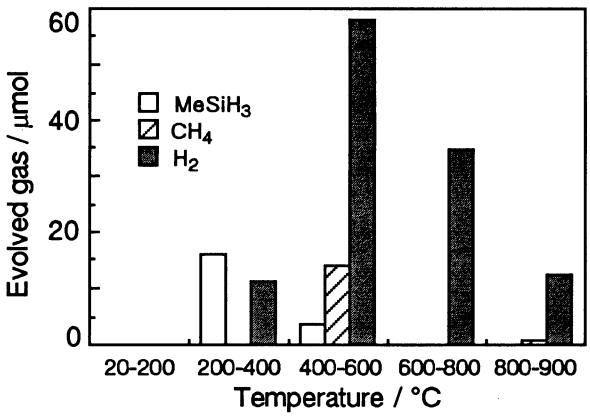
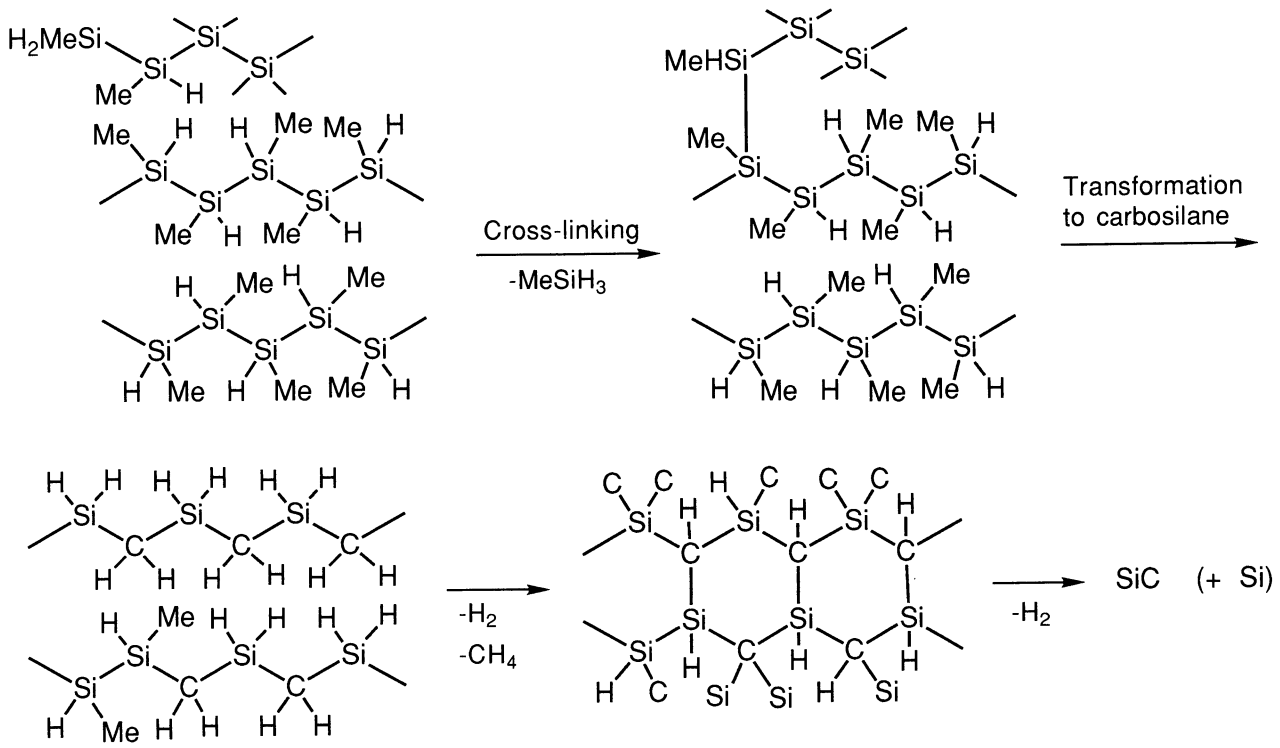


Fig. 1. Gaseous products generated during pyrolysis of poly(methylsilylene). Conditions: polymer 6.7 mg (synthesized at 100 °C, see Table 1), heating rate 10 °C/min, under N_2.

The ceramic powder obtained by pyrolysis of poly(methylsilylene) up to 1400 °C was analyzed by XRD (Cu Kα with a Ni filter). The powder consisted of β-SiC and metallic silicon (Fig. 2-(a)).



Scheme 1.

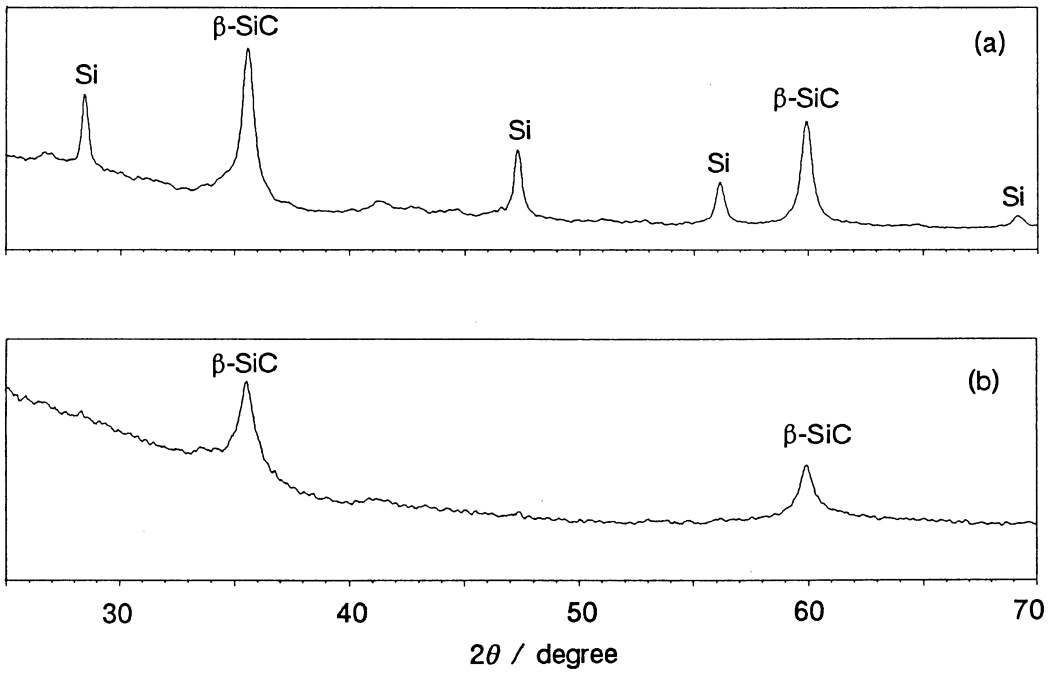


Fig. 2. X-Ray diffraction patterns of the solid resulting from pyrolysis of polysilanes: (a) poly(methylsilylene); (b) poly(methylsilylene) + poly(phenylsilylene).

The formation of metallic silicon corresponds with the loss of methane during the polymerization and pyrolysis (*vide supra*). In order to balance the Si/C ratio in the ceramics, we blended poly(methylsilylene) with a carbon rich polymer, poly(phenylsilylene) (Mw = 1600). The pyrolysis of poly(methylsilylene) containing 22 weight % of poly(phenylsilylene) gave ceramics which showed only signals assignable to β-SiC (Fig. 2-(b)): ceramic yield 58%.

To summarize, poly(methylsilylene) synthesized *via* Nd-catalyzed dehydrogenative condensation of methylsilane was shown to be a very good precursor of β-SiC. In view of simpleness and high ceramic yields, the present method surpasses the current industrial process that starts with poly(dimethylsilylene) prepared by the Wurtz-type coupling. Processing to make fibers or films and economical supply of the starting material ($MeSiH_3$) are the next subjects for industrialization.

References

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