

## Modification of Thermal Degradation of Oligo(methylsilene) Catalyzed by Group 4 and 6 Transition Metal Complexes

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Received April 13, 1998

The oligo(methylsilene) (1) was treated with the group 4 metallocene  $Cp_2MCl_2/Red-Al$  ( $M = Ti, Zr, Hf$ ) combination catalysts and with the group 6 metal carbonyl  $M(CO)_6$  ( $M = Cr, W$ ) catalysts, producing the modified, cross-linked polymers. The average molecular weights and percent ceramic residue yields of modified polymers increase as the catalyst goes down from Ti to Hf and similarly as the catalyst goes down from Cr to W. An interrelationship between average molecular weights and percent ceramic residue yield is found within the respective group of catalysts, but is not observed as the catalyst goes down from Ti to W. The polymers modified with the group 4 metallocene combination catalysts have higher molecular weights and similar percent ceramic residue yields as compared to the polymers modified with the group 6 metal carbonyl catalysts. The catalytic activities of group 4 metallocene combinations appear to be higher  $\sim 100$  °C, but to be lower at very high temperature than those of group 6 metal carbonyls.

### Introduction

Silicon-containing ceramics such as silicon carbide (SiC), silicon nitride ( $Si_3N_4$ ), silicone carbonitride ( $Si_xC_yN_z$ ), and silica ( $SiO_2$ ) have received a great deal of attention for diverse applications.<sup>1</sup> *Inter alia*, silicon carbide, a silicon-containing non-oxide ceramic, has been known as a stronger material than carbon ceramic<sup>2</sup> and has been widely employed as a reinforcement in advanced ceramics and composites.<sup>3</sup> In 1975, Yajima and coworkers first developed a revolutionary process for fabricating SiC fiber,<sup>4</sup> including pyrolytic conversion in the 400-470 °C temperature range under an argon atmosphere of insoluble polydimethylsilane into soluble polycarbosilane (PCS), which is melt-spun into fiber form (trade name "Nicalon" manufactured by Nippon Carbon Co., Tokyo, Japan and distributed globally by Dow Corning Co., U.S.A.) and then undergoes radical cross-linking under an air atmosphere in the 300-350 °C temperature range, followed by its final pyrolytic transformation at 1200 °C or higher under an inert atmosphere into SiC fiber. The oxidative (cross-linking) curing process permits the conversion of PCS fiber to SiC ceramic in high ceramic residue yield without softening during the pyrolysis, but may cause fiber degradation at high temperature due to the presence of residual oxygen. Introduction of cross-linking additives may result in the unnecessary contamination of SiC ceramics or in the carbon-oversupply to SiC ceramics.<sup>5</sup> Alternative curing method should be considered in order to overcome such disadvantages.

The Si-H groups in PCS backbone permit cross-linking between PCS chains in the Yajima process. Harrod discovered titanocene- and zirconocene-catalyzed dehydrocoupling of hydrosilanes to poly(hydrosilane)s.<sup>6</sup> Subsequently, Tilley *et al.* reported studies on the catalysts and mechanism for the dehydropolymerization of various hydrosilanes catalyzed by group 4 metallocene complexes.<sup>7</sup> One of us recently reported the catalytic redistribution/dehydrocoupling of various aryl

group-containing alkylsilanes by  $Cp_2MCl_2/Red-Al$ ,  $Cp_2MCl_2/n-BuLi$  ( $M = Ti, Zr, Hf$ ), and  $Cr(CO)_6$  catalysts.<sup>8</sup> Recently, Seyferth and coworkers described the preparation of near-stoichiometric silicon carbide by pyrolyzing a polymethylsilane,  $(MeSiH)_x$  modified with zirconocenes.<sup>9</sup> They also reported the preparation of SiC/MoSi<sub>2</sub> composite by pyrolyzing a polymethylsilane modified by  $Mo(CO)_6$ -catalyzed dehydrocoupling of Si-H bonds.<sup>10</sup> Very recently, one of us reported the synthesis of SiC/Mo<sub>2</sub>C and SiC/Mo<sub>x</sub>Si<sub>y</sub>C<sub>z</sub> composites by pyrolyzing the mixture of PCS with different weight percents of Mo and  $Mo(CO)_6$ , respectively.<sup>11</sup> To the best of our knowledge, the group 4 and 6 transition metal complexes have never been directly used as a catalyst for modification of oligo(methylcarbosilane). Oligo(carbosilane) should be a better precursor for SiC ceramic than oligosilane because oligosilane should lose less organic volatiles during the thermal transformation into oligo(carbosilane) and than polycarbosilane in terms of steric effect in the dehydrocoupling curing process. Here we report the catalytic modification and thermal degradation of oligo(methylcarbosilane) preceramic polymer, oligo(methylsilene), by the group 4  $Cp_2MCl_2/Red-Al$  ( $M = Ti, Zr, Hf$ ) combination catalyst and by the group 6  $M(CO)_6$  ( $M = Cr, W$ ) catalysts to compare their catalytic effects.

### Experimental Section

All reactions and manipulations were performed under prepurified nitrogen using Schlenk techniques. Dry, oxygen-free solvents were employed throughout. Glassware was flame-dried or oven-dried before use. Infrared spectra were obtained using a Perkin-Elmer 1600 Series FT-IR or a Nicolet 520P FT-IR spectrometer. Proton NMR spectra were recorded on a Varian Gemini 300 spectrometer using  $CDCl_3/CHCl_3$  as a reference at 7.24 ppm downfield from TMS. The relaxation time was set as 20 second because of inherent long relaxation time of Si-H bond<sup>14</sup> to get a better CH/SiH

integral ratio. Silicon-29 NMR spectra were obtained on a Varian XL-300 spectrometer operating at 59.59 MHz with  $\text{CDCl}_3$  as a solvent utilizing a DEPT (Distortionless Enhancement of Polarization Transfer) pulse sequence. An external reference of 50/50 by volume of TMS (0.00 ppm) in  $\text{CDCl}_3$  was used. Gel permeation chromatography (GPC) was carried out on a Waters Millipore GPC liquid chromatograph. The calibrant (monodisperse polystyrenes) and the sample were dissolved in toluene and separately eluted from an Ultrastaygel GPC column series (sequence 500,  $10^3$ ,  $10^4$ ,  $10^5$  Å columns). Molecular weights were extrapolated from the calibration curve derived from the polystyrene standards. Data analyses were carried out using a Waters Data Module 570. Thermogravimetric analyses (TGA) of samples were performed on a Perkin Elmer 7 Series Thermal Analysis System under an argon flow. The sample in a platinum boat was heated from 25 °C to 800 °C at a rate of 10 °C/min. Ceramic residue yield is reported as the percentage of the weight of the residue remaining after completion of the heating cycle divided by the original sample weight.  $\text{Cp}_2\text{MCl}_2$  (M = Ti, Zr, Hf),  $\text{M}(\text{CO})_6$  (M = Cr, W), and Red-Al (or Vitride; sodium bis(2-methoxyethoxy)aluminum hydride; 3.4 M in toluene) were purchased from Aldrich Chemical Co. and were used without further purification. The oligo(methylsilene) **1**, IR (neat, KBr,  $\text{cm}^{-1}$ ): 2957 s, 2899 m ( $\nu_{\text{CH}}$ ), 2103 s ( $\nu_{\text{SiH}}$ ), 1252 m ( $\nu_{\text{SiC}}$ ), 1410 s ( $\delta_{\text{CH}}$ );  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ , 300 MHz): -1.0-0.5 (br,  $\text{SiCH}_2$ ,  $\text{SiCH}_3$ ), 3.5-4.8 (br, SiH), CH/SiH integral ratio = 9.8;  $^{29}\text{Si}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ , 59.59 MHz): -17.2 (br, SiH,  $\text{SiCH}_2$ ,  $\text{SiCH}_3$ ); GPC:  $M_w = 1100$ ,  $M_n = 630$ ,  $M_w/M_n = 1.7$ ; TGA ceramic residue yield: 26% (black solid, theoretical ceramic residue yield =  $\text{SiC}/\text{C}_2\text{H}_6\text{Si} = 69\%$ ), which was obtained from fractional precipitation, was prepared according to the literature procedure.<sup>12</sup>

#### Modification of **1** Catalyzed by $\text{Cp}_2\text{TiCl}_2/\text{Red-Al}$ .

Oligo(methylsilene) **1**, 1.0 g, 17.2 mmol equiv) in 1.0 mL of toluene was added to a Schenk flask containing  $\text{Cp}_2\text{TiCl}_2$  (0.085 g, 0.34 mmol) and Red-Al (0.10 mL, 0.34 mmol). The light green reaction mixture was heated at 90 °C to turn dark green instantly, and the reaction medium became slowly viscous. The amount of evolved gas during the reaction was measured by using a Topler pump. The catalyst was inactivated 24 h later by exposure to the air for 2 h. The resulting mixture was passed rapidly through a silica gel column (70-230 mesh, 20 cm  $\times$  2 cm) with 200 mL of toluene used as the eluent: Permaphase-ODS<sup>TM</sup> with Si-O-Si bonds as bonded phase packing material and mixed solvent (100 mL) of THF/toluene (1/1) as eluent were used for reverse phase chromatography.<sup>13</sup> The effluent was evaporated *in vacuo* to yield 1.0 g (100% yield) of an off-white solid which was soluble in toluene, THF, methylene chloride, and chloroform. IR (film, KBr,  $\text{cm}^{-1}$ ): 2102 s ( $\nu_{\text{SiH}}$ );  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ , 300 MHz): -1.0-0.5 (br,  $\text{SiCH}_2$ ,  $\text{SiCH}_3$ ), 3.3-4.8 (br, SiH), CH/SiH integral ratio = 15.6;  $^{29}\text{Si}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ , 59.59 MHz): -17.0 (br, SiH,  $\text{SiCH}_2$ ,  $\text{SiCH}_3$ ); GPC:  $M_w = 5300$ ,  $M_n = 4000$ ,  $M_w/M_n = 1.3$ ; TGA ceramic residue yield: 62% (black solid).

**Modification of **1** Catalyzed by  $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$  (M = Zr, Hf).** As a typical modification reaction, **1** (1.0 g, 17.2 mmol equiv) in 1.0 mL of toluene was injected to a Schenk flask containing  $\text{Cp}_2\text{ZrCl}_2$  (0.10 g, 0.34 mmol) and Red-Al (0.10 mL, 0.34 mmol). The reaction mixture was

heated at 90 °C to turn brown instantly, and the reaction medium became slowly gelatinous. The amount of evolved gas during the reaction was measured by using a Topler pump. The catalyst was destroyed 24 h later by exposure to the air for 2 h. The brown gelatinous material was washed well with toluene and diethyl ether and dried under vacuum to afford 1.0 g (100% yield) of a pale chocolate solid which was insoluble in most organic solvents. IR (KBr pellet,  $\text{cm}^{-1}$ ): 2102 s ( $\nu_{\text{SiH}}$ ); TGA ceramic residue yield: 77% (black solid).

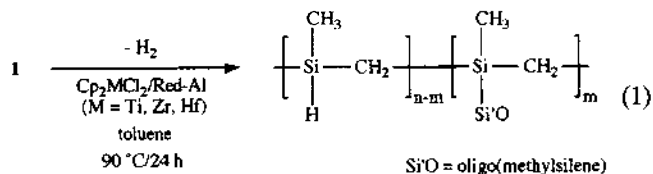
**Modification of **1** Catalyzed by  $\text{M}(\text{CO})_6$  (M = Cr, W).** The following procedure is the representative of the modification reactions with the group 6 metal carbonyls. A Schenk flask was charged with **1** (1.0 g, 17.2 mmol equiv),  $\text{Cr}(\text{CO})_6$  (0.075 g, 0.34 mmol), and 5 mL of dioxane. The reaction mixture was slowly heated up to 90 °C in order to minimize the sublimation of  $\text{Cr}(\text{CO})_6$  and turned light green. The amount of evolved gas during the reaction was measured by using a Topler pump. After 24 h, the resulting mixture was passed rapidly through a silica gel column (70-230 mesh, 20 cm  $\times$  2 cm) with 200 mL of toluene: Permaphase-ODS<sup>TM</sup> with Si-O-Si bonds as bonded phase packing material and mixed solvent (100 mL) of THF/toluene (1/1) as eluent were used for reverse phase chromatography.<sup>13</sup> The effluent was evaporated at reduced pressure to give 1.0 g (100% yield) of a pale green solid which was soluble in toluene, THF, methylene chloride, and chloroform. IR (film, KBr,  $\text{cm}^{-1}$ ): 2109 s ( $\nu_{\text{SiH}}$ );  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ , 300 MHz): -1.0-0.5 (br,  $\text{SiCH}_2$ ,  $\text{SiCH}_3$ ), 3.3-4.9 (br, SiH), CH/SiH integral ratio = 18.5;  $^{29}\text{Si}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ , 59.59 MHz): -17.0 (br, SiH,  $\text{SiCH}_2$ ,  $\text{SiCH}_3$ ); GPC:  $M_w = 2000$ ,  $M_n = 1100$ ,  $M_w/M_n = 1.8$ ; TGA ceramic residue yield: 75% (black solid).

## Results and Discussion

A soluble and fusible oligo(methylsilene) **1**,  $[\text{MeSi}(\text{H})\text{CH}_2]_{x,y}[\text{MeSiCH}_2]_z$ , was prepared by pyrolytic Kumada rearrangement of a mixture of organic solvent-insoluble polydimethylsilane,  $(\text{SiMe}_2)_n$ , and hexane-soluble cyclic hexamer,  $(\text{SiMe}_2)_6$ , at 400-450 °C temperature range in autoclave and by subsequent fractional precipitation.<sup>12</sup> The weight average molecular weight and TGA ceramic residue yield of **1** were 1100 (polydispersity index = 1.7) and 26%, respectively. The theoretical ceramic residue yield ( $\text{SiC}/\text{C}_2\text{H}_6\text{Si}$ ) of **1** is 69%, and 44% of its composition to be SiC ceramic was thus lost as volatiles during pyrolysis at 800 °C. The oligo(methylsilene) is known to possess some degree of cross-linking in its chain because of intermolecular Kumada rearrangement during pyrolysis.<sup>14</sup> The  $^1\text{H}$  NMR spectrum of **1** shows three broad unresolved mountain-like resonances centered at -0.5, 0.2, and 4.0 ppm assigned to  $\text{SiCH}_2$ ,  $\text{SiCH}_3$ , and SiH, respectively. The CH/SiH integral ratio is 9.8 instead of 5.0 because of some degree of cross-linking in the oligomer chain and inherent long relaxation time of Si-H bond.<sup>15</sup> The  $^{29}\text{Si}$  NMR spectrum of **1** shows one broad unresolved mountain-like resonances centered at -17.2 ppm in the typical chemical shift range of carborane macromolecules. The IR spectrum of **1** exhibits a typical intense  $\nu_{\text{SiH}}$  band at ca. 2100  $\text{cm}^{-1}$ .

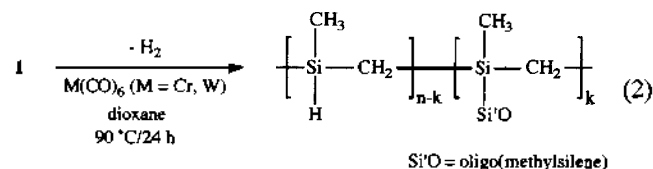
The dehydrocoupling reactivity of hydrosilanes is well known to decrease drastically in the order of primary > secondary >> tertiary.<sup>7,8</sup> As expected, dehydrocoupling

modification of **1** with 2 mol% of the  $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$  ( $\text{M} = \text{Zr}, \text{Hf}$ ) combination catalysts took place very slowly at ambient temperature, but upon heating at 90 °C the reaction medium became slowly gelatinous over 24 h (eq 1).



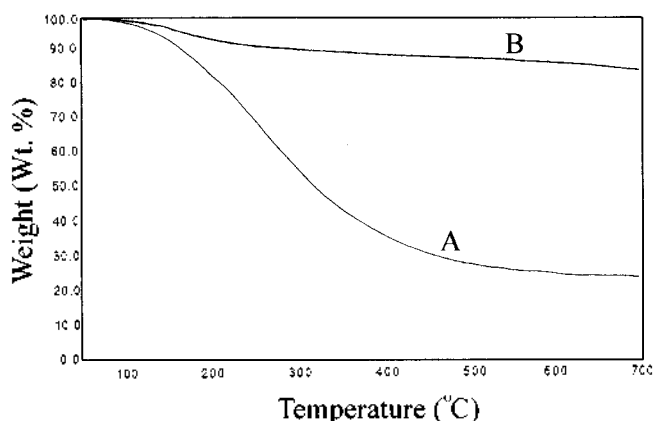
The modified polymers were isolated in ~100% yield as a pale chocolate solid for Zr and as a pale yellow solid for Hf, which were insoluble in most organic solvents, after workup including washing with toluene and diethyl ether. The TGA ceramic residue yield of the insoluble solids was 77% for Zr and 83% for Hf. In contrast, dehydrocoupling modification of **1** with 2 mol% of  $\text{Cp}_2\text{TiCl}_2/\text{Red-Al}$  combination catalyst occurred very slowly at ambient temperature and upon heating at 90 °C. The reaction medium became slowly viscous over 24 h. The modified polymer was obtained in ~100% yield as an off-white solid (TGA ceramic residue yield = 62%), which was soluble in most organic solvents, after workup including column chromatography. The TGA ceramic residue yields (62–83%) of modified **1** are much higher than that of unmodified **1** (26%) and are close to or higher than the theoretical ceramic residue yield of 69%. The IR spectra of the modified poly(methylsilene)s exhibit an intense  $\nu_{\text{Si-H}}$  band at ca. 2100  $\text{cm}^{-1}$  of which the intensity is somewhat decreased as compared with **1**. The CH/SiH integral ratio of modified **1** increased as compared to the unmodified **1**. The experimental data strongly suggest that some degree of cross-linking occurred during the modification process. The modification may first produce a weakly cross-linked polymer which then undergoes an extensive cross-linking reaction of backbone Si-H bonds, leading to an insoluble polymer. As a control experiment, modification of **1** with 2 mol% of Red-Al was attempted under the same reaction conditions, resulting in no appreciable change of  $^1\text{H}$  NMR spectrum and molecular weight (confirmed by  $^1\text{H}$  NMR spectroscopy and GPC analysis).

Dehydrocoupling modification of **1** with 2 mol% of the  $\text{M}(\text{CO})_6$  ( $\text{M} = \text{Cr}, \text{W}$ ) catalysts was carried out at 90 °C for 24 h (eq 2).



The modified polymers were isolated in ~100% yield as a pale green solid for Cr and as a pale yellow solid for W, which were soluble in most organic solvents, after workup including column chromatography. The TGA ceramic residue yield of the modified polymer was 75% for Cr and 84% for W. The TGA ceramic residue yields of the modified **1** are much higher than that of unmodified **1** (26%) and higher than the theoretical ceramic residue yield of 69% as seen in Figure 1.

The weight average molecular weights ( $M_w$ ) of the modi-



**Figure 1.** TGA thermograms of **1** before (A) and after (B) catalytic modification with  $\text{W}(\text{CO})_6$  under argon atmosphere.

fied polymers were 2000 for Cr and 2500 for W. The characterization data are given in Table 1.

The IR spectra of the modified poly(methylsilene)s exhibit an intense  $\nu_{\text{Si-H}}$  band at ca. 2100  $\text{cm}^{-1}$  of which the intensity is somewhat decreased as compared with **1**. The CH/SiH integral ratio of modified **1** increased as compared to the unmodified **1**. The  $^{29}\text{Si}$  NMR spectrum of **1** shows one broad unresolved mountain-like resonances centered at -17.2 ppm. There was no significant change in the  $^{29}\text{Si}$  NMR spectra of **1** before and after their catalytic modification except that the single broad resonance had shifted downfield only by 0.2 ppm. The amount of evolved gas during the reaction was measured by using a Topley pump, but a stoichiometric relationship between amount of evolved gas and degree of cross-linking was not found for uncertain reason. Nonetheless, we may conclude based on the  $^1\text{H}$  NMR, IR, GPC, and TGA data that some degree of cross-linking exists in the polymer chain.

As shown in Table 1, the modification of **1** with the group 4 metallocene  $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$  ( $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ ) combination catalysts yielded the soluble polymer (for Ti) and insoluble polymers (for Zr, Hf). The molecular weight and percent ceramic residue yield of modified polymers increase as the catalyst goes down from Ti to Hf. Red-Al for itself did not have an appreciable effect on the modification of **1** although bis(silyl)methanes  $\text{RCH}(\text{SiH}_3)_2$  are known to transform into  $\text{RCH}_2\text{SiH}_3$  in the presence of Red-Al<sup>16</sup> and bis(silyl)methanes  $\text{CH}_2(\text{SiR}_3)_2$  are known to

**Table 1.** Characterization of Catalytic Modification of **1** with  $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$  ( $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ ) Combination and  $\text{M}(\text{CO})_6$  ( $\text{M} = \text{Cr}, \text{W}$ ) Catalysts<sup>a</sup>

Catalyst (M)	mol wts <sup>b</sup>		% ceramic residue yield <sup>c</sup>
	$M_w$	$M_n$	
no catalyst	1100	630	26
Ti	5300	4000	62
Zr	insoluble		77
Hf	insoluble		83
Cr	2000	1100	75
W	2500	1400	84

<sup>a</sup>  $[\text{M}]/[\mathbf{1}] = 0.02$ ; at 90 °C for 24 h. <sup>b</sup> Measured with GPC (vs polystyrene) in toluene. <sup>c</sup> Measured with TGA up to 800 °C.

transform into  $\text{KCH}(\text{SiR}_3)_2$  in the presence of 1:1  $^n\text{BuLi}/^n\text{BuOK}$ .<sup>17</sup> The group 6 metal carbonyl  $\text{M}(\text{CO})_6$  ( $\text{M}=\text{Cr}, \text{W}$ ) catalysts produce the modified soluble polymers. The molecular weight and percent ceramic residue yield of modified polymers increase as the catalyst goes down from Cr to W. The molecular weight and percent ceramic residue yield of modified polymers increase as compared to unmodified **1**. An interrelationship between molecular weight and percent ceramic residue yield is found among the respective group of catalysts. However, as seen in Table 1, an exact interrelationship between molecular weight and percent ceramic residue yield is not found as the catalyst goes down from Ti to W. Interestingly, while the molecular weights (or degree of cross-linking in view of their solubilities) of the polymers modified with the group 4 metallocene combination catalysts were higher than those of the polymers modified with the group 6 metal carbonyl catalysts, the percent ceramic residue yields of the polymers modified with the group 4 metallocene combination catalysts were similar to those of the polymers modified with the group 6 metal carbonyl catalysts. This is inconsistent with the general fact that the percent ceramic residue yield of highly cross-linked polymer is higher than that of lowly cross-linked polymers. Although the following explanation is just a speculation, we may rationalize as follows. The group 4 and 6 catalytic species could still remain within the polymer body in view of hues of the modified polymer products because we were unable to remove the catalysts completely from the polymer body despite carefully extensive workup. We are not sure at present how the catalysts can attach strongly to the polymer body. The group 6 metal carbonyl moiety such as  $\text{M}(\text{CO})_6$  is known to anchor firmly to the aromatic groups although group 6 metal hexacarbonyls in themselves sublime readily.<sup>18</sup> The group 4 and 6 transition metal complexes are reported to be weakly bound to the Si-H bond.<sup>19</sup> The dehydrocoupling catalytic activities of group 4 metallocene combinations appear to be higher than those of group 6 metal carbonyl catalysts at  $\sim 100^\circ\text{C}$  in the dehydrocoupling of the poly-methylcarbosilane. Heating of **1** at  $200^\circ\text{C}$  for 6 days without catalyst did not effect any change of the  $^1\text{H}$  NMR, GPC, and TGA data. However, the cross-linking catalytic activities of group 4 metallocene combinations appear to be lower than those of group 6 metal carbonyls at very high temperature ( $400^\circ\text{C}$  or higher?) in the pyrolytic transformation of the modified **1**. The group 4 and 6 catalytic species may survive at the high temperature during the catalysis because they may be protected within the polymer matrix even at the high temperature.<sup>6,10,11</sup> We believe that the group 4 catalytic species could be less stable at the high temperature than the group 6 catalytic species. One can imagine that the cross-linking mode of catalysis may change with catalyst, temperature, and physical state (*i.e.*, in solution and in solid).<sup>20</sup> The modified polymers were not pyrophoric and were found to be quite stable at air atmosphere for a long period: the noticeable growth of Si-O stretching bands by oxidation of the Si-H bonds was not observed for several months. Thermogravimetric analysis (TGA) of these modified oligo(methylsilene)s remained unchanged after and before irradiation for 2 h using a medium-pressure mercury lamp, indicating that the polymers are not appreciably photodegradable. The higher ceramic

residue yields (for Zr, Hf, Cr, W), as shown in Table 1, than the theoretical yield (*i.e.*,  $\text{SiC}/\text{SiC}_2\text{H}_6 = 69\%$  for **1**) mean an extra free carbon formation, promoted by the cross-linking, along with SiC formation under the pyrolysis conditions.

## Conclusion

Oligo(methylsilene) **1**,  $[\text{MeSi}(\text{H})\text{CH}_2]_x$ , was modified by using the group 4 metallocene  $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$  ( $\text{M}=\text{Ti}, \text{Zr}, \text{Hf}$ ) combination catalysts and the group 6 metal carbonyl  $\text{M}(\text{CO})_6$  ( $\text{M}=\text{Cr}, \text{W}$ ) catalysts. The molecular weight and percent ceramic residue yield of modified polymers increase as the catalyst goes down from Ti to Hf and similarly as the catalyst goes down from Cr to W. An interrelationship between molecular weight and percent ceramic residue yield is found among the respective group of catalyst. However, an exact interrelationship between molecular weight and percent ceramic residue yield is not found as the catalyst goes down from Ti to W. The catalytic activities of group 4 metallocene combinations seem to be higher than those of group 6 metal carbonyl catalysts at  $\sim 100^\circ\text{C}$  in the dehydrocoupling of **1**. However, the catalytic activities of group 4 metallocene combinations appear to be lower than those of group 6 metal carbonyls at very high temperature in the pyrolytic transformation of the modified oligo(methylsilene).

**Acknowledgment.** This research was supported by the Korea Research Foundation through the International Collaborative Research Program (1997) and by the Korea Ministry of Education through the Basic Science Research Institute Program (Project No. BSRI-97-3426).

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## Molecular Orbital Studies of Bonding Characters of Al-N, Al-C, and N-C Bonds in Organometallic Precursors to AlN Thin Films

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Received May 19, 1998

Electronic structures and properties of the organometallic precursors  $[\text{Me}_2\text{AlNHR}]_2$  (R = Me, 'Pr, and 'Bu) have been calculated by the semiempirical (ASED-MO, MNDO, AM1 and PM3) methods. Optimized structures obtained from the MNDO, AM1, and PM3 calculations indicate that the N-C bond lengths are considerably affected by the change of the R groups bonded to nitrogen, but the bond lengths of the Al-N and Al-C bonds are little affected. This result is useful in explaining the experimental results for the elimination of the R groups bonded to nitrogen, and could serve as a guide in designing an optimum precursor for the AlN thin film formation.

### Introduction

Aluminum nitride (AlN) exhibits interesting properties for electronic applications (chemical inertness, good thermal

stability, piezoelectricity, etc.). The thermal expansion coefficient of AlN is very similar to that of silicon in the range from room temperature to 200 °C (AlN:  $3.5 \times 10^{-6}/\text{K}$ , Si:  $3.4 \times 10^{-6}/\text{K}$ ). Its flexural strength at room temperature is 5,000 kg/cm<sup>2</sup> which is extremely higher than those of Al<sub>2</sub>O<sub>3</sub> (3,100–3,200 kg/cm<sup>2</sup>) and BeO (2,500 kg/cm<sup>2</sup>).<sup>1</sup> It also has a high

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