

- zhendler, J.; Sarel, *J. Org. Chem.* 1977, 42, 3279. (b) Bunton, C. A.; Romsted, L. S.; Smith, H. H. *ibid.* (c) Bunton, C. A.; Carrasco, N.; Haung, S. K.; Paik, C. H.; Romsted, L. S. *J. Am. Chem. Soc.* 1978, 100, 5420.
11. Piskiewicz, D. *J. Am. Chem. Soc.* 1977, 99, 7695.
12. Okahala, Y.; Ando, R.; Kunitake, T. *J. Am. Chem. Soc.* 1977, 99, 3067.
13. Weber, W. P.; Gokel, G. W. *Phase Transfer Catalysis in Organic Synthesis*; Springer-Verlag: New York, 1977.
14. We used the acronym ETABr for ethyltri-*n*-octylammonium bromide, instead of TEABr used by Kunitake,¹² for following that of IUPAC system.
15. In diluted NaOH we estimated $pK_a=12.8$.^{1a,16}
16. (a) Bunton, C. A.; Romsed, L. S.; Sepulveda, L. J. *Phys. Chem.* 1980, 84, 2611. (b) Hisano, T.; Ichikawa, M. *Chem. Pharm. Bull.* 1974, 22, 1974. (c) Yatsimirski, A. K.; Osipov, A. P.; Martinek, K.; Berzin, I. V. *Kolloidn. Zh.* 1975, 37, 470.

Modification of Poly(methylsilene) Catalyzed by Group 4 and 6 Transition Metal Complexes and Its Pyrolysis

Soo-Yeon Yang, Jong-Mok Park, Hee-Gweon Woo*, Whan-Gi Kim[†],
Ik-Sik Kim[‡], Dong-Pyo Kim[†], and Taek-Sung Hwang*

Department of Chemistry, Chonnam National University, Kwangju 500-757, Korea

[†]Department of Applied Chemistry, Kon-Kuk University, Choongju 380-701, Korea

[‡]Kumho Group R & D Center, Kwangju 543-940, Korea

[†]Department of Fine Chemical Engineering and Chemistry, Chungnam National University, Taejon 305-764, Korea

**Department of Chemical Engineering, Chungnam National University, Taejon 305-764, Korea*

Received June 10, 1997

The poly(methylsilene) (1) was modified with the group 4 metallocene $Cp_2MCl_2/Red-Al$ ($M = Ti, Zr, Hf$) combination catalyst and with the group 6 metal carbonyl $M(CO)_6$ ($M = Cr, Mo, W$) catalyst, producing the highly cross-linked insoluble polymer and the lowly cross-linked soluble polymer, respectively. An interrelationship between molecular weight and percent ceramic residue yield with metal within the respective group was not found. The polymers modified with the group 4 metallocene combination catalysts have higher molecular weight and lower percent ceramic residue yield than the polymers modified with the group 6 metal carbonyl catalysts do. The catalytic activity of group 4 metallocene combinations appears to be higher at ~ 100 °C, but to be lower at very high temperature than those of group 6 metal carbonyls. The pyrolysis of the modified 1 yielded SiC ceramic.

Introduction

There are two kinds of ceramics known: oxide type and non oxide type.¹ Silicon-containing ceramics have attracted a great deal of attention for many special applications. Silicon-containing non-oxide ceramics such as silicon carbide (SiC) and silicon nitride (Si_3N_4) have been known for some time.² In particular, silicon carbide ceramic has been widely used as a reinforcement in advanced ceramics and composites.³ A process of fabricating silicon carbide fiber was developed by Yajima *et al.*⁴ The process includes pyrolytic conversion (in the 400–470 °C temperature range) of polydimethylsilane into polycarbosilane (PCS), which is melt-spun into fiber form (trade name "Nicalon" manufactured by Nippon Carbon Co., Tokyo, Japan) and is then cross-linked under an air atmosphere (in the 300–350 °C temperature range), followed by its final pyrolysis (at 1200 °C or higher) under an inert atmosphere into SiC fiber. The cross-linking process by oxidative curing allows the con-

version of PCS fiber to SiC with minimal loss of organic constituent molecules without softening. However, the oxygen introduced during the oxidative curing process may cause fiber degradation at high temperature. In order to improve heat resistivity of PCS some doping agents (*e.g.*, BCl_3) or cross-linking agents (*e.g.*, vinyl derivatives) were added, resulting in the contamination of SiC ceramics and in the oversupply of carbon source to SiC ceramics, respectively.⁵ Another cross-linking method should be considered as an alternative of the disadvantageous curing processes by oxidation and hydrosilation.

The role of Si-H groups in PCS in the Yajima process is very important because Si-H groups permit cross-linking between PCS chains. Recently, Seyferth *et al.* described the preparation of near-stoichiometric silicon carbide by pyrolyzing a polymethylsilane modified by zirconocene-catalyzed dehydrocoupling of Si-H bonds.⁶ Harrod discovered an alternative group 4 metallocene-catalyzed dehydropolymerization leading to great progress in poly (organosilane) synthesis.⁷ Subsequently, Tilley *et al.* reported the catalytic dehydropolymerization of various silanes by

*Author to whom correspondence should be addressed.

(CpCp*ZrH₂)₂ and CpCp*Zr[Si(SiMe₃)₃]Me.⁸ We recently reported the catalytic redistribution/dehydrocoupling of various aryl group-containing alkylsilanes by Cp₂MCl₂/Red-Al, Cp₂MCl₂/*n*-BuLi (M = Ti, Zr, Hf), and Cr(CO)₆ catalysts.⁹ Seyferth *et al.* reported the preparation of SiC/MoSi₂ composite by pyrolyzing a polymethylsilane modified by Mo(CO)₆-catalyzed dehydrocoupling of Si-H bonds.¹⁰ Very recently, one of us described the synthesis of SiC/Mo₂C and SiC/Mo₃Si₇C₂ composites by pyrolyzing the mixture of PCS with different weight percents Mo and Mo(CO)₆, respectively.¹¹ 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 polymethylcarbosilane. In this paper, we report the catalytic modification and pyrolysis of polymethylcarbosilane preceramic polymer, poly(methylsilane), by the group 4 Cp₂MCl₂/Red-Al (M = Ti, Zr, Hf) combination catalyst and by the group 6 M(CO)₆ (M = Cr, Mo, W) catalyst to compare their catalytic effects at different temperature.

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 CDCl₃/CHCl₃ as a reference at 7.24 ppm downfield from TMS. Silicon-29 NMR spectra were obtained on a Varian XL-300 spectrometer operating at 59.59 MHz with CDCl₃ 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 CDCl₃ was used. Gel permeation chromatography (GPC) was carried out on a Waters Millipore GPC liquid chromatograph. The calibrant (monodisperse polystyrene) and the sample were dissolved in toluene and separately eluted from an Ultrastaygel GPC column series (sequence 500, 10³, 10⁴, 10⁵ Å columns). Molecular weights were extrapolated from the calibration curve derived from the polystyrene standard. 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. Pyrolysis under an argon atmosphere to 1500 °C using a Lindberg Model 59545 single zone tube furnace, equipped with a mullite tube and a carbon pyrolysis boat supported on a 6" alumina tube dec. Percent ceramic residue yield was calculated as change in weight before and after pyrolysis. X-ray powder diffraction (XRD) measurements were done on an APD 3600 X-ray powder diffractometry. The d-spacings were matched to computer-generated patterns based on referenced files.¹² Cp₂MCl₂ (M = Ti, Zr, Hf), M(CO)₆ (M = Cr, Mo, W), and Red-Al (or Vitride; sodium bis(2-methoxyethoxy)aluminum hydride; 3.4 M in toluene) were

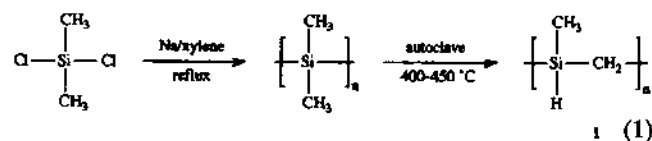
purchased from Aldrich Chemical Co. and were used without further purification. The poly(methylsilene) [1, IR (film, KBr, cm⁻¹): 2900 s, 2950 m (ν_{CH}), 2100 s (ν_{SiH}), 1250 m (ν_{SiC}), 1410 s (δ_{CH}); ¹H NMR (δ, CDCl₃, 300 MHz): -0.9-0.8 (br, SiCH₂, SiCH₃), 3.8-5.0 (br, SiH), CH/SiH integral ratio=12.2; ²⁹Si NMR (δ, CDCl₃, 59.59 MHz): -17.23 (br, SiH, SiCH₂, SiCH₃); GPC: M_w=2200, M_n=750, M_w/M_n=2.9; TGA ceramic residue yield: 65% (black solid)], which was obtained from fractional precipitation, was prepared according to the literature procedure.¹³

Modification of 1 Catalyzed by Cp₂MCl₂/Red-Al (M = Ti, Zr, Hf). The following procedure is the representative of the modification reactions with the group 4 metallocene Cp₂MCl₂/Red-Al (M = Ti, Zr, Hf) combination catalysts. Poly(methylsilene) (1) (1.0 g, 17.2 mmol equiv) in 1.0 mL of toluene was injected to a Schenk flask containing Cp₂TiCl₂ (0.085 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 catalyst was inactivated 24 h later by exposure to the air for a few hours. The brown gelatinous material was washed well with toluene and diethyl ether and dried at reduced pressure to give 1.0 g (100% yield) of light chocolate solid which was insoluble in most organic solvents. IR (KBr pellet, cm⁻¹): 2100 s (ν_{SiH}); TGA ceramic residue yield: 73% (black solid).

Modification of 1 Catalyzed by M(CO)₆ (M = Cr, Mo, W). As a typical modification reaction, a Schlenk flask was charged with 1 (1.0 g, 17.2 mmol equiv), Cr(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 Cr(CO)₆ and turned light green. After 24 h, the resulting mixture was passed rapidly through a reverse phase silica gel column (70-230 mesh, 20 cm × 2 cm) with 200 mL of toluene used as the eluent. The effluent was evaporated at reduced pressure to yield 1.0 g (100% yield) of a pale green solid which was soluble in toluene, THF, methylene chloride, and chloroform. IR (film, KBr, cm⁻¹): 2100 s (ν_{SiH}); ¹H NMR (δ, CDCl₃, 300 MHz): -0.9-0.8 (br, SiCH₂, SiCH₃), 3.8-5.0 (br, SiH), CH/SiH integral ratio=13.6; ²⁹Si NMR (δ, CDCl₃, 59.59 MHz): -17.16 (br, SiH, SiCH₂, SiCH₃); GPC: M_w=3600, M_n=1300; TGA ceramic residue yield: 90% (black solid).

Results and Discussion

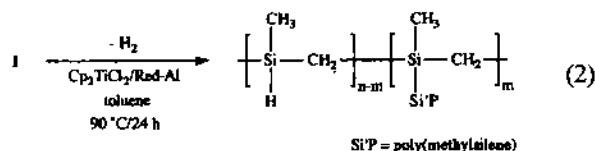
Wurtz-coupling reaction of dichlorodimethylsilane using sodium metal dispersion in xylene-refluxing temperature produced an insoluble and infusible polydimethylsilane in high yield. A soluble and fusible poly(methylsilene) was then prepared by pyrolytic Kumada rearrangement of the polydimethylsilane at 400-450 °C in autoclave (eq. 1).



The polymethylsilene (1) with weight average molecular weight of 2200 (polydispersity index = 2.9) and TGA ceramic residue yield of 65% was obtained from fractional pre-

cupitation.¹³ The polymethylsilene is known to possess some degree of cross-linking in the polymer chain because of intermolecular Kumada rearrangement during pyrolysis.¹⁴ The ¹H NMR spectrum of **1** shows three broad unresolved mountain-like resonances centered at -0.1, 0.2, and 4.4 ppm assigned to SiCH₂, SiCH₃, and SiH, respectively. The CH/SiH integral ratio was 12.2 instead of 5.0 because of some degree of cross-linking in the polymer chain and long relaxation time of Si-H bond.¹⁵ The ²⁹Si NMR spectrum of **1** shows one broad unresolved mountain-like resonances centered at -17.23 ppm assigned to SiCH₂, SiCH₃, and SiH. The IR spectrum of **1** exhibits a typical intense ν_{SiH} band at ca. 2100 cm⁻¹.

One may expect that the tertiary silyl groups of **1** should seldom undergo dehydrocoupling due to their steric bulkiness because the dehydrocoupling reactivity of hydrosilanes is well known to decrease drastically in the order of primary > secondary >> tertiary.^{7,8} As expected, dehydrocoupling modification of **1** with 2 mol% of the Cp₂TiCl₂/Red-Al combination catalyst took place very slowly at ambient temperature and upon heating at 90 °C the reaction medium became slowly gelatinous over 24 h (eq. 2).



The modified polymer was isolated in ~100% yield as a light chocolate solid, which was insoluble in most organic solvents, after workup including washing with toluene and diethyl ether. The TGA ceramic residue yield of the insoluble solid was 73%. Similarly, dehydrocoupling modification of **1** with 2 mol% of the other Cp₂MCl₂/Red-Al (M = Zr, Hf) combination catalysts occurred very slowly at a ambient temperature and upon heating at 90 °C the reaction medium became slowly gelatinous over 24 h. The modified polymers were obtained in ~100% yield as a light chocolate insoluble solid (TGA ceramic residue yield=76%) for Zr and a pale orange insoluble solid (TGA ceramic residue yield=74%) for Hf. The characterization data are summarized in Table 1.

The IR spectra of the modified poly(methylsilene)s exhibit an intense ν_{SiH} band at ca. 2100 cm⁻¹ of which the intensity was somewhat decreased as compared with **1**. 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 po-

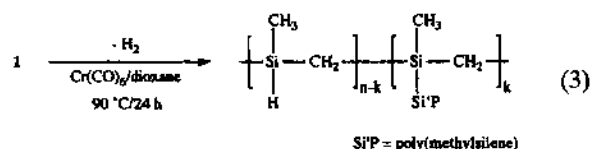
Table 1. Characterization of Catalytic Modification of **1** with Cp₂MCl₂/Red-Al (M = Ti, Zr, Hf) Combination Catalysts^a

Catalyst (M)	mol wt ^b		% ceramic residue yield ^c
	M _w	M _n	
no catalyst	2200	750	65
Ti	insoluble		73
Zr	insoluble		76
Hf	insoluble		74

^a [M]/[**1**]=0.02; at 90 °C for 24 h. ^b Measured with GPC (vs polystyrene) in toluene. ^c Measured with TGA up to 800 °C.

lymer. 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 ¹H NMR spectrum and molecular weight (confined by ¹H NMR spectroscopy and GPC analysis).

Dehydrocoupling modification of **1** with 2 mol% of the Cr(CO)₆ catalyst was carried out at 90 °C for 24 h (eq. 3).



The modified polymer was isolated in ~100% yield as a pale green solid, which was soluble in most organic solvents, after workup including column chromatography. The TGA ceramic residue yield of the modified polymer was 90%. The weight average molecular weight (M_w) and number average molecular weight (M_n) of the modified polymer were 3600 and 1300, respectively. Similarly, dehydrocoupling modification of **1** with 2 mol% of the other M(CO)₆ (M = Mo, W) catalysts was performed at 90 °C for 24 h. The modified polymers were obtained in ~100% yields as a light chocolate soluble solid (TGA ceramic residue yield=87%) for Mo and a light yellow soluble solid (TGA ceramic residue yield=88%) for W. The weight average molecular weight and number average molecular weight of the resulting modified polymers were 3500 and 1200 for Mo and 4500 and 1300 for W, respectively. The characterization data are given in Table 2.

The IR spectra of the modified poly(methylsilene)s exhibit an intense ν_{Si-H} band at ca. 2100 cm⁻¹ of which the intensity was somewhat decreased as compared with **1**. The ¹H NMR spectra of the modified poly(methylsilene)s show that the CH/SiH integral ratios are in the 13-14 range. The ²⁹Si NMR spectrum of **1** shows one broad unresolved mountain-like resonances centered at -17.16 ppm assigned to SiCH₂, SiCH₃, and SiH. We may conclude based on the ¹H NMR, IR, GPC, and TGA data that some degree of cross-linking exists in the polymer chain. There was no significant change in the ²⁹Si NMR spectra of **1** before and after their catalytic modification except that the single broad resonance had shifted downfield by 0.07 ppm. **1** was catalytically modified by using 2 mol% of Mo(CO)₆ at 90 °C for 6 d, yielding a modified polymer with molecular weights of 5200 (M_w) and 1500 (M_n) and with TGA ceramic residue yield of 91%. Pyrolysis at 1500 °C of the modified polymer produced a

Table 2. Characterization of Catalytic Modification of **1** with M(CO)₆ (M = Cr, Mo, W) Catalysts^a

Catalyst (M)	mol wt ^b		% ceramic residue yield ^c
	M _w	M _n	
Cr	3600	1300	90
Mo	3500	1200	87
Mo ^b	5200	1500	91(84)
W	4500	1300	88

^a [M]/[**1**]=0.02; at 90 °C for 1 d. ^b [M]/[**1**]=0.02; at 90 °C for 6 d. ^c Measured with GPC (vs polystyrene) in toluene. ^d Measured with TGA up to 800 °C. ^e Bulk pyrolysis at 1500 °C.

black ceramic solid in 84% yield which turned out to be SiC ceramic along with small amount of $\text{Mo}_x\text{Si}_y\text{C}_z$ (confirmed by X-ray powder diffraction analysis).¹¹

As shown in Table 1, the group 4 metallocene $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$ ($\text{M}=\text{Ti}, \text{Zr}, \text{Hf}$) combination catalysts produce the modified insoluble polymers with similar percent ceramic residue yields in the 73-76% range: any notable tendency toward solubility and percent ceramic residue yield with the group 4 metal was not found. 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 RCH_2SiH_3 in the presence of Red-Al¹⁶ and bis(silyl)methanes $\text{CH}_2(\text{SiR}_3)_2$ are known to transform into $\text{KCH}(\text{SiR}_3)_2$ in the presence of 1:1 $^t\text{BuLi}/^t\text{BuOK}$.¹⁷ As shown in Table 2, the group 6 metal carbonyl $\text{M}(\text{CO})_6$ ($\text{M}=\text{Cr}, \text{Mo}, \text{W}$) catalysts produce the modified soluble polymers with similar weight average molecular weights in the range of 3500-4500 and with similar percent ceramic residue yields in the range of 87-90%. Compared with **1**, the increase of molecular weights was not pronounced. Any marked trend toward molecular weight and percent ceramic residue yield with the group 6 metal was not observed, *albeit* longer reaction time and $\text{W}(\text{CO})_6$ gave somewhat higher molecular weight polymers. An interrelationship between molecular weight and TGA ceramic residue yield was neither shown. Interestingly, as shown in Table 1 and 2, 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 lower than those of the polymers modified with the group 6 metal carbonyl catalysts. This is opposite to 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 only a speculation, we may rationalize the fact (*vide infra*). The group 4 and 6 catalytic species still remain within the polymer body in view of colors of the modified polymer products because we were unable to remove the catalysts completely from the polymer body in spite of carefully extensive workup. We are not sure at present how the catalysts can attach strongly to the polymer body without aromatic substituents. The group 6 metal carbonyl moiety such as $\text{M}(\text{CO})_3$ is known to anchor strongly to the aromatic groups although group 6 metal hexacarbonyls for themselves sublime readily.¹⁸ The group 4 and 6 transition metal complexes are known to be weakly bound to the Si-H bond.¹⁹ A transition metal complex-coordinated polymer could be different from a transition metal complex-free polymer.²⁰ 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 polymethylcarbosilane. Heating of **1** at 200°C for 6 days without catalyst did not effect any change of the ^1H 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°C or higher?) in the pyrolytic transformation of the modified poly

(methylsilene). 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.^{6,10,11} 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).²¹ The modified poly(methylsilene)s 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 poly(methylsilene)s remained unchanged after and before irradiation for 2 h using a medium-pressure mercury lamp, indicating that polymers are not appreciably photodegradable. The TGA data of the modified polycarbosilanes showed that the ceramic residue yields were consistently higher than theoretical yields (*i.e.*, $\text{SiC}/\text{SiC}_2\text{H}_6=69\%$ for **1**), probably due to extra free carbon formation, promoted by the cross-linking, along with SiC formation under the pyrolysis conditions.

Conclusion

The poly(methylsilene) (**1**) was prepared in high yield by Wurtz coupling of dichlorodimethylsilane and Kumada rearrangement of polydimethylsilane. The poly(methylsilene) (**1**) was modified by the group 4 metallocene $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$ ($\text{M}=\text{Ti}, \text{Zr}, \text{Hf}$) combination catalysts and by the group 6 metal carbonyl $\text{M}(\text{CO})_6$ ($\text{M}=\text{Cr}, \text{Mo}, \text{W}$) catalysts to produce the highly cross-linked insoluble polymers and the lowly cross-linked soluble polymers, respectively. Any marked trend toward molecular weight and TGA ceramic residue yield with metal within the respective group was not observed. The polymers modified with the group 4 metallocene combination catalysts possess higher molecular weight and lower percent ceramic residue yield than the polymers modified with the group 6 metal carbonyl catalysts do. The 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(methylsilene). 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 poly(methylsilene). The pyrolysis of the modified poly(methylsilene) yielded SiC ceramic.

Acknowledgment. H. G. W. is grateful to the Ministry of Education, Korea through the Basic Science Research Institute Program (Project No. BSRI-96-3426) and the Center for Inorganic Materials Chemistry, Chungnam National University (1997) for the financial support. D. P. K. gratefully acknowledges the Korea Science and Engineering Foundation (Project No. 0306-066-2) for support of this work. H. G. W. especially thanks the Dow Corning Corporation for a gift.

References

1. Hench, L. L.; West, J. K. *Chem. Rev.* 1992, 90, 33.

2. (a) *Gmelin Handbook of Inorganic Chemistry*, 8th ed.; Springer-Verlag: Berlin (FRG), 1984; Supplement volume B2. (b) Messier, D. R.; Croft, W. J. In *Preparation and Properties of Solid-State Materials*; Wilcox, W. R., Ed.; Marcel Dekker: New York, 1982; Volume 7, Chapter 2.
3. (a) Fizer, E.; Gadow, R. *Am. Ceram. Soc. Bull.* 1986, 65, 326. (b) Sheppard, L. M. *Am. Ceram. Soc. Bull.* 1990, 69, 666.
4. (a) Yajima, S.; Hayashi, J.; Omori, M. *Chem. Lett.* 1975, 931. (b) Yajima, S.; Okamura, K.; Hayashi, J.; Omori, M. *J. Am. Ceram. Soc.* 1976, 59, 324.
5. (a) Lipowitz, J.; Barnard, T.; Bujalski, D.; Rade, J.; Zank, G.; Zangvil, A.; Xu, Y. *Compos. Sci. Technol.* 1994, 51, 167. (b) Toreki, W.; Creed, N. M.; Batich, C. D. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1990, 31, 611.
6. Seyferth, D.; Wood, T. G.; Tracy, H. J.; Robison, J. L. *J. Am. Ceram. Soc.* 1992, 75, 1300.
7. (a) Aitken, C.; Harrod, J. F.; Gill, U. S. *Can. J. Chem.* 1987, 65, 1804. (b) Harrod, J. F.; Yun, S. S. *Organometallics* 1987, 6, 1381. (c) Aitken, C.; Barry, J.-P.; Gauvin, F.; Harrod, J. F.; Malek, A.; Rousseau, D. *Organometallics* 1989, 8, 1732. (d) Harrod, J. F.; Ziegler, T.; Tschinke, V. *Organometallics* 1990, 9, 897. (e) Woo, H.-G.; Harrod, J. F.; Henique, J.; Samuel, E. *Organometallics* 1993, 12, 2883. (f) Britten, J.; Mu, Y.; Harrod, J. F.; Polowin, J.; Baird, M. C.; Samuel, E. *Organometallics* 1993, 12, 2672.
8. (a) Woo, H.-G.; Tilley, T. D. *J. Am. Chem. Soc.* 1989, 111, 3757. (b) Woo, H.-G.; Tilley, T. D. *J. Am. Chem. Soc.* 1989, 111, 8043. (c) Woo, H.-G.; Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* 1992, 114, 5698. (d) Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *J. Am. Chem. Soc.* 1992, 114, 7047. (e) Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *Macromolecules* 1991, 24, 6863. (f) Imori, T.; Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *Chem. Mater.* 1993, 5, 1487. (g) Tilley, T. D. *Acc. Chem. Res.* 1993, 26, 22.
9. (a) Woo, H.-G.; Kim, S.-Y.; Han, M.-K.; Cho, E. J.; Jung, I. N. *Organometallics* 1995, 14, 2415. (b) Woo, H.-G.; Kim, S.-Y.; Kim, W.-G.; Cho, E. J.; Yeon, S. H.; Jung, I. N. *Bull. Korean Chem. Soc.* 1995, 16, 1109. (c) Woo, H.-G.; Song, S.-J.; You, H.; Cho, E. J.; Jung, I. N. *Bull. Korean Chem. Soc.* 1996, 17, 475. (d) Woo, H.-G.; Song, S.-J. *Bull. Korean Chem. Soc.* 1996, 17, 494.
10. Seyferth, D.; Sobon, C. A.; Borm, J. *New J. Chem.* 1990, 14, 545.
11. Kim, D.-P.; Lee, J.-D. *Korean J. Mater. Res.* 1996, 6, 515.
12. Smith, D. K. *Modern Powder Diffraction*; Bish, D. L., Post, J. E., Eds.; The Mineralogical Society of America: Washington, D. C., 1989.
13. Yajima, S.; Shishido, T.; Okamura, K. *Am. Ceram. Soc. Bull.* 1977, 56, 1060.
14. Yajima, S.; Okamura, K.; Hayashi, J. *J. Am. Ceram. Soc.* 1975, 58, 1209.
15. Harris, R. K.; Kennedy, J. D.; McFarlane, W. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978; Chapter 10.
16. Woo, H.-G.; Song, S.-J.; Cho, E. J.; Jung, I. N. *Bull. Korean Chem. Soc.* 1996, 17, 123.
17. Seyferth, D.; Lang, H. *Organometallics* 1991, 10, 551.
18. Wiseman, A. I.; Jones, R. G.; Swain, A. C.; Went, M. J. In *Silicon-containing Polymers*; Jones, R. G., Ed.; The Royal Society of Chemistry: Cambridge (UK), 1995; p 191.
19. Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, California, 1987.
20. Ley, K. D.; Whittle, C. E.; Bartberger, M. D.; Schanze, K. S. *J. Am. Chem. Soc.* 1997, 119, 3423.
21. Woo, H.-G.; Song, S.-J. Unpublished results.