Poly(methylsilane) and Other Polymeric Ceramic Precursors. Their Chemistry and Application in Preparation of Advanced Materials

by

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B.S., The American University, Washington, DC
(1990)

Submitted to the Department of Chemistry
in partial fulfillment
of the requirements for the
degree of

DOCTOR OF PHILOSOPHY
in Inorganic Chemistry

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
February 1995

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This dissertation is dedicated to
my lovely wife Danuta,
to my parents Nonna and Włodzimierz Czubarow,
and to
Ken and Fran Valentine
Poly(methylsilane) and Other Polymeric Ceramic Precursors. Their Chemistry and Application in Preparation of Advanced Materials

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Paweł Czubarow

Submitted to the Department of Chemistry on December 16, 1994 in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

ABSTRACT

Chapter One. Synthesis, Characterization, Derivatization, and Application of Poly(methylsilane) Ceramic Precursor

Oligo(methylsilane) (OMS) of structure \[(\text{MeSiH})_x(\text{MeSi})_y(\text{MeSiH}_2)_z\]_n where \(x + y + z = 1\) and \(0.94 \geq (x + z) \geq 0.75\) and poly(methylsilane) (PMS) where \(0.60 \geq (x + z) \geq 0.30\) have been synthesized by the sodium polycondensation reaction of MeSiHCl\(_2\) in a solvent mixture of hexane or toluene and THF using ultrasonic activation. This polycondensation reaction takes place in two stages (1) (10 - 20 h of reaction) yielding the OMS oil which gives low ceramic residue yields on pyrolysis and (2) (30 - 40 h of reaction) yielding PMS solid which gives high ceramic residue yields of near stoichiometric SiC on pyrolysis. PMS was also made by ultrasonication (about 5 h) of OMS with sodium in toluene and THF solvent mixture. PMS is soluble in hexane and toluene and has a ceramic residue yield in the range of 80 to 85%. Ceramic fibers, films, and solid monoliths without requiring a curing step were prepared from PMS. Cocondensation of MeSiHCl\(_2\) and CH\(_2\)Br\(_2\) with sodium was performed to increase the molecular weight of the oligomer. Various transition metal dehydrogenative coupling catalysts were exploited to increase the molecular yield and ceramic residue yield of OMS. Quantitative chlorination of the OMS was accomplished through photolysis of the oligomer with CH\(_2\)Cl\(_2\) and UV irradiation.
Chapter Two. Application of Poly(methylsilane) and Other Polymeric Ceramic Precursors to in situ Preparation of Metal Matrix Composites and Cermets

Polymeric ceramic precursors such as poly(methylsilane), polycarbosilanes, polysilazanes, and poly(borazinylamine) were used as binders for metal powders such as Ti, Al, Zr, V, Mo, W, Fe, Ni, and Cu in powder metallurgy (P/M) preparation of near-net-shape metal matrix composites and cermets. The main advantage of using polymeric ceramic precursors instead of commercially used organic polymers is that the costly and tedious debinding step in avoided and the resulting composites have diminished void volume. In the current application the polymeric ceramic precursor plays two roles 1) as a binder and lubricant and 2) as a source of ceramics. The MMCs had high moduli of rupture, high hardness, oxidation and corrosion resistance. In some cases the polymeric ceramic precursors proved to be convenient in cermet preparation. In almost all of the cases the final ceramic phases resulted from a high temperature solid state reaction between amorphous ceramics resulting from the pyrolysis of the polymer and the metal matrix. Metal silicides, carbides, nitrides, or borides were formed and finely dispersed in the metal matrix.

Chapter Three. Application of Poly(methylsilane) and Nicalon® Polycarbosilane Precursor as Binders for Metal/Ceramic Powders in preparation of Functionally Graded Materials

For the first time, ceramic precursors were applied in P/M preparation of Functionally Graded Materials (FGM). Two types of FGMs were prepared: Al/ SiC for possible aerospace applications and Cu/ SiC for dynamic seal applications. There are two main advantages of using ceramic precursors for P/M preparation of FGMs 1) avoidance of the commercially used debinding step and 2) shrinkage control of the individual layers of the composite.

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TABLE OF CONTENTS

Abstract .................................................................................................................. 4

Chapter One. Synthesis, Characterization, Derivatization, and Application of Poly(methylsilane) Ceramic Precursor

Section A. Introduction .......................................................................................... 20

Section B. Synthesis of Oligo(methylsilane) .......................................................... 29

Section C. The Composition of Oligo(methylsilane) .............................................. 41

Section D. Proposed Mechanism of Oligo(methylsilane)
Synthesis. The Effect of Chain Transfer
Agent on Growth of Oligo(methylsilane) ................................................................. 58

Section E. Photochlorination of Oligo(methylsilane) ............................................. 76

Section F. Crosslinking of Oligo(methylsilane) by Catalyzed
Dehydrogenative Coupling Reactions .................................................................. 106

Section G. High Molecular Weight Poly(methylsilane) -
a Precursor to Near-Stoichiometric SiC ................................................................. 136

Section H. Experimental ......................................................................................... 176

General Comments ................................................................................................ 177

Reaction Between Methyldichlorosilane and 2.5 Na in
Refluxing Hexane/THF 7/1 v/v. (PC/2/47)............................................................... 180

Reaction Between MeSiHCl₂ (Gradual Addition) and
2.5 Na in 7/1 v/v Ratio of Hexane/THF Using Ultrasonic
Activation at 20°C. (PC/2/55) ................................................................................ 181
Recommended Procedure for Synthesis of Oligo(methylsilane).
Reaction Between MeSiHCl₂ and 2.5 Na in 7/1 v/v of
Hexane/THF Using Ultrasonic Activation at 45°C.
(PC/3/61; PC/4/14, 18, 19, 28, 51; PC/5/12, 29, 59, 66;
PC/7/19, 26, 60; PC/8/12, 17) ........................................... 182

Reaction Between MeSiHCl₂ (Stepwise Addition)
and 2.5 Na in 7/1 v/v of Hexane/THF Using
Ultrasonic Activation at 50°C. (PC/4/34; PC/6/70) ................. 184

Reaction Between MeSiHCl₂ and 2.5 Na in
15/1 v/v of Hexane/THF Using Ultrasonic
Activation at 28°C. (PC/3/39) ........................................... 185

Reaction Between MeSiHCl₂ and 2.5 Na in
Concentrated (12.4 M) Solution in 7/1 v/v of
Hexane/THF Using Ultrasonic Activation
at 28°C. (PC/8/28) .................................................... 186

Reaction Between MeSiHCl₂ and 2.5 Na in
Hexane and Toluene Using Ultrasonic
Activation at 28°C. (PC/3/21, 23) ..................................... 187

Reaction Between MeSiHCl₂ and Minimum
Surface Area of Na in 7/1 v/v Hexane/THF
Using Ultrasonic Activation at 28°C. (PC/8/19) ..................... 188

Reaction Between MeSiHCl₂ and 0.25 Na in
7/1 v/v Hexane/THF Using Ultrasonic Activation
at 28°C. (PC/6/16) ..................................................... 189

Reaction Between MeSiHCl₂ and 12.5 Na in
1/7 v/v THF/Hexane Using Ultrasonic Activation
at 28°C. (PC/8/22) ..................................................... 190

Reaction Between MeSiHCl₂ and 2.5 Na with 2 wt%
of Ethyl Acetate Using Ultrasonic Activation
at 28°C. (PC/8/49) ..................................................... 191

Reaction Between MeSiHCl₂ and 2.5 Na with 4 wt%
of THF Using Ultrasonic Activation at 28°C. (PC/8/29) ............. 192
Reaction Between PhSiHCl₂ and 2.5 Na in 7/1 v/v Hexane/THF Using Ultrasonic Activation. (PC/3/41) .................................193

Reaction Between MeSiHCl₂ and CH₂Br₂ in 1:1 Molar Ratio and 2.5 Na in Refluxing Toluene. (PC/2/73; PC/3/2) .................................................................194

Reaction Between MeSiHCl₂ and Various Amounts of CH₂Br₂ and 2.5 Na in Refluxing Octane. (PC/3/4,5,6) .........................196

Reaction Between MeSiHCl₂ and 5 wt% (PC/3/9) and 15 wt% (PC/3/10) of CH₂Br₂ and 2.5 Na in 7/1 v/v of Hexane/THF Using Ultrasonic Activation at 20°C. (PC/3/9,10) ..................................................................................198

Reaction of Oligo(methyilsilane) With 0.5 mol% (Cp₂ZrH₂)ₙ in Refluxing Toluene. (PC/4/50, 64, 67; PC/5/43, 56; PC/6/69) ..........................................................199

Reaction of Oligo(methyilsilane) With 0.5 mol% (Cp₂ZrH₂)ₙ in Hexane at 70°C Under Vacuum. (PC/4/9) .........................200

UV Photolysis of Oligo(methyilsilane) With 0.5 mol% of (Cp₂ZrH₂)ₙ in Hexane Under Vacuum. (PC/4/10) ..................201

A Blend of Oligo(methyilsilane) With 0.57 mol% of Cp₂ZrCl₂. (PC/3/43, 45, 47) .................................................................202

Reaction of Oligo(methyilsilane) With 0.57 mol% of Cp₂ZrCl₂ in Refluxing Toluene. (PC/3/58, 46) .........................203

Reaction of Oligo(methyilsilane) With 0.57 mol% of Cp₂TiCl₂ in Refluxing Toluene. (PC/3/59; PC/4/17) .........................203

A Blend of Oligo(methyilsilane) With 0.57 mol% of Cp₂ZrHCl. (PC/3/52) .................................................................204

Reaction of Oligo(methyilsilane) With 0.5 mol% of Cp₂ZrHCl in Refluxing Toluene. (PC/3/66, 70) .........................204
Reaction of Oligo(methylsilane) With 0.5 mol% of Cp₂TiMe₂ in Toluene at Room Temperature. (PC/7/73) ........................................... 205

UV Photolysis of Oligo(methylsilane) With 0.5 mol% of Cp₂ZrMe₂ in Hexane Under Vacuum. (PC/3/69; PC/4/1) ........................................... 206

Reaction of Oligo(methylsilane) With 0.5 mol% of Cp₂ZrMe₂ in Refluxing Hexane. (PC/3/68) ................................................................. 207

Reaction of Oligo(methylsilane) With 0.5 mol% of (Ph₃P)₃RhCl in Toluene at Room Temperature. (PC/4/16, TS/3/31) ................................................................. 207

Reaction of Oligo(methylsilane) With 0.5 mol% of [Rh(COD)Cl]₂ in Toluene at Ambient Temperature Under Vacuum. (PC/4/20) .................................................................................. 208

Reaction of Oligo(methylsilane) With 0.5 mol% of (Ph₃P)₂Rh(CO)Cl in Toluene at Room Temperature Under Vacuum. (PC/4/21, 29, 57) .................................................................................. 209

Thermolysis of Oligo(methylsilane) With 1.0 mol% of Ti(OPr-i)₄ in Toluene at 105°C Under Vacuum. (PC/4/11) ........................................... 210

Solvent Free Thermolysis of Oligo(methylsilane) With 1.0 mol% of Ti(OPr-i)₄ at 200°C. (PC/4/12) ................................................................. 211

Thermolysis of Oligo(methylsilane) With 1.0 mol% of Ti(OPr-i)₄ at 250°C in a Sealed Tube. (PC/4/13) ................................................................. 212

UV Photolysis of Oligo(methylsilane) With 1.0 mol% of Ti(OPr-i)₄ in Hexane Under Vacuum. (PC/4/15) ................................................................. 212

Reaction of Oligo(methylsilane) With 1.0 mol% of B(OEt)₃ in Refluxing Undecane (b.p. 196°C). (PC/7/33, 34) ........................................... 213

Thermolysis of Neat Oligo(methylsilane) at 190°C in a Sealed Tube. (PC/2/74) ................................................................. 214

Thermolysis of Neat Oligo(methylsilane) at 250°C in a Sealed Tube. (PC/4/22) ................................................................. 215
Thermolysis of Neat Oligo(methylsilane) at 300°C in a Sealed Tube. (PC/4/8) ................................................................. 215

Thermolysis of Neat Oligo(methylsilane) at 400°C in a Sealed Tube. (PC/4/6) ................................................................. 216

Irradiation With γ-Rays of Neat Oligo(methylsilane) in a Sealed Tube. (PC/4/35) ................................................................. 217

UV Photochlorination of Oligo(methylsilane) in CH₂Cl₂ Under Vacuum. (PC/5/23, 42) ................................................................. 217

UV Photochlorination of Oligo(methylsilane) in CH₂Cl₂. (PC/7/13, 27, 29, 30, 31, 32, 72; PC/8/5) ................................................................. 218

UV Photochlorination of Oligo(methylsilane) in CH₂Cl₂ at Various Time Intervals. (TS/2/15, 16, 17, 20, 38) ................................................................. 219

UV Photochlorination of Poly(methylsilane) (TS-2 Quenched with Mel) and 1.0 CH₂Cl₂ in Hexane and Its Subsequent Reduction with LiAlH₄. (TS/3/43, 48) ................................................................. 220

UV Photolysis of Oligo(methylsilane) in Hexane. (PC/8/18) ................................................................. 221

UV Photochlorination of Oligo(methylsilane) With 0.5 Mol of CH₂Cl₂ in Hexane. (PC/8/15, 14) ................................................................. 222

Recommended Least Destructive to the Si-Si Bond UV Photochlorination of Oligo(methylsilane) With 1.0 Mol of CH₂Cl₂ in Hexane. (TS/3/21) ................................................................. 223

Daylight Photochlorination of Oligo(methylsilane) With CH₂Cl₂. (PC/8/40) ................................................................. 224

UV Photochlorination of the Nicalon® Fiber Polycarboasilane Precursor in CH₂Cl₂ at Various Time Intervals. (PC/6/14, 19, 24; PC/8/30) ................................................................. 224

UV Photochlorination of the Nicalon® Fiber Polycarboasilane Precursor in CCl₄. (PC/6/31) ................................................................. 225
UV Photochlorination of Oligo(methylsilane)
Using Various Chlorinating Agents. (TS/1/58, 70, 57) .................................. 226

Reaction of Oligo(methylchlorosilane) With an Excess
of Ammonia at 4°C in Diethyl Ether. (PC/8/8, 16) ................................. 227

Reaction of Oligo(methylchlorosilane) With an Excess
of NH₂CH₃ at 4°C in Diethyl Ether. (PC/8/7) ........................................... 228

Reaction of Oligo(methylchlorosilane) With an Excess
of PhLi at 4°C in Diethyl Ether. (TS/2/47) ............................................ 229

Reaction of Oligo(methylchlorosilane) With an Excess
of MeOH at 4°C in Diethyl Ether (TS/3/23) ........................................... 230

Extended Reaction Time Experiment of MeSiHCl₂
and 2.5 Na in 7/1 v/v Hexane/THF
by Ultrasonic Activation. (TS/1/52) .................................................. 231

Extended Reaction Time Experiment of MeSiHCl₂
and 2.5 Na in 7/1 v/v Hexane/THF
by Ultrasonic Activation. (PC/7/58) .................................................. 232

Extended Reaction Time Experiment of MeSiHCl₂
and 2.5 Na in 7/1 v/v Toluene/THF
by Ultrasonic Activation. Synthesis of TS-1. (PC/7/59) ....................... 233

Extended Reaction Time Experiment of MeSiHCl₂
(Gradually Added) and 2.5 Na in 7/1 v/v Toluene/THF
by Ultrasonic Activation.
Synthesis of TS-1. (TS/2/51, TS/3/01) ............................................. 235

Extended Reaction Time Experiment of MeSiHCl₂
and 5.0 Na in 7/1 v/v Toluene/THF
by Ultrasonic Activation. (TS/3/6) .................................................. 236

Extraction of the High Molecular Weight
Poly(methylsilane) PC-1 From NaCl Crystals
Obtained From TS-1 Synthesis (TS/2/51). (PC/8/34) .............................. 237
Extraction of the High Molecular Weight Poly(methylsilane) PC-1 From NaCl Crystals Obtained From Synthesis of Oligo(methylsilane). (TS/2/39, PC/8/12, PC/8/17, PC/8/19, PC/8/23) .............................................. 239

Wurtz Coupling Reaction of MeSiHCl₂ and 2.05 Na in 7/1 v/v Toluene/THF by Ultrasonic Activation and Subsequent Cross-Linking of the Oligomer With 0.5 Na. Synthesis of TS-2. (TS/2/68, 72t, 72h) .................................................. 240

Extended Reaction Time Experiment of MeSiHCl₂ and 2.5 Na in Refluxing 7/1 v/v Toluene/THF. (TS/2/73) ........................................... 242

Recommended Procedure for the Preparation of Poly(methylsilane) (TS-2) by Reaction of Oligo(methylsilane) With 0.5 Na in 7/1 v/v Toluene/THF Using Ultrasonic Activation and Subsequent Quenching of the Polymer with MeI. (PC/8/42, 55; TS/3/22, 39) .......................................................... 244

Blend of Oligo(methylsilane) and Ploy(methylsilane) with BHT to Prevent Their Oxidation Upon Exposure to Air. (TS/2/48, 57) .................................................. 247

Control Experiment of Oligo(methylsilane) Ultrasonication in 7/1 v/v Hexane/THF. (PC/8/37) .................................................. 248

Reaction of Oligo(methylsilane) With 15 mol% NaH in THF and Using Ultrasonic Activation. (PC/8/54; PC/8/41) .................................................. 248

Wurtz Coupling Reaction of MeSiHCl₂ and 2.5 Na in THF by Ultrasonic Activation. (PC/3/22, 63; PC/8/45, 46) .................................................. 249

Wurtz Coupling Reaction of MeSiHCl₂ and 2.5 Na in Refluxing THF.³⁶ (PC/8/50; TGW-VIII-39³⁶) ........................................... 250

Coating of an Alumina Substrate With Poly(methylsilane) (TS-2H). (PC/8/52) .................................................. 251
Spinning SiC Fibers From High Molecular Weight Poly(methylsilane) (TS-2H). ........................................... 252

Preparation of Monolithic SiC From TS-2T. ........................................... 252

References ......................................................................................... 253

Chapter Two. Application of Poly(methylsilane) and Other Polymeric Ceramic Precursors to *in situ* Preparation of Metal Matrix Composites and Cermets

Introduction ....................................................................................... 262

Results and Discussion ...................................................................... 270

Poly(methylsilane) and Other Polymeric Ceramic Precursors Containing Silicon, Carbon, Nitrogen, or Boron as Binders for Ti, Al, Cu, Mo, W, V, and Zr Powders ...................................................... 274

Precursor to Near-Stoichiometric BN (PBA) as Binder for Ti, Al, Cu, Fe, Ni, and W Metal Powders ...................................................................................... 314

A TiN Precursor as a Binder for Ti and Si$_3$N$_4$ Powders and as a Precursor for Continuous TiN Thin Films on an Alumina Substrate ......................................................... 327

Conclusion ......................................................................................... 336

Appendix A ......................................................................................... 338

Appendix B ......................................................................................... 339

Experimental .................................................................................... 348

General Comments ............................................................................ 348

Preparation of Ti/PMS 9:1 Mol Ratio Green Body. (PC/5/17, 21, 24, 68) ................................................................................ 350
Preparation of Ti/PMS 9:1 Mol Ratio Green Body by 100°C Isostatic Pressing. (PC/6/5) ........................................351

Preparation of Ti/PCS 9:1 Mol Ratio Green Body. (PC/5/30) ........................................................................351

Preparation of Ti/PVS 26:1 Mol Ratio Green Body. (ML 13) ....................................................................352

Preparation of Ti/DBA 9:1 Mol Ratio Green Body. (ML 14) .................................................................352

Coreductive Coupling of 1.0 MeHSiCl₂ and 0.4 Me₂SiCl₂ and 2.5 Na and Subsequent Crosslinking With (C₅₂ZrH₂)ₙ. Synthesis of PMSII. (ML 1, 6) .................................................................353

Preparation of Ti/FMSII 19:1 Mol Ratio Green Body. (ML 21) .................................................................354

Preparation of Ti/PSZ 9:1 Mol Ratio Green Body. (SWK/1/23) .................................................................354

Preparation of Ti/PSZ 9:1 Mol Ratio Green Body and Its Isopressing at 100°C. (SWK/1/34) .........................355

Preparation of Ti/PSZ 9:1 Mol Ratio Green Body and Its Isopressing at 100°C. (SWK/1/42) .........................355

Preparation of Ti/PBA 9:1 Mol Ratio Green Body. (PC/7/40/A, C) ..........................................................356

Preparation of Al/PMS 9:1 Mol Ratio Green Body. (PC/5/31, 39) .............................................................356

Preparation of Al/PMS 9:1 Mol Ratio Green Body and Its Isopressing at 100°C. (PC/6/6) .........................357

Preparation of Al/PMS(with 0.5 wt% BHT) 9:1 Mol Ratio Green Body. (TS/2/60) .........................358
Preparation of Al/PMSII 20:1 Mol Ratio
Green Body. (ML 10) ................................................................. 358

Preparation of Al/PVS 28:1 Mol Ratio
Green Body. (ML 12) ................................................................. 359

Preparation of Al/PBA 9:1 Mol Ratio Green
Body. (PC/7/36/A, B, 39/A, 39/B, CKN/1/3/A) .................. 359

(PC/5/57) ................................................................................. 360

(PC/5/58/A) ................................................................................. 360

(ML 5) .......................................................................................... 361

(ML 18) .......................................................................................... 361

(ML 19) .......................................................................................... 362

(PC/7/43, CKN/1/5/A) ................................................................. 362

Preparation of Zr/PMS 9:1 Mol Ratio Green Body.
(PC/5/71) .......................................................................................... 363

Preparation of Zr/PCS 9:1 Mol Ratio Green Body.
(PC/6/4) .......................................................................................... 364

(SWK/1/22z) ................................................................................. 364

Preparation of Zr/PVS 18:1 Mol Ratio Green Body.
(ML 25) .......................................................................................... 365

(PC/5/72) ....................................................................................... 365
Preparation of V/PCS 9:1 Mol Ratio Green Body. (PC/5/74) ................................................................. 366

Preparation of V/PVS 18:1 Mol Ratio Green Body. (ML 26) ....................................................................... 366

Preparation of V/DBA 9:1 Mol Ratio Green Body. (ML 28) ....................................................................... 367

Preparation of V/PSZ 9:1 Mol Ratio Green Body. (SWK/1/22v) ................................................................. 367

Preparation of Mo/PMS 9:1 Mol Ratio Green Body. (PC/5/70) ................................................................. 368

Preparation of Mo/PCS 9:1 Mol Ratio Green Body. (SWK/1/1) ................................................................. 368

Preparation of Mo/PSZ 9:1 Mol Ratio Green Body. (SWK/1/20) ................................................................. 369

Preparation of W/PMS 9:1 Mol Ratio Green Body. (PC/5/63) ................................................................. 369

Preparation of W/PCS 9:1 Mol Ratio Green Body. (PC/5/65) ................................................................. 370

Preparation of W/PCS 97:3 Mol Ratio Green Body. (PC/5/69) ................................................................. 371

Preparation of W(<1μ)/PMS 9:1 Mol Ratio Green Body. (PC/7/67) ................................................................. 371

Preparation of W/PVS 19:1 Mol Ratio Green Body. (ML 4) ................................................................. 372

Preparation of W/PMSII 20:1 Mol Ratio Green Body. (ML 9) ................................................................. 372

Preparation of W/PSZ 9:1 Mol Ratio Green Body. (SWK/1/18) ................................................................. 373
Preparation of W/PBA 9:1 Mol Ratio Green Body. (PC/7/65, CKN/1/11/A) ............................................................. 373

Preparation of Fe/PBA 9:1 Mol Ratio Green Body. (PC/7/44, CKN/1/3/C) ............................................................. 374

Preparation of Ni/PBA 9:1 Mol Ratio Green Body. (PC/7/46, CKN/1/5/B) ............................................................. 374

Oxidation Resistance Study of Some MMCs. .................................................. 375

Corrosion Resistance Test for Al/PMS Containing Al₄C₃ Dispersoid. (PC/6/59) ............................................................. 376

Preparation of Si₃N₄-TiN Composite with (CH₃)₃SiNHTiCl₃ as a Binder. (PC/7/68, CKN/1/11/B) ................................................ 377

Preparation of Ti-TiN Composite With (CH₃)₃SiNHTiCl₃ as a Binder. (PC/7/48, 68; CKN/1/6/A) ................................................ 378

Preparation of a TiN Thin Film on an Alumina Substrate Using the (CH₃)₃SiNHTiCl₃ Precursor. (PC/8/51, 56) ................................................ 378

References ................................................................................. 380

Chapter Three. Application of Poly(methylsilane) and Nicalon® Polycarbosilane Precursor for Metal/Ceramic Powders in Preparation of Functionally Graded Materials

Introduction ............................................................................. 387

Results and Discussion ................................................................. 395

Conclusion ................................................................................ 412

Experimental ............................................................................ 413

General Comments .................................................................... 413

17
Chapter One

Synthesis, Characterization, Derivatization, and Application of

Poly(methylsilane) Ceramic Precursor
Section A

Introduction
Polyorganosilanes are a unique class of polymers from both a physical and a chemical standpoint. In the last decade great effort has been made to understand the chemistry, physics, and applications of polysilanes.\textsuperscript{1,2}

Historically, the first polysilanes were prepared by F. S. Kipping and coworkers,\textsuperscript{3} who found that the reaction of diphenyldichlorosilane with sodium resulted in a complex mixture of halogen-free products. This mixture contained crystalline cyclic species (\(\text{Ph}_2\text{Si}_n\)) where \(n = 4, 6, 8\) and polymeric species where \(n > 8\). The crystalline poly(diphenylsilanes) were soluble in most organic solvents while the polymeric ones were described as colorless, slightly gelatinous powders insoluble in most organic solvents. The polysilanes were believed to be a mixture of saturated and "unsaturated" (containing Si=Si double bond) silanes. Due to the lack of solubility of the first polysilanes, the field was not further explored for about 25 years.

In 1949 the field of polysilanes was revisited by Burkhard\textsuperscript{4} who reported the synthesis of (\(\text{Me}_2\text{Si}_n\)) where \(n = 55\) by ebulliometry in biphenyl. Due to its high crystallinity the poly(dimethylsilane) was infusible and insoluble in most hydrocarbon solvents. It is believed that this intractability and the very harsh experimental conditions used (the reaction was carried out in an autoclave at 200\(^\circ\)C and 220 psi) may have contributed to the neglect of the field for the next 20 years. In 1968 Kumada and Tamao\textsuperscript{5} synthesized a permethylpolysilane having 12 silicon units: \(\text{Me} (\text{SiMe}_2)_{12} \text{Me}\). Later Yajima and coworkers\textsuperscript{6,7} found that
(Me₂Si)n may be used as a precursor to β-SiC. They found that thermolysis of (Me₂Si)n affords a soluble polycarbosilane from a Kumada rearrangement⁸ which destroys the crystallinity and resulting intractability of the original polymer.

**Scheme A1** shows the Kumada rearrangement in the case of the gas phase thermolysis of hexamethylidisilane.⁸

\[
\Delta \\
(\text{CH}_3)_3\text{SiSi(\text{CH}_3)_3} \rightarrow 2 (\text{CH}_3)_3\text{Si}^* \\
(\text{CH}_3)_3\text{Si}^* + (\text{CH}_3)_3\text{SiSi(\text{CH}_3)_3} \rightarrow (\text{CH}_3)_3\text{SiH} + \cdot\text{CH}_2(\text{CH}_3)_2\text{SiSi(\text{CH}_3)_3} \\
\cdot\text{CH}_2(\text{CH}_3)_2\text{SiSi(\text{CH}_3)_3} \rightarrow (\text{CH}_3)_2\cdot\text{SiCH}_2\text{Si(\text{CH}_3)_3} \\
(\text{CH}_3)_2\cdot\text{SiCH}_2\text{Si(\text{CH}_3)_3} + (\text{CH}_3)_3\text{SiSi(\text{CH}_3)_3} \rightarrow \\
(\text{CH}_3)_2\text{HSiCH}_2\text{Si(\text{CH}_3)_3} + \cdot\text{CH}_2(\text{CH}_3)_2\text{SiSi(\text{CH}_3)_3}
\]

**Scheme A1**

In 1978 West and coworkers⁹ synthesized a soluble copolysilane by reductively coupling a mixture of Me₂SiCl₂ and PhMeSiCl₂. In the last and current decade, interest in polysilanes has blossomed as is depicted by a bar-graph based on Chemical Abstracts Service on-line data (Fig. A1).

Many interesting properties and uses have been found for polysilanes. As precursors to SiC,¹⁰ they were pioneered by Yajima, Seyferth, Worsfold, and West. Other uses include: ceramic reinforcing agents,⁹ liquid crystals,¹¹ oxygen-
Insensitive initiators for polymerization of vinyl monomers,\textsuperscript{12} non-linear optical materials,\textsuperscript{13} UV-resists for high resolution microlithography,\textsuperscript{14} imageable etch barriers,\textsuperscript{15} contrast enhancement layers,\textsuperscript{16} photoconductors,\textsuperscript{17} or, when doped, as semiconductors.\textsuperscript{18}

From an electronic standpoint, polysilanes resemble polyacetylenes rather then polyolefins.\textsuperscript{19} The UV absorption of alkyl-substituted polysilanes as well as the nature of their easily promoted Si-Si bonding $\sigma$ electrons and low energy delocalized antibonding $\sigma^*$ orbitals are diagnostic of this resemblance. It is believed that the UV absorption of these polymers is due to $\sigma_{\text{Si-Si}} - \sigma^*_{\text{Si-Si}}$ or $\sigma_{\text{Si-Si}} - \pi(3d_{\text{Si-Si}})$ excitations of the delocalized electrons in the main backbone.\textsuperscript{20}

There are a number of synthetic routes used for the preparation of polysilanes. Historically, the first and still the most common procedure is based on the reductive coupling of dichlorosilanes using an alkali metal as a reducing agent. The most commonly used reagent is a sodium dispersion in refluxing toluene\textsuperscript{3} (eq. A1). However, an ultrasonic activation at a much lower temperature also has been reported.\textsuperscript{21}

$$n \text{R}_2\text{SiCl}_2 + 2 n \text{Na} \rightarrow 2 n \text{NaCl} + (\text{R}_2\text{Si}) $$ \hspace{1cm} (A1)

Dow Corning adopted a redistribution reaction for the synthesis of polysilanes.\textsuperscript{22} This process involves the redistribution of methylchlorodisilanes to volatile methylchlorosilanes and a chlorine-containing polysilane using
tetraalkylammonium or phosphonium salts as catalysts. The resulting chloropolysilane then can be alkylated with Grignard or lithium reagents or reduced to yield a polymeric SiC ceramic precursor.

**Interest in Polysilanes**

![Graph showing the number of publications by year](image)

**Figure A1** Literature activity in the field of polysilanes.

Dehydrogenative coupling, pioneered by the research groups of Harrod

24
and Tilley,\textsuperscript{24} is another efficient way of joining silicon atoms into chains. This method uses primary (RSiH\textsubscript{3}) or secondary (R\textsuperscript{1}R\textsuperscript{2}SiH\textsubscript{2}) silanes as monomers and early transition metalloccenes such as Cp\textsubscript{2}TiMe\textsubscript{2} or (Cp\textsubscript{2}ZrH\textsubscript{2})\textsubscript{n} as catalysts (eq. A2). This dehydrogenative coupling polymerization may also be stereoselective when optically active catalysts are used.\textsuperscript{25}

\[ n \text{R}_2\text{SiH}_2 + M_{\text{complex}} \rightarrow \text{cyclo}-(\text{R}_2\text{Si})_n + \text{H}((\text{SiR}_2)_m\text{H} + (n + m) \text{H}_2 \downarrow \] (A2)

Among other, less generally applicable procedures for polysilane synthesis have been the following: 1) ring-opening polymerization of strained silane ring systems,\textsuperscript{26} although this is of limited usefulness; 2) electrochemical reductive coupling of chlorosilanes,\textsuperscript{27} which can give high product yields; 3) cocondensation of chlorinated and lithiated oligomers, which has been used to prepare micro-block copolysilanes (eq. A3);\textsuperscript{28}

\[ \text{Li(Ph}_2\text{Si)}_n\text{Li} + \text{Cl(Me}_2\text{Si)}_x\text{Cl} \rightarrow [(\text{Ph}_2\text{Si})_x(\text{Me}_2\text{Si})_y]_n \] (A3)

4) thermolytic extrusion of Hg(0) from (PhMeSiHg)\textsubscript{n} used to obtain (PhMeSi)\textsubscript{n};\textsuperscript{29}

5) the anionically initiated cleavage/polymerization of a variety of 2,3-disilylbicyclo[2.2.2]octa-5,7-diene derivatives (eq. A4).\textsuperscript{30}
Some branched and ladder polysilanes also have been synthesized for possible preceramic use (eq. A5). The ladder polysilanes give pyrolytic ceramic residue yields on the order of 65% where most of the silicon is retained.\textsuperscript{31}

\[
\text{Cl}_2\text{R}_2\text{SiSiRCl}_2 + \text{ClR}_2\text{SiSiR}_2\text{Cl} \xrightarrow{\text{Li, THF}} \text{R}_2\text{Si-Si-R}_2 + \text{R}_2\text{Si-Si-R}_2 + \text{other structures} \quad (A5)
\]

Another useful preceramic system was prepared at Union Carbide by Schilling and coworkers.\textsuperscript{32} This polysilane was prepared by sodium condensation of CH\textsubscript{2}=CHSiMeCl\textsubscript{2}, Me\textsubscript{3}SiCl, and either MeSiHCl\textsubscript{2} or Me\textsubscript{2}SiCl\textsubscript{2}. This polymer proved to be an effective precursor to SiC.

The synthesis of poly(methylsilane), (CH\textsubscript{3}SiH)\textsubscript{n}, which has Si:C ratio of 1, as a precursor to SiC has previously been studied by several groups. Synthesis of poly(methylsilane) by Wurtz reductive coupling of MeSiHCl\textsubscript{2} with sodium was explored by Brown-Wensley and Sinclair\textsuperscript{33} and at M.I.T. by Wood.\textsuperscript{36} The dehydrogenative coupling of MeSiH\textsubscript{3} was studied by Harrod and coworkers,\textsuperscript{34} and Tanaka and coworkers.\textsuperscript{35} The current work is an extension of a study initiated by Wood.\textsuperscript{36}

This chapter considers the reductive coupling of MeSiHCl\textsubscript{2} with sodium using heat and ultrasonic activation. Particular attention is given to the sonochemical reductive coupling since it gives a high yield of a high purity
product. Sodium metal and methyldichlorosilane in a cosolvent mixture of hexane/THF or toluene/THF reacted to yield an oligo or poly(methylsilane). The polymerization of methyldichlorosilane with sodium is a two stage process. The first stage takes 10 - 20 hours of ultrasonication and yields an oily oligo(methylsilane) (OMS). The second stage takes 20 - 60 hours of ultrasonication and yields a high molecular weight poly(methylsilane) (PMS). When care is taken to make sure that the solvents and the metal are oxygen free, the oligo(methylsilane) is a clear oil of monomodal molecular weight distribution (\(M_w = 1540\) and \(PDI = M_w/M_n = 1.7\) (relative to polystyrene standard) by GPC). Poly(methylsilane) is an orange solid with a trimodal molecular weight distribution of \(~10,000; ~1,000;\) and \(~500\) (relative to polystyrene standard).

There is evidence that initially the reaction follows a radical path rather than an anionic one. However, later in the reaction (second stage) probably silyl anion and NaH are generated which act as a dehydrogenative coupling catalyst affording higher molecular weights polymers. The structure of the oligo(methylsilane) seems to be mostly linear with some degree of branching. Although ultrasonication and heating are somewhat different in terms of the activation mode, the oligo(methylsilane) structures obtained by both processes are nearly identical.

Poly(methylsilane) is particularly interesting as a ceramic precursor since its carbon to silicon ratio is 1.0, the same as that found in silicon carbide (SiC).
Indeed, pyrolysis of poly(methylsilane) affords nearly stoichiometric SiC in high yield (85%).

Oligo(methylsilane) also is an attractive starting point for very versatile derivatization chemistry. Photochlorination using chlorinated hydrocarbons as a chlorine source as well as the derivatization of the resulting chlorinated polysilane were studied.
Section B

Synthesis of Oligo(methylsilane)
In the last decade great effort has been made to understand the polymerization reaction which yields polysilanes.\textsuperscript{1,2} The main effort has been directed towards understanding the Wurtz reductive coupling of arylalkyldichlorosilanes.\textsuperscript{37} Various factors such as solvent, temperature, rate and sequence of reagent addition, size and shape of alkali metal particles, alkali metal/chlorosilane ratio, as well as the nature of the monomer (i.e., functional groups on silicon) were found to influence molecular weight and its distribution, conversion yield, and the structure of the polysilanes.\textsuperscript{38}

Many research groups have extensively explored variables which govern the polysilane formation. Recently Oka, West and coworkers\textsuperscript{39} closely examined the molecular weight control conditions for the Wurtz reductive coupling synthesis of polysilanes. In particular the synthesis of (PhMeSi)\textsubscript{n} from PhMeSiCl\textsubscript{2} and sodium was considered. They have concluded the following: 1) the yield and molecular weight of polymers depend on the rate of the addition of chlorosilane (i.e., fast addition affords low yield of high molecular weight polymer); 2) the use of a polar solvent helps to increase the yield; 3) the yield increases with temperature, but the molecular weight decreases with temperature; 4) dilution reduces the molecular weight and yield. Matyjaszewski and coworkers also observed that the yield, degree of polymerization, and polydispersity depend on temperature and power of ultrasonication.\textsuperscript{40} They noticed that by using ultrasonic activation high molecular weights and low polydispersed polysilanes are achieved.
Worsfold observed that molecular weight changes with the rate of stirring of the reaction mixture.\textsuperscript{41a} Usually, low molecular weight polysilanes were obtained when high surface area sodium was used (high speed stirring). Gauthier and Worsfold found that the rate of formation of polysilanes increases with the amount of crown ether.\textsuperscript{41b} Miller and coworkers concluded that diglymes and crown ethers increase the yield of the final polysilanes.\textsuperscript{37} Zeigler and coworkers\textsuperscript{38} showed that the cosolvent such as diglyme or THF has a bulk effect and that it does not provide selective stabilization of reactive intermediates. It was concluded by many investigators that no single procedure for Wurtz-type polymerization of chlorosilanes seems to be optimal for all structural monomer types. The appropriate procedure to optimize yields and polymer properties still must be determined empirically.

This section is devoted to the synthesis of oligo(methylsilane). Previously Wood prepared oligo(methylsilane) by using reflux conditions and Na metal dispersion. He found that 1) the optimum conditions for synthesis of oligo(methylsilane) (OMS) required use of a 7/1 v/v hexane/THF solvent mixture; 2) prolonged reflux ( \( > 16 \) h) afforded highly crosslinked products; 3) use of a stoichiometric ratio of Si-Cl to Na yielded chlorine-containing polysilanes; therefore, at least 2.5 molar equivalents of Na were employed; 4) the value of \((x + z)\) varied from 0.76 to 0.85 and was directly proportional to the rate of chlorosilane addition, where \((x + z)\) is derived from the oligo(methylsilane) compositional unit.
of \([(\text{MeSiH})_x(\text{MeSi})_y(\text{MeSiH}_2)_z]_n\) where \(x + y + z = 1\); 5) addition of THF as a cosolvent increased the conversion yield; 6) use of THF alone yielded high molecular weight poly(methylsilane).\(^{36}\) In the current study a number of different conditions for polymerizing MeSiHCl\(_2\) with Na were examined. The general procedure involved ultrasonic activation of MeSiHCl\(_2\) and sodium in a cosolvent mixture of 7/1 v/v hexane/THF where the mode of addition of chlorosilane to sodium was used.

The entire reductive coupling of MeSiHCl\(_2\) with sodium is a process which can be divided into two stages. The first stage consists of 10 - 20 hours of ultrasonication. During this stage an oily oligo(methylsilane) is formed. In the second stage, the ultrasonication continues for over 20 hours (preferably 30 - 40 hours), and a solid, high molecular weight poly(methylsilane) is afforded. The latter will be discussed in greater detail in the section on high molecular weight poly(methylsilane) (Section G).

On the basis of prior\(^{36}\) and present NMR studies, the oligomer has a general composition: \([(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y(\text{CH}_3\text{SiH}_2)_z]_n\) where \(x/z = 4\), \(x + y + z = 1\) and \(0.94 \geq (x + z) \geq 0.75\), depending on various factors such as concentration, solvents used, and time of the reaction. The silicon atoms in the MeSi units are bonded to three other silicon atoms, hence are branching sites. The MeSiH\(_2\) units are end groups. At high concentrations (\(\geq 12.4\) M) of MeSiHCl\(_2\) the \((x + y)\) value approaches 0.94, and in dilute systems (\(\leq 4.1\) M) \((x + z)\) approaches 0.75. In all
cases, the molecular weight is approximately the same unless the time of the reaction is extended for more than 20 hours, in which case a high degree of branching is observed and values of \((x + z) = 0.4\) are obtained. In addition to the main products, in both stages about 10% of the product is entrapped within a matrix of large yellow NaCl crystals which adhere to the surface of sodium particles (Fig. B1). This product is a high molecular weight poly(methylsilane) with \((x + z)\) values in the order of 0.4 - 0.6. Both of the high molecular weight poly(methylsilane) cases will be addressed *vide infra* (Section G).

It was observed that the rate of addition of chlorosilane affected the yield of the final product. The reaction yields when one molar equivalent of MeSiHCl₂ and 2.5 molar equivalents of sodium are used were between 65 and 91% and are dependent on the rate of addition of the chlorosilane. With the slow addition of chlorosilane at 20°C and ultrasonication activation, yields of up to 91% conversion of monomer to polymer were achieved. When all the reactants are present together in the reaction vessel prior to ultrasonication, oligosilane in yields between 65 and 80% was obtained. The stepwise addition of the chlorosilane by first adding one half of the entire amount and after several hours introducing the rest of the monomer did not affect the composition of the resulting oligomer; however, it slightly lowered its yield to about 64%.

There also is a strong dependence of the yield of the oligomer on the reaction activation mode. It appears that, in general, ultrasonic activation at 28 -
47°C affords higher conversion yields (65 - 80%) of oligomer than reflux conditions (~ 70°C) with no ultrasonication (55 - 65%). Usually ultrasonication results in close to 80% conversion when it is carried out 28°C. In the reactions where the ultrasonication bath is at constant 28°C the actual temperature of the reaction mixture fluctuates between 34 and 38°C.

The effect of varying the amount of sodium used in the reaction on the molecular weight of the oligo(methylsilane) also was explored. The reaction involving the use of 0.25 molar equivalent of sodium to one of MeSiHCl₂ afforded a 15% yield of a clear oil (but quantitative relative to Na consumed). Based on ¹H NMR and IR spectroscopy obtained, the oligomer oil had unchanged composition \((x + z) = 0.86\) as compared to the one obtained with 2.5 molar equivalent of Na per molar equivalent of MeSiHCl₂ and also contained SiH₂ functionalities. Increasing the amount of sodium to 12.5 molar equivalents per molar equivalent of MeSiHCl₂ yielded in 81% an oil with unchanged structure \((x + z) = 0.81\) based on ¹H NMR spectrum as compared to oligomer obtained with 2.5 molar equivalent of Na per molar equivalent of MeSiHCl₂.

The sodium particle size in the reductive coupling of MeSiHCl₂ with sodium also was explored. A reaction with a minimum surface area (i.e., one solid, carefully cleaned piece of sodium) of sodium afforded slightly lower yields (62%), probably because most of the sodium surface was unexposed. The same reaction conditions involving sodium pieces (~ 10 mm in diameter) gave a higher
yield (75%) of clear oil. The overall composition of the clear OMS oil was comparable in both cases, within the experimental error based on \textsuperscript{1}H NMR, with $(x + z)$ values being 0.86 and 0.91, respectively.

\textbf{Figure B1} NaCl crystals occluding a sodium particle from ultrasound activated reductive coupling of MeSiHCl\textsubscript{2}.
The ethereal cosolvent is an important variable in the ultrasonically activated reductive coupling of methyldichlorosilane with sodium. Reaction in pure toluene using ultrasonication for 42.5 hours did not yield any oligomer nor any NaCl. However, the same reaction in hexane for 23 hours afforded a trace of white oil. The present study found that the addition of a cosolvent such as THF increases the yield of oligomer, confirming the observation of Wood.\textsuperscript{36} For example, using a 15/1 volume ratio of hexane/THF resulted in a 30\% yield of white oil with (x + z) = 0.79, while use of a 7/1 volume ratio under the same reaction conditions gave a 65 - 80\% yield of clear oil with (x + z) = 0.85. In addition, when pure THF was used, a higher molecular weight, soluble, pink-white solid polymer was formed in about 40\% yield with (x + z) = 0.45 after reflux for 48 hours (0.63 after ultrasonication), along with a large quantity of insoluble, white solid. Poly(THF) was a byproduct which was especially abundant when ultrasonication was used as a mode of initiation in pure THF medium.

Reactions carried out without solvent also were explored in an attempt to entrap the high molecular weight polysilane in NaCl crystals. It was observed that pure chlorosilane does not react with sodium in the absence of a solvent; however, when 4 wt\% of THF or 2 wt\% of ethyl acetate were added, the reaction afforded a 43\% yield of oligo(methylsilane) in the case of THF with (x + z) = 0.86 and a 37\% yield of oligo(methylsilane) with (x + z) = 0.76 in the case of ethyl acetate. Also, in the case of ethyl acetate, the oligo(methylsilane) product contained some
residual Si-Cl bonds according to the IR spectrum of the product (Fig. B2). The amount of high molecular weight poly(methylsilane) occluded in the NaCl crystals was small (2.4 - 6.2 wt%), regardless of the amount of THF present.
Figure B2 IR spectrum of solvent free reductive coupling of MeSiHCl$_2$ with a trace of a) THF; b) ethyl acetate.
Oligo(methylsilane) is a very air-sensitive substance. Upon exposure to air it becomes an insoluble solid in a matter of hours. Conflagration occurs when it comes in contact with combustible materials such as paper or cloth in air. In order to prevent the facile air oxidation, a procedure developed by Bryson involving the use of antioxidants was employed.\textsuperscript{42} Bryson found that 2,6-di-tert-butyl-4-methylphenol (BHT) or its derivatives effectively halt oxidation of very air-sensitive polysilanes such as the Schilling polymer.\textsuperscript{32} We found that about 5 wt\% (\sim 1 \text{ mol\%}) of BHT blended with the oligo(methylsilane) prevents its air oxidation for weeks (Fig. B3). After about two weeks of air exposure the oil containing BHT is covered with a solid film while the bulk still remains oily.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{graph.png}
\caption{A graph depicting an effect of BHT on oligo(methylsilane) exposed to air.}
\end{figure}
In conclusion, using ultrasonic activation, a high conversion (91%) of monomer to oligomer can be obtained if the entire synthesis is carried out at about 20°C with a slow addition of MeSiHCl₂. For the maximum \((x + z) = 0.94\) value, a concentrated \((\geq 12.4 \text{ M solution of MeSiHCl}_2)\) reaction mixture of the chlorosilane in 7/1 v/v hexane/THF should be used. However, the recommended, most convenient preparation of the oligo(methylsilane) involves having all the reactants in 7/1 v/v hexane/THF present in the reaction vessel prior to ultrasonication and using Na pieces about 10 mm in diameter. Subsequent ultrasonicatcon for 10 - 20 hours in that case gives the oligomer clear oil in about 65 - 80% yield with \((x + z)\) between 0.85 and 0.92.
Section C

The Composition of Oligo(methyilsilane)
Since polymers almost never crystallize to give X-ray quality single crystals except for some regular dendrimers\textsuperscript{43a} and a large variety of biopolymers,\textsuperscript{43b} it is necessary to utilize other means of structural elucidation. To extract the maximum information about the polymer structure spectroscopy is employed. The first determination of the composition of the oligo(methylsilane) (OMS) was reported in 1984 by Wood.\textsuperscript{36} Based on \(^1\text{H}\) NMR studies, two types of units were recognized as being present: the difunctional MeSiH unit and MeSi unit, in which the silicon atom is bonded to three other silicon atoms. The latter unit thus is a branching site. The NMR spectrum did not give any information concerning the connectivity of these units, although the mole fraction of each could be determined by integration of the \(^1\text{H}\) NMR spectrum. Thus Wood wrote the composition of the oligo(methylsilane) as \([\text{MeSiH}]_x(\text{MeSi})_y\] \(_n\) where \(x + y = 1\). Based on molecular weight measurements by freezing point depression Wood proposed that \(n = 11\) to \(13\).\textsuperscript{36}

The present study gave slightly different results. The structural characterization of the polysilane is not simple because each silicon is a stereocenter and the polymer is a mixture of a large number of stereoisomers strung in a chain. Consequently, \(^1\text{H}\), \(^{13}\text{C}\), and \(^{29}\text{Si}\) NMR spectra give broad signals with little information on fine details of the structure of the oligomer.

The 300 MHz \(^1\text{H}\) NMR spectrum of the polysilane shows two broad resonances. One between 0 - 1 ppm \((W_{1/2} = 90\ \text{Hz})\), corresponding to the protons
of the methyl group attached to silicon (MeSi), and another between 3.8 - 4.5 ppm 
($W_{1/2} = 75$ Hz), corresponding to the protons attached directly to the silicon atom 
(SiH$_x$) (Fig. C1). Integration of these signals in the $^1$H NMR spectrum of the 
oligo(methylsilane) varies with the reaction conditions used to prepare the 
oligomer between SiCH$_3$/SiH$_x$ = 3.8/1 for branched and SiCH$_3$/SiH$_x$ = 3.2/1 for 
oligomers with only a small amount of branching, while in theory SiCH$_3$/SiH$_x$ 
should be 3.0/1. The resonance between 3.8 - 4.5 ppm shows a small upfield 
shoulder at 3.9 ppm which becomes better resolved using a 500 MHz instrument 
(Fig. C3). Based on model compounds,$^{44}$ CH$_3$SiH$_2$SiH$_2$CH$_3$ and 
(CH$_3$)$_2$SiHSiH(CH$_3$)$_2$, resonances for SiH$_2$ and SiH are expected to be found at 
3.58 ppm and 3.72 ppm, respectively. This suggests that the shoulder is a part of 
an SiH$_2$ signal. This observation was confirmed by $^{29}$Si DEPT NMR and IR 
spectra (vide infra). When deconvolution techniques were applied to the SiH$_x$ 
signal of the $^1$H NMR spectrum, the integral ratio of SiH protons to SiH$_2$ protons 
was found to be 4/1 which indicates a ratio of 8 SiH groups to 1 SiH$_2$ group (Fig. 
C2).

The choice of the NMR solvent also is an important issue. It has been 
observed that polar solvents such as CD$_2$Cl$_2$ improve the separation of SiH and 
SiH$_2$ signals when compared with C$_6$D$_6$ (compare Fig. C1 and Fig. C3).

With these new observations, the structural unit composition of the OMS
becomes: \[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y(\text{CH}_3\text{SiH}_2)_z\]_n where x/z = 4; x + y + z = 1; and 0.94 ≥ (x + z) ≥ 0.75, depending on the reaction conditions (for the recommended synthesis 0.85 ≥ (x + z) ≥ 0.92). The variable z denotes the mole fraction of end groups of the oligomer, x indicates the mole fraction of difunctional main chain units and y represents the mole fraction of trifunctional branched units. During acquisition of the NMR spectrum care must be taken in choosing a proper relaxation time for SiH_x and SiCH_3. Since silicon has a long relaxation time, protons attached to it will require longer delays between pulses than will the SiCH_3 protons. A spin-lattice relaxation experiment of OMS in C_6D_6 at ambient temperature showed T1 to be 3.5, 4.5 and 1.5 seconds for SiH, SiH_2 and SiCH_3, respectively. The higher the molecular weight becomes, the shorter the relaxation time since there are more degrees of freedom available in the system.

The $^{13}$C NMR spectrum shows a broad resonance at -12.3 to -7.1 ppm with $W_{1/2} = 230$ Hz corresponding to SiCH_3 functionalities.

The $^{29}$Si NMR spectroscopy proved to be a useful technique for obtaining detailed information on the conformation (i.e., tacticity) and structure (i.e., end groups) of polysilane chains. The $^{29}$Si NMR technique is particularly applicable considering its recent advances. There are, however, several barriers which have to be surmounted when using this technique. In general, $^{29}$Si NMR measurements are difficult because: 1) the $^{29}$Si isotope natural abundance is low (4.67%); 2) the
magnetogyric ratio is small and negative ($\gamma = -0.55477$), meaning that the energy difference between spin states as well as the Boltzmann population difference are small; 3) the Nuclear Overhauser Effect is negative and leads to a reduced, null, or negative $^{29}\text{Si}$ signal; 4) the spin-lattice relaxation time is long, so the intervals at which Fourier Transform pulses can repeat lengthens, leading to long acquisition times. Therefore, special techniques are required to enhance the $^{29}\text{Si}$ signal. For example if a silicon atom is bonded to a hydrogen, possessing a large Boltzmann population difference, nuclear spin polarization transfer from $^{1}\text{H}$ to $^{29}\text{Si}$ will increase the $^{29}\text{Si}$ signal.$^{47}$
Figure C1 $^1$H NMR spectrum of oligo(methylsilane) in $C_6D_6$ using 300 MHz instrument. The residual signals downfield from SiMe are due to residual hexane from the Wurtz coupling.
Figure C2: $^1$H NMR spectrum deconvoluted for SiH$_x$ signal using 500 MHz instrument.
Figure C3 $^1$H NMR spectrum of oligo(methylsilane) in CD$_2$Cl$_2$ using 500 MHz instrument.
Another very important feature is that protons have short relaxation times which governs the pulse repetition so the acquisition may be done more rapidly. There are two multipulse NMR polarization transfer techniques commonly used: INEPT (Insensitive Nuclei Enhanced by Polarization Transfer) and DEPT (Distortionless Enhancement by Polarization Transfer).\textsuperscript{46, 47} In this thesis, the DEPT sequence was used to analyze the polysilane. Coupling constants of 140 Hz for Si-H; 60 Hz or lower for SiCH\textsubscript{x} and different pulse angles [MULT = 0.5 (all peaks up), 1.0 (only odd number of protons coupled with silicon contribute to the signal), and 1.5 (odd number of protons show a positive signal and an even one a negative)] were employed. Spectra at MULT = 0.5 (Fig. C4c) showed two sets of broad resonances with two sharp signals each at -61.5 and -64 ppm (\(W_{1/2} = 400\) Hz) corresponding to SiH\textsubscript{2}; -68.2 ppm and -71.5 ppm (\(W_{1/2} = 700\) Hz), probably corresponding to SiH. In the spectrum at MULT = 1.0 (Fig. C4b) these two sharp peaks of strong intensity became of medium intensity; the intensity of the other two broad resonances remained unchanged. The spectrum at MULT = 1.5 (Fig. C4a) showed two negative resonances at -62 and -64 ppm (SiH\textsubscript{2}), and the rest of the broad resonances remained unchanged.

Harrod and coworkers reported similar chemical shifts for SiH\textsubscript{2} (-57 and -60 ppm) in their DEPT sequence \textsuperscript{29}Si NMR spectra of poly(n-hexylsilane). They also observed that the relative position of the silicon resonances of SiH and SiH\textsubscript{2}
are reversed relative to the position of the proton resonances.\textsuperscript{48} In addition, these chemical shifts agree with the $\delta_{\text{Si}}$ -57 ppm reported by Bianconi and Weidman\textsuperscript{49} for a soluble poly(n-hexylsilylene), (RSi)$_n$, network having ternary Si units. This agreement exists probably because the electronegativitiey of Si and H are close (i.e. 1.90 and 2.20, respectively) compared with the C: 2.55 on Pauling's scale.

The FT-IR spectrum of oligo(methylsilane) (Fig. C5) showed the usual C-H absorptions, ($v_{\text{C-H}}$) at 2957(antisym.), 2894(sym.), 2796 cm$^{-1}$ and a large, broad Si-H absorption ($v_{\text{Si-H}}$) centered at 2107 cm$^{-1}$. The Si-H absorption is rather broad since it probably consists of at least two overlapping peaks due to SiH and SiH$_2$.\textsuperscript{50} There are strong and sharp absorptions at 1410 and 1248 cm$^{-1}$ assignable to C-H antisymmetric and symmetric bends ($\delta_{\text{Si-Me}}$) of the methyl groups, respectively.\textsuperscript{51b} A small but sharp band at 931 cm$^{-1}$ corresponds to the $\gamma$SiH$_2$ scissoring mode. The presence of this band provides further evidence for the presence of the -MeSiH$_2$ group. A sharp, strong and broad absorption at 865 cm$^{-1}$ is due to the $\rho$CH$_3$ rocking mode.\textsuperscript{51a} Finally, there are absorptions due to the stretch ($v_{\text{Si-C}}$) of the methyl group at 770(antisym.), 688(sym.), and 650 cm$^{-1}$.\textsuperscript{51b, c} Noteworthy is the absence of residual Si-Cl in the OMS as evidenced by the absence of bands in the 498 - 525 cm$^{-1}$ region;\textsuperscript{52} this absorption, however, is well visible in the IR spectrum of the chlorinated polymers (\textit{vide infra}). This spectrum of OMS is identical to one reported by Mu and Harrod.\textsuperscript{34a}
Figure C4 $^{29}$Si NMR DEPT sequence spectrum of oligo(methylsilane), MULT = a) 1.5; b) 1.0; c) 0.5.
Figure C5 FT-IR spectrum of oligo(methylsilane) on NaCl disk (compare with ref. 34a).
The mass spectrum of the OMS (Fig. C6) was measured in the electron impact (EI) ionization mode at 60°C and 70eV. It showed that the parent ion is present in very small abundance. Such an ion would have a higher intensity if the species was cyclic or cage-like. In the case of a cyclic polysilane the primary event probably is cleavage of an Si-Si bond of the ring, a process which does not result in a significant mass loss and yields the parent ion in high abundance. In the linear case, the primary event also is cleavage of the Si-Si bond which leads to multiple fragmentation and a low abundance of the parent ion. In addition, the mass spectra showed a peculiar pattern of clusters of intensity every 15 g/mol (Fig. C6). Such clusters may correspond to the loss of methyl groups from the silicon backbone.

Plasma Desorption / Time Of Flight (PD/TOF) is a relatively mild mass spectrometric technique which is used in determining the molecular weight of biopolymers such as proteins. The PD/TOF at acceleration voltage of 13 kV experiment showed two molecular ion peaks commencing at 395 and 667 (Fig. C7), possibly indicating two different molecular weights which normally are not resolvable by GPC of OMS.

Gel permeation chromatography (GPC) in toluene using Ultrastyragel™ columns (Fig. C8) of OMS showed a monomodal molecular weight distribution with $M_w = 1540$ and $PDI = M_w/M_n = 1.7$ (relative to the monodispersed
polystyrene standards). The Polydispersity Index (PDI) is approaching a value of 2, typical of the most probable Flory-Huggins distribution which is characteristic of the free radical polymerization mechanism. Keeping in mind that the covalent radius ratio\textsuperscript{53} of carbon to silicon is C/Si = 0.6, the approximate average molecular weights for the all silicon backbone obtained using polystyrene standards are $M_n = 550$ and $M_w = 924$. The value of $M_n = 520$ was measured by Wood\textsuperscript{36} using cryoscopy in benzene and corresponds to the number average degree polymerization of $P_n = 13$. The Signar method,\textsuperscript{54} which is based on colligative properties (only $M_n$ can be obtained), also was used to determine the molecular weight of OMS. The Signar method involves the principle of isothermal distillation and it is applicable to measure molecular weights of about 25,000. By the Signar method a molecular weight of OMS was 957 g/mol. The Signar method is cumbersome and not a very popular one; however it is rather accurate within 1-2%.
Figure C6 Mass spectrum of oligo(methylsilane) by electron impact.
Figure C7 Mass spectrum of oligo(methylsilane) by PD/TOF.
Figure C8 GPC trace of oligo(methylsilane); $M_w = 1540$; PDI = 1.7, (relative to polystyrene).

Based on NMR, IR, and mass spectroscopy measurements, the structure of oligo(methylsilane) is mostly linear with some degree of branching. The description of OMS in terms of compositional units is $([(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y(\text{CH}_3\text{SiH}_2)_z]_n$, where $x/z = 4$; $x + y + z = 1$; and $0.94 \geq (x + z)$ $\geq 0.75$, depending on the reaction conditions. By $^1$H NMR, it was observed that there is an 8:1 ratio of SiH/SiH$_2$ units. If the assumption is made that two end groups are required per molecule, then the average degree of polymerization would be about 16 units. If account is taken for some branches, the degree of polymerization should be about 16 - 20 units. This prediction is in agreement with the molecular weight measurements within experimental error.
Section D

Proposed Mechanism of Oligo(methylsilane) Synthesis. The Effect of Chain Transfer Agents on Growth of Oligo(methylsilane)
Polysilanes such as poly-dialkylsilane, -diarylsilane, and -alkylarylsilane typically are prepared by Wurtz reductive coupling with a molten alkali metal, usually sodium (m.p. 97.81°C), in boiling toluene (b.p. 110°C) or xylene (b.p. 144°C). 1,2,3 The use of solvents with such high boiling points leads to lower yields and contamination with siloxanes. 55 The products have polymodal molecular weight distributions and contain cyclic oligomers (Si₅, Si₆), low molecular weight polymers (Mₙ ~ 10³), and high molecular weight polymers (Mₙ ~ 10⁵). The origin of the bimodal distribution may lie in a diffusion phenomenon 38a or may be due to various reaction intermediates occurring simultaneously. A number of reactive intermediates such as silyl radicals, radical anions, silylenes, disilenes, strained cyclosilanes, or masked disilenes are suspected to participate in polysilane formation. 40 Because formation of the various intermediates will have different activation energies, temperature changes may favor or suppress a particular intermediate.

Reductive coupling at ambient temperatures also may be accomplished by using ultrasonic activation. Sonochemistry is based on the principle of implosive collapse of cavities with high pressures and temperatures existing locally for short periods of time. The afforded products possess monomodal polymer molecular weight distributions, are high molecular weight polymers, and have a value of polydispersities approaching one. 21 Kim and Matyjaszewski 56 have reported that only aryl-substituted chlorosilanes may successfully be polymerized in aromatic
hydrocarbons using ultrasonic activation at ambient temperature. Scheme D1 depicts a proposed mechanism.

\[
\text{---Si-Cl} \quad + \quad \text{Na} \quad \rightarrow \quad \text{---Si-Cl}^- \quad + \quad \text{Na}^+ \quad \rightarrow \quad \text{---Si}^- \quad + \quad \text{NaCl}^{-}_{\text{aq}}
\]

\[
\text{---Si}^- \quad + \quad \text{Na} \quad \rightarrow \quad \text{---Si}^- \quad + \quad \text{Na}^+ \quad \rightarrow \quad \text{---Si-Si}^{-}_{\text{aq}} \quad + \quad \text{NaCl}^{-}_{\text{aq}}
\]

**Scheme D1**

In Scheme D1 the polymeric silyl radical can be transformed easily to a silyl anion. The resulting polysilyl anion will react in an $S_N2$ fashion with a stronger electrophile, the $R_2SiCl_2$ monomer (two electron-withdrawing groups) rather than with a weaker electrophile, a mono chloro-terminated chain (one electron withdrawing group). The reaction product obtained in such fashion has a Polydispersity Index approaching one (1.2) typical of an anionic "horse race polymerization".$^{57}$

Kim and Matyjaszewski believe that only an aryl-substituted chloro-terminated chain end can participate in a two-electron transfer process with sodium.$^{58}$ However, the silyl anion itself can react with a dialkyl- or diaryl-dichlorosilane. The dialkyldichlorosilane is suspected to react with sodium exclusively by a free radical path; therefore, it does not homopolymerize under the conditions mentioned.$^{56}$ The reductive coupling polymerization must start with a slow electron-transfer reaction between sodium and a $R_2SiCl_2$ monomer (rate determining step) and is followed by much faster reactions involving a polymeric
species. Otherwise, no high polymer could be found if an excess of sodium was used. Ultrasonic activation accelerates the electron transfer process. It increases the sodium surface area and creates a fine dispersion of sodium particles and lowers the barrier to electron transfer as a result of the ultra-clean sodium surface as well as the heat and pressure generated locally.

Zeigler proposed a radical type path for the reductive coupling polymerization of dichlorosilanes with sodium.\textsuperscript{38b} He found that phenylmethyl- and 4-dimethylaminophenylmethyl polysilanes were hydrogen terminated (Si-H) suggesting some kind of a chain transfer process which also contributed to limit their molecular weights.

It appears that the reductive coupling of CH\textsubscript{3}SiHCl\textsubscript{2} with sodium using ultrasonic activation takes place in two stages. The first stage (after 10-20 hours of reaction) results in an oily oligomeric product which contains SiH\textsubscript{2} functionalities. The second stage (above 20 hours of reaction) results in the production of a high molecular weight polymeric product. The second stage is believed to involve a silyl anion intermediate and will be discussed in detail in the section on the high molecular weight poly(methylsilane) (Section G). There is some evidence that the first stage of reductive coupling of MeSiHCl\textsubscript{2} with sodium proceeds by a free radical path. The oligomer does not appear to have any anionic living chain ends as is expected in most anionic polymerizations. For example, after the oligomer was isolated, addition of PhMe\textsubscript{2}SiCl did not result in
incorporation of PhMe₂Si groups into the structure of the oligomer.

Recently Sartori and coworkers⁵⁹,⁶⁰ have explored the direct synthesis of polycarbosilanes by co-reductively coupling chlorosilanes and brominated hydrocarbons with sodium (eq. D1).

\[ n \text{Ph}_2\text{SiCl}_2 + n \text{CH}_2\text{Br}_2 + 4n \text{Na}^- (\text{Ph}_2\text{Si}^-\text{CH}_2^-)_n + 2n \text{NaCl} + 2n \text{NaBr} \]  \hspace{1cm} (D1)

Sartori’s group thus has introduced a short cut in the pyrolysis process of obtaining SiC ceramics from R₂SiCl₂ starting materials by intercalating a carbon atom between two silicon atoms and hence arriving at a pyrolysis intermediate obtainable normally in the case of polysilanes through a Kumada rearrangement.⁸

In the current study it was of interest to investigate the effect of brominated hydrocarbons as transfer agents and as a means of possibly increasing the molecular weight of oligo(methylsilane) in the first stage of the reaction. In this respect a brominated hydrocarbon chain transfer agent possibly would prevent the radical driven isomerization of the oligo(methylsilane) which results in chain terminating SiH₂ formation. The effect of chain transfer agents also was explored in order to elucidate the polymerization mechanism of MeSiHCl₂ and sodium. The brominated hydrocarbons were used to first "cap" the growing chain and again reactivate it for further polymerization. It was found that with the addition of a chain transfer agent such as CH₂Br₂ the molecular weight of the oligomer increased. For example, use of MeSiHCl₂ and CH₂Br₂ 1/1 and 2/1 molar ratio
yielded a higher molecular weight copolymer compared with the base oligomer as depicted by the GPC trace (Fig. D1).
Figure D1 GPC trace of oligo(methysilane): a) without a transfer agent, b) copolymer made with 2/1 molar ratio of MeSiHCl₂/CH₂Br₂, c) 1/1 molar ratio of MeSiHCl₂/CH₂Br₂ with Na in refluxing octane (relative to polystyrene).
The reaction involving CH$_2$Br$_2$ and MeSiHCl$_2$ in 1/1 to 3/1 molar ratio of MeSiHCl$_2$/CH$_2$Br$_2$ with sodium in refluxing octane afforded a product containing Si-Si linkages as well as Si-(CH$_2$)$_n$-Si and -(SiCH$_2$Si)$_n$- linkages as shown by the $^1$H NMR spectra (Fig. D2). The Si-(CH$_2$)$_n$-Si $^1$H NMR resonances were downfield (1.5 and 1.0 ppm) from the SiMe signal (0.5 ppm) and the -(SiCH$_2$Si)$_n$- resonance appeared as a shoulder upfield (-0.2 ppm) from the SiMe signal. This assignment is in agreement with $^1$H NMR spectra of model compounds such as Me$_3$SiCH$_2$SiMe$_3$ whose proton chemical shift due to SiCH$_2$Si is at -0.3 ppm.\textsuperscript{61} The $^1$H NMR spectrum of the other model compound, Me$_3$Si(CH$_2$)$_3$SiMe$_3$ shows proton chemical shifts due to SiCH$_2$- at 0.8 ppm and -CH$_2$CH$_2$CH$_2$- at 1.8 ppm.\textsuperscript{62} Judging from the $^1$H NMR spectrum (Fig. D2), the formation of Si-(CH$_2$)$_n$-Si linkages is more facile in this reductive coupling than the insertion of a methylene group between silicon atoms -(SiCH$_2$Si)$_n$-. The ultrasonication reaction of 5 and 10 wt% of CH$_2$Br$_2$ with MeSiHCl$_2$ and Na afforded primarily Si-(CH$_2$)$_n$-Si units in addition to Si-Si linkages as evidenced by the $^1$H NMR spectrum of the product (Fig. D3).

Interestingly, homopolymerization of PhSiHCl$_2$ using sodium, 7/1 hexane/THF, and ultrasonic activation also yielded a product containing SiH$_2$ end groups as shown by the $^{29}$Si NMR DEPT spectrum (Fig. D4). The shape and the chemical shift of the silicon resonance (-50 to -70 ppm) of this poly(phenylsilane)
is identical to the one of the H(PhSiH)ₙH polysilane prepared by Waymouth and coworkers by reaction of PhSiH₃ with an optically active dehydrogenative coupling catalyst.²⁵,⁷²b It is believed that also in our case reaction takes place through a radical rather than anionic path. Recently, Harrod and coworkers³⁴b proposed that because PhSiH₂⁻ (through resonance stabilization) is more stable than MeSiH₂⁻ it was possible to observe dehydrogenative coupling activity of LiAlH₄ towards MeSiH₃ but not towards PhSiH₃ (Scheme D3).

\[
\text{Li}^+\text{H}^- + \text{P-SiR'H}_2 \rightarrow \text{Li}^+\text{[P-SiR'H]}^- + \text{H}_2
\]

\[
\text{Li}^+\text{[P-SiR'H]}^- + \text{P-SiR'H}_2 \rightarrow \text{Li}^+\text{H}^- + \text{P-SiR'HSiR'H-P}
\]

**Scheme D3**

Other evidence in favor of a free radical mechanism was obtained in a reaction of MeSiHCl₂ and CH₂Br₂ in 1:1 molar ratio with molten sodium in toluene. The product was a polymer containing incorporated toluene-derived benzyl groups (Fig. D5). A possible mechanism for this process is depicted on Scheme D4. This reaction does not take place in the absence of a transfer agent. A transfer agent such as CH₂Br₂ is needed to raise the chain transfer constant of the macroradical so it can react with toluene. Toluene and the polysilyl radical have rather small transfer constants so they do not interfere with each other. This reaction also does not take place at ambient temperature using ultrasonic activation.
Scheme D4
The following scheme (Scheme D5a) represents a proposed mechanism for the polymerization of methyldichlorosilane without a chain transfer agent.

1) \[
\text{C}_1\text{SiCl}_2 + \text{Na} \xrightarrow{\text{slow}} \text{C}_1\text{SiCl}^- + \text{Na}^+ 
\]

2) \[
\text{C}_1\text{SiCl}^- + \text{Na}^+ \rightarrow \text{C}_1\text{Si}^- + \text{NaCl}
\]

3) \[
2 \text{C}_1\text{Si}^- \rightarrow \text{C}_1\text{SiSiCl}_2
\]

4) \[
\text{SiSi}^- \xrightarrow{\text{Cyclization}} \text{SiSiH}
\]

Scheme D5a

Possible termination modes:
- disproportionation
- branching by coupling
- cyclization (back biting)
Scheme D5b depicts a proposed reaction mechanism of MeSiHCl₂ and Na in the presence of a transfer agent.

5) \[ \text{Me} - \text{Si} - \text{Si}^* + \text{CH}_2\text{Br}_2 \rightarrow \text{Me} - \text{Si} - \text{Si} - \text{Br} + \cdot \text{CH}_2\text{Br} \]

6) \[ \text{Me} - \text{Si} - \text{Si} - \text{Br} + \cdot \text{Na} \rightarrow \]

7) propagation to form homopolymer

\[ \text{Me} - \text{Si} - \text{Cl} + \cdot \text{CH}_2\text{Br} \rightarrow \text{Me} - \text{Si} - \text{Si} - \text{Si} - \text{Cl} \rightarrow \text{Me} - \text{Si} - \text{Si} - \text{CH}_2\text{Br} \]

propagation to form copolymer

Scheme D5b
The first step (rate determining) involves electron transfer from sodium to monomer to form a monomeric radical anion (1). This species is transformed to a monomeric radical (2). Two such radicals then dimerize (3) and in the presence of the excess of sodium metal this process repeats until the radical is long enough to isomerize. The uninterrupted polymer radical, stabilized by extensive σ conjugation, then isomerizes from a secondary to a tertiary (more stable) radical (4) which then can either terminate by hydrogen atom capture from another macrosilane (disproportionation), branch by coupling to another polyradical, or cyclize by reacting with itself. In order to avoid termination, a chain transfer agent such as CH₂Br₂ is employed. Such agents have rather high chain transfer constants, namely CBr₄ (420) >> CCl₄ (0.0148) > CH₂Br₂ (0.0110) > Me₂SiCl₂ (0.00178) > toluene (0.000205) for styrene at 60°C. In order for the chain transfer to function effectively, reaction between the chain transfer agent and a macroradical must be faster than the isomerization of the macroradical (5). When the chain end happens to be bromine-terminated (by the chain transfer agent), the excess of sodium allows an electron transfer to occur again and, subsequently, formation of another macroradical is facilitated (6). This macroradical then may happen to be in the immediate vicinity of a chain transfer agent radical with which it reacts (7). The possibility of having the macroradical react with its monomer also exists (7). The lower Si-H bond energy (90 kcal/mol) compared with C-H (104 kcal/mol) probably is responsible for the increased chain transfer affinity of
Si-H compounds over C-H compounds in reductive coupling polymerization reactions. This is why in the homopolymerization process transfer occurs only to the polymer and not to the solvent. Thus the use of brominated hydrocarbons as chain transfer agents leads to formation of longer polymers with less branching. This also serves to decrease ceramic residue yields of the polymer thus formed. The polymers obtained from 1/1, 2/1, and 3/1 MeSiHCl₂/CH₂Br₂ reactions with sodium afford 25%, 35%, and 16% ceramic residue yields upon pyrolysis, respectively.

It would be rather unlikely to have a silyl anion (or NaH) intermediate present in the initial stages of the polymerization reaction of MeSiHCl₂. At this stage NaH probably would first react with CH₃SiHCl₂ to yield CH₃SiH₂Cl which would then act as a terminating capping group in the terminating step of the polymerization. The presence of NaH also would catalyze dehydrogenative coupling yielding a high molecular weight polymer, whose pyrolysis gives high ceramic yields. The silyl anion mechanism is more pronounced after long reaction times. Also, initially the reaction mixture is clear in color (except for large yellow NaCl crystals containing some high molecular weight poly(methylsilane)); however, only later (above 20 hours of ultrasonication) does this solution become yellow-orange, indicating the possible presence of silyl anion intermediates. The NaH mechanism will be discussed in greater detail in the section on high molecular weight poly(methylsilane) (Section G).
Figure D2 $^1$H NMR spectra of copolymers prepared by reflux in octane a) 1:1, b) 1:2, c) 1:3 of CH$_2$Br$_2$/MeSiHCl$_2$. 
Figure D3 $^1$H NMR spectra of copolymer prepared by ultrasonication of MeSiHCl$_2$ and Na with a) 5 wt% and b) 10 wt% CH$_2$Br$_2$. 
Figure D4 $^{29}$Si NMR spectrum (DEPT mode) of oligo(phenylsilane) with MULT = a) 1.5, b) 1.0, and c) 0.5.
**Figure D5** a) $^1$H NMR spectrum, b) $^{13}$C NMR spectrum (decoupled) of oligo(methylsilane) with incorporated tolyl group.
Section E

Photochlorination of Oligo(methylsilane)
Changing polymer properties such as $T_g$, $T_m$ or solid mechanical behavior such as crazing vs. sheer bending, requires altering the functional groups attached to the polymer backbone. There are various ways of altering the substituents of polysilanes. The most common way is via cleavage of the substituents on the silicon backbone by reagents that introduce chlorine. This results in highly reactive Si-Cl functionalities. In such reactions it is desirable to avoid Si-Si chain scission.

There are various ways of chlorinating monomeric or polymeric silanes. One of the routes extensively explored by Kumada and Sakurai and coworkers was the interchange reaction of methyl or aryl groups with chloride catalyzed by aluminum chloride$^{65}$ as depicted in equation E1 and E2.

$$\text{Me}_3\text{Si-SiR}_3 + \text{ClMe}_2\text{Si-SiMe}_3 \rightleftharpoons \text{ClMe}_2\text{Si-SiR}_3 + \text{Me}_3\text{Si-SiMe}_3 \quad (\text{E1})$$

$$\text{ArSiMe}_3 + \text{ClMe}_2\text{Si-SiMe}_3 \rightarrow \text{ArMe}_2\text{Si-SiMe}_3 + \text{Me}_3\text{SiCl} \quad (\text{E2})$$

Another method for introducing chlorine into silicon was developed by Hengge and coworkers who studied the removal of phenyl groups from disilanes with HCl, HBr, or HI to form silicon-halide bonds (eq. E3). This reaction can be performed either under high pressure of HCl, HI, or HBr$^{66}$ or at atmospheric pressure with an AlCl$_3$ catalyst.$^{67}$ The latter reaction is particularly useful for chlorinating cyclosilanes since it occurs without Si-Si chain scission.

$$\text{Me}_3\text{Si-SiPh}_3 + \text{HCl} \rightarrow \text{Me}_3\text{Si-SiPh}_2\text{Cl} + \text{PhH} \quad (\text{E3})$$
Dunoguès and coworkers used Kumada’s and Sakurai’s method of AlCl₃ catalyzed interchange of methyl and chlorine on silicon to synthesize the first polychlorocarbosilane.⁶⁸a Recently, Sartori and coworkers⁶⁸b applied Hengge’s procedure to cleave phenyl groups from poly(methylphenylcarbosilane) with HCl or HBr in the presence of AlCl₃ or AlBr₃. The exchange reaction of aryl groups gave nearly quantitative yields of halogenated polysilane.

In addition, the chlorination of Si-H bonds with SnCl₄ is known in the case of monosilanes.⁶⁹ This reaction also was explored by Wood⁴⁶ for the chlorination of oligo(methylsilane). The resulting oligo(methylchlorosilane) was only partially chlorinated and was of considerably higher molecular weight than the starting oligomer, indicating some Si-Si bond redistribution had occurred.

A free radical route for synthesis of Si-Cl groups also is known. Abstraction of chlorine from chlorobenzene by triphenylsilane initiated by tert-butyl peroxide is such a process.⁷⁰ Later, a Japanese group led by Nagai⁷¹ found that Si-H containing alkylsilanes and arylsilanes react with CCl₄ in the presence of benzoyl peroxide to yield the corresponding alkyl- or arylchlorosilanes as shown on Scheme E1.
\[ R(O)COOC(O)R \rightarrow 2 R(O)CO^* \]

\[ R(O)CO^* + R_3Si-H \rightarrow R(O)COH + R_3Si^* \]

\[ R_3Si^* + CCl_4 \rightarrow R_3Si-Cl + Cl_3C^* \]

\[ 2 Cl_3C^* \rightarrow Cl_3C-CCl_3 \]

etc.

**Scheme E1**

Recently, Waymouth and coworkers\(^{72}\) reported the synthesis of poly(phenylchlorosilane) from poly(phenylsilane). Poly(phenylsilane) was dissolved in CCl\(_4\) and maintained in daylight for several days. Chlorine-for-hydrogen substitution was observed. The final polymer had an unchanged molecular weight which would indicate that Si-Si bond cleavage did not take place. This chlorination reaction takes place with retention of configuration at the silicon atom which is not surprising since silyl radicals are known not to invert as opposed to carbon radicals.\(^ {73}\)

About the same time and independently of Waymouth, our group discovered the photochlorination of oligo(methylsilane) (OMS) in a quartz vessel using CH\(_2\)Cl\(_2\) as a chlorine source and UV (\(\lambda = 254\) nm) irradiation. A solution of the oligo(methylsilane) in CH\(_2\)Cl\(_2\) on irradiation with UV in an air-free atmosphere for more than 10 hours yielded an oily oligo(methylchlorosilane). The chlorination reaction was quantitative and CH\(_3\)Cl was formed according to IR, and
\(^1\)H NMR spectroscopy and GLC. An NMR tube reaction involving oligo(methylsilane), \(\text{CD}_2\text{Cl}_2\) and UV irradiation yielded quantitative chlorination after 10 hours of irradiation as shown by the final \(^1\)H NMR spectrum (Fig. E1). The chlorination reaction proceeded only when the solution was irradiated. When the irradiation was stopped, the reaction ceased as well. This observation indicates that there is no continuous, self-initiating radical chain growth in this reaction.

One of the products detected by \(^1\)H NMR was \(\text{CD}_2\text{HCl}\) (Fig. E1). The IR spectrum of this reaction mixture, revealing Si-Cl formation and Si-H disappearance, is shown on Fig. E2. The solid poly(methylsilane) (TS-2 (Section G) quenched with MeI) with 1.0 molar equivalents of \(\text{CH}_2\text{Cl}_2\) and UV irradiation gave a tacky solid, hinting at a decrease in molecular weight. Indeed, after its reduction with \(\text{LiAlH}_4\), based on the GPC data, molecular weight is drastically reduced (Fig. E7).

The \(^29\)Si and \(^13\)C NMR spectra of the chlorinated oligo(methylsilane) showed two sharp signals in the downfield region and one broad signal in the upfield region \textit{vide infra}. Due to scarcity of \(^29\)Si and \(^13\)C NMR data on polysilanes bearing electronegative substituents on Si such as O, N, or halogen, a comparison was made with structural data provided on macromolecules such as silicones and silicates. In the \(^29\)Si NMR spectra of both silicones\(^74\) and soluble silicates\(^75\) the resonance due to the end group silicon atom is about 7 ppm.
downfield from the signal due to the second to last silicon atom in the chain. The signals due to the rest of the Si atoms in the backbone are grouped together upfield from these two. If an extrapolation is made of these results to the current ones, the DEPT $^{29}$Si NMR spectrum of oligo(methylchlorosilane), has a broad signal between -2 and 20 ppm due to Cl-SiMe groups of the backbone and signals due to the first ClSiMe to the end group and Cl$_2$SiMe the end group at 22 and 26 ppm, respectively (Fig. E3).

Choice of the solvent is also an important factor in determining the structure of chlorinated OMS by NMR spectroscopy. For example, when a nonpolar solvent such as C$_6$D$_6$ is used, the $^1$H NMR signal of Si-CH$_3$ is not well resolved. However, when polar solvents are used (such as CD$_2$Cl$_2$), signals due to Cl$_2$SiCH$_3$ (1.0 ppm; $W_{1/2} = 90$ Hz) and ClSiCH$_3$ (0.6 ppm; $W_{1/2} = 100$ Hz) are well resolved (Fig. E4). The model compounds depicted in Table E1 were employed in the elucidation of the structure and in spectral peak assignments of oligo(methylchlorosilane). Based on the integration of the $^1$H NMR spectrum, a large amount of Cl$_2$SiMe was present compared with ClSiMe (Fig. E4), indicating possible Si-Si chain scission.

A closer look at the $^{13}$C DEPT NMR spectrum of the oligo(methylchlorosilane) reveals the presence of the main backbone groups (ClSiMe) which give a broad signal between -2 and 5 ppm, and two sharp
resonances at 10 and 8 ppm which probably correspond to the end and penultimate Cl₂SiMe and ClSiMe groups, respectively. There also is a broad signal due to CH₂ functionalities at -30 ppm (Fig. E5). When the chlorination was repeated using ¹³CH₂Cl₂, incorporation of the ¹³C isotope into the oligosilane structure was negligible, according to the intensity of the CH₂ signal in the ¹³C NMR DEPT spectrum (Fig. E6). Judging from the chemical shifts of about 30 ppm (¹³C NMR DEPT (Fig. E6), Table E1), the methylene group present in the final product most likely arose from the chlorination of methyl groups on silicon to give SiCH₂Cl groups and not from the Kumada rearrangement. Also, the CH₂ signal becomes progressively less intense with further chlorination (Fig. E6), possibly because SiCH₂Cl becomes further chlorinated to SiCHCl₂.

To avoid the chlorination of methyl groups attached to the silicon backbone, the chlorination may be carried out in hexane solution with a 1:1 or 1:0.5 molar ratio of MeSiH to CH₂Cl₂. A UV irradiation of this solution for about 16 h yielded a nearly quantitative chlorination OMS and an absence of -CH₂Cl functionalities based on the DEPT ¹³C NMR (Fig. E8), IR, and elemental analysis.
Figure E1 $^1$H NMR spectrum of oligo(methylsilane) photolysis with CD$_2$Cl$_2$. 
Figure E2 FT-IR spectrum of gradual photochlorination of oligo(methylsilane).
Figure E3: $^{29}$Si NMR DEPT spectrum of oligo(methylchlorosilane) (broad peak at -60 ppm corresponds to residual HSiMe and crosslinked units).
Figure E4 $^1$H NMR spectrum of oligo(methylchlorosilane) in a) $C_6D_6$; b) $CD_2Cl_2$. 

-MeSiCl$_2$

(MeSiCl)$_n$

2.  

b)
Figure E5 $^{13}$C NMR DEPT spectrum of oligo(methylchlorosilane) (broad peak at -10 ppm corresponds to residual HSiMe).
Figure E6 $^{13}$C NMR DEPT (MULT = 1.5) spectrum of gradual chlorination of oligo(methylsilane) with $^{13}$CH$_2$Cl$_2$ in C$_6$D$_{12}$. 
Figure E7 GPC traces of poly(methylsilane) (TS-2) (a) and of TS-2 photochlorinated with CH₂Cl₂ and subsequently reduced with LiAlH₄ (b).

Figure E8 ¹³C NMR DEPT (MULT = 1.5) spectra of photochlorinated OMS in SiH/CH₂Cl₂ 1/1 molar ratio (Note absence of signal due to -CH₂Cl at about 30 ppm).
Various background experiments also were attempted in order to shed some light on the mechanism of this reaction. A reaction of \( \text{Ph}_2\text{SiH}_2 \) and \( \text{CH}_2\text{Cl}_2 \) with UV irradiation carried out in a quartz NMR tube revealed the formation of \( \text{Ph}_2\text{SiHCl} \) and \( \text{Ph}_2\text{SiCl}_2 \) as well as of \( \text{CH}_3\text{Cl} \). In order to determine the effect of UV irradiation on the oligo(methylsilane), it \( ((x + z) = 0.85) \) was irradiated in hexane solution, yielding a solid product (ceramic residue yield on pyrolysis was 33%) with diminished SiH functionality \( ((x + z) = 0.53) \), indicating that a crosslinking reaction had taken place. However, SiCH\(_2\)Si linkages, which would result from free radical based Kumada rearrangement,\(^8\) were not present. The current findings are in agreement with the experimental results obtained by Wood who reported a gummy product from the irradiation of a hexane solution of OMS oil.\(^{36}\)

The efficiency of the chlorination reaction also was explored. UV irradiation of a hexane solution of the oligosilane with 1.0 and 0.5 molar equivalent of \( \text{CH}_2\text{Cl}_2 \) afforded a fully chlorinated oligomer after 16 - 17 hours of irradiation (Fig. E9a). Exposure of a \( \text{CH}_2\text{Cl}_2 \) oligomer solution to daylight resulted in a very sluggish chlorination as shown by IR (Fig. E9b). The Si-Cl absorption was very weak even after 166 hours of exposure to daylight compared to UV irradiation and the Si-H absorption still was very strong.
Based on the structural evidence and sequential irradiation reactions, as well as some background experiments, the following chlorination mechanism is proposed (Scheme E2a).

\[
\begin{align*}
\text{CH}_3 & \quad \text{UV} \quad \text{CH}_3 \\
\text{Si} & + \text{CH}_2\text{Cl}_2 \quad \rightarrow \quad \text{Si} + \cdot\text{CH}_2\text{Cl} \\
\text{CH}_3 & + \cdot\text{CH}_2\text{Cl} \quad \rightarrow \quad \text{Si} + \text{CH}_3\text{Cl}
\end{align*}
\]

etc.

**Scheme E2a - the major reaction**

Based on the physical nature of low viscosity oily oligo(methylchlorosilane) product one may ascertain that during the photochlorination reaction Si-Si bond scission takes place (Scheme E2b).
The final product has a following structure:

\[
\begin{align*}
\text{CH}_3 &\text{CH}_3 \\
\text{Si-Si} &\text{Cl} \quad + \quad \text{.Cl} \\
\text{Cl} &\text{Cl} \\
\end{align*}
\rightarrow
\begin{align*}
\text{CH}_3 &\text{Si-Cl} \\
\text{Cl} &\text{Cl} \\
\end{align*}
\begin{align*}
\text{Si-Cl} &\text{Cl} \\
\text{Cl} &\text{Cl} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 &\text{Si-Cl} \\
\text{Cl} &\text{Cl} \\
\end{align*}
\rightarrow
\begin{align*}
\text{CH}_2 &\text{Si-Cl} \\
\text{Cl} &\text{Cl} \\
\end{align*}
\begin{align*}
\text{CH}_2 &\text{Cl} \\
\text{Cl} &\text{Cl} \\
\end{align*}
\]

\[
\begin{align*}
\text{Si-Cl} &\text{Cl} \\
\text{Cl} &\text{Cl} \\
\end{align*}
\rightarrow
\begin{align*}
\text{CH}_2 &\text{Si-Cl} \\
\text{Cl} &\text{Cl} \\
\end{align*}
\]

Scheme E2b - the minor reaction
The unit marked with the variable z denotes the branched unit of the oligomer. The y unit is absent when the reaction is carried out in a 1/1 or 1/0.5 molar ratio of MeSiH to CH$_2$Cl$_2$.

A comparison of the photochlorination of oligosilane with that of other organosilicon polymers was performed. For example, UV-radiation-induced chlorination of the Nicalon® fiber precursor polycarbosilane with CH$_2$Cl$_2$ was very slow. Even after 66 hours of irradiation with UV some SiH groups remained (Fig. E10) and the $^1$H NMR integral signal ratio was SiCH$_3$/SiH = 14.5 (SiCH$_3$/SiH = 7.8 of the starting polymer). More facile is the chlorination when CCl$_4$ is employed. Nearly complete chlorination resulted after 15 hours of irradiation (SiCH$_3$/SiH = 30.0). Other polymers such as a polysilazane (MeSi(H)NMe)$_n$ or a polysiloxane (MeSi(H)O)$_n$ did not show any tendency for photochlorination with CH$_2$Cl$_2$, possibly due to some radical chain transfer process.

A comparison of the efficiency of chloromethane chlorinating agents, CCl$_4$,
CHCl₃, and CH₂Cl₂, was explored. Based on the IR and NMR spectroscopy study, the following sequence of effectiveness in photochlorination of OMS was established: CCl₄ > CHCl₃ > CH₂Cl₂. Interestingly, the molecular weight of the oligo(methylchlorosilane) produced decreased as the halomethane was changed from CH₂Cl₂ to CCl₄ as observed by the relative decrease in the viscosity of the product. The IR spectra depict progressive Si-H depletion and an Si-Cl increase, occurring as the halomethane is changed from CH₂Cl₂ to CCl₄ in Fig. E11.

Figure E12 shows ¹H NMR spectra depicting the increase in -SiMeCl₂ signals for different chlorine sources, with CH₂Cl₂ yielding the least amount of terminal -SiMeCl₂ units in the chlorination compared with the other free radical chlorine sources. Since the -SiMeCl₂ groups are indicative of Si-Si chain scission, CH₂Cl₂ is the mildest and least destructive chlorinating agent.
Figure E9 FT-IR spectra of photochlorinated oligo(methylsilane) product by a) 0.5 molar equivalent of CH$_2$Cl$_2$ using UV irradiation for 17 h; b) excess of CH$_2$Cl$_2$ using daylight for 166 h.
Figure E10 FT-IR spectrum of photochlorinated Nicalon® polycarbosilane using CCl₄ and UV irradiation for 15 h.
Figure E11 FT-IR spectra of photochlorinated oligo(methylsilane) with UV light for 22 h in b) CH$_2$Cl$_2$; c) CHCl$_3$; d)CCl$_4$. Spectrum (a) is that of the OMS starting material.
Figure E12 $^1$H NMR spectra of photochlorinated oligo(methylsilane) with UV radiation for 22 h in a) CH$_2$Cl$_2$; b) CHCl$_3$; c) CCl$_4$. 
The crosslinking of oligo(methylsilane) with nitrogen bridging units is of interest since the pyrolysis product would afford an SiC/Si-C-N composite material. Such materials have useful bulk mechanical properties as reported by Semen and Loop.\textsuperscript{76} The most convenient route for crosslinking of oligo(methylsilane) with nitrogen would be through ammonolysis of oligo(methylchlorosilane). The reaction of oligo(methylchlorosilane) in ether with an excess of ammonia at 4°C afforded a solid, soluble, crosslinked polymeric network whose pyrolysis gave a ceramic residue yield on pyrolysis in argon (TGA) of 82%. This network appeared to have many Si-N-Si linkages based on low nitrogen content by elemental analysis and absence of Si-Cl band in its IR spectrum. Recovered NH\textsubscript{4}Cl indicated that the reaction proceeded to the extent of about 97% based on a one-to-one reaction of Si-Cl and N-H. The IR spectrum of the product indicated the presence of some N-H functionalities. The powder X-ray diffraction pattern of the pyrolyzed product (1500°C, Ar) of this polymer showed that a mixture of SiC (JCPDS card # 29-1129 and 19-1138) and Si\textsubscript{3}N\textsubscript{4} (JCPDS card # 9-250) had been formed. A similar reaction of oligo(methylchlorosilane) with methyamine also afforded a partly crosslinked network; however, its ceramic residue yield on pyrolysis in argon (TGA) was only 30%.

Other substitution reactions of oligo(methylchlorosilane) were attempted such as methoxylation and arylation (equations E4 and E5). In general, the
substitution reactions proceeded to > 90% completion judging by the $^1$H NMR spectra of the products.

$$ (\text{MeSiCl})_n + \text{MeOH} \rightarrow (\text{MeSiOMe})_n + \text{HCl} \quad (\text{E4}) $$

$$ (\text{MeSiCl})_n + \text{PhLi} \rightarrow (\text{MeSiPh})_n + \text{LiCl} \downarrow \quad (\text{E5}) $$

The most significant difference between the described chlorination procedure and that of Waymouth was the decrease in molecular weight of the chlorinated species due to Si-Si bond scission as indicated by the GPC trace (Fig. E7) and the decrease in viscosity of the product compared with that of the starting OMS. This observation is in agreement with the report describing Si-Si bond cleavage of dodecamethylcyclohexasilane by irradiation with $\lambda > 300$ nm in a cosolvent mixture of CCl$_4$/CH$_2$Cl$_2$ (eq. E6).$^{77}$

$$ \text{CCl}_4/\text{CH}_2\text{Cl}_2, \text{hv} \quad (\text{Me}_2\text{Si})_6 \rightarrow \text{Cl}-(\text{SiMe}_2)_6\text{-Cl} + \text{Cl}_3\text{C-CCl}_3 \quad (\text{E6}) $$

In addition, the described photochlorination is a much more complicated process than the reaction described by Waymouth and coworkers, as evidenced by the fact that various competing free radical reactions are taking place.
### Table E1 Model Compounds Used in Structural Determination of Photochlorinated OMS

<table>
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<tr>
<th>Model Compound</th>
<th>IR Data (cm(^{-1}))</th>
<th>(^1\text{H NMR Data}) (\delta) (ppm)</th>
<th>Reference</th>
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<td>Me Me H-Si-Si-H Cl Cl</td>
<td>2990(w), 2160(s), 1410(w), 1265(m), 872(s), 788(s), 735(s), 705(w), 625(w), 542(w), 509(s)</td>
<td>(neat) CH(_3)(d) 0.70 SiH(q) 4.93</td>
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<td>Me Me H-Si-Si-H H Cl</td>
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<td>(CCl(_4)) CH(_3)(t) 0.38 SiH(_2)Cl(t) 4.83 SiH(_2)Me(m) 3.76</td>
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<td>(CDCl₃)</td>
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<tr>
<td>H-Si-CH₂-Si-Me</td>
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<td><strong>(-SiH₂CH₂-)ₙ</strong></td>
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<td><strong>CH₂(s)</strong> 0.532</td>
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<td>Me</td>
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References for Table E1


Section F

Crosslinking of Oligo(methylsilane) by Catalyzed Dehydrogenative Coupling

Reactions
Poly(methylsilane) would seem to be an ideal precursor to SiC ceramics due to its ease of synthesis and its carbon-to-silicon ratio of 1 which is the same as that found in SiC. However, when pyrolyzed in an inert atmosphere, the clear oil oligo(methylsilane) (OMS), the first stage product of the reductive coupling of MeSiHCl₂, afforded only between 13 to 26% ceramic residue yield. The ceramic produced contained SiC with 22 wt% Si.³⁶

The OMS has a great number of reactive centers, namely SiH groups and Si-Si bonds. Among the diverse reactions that Si-H and Si-Si bonds undergo are a large variety of stoichiometric and catalytic reactions with coordinatively unsaturated transition metal species.¹ Harrod and coworkers found that Group 4 metalloocene compounds catalyze the dehydrogenative coupling of primary silanes to form polysilanes.²³a The molecular weight of the polysilanes derived from such dehydrogenative coupling varied with the size of the functional group on silicon. Polysilanes derived from silanes with small substituents such as methyl afforded high molecular weight polymers and even insoluble gels. For example, Harrod and coworkers³⁴ synthesized high molecular weight poly(methylsilane) from MeSiH₃ utilizing a Cp₂MMe₂ where M = Ti or Zr catalyst (eq. F1). Under carefully controlled conditions, the resulting poly(methylsilane) was soluble in most common organic solvents and its pyrolysis at 1000°C afforded a ceramic in 70 - 80% yield with a composition of Si₁C₀.₉. Unfortunately it took about 8 days for the synthesis of this polymer to proceed to completion and the synthesis uses
gaseous and pyrophoric MeSiH$_3$ as the starting material.

\[
\text{Cp}_2\text{MMe}_2 \text{ (cat.)}, \ M = \text{Ti, Zr} \\
\text{MeSiH}_3 - \text{H}-[(\text{MeSiH})_a(\text{MeSi})_b]_x-\text{H} \quad (F1)
\]

Woo and Tilley$^{24}$ have proposed a mechanism for the catalytic polymerization of RSiH$_3$ silanes which involves the generation of a coordinatively unsaturated metal hydride and proceeds through a four-center transition state leading to a $\sigma$-bond metathesis. A stepwise insertion of SiMeH in to the M-Si bond results (**Scheme F1**). Corey and coworkers$^{78}$ have dehydrogenatively coupled primary and secondary silanes using an *in situ* generated Cp$_2$ZrCl$_2$/2 n-BuLi catalyst. Addition of 2 n-BuLi to Cp$_2$ZrCl$_2$ yields Cp$_2$ZrBu$_2$ which, upon warming to room temperature, is converted to Cp$_2$Zr(butene)$^{79}$ which is the catalyst active in the dehydrogenative coupling of PhMeSiH$_2$. During this reaction PhMeBuSiH was formed as a minor by-product.
The use of dehydrogenative coupling catalysts as crosslinking agents for OMS to yield poly(methylsilane) was explored by Tracy. He found that refluxing a hexane solution containing OMS oil and a 0.9 mol% of (Cp₂ZrH₂)ₙ produced an orange solid which on pyrolysis gave a 62% ceramic residue yield (by TGA) of 98% pure β-SiC. A number of other potential crosslinking agents such as KH (36% ceramic residue yield) or MeLi (67% ceramic residue yield) were tried by Wood. More recently, Robison explored the use of other Group 4 metalloccenes such as (Cp₂ZrH₂)ₙ, Cp₂TiMe₂, Cp₂ZrMe₂, Cp₂ZrHCl, and
Cp₂ZrCl₂/2 n-BuLi for crosslinking of polysilanes and polycarbosilanes in order to obtain higher molecular weight polymers. It was observed that, in general, soluble polymers of higher molecular weight were obtained which gave higher ceramic residue yields upon pyrolysis.

The current study has shown very diverse catalytic behavior of early transition metallocones towards OMS. A variety of reaction conditions were investigated. In general, a Schlenk flask was charged with the air-sensitive OMS and the catalyst in a dry box. Usually 0.5 mol% of the catalyst was used relative to the oligomer repeat unit (CH₃SiH). The solvent (hexane or toluene) then was added and the flask fitted with a reflux condenser. Subsequently, the reaction mixture was heated at reflux or UV irradiated under argon for 2 to 20 hours. In another procedure, a Schlenk flask was fitted with a high vacuum stopper and the reaction was carried out in vacuo or, in the closed system, at the vapor pressure of solvent used. The final products then were isolated by removal of the solvent and dried in vacuo. In two cases the catalysts (Cp₂ZrHCl and Cp₂ZrCl₂) were removed by precipitation or sublimation. In both instances, the retrieved compounds were the starting catalysts based on their ¹H NMR spectra. Control experiment of heating OMS up to 190°C for 12 hours without catalysts did not result in a product with significant alteration in the molecular weight or molecular complexity of the polymer as compared with the OMS containing catalysts.

The instrumental methods used for polymer analysis were ¹H NMR
spectroscopy to determine the extent of cross-linking, i.e., the increase of the CH/SiH ratio, $^{29}$Si NMR spectroscopy to determine the selectivity of the catalyst towards SiH and SiH$_2$ groups and thermogravimetric analysis (TGA) to determine the yield of ceramic residue after pyrolysis. Gel permeation chromatography (GPC) was used for molecular weight determination (Section G). Powder X-ray diffraction (XRD) also was utilized to determine the extent of crystalline ceramic phases.

The following diagram (Fig. F1) depicts a proposed classification of catalysts according to their effect on the OMS.

![Diagram of catalyst classification]

**Dehydrogenative Coupling Catalysts**

Conventional \( \rightarrow \) Pyrolysis \( \rightarrow \) Conventional/Pyrolysis

**Figure F1**

The conventional catalysts form Si-Si bonds in a dehydrogenative coupling reaction under relatively mild conditions such as temperatures between room temperature and about 200°C. The conventional/pyrolysis catalysts cause limited crosslinking of silanes under mild conditions but their major effect is during the pyrolysis of the polymer where they appear to cause further Si-Si bond formation.

111
The pyrolysis catalysts have no or little effect on the polymer under mild conditions but they induce Si-Si bond formation at higher temperatures during the pyrolysis (200°C and above). Use of the latter catalysts may be practical when crosslinking is undesirable before pyrolysis for intended application. An anticipated application would be the use of an oil (normally of low molecular weight and giving a low yield of ceramic residue on pyrolysis) as a binder for injection molding of ceramic, metal/ceramic, or metal powders. A similar idea was explored by Lukacs who used a liquid poly(methylvinylsilazane) and a peroxide curing agent for injection molding of ceramic powders.82

Studies by Robison81 revealed that \((\text{Cp}_2\text{ZrH}_2)_n\) could induce dehydrogenative coupling at room temperature as well as at elevated temperatures, qualifying it as a conventional catalyst. In both cases, the product was an orange solid polymer which was soluble in most common organic solvents and gave ceramic residue yields on pyrolysis in the range of 65 to 84%. This span in ceramic residue yield is a result of varying degrees of crosslinking. It was observed in the current study that extensive reflux of a hexane solution of OMS with \((\text{Cp}_2\text{ZrH}_2)_n\) yielded some insoluble products and if the reflux was not stopped in time, eventually crosslinking occurred to such an extent that an insoluble polymeric network was formed. In the current study, thermolysis of OMS in hexane at 70°C for 1 h in the presence of 0.5 mol% of \((\text{Cp}_2\text{ZrH}_2)_n\) in vacuo afforded a soluble, yellow solid \(((x + z) = 0.75)\) with a ceramic residue yield...
of 65% (without removal of the catalyst). Reflux for 3 h in toluene at atmospheric pressure gave a orange solid with \((x + z) = 0.42\) whose pyrolysis gave an 84% ceramic residue yield. Ultraviolet irradiation for 6 h of the OMS with \((\text{Cp}_2\text{ZrH}_2)_n\) in hexane, however, afforded an unchanged oil \((x + z) = 0.91\) but with a ceramic yield of 70% since the catalyst was present during the pyrolysis. As expected, \((\text{Cp}_2\text{ZrH}_2)_n\) also can act as a pyrolysis catalyst. The extent of dehydrogenative coupling can be observed in the \(^{29}\text{Si}\) NMR spectrum (Fig. F2) which compares negative signals (\(\text{SiH}_2\)) at -60 ppm of photolyzed (Fig. F2b) and thermal (Fig. F2a) reaction products. In the thermal case almost complete disappearance of the \(\text{SiH}_2\) resonance was observed (Fig. F2a). In the overall description, then, \((\text{Cp}_2\text{ZrH}_2)_n\) qualifies as a conventional/pyrolysis catalyst.

When OMS was refluxed in toluene for 3.5 h with 0.5 mol\% of \(\text{Cp}_2\text{ZrHCl}\), the reaction mixture turned orange almost immediately, as had been observed in the case of the \((\text{Cp}_2\text{ZrH}_2)_n\) catalyst. The product of this reaction was a pink-white solid \((x + z) = 0.77\) whose pyrolysis gave a ceramic residue yield of only 45% after the catalyst had been removed by precipitating it with hexane. The precipitate was \(\text{Cp}_2\text{ZrHCl}\) based on its \(^1\text{H}\) NMR spectrum. Unlike \((\text{Cp}_2\text{ZrH}_2)_n\), \(\text{Cp}_2\text{ZrHCl}\) does not react with OMS at room temperature to yield a solid product. Instead, it yields an oil \((x + z) = 0.88\) containing the unreacted catalyst. This blend of OMS and the catalyst, however, yields a 70% ceramic residue when
pyrolyzed. Thus Cp₂ZrHCl is another example of a conventional/pyrolysis
catalyst since it induces some dehydrogenative coupling at the boiling point of
toluene, thus crosslinking OMS, and affords high ceramic yields of SiC when it is
blended with OMS before pyrolysis.

Since Cp₂ZrHCl showed catalytic activity for crosslinking OMS by
dehydrogenative coupling, it was also of interest to explore the effect of
metallocene dichlorides on the OMS. Both Cp₂TiCl₂ and Cp₂ZrCl₂ proved to be
good pyrolysis catalysts. Reflux in toluene for 24 h of OMS with 0.5 mol%
Cp₂TiCl₂ yielded oily products with virtually unchanged CH/SiH ratio ((x - z ) =
0.91). The ceramic residue yield of this polysilane/catalyst mixture, was 63%.
Refluxing of OMS with 0.57 mol% of Cp₂ZrCl₂ in toluene solution for 43.5 h also
afforded oily products with little change in CH/SiH ratio ((x + y) = 0.88).
Thermogravimetric analysis of this OMS/Cp₂ZrCl₂ mixture gave a 67% ceramic
residue yield. Simply blending 0.5 mol% of Cp₂ZrCl₂ with the OMS oil prior to
pyrolysis increased the ceramic residue yield from 26% to 70% (Fig. F3) of near
stoichiometric SiC as determined by elemental analysis. In addition, these
ceramics and the ones derived from (Cp₂ZrH₂)n-catalyzed crosslinked OMS
appeared to be identically crystalline judging from the X-ray diffraction (XRD)
patterns (Fig. F4). A comparison of XRD patterns of the ceramics derived from
the pure OMS oil and the ceramic derived from the oil containing Cp₂ZrCl₂
showed that the latter ceramic has a finer particle size (judging from the broadness of the XRD peaks) and contains much less elemental silicon (Fig. F5). A control experiment in which the oil was heated with Cp₂ZrCl₂ in refluxing toluene for 3 hours and the catalyst subsequently was removed by sublimation in vacuum at 150°C afforded an oil \((x + z) = 0.88\) which on pyrolysis gave a ceramic residue yield of only 30%. The oligomer resulting from such a treatment is structurally identical to the starting oil. This observation would qualify Cp₂ZrCl₂ as a pyrolysis catalyst. It is very probable that Cp₂TiCl₂ and Cp₂ZrCl₂ are reduced at higher temperatures by the OMS Si-H units and only then become effective crosslinking catalysts (eq. F2).

\[
\text{Cp}_2\text{MCl}_2 + n \text{Si-H} \xrightarrow{\Delta} \text{Cp}_2\text{MHCl} + (n-1) \text{Si-H} \xrightarrow{\Delta} \text{Cp}_2\text{MH}_2 \quad (\text{F2})
\]

Dimethyltitanocene also was explored as a possible dehydrogenative coupling catalyst for OMS. This compound had been shown by Harrod to catalyze poly(methylsilane) formation.\(^{34}\) A reaction of 0.5 mol% of Cp₂TiMe₂ with OMS in toluene at room temperature after 19 h afforded a green, soluble solid \((x + z) = 0.63\) which, upon pyrolysis, gave a 72% yield of ceramic residue. The high reactivity of Cp₂TiMe₂ as a dehydrogenative coupling catalysts results from very facile \(\alpha\)-hydride elimination from Cp₂TiMe₂, leading to formation of \([\text{Cp}_2\text{TiH}]_2\text{H}\) in the presence of silane species, as previously reported by Harrod and coworkers.\(^{83}\)
In contrast to dimethyltitanocene, use of Cp₂ZrMe₂ does not result in sufficient crosslinking at milder conditions. For example, refluxing of OMS with 0.5 mol% of Cp₂ZrMe₂ in hexane for 7 h, afforded an oil with (x + z) = 0.88. This oil, together with the catalyst, gave a ceramic residue yield of 77% on pyrolysis. Ultraviolet irradiation of OMS with Cp₂ZrMe₂ yielded an essentially unchanged (by IR and ¹H NMR spectroscopy) oil ((x + z) = 0.91) which, together with the catalyst, gave a 73% ceramic residue yield on pyrolysis. Since there was essentially no molecular weight increase of the oligomer but the ceramic residue yield of the oil was high, Cp₂ZrMe₂ is a pyrolysis catalyst.

Many Pt, Pd, Rh, and Ir complexes are known to catalyze the hydrosilylation of alkenes as well as the formation of Si-Si bonds from hydrosilanes.⁸⁴ Some examples of conventional catalysts for the dehydrogenative coupling reaction of RSiH₃ to give oligosilanes are Wilkinson's catalyst⁸⁵ and its derivatives. A room temperature reaction of 0.5 mol% of (Ph₃P)₃RhCl with OMS in toluene for 18 hours afforded a solid product with (x + z) = 0.50. The ceramic residue yield obtained on pyrolysis of this solid (still containing the catalyst) was 74%. A room temperature reaction in a evacuated flask in toluene solution, using 0.5 mol% of [Rh(COD)Cl]₂ as catalyst, afforded, after 19 h of stirring, an amber solid with (x + z) = 0.71. A ceramic residue of 74% was obtained upon pyrolysis of this solid which still contained the catalyst. Using similar reaction conditions and 0.5 mol% of (Ph₃P)₂Rh(CO)Cl as a catalyst, an amber solid polymer with (x +
$z) = 0.51$ was obtained. This polymer (together with the catalyst), gave an 85% yield of ceramic residue on pyrolysis. Pyrolysis of the latter polymer at 1500°C in Ar afforded a Si-rich $\beta$-SiC as well as some RhSi (JCPDS card# 35-1074) (Fig. F6). In all three cases, the solution turned amber in color and was accompanied by evolution of gas bubbles, presumably hydrogen, almost immediately after addition of the catalyst. In all three cases, the solid polymers were soluble in most common organic solvents. Based on the above data these catalysts can be classified as conventional and possibly pyrolysis catalysts. Although these rhodium complexes are not stable thermally, their Rh-containing dehydrogenative coupling products could serve as pyrolysis catalysts.
Figure F2a $^{29}$Si NMR DEPT spectrum of OMS thermolyzed with $(\text{Cp}_2\text{ZrH}_2)_n$, MULT = a) 1.5; b) 1.0; c) 0.5.
Figure F2b $^{29}$Si NMR DEPT spectrum of OMS photolyzed with $(\text{Cp}_2\text{ZrH}_2)_n$. MULT = a) 1.5; b) 1.0; c) 0.5.
Figure F3 TGA trace of OMS a) neat; b) blended with 0.5 mol% Cp₂ZrCl₂.
Figure F4 XRD pattern of pyrolysis (1500°C, Ar) product from a) thermolyzed OMS with \((\text{Cp}_2\text{ZrH}_2)_n\); b) OMS blended with \(\text{Cp}_2\text{ZrCl}_2\).
Figure F5 XRD patterns of pyrolysis (1500°C) products derived from: a) neat OMS; b) OMS blended with Cp₂ZrCl₂.
Figure F6 XRD pattern of ceramics derived from OMS reacted with (Ph₃P)₂Rh(CO)Cl after 1500°C pyrolysis in Ar.
It was of interest to determine whether metal alkoxides might induce
dehydrogenative crosslinking since it was found earlier that several alkoxides, in
conjunction with organosilicon polymers, protected carbon/carbon composites
against oxidation at high temperatures.\textsuperscript{86} In addition, Yajima and coworkers
explored the use of titanium tetrabutoxide as a crosslinking agent for
polycarbosilane. This polymer proved to be a good precursor for SiC/TiC fibers
(Tyranno\textsuperscript{TM} precursor).\textsuperscript{87} A number of alkoxides were considered for
dehydrogenative crosslinking of OMS. In all cases the compounds appeared to
have little or no effect on the oligomer. A catalytic amount (1.0 mol\% of
\text{Ti(OPr-i)}\textsubscript{4} was added to OMS and the mixture was heated in refluxing toluene in
one experiment and UV irradiated in hexane in another. In both cases an oily
product with almost no change in CH/SiH ratio (by \textsuperscript{1}H NMR) compared with the
original oil ((x + z) = 0.91) was obtained. The ceramic residue yield obtained in
pyrolysis of the oil (still containing the catalyst) was only 26\%. At 200\textdegree C, a
soluble, blue, tacky solid product with (x + z) = 0.48 was obtained. The ceramic
residue yield of the solid containing the catalyst obtained \textit{ex situ} pyrolysis was only
47\%. At 250\textdegree C, a sealed tube reaction of 1.0 mol\% \text{Ti(OPr-i)}\textsubscript{4} with OMS yielded
a sparingly soluble, black solid polymer with (x + z) = 0.45. The ceramic residue
yield of this polymer (with the catalyst) was 72\%. Similar behavior was found for
other early transition metal alkoxides, \text{Ti(OEt)}\textsubscript{4}, \text{Zr(OEt)}\textsubscript{4}, \text{Nb(OEt)}\textsubscript{5}, and
\text{Ta(OEt)}\textsubscript{5}. All yielded sparingly soluble solids and whose pyrolysis gave ceramic
residue yields of between 53-77%. Somewhat different behavior was exhibited by a boron alkoxide. A reaction of 1.0 mol% of B(OEt)$_3$ and OMS in refluxing undecane (b.p. 196°C) yielded a soluble, yellow solid with $(x + z) = 0.26$ whose pyrolysis gave a ceramic residue yield of 78%. However, a reaction in refluxing toluene yielded only a low molecular weight oligomer oil ($(x + z) = 0.78$).

Pyrolysis of a blend of 1.0 mol% of B(OEt)$_3$ with OMC afforded a 58% ceramic residue yield.

The selectivity of the catalysts towards the crosslinking sites of the OMS, SiH vs SiH$_2$, also was examined. To analyze the extent of selectivity, a $^{29}$Si NMR DEPT sequence was employed. A decrease in negative signal intensity (SiH$_2$) vs. the positive one (SiH) and comparison of this relative ratio with $^1$H NMR $(x + z)$ values aided in distinguishing the selectivity of each catalyst. For example, if the negative signal appeared to be very small and $(x + z) < 0.75$, the catalyst was considered to be selective. If, on the other hand, $(x + z) < 0.75$ and the negative signal intensity was comparable to the one observed in the original OMS, the catalyst would not appear to be selective. Cp$_2$ZrHCl and Ti(OPr-i)$_4$ were very indiscriminate, reacting equally with SiH and SiH$_2$ sites as observed by $^{29}$Si DEPT sequence NMR (Fig. F7). A generic example of random crosslinking is a neat thermolysis (Table F1) of the oligomer in a sealed tube at 250°C (Fig. F8).

However, Cp$_2$ZrH$_2$ (Fig. F2a) and (Ph$_3$P)$_2$Rh(CO)Cl (Fig. F9) were very
selective and reacted predominantly with SiH₂ functionalities. Selective catalysts can afford soluble polymers of higher molecular weight than unselective catalysts which randomly form Si-Si bonds and yield insoluble gels in large amounts.
Figure F7 $^{29}$Si NMR DEPT spectrum of OMS reacted with Cp$_2$ZrHCl, MULT = a) 1.5; b) 1.0; c) 0.5.
Figure F8 $^{29}$Si NMR DEPT spectrum of OMS thermolyzed at 250°C, MULT = a) 1.5; b) 1.0; c) 0.5.
Figure F9 $^{29}$Si NMR DEPT spectrum of OMS reacted with (Ph$_3$P)$_2$Rh(CO)Cl, MULT= a) 1.5; b) 1.0; c) 0.5.
A number of control experiments also were performed with neat OMS.

Irradiation of the oligomer with 2 MRad of $\gamma$-rays apparently cleaved Si-Si bonds, yielding an oil of lower viscosity than the original one ($\langle x + z \rangle = 0.94$). This oil gave a ceramic residue yield of 18% on pyrolysis. The oligomer oil also was thermolyzed in evacuated sealed vessels at temperatures stated in Table F1.

**Table F1 Results of OMS Heat Treatments in Sealed Tubes**

<table>
<thead>
<tr>
<th>Reaction Temp. ($^\circ$C)</th>
<th>Reaction Time (h)</th>
<th>Yield</th>
<th>(x+z) from $^1$H NMR</th>
<th>Ceramic yield by TGA (%)</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>190</td>
<td>12</td>
<td>95%</td>
<td>0.54</td>
<td>25</td>
<td>viscous oil</td>
</tr>
<tr>
<td>250</td>
<td>3</td>
<td>92%</td>
<td>0.58</td>
<td>43</td>
<td>tacky white solid</td>
</tr>
<tr>
<td>300</td>
<td>0.5</td>
<td>86%</td>
<td>0.36</td>
<td>71</td>
<td>white solid</td>
</tr>
<tr>
<td>400</td>
<td>0.5</td>
<td>68%</td>
<td>-</td>
<td>91</td>
<td>insoluble canary yellow solid</td>
</tr>
</tbody>
</table>

It appears that extensive thermal cross-linking of the oligomer in the absence of any catalyst takes place between 300 and 400$^\circ$C. Based on the IR spectra of samples pyrolyzed at 300 and 400$^\circ$C a possible Kumada rearrangement is taking place at these temperatures at which the transformation from a polysilane (CH$_3$Si-Si) to a polycarbosilane (HSiCH$_2$Si) is known to occur.\textsuperscript{6, 7} Figure F10 shows an IR spectrum (fingerprint region) with a CH$_2$ deformation mode commencing at 1348 cm$^{-1}$ in the sample pyrolyzed at 400$^\circ$C. Figure F11 depicts an overlaid increase in ceramic residue yields with an increase of pyrolysis temperature for the thermolyzed OMS described in Table F1. It is noteworthy
that OMS prepyrolyzed to 400°C gives a ceramic yield of 91%, which is the theoretical ceramic residue yield for (MeSiH)ₙ.

It also was observed that different OMS pyrolysis conditions yield ceramics of differing purities. For example, prepyrolysis of OMS in a thick-walled glass tube at 450°C for two hours yielded an insoluble yellow solid product which on pyrolysis to 1500°C in argon afforded SiC almost free of elemental silicon (based on XRD), as compared with ceramics derived from the untreated OMS oil (not prepyrolyzed) (Fig. F12). The overall heating program for the pyrolysis of the ceramic precursors plays an important role in the purity of final ceramics and will be further addressed *vide infra*.

It seems, judging from the results of thermolysis control experiments, that the transition metal alkoxides have an almost negligible effect on the dehydrogenative coupling of oligosilane.
Figure F10 FT-IR spectrum (fingerprint region, KBr pellet) of OMS pyrolyzed at a) 300°C and b) 400°C in a sealed tube (note the CH₂ deformation mode at 1348 cm⁻¹).
Figure F11 TGA traces of OMS thermolyzed at a) 400°C; b) 300°C; c) 250°C; d) 190°C.
Figure F12 XRD patterns of 1500°C in Ar pyrolysis product of a) OMS prepyrolyzed to 450°C; b) neat OMS oil.
This classification of dehydrogenative coupling catalysts may prove useful when different rheologies of polymeric precursors are desired for specific applications. For example, if a low viscosity, high ceramic yield oil is required as a lubricant for injection molding of a ceramic part, a pyrolysis catalyst such as Cp₂ZrCl₂, Cp₂TiCl₂ or Cp₂ZrMe₂ may be useful. On the other hand, if a high molecular weight solid polymer is needed for fiber spinning or film casting, a conventional or conventional/pyrolysis catalyst such as (Cp₂ZrH₂)ₙ or (Ph₃P)₂RhCl(CO) may be employed.

In many cases the catalyst unavoidably becomes a part of the polymer network after the crosslinking reaction. Nevertheless, in the case of Cp₂ZrHCl, the unchanged catalyst could be retrieved by precipitation in hexane in close to 100% yield.
Section G

High Molecular Weight Poly(methylsilane) - a Precursor to Near-Stoichiometric SiC
A high molecular weight poly(methylsilane) that is a stoichiometric SiC precursor is a worthwhile goal. It is generally believed that branching and crosslinking of the polysilane is necessary to afford high ceramic yields of SiC when the polymer is pyrolyzed.

There are various ways of achieving high molecular weight polysilanes and hence high ceramic yields. One route explored by Bianconi and Weidman$^{49}$ involved the reductive coupling of RSiCl$_3$ compounds by Na/K alloy, which yields a soluble polymeric network, $(RSi_{1.5})_n$. More recently, Seyferth et al.$^{81b}$ reported high molecular weight poly(methylsilane)s which were synthesized by reacting oligo(methylsilane) with a catalytic amount of an early transition metallocene derivative. Such catalysts, as shown in the previous section, induce a dehydrogenative coupling reaction which yields branching and crosslinking and consequently affords a polymer whose pyrolysis gives a high ceramic yield of near-stoichiometric SiC. An extension of this work was presented in Section F of this chapter. Also, Harrod et al.$^{34b}$ utilized LiAlH$_4$ as a cross-linking catalyst for oligo(methylsilane) to produce a high molecular weight poly(methylsilane).

Several investigators, as noted in an earlier section, have explored the use of alkali metals for the combined reductive-dehydrogenative coupling of silanes. Schilling and coworkers at Union Carbide discovered a useful way of making an efficient SiC precursor.$^{88}$ They explored the reaction of K with MeSiHCl$_2$ and vinyl chlorosilanes to prepare a soluble polysilane-polycarbosilane preceramic
network (eq. G1). When sodium was used in stead of K only linear polysilanes resulted (eq. G2).

\[
\text{MeSiHCl}_2 + \text{ViSiMeCl}_2 \overset{K}{\rightarrow} (\text{MeSiH})_x(\text{CH}_2 \text{CHSiMe})_y(\text{MeSi})_z \quad (G1)
\]

\[
\text{MeSiHCl}_2 + \text{ViSiMeCl}_2 \overset{Na}{\rightarrow} (\text{MeSiH})_x(\text{ViSiMe})_y \quad (G2)
\]

Preceding Schilling's work, Peterson and Arkles had found an economic way of synthesizing cyclic polysilanes by using chlorohydro silanes and lithium or lithium-alkali metal alloys. In this reaction Si-Si bonds are formed by the removal of halogen and hydrogen from the chlorohydro silane by action of alkali metals (eq. G3).

\[
2 \text{RR'SiHX} + 2 \text{M} \rightarrow (\text{RR'Si})_n + 2 \text{MX} + \text{H}_2 \quad ! (G3)
\]

Brown-Wensley and Sinclair at 3M and Wood at MIT have independently prepared partly crosslinked poly(methylsilane) by the reaction of MeSiHCl₂ and Na in THF (eq. G4).

\[
\text{MeSiHCl}_2 \overset{Na}{\underset{\text{THF}}{\rightarrow}} [(\text{MeSiH})_x(\text{MeSi})_y]_n \quad (G4)
\]

In the present study an in situ branching and crosslinking of oligo(methylsilane) (OMS) by Na and ultrasonic activation was explored. The use of Na instead of K provides some practical and economic advantages. Sodium is about 20 times less expensive than potassium and is safer to handle. This section examines more closely the second stage product of the reductive coupling of CH₂SiHCl₂ by Na using ultrasonic activation. This high molecular weight, high
ceramic yield poly(methylsilane) is obtained by ultrasonication of CH₃SiHCl₂ and Na in hexane/THF or toluene/THF 7/1 v/v for more than about 22 hours at 47°C. Crosslinking of the oligo(methylsilane) oil with Na at the same reaction conditions also will be discussed.

The Wurtz reductive coupling of CH₃SiHCl₂ using sodium and ultrasonic activation (350 W, 45-56 kHz) in its first stage (10-20 hours of ultrasonication) afforded the usual 65-91% yield of clear oil oligo(methylsilane). In addition, a high molecular weight solid poly(methylsilane) (PC-1), formed in about 10% yield, was found entrapped within the large, yellow NaCl crystals adhering to the unreacted sodium (Fig. B1). According to the ¹H NMR spectrum value of (x+z) = 0.65 (Fig. G1). This polymer was isolated by first removing the NaCl crystals from the unreacted sodium and then extracting the NaCl crystals with oxygen-free water. The polymer is a white powder that is soluble in most common organic solvents and which is extremely pyrophoric in air. According to its IR spectrum, the polymer does not contain any Si-O-Si bonds which would result from reaction of the polymer with water (Fig. G2). Pyrolysis of this polymer afforded a 77% yield of ceramic residue whose only crystalline phase is β-SiC according to XRD pattern (Fig. G3). Based on the elemental analysis the polymer still contains 0.14% sodium. By GPC this polymer shows a trimodal molecular weight behavior with the highest molecular weight at about 10⁵ relative to polystyrene (Fig. G6d).
Figure GI \(^1\)H NMR spectrum of poly(methyl)silane) extracted from NaCl crystals.
Figure G2 FT-IR spectrum of poly(methylsilane) extracted with water from NaCl crystals (NaCl disks).
Figure G3 XRD patterns of ceramics obtained from 1500°C in Ar pyrolysis of poly(methylsilane) extracted from NaCl where the main product was a) solid poly(methylsilane); b) oligo(methylsilane) oil
A higher yield (50 - 65%) of a high molecular weight poly(methylsilane) was obtained from the CH$_3$SiHCl$_2$ and sodium reaction in 7/1 v/v hexane/THF or toluene/THF (TS-1) using ultrasonication for more than 22 h (preferably 30 - 40 h). Possibly if high power ultrasonication is utilized the time of reaction may decrease. This polymer (TS-1) was isolated as highly pyrophoric, orange-yellow solid ((x + z) = 0.33 - 0.41) which is soluble in toluene and partly soluble in hexane. It afforded the ceramic residue in 75 to 87% yield upon pyrolysis. The elemental analysis of TS-1 indicated the presence of residual Na in 0.64%. Pyrolysis of this polymer in Ar at 1000°C afforded a ceramic containing 0.41% Na. After pyrolysis in argon at 1500°C for 3 h only 0.14% Na remained. Probably, if the pyrolysis of this polymer was carried out for longer periods of time or at higher temperature, the amount of Na would diminish to ppm levels since NaH decomposes at 800°C and elemental Na (b.p. 882.9°C) probably would volatilize.$^{90}$ The products from both stages of the reductive coupling reaction (i.e., oligomer oil and solid poly(methylsilane) have almost identical "structure" based on their IR spectra (Fig. G4). However, the IR spectrum of the second stage product shows a diminished absorption due to γSiH$_2$ at 930 cm$^{-1}$. The diminished content of SiH$_2$ was confirmed by DEPT $^{29}$Si NMR vide infra. Also, the pyrolysis product of the first and second stage showed almost identical XRD patterns (Fig. G5a, b).
Some reaction conditions were also investigated. It was observed that the presence of aromatic hydrocarbons such as toluene affords higher molecular weight polymer (hence higher ceramic residue yields) than when hexane is used (Fig. G18). The highest yield of high molecular weight, soluble product is obtained when the duration of ultrasonication is 40 to 60 h. Above 60 h of ultrasonication some insoluble, crosslinked product is formed. Gradual addition of the chlorosilane to 2.5 Na in 7/1 v/v toluene/THF affords higher conversion to product. An excess of Na (≥ 2.5 molar equivalents) is required to obtain the high molecular weight poly(methylsilane). Use of a stoichiometric amount of Na yields only an oil product with Si-Cl bonds, even after 40 h of ultrasonication.

The extended time reductive coupling reaction also affords large NaCl crystals which contain high molecular weight poly(methylsilane) \((x + z = 0.36)\) whose pyrolysis gives a ceramic residue yield of 73%. Based on the GPC trace (Fig. G6b), the polymer extracted from the NaCl has a lower molecular weight distribution than the one extracted from the NaCl in the reaction yielding the oligomer oil (Fig. G6d). Pyrolysis of the former yields a Si-rich \(\beta\)-SiC based on its XRD pattern (Fig. G3). In contrast, almost pure \(\beta\)-SiC is obtained in the pyrolysis of the polymer extracted from the NaCl crystals from the reaction which gives the OMS oil (Fig. G3).
Figure G4 FT-IR spectrum of a) oligo(methylsilane) oil and b) TS-1 (NaCl disks).
Figure G5a XRD pattern of ceramics derived from pyrolysis in argon of oligo(methylsilane).
Figure G5b XRD pattern of ceramics derived from pyrolysis in argon of poly(methylsilane) TS-1.
Figure G6 GPC traces of: a) TS-1 synthesized by prolonged ultrasonication in toluene/THF; b) NaCl extracted PC-1 where the main products was TS-1 depicted in a); c) original oligo(methylsilane) clear oil; d) NaCl extracted PC-1 where the main product was an oil depicted in c) (relative to polystyrene).
A third type of high molecular weight poly(methylsilane) is obtained by the action of Na with ultrasonication on previously synthesized oligo(methylsilane). In this reaction 0.5 molar equivalent of Na and 1.0 molar equivalent of oligo(methylsilane) in 7/1 v/v toluene/THF were ультразонicated for about 5 hours. This reaction does not take place in the absence of ethereal cosolvent. This reaction yields a toluene-soluble, pyrophoric, pumpkin-yellow-orange solid polymer (TS-2) which, upon exposure to daylight changes color to green \((x + z) = 0.36\). Upon pyrolysis in Ar, this polymer affords near-stoichiometric SiC in about 87% yield. The GPC trace of this polymer depicts a trimodal molecular weight distribution with a broad, high molecular weight region (~10,000) and two narrow low molecular weight regions (~1,000 and ~500 respectively) (Fig. G7a). The low molecular weight end can be extracted with hexane (TS-2H) as shown in the GPC trace (Fig. G7b) and the high molecular weight is soluble in toluene (TS-2T) (Fig. G7c). About 80% of TS-2 was soluble in hexane. The TS-2 polysilane appears to have a higher molecular weight than TS-1 polymer (Fig. G18). Such molecular weight behavior appears to be unique to crosslinked systems induced by sodium. It also was observed that, in general, high molecular weight poly(methylsilane) gives higher purity β-SiC on pyrolysis (less elemental Si) compared to the lower molecular weight species, as shown by the XRD's (Figs. G3, G8). The elemental analysis of TS-2 indicated the presence of 1.45% residual
Na. The hexane-soluble fraction (TS-2H), however, contained only 0.096% Na. Pyrolysis of TS-2 in Ar at 1000°C afforded a ceramic that contained 0.68% Na. After pyrolysis at 1500°C for 3 h only 0.055% Na remained. The orange color of the polymer is indicative of living silyl anion intermediate. To terminate -Si Na⁺ isolated polymer was redissolved in toluene and enough Mel was added to change the color of the solution from yellow-orange to clear, hence quenching the living intermediate. After removal of insoluble material, the solvent was removed at reduced pressure, leaving a white solid polymer which, based on elemental analysis, contained 1.11% Na (before quenching the polymer contained 1.72% Na) and which upon pyrolysis in Ar afforded a ceramic residue in 74-79% yield. This polymer appeared to be more air sensitive and pyrophoric than the starting yellow-orange polymer (Fig. G13). The molecular weights and their distributions of Mel quenched and of unquenched polysilanes are identical. The Mel quenched polymer also does not show any melting behavior.

The present study revealed that the heating program for pyrolysis of poly(methylsilane) is an important factor in achieving stoichiometric SiC. Special attention should be paid to the temperature range at which a transition from polysilane to polycarbosilane takes place. Judging from the literature and present results, a possibility arises that the temperature of the Kumada rearrangement depends on the molecular weight of a silane. The original rearrangement was performed on a Me₆Si₂ in the gas phase and did not take place until 600°C. The
rearrangement of the OMS oil in a sealed tube occurred between 300 and 400°C as evidenced by the fingerprint region of their IR spectrum (Fig. F10). The heat treatment of TS-2 polymer in an open tube furnace in argon showed that a Kumada rearrangement takes place between 200 and 300°C as depicted in the IR spectrum (fingerprint region) by the appearance of the CH₂ deformation band at 1349 cm⁻¹ (Fig. G9). Unfortunately further evidence by solution NMR spectroscopy is limited by non-solubility of the rearranged polymers. This observation is in close agreement with recent results of Harrod, Butler, and coworkers who reported based on IR spectra a Kumada rearrangement of a poly(methylsilane) film cast on a silicon wafer at about 200°C. Therefore, when during the pyrolysis of poly(methylsilane) a 2 h hold is incorporated into the pyrolysis program at about 300°C, on the way to 1000°C and higher, the final SiC is almost free of elemental silicon based on the XRD patterns (Fig. G10).

The current study showed that the sum of elemental analyses of poly(methylsilane) (Si, C, H) and ceramics (Si, C) derived from it generally was between 93 and 97%. A similar observation can be seen throughout the literature. For example, Yajima reported values for the elemental analysis of the polycarbosilane that added up to 93.12%. Schilling's polycarbosilane network on pyrolysis to 1200°C gave ceramics whose elemental analysis added up to only 86.10%. More recently, Harrod and coworkers reported elemental analyses
performed by Galbraith Laboratories of ceramics derived poly(methylsilane) not containing any catalyst that added up to 95.89% and 95.94%. There are several factors which may influence the poor analysis results: the difficulty of complete combustion of high silicon content precursors and the refractory ceramic samples; the difficulty associated with handling of very air sensitive samples; the particle size (i.e., surface area of the ceramics). The Si analysis of the precursor and of the ceramic derived from it seems to be a special challenge. In some cases varying the weight of the analytical sample may improve the recovery even by 10%.

Therefore, a close collaboration is advisable with the elemental analysis services for a possible process development of Si and C analysis.

The UV absorption spectrum can be a measure of the Si-Si chain length as reported by West and coworkers. In general, the longer the (Si)$_n$ chain length, the higher is $\lambda_{\text{max}}$ of the UV absorption. In the case of the oligo(methylsilane) oil, two absorptions are present, the main one at 234 nm with a shoulder at 262 nm. The hexane-soluble fraction of the poly(methylsilane) (TS-2H) also shows two UV absorptions, with the main one at 230 nm and a smaller one at 278 nm. Finally, the toluene-soluble fraction (TS-2T) shows three UV maxima at: 230 nm, 258 nm, and 278 nm. This indicates that (1) probably due to the polymodal character of the polymer several $\lambda_{\text{max}}$ are seen and (2) $\lambda_{\text{max}}$ at 278 nm is due to the higher molecular weight fraction. Both quenched with MeI and unquenched TS-2 polymers show identical UV absorption spectra.
Figure G7 GPC traces of poly(methylsilane) (TS-2) crosslinked with Na, a) the entire molecular weight distribution; b) hexane extracted fraction; c) toluene extracted fraction (relative to polystyrene).
Figure G8 XRD patterns of the ceramics derived from 1500°C in Ar pyrolysis of TS-2, a) hexane extracted fraction (low molecular weight); b) toluene soluble fraction (higher molecular weight).
Figure G9 The fingerprint region of the IR spectrum of TS-2 poly(methylsilane) heated under Ar for 0.5 h at a) 200°C and b) 300°C (KBr pellet) (Note the splitting of the 1240 cm\(^{-1}\) band and broadening of 1030 cm\(^{-1}\) band is indicative of reaction of the polymer with a trace of oxygen\(^{91}\) after the heat treatment).
Figure G.10 XRD patterns of ceramics derived from Ar pyrolysis of TS-2.
A comparison of TS-1 and TS-2 solid polymers and the one obtained by Wood\textsuperscript{36} from the Wurtz reductive coupling of CH\textsubscript{3}SiHCl\textsubscript{2} and Na in THF ((x + z) = 0.45) shows that the current polymer has considerably higher molecular weight and a trimodal molecular weight distribution while Wood's polymer has a bimodal distribution (Fig. G11). Also, the current polymers gives higher yields of ceramic residue 75 - 87\% as opposed to the original Wood's "THF" polylsiline, 48 - 55\% (Fig. G12). In addition, Wood's polymer spatters from the pyrolysis boat during pyrolysis while TS-1 or TS-2 exhibits overall shrinkage without such spattering.
Figure G11 GPC traces of: a) PMS obtained by reflux in THF of MeSiHCl$_2$ and Na (Wood's polymer); b) TS-2; c) PMS obtained from ultrasonication MeSiHCl$_2$ and Na in THF (relative to polystyrene).
Figure G12 TGA traces of: a) TS-1 synthesized by prolonged reductive coupling; b) PMS synthesized by reductive coupling of MeSiHCl₂ with Na in THF; c) oligo(methylsilane) oil.
The present high molecular weight poly(methylsilane) has one problem, namely its pyrophoricity. However, this problem can be circumvented by the addition of an antioxidants. It was found recently by Bryson that the addition of 1 wt% of 2,6-di-tert-butyl-4-methylphenol (BHT) or its derivatives improve the air stability of highly air-sensitive Schilling-type polysilanes. Addition of about 5 wt% (1 mol%) of BHT to TS-1 eliminates its pyrophoricity and inhibits its air oxidation for weeks (Fig. G13). After the addition of BHT polymer becomes white because the phenol reacts with the silyl anion groups. Also, the $^{29}\text{Si}$ NMR spectra of TS-1 that had not been exposed to air and of a sample containing BHT that had been exposed to air were identical.

![Graph](image)

**Figure G13** A graph depicting an effect of BHT on poly(methylsilane) exposed to air.

Application of this polymer system as a precursor to ceramic fibers and films also has been explored. Thin polymer films of the TS-2H (hexane-soluble)
fraction have been cast on an alumina substrate by dip coating and pyrolyzed at 1000°C in Ar, affording a partly crystalline SiC film. The film appears to be mostly uniform with the exception of a few flaws as depicted in Fig. G14. Recently, Harrod's poly(methylsilane) derived from dehydrogenative coupling of MeSiH₃ with Cp₂TiMe₂ was spun into fibers. Addition of a curing agent was necessary to prevent the fiber from melting during the pyrolysis. In the present study, fibers were formed by manually pulling them from a viscous toluene solution of TS-2H and subsequently were pyrolyzed at 1000°C in Ar (Fig. G15). The resulting ceramic fibers were homogenous and solid inside. The fibers did not require prior curing by irradiation or exposure to oxygen before their pyrolysis since TS-2 does not show a melting behavior. Monolithic pellets also were prepared from the TS-2T fraction. The monoliths were observed to shrink 70% by volume without a sign of melting after being pyrolyzed in Ar at 1500°C for 3 hours. The density changed from 1.03 g/cc (green body) to 2.27 g/cc (71 % of the theoretical of density!) for the final monolith. The Vickers microhardness of the monolith was about 2400 HV which is comparable with the hardness of commercially available SiC. A study of morphology of the monolith revealed the presence of elemental silicon in the bulk β-SiC matrix. The silicon deposits occurred in regularly arranged veins (~1 μm in diameter) as depicted in the optical micrograph as well as in the SEM image and its silicon map (Fig. G16).
**Figure G14** SEM micrographs of SiC film on alumina substrate prepared from TS-2H and pyrolyzed in Ar at 1000°C.
Figure G14 SEM micrographs of SiC film on alumina substrate prepared from TS-2H and pyrolyzed in Ar at 1000 °C.
Figure G15 SEM micrograph of SiC fiber span from TS-2H and pyrolyzed in Ar at 1000°C.
Figure G16 Morphology of SiC monolith derived from TS-2T a) SEM micrograph (note the silicon veins), b) (A) the size of the green monolith before pyrolysis, (B) cross-section of the monolith after pyrolysis.
Figure G16 ESEM micrograph: a) image of the monolith's morphology with a vertical silicon deposit; b) silicon map of image a) (lighter areas indicate Si rich regions).
Various background experiments have been performed to determine the nature of the reaction of oligo(methylsilane) with sodium. Reflux conditions in place of ultrasonication yielded mostly insoluble products with only a trace of a soluble, tacky solid. Likewise, a 65.5 h ultrasonication of \((\text{CH}_3)_2\text{SiHCl}\) with sodium has yielded only \([(\text{CH}_3)_2\text{SiH}]_2\) and no high polymers. Also an ultrasonication for 89.5 hours of the oligo(methylsilane) in 7/1 v/v hexane/THF in the absence of sodium did not result in any appreciable structural alteration of the original oligomer. It would appear that the dehydrogenative coupling reaction of silanes with Na is specific only for species having extensive Si-Si linkages.

Noteworthy is that the molecular weight characteristics such as distribution, relative abundance, and modality of the GPC traces appear to be unique for each individual dehydrogenative coupling catalyst system (discussed in Section F) used to crosslink the oligo(methylsilane) (Fig. G17). More study is required to determine whether or not the GPC trace may be used as a fingerprint of a particular catalyst/polymer system. There is a striking resemblance between the GPC traces of oligo(methylsilane) crosslinked by NaH and the one crosslinked by Na alone or by prolonged Wurtz coupling (Fig. G18). NaH was examined as a possible crosslinking catalyst for OMS. A reaction of 15 mol% of NaH with OMS in THF (or at least 2/7 THF/hexane v/v ratio) using ultrasonication at 27°C for 5 hours gave a soluble solid polymer in 84% yield. Its pyrolysis in argon gave a
ceramic residue in 53% yield. The most reasonable choice for the reaction mechanism in crosslinking reaction of oligo(methylsilane) with Na would involve a silyl anion intermediate generated by Na and NaH formed *in situ.*
Figure G17 GPC traces of oligo(methyilsilane) crosslinked with: a) NaH; b) (Ph₃P)₂Rh(CO)Cl; c) Cp₂ZrHCl; d) (Cp₂ZrH₂)ₙ (relative to polystyrene).
Figure G18 GPC traces of oligo(methyilsilane) crosslinked with a) Na (TS-2) and d) NaH. Poly(methyilsilane) synthesized by extensive ultrasonication in b) toluene/THF system (TS-1), c) hexane/THF system (relative to polystyrene).
Corriu and coworkers\textsuperscript{94} have explored reaction of the Si-H bond with alkali metal hydrides, NaH, KH, or LiAlH\textsubscript{4}, and subsequent formation of Si-Si bonds. The proposed reaction mechanism involved hypervalent silicon intermediates. In all three cases of crosslinking the oligo(methylsilane) with Na, NaH, or simply prolonged Wurtz coupling of the chlorosilane, yellow orange solutions are formed. In the case of prolonged ultrasonication, the yellow-orange color emerges after about 22 h of reaction at 47°C. The appearance of the yellow-orange color probably is due to a solvated silyl anion. These observations, in conjunction with Corriu's work, would suggest the reaction mechanism depicted on Scheme G1.

The first step of this mechanism involves ultrasonication-activated electron transfer from Na which in the presence of neighboring Na forms a silyl anion and eliminates NaH. The NaH elimination probably is aided by its solvation in THF since these reactions do not take place in pure hydrocarbon solvents. The generated NaH then participates in further crosslinking. It appears that this current crosslinking mechanism is rather selective towards SiH\textsubscript{2} functionalities of the oligomer as shown in the DEPT $^{29}$Si NMR (Fig. G19).
Scheme G1 - Initiation
Scheme G1 - Propagation
Figure G19 DEPT $^{29}$Si NMR spectrum of TS-1. MULT = a) 1.5, b) 1.0, c) 0.5.
The recommended procedure for synthesis of high molecular weight poly(methylsilane) (TS-2) would involve crosslinking of oligo(methylsilane) with Na in 7/1 v/v toluene/THF and using ultrasonication. The high molecular weight poly(methylsilane) may be prepared from previously synthesized oligomer (about 10 - 20 h) and subsequently crosslinked with Na (about 5 h) using ultrasonic activation. As compared with other means of synthesis of high molecular weight poly(methylsilane), namely, crosslinking of oligo(methylsilane) with expensive catalysts or dehydrogenative coupling of pyrophoric MeSiH₃, the current route, due to its simplicity, appears to be very efficient and cost effective. The SiC ceramics prepared from the TS-2 poly(methylsilane) can be nearly pure and not containing any transition metal ceramic impurities as it is the case with the current state of the art.
Section H

Experimental
General Comments

All glassware was oven or heat gun-dried under vacuum or under a stream of nitrogen or argon prior to use. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium/benzophenone. Toluene was distilled from sodium and hexane from LiAlH₄. Solvents and liquid reagents were deoxygenated by bubbling nitrogen or argon through them for ca. 30 min to an h prior to use. Chlorosilanes were obtained from Aldrich, Petrarch Systems, Hüls America, or Silar Inc. and were distilled from magnesium under Ar prior to use. Reagent grade sodium was further purified by melting it in stirred, refluxing xylene, and allowing it to set in one large mass upon cooling.

The polycarbosilane precursor to Nicalon® fiber was purchased from Dow Corning Co., X9-6348, lot # PG110064.

Dehydrogenative coupling catalysts were prepared according to published procedures: \((\text{Cp}_2\text{ZrH}_2)_n\),\(^{95}\) \(\text{Cp}_2\text{ZrMe}_2\),\(^{96}\) \(\text{Cp}_2\text{TiPh}_2\),\(^{97}\) \(\text{Cp}_2\text{TiMe}_2\).\(^{98}\) Other reagents were purchased from Aldrich Chemical Company, Inc. (\(\text{Cp}_2\text{ZrHCl}\), \(\text{Cp}_2\text{HfCl}_2\), \((\text{Ph}_3\text{P})_3\text{RhCl}\), \(\text{PhLi}\) (1.8 M solution in cyclohexane/ether), \(\text{MeLi}\) (1.4 M solution in diethyl ether), \(\text{PhOH}\), \(\text{B(OEt)}_3\), \(\text{Ti(OPr-i)}_4\), \(\text{Ti(OEt)}_4\), \(\text{Zr(OEt)}_4\), \(\text{Nb(OEt)}_5\), and \(\text{Ta(OEt)}_5\). Boulder Scientific Co., donated \(\text{Cp}_2\text{TiCl}_2\) (lot # BSC-146-0120) and \(\text{Cp}_2\text{ZrCl}_2\) (lot # BSC-153-0109). The catalysts \((\text{Ph}_3\text{P})_2\text{RhCl(CO)}\) and \([\text{Rh(COD)Cl}]_2\) were kindly provided by Dr. T. Craig Masterman.

Ultrasonic activation was accomplished using an internally cooled Branson
3200 ultrasonic cleaner operating at 45-56 kHz, 300 W.

The coating of alumina substrate was done using a modified syringe pump model 341A made by Sage Instrument division of Orion Research Inc. with a draw rate of 0.01 mm/s.

The UV photolysis experiments were performed using a Hanovia medium pressure mercury lamp (200 W, λ = 254 nm, surrounded by quartz water-cooled jacket) in quartz glassware. The distance of a lamp from the reaction flask was about 15 cm.

$^1$H NMR spectra were recorded on a Varian XL-300 spectrometer operating at 300 MHz. They were obtained using solutions in $C_6D_6$, $CD_2Cl_2$, or $CDCl_3$ and are reported in $\delta$ units, ppm downfield from TMS.

The heteronuclear NMR spectra were recorded on the same instrument operating at 75.5 MHz for $^{13}C$ and 59.6 MHz for $^{29}Si$ NMR and using the default setting. In the DEPT $^{29}Si$ NMR mode, 140 Hz coupling constant was used and three different pulse angles: MULT = 0.5, 1.0, 1.5 were applied.

Infrared spectra were obtained using a Perkin-Elmer 1600 Series FT-IR in the single mode, and gathering 16 signals per scan with 4 cm$^{-1}$ resolution.

Ultraviolet spectra were obtained of n-hexane solutions (1.0 cm quartz cuvettes) using a Hewlett-Packard 8452A Diode Array Spectrophotometer.

Mass spectra were obtained using a Finnigan MAT System 8200 instrument operating at 70eV and 60°C in electron impact mode. Plasma Disortion/Time Of
Flight experiment was performed on BIOION™ 20 using ionization source of
252Cf and Acc voltage 13 kV.

Gel permeation chromatography (GPC) was performed using a
Waters/Millipore 150-C ALC/GPC instrument, equipped with 10³ and 10⁴ Å
Ultrastyragel and 60 Å μ-Porasil columns. Toluene (HPLC grade) was used as
eluent at 1 mL/min flow rate at 25°C. The molecular weights reported are relative
to the monodisperse polystyrene standards purchased from Polysciences Inc.

Signar molecular weight measurements were conducted according to
published procedure.⁵⁴

Elemental analyses were performed by the Galbraith Laboratories and
Scandinavia Microanalytical Laboratoys, Denmark (only C, H, and N). Estimated
error ranges for analysis of ceramic samples are ±1.5% for carbon and ±3.0% for
silicon.

Thermogravimetric analysis (TGA) data were obtained using a Perkin-
Elmer System 4 connected to a Perkin-Elmer TGS-2 Thermal Analyzer. Samples
(3 - 8 mg) were heated, in argon, from 50 - 950°C at a rate of 10°C/min.

Scanning electron micrographs were obtained using an Environmental
Scanning Electron Microscope (Electro Scan) and a Hitachi S-530 model operating
with Acc of 20 kV. The HNU EDX detector in conjunction with System 5000.

X-Ray diffraction was performed on a Rigaku Rotaflex RU-300 powder X-
ray diffractometer using Cu Kα (λ = 1.5418 Å) radiation from a rotating anode
source (50 kV, 200 mA). Identification of crystalline phases in the powder diffraction patterns was made by comparison with JCPDS file.

Reaction Between MeSiHCl$_2$ and 2.5 Na in Refluxing Hexane/THF 7/1 v/v.

(PC/2/47).

This experiment was performed in order to reproduce the original oligo(methylsilane) made by Wood.$^{36}$

A 500 mL, three-necked round-bottomed flask equipped with a reflux condenser, a pressure-equalizing addition funnel, a magnetic stir-bar, and a rubber septum was charged with 29.2 g (1.27 mol) of Na shot (~10 mm in diameter), 15 mL of THF and 105 mL of hexane. The addition funnel was charged with 52.5 mL (57.7 g, 0.502 mol) of MeSiHCl$_2$. The chlorosilane was added dropwise to the sodium during 2 h at room temperature. Subsequently, the reaction mixture was heated at reflux for 16.5 h. The flask was allowed to cool to room temperature. The contents, together with three 30 mL hexane washings, were cannulated into a thick walled centrifuge bottle and centrifuged for 1 h. The clear supernatant solution was cannulated into a Schlenk flask and trap-to-trap distilled at reduced pressure into a cooled receiver. A residue of 12.3 g (55% yield) of a milky, white oil (soluble in most organic solvents) remained.

$^1$H NMR (300 MHz, C$_6$D$_6$): $\delta$ 0.5 ($W_{1/2}$ = 90 Hz, 3.5 H, SiCH$_3$),

4.0 ($W_{1/2}$ = 60 Hz, 1.0 H, SiH, SiH$_2$);

CH/SiH = 3.5.
IR (thin film, NaCl, cm⁻¹): 2956(s), 2892(s), 2794(w), 2105(vs), 1918(w), 1409(m), 1247(s), 1046(m), 931(s), 863(vs), 774(vs), 683(vs), 584(s).

The product was identical to the one obtained by Wood.³⁶

Reaction Between MeSiHCl₂ (Gradual Addition) and 2.5 Na in 7/1 v/v Ratio of Hexane/THF Using Ultrasonic Activation at 20°C. (PC/2/55).

This experiment was performed in order to synthesize oligo(methylsilane) using ultrasonic activation.

A 500 mL, three-necked round-bottomed flask equipped with a reflux condenser, a pressure-equalizing addition funnel, and a rubber septum was charged with 29.2g (1.27 mol) of Na shot (~10 mm in diameter), 15 mL of THF and 105 mL of hexane. The addition funnel was charged with 52.5 mL (57.7 g, 0.502 mol) of MeSiHCl₂. Then the flask was placed in the ultrasonic bath and the MeSiHCl₂ was added dropwise, with ultrasonication over the course of 2 h. Ultrasonication was continued for an additional 16 h. Upon completion of the reaction, the solution was blue, more viscous than the starting solution and the Na chunks were broken up and covered with large crystals. The solution and small solid particles were cannulated into a thick walled centrifuge bottle and the remaining solids were washed three times with 30 mL portions of hexane and the washings were added to the bottle. The mixture was centrifuged for 1 h. The clear supernatant solution was cannulated into a Schlenk flask and trap-to-trap distilled to remove solvents.
A residue of 20.4 g (91% yield) of a translucent oil (soluble in most organic solvents) remained.

$^1$H NMR (300 MHz, C$_6$D$_6$): $\delta$ 0.5 ($W_{1/2} = 90$ Hz, 3.4 H, SiCH$_3$),
4.1 ($W_{1/2} = 90$ Hz, 1.0 H, SiH, SiH$_2$).
CH/SiH = 3.4.

$^{13}$C NMR (75.5 MHz, C$_6$D$_6$): $\delta_c$ -12.3 to -5.1 ($W_{1/2} = 230$ Hz, SiCH$_3$).

$^{29}$Si NMR (59.59 MHz, C$_6$D$_6$): $\delta_{Si}$ -71, -67 ($W_{1/2} = 300$ Hz, SiH);
-64, -61 ($W_{1/2} = 300$ Hz, SiH$_2$)

IR (thin film on NaCl, cm$^{-1}$): 2957(s), 2894(s), 2797(w), 2107(vs), 1920(w),
1410(s), 1247(s), 1083(w), 931(vs), 862(vs),
771(vs), 685(vs), 584(s).

Ceramic Residue Yield (TGA): 11%

This reaction yielded oligo(methylsilane) in highest yield.

Recommended Procedure for Synthesis of Oligo(methylsilane). Reaction Between MeSiHCl$_2$ and 2.5 Na in 7/1 v/v of Hexane/THF Using Ultrasonic Activation at 45°C. (PC/3/61; PC/4/14, 18, 19, 28, 51; PC/5/12, 29, 59, 66; PC/7/19, 26, 60;
PC/8/12, 17)

This experiment explored an effect of having all reactants present at the beginning.

A 100 mL Schlenk flask was charged with 14.6 g (0.635 mol) of Na shot
(~10 mm in diameter), 7.5 mL of THF, 52.5 mL of hexane, and 26 mL (28.6 g,
0.249 mol) of MeSiHCl$_2$. The flask then was placed in the ultrasonic bath for
19 h. The reaction mixture and three 20 mL hexane washings then were cannulated into a thick walled centrifuge bottle and centrifuged for 1 h. The clear supernatant solution was cannulated into a Schlenk flask and trap-to-trap distilled at reduced pressure leaving 8.2 g (75% yield) of clear oil which was soluble in most common organic solvents. The rest of the solids (Na + NaCl) amounted to 33.0 g.

$^1$H NMR (300 MHz, C$_6$D$_6$): $\delta$ 0.5 ($W_{1/2} = 90$ Hz, 3.3 H, SiCH$_3$),

$\quad$ 4.1 ($W_{1/2} = 75$ Hz, 1.0 H, SiH, SiH$_2$); CH/SiH = 3.3; in general CH/SiH = 3.3 - 3.6.

$^{13}$C NMR (75.5 MHz, C$_6$D$_6$): $\delta_C$ -12.2 to -5.1 ($W_{1/2} = 230$ Hz, SiCH$_3$).

$^{29}$Si NMR (59.59 MHz, C$_6$D$_6$): $\delta_Si$ -71, -67 ($W_{1/2} = 300$ Hz, SiH);

$\quad$ -64, -61 ($W_{1/2} = 300$ Hz, SiH$_2$), (Fig. C4).

IR (thin film on NaCl, cm$^{-1}$): 2957(s), 2894(s), 2796(w), 2107(vs), 1918(vw), 1410(s), 1247(vs), 1037(vw), 931(vs), 867(vs), 770(vs), 685(vs), 584(s).

Ceramic Residue Yield (TGA): 18%

Molecular Weight by GPC: Fig. C8

X-ray Diffraction Pattern: Fig. G5 a

The this reaction proved to be the least complicated, giving the highest purity product in high yield.
Reaction Between MeSiHCl₂ (Stepwise Addition) and 2.5 Na in 7/1 v/v of Hexane/THF Using Ultrasonic Activation at 50°C. (PC/4/34; PC/6/70)

The effect of stepwise addition of chlorosilane on the oligo(methyilsilane) synthesis was explored.

A 250 mL Schlenk flask was charged with 14.6 g (0.635 mol) of Na shot (~10 mm in diameter), 7.5 mL of THF 52.5 mL of hexane, and 13 mL (14.3 g, 0.124 mol) of MeSiHCl₂. The flask then was placed in the ultrasonic bath and after 3 h of ultrasonication an additional 13 mL (14.3 g, 0.124 mol) of MeSiHCl₂ was added. The ultrasonication was terminated after 17 h. The contents of the flask, together with three 20 mL hexane washings, were cannulated into a thick walled centrifuge bottle and centrifuged for 1 h. The clear supernatant solution was cannulated then into a Schlenk flask and trap-to-trap distilled at reduced pressure, leaving 7.5 g (70% yield) of a clear oil which was soluble in most common organic solvents.

\[ ^1H \text{ NMR} \text{ (300 MHz, } C_6D_6) : \delta 0.5 (W_{1/2} = 90 \text{ Hz, } 3.4 \text{ H, SiCH}_3), \]
\[ 4.1 (W_{1/2} = 75 \text{ Hz, } 1.0 \text{ H, SiH, SiH}_2); \]
\[ \text{CH/SiH = 3.4.} \]

\[ \text{IR (thin film on NaCl, cm}^{-1}) : 2957(s), 2894(s), 2796(w), 2107(vs), 1918(w), 1410(s), 1247(vs), 1040(vw), 931(s), 867(vs), 770(vs), 685(vs), 584(s). \]

The stepwise addition appears not to have any effect on the course of the reaction.
Reaction Between MeSiHCl$_2$ and 2.5 Na in 15/1 v/v of Hexane/THF Using

Ultrasonic Activation at 28°C. (PC/3/39)

The effect of increasing hexane/THF ratio on the reaction was explored.

A 100 mL Schlenk flask was charged with 7.3 g (0.317 mol) of Na shot (~10 mm in diameter), 1.75 mL of THF 26.25 mL of hexane, and 13 mL (14.3 g, 0.124 mol) of MeSiHCl$_2$. The flask then was placed in the ultrasonic bath for 17 h. The solution, together with three 10 mL hexane washings, was cannulated into a thick-walled centrifuge bottle and centrifuged for 1 h. The clear supernatant solution then was cannulated into a Schlenk flask and trap-to-trap distilled at reduced pressure leaving 1.6 g (30% yield) of a milky white oil that was soluble in most common organic solvents.

$^1$H NMR (300 MHz, C$_6$D$_6$): $\delta$ 0.5 ($W_{1/2} = 9\nu$ Hz, 3.8 H, SiCH$_3$),

4.0 ($W_{1/2} = 75$ Hz, 1.0 H, SiH, SiH$_2$);  
CH/SiH = 3.8.

$^{29}$Si NMR (59.59 MHz, C$_6$D$_6$): $\delta_{Si} -72$, -68 ($W_{1/2} = 300$ Hz, SiH);

-64, -61 ($W_{1/2} = 300$ Hz, SiH$_2$).

IR (thin film on NaCl, cm$^{-1}$): 2957(s), 2894(s), 2797(w), 2108(vs), 1921(vw), 1410(s), 1248(vs), 1037(w), 931(vs), 869(vs), 768(vs), 686(vs), 584(s).

Ceramic Residue Yield (TGA): 13%

Increasing the hexane/THF ratio from 7/1 to 15/1 decreases the overall product yield.
Reaction Between MeSiHCl₂ and 2.5 Na in Concentrated (12.4 M) Solution in 7/1 v/v of Hexane/THF Using Ultrasonic Activation at 28°C. (PC/8/28)

The effect of a more concentrated reaction mixture on SiH content of the oligomer was explored.

A 100 mL Schlenk flask was charged with 7.3 g (0.317 mol) of Na shot (~10 mm in diameter), 1.25 mL of THF and 8.75 mL of hexane, and 13 mL (14.3 g, 0.124 mol) of MeSiHCl₂. The flask then was placed in the ultrasonic bath for 19.5 h. The solution, together with three 10 mL hexane washings, then was cannulated into a thick-walled centrifuge bottle and centrifuged for 1 h. The clear supernatant solution then was cannulated into a Schlenk flask and trap-to-trap distilled at reduced pressure leaving 2.98 g (54% yield) of a clear oil that was soluble in most common organic solvents. The remaining solids (Na + NaCl) amounted to 15.76 g. After extraction with water 0.65 g (12% yield) of pyrophoric white solid was obtained from 10.01 g of NaCl crystals; this product will be considered in detail *vide infra*.

\[ ^1H \text{NMR (300 MHz, } C_6D_6) \]: \( \delta \) 0.5 \( (W_{1/2} = 90 \text{ Hz, } \text{SiCH}_3) \),

4.0, 3.9 \( (W_{1/2} = 75 \text{ Hz, } \text{SiH, SiH}_2) \);

\( \text{CH/SiH} = 3.2 \).

**IR (thin film on NaCl, cm}^{-1})**: 2955(m), 2892(m), 2794(w), 2105(vs),

1409(m), 1247(m), 1050(w), 930(s), 860(vs),

769(vs), 682(vs), 643(s), 585(m).
Analysis of the oil: C: 26.86%; H: 8.73%
Calc. (MeSiH_x)_{0.94}(MeSi)_{0.06}: C: 27.26%; H: 8.99%

The concentrated reaction yields higher (x + z) value based on $^1$H NMR.

Reaction Between MeSiHCl₂ and 2.5 Na in Hexane and Toluene Using Ultrasonic Activation at 28°C. (PC/3/21, 23)

Reaction in absence of ethereal cosolvent was explored.

A 100 mL Schlenk flask was charged with 7.3 g (0.317 mol) of Na metal shot (~10 mm in diameter), 20 mL of hexane or 20 mL of toluene, and 13 mL (14.3 g, 0.124 mol) of MeSiHCl₂. The flask then was placed in the ultrasonic bath for 23 h (hexane) and 42.5 h (toluene). The solution, together with three 10 mL hexane washings, was cannulated into a thick-walled centrifuge tube and centrifuged for 1 h. The clear supernatant solution was cannulated into a Schlenk flask and trap-to-trap distilled at reduced pressure leaving 1.0 g (18% yield) of a white oil that was soluble in most common organic solvents. In the case of toluene as a solvent no polymer or any NaCl was obtained.

$^1$H NMR (300 MHz, C₆D₆): δ 1.0 (4.1 H, SiCH₂), 1.4 (1.0 H, CH₂, SiH₂).

The absence of an ether cosolvent gives a very low yield of impure product.
Reaction Between MeSiHCl₂ and Minimum Surface Area of Na in 7/1 v/v

Hexane/THF Using Ultrasonic Activation at 28°C. (PC/8/19)

The effect of minimum surface area was explored on the yield and molecular weight of the oligomer.

A 190 mL Schlenk flask was charged with 7.24 g (0.315 mol) of a single shiny chunk of Na metal, 3.75 mL of THF, 26.25 mL of hexane, and 13 mL (14.3 g, 0.124 mol) of MeSiHCl₂. The flask then was placed in the ultrasonic bath for 18 h. The solution, together with three 20 mL hexane washings, was cannulated into a thick-walled centrifuge tube and centrifuged for 1 h. The clear supernatant solution then was cannulated into a Schlenk flask and trap-to-trap distilled at reduced pressure leaving 3.4 g (62% yield) of a clear oil (soluble in most common organic solvents). The remaining solids (Na + NaCl) amounted to 15.42 g.

^1H NMR (300 MHz, C₆D₆): δ 0.5 (W₁/₂ = 90 Hz, 3.5 H, SiCH₃),
4.1 (W₁/₂ = 75 Hz, 1.0 H, SiH, SiH₂);
CH/SiH = 3.5.

IR (thin film on NaCl, cm⁻¹): 2957(s), 2894(s), 2795(w), 2108(vs), 1921(vv), 1410(s), 1248(vs), 1045(w), 931(vs), 868(vs), 769(vs), 687(vs), 587(s).

Minimum surface area does not affect the composition but gives about 10% lower yield of the oligomer.
Reaction Between MeSiHCl₂ and 0.25 Na in 7/1 v/v Hexane/THF Using

Ultrasonic Activation at 28°C. (PC/6/16)

Effect of excess of MeSiHCl₂ the structure and yield of the product.

A 100 mL Schlenk flask was charged with 0.73 g (0.032 mol) of Na metal chunks (~10 mm in diameter), 3.75 mL of THF, 26.25 mL of hexane, and 13 mL (14.3 g, 0.124 mol) of MeSiHCl₂. The flask then was placed in the ultrasonic bath for 19 h. The solution, together with three 20 mL hexane washings, was cannulated into a thick-walled centrifuge tube and centrifuged for 1 h. The clear supernatant solution was then cannulated into a Schlenk flask and trap-to-trap distilled at reduced pressure leaving 0.8 g (0.018 mol, 14.7% yield based on MeSiHCl₂, or ca. 100% based on Na) of a clear oil (soluble in most common organic solvents).

\(^1\text{H NMR}\) (300 MHz, C₆D₆): \(\delta\) 0.5 (\(W_{1/2} = 90\) Hz, 3.5 H, SiCH₃),
4.0, 3.9 (\(W_{1/2} = 75\) Hz, 1.0 H, SiH, SiH₂),
1.3, 3.1 (from poly(THF) CH₂); CN/SiH = 3.5.

\(^{13}\text{C NMR}\) (75.5 MHz, C₆D₆): \(\delta_C\) -9 (\(W_{1/2} = 180\) Hz, SiCH₃), 30, 44, 70 (CH₂)

\(^{29}\text{Si NMR}\) (59.59 MHz, C₆D₆): \(\delta_{Si}\) -71, -67 (\(W_{1/2} = 300\) Hz, SiH);
-64, -61 (\(W_{1/2} = 300\) Hz, SiH₂).

\(\text{IR (thin film on NaCl, cm}^{-1}\): 2956(s), 2923(s), 2894(s), 2853(m), 2796(w),
2107(vs), 1920(vv), 1727(vv), 1410(s),
1247(s), 1099(m), 931(vs), 867(vs), 770(vs),
685(vs), 584(s).

The excess of MeSiHCl₂ yields quantitative conversion of chlorosilane to
oligosilane oil.

Reaction Between MeSiHCl₂ and 12.5 Na in 1/7 v/v THF/Hexane Using Ultrasonic Activation at 28°C. (PC/8/22)

The effect of an excess of Na on the yield of the oligomer was explored.

A 100 mL Schlenk flask was charged with 7.5 g (0.326 mol) of Na metal chunks (~10 mm in diameter), 3.75 mL of THF, 26.25 mL of hexane, and 6.5 mL (7.15 g, 0.062 mol) of MeSiHCl₂. The flask then was placed in the ultrasonic bath for 17 h. The contents of the flask, together with three 10 mL hexane washings, were cannulated into a thick-walled centrifuge tube and centrifuged for 1 h. The clear supernatant then was cannulated into a Schlenk flask and trap-to-trap distilled at reduced pressure leaving 2.2 g (81% yield) of a white oil (soluble in most common organic solvents). The remaining solids (Na + NaCl) amounted to 12.20 g.

**¹H NMR** (300 MHz, C₆D₆): δ 0.5 (W₁/₂ = 120 Hz, 3.7 H, SiCH₃), 4.0, 3.9 (W₁/₂ = 75 Hz, 1.0 H, SiH, SiH₂); CH/SiH = 3.7.

**IR** (thin film on NaCl, cm⁻¹): 2956(s), 2893(s), 2795(w), 2106(vs), 1918(vw), 1410(s), 1247(s), 1043(w), 931(vs), 858(vs), 770(vs), 685(vs), 586(s).

The use of excess Na leads to marginally higher yields of the oligomer.
Reaction Between MeSiHCl$_2$ and 2.5 Na with 2 wt% of Ethyl Acetate Using Ultrasonic Activation at 28°C. (PC/8/49)

Solvent free synthesis of the oligomer with long ultrasonication times and a trace of ethyl acetate.

A 100 mL Schlenk flask was charged with 7.3 g (0.317 mol) of Na metal shot (~10 mm in diameter), 0.43 g (2 wt%) of ethyl acetate, and 13 mL (14.3 g, 0.124 mol) of MeSiHCl$_2$. The flask then was placed in the ultrasonic bath for 75.5 h. The contents of the flask, together with three 10 mL toluene washings, were cannulated into a thick-walled centrifuge tube and centrifuged for 1 h. The clear supernatant solution then was cannulated into a Schlenk flask and trap-to-trap distilled at reduced pressure leaving 2.05 g (37% yield) of a clear oil (soluble in most common organic solvents). The remaining solids (Na + NaCl) amounted to 9.91 g.

$^1$H NMR (300 MHz, C$_6$D$_6$): δ 0.5 (W$_{1/2}$ = 105 Hz, 3.9 H, SiCH$_3$),

4.0, 3.9 (W$_{1/2}$ = 75 Hz, 1.0 H, SiH, SiH$_2$);

CH/SiH = 3.9.

IR (thin film on NaCl, cm$^{-1}$): 2957(s), 2894(s), 2796(w), 2108(vs), 1921(vw),

1409(s), 1248(s), 1067(m), 931(vs), 870(vs),

770(vs), 686(vs), 587(s), 500(m).

The "solvent free" ultrasonicated reductive coupling of MeSiHCl$_2$ with Na for over 70 h gives a low yield of an oligomer.
Reaction Between MeSiHCl₂ and 2.5 Na with 4 wt% of THF Using Ultrasonic Activation at 28°C. (PC/8/29)

Solvent free reductive coupling reaction with a trace of THF was explored.

A 100 mL Schlenk flask was charged with 7.25 g (0.317 mol) of Na metal shot (~10 mm in diameter), 1 mL (0.88 g) of THF and 13 mL (14.3 g, 0.124 mol) of MeSiHCl₂. The flask then was placed in the ultrasonic bath for 17.5 h. The contents of the flask, with three 20 mL hexane washings, were cannulated into a thick-walled centrifuge tube and centrifuged for 1 h. The clear supernatant solution then was cannulated into a Schlenk flask and trap-to-trap distilled at reduced pressure leaving 2.35 g (43% yield) of clear, low viscosity oil (soluble in most common organic solvents). The remaining solids (Na + NaCl) amounted to 14.5 g. From 9.13 g of NaCl 0.57 g of soluble solid polymer (Ceramic Residue Yield (TGA) = 23%) was extracted with water.

\(^1\text{H NMR}\) of oil (300 MHz, C₆D₆): \(\delta 0.5 (W_{1/2} = 105 \text{ Hz}, 3.5 \text{ H, SiCH}_3),\)

\(4.0, 3.9 (W_{1/2} = 75 \text{ Hz}, 1.0 \text{ H, SiH, SiH}_2);\)

\(\text{CH/SiH} = 3.5.\)

\(^1\text{H NMR}\) of solid (300 MHz, C₆D₆): \(\delta 0.5 (W_{1/2} = 120 \text{ Hz}, 4.3 \text{ H, SiCH}_3),\)

\(4.0, 3.9 (W_{1/2} = 90 \text{ Hz}, 1.0 \text{ H, SiH, SiH}_2);\)

\(\text{CH/SiH} = 4.3.\)

\(\text{IR}\) of oil

(thin film on NaCl, cm\(^{-1}\)): 2955(s), 2892(s), 2799(w), 2108(vs), 1921(vw),

1409(s), 1247(s), 1097(w), 931(vs), 865(vs), 768(vs),
684(vs), 584(s).

192
**IR of solid**  
(thin film on NaCl, cm⁻¹): 2955(m), 2893(m), 2794(w), 2080(vs), 1921(vw),  
1408(m), 1247(s), 1037(m), 931(s), 865(vs), 766(vs),  
684(vs), 586(s).  

**Analysis of the oil:** C: 26.43%; H: 8.60%  
Calc. \((\text{MeSiH}_x\text{MeSi})_{0.86}\text{MeSi})_{0.14}: C: 27.32\%; H: 8.80%  

The solvent free reductive coupling gives a low yield of oligomer.

**Reaction Between PhSiHCl₂ and 2.5 Na in 7/1 v/v Hexane/THF Using Ultrasonic Activation** (PC/3/41)

This experiment was performed in order to determine the presence of SiH₂ functionalities in poly(phenylsilane).

A 100 mL Schlenk flask was charged with 3.65 g (0.160 mol) of mirror clean Na metal (~10 mm in diameter), 30 mL of hexane, 4.25 mL of THF, and 9.35 mL (11.2 g, 0.063 mol) of PhSiHCl₂. The flask then was placed in the ultrasonic bath for 19 h. The contents of the flask were washed three times with 20 mL portions of hexane and cannulated into a thick-walled centrifuge bottle and centrifuged for 1 h. The clear supernatant solution then was cannulated into a Schlenk flask and trap-to-trap distilled at reduced pressure leaving 2.0 g (30%) of a transparent oil (soluble in most common organic solvents).

**¹H NMR (300 MHz, C₆D₆):** δ 4.6 \((W_{1/2} = 105 \text{ Hz}, 1.0 \text{ H, SiH, SiH}_2)\);  
7.0, 7.4 \((W_{1/2} = 120\text{Hz}, 9.2 \text{ H, SiPh})\).
\(^{29}\text{Si NMR}\) (59.59 MHz, C\(_6\)D\(_6\)): \(\delta_{\text{Si}} -65, -64, -61\) (W1/2 = 360 Hz, SiH); 
-58, -56 (W1/2 = 120 Hz, SiH\(_2\)).

\textbf{IR} (thin film on NaCl, cm\(^{-1}\)): 3131(w), 3066(s), 3048(s), 3010(m), 2995(m), 2926(w), 2106(s), 1953(w), 1880(w), 1815(w), 1761(vv), 1647(vv), 1585(m), 1566(m), 1482(s), 1427(s), 1376(m), 1331(m), 1299(m), 1260(m), 1189(m), 1157(m), 1101(s), 1065(m), 1026(m), 998(s), 913(s).

**Ceramic Residue Yield (TGA):** 33%

The product contained SiH\(_2\) functionalities.

**Reaction Between MeSiHCl\(_2\) and CH\(_2\)Br\(_2\) in 1:1 Molar Ratio and 2.5 Na in Refluxing Toluene.** (PC/2/73; PC/3/2)

The effect of brominated hydrocarbons on reductive coupling of MeSiHCl\(_2\) was explored.

A 500 mL three necked round-bottomed flask, equipped with a magnetic stir-bar, a reflux condenser, and three rubber septa was charged with 16.67 g (0.725 mol) of Na metal shot (~10 mm in diameter) and 300 mL of toluene. The flask then was placed in the ultrasonic bath until most of the Na chunks became a fine suspension. The flask was charged with 10 mL (15.4 g, 0.144 mol) of CH\(_2\)Br\(_2\) and 15 mL (16.5 g, 0.143 mol) of MeSiHCl\(_2\) and was heated at reflux with stirring for 19.5 h. After cooling to room temperature, the contents (brown slurry) of the flask, with three 20 mL hexane washings, were cannulated into a
thick-walled centrifuge bottle and centrifuged for 2 h. The clear supernatant
solution then was cannulated into a Schlenk flask and trap-to-trap distilled at
reduced pressure leaving 2.0 g (24% yield) of a yellow transparent oil. The oil
was soluble in toluene, hexane, benzene, and THF.

$^1$H NMR (300 MHz, C$_6$D$_6$): $\delta$ -0.2 (shoulder, SiCH$_2$Si),

0.3 ($W_{1/2} = 120$ Hz, 8.45 H, SiCH$_3$),
1.0, 1.5 (0.1 H, (CH$_2$)$_n$), 2.1 (0.2 H, CH),
4.1 ($W_{1/2} = 180$ Hz, 1.0 H, SiH, SiH$_2$),
7.1 ($W_{1/2} = 60$ Hz, 0.9 H C$_6$H$_5$).

$^{13}$C NMR (75.5 MHz, C$_6$D$_6$): $\delta_C$ -10, -6, 0 ($W_{1/2} = 1060$ Hz, SiCH$_3$, CH$_2$, CH);
127 ($W_{1/2} = 300$ Hz, C$_6$H$_5$).

$^{29}$Si NMR (59.59 MHz, C$_6$D$_6$): $\delta_{Si}$ -71, -67 ($W_{1/2} = 360$ Hz, SiH);
-64, -61($W_{1/2} = 400$ Hz, SiH$_2$);
-34, -16 ($W_{1/2} = 300$ Hz SiCH$_2$, SiCH).

IR (thin film on NaCl, cm$^{-1}$): 2954(s), 2893(s), 2100(vs), 1601(w),1493(w),
1452(m), 1409(m), 1351(w), 1248(vs), 1039(s),
934(m), 868(vs), 835(s), 777(vs), 697(s).

Ceramic Residue Yield (TGA): 18%

The incorporation of phenyl and methylene groups in to the silicon
backbone took place.
Reaction Between MeSiHCl₂ and Various Amounts of CH₂Br₂ and Na in Refluxing Octane. (PC/3/4,5,6)

The effect of various amounts of CH₂Br₂ on the synthesis of oligomers was explored.

A 500 mL Schlenk flask, equipped with a magnetic stir-bar and a reflux condenser was charged with 16.67 g (0.725 mol) of Na shot (~10 mm in diameter), 210 mL of octane, and 15 mL (16.5 g, 0.143 mol) of MeSiHCl₂ and the following amounts of CH₂Br₂ from Table H1.

<table>
<thead>
<tr>
<th>ID</th>
<th>MeSiHCl₂/CH₂Br₂ molar ratio</th>
<th>volume (mL) CH₂Br₂</th>
<th>moles CH₂Br₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC/3/4</td>
<td>1/1</td>
<td>10</td>
<td>0.143</td>
</tr>
<tr>
<td>PC/3/5</td>
<td>2/1</td>
<td>5</td>
<td>0.072</td>
</tr>
<tr>
<td>PC/3/6</td>
<td>3/1</td>
<td>3.25</td>
<td>0.048</td>
</tr>
</tbody>
</table>

The reaction mixture was stirred and heated at reflux for 19.5 h. After the flask was allowed to cool to room temperature, its contents (brown slurry), together with three 20 mL hexane washings, were cannulated into a thick-walled centrifuge bottle and centrifuged for 2 h. The clear supernatant solution was cannulated into a Schlenk flask and trap-to-trap distilled at reduced pressure leaving the following amounts of products (Table H2):
<table>
<thead>
<tr>
<th>MeSiHCl₂(CH₂Br₂)</th>
<th>Yield (g)</th>
<th>Yield (%)</th>
<th>TGA (%)</th>
<th>SiMe/SiH by (^1)H NMR</th>
<th>GPC: see Fig.</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/1</td>
<td>1.7</td>
<td>20</td>
<td>25</td>
<td>49</td>
<td>D1 c</td>
<td>yellow solid, partly soluble</td>
</tr>
<tr>
<td>2/1</td>
<td>1.8</td>
<td>25</td>
<td>35</td>
<td>24.6</td>
<td>D1 b</td>
<td>yellow solid, well soluble</td>
</tr>
<tr>
<td>3/1</td>
<td>1.5</td>
<td>22</td>
<td>16</td>
<td>28</td>
<td>-</td>
<td>yellow tacky solid, well soluble</td>
</tr>
</tbody>
</table>

\(^1\)H NMR (300 MHz, C₆D₆): \(\delta\) -0.3 (shoulder, SiCH₂Si), 0.5 (\(W_{1/2} = 180\) Hz, SiCH₃); 1.0, 1.5 (\(W_{1/2} = 60\) Hz, (CH₂)ₙ); 4.2 (\(W_{1/2} = 75\) Hz, SiH, SiH₂), 5.1 (trace, SiCH₂Br); CH/SiH ratio see Table H2.

\(^{13}\)C NMR (75.5 MHz, C₆D₆): \(\delta\) C 2 (\(W_{1/2} = 600\) Hz, SiCH₃); 14.5 (\(W_{1/2} = 130\) Hz, CH₂); 23, 30, 32 (\(W_{1/2} = 130\) Hz, CH₂).

\(^{29}\)Si NMR (59.59 MHz, C₆D₆): \(\delta\) Si -70, -65 (\(W_{1/2} = 360\) Hz, SiH, SiH₂); -34, -17, 0 (\(W_{1/2} = 120\) Hz, H₂CSiCH₃).

IR (essentially the same for all 3 cases) (thin film on NaCl, cm\(^{-1}\)): 2956(s), 2925(s), 2107(m), 1465(m), 1406(m), 1377(m), 1248(s), 1044(s), 836(s), 770(s), 685(s).

Ceramic Residue Yield (TGA): see Table H2

The reaction yields were low but the molecular weight increased as the ratio MeSiHCl₂(CH₂Br₂) decreased.
Reaction Between MeSiHCl₂ and 5 wt% (PC/3/9) and 15 wt% (PC/3/10) of CH₂Br₂ and 2.5 Na in 7/1 v/v of Hexane/THF Using Ultrasonic Activation at 20°C. (PC/3/9,10)

The effect of substoichiometric amounts of CH₂Br₂ on synthesis of the oligomer was investigated.

A 300 mL Schlenk flask was charged with 14.6 g (0.635 mol) Na metal shot (~10 mm in diameter), 7.5 mL of THF and 52.5 mL of hexane. The flask was equipped with an addition funnel containing 26 mL (28.6 g, 0.248 mol) of MeSiHCl₂ and 0.57 mL (0.0082 mol) of CH₂Br₂ in PC/3/9 experiment and 1.71 mL (0.0246 mol) of CH₂Br₂ in PC/3/10 experiment. The flask then was placed in the ultrasonic bath for 17.5 h after which the contents (blue solution) with three 20 ml hexane washings, were cannulated into a thick-walled centrifuge bottle and centrifuged for 1 h. The clear supernatant solution was cannulated into a Schlenk flask and trap-to-trap distilled at reduced pressure leaving 6.5 g (60% yield) of a yellow-white oil (PC/3/9) and 7.2 g (66% yield) of a yellow oil (PC/3/10). Both of the products are soluble in common organic solvents.

PC/3/9

¹H NMR (300 MHz, C₆D₆): δ 0.5 (W₁/₂ = 90 Hz, 4.9 H, SiCH₃);
1.0, 1.5 (trace (CH₂)ₙ),
4.0 (W₁/₂ = 75 Hz, 1.0 H, SiH, SiH₂);
CH/SiH = 4.9.
PC/3/10

$^1$H NMR (300 MHz, C$_6$D$_6$): $\delta$ 0.5 ($W_{1/2} = 210$ Hz, 7.4 H, SiCH$_3$);
   1.0, 1.5 (trace (CH$_2$)$_n$),
   4.0 ($W_{1/2} = 150$ Hz, 1.0 H, SiH, SiH$_2$);
   CH/SiH = 7.4.

PC/3/9 and PC/310

$^{13}$C NMR (75.5 MHz, C$_6$D$_6$): $\delta$C -9.0 ($W_{1/2} = 250$ Hz, SiCH$_3$);
   2.0 ($W_{1/2} = 200$ Hz, CH$_2$).

$^{29}$Si NMR (59.59 MHz, C$_6$D$_6$): $\delta$Si -71, -67 ($W_{1/2} = 400$ Hz, SiH);
   -63, -61 ($W_{1/2} = 200$ Hz, SiH$_2$).

IR (thin film on NaCl, cm$^{-1}$): 2957(m), 2894(m), 2794(w), 2107(s), 1409(m),
   1248(m), 1038(w), 931(s), 865(vs), 770(s), 686(s).

Ceramic Residue Yield (TGA): ca. 22%

The (CH$_2$)$_n$ groups were incorporated into the polymeric backbone, but no
SiCH$_2$Si groups were observed.

Reaction of Oligo(methylsilane) With 0.5 mol% (Cp$_2$ZrH$_2$)$_n$ in Refluxing

Toluene. (PC/4/50, 64, 67; PC/5/43, 56; PC/6/69)

A 100 mL Schlenk flask fitted with a reflux condenser and equipped with
magnetic stir-bar was charged with 1.14 g (0.026 mol) of oligo(methylsilane)
(CH/SiH = 3.5), 0.030 g (0.134 mmol) of (Cp$_2$ZrH$_2$)$_n$ and 20 mL of toluene. The
solution almost immediately became orange was heated at reflux for 2 to 3 h.
Subsequently, toluene was removed by trap-to-trap distillation at reduced pressure
leaving 1.16 g (101% yield, PC/4/50) of orange solid which was soluble in most common organic solvents.

PC/4/50 (2 h reflux)

$^1$H NMR (300 MHz, C$_6$D$_6$): δ 0.5 (W$_{1/2}$ = 90 Hz, 6.56 H, SiCH$_3$),
4.1 (W$_{1/2}$ = 120 Hz, 1.0 H, SiH, SiH$_2$),
5.9, 6.0 (trace, Cp rings); CH/SiH = 6.56.

Ceramic Residue Yield (TGA): 72%

PC/6/69 (3 h reflux)

$^1$H NMR (300 MHz, C$_6$D$_6$): δ 0.5 (W$_{1/2}$ = 120 Hz, 7.06 H, SiCH$_3$),
4.1 (W$_{1/2}$ = 120 Hz, 1.0 H, SiH, SiH$_2$),
5.9, 6.0 (trace, Cp rings); CH/SiH = 7.06.

Ceramic Residue Yield (TGA): 84%

Molecular Weight by GPC: Fig. G17 d

X-ray Diffraction Pattern: Fig. F4 a

Reaction of Oligo(methylsilane) With 0.5 mol% (Cp$_2$ZrH$_2$)$_n$ in Hexane at 70°C

Under Vacuum. (PC/4/9)

A 100 mL Schlenk flask equipped with a high vacuum stopper and a magnetic stir-bar was charged with 0.93 g (0.021 mol) of oligo(methylsilane) (CH/SiH = 3.3), 0.023 g (0.103 mmol) of (Cp$_2$ZrH$_2$)$_n$, and 20 mL of hexane. After evacuation by three freeze-pump-thaw cycles, the flask with a clear yellow solution was placed in a 70°C constant temperature bath for 1 h. Subsequently the hexane was removed at reduced pressure and 20 mL of toluene was introduced to
redissolve soluble portion of the polymer. After filtration of the insoluble gel the solution was trap-to-trap distilled, leaving 0.50 g (52%) of a yellow solid which was soluble in most common organic solvents.

$^1$H NMR (300 MHz, C₆D₆): $\delta$ 0.5 (W$_{1/2}$ = 90 Hz, 3.9 H, SiCH₃),

4.1 (W$_{1/2}$ = 90 Hz, 1.0 H, SiH, SiH₂),

6.1 (trace, Cp rings); CH/SiH = 3.9.

$^{13}$C NMR (75.5 MHz, C₆D₆): $\delta$C -8 (W$_{1/2}$ = 400 Hz, SiCH₃, CH).

$^{29}$Si NMR (59.59 MHz, C₆D₆): $\delta$Si -72 (W$_{1/2}$ = 480 Hz, SiH);

-60 (W$_{1/2}$ = 400 Hz, SiH₂). (Fig. F2 a).

IR (KBr pellet, cm⁻¹): 2953(s), 2893(s), 2073(vs), 1406(s), 1247(vs), 1038(s),

931(s), 866(vs), 760(vs), 682(vs).

Ceramic Residue Yield (TGA): 65%

UV Photolysis of Oligo(methylsilane) With 0.5 mol% of (Cp₂ZrH₂)$_n$ in Hexane Under Vacuum. (PC/4/10)

A 100 mL quartz Schlenk flask equipped with a magnetic stir-bar and a high vacuum stopper was charged with 0.82 g (0.019 mol) of oligo(methylsilane) (CH/SiH = 3.3), 0.021 g (0.094 mmol) of (Cp₂ZrH₂)$_n$, and 20 mL of hexane.

After the evacuation by three freeze-pump-thaw cycles, the flask was irradiated by Hanovia UV lamp for 6 h. The resulting cloudy, deep orange solution was centrifuged to remove some gelled polymer. The clear orange solution then was trap-to-trap distilled, leaving 0.70 g (84%) of brown oil, which was soluble in
most common organic solvents.

\[ ^1H \text{ NMR} \ (300 \text{ MHz, C}_6\text{D}_6): \delta \ 0.5 \ (W_{1/2} = 105 \text{ Hz, } 3.3 \text{ H, SiCH}_3), \]
\[ 4.1 \ (W_{1/2} = 75 \text{ Hz, } 1.0 \text{ H, SiH, SiH}_2), \]
\[ 6.0 \ (\text{trace, Cp rings); CH/SiH = 3.3}. \]

\[ ^{29}\text{Si NMR} \ (59.59 \text{ MHz, C}_6\text{D}_6): \delta_{\text{Si}} -71, -67 \ (W_{1/2} = 300 \text{ Hz, SiH}); \]
\[ -61, -64 \ (W_{1/2} = 300 \text{ Hz, SiH}_2), \ (\text{Fig. F2 b}). \]

\[ \text{IR (thin film on NaCl, cm}^{-1}): 2956(s), 2893(s), 2795(w), 2104(vs), 1919(vw), \]
\[ 1410(s), 1247(s), 1019(w), 931(vs), 862(vs), \]
\[ 773(vs), 687(vs), 587(s). \]

\[ \text{Ceramic Residue Yield (TGA): 70\%} \]

**A Blend of Oligo(methylsilane) With 0.57 mol\% of Cp}_2\text{ZrCl}_2. (PC/3/43, 45, 47)**

A 100 mL Schlenk flask equipped with magnetic stir-bar was charged with
0.70 g (0.016 mol) of oligo(methylsilane) (CH/SiH = 3.3), 0.0266 g (0.091 mmol) of Cp}_2\text{ZrCl}_2, and 20 mL of hexane. The flask then was placed in ultrasonic bath
for 1 h to assure a uniform dispersion of the catalyst. The suspension was trap-to-
trap distilled leaving 0.72 g of white oil.

\[ ^1H \text{ NMR} \ (300 \text{ MHz, C}_6\text{D}_6): \delta \ 0.5 \ (W_{1/2} = 90 \text{ Hz, } 3.4 \text{ H, SiCH}_3), \]
\[ 4.1 \ (W_{1/2} = 75 \text{ Hz, } 1.0 \text{ H, SiH, SiH}_2), \]
\[ 6.0 \ (\text{trace, Cp rings); CH/SiH = 3.4}. \]

\[ \text{Ceramic Residue Yield (TGA): 70\%} \]

\[ \text{Analysis of Ceramics (1500°C, Ar): C: 27.80\%; Si: 69.79\%; } \]
\[ \Sigma = 97.59\% \]
\[ \text{Calc. (SiC): C: 29.95\%; Si: 70.05\%} \]

**X-ray Diffraction Pattern: Figs. F4 b; F5 b**
Reaction of Oligo(methylsilane) With 0.57 mol% of Cp₂ZrCl₂ in Refluxing Toluene. (PC/3/58, 46)

A 100 mL Schlenk flask equipped with a reflux condenser and a magnetic stir-bar was charged with 0.95 g (0.022 mol) of oligo(methylsilane) (CH/SiH = 3.3), 0.035 g (0.12 mmol) of Cp₂ZrCl₂, 20 mL of toluene. The solution was heated at reflux for 43.5 h. After cooling to room temperature, the yellow solution was trap-to-trap distilled leaving 0.97 g (100%) of yellow oil.

¹H NMR (300 MHz, C₆D₆): δ 0.5 (W₁/₂ = 90 Hz, 3.4 H, SiCH₃), 4.1 (W₁/₂ = 75 Hz, 1.0 H, SiH, SiH₂), 6.1 (trace, Cp rings); CH/SiH = 3.4.

IR (thin film on NaCl, cm⁻¹): 2957(s), 2894(s), 2796(w), 2109(vs), 1918(vw), 1410(s), 1247(vs), 1040(vw), 931(vs), 867(vs), 770(vs), 685(vs), 584(s).

Ceramic Residue Yield (TGA): 67%

Reaction of Oligo(methylsilane) With 0.57 mol% of Cp₂TiCl₂ in Refluxing Toluene. (PC/3/59; PC/4/17)

A 100 mL Schlenk flask equipped with a reflux condenser and a magnetic stir-bar was charged with 0.89 g (0.020 mol) of oligo(methylsilane) (CH/SiH = 3.3), 0.029 g (0.12 mmol) of Cp₂TiCl₂, and 20 mL of toluene. The solution then was heated to refluxed for 24 h. After cooling to room temperature the red solution was trap-to-trap distilled leaving 0.92 g (102%) of red oil.
$^1$H NMR (300 MHz, C$_6$D$_6$): $\delta$ 0.5 ($W_{1/2} = 90$ Hz, 3.3 H, SiCH$_3$),
4.0 ($W_{1/2} = 80$ Hz, 1.0 H, SiH, SiH$_2$),
6.0 (trace, Cp rings); CH/SiH = 3.3.

Ceramic Residue Yield (TGA): 63%

A Blend of Oligo(methylsilane) With 0.57 mol% of Cp$_2$ZrHCl. (PC/3/52)

A 100 mL Schlenk flask equipped with magnetic stir-bar was charged with
0.99 g (0.023 mol) of oligo(methylsilane) (CH/SiH = 3.4), 0.033 g (0.13 mmol) of
Cp$_2$ZrHCl, and 10 mL of toluene to assure the uniform dispersion of the catalyst.
The yellow solution then was evaporated by trap-to-trap distillation leaving 1.02 g
(100%) of yellow oil.

$^1$H NMR (300 MHz, C$_6$D$_6$): $\delta$ 0.5 ($W_{1/2} = 90$ Hz, 3.4 H, SiCH$_3$),
4.1 ($W_{1/2} = 75$ Hz, 1.0 H, SiH, SiH$_2$),
6.0 (trace, Cp rings); CH/SiH = 3.4.

Ceramic Residue Yield (TGA): 70%

Reaction of Oligo(methylsilane) With 0.5 mol% of Cp$_2$ZrHCl in Refluxing
Toluene. (PC/3/66, 70)

A 100 mL Schlenk flask equipped with magnetic stir-bar and a reflux
condenser was charged with 1.08 g (0.025 mol) of oligo(methylsilane) (CH/SiH =
3.3), 0.032 g (0.125 mmol) of Cp$_2$ZrHCl, and 20 mL of toluene. The solution was
heated at reflux for 3.5 h, after which toluene was trap-to-trap distilled. Then 10
mL of hexane was added to precipitate the catalyst. The suspension was centrifuged to remove the catalyst. The supernatant solution was cannulated into a Schlenk flask and was trap-to-trap distillation leaving 1.1 g (100%) of pink-white solid which is soluble in most common organic solvents. The precipitated solid was a Cp₂ZrHCl catalyst according to ¹H NMR (0.29 (1H), 5.86, 6.00 (10.6 H, Cp)).

¹H NMR (300 MHz, C₆D₆): δ 0.5 (W₁/₂ = 120 Hz, 3.9 H, SiCH₃),
4.1 (W₁/₂ = 90 Hz, 1.0 H, SiH, SiH₂),
CH/SiH = 3.9.

¹³C NMR (75.5 MHz, C₆D₆): δ C -7 (W₁/₂ = 375 Hz, SiCH₃).

²⁹Si NMR (59.59 MHz, C₆D₆): δ Si -67 (W₁/₂ = 540 Hz, SiH);
-61 (W₁/₂ = 200 Hz, SiH₂), (Fig. F7).

IR (KBr pellet, cm⁻¹): 2954(s), 2894(s), 2078(s), 1406(m), 1247(s), 1043(s),
931(s), 865(vs), 760(vs), 682(s).

Ceramic Residue Yield (TGA): 45% (without Cp₂ZrHCl)

Molecular Weight by GPC: Fig. G17 c

Reaction of Oligo(methylsilane) With 0.5 mol% of Cp₂TiMe₂ in Toluene at Room Temperature. (PC/7/73)

A 100 mL Schlenk flask equipped with a magnetic stir-bar was charged with 0.89 g (0.020 mol) of oligo(methylsilane) (CH/SiH = 3.3), 0.022 g (0.105 mmol) of Cp₂TiMe₂, and 20 mL of toluene. The solution turned green after about 1 h of stirring and later became brown-green. After 19 h of stirring at room
temperature toluene was trap-to-trap distilled leaving 0.91 g (103%) of brown, soluble solid.

\textbf{\textsuperscript{1}H NMR} (300 MHz, C\textsubscript{6}D\textsubscript{6}): \(\delta 0.5\) (\(W_{1/2} = 105\) Hz, 4.8 H, SiCH\textsubscript{3}),

4.1 (\(W_{1/2} = 75\) Hz, 1.0 H, SiH, SiH\textsubscript{2}),

CH/SiH = 4.8.

\textbf{Ceramic Residue Yield (TGA):} 72%

**UV Photolysis of Oligo(methylsilane) With 0.5 mol\% of Cp\textsubscript{2}ZrMe\textsubscript{2} in Hexane**

\textbf{Under Vacuum}, (PC/3/69; PC/4/1)

A 100 mL Schlenk quartz flask equipped with a magnetic stir-bar and high vacuum stopper was charged with 0.36 g (0.0082 mol) of oligo(methylsilane) (CH/SiH = 3.3) clear oil, 0.011 g (0.0438 mmol) of Cp\textsubscript{2}ZrMe\textsubscript{2}, and 20 mL of hexane. After three freeze-pump-thaw cycles the flask was irradiated with a Hanovia UV lamp for 5 h. The cloudy orange solution then was cannulated into a thick-walled centrifuge tube and centrifuged for 1 h to remove the gelled polymer. The supernatant solution was then trap-to-trap distilled leaving 0.30 g (83%) of yellow oil, which was soluble in most common organic solvents.

\textbf{\textsuperscript{1}H NMR} (300 MHz, C\textsubscript{6}D\textsubscript{6}): \(\delta 0.5\) (\(W_{1/2} = 90\) Hz, 3.4 H, SiCH\textsubscript{3}),

4.1 (\(W_{1/2} = 75\) Hz, 1.0 H, SiH, SiH\textsubscript{2}),

6.0 (trace, Cp rings); CH/SiH = 3.4.

\textbf{IR} (thin film on NaCl, cm\textsuperscript{-1}): 2956(s), 2894(s), 2796(w), 2107(vs), 1919(vw), 1409(s), 1247(vs), 1017(w), 931(vs), 871(vs), 773(vs),
685(vs), 584(s).

Ceramic Residue Yield (TGA): 73%

Reaction of Oligo(methylsilane) With 0.5 mol% of Cp₂ZrMe₂ in Refluxing Hexane. (PC/3/68)

A 100 mL Schlenk flask equipped with a reflux condenser and a magnetic stir-bar was charged with 1.04 g (0.024 mol) of oligo(methylsilane) (CH/SiH = 3.4), 0.030 g (0.12 mmol) of Cp₂ZrMe₂, and 20 mL of hexane. The solution was heated at reflux for 7 h after which hexane was trap-to-trap distilled leaving 1.1 g (103%) of yellow oil which was soluble in most common organic solvents.

\(^1\)H NMR (300 MHz, C₆D₆): \(\delta 0.5 \ (W_{1/2} = 90 \text{ Hz, SiCH}_3)\),

\(4.1 \ (W_{1/2} = 60 \text{ Hz, SiH, SiH}_2)\),

\(5.7, 5.8, 5.9, 6.0 \) (trace, Cp rings); CH/SiH = 3.4.

IR (thin film on NaCl, cm\(^{-1}\)): 2956(s), 2894(s), 2795(w), 2107(vs), 1919(vw),

1410(s), 1248(vs), 1017(w), 931(vs), 865(vs), 766(vs),

685(vs), 584(s).

Ceramic Residue Yield (TGA): 77%

Reaction of Oligo(methylsilane) With 0.5 mol% of (Ph₃P)₃RhCl in Toluene at Room Temperature. (PC/4/16, TS/3/31)

A 100 mL Schlenk flask equipped with a magnetic stir-bar was charged with 0.44 g (0.010 mol) of oligo(methylsilane) (CH/SiH = 3.4) clear oil, 0.092 g
(0.1 mmol) of \((\text{Ph}_3\text{P})_3\text{RhCl}\), and 20 mL of toluene. For about 10 min. there was no change in the reaction mixture but then the colorless solution became yellow and then dark red. Also evolution of gas bubbles took place. Also, the initially insoluble catalyst dissolved after about of 15 min. of reaction. The solution was stirred at room temperature for 18 h after which the solution was trap-to-trap distilled leaving 0.57 g (107%) of brown, tacky solid, which was soluble in most common organic solvents.

\[ ^1\text{H NMR} \ (300 \text{ MHz, C}_6\text{D}_6): \delta \ 0.5 \ (W_{1/2} = 135 \text{ Hz, 6.0 H, SiCH}_3), \]
\[ 4.1 \ (W_{1/2} = 90 \text{ Hz, 1.0 H, SiH, SiH}_2), \]
\[ 7.0, 7.2, 7.4, 7.7 \text{ (trace, PPh}_3\text{ groups); CH/SiH} = 6.0. \]

\[ ^29\text{Si NMR} \ (59.59 \text{ MHz, C}_6\text{D}_6): \delta_{\text{Si}} -67 \ (W_{1/2} = 600 \text{ Hz, SiH}); \]
\[ -61 \text{ (diminished, } W_{1/2} = 300 \text{ Hz, SiH}_2) \]

\[ \text{IR} \ (\text{thin film on NaCl, cm}^{-1}): 2957(s), 2894(s), 2795(w), 2104(vs), 1919(vv), \]
\[ 1409(s), 1248(vs), 1045(s), 931(s), 864(vs), 766(vs), 685(vs). \]

**Ceramic Residue Yield (TGA): 74%**

**Reaction of Oligo(methyilsilane) With 0.5 mol% of [Rh(COD)Cl]$_2$ in Toluene at Ambient Temperature Under Vacuum. (PC/4/20)**

A 100 mL Schlenk flask equipped with magnetic stir-bar and a high vacuum stopper was charged with 0.50 g (0.011 mol) of oligo(methyilsilane) (CH/SiH = 3.3) clear oil, 0.030 g (0.061 mmol) of [Rh(COD)Cl]$_2$, and 20 mL of toluene. The
flask underwent three freeze-pump-thaw cycles. After 10 min. the solution became yellow and then dark brown. Also evolution of gas bubbles took place. The solution was stirred at room temperature for 18.5 h after which the solution was trap-to-trap distilled leaving 0.55 g (103%) of brown, tacky solid, which was soluble in most common organic solvents.

$^{1}H$ NMR (300 MHz, C$_6$D$_6$): $\delta$ 0.5 ($W_{1/2} = 120$ Hz, 4.2 H, SiCH$_3$); 1.0, 1.5 (trace, (CH$_2$)$_n$), 4.1 ($W_{1/2} = 60$ Hz, 1.0 H, SiH, SiH$_2$), CH/SiH = 4.2.

$^{29}$Si NMR (59.59 MHz, C$_6$D$_6$): $\delta$$_{Si}$ -68 ($W_{1/2} = 300$ Hz, SiH); -61 ($W_{1/2} = 200$ Hz, SiH$_2$)

Ceramic Residue Yield (TGA): 74%

Reaction of Oligo(methylsilane) With 0.5 mol% of (Ph$_3$P)$_2$Rh(CO)Cl in Toluene at Room Temperature Under Vacuum. (PC/4/21, 29, 57)

A 100 mL Schlenk flask equipped with magnetic stir-bar and a high vacuum stopper was charged with 0.87 g (0.020 mol) of oligo(methylsilane) (CH/SiH = 3.3) clear oil, 0.070 g (0.101 mmol) of (Ph$_3$P)$_2$Rh(CO)Cl, and 20 mL of toluene. The flask then underwent three freeze-pump-thaw cycles. After 10 min. the solution became yellow and then dark brown. Also evolution of gas bubbles took place. The solution was stirred at room temperature for 19 h after which time the solution was trap-to-trap distilled leaving 0.92 g (98%) of brown solid, which was
soluble in most common organic solvents.

\[ ^1H \text{ NMR (300 MHz, C}_6\text{D}_6\text{): } \delta \text{ 0.5 (W}_1/2\text{ = 120 Hz, 5.9 H, SiCH}_3\text{), 4.1 (W}_1/2\text{ = 105 Hz, 1.0 H, SiH, SiH}_2\text{), 7.0, 7.2, 7.4 (trace, PPh}_3\text{ groups); CH/SiH = 5.9.} \]

\[ ^13C \text{ NMR (75.5 MHz, C}_6\text{D}_6\text{): } \delta \text{C -9 (W}_1/2\text{ = 300 Hz, SiCH}_3\text{); 1.5 (W}_1/2\text{ = 75 Hz, CH).} \]

\[ ^29\text{Si NMR (59.59 MHz, C}_6\text{D}_6\text{): } \delta \text{Si -66 (W}_1/2\text{ = 720 Hz, SiH); -62 (diminished, W}_1/2\text{ = 300 Hz, SiH}_2\text{), (Fig. F9).} \]

\[ \text{IR (KBr pellet, cm}^{-1}\text{): 2955(s), 2894(s), 2796(w), 2071(s), 1410(s), 1246(vs), 1045(s), 931(vw), 865(vs), 760(vs), 683(vs).} \]

\text{Ceramic Residue Yield (TGA): 85%}

\text{Analysis of Ceramics}

\( (1500^\circ\text{C, Ar, with the catalyst): C: 21.38\%, Si: 71.22\%; } \Sigma = 92.60\% \)

\( \text{Calc. (SiC): C: 29.95\%; Si: 70.05\%} \)

\text{Molecular Weight by GPC: Fig. G17 b}

\text{X-ray Diffraction Pattern: Fig. F6}

\text{Thermolysis of Oligo(methylsilane) With 1.0 mol\% of Ti(OPr-i)_4 in Toluene at 105}^\circ\text{C Under Vacuum, (PC/4/11)}

A 100 mL Schlenk flask equipped with magnetic stir-bar and a high vacuum stopper was charged with 1.14 g (0.026 mol) of oligo(methylsilane) (CH/SiH = 3.3) clear oil, 0.077 mL (0.272 mmol) of Ti(OPr-i)_4, and 20 mL of toluene. The flask then underwent three freeze-pump-thaw cycles after which the solution turned purple-blue. The evacuated flask then was placed in a 105^\circ\text{C oil bath for}
3.5 h. The blue solution then was trap-to-trap distilled leaving 1.2 g (99%) of a blue oil, which was soluble in most common organic solvents.

**1H NMR** (300 MHz, C₆D₆): δ 0.5 (W₁/₂ = 105 Hz, 3.3 H, SiCH₃), 4.1 (W₁/₂ = 75 Hz, 1.0 H, SiH, SiH₂), CH/SiH = 3.3.

**IR** (thin film on NaCl, cm⁻¹): 2957(s), 2894(s), 2796(w), 2107(s), 1918(vv), 1410(s), 1247(vs), 1129(w), 1018(w), 931(vs), 864(vs), 771(vs), 685(vs), 585(vs).

**Ceramic Residue Yield (TGA):** 26%

Solvent Free Thermolysis of Oligo(methylsilane) With 1.0 mol% of Ti(OPr-i)₄ at 200°C. (PC/4/12)

A graphite boat was charged with 0.57 g (0.013 mol) of oligo(methylsilane) (CH/SiH = 3.3) clear oil and 0.04 mL (0.14 mmol) of Ti(OPr-i)₄ and was placed in the Ar purging furnace tube. The sample then was pyrolyzed using the following program: ramp I: 5°C/min.; dwell I: 100°C (1 h); ramp II: 5°C/min.; dwell II: 200°C (2 h). After pyrolysis, 0.49 g (80%) tacky blue solid which was soluble in most common organic solvents was obtained.

**1H NMR** (300 MHz, C₆D₆): δ 0.5 (W₁/₂ = 105 Hz, 4.1 H, SiCH₃), 4.1 (W₁/₂ = 75 Hz, 1.0 H, SiH, SiH₂); CH/SiH = 4.1.

**²⁹Si NMR** (59.59 MHz, C₆D₆): δ_Si -68, -71 (W₁/₂ = 600 Hz, SiH); -62 (W₁/₂ = 300 Hz, SiH₂).

**IR** (KBr pellet, cm⁻¹): 2956(s), 2894(s), 2796(w), 2104(s), 1409(s), 1251(vs), 1050(s), 931(vv), 866(vs), 761(vs), 683(s).
Ceramic Residue Yield (TGA): 47%

Thermolysis of Oligo(methylsilane) With 1.0 mol% of Ti(OPr-i)₄ at 250°C in a Sealed Tube. (PC/4/13)

A 100 mL thick-walled tube was charged with 0.77 g (0.0175 mol) of oligo(methylsilane) (CH/SiH = 3.3) clear oil and 0.05 mL (0.180 mmol) of Ti(OPr-i)₄. The tube was sealed under vacuum and placed in the furnace programmed: ramp: 5°C/min.; dwell: 250°C (3 h). After pyrolysis, 0.65 g (80%) of a black, sparingly soluble solid was obtained.

¹H NMR (300 MHz, C₆D₆): δ 0.5 (W₁/₂ = 75 Hz, 6.6 H, SiCH₃),

4.1 (W₁/₂ = 90 Hz, 1.0 H, SiH, SiH₂); CH/SiH = 6.6.

²⁹Si NMR (59.59 MHz, C₆D₆): δ Si -66 (W₁/₂ = 540 Hz, SiH);

-61, -64 (W₁/₂ = 300 Hz, SiH₂)

IR (KBr pellet, cm⁻¹): 2950(s), 2887(s), 2796(w), 2063(s), 1406(s), 1242(s),

1040(s), 931(m), 866(vs), 762(vs), 680(vs).

Ceramic Residue Yield (TGA): 72%

UV Photolysis of Oligo(methylsilane) With 1.0 mol% of Ti(OPr-i)₄ in Hexane Under Vacuum. (PC/4/15)

A 100 mL Schlenk quartz flask equipped with magnetic stir-bar and a high vacuum stopper was charged with 0.73 g (0.0166 mol) of oligo(methylsilane) (CH/SiH = 3.3 clear oil, 0.05 mL (0.180 mmol) of Ti(OPr-i)₄, and 20 mL of
hexane. The flask then underwent three freeze-pump-thaw cycles. The evacuated flask was irradiated with a Hanovia UV lamp for 4.5 h. After the photolysis the cloudy, navy blue solution was trap-to-trap distilled after which the solids were redissolved in toluene and centrifuged for 1 h. The supernatant solution was then trap-to-trap distilled leaving 0.73 g (93%) of blue oil, which was soluble in most common organic solvents. The trace of black insoluble solid residue was not analyzed.

\[ ^1H \text{NMR (300 MHz, C}_6\text{D}_6): \delta 0.5 \ (W_{1/2} = 120 \text{ Hz, SiCH}_3), \]

\[ 4.1 \ (W_{1/2} = 75 \text{ Hz, SiH, SiH}_2), \text{ CH/SiH = 3.3.} \]

Ceramic Residue Yield (TGA): 25%

Reaction of Oligo(methylsilane) With 1.0 mol% of B(OEt)_3 in Refluxing

Undecane (b.p. 196°C). (PC/7/33, 34)

A 100 mL Schlenk flask equipped with magnetic stir-bar and a reflux condenser was charged with 0.78 g (0.0177 mol) of oligo(methylsilane) (\text{CH/SiH} = 3.5), 0.020 g (0.137 mmol) of B(OEt)_3, and 15 mL of undecane. The solution then was heated at reflux for 3.5 h. The solution was trap-to-trap distilled leaving 0.86 g (107%) of yellow solid which was soluble in most common organic solvents.

\[ ^1H \text{NMR (300 MHz, C}_6\text{D}_6): \delta 0.5 \ (W_{1/2} = 90 \text{ Hz, SiCH}_3), \]

\[ 0.9, 1.3 \ (\text{trace, (CH}_2)_n \text{ of undecane}), \]

\[ 4.1 \ (W_{1/2} = 120 \text{ Hz, SiH, SiH}_2); \]

\[ \text{CH/SiH = 11.2.} \]
$^{29}$Si NMR (59.59 MHz, C₆D₆): δ₁₋₆ -66 ($W_{1/2} = 920$ Hz, SiH); -61, -64 ($W_{1/2} = 300$ Hz, SiH₂)

IR (KBr pellet, cm⁻¹): 2950(s), 2887(s), 2796(w), 2063(s), 1406(s), 1242(s), 1043(s), 931(vw), 868(vs), 764(vs), 682(vs).

Ceramic Residue Yield (TGA): 78%

Thermolysis of Neat Oligo(methylsilane) at 190°C in a Sealed Tube. (PC/2/74)

A 100 mL thick-walled tube was charged with 2.0 g (0.045 mol) of oligo(methylsilane) (CH/SiH = 3.3) clear oil. The tube was sealed under vacuum and placed in the 190°C constant temperature oil bath for 12 h. A two layer system with very viscous oil covered with transparent liquid was obtained. The oil was redissolved in 40 mL of toluene and the solution was transferred to 100 mL Schlenk flask where it was trap-to-trap distilled leaving 1.9 g (95%) of translucent, viscous oil.

$^1$H NMR (300 MHz, C₆D₆): δ 0.5 ($W_{1/2} = 120$ Hz, 5.6 H, SiCH₃), 4.0 ($W_{1/2} = 105$ Hz, 1.0 H, SiH, SiH₂), CH/SiH = 5.6.

IR (thin film NaCl, cm⁻¹): 2956(s), 2892(s), 2793(w), 2109(s), 1918(vw), 1409(s), 1247(s), 1039(m), 931(s), 861(s), 762(s), 634(s), 584(s).

Ceramic Residue Yield (TGA): 25%
Thermolysis of Neat Oligo(methylsilane) at 250°C in a Sealed Tube. (PC/4/22)

A 100 mL thick-walled tube was charged with 0.87 g (0.020 mol) of oligo(methylsilane) (CH/SiH = 3.5) clear oil. The tube was sealed under vacuum and placed in the furnace which was programmed: ramp: 5°C/min.; dwell: 250°C (3 h). After heating, the tube must be handled with great care since their contents are under pressure. A tacky solid product was obtained which was redissolved in 40 mL of toluene. The solution was transferred to 100 mL Schlenk flask where it was trap-to-trap distilled leaving 0.80 g (92%) of translucent tacky solid soluble in most common organic solvents.

$^1$H NMR (300 MHz, C$_6$D$_6$): $\delta$ 0.5 ($W_{1/2} = 90$ Hz, 5.2 H, SiCH$_3$), 4.1 ($W_{1/2} = 120$ Hz, 1.0 H, SiH, SiH$_2$), CH/SiH = 5.2.

$^{29}$Si NMR (59.59 MHz, C$_6$D$_6$): $\delta$ Si -66 ($W_{1/2} = 840$ Hz, SiH); -61, -64 ($W_{1/2} = 300$ Hz, SiH$_2$), (Fig. F8).

IR (thin film NaCl, cm$^{-1}$): 2954(s), 2890(s), 2791(w), 2074(s), 1408(s), 1246(s), 1046(w), 931(s), 865(s), 770(s), 682(s).

Ceramic Residue Yield (TGA): 43%

Thermolysis of Neat Oligo(methylsilane) at 300°C in a Sealed Tube. (PC/4/8)

A 100 mL thick-walled tube was charged with 0.70 g (0.016 mol) of oligo(methylsilane) (CH/SiH = 3.5) clear oil. The tube was sealed under vacuum and placed in the furnace which was programmed: ramp: 5°C/min.; dwell: 300°C (0.5 h). The tacky solid product was redissolved in 40 mL of toluene. The
solution was transferred to a 100 mL Schlenk flask and trap-to-trap distilled
leaving 0.60 g (86%) of pale yellow-white, which tacky solid sparingly soluble in
benzene and toluene.

$^1$H NMR (300 MHz, C$_6$D$_6$): $\delta$ 0.5 ($W_{1/2} = 75$ Hz, 8.5 H, SiCH$_3$),
4.1 ($W_{1/2} = 120$ Hz, 1.0 H, SiH, SiH$_2$), CH/SiH = 8.5.

IR (KBr pellet, cm$^{-1}$): 2949(s), 2888(s), 2791(vw), 2060(s), 1405(s), 1242(s),
930(w), 866(vs), 788(vs), 682(vs).

Analysis of Ceramics: (1500°C) C: 25.86%; Si: 61.79%; $\sum$ = 87.65%
Calc. (SiC): C: 29.95%; Si: 70.05%

Ceramic Residue Yield (TGA): 71%

Thermolysis of Neat Oligo(methyilsilane) at 400°C in a Sealed Tube. (PC/4/6)

A 100 mL thick-walled tube was charged with 0.73 g (0.016 mol) of
oligo(methyilsilane) (CH/SiH = 3.5) clear oil. The tube was sealed under vacuum
and placed in the furnace which was programmed: ramp: 5°C/min.; dwell: 400°C
(0.5 h). After the elapsed period of time 0.50 g (68%) of insoluble, infusible,
canary yellow solid was obtained.

Ceramic Residue Yield (TGA): 91%

IR (KBr pellet, cm$^{-1}$): 2950(w), 2886(m), 2790(vw), 2060(m), 1404(m), 1348(w),
1242(s), 868(w), 761(vs), 678(vs).
Irradiation With γ-Rays of Neat Oligo(methylsilane) in a Sealed Tube. (PC/4/35)

A 100 mL thick-walled tube was charged with 0.45 g (0.0102 mol) of oligo(methylsilane) (CH/SiH = 3.4) clear oil. The tube was sealed under vacuum and placed in the γ cell for a 2 MRad dose from $^{60}$Co source. After irradiation, 0.44 g of a clear, low viscosity oil was obtained.

$^1$H NMR (300 MHz, C$_6$D$_6$): $\delta$ 0.5 ($W_{1/2}$ = 120 Hz, 3.2 H, SiCH$_3$), 4.0 ($W_{1/2}$ = 75 Hz, 1.0 H, SiH, SiH$_2$), CH/SiH = 3.2.

$^{29}$Si NMR (59.59 MHz, C$_6$D$_6$): $\delta_{Si}$ -68, -71 ($W_{1/2}$ = 620 Hz, SiH); -61, -64 ($W_{1/2}$ = 300 Hz, SiH$_2$)

Ceramic Residue Yield (TGA): 18%

UV Photochlorination of Oligo(methylsilane) in CH$_2$Cl$_2$ Under Vacuum. (PC/5/23, 42)

A 100 mL Schlenk quartz flask equipped with a high vacuum stopper and a magnetic stir-bar was charged with 0.48 g (0.0110 mol) of oligo(methylsilane) (CH/SiH = 3.3) clear oil and 15 mL of CH$_2$Cl$_2$. The flask then was evacuated and underwent three freeze-pump-thaw cycles and was placed under Hanovia UV lamp for 18 h. The light yellow solution then was trap-to-trap distilled leaving 0.97 g (0.0123 mol based on (MeSiCl)$_n$) of translucent yellow oil, which was soluble in most common organic solvents. The product showed a positive Beilstein test for the presence of chlorine.
$^1$H NMR (300 MHz, C$_6$D$_6$): $\delta$ 0.8 ($W_{1/2} = 120$ Hz, ClSiCH$_3$, Cl$_2$SiCH$_3$).

$^{13}$C NMR (75.5 MHz, C$_6$D$_6$): $\delta$ C -9 ($W_{1/2} = 300$ Hz, SiCH$_3$);

$\begin{array}{l}
2 \quad (W_{1/2} = 320$ Hz, (CH$_3$SiCl)$_n$);
10 \quad (W_{1/2} = 80$ Hz, CH$_3$SiCl);
7 \quad (W_{1/2} = 80$ Hz, CH$_3$SiCl$_2$);
29 \quad (W_{1/2} = 300$ Hz, SiCH$_2$Cl).
\end{array}$

$^{29}$Si NMR (59.59 MHz, C$_6$D$_6$): $\delta$ Si -60 ($W_{1/2} = 540$ Hz, SiH, SiH$_2$);

$\begin{array}{l}
5 \quad (W_{1/2} = 840$ Hz, (ClSiMe)$_n$);
24 \quad (W_{1/2} = 240$ Hz, ClSiMe);
32 \quad (W_{1/2} = 300$ Hz, Cl$_2$SiMe).
\end{array}$

IR (thin film on NaCl, cm$^{-1}$): 2963(s), 2898(s), 2789(w), 2167(w), 1946(w),

$\begin{array}{l}
1400(s), 1253(s), 1055(s), 844(s), 762(s), 532(s).
\end{array}$

Analysis:

C: 14.31%; Si: 30.06%; Cl: 44.00%

Calc. based on (CH$_3$SiCl)$_n$: C: 15.28%; Si: 35.74%; Cl: 45.13%

UV Photochlorination of Oligo(methylsilane) in CH$_2$Cl$_2$: (PC/7/13, 27, 29, 30, 31, 32, 72; PC/8/5)

A solution of 1.93 g (0.0439 mol based on MeSiH) of the oligo(methylsilane) (CH/SiH = 3.3) clear oil in 20 mL of CH$_2$Cl$_2$ in a quartz flask equipped with a Claisen adapter containing a cold finger, a gas adapter for Ar inlet, and a magnetic stir-bar was irradiated with a Hanovia UV lamp for 22 h (the solution became slightly warm but did not reflux). The resulting light yellow solution was distilled at reduced pressure to remove solvent, leaving 3.3 g (0.0420 mol based on (MeSiCl)$_n$) of a clear oil, which was soluble in most common
organic solvents. The product showed a positive Beilstein test for the presence of chlorine.

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 0.6 (W$_{1/2}$ = 75 Hz, 1.0 H, ClSiCH$_3$);
1.0 (W$_{1/2}$ = 75 Hz, 1.4 H, Cl$_2$SiCH$_3$).

IR (thin film on NaCl, cm$^{-1}$): 2962(m), 2899(m), 2790(vw), 2144(vw), 1400(s),
1255(vs), 1057(m), 845(m), 772(vs), 727(vs), 532(vs).

UV Photochlorination of Oligo(methylsilane) in CH$_2$Cl$_2$ at Various Time Intervals. (TS/2/15, 16, 17, 20, 38)

A 100 mL quartz flasks equipped with a Claisen adapters containing a cold fingers, a gas adapters for an Ar inlet, and a magnetic stir-bar was charged with the amounts of oligo(methylsilane) (CH/SiH = 3.3) shown in Table H3 and 30 mL of CH$_2$Cl$_2$. The flasks then was irradiated with a Hanovia UV lamp for the times indicated in Table H3. The resulting light yellow solutions were trap-to-trap distilled leaving the amounts of oligo(methylchlorosilane) indicated in Table H3. The products were soluble in most common organic solvents. The products showed a positive Beilstein test for presence of chlorine.
Table H3

<table>
<thead>
<tr>
<th>Amount of Oligomer (g)</th>
<th>Mol Based on (CH₃SiH)ₙ</th>
<th>Hours of Irradiation</th>
<th>Yield (g)</th>
<th>SiCH₃/SiH by ¹H NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>0.0227</td>
<td>2</td>
<td>1.47</td>
<td>14.4</td>
</tr>
<tr>
<td>0.99</td>
<td>0.0224</td>
<td>4</td>
<td>1.68</td>
<td>30.2</td>
</tr>
<tr>
<td>1.06</td>
<td>0.0240</td>
<td>8</td>
<td>1.94</td>
<td>84.7</td>
</tr>
<tr>
<td>1.16</td>
<td>0.0263</td>
<td>12</td>
<td>2.16</td>
<td>188.7</td>
</tr>
<tr>
<td>0.55</td>
<td>0.0125</td>
<td>16</td>
<td>0.75</td>
<td>∞</td>
</tr>
</tbody>
</table>

¹H NMR (300 MHz, CD₂Cl₂): δ 0.6 (W₁/₂ = 75 Hz, ClSiCH₃);
1.0 (W₁/₂ = 75 Hz, Cl₂SiCH₃),
3.8 (50 Hz, SiH, SiH₂);

Table H3 shows values of SiCH₃/SiH ratios.
IR (thin film, NaCl, cm⁻¹): 2962(m), 2896(m), 2125(s), 1402(s), 1251(s), 1085(w), 929(s), 866(vs), 766(vs), 704(vs), 541(vs).

UV Photoclorination of Poly(methyilsilane) (TS-2 Quenched with MeI) and 1.0 CH₂Cl₂ in Hexane and Its Subsequent Reduction with LiAlH₄ (TS/3/43, 48)

A solution of 0.36 g (8.2 mmol) of poly(methyilsilane) (CH/SiH = 13.0) solid in 50 mL hexane and 1.0 mL of CH₂Cl₂ in a quartz flask equipped with a Claisen adapter containing a cold finger, a gas adapter for an Ar inlet, and a magnetic stir-bar was irradiated with a Hanovia UV lamp for 16 h. The resulting solution was trap-to-trap distilled leaving 0.661 g (8.4 mmol based on (MeSiCl)ₙ) of clear, tacky solid, which was soluble in most common organic solvents.
$^{1}H$ NMR (300 MHz, C$_6$D$_6$): $\delta$ 0.7 ($W_{1/2} = 175$ Hz, ClSiCH$_3$, Cl$_2$SiCH$_3$).

IR (thin film on NaCl, cm$^{-1}$): 2959(s), 2897(m), 2120(vw), 1400(s), 1254(vs), 1056(s), 840(m), 776(vs), 700(s), 617(m), 605(m), 524(s).

**Reduction of the photochlorinated TS-2**

A 100 mL Schlenk flask equipped with a magnetic stir-bar was charged with 0.312 g (3.9 mmol) of oligo(methylchlorosilane) tacky solid, 30 mL of THF, and 20 mL of concentrated LiAlH$_4$ THF solution. After the solution was stirred for 24 h THF was removed by trap-to-trap distillation and the remaining solid was redissolved in 20 mL of toluene to precipitate the salts. After centrifuging the clear solution was trap-to-trap distilled leaving 0.17 g (3.8 mmol) of clear tacky solid.

$^{1}H$ NMR (300 MHz, C$_6$D$_6$): $\delta$ 0.5 ($W_{1/2} = 75$ Hz, 4.9 H, SiCH$_3$), 4.2 ($W_{1/2} = 75$ Hz, 1.0 H, SiH, SiH$_2$).

IR (thin film on NaCl, cm$^{-1}$): 2956(s), 2892(m), 2104(vs), 1409(m), 1248(s), 1036(s), 931(s), 867(vs), 776(vs), 686(s).

**Molecular Weight by GPC: Fig. E7 b**

**UV Photolysis of Oligo(methylsilane) in Hexane. (PC/8/18)**

A solution of 0.75 g (0.0170 mol) of oligo(methylsilane) (CH/SiH = 3.4) clear oil in 30 mL of hexane in a quartz flask equipped with a Claisen adapter containing a cold finger, a gas adapter for an Ar inlet, and a magnetic stir-bar was
irradiated with a Hanovia UV lamp for 17 h. The resulting light yellow solution was trap-to-trap distilled leaving 0.62 g of solid, which was soluble in most common organic solvents.

\[ ^1H \text{ NMR} \ (300 \text{ MHz, } \text{CD}_2\text{Cl}_2): \delta \ 0.3 \ (W_{1/2} = 60 \text{ Hz, } 6.0 \text{ H, SiCH}_3), \]
\[ \quad 3.7 \ (W_{1/2} = 40 \text{ Hz, } 1.0 \text{ H, SiH, SiH}_2), \text{ CH/SiH} = 6.0. \]

IR (thin film on NaCl, cm\(^{-1}\)): 2955(s), 2890(s), 2791(w), 2105(s), 1407(m), 1247(s), 1044(s), 966(m), 931(s), 865(vs), 769(vs), 685(s).

**Ceramic Residue Yield (TGA):** 33%

**UV Photochlorination of Oligo(methylsilane) With 0.5 Molar Equivalent of CH\(_2\)Cl\(_2\) in Hexane.** (PC/8/15, 14)

A solution of 0.64 g (0.0145 mol) of oligo(methylsilane) (CH/SiH = 3.4) clear oil in 0.50 mL (0.66 g, 7.8 mmol) of CH\(_2\)Cl\(_2\) and 9.5 mL of hexane in a quartz flask equipped with a Claissen adapter containing a cold finger, a gas adapter for an Ar inlet, and a magnetic stir-bar was irradiated with a Hanovia UV lamp for 17 h. The resulting light yellow solution was trap-to-trap distilled leaving 1.123 g (0.0143 mol based on (MeSiCl)\(_n\)) of a solid which was soluble in most common organic solvents. The product showed a positive Beilstein test for presence of chlorine.

\[ ^1H \text{ NMR} \ (300 \text{ MHz, } \text{CD}_2\text{Cl}_2): \delta \ 0.6 \ (W_{1/2} = 75 \text{ Hz, } 1.0 \text{ H, ClSiCH}_3), \]
\[ \quad 1.0 \ (W_{1/2} = 75 \text{ Hz, } 1.4 \text{ H, Cl}_2\text{SiCH}_3). \]

IR (thin film on NaCl, cm\(^{-1}\)): 2959(s), 2899(s), 2871(s), 2790(w), 2151(vw),
1943(vw), 1400(s), 1253(vs), 1053(m), 844(s),
770(vs), 725(s), 704(s), 515(vs), 503(vs).

Recommended Least Destructive to the Si-Si Bond UV Photochlorination of
Oligo(methylsilane) With 1.0 Molar Equivalent of CH₂Cl₂ in Hexane. (TS/3/21)

A solution of 1.05 g (0.0239 mol) of oligo(methylsilane) clear oil in 1.50
mL (1.99 g, 0.0234 mol) of CH₂Cl₂ and 50 mL of hexane in a quartz flask
equipped with a Claisen adapter containing a cold finger, a gas adap-
tor for a Ar
inlet, and a magnetic stir-bar was irradiated with a Hanovia UV lamp for 16 h.
The resulting light yellow solution was trap-to-trap distilled leaving 1.7061 g of a
clear oil, soluble in most common organic solvents.

**¹H NMR** (300 MHz, C₆D₆): δ 0.6 (W₁/₂ = 150 Hz, 1.0 H, ClSiCH₃);
0.8 (W₁/₂ = 100 Hz, 1.4 H, Cl₂SiCH₃).

**IR** (thin film on NaCl, cm⁻¹): 2962(m), 2900(m), 2142(vw), 1400(s), 1255(s),
1057(m), 874(m), 845(s), 771(vs), 727(vs),
517(vs).

**³¹C NMR** (75.5 MHz, C₆D₆): δC -9 (W₁/₂ = 300 Hz, SiCH₃);
2 (W₁/₂ = 320 Hz, (CH₃SiCl)ₙ);
10 (W₁/₂ = 80 Hz, CH₃SiCl),
7 (W₁/₂ = 160 Hz, CH₃SiCl₂);
(Note absence of SiCH₂Cl).

**²⁹Si NMR** (59.59 MHz, C₆D₆): δSi -60 (W₁/₂ = 540 Hz, SiH, SiH₂);
5 (W₁/₂ = 840 Hz, (ClSiMe)n),
24, (W₁/₂ = 300 Hz, ClSiMe),
32 (W₁/₂ = 240 Hz, MeSiCl₂).

223
Analysis: C: 16.76%; H: 4.23%; Cl: 44.09%
Calc. (MeSiCl)₄: C: 15.29%; H: 3.85%; Cl: 45.12%

**Daylight Photochlorination of Oligo(methylsilane) With CH₂Cl₂ (PC/8/40)**

A solution of 0.37 g (0.0084 mol) of oligo(methylsilane) (CH/SiH = 3.4) clear oil in 20 mL of CH₂Cl₂ in a quartz flask equipped with a magnetic stirrer and a rubber septum was exposed to daylight for 166 h. The resulting solution was trap-to-trap distilled leaving 0.39 g of translucent oil, which was soluble in most common organic solvents. The product shows a positive Beilstein test for presence of chlorine but still a large amount of Si-H bonds were present based on the IR and ¹H NMR spectra.

**¹H NMR** (300 MHz, C₆D₆): δ 0.5 (W₁/₂ = 120 Hz, 3.9 H, SiCH₃), 4.0 (W₁/₂ = 75 Hz, 1.0 H, SiH, SiH₂).

**IR** (thin film on NaCl, cm⁻¹): 2957(s), 2894(s), 2794(w), 2109(s), 1920(vw), 1409(s), 1247(s), 1034(w), 930(s), 864(s), 769(s), 686(s), 587(s), 496(m).

**UV Photochlorination of the Nicalon® Fiber Polycarbosilane Precursor in CH₂Cl₂ at Various Time Intervals.** (PC/6/14, 19, 24; PC/8/30)

The solutions of the polycarbosilane shown in **Table H4** in 50 mL of CH₂Cl₂ in quartz flasks equipped with a Claisen adapters containing a cold finger, a gas adapters for an Ar inlet, and magnetic stir-bar were irradiated with a Hanovia
UV lamp for the times indicated in Table H4. The resulting light yellow solutions were trap-to-trap distilled leaving the amounts of chlorinated polycarbosilane indicated in Table H4. The products were soluble in most common organic solvents. The products showed a positive Beilstein test for the presence of chlorine.

<table>
<thead>
<tr>
<th>Amount of PCS (g)</th>
<th>Mol of PCS</th>
<th>Hours of Irradiation</th>
<th>Yield (g)</th>
<th>SiCH₃/SiH by ¹H NMR*</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.10</td>
<td>0.0534</td>
<td>17</td>
<td>3.41</td>
<td>-</td>
</tr>
<tr>
<td>3.00</td>
<td>0.0517</td>
<td>19</td>
<td>3.9</td>
<td>13.5</td>
</tr>
<tr>
<td>3.00</td>
<td>0.0517</td>
<td>37</td>
<td>3.4</td>
<td>15.0</td>
</tr>
<tr>
<td>4.00</td>
<td>0.0690</td>
<td>66</td>
<td>4.8</td>
<td>14.5</td>
</tr>
</tbody>
</table>

* - SiCH₃/SiH ration of the starting material is 7.75

¹H NMR (300 MHz, C₆D₆): δ 0.3 (W₁/₂ = 150 Hz, SiCH₃),

4.6 (W₁/₂ = 210 Hz, SiH, SiH₂),

Table H4 shows SiCH₃/SiH ratios.

IR (KBr pellet, cm⁻¹): 2951(s), 2897(s), 2102(s), 1409(m), 1357(m), 1255(s), 1023(vs), 830(vs), 493(m).

Ceramic Residue Yield (TGA): ~ 74%

UV Photoclorination of the Nicalon® Fiber Polycarbosilane Precursor in CCl₄. (PC/6/31)

A solution of 2.0 g (0.0344 mol) of the polycarbosilane (CH/SiH = 7.75) in 15 mL of CCl₄ in a quartz flask equipped a Claisen adapter containing a cold
finger, a gas adapter for an Ar inlet, and a magnetic stir-bar was irradiated with
Hanovia UV lamp for 15 h. The resulting amber solution was trap-to-trap distilled
leaving 3.4 g of yellow solid, which was soluble in most common organic solvents.
The product showed a positive Beilstein test for presence of chlorine.

$^1$H NMR (300 MHz, C$_6$D$_6$): $\delta$ 0.4 (W$_{1/2}$ = 210 Hz, 30 H, SiCH$_3$),
5.0 (1.0 H, SiH, SiH$_2$), CH/SiH = 30.

IR (KBr pellet, cm$^{-1}$): 2951(m), 2896(m), 2108(m), 1406(m), 1356(m), 1257(s),
1024(s), 827(vs), 480(m).

Ceramic Residue Yield (TGA): 61%

UV Photochlorination of Oligo(methylsilane) Using Various Chlorinating Agents.

(TS/1/58, 70, 57)

The solutions of the OMS shown in Table H5 in 50 mL of chlorocarbon in
quartz flasks equipped with a Claisen adapters containing a cold finger, a gas
adapters for an Ar inlet, and magnetic stir-bar were irradiated with a Hanovia UV
lamp for 22 h. The resulting light yellow solutions were trap-to-trap distilled
leaving the amounts of chlorinated polycarboxilane indicated in Table H5. The
products were soluble in most common organic solvents. The products showed a
positive Beilstein test for the presence of chlorine.
Table H5

<table>
<thead>
<tr>
<th>solvent</th>
<th>weight (g) of OMS</th>
<th>weight (g) of chlorinated OMS</th>
<th>Cl₂SiMe/ClSiMe ratio by ¹H NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂Cl₂</td>
<td>4.5</td>
<td>6.95</td>
<td>1.82</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>5.44</td>
<td>10.2</td>
<td>2.07</td>
</tr>
<tr>
<td>CCl₄</td>
<td>2.33</td>
<td>5.11</td>
<td>2.97</td>
</tr>
</tbody>
</table>

¹H NMR (300 MHz, CD₂Cl₂): δ 0.6 (W₁/₂ = 75 Hz, ClSiCH₃);
1.0 (W₁/₂ = 75 Hz, Cl₂SiCH₃),

for Cl₂SiMe/ClSiMe ratio see Table H5.

IR (thin film on NaCl, cm⁻¹)

(CH₂Cl₂) : 2964(m), 2899(m), 2142(w), 1400(s), 1254(vs), 1050(w), 874(m),
771(vs), 706(s), 523(vs).

(CHCl₃) : 2964(m), 2899(m), 2140(vw), 1400(s), 1254(vs), 1041(w), 874(w),
770(vs), 707(s), 522(vs).

(CCl₄) : 2964(w), 2900(w), 1400(s), 1254(vs), 1079(w), 867(w), 780(vs), 727(s),
530(vs).

Reaction of Oligo(methylchlorosilane) With an Excess of Ammonia at 4°C in

Diethyl Ether. (PC/8/8, 16)

A 100 mL, three-necked, round bottomed flask equipped with a dry
ice/acetone condenser, mechanical stir-bar, and a gas adapter for an ammonia inlet
was charged with 1.2 g (0.0153 mol) of oligo(methylchlorosilane) oil (PC/8/15)
and 30 mL of Et₂O. The flask was placed in a slush bath at 4°C and dry ammonia
gas was bubbled in until it started to condense on the dry ice-acetone condenser
(about 1 h). The mixture was allowed to warm to room temperature. NH₄Cl was filtered (0.79 g, 0.0148 mol, 97%) and the filtrate was trap-to-trap distilled leaving 0.60 g of a white solid which was soluble in most common organic solvents.

**¹H NMR** (300 MHz, C₆D₆): δ 0.5 (W₁/₂ = 170 Hz, HNSiCH₃, (HN)₂SiCH₃); 3.0 (trace, SiH).

**IR** (thin film on NaCl, cm⁻¹): 3358(m), 2947(s), 2889(s), 2073(w), 1540(m), 1407(m), 1349(m), 1245(m), 1135(s), 1020(s), 882(vs), 754(vs).

**Ceramic Residue Yield (TGA):** 82%

**Analysis:**

C: 20.82%; H: 6.58%; N: 11.03%

Calc. (CH₃Si(NH)₀.₅)n: C: 23.72%; H: 6.97%; N: 13.83%

**Reaction of Oligo(methylchlorosilane) With an Excess of NH₂CH₃ at 4°C in Diethyl Ether.** (PC/8/7)

A 100 mL, three-necked, round bottomed flask equipped with a dry ice/acetone condenser, mechanical stir-bar, and a gas adapter for methylamine inlet was charged with 1.2 g (0.0153 mol) of oligo(methylchlorosilane) oil (PC/7/13) and 30 mL of Et₂O. The flask was placed in a slush bath at 4°C and dry methylamine gas was bubbled in until it started to condensed on the dry ice/acetone condenser (about 1 h). The mixture was allowed to warm to room temperature, then CH₃NH₃Cl was filtered. The filtrate was trap-to-trap distilled leaving 1.0 g (0.0172 mol) of yellowish oil which was soluble in most common
organic solvents. The oil gave a negative Beilstein test for chlorine.

$^{1}H$ NMR (300 MHz, C$_6$D$_6$): $\delta$ 0.3 (W$_{1/2}$ = 105 Hz, 3.5 H, HNSiCH$_3$,

(HN)$_2$SiCH$_3$); 2.5 (W$_{1/2}$ = 60 Hz, 3 H, NCH$_3$).

$^{29}$Si NMR (59.59 MHz, C$_6$D$_6$): $\delta$ _Si_-5, -2 (W$_{1/2}$ = 600 Hz, SiHNCH$_3$,

Si(HNCH$_3$)$_2$)

IR (thin film on NaCl, cm$^{-1}$): 3416(m), 2948(s), 2885(s), 2800(s), 2080(vw),

1576(vw), 1536(w), 1464(m), 1425(m), 1367(s),

1246(s), 1175(s), 1094(vs), 884(vs), 758(vs), 711(s),

573(s), 523(vw).

Ceramic Residue Yield (TGA): 30%

Analysis:

C: 32.88%; H: 8.86%; N: 16.57%

Calc. (CH$_3$Si(NHCH$_3$)$_{0.5}$)$_n$: C: 30.99%; H: 8.67%; N: 12.04%

Reaction of Oligo(methylchlorosilane) With an Excess of PhLi at 4°C in Diethyl Ether. (TS/2/47)

A 100 mL Schlenk flask containing a magnetic stir-bar and 15 mL of ether was charged with 15 mL of a 1.3 M ether solution of PhLi (0.0195 mol) and was fitted with an addition funnel containing 0.98 g (0.0125 mol) of oligo(methylchlorosilane) oil (PC/7/13) diluted by 10 mL of ether. The flask was placed in a slush bath at 4°C and the contents of the funnel were added dropwise over 20 min. into the stirred PhLi solution. The brown suspension was allowed to warm to room temperature and was stirred overnight. Filtration was followed by treatment of the filtrate with 10 mL of methanol to react all remaining Si-Cl
functionalities. The resulting suspension was treated with 50 mL of hexane and filtered. The filtrate was trap-to-trap distilled leaving 1.08 g of transparent yellow oil which was soluble in most common organic solvents. The oil gave a negative Beilstein test for chlorine.

$^1\text{H NMR}$ (300 MHz, C$_6$D$_6$): δ 0.7 (W$_{1/2}$ = 220 Hz, 1.7 H, SiCH$_3$),

3.5 (W$_{1/2}$ = 80 Hz, 0.2 H, OCH$_3$),

7.4 (W$_{1/2}$ = 80 Hz, 5.0 H C$_6$H$_5$).

$\text{IR}$ (thin film, NaCl, cm$^{-1}$): 2953(s), 2073(vv), 1954(vv), 1884(vv), 1819(vv), 1594(m), 1482(s), 1427(s), 1250(m), 1110(vs), 789(vs), 735(vs), 698(vs).

**Reaction of Oligo(methylchlorosilane) With an Excess of MeOH at 4°C in Diethyl Ether.** (TS/3/23)

A 100 mL Schlenk flask was equipped with a magnetic stir-bar and an addition funnel containing 50 mL of methanol was charged with 2.4 g (0.0545 mol) of oligo(methylchlorosilane) oil (TS/3/21) and 20 mL diethyl ether. The flask was placed in a slush bath at 4°C. Methanol was dropwise added into stirring OMS/ether solution during 20 min and immediately addition of 2.5 mL of pyridine followed. The resulting white suspension was allowed to warm to room temperature and stirred overnight. Filtration to remove solid followed. The solvent was removed from the filtrate by trap-to-trap distillation leaving 2.13 g of a clear yellow oil which was soluble in most common organic solvents.
\[^1\text{H NMR}\] (300 MHz, C\(_6\)D\(_6\)): \(\delta 0.6\) (\(W_{1/2} = 210\ \text{Hz}\), 1.0 H, SiCH\(_3\)), 
\(3.5\) (\(W_{1/2} = 30\ \text{Hz}\), 0.96 H, OMe).

IR (thin film, NaCl, cm\(^{-1}\)): 2935(vs), 2831(s), 1458(m), 1405(m), 1249(s), 
1183(s), 1072(vs), 814(s), 750(vs), 654(s), 503(vw).

Analysis: C: 30.15%; H: 8.10%; Cl: 2.23%
Calc. (CH\(_3\)SiOCH\(_3\))\(_n\): C: 32.39%; H: 8.16%; O: 21.58%

Extended Reaction Time Experiment of MeSiHCl\(_2\) and 2.5 Na in 7/1 v/v
Hexane/THF by Ultrasonic Activation. (TS/1/52)

The effect of long ultrasonication on the reaction was explored.

A 300 mL Schlenk tube was charged with 41.0 g (1.78 mol) of shiny Na metal (~ 10 mm in diameter), 140 mL of hexane, 20 mL of THF, and 73 mL (80.3 g, 0.70 mol) of MeSiHCl\(_2\). As soon as the chlorosilane was added the Na surface turned black. The flask was placed in the ultrasonic bath at 47°C for 24 h. The originally, clear, colorless solution became yellow after about 22 h of ultrasonication. After termination of ultrasonication the solid phase was filtered and washed three times with 50 mL portions of hexane. The yellow filtrate was trap-to-trap distilled to leave 14.7 g (0.33 mol, 48%) of a light-yellow solid, which was pyrophoric and soluble in most common organic solvents. Melting behavior was observed under a flow of Ar in the pyrolysis furnace and revealed softening at 140°C and melting with evolution of bubbles at 185°C.

\[^1\text{H NMR}\] (300 MHz, C\(_6\)D\(_6\)): \(\delta 0.45\) (\(W_{1/2} = 75\ \text{Hz}\), 5.9 H, SiCH\(_3\));
\[ W_{1/2} = 90 \text{ Hz}, \ 1.0 \text{ H, SiH, SiH}_2. \]

\[^{13}\text{C NMR} (75.5 \text{ MHz, C}_6\text{D}_6): \ \delta_C -8 \text{ to } -9.5 (W_{1/2} = 290 \text{ Hz, SiCH}_3).\]

\[^{29}\text{Si NMR} (59.59 \text{ MHz, C}_6\text{D}_6): \ \delta_{\text{Si}} -62 (W_{1/2} = 530 \text{ Hz, SiH}); -60 \text{ (trace peak, SiH}_2).\]

\textbf{IR} (thin film on NaCl, cm\(^{-1}\)):
- 2951(m), 2887(s), 2787(w), 2057(s), 1405(m),
- 1243(m), 1076(m), 928(w), 866(vs), 789(vs), 684(vs),
- 640(s).

\textbf{Ceramic Residue Yield (TGA)}: 44%

\textbf{Analysis}:
- C: 22.96%; H: 6.79%
- Calc.\((\text{MeSiH}_x)_{0.51}(\text{MeSi})_{0.49}\): C: 27.53%; H: 8.09%

\textbf{Analysis of ceramics}
- \((1500^\circ C, \text{ Ar})\): C: 28.85%; Si: 63.63%; Na: 0.14%; \(\sum = 92.62\%\)
- Calc.(SiC): C: 29.95%; Si: 70.05%

\textbf{Molecular Weight by GPC}: Fig. G18 c

Long time reductive coupling affords high molecular weight product.

\textbf{Extended Reaction Time Experiment of MeSiHCl}_2\text{ and 2.5 Na in 7/1 v/v} \textbf{Hexane/THF by Ultrasonic Activation}, (PC/7/58)

The effect of 2.5 days of ultrasonication on reductive coupling was investigated.

A 200 mL Schlenk tube was charged with 14.6 g (0.635 mol) of shiny Na metal (~ 5 mm in diameter), 52.3 mL of hexane, 7 mL of THF, and 26 mL (28.6 g, 0.249 mol) of MeSiHCl\(_2\). As soon as the chlorosilane was added the Na surface turned black. The flask then was placed in the ultrasonic bath operating at 47°C
for 64 h. After termination of ultrasonication the solids were filtered and washed three times with 50 mL portions of toluene. The yellow filtrate was trap-to-trap distilled leaving 4.6 g (0.104 mol, 42%, rest of the product was insoluble) of a light-yellow solid which was pyrophoric and soluble in most common organic solvents.

$^{1}$H NMR (300 MHz, C$_6$D$_6$): $\delta$ 0.5 ($W_{1/2}$ = 60 Hz, 9.0 H, SiCH$_3$);

$\delta$ 4.2 ($W_{1/2}$ = 90 Hz, 1.0 H, SiH, SiH$_2$), CH/SiH = 9.0.

$^{29}$Si NMR (59.59 MHz, C$_6$D$_6$): $\delta$$_{Si}$ -64 ($W_{1/2}$ = 400 Hz, SiH);

$\delta$ -60 (trace peak, SiH$_2$).

Ceramic Residue Yield (TGA): 80%

Analysis of Ceramics (1500°C, Ar): C: 26.22%; Si: 68.65%; $\sum$ = 94.87%

Calc.(SiC): C: 29.95%; Si: 70.05%

Molecular Weight by GPC: Fig. G18 c

Longer ultrasonication gives lower yields of soluble crosslinked higher molecular weight product.

Extended Reaction Time Experiment of MeSiHCl$_2$ and 2.5 Na in 7/1 v/v

Toluene/THF by Ultrasonic Activation. Synthesis of TS-1. (PC/7/59)

The effect of aromatic hydrocarbons on the long reductive coupling product.

A 300 mL Schlenk tube was charged with 14.6 g (0.635 mol) of shiny Na metal (~ 10 mm in diameter), 52.3 mL of hexane, 7 mL of THF, and 26 mL (28.6
g, 0.249 mol) of MeSiHCl₂. As soon as the chlorosilane was added the Na surface turned black. The flask was placed in the ultrasonic bath operating at 47°C for 43 h. After termination of ultrasonication, the solid phase was filtered and washed three times with 50 mL portions of toluene. The yellow-orange filtrate was trap-to-trap distilled yielding 5.6 g (0.127 mol, 51%, rest of the product was insoluble) of yellow-orange solid, which was pyrophoric and soluble in most common organic solvents.

**¹H NMR (300 MHz, C₆D₆):** δ 0.5 (W₁/₂ = 60 Hz, 7.35 H, SiCH₃);
4.2 (W₁/₂ = 120 Hz, 1.0 H, SiH, SiH₂),
CH/SiH = 7.35.

**IR (thin film on NaCl, cm⁻¹):** 2953(s), 2889(s), 2790(w), 2065(s), 1893(vw),
1456(w), 1407(m), 1244(s), 1044(s), 930(m), 868(vs),
765(vs), 684(vs), 584(w), 466(m).

**Ceramic Residue Yield (TGA):** 85%

**Analysis of the Polymer:**
C: 25.24%; H: 7.21%

Calc. (MeSiHₓ)₀.₄₁(MeSi)₀.₅₉: C: 27.67%; H: 7.86%

**Analysis of Ceramics (1500°C, Ar):** C: 27.39%; Si: 66.93%; Σ = 94.32%

Calc.(SiC): C: 29.95%; Si: 70.05%

**Molecular Weight by GPC: Fig. G18 b**

In another reaction (TS/4/50) in a 7/1 v/v toluene/THF ultrasonicated for 29 h at 45°C a yellow-greenish powder was obtained in 77% yield.

**¹H NMR (300 MHz, C₆D₆):** δ 0.5 (W₁/₂ = 90 Hz, 4.9 H, SiCH₃);
4.0 (W₁/₂ = 75 Hz, 1.0 H, SiH, SiH₂), CH/SiH = 4.9.

**Ceramic Residue Yield (TGA):** 50%

The presence of aromatic hydrocarbons increases the yield, molecular
weight, and gives precursors which yield higher ceramic residue on pyrolysis.

**Extended Reaction Time Experiment of MeSiHCl₂ (Gradually Added) and 2.5 Na**

in 7/1 v/v Toluene/THF by Ultrasonic Activation. Synthesis of TS-1. (TS/2/51, TS/3/01)

The effect of gradual addition of chlorosilane on the long reductive coupling final product was explored.

A 300 mL Schlenk flask equipped with an addition funnel containing 56 mL (61.6 g, 0.54 mol) of MeSiHCl₂ was charged with 30.5 g (1.33 mol) of shiny Na metal (~10 mm in diameter), 105 mL of toluene and 15 mL of THF. The flask was placed in the ultrasonic bath and the chlorosilane was added dropwise over a period of 1.5 h. The mixture was ultrasonicated at 28°C for 40 h. During ultrasonication the temperature inside the reactor was between 34 - 38°C. After termination of ultrasonication the solids were washed three times with 50 mL portions of toluene and together with the yellow-orange solution were cannulated into a thick-walled bottle which was then centrifuged for 1 h. The yellow-orange supernatant solution was trap-to-trap distilled yielding 14.5 g (0.33 mol, 61%) of yellow-orange solid which was pyrophoric (when compressed or in a heap, but not when spread out) and soluble in most organic solvents. (The same reaction after 139 h of ultrasonication yielded 8.9 g (0.20 mol, 37%) of yellow-orange solid residue which was soluble in most common organic solvents, in addition to a large
amount of insoluble, highly crosslinked polysilane.) The insoluble solids (NaCl and Na) weighted 74.76 g. Melting behavior of the yellow-orange polymer was observed under a flow of Ar in the pyrolysis furnace and revealed softening at 150°C and melting with evolution of bubbles at 185°C.

\[ ^1H \text{NMR} \ (300 \text{ MHz, } C_6D_6): \delta \ 0.5 \ (W_{1/2} = 80 \text{ Hz, } 6.9 \ H, \text{ SiCH}_3); \]
\[ \quad 4.1 \ (W_{1/2} = 86 \text{ Hz, } 1.0 \ H, \text{ SiH, SiH}_2), \text{ CH/SiH} = 6.9. \]

\[ ^{29}\text{Si NMR} \ (59.59 \text{ MHz, } C_6D_6): \delta_{\text{Si}} \ -63 \ (W_{1/2} = 400 \text{ Hz, SiH}); \]
\[ \quad -60 \ (\text{trace peak, SiH}_2), \ (\text{Fig. G9}). \]

\[ \text{IR} \ (\text{thin film on NaCl, } \text{cm}^{-1}): 2952(s), 2890(s), 2790(w), 2065(s), 1406(m), \]
\[ \quad 1245(m), 1046(m), 930(m), 867(vs), 764(vs), 684(vs), \]
\[ \quad 640(s). \]

\[ \text{Ceramic Residue Yield (TGA): } 75\% \ (86\% \text{ after } 139 \text{ h of ultrasonication}) \]

\[ \text{Analysis:} \quad \text{C: } 26.41\%; \text{ H: } 7.87\% \]

\[ \text{Calc.}\ (\text{MeSiH}_x)_{0.43}(\text{MeSi})_{0.57}: \text{C: } 27.56\%; \text{ H: } 7.98\% \]

\[ \text{Analysis of Ceramics (1500°C, Ar):} \quad \text{C: } 28.63\%; \text{ Si: } 64.54\%; \Sigma = 93.17\% \]

\[ \text{Calc.}\ (\text{SiC}): \text{C: } 29.95\%; \text{ Si: } 70.05\% \]

\[ \text{X-ray Diffraction Pattern:} \ (\text{Fig. G5 b}) \]

The gradual addition of the chlorosilane in long reductive coupling results in higher product yields.

\[ \text{Extended Reaction Time Experiment of MeSiHCl}_2 \text{ and } 5.0 \text{ Na in } 7/1 \text{ v/v} \]

\[ \text{Toluene/THF by Ultrasonic Activation.} \ (\text{TS/3/6}) \]

The effect of excess sodium on the reductive coupling reaction was explored. A 300 mL Schlenk flask was charged with 20.7 g (0.90 mol) of shiny
Na metal (~ 10 mm in diameter), 38 mL of toluene, 5 mL of THF, and 18.7 mL (20.6 g, 0.180 mol) of MeSiHCl₂. The flask was placed in the ultrasonic bath at 28°C for 40 h. After termination of ultrasonication the solids were washed three times with 50 mL portions of toluene and the washings, together with the yellow-orange solution, were cannulated into a thick-walled centrifuge bottle and centrifuged for 1 h. The yellow-orange supernatant solution was trap-to-trap distilled leaving 2.4 g (0.055 mol, 30%) of yellow-orange pyrophoric solid which was soluble in most common organic solvents.

\[ {^1}H\text{ NMR (300 MHz, C}_6\text{D}_6\text{): } \delta 0.5 (W_{1/2} = 70 \text{ Hz}, 6.9 \text{ H, SiCH}_3); \]
\[ 4.1 (W_{1/2} = 100 \text{ Hz}, 1.0 \text{ H, SiH, SiH}_2), \text{ CH/SiH} = 6.9. \]

IR (thin film on NaCl, cm\(^{-1}\)): 2952(s), 2890(s), 2790(w), 2062(s), 1406(m), 1245(m), 930(m), 867(vs), 790(vs), 684(vs).

**Ceramic Residue Yield (TGA):** 85%

Excess of Na affords low yield of soluble, high molecular weight product.

**Extraction of the High Molecular Weight Poly(methylsilane) PC-1 From NaCl**

**Crystals Obtained From TS-1 Synthesis (TS/2/51).** (PC/8/34)

Extraction of the high molecular weight polymer from the NaCl crystals in the experiment in which the main reaction product was a solid polymer.

A 300 mL round-bottomed flask equipped with a magnetic stirrer was charged with 65.45 g of green NaCl crystals freshly scraped from the unreacted Na
metal surface. A 200 mL of deoxygenated water (Ar was bubbled for 1 h) was added very slowly, to avoid run-a-way reactions, especially when traces of unreacted Na are present. In the process of water addition the flask contents warmed up to about 80°C. The resulting suspension of a fluffy white solid was stirred overnight at room temperature. The solid was filtered and subsequently dried in vacuo. It was redissolved in 100 mL of toluene to separate it from any remaining NaCl. After filtration, the filtrate was trap-to-trap distilled, leaving 1.6 g of a white solid which was soluble in most common organic solvents. The solid was pyrophoric in air and melted at about 250°C.

\textsuperscript{1}H NMR (300 MHz, C\textsubscript{6}D\textsubscript{6}): \delta 0.6 (W\textsubscript{1/2} = 90 Hz, 8.4 H, SiCH\textsubscript{3});

4.2 (W\textsubscript{1/2} = 120 Hz, 1.0 H, SiH, SiH\textsubscript{2}), CH/SiH = 8.4.

IR (thin film, NaCl, cm\textsuperscript{-1}): 2955(s), 2890(s), 2791(w), 2075(s), 1910(w), 1407(m), 1249(s), 1053(s), 931(m), 868(s), 761(vs), 682(s), 586(m).

**Ceramic Residue Yield (TGA)** (10°C/min., 1000°C, Ar, 3 h): 73%;

(5°C/min., 1500°C, Ar, 3 h): 64%

**Analysis:**

C: 28.39%; Si: 64.44%; H: 7.93%; \(\sum = 100.76\%\)

Calc.(MeSiH\textsubscript{x})\textsubscript{0.36}(MeSi)\textsubscript{0.64}: C: 27.62%; Si: 64.59%; H: 7.79%

**Analysis of Ceramic**

(1500°C, Ar): C: 26.51%; Si: 72.93%; \(\sum = 99.44\%\) (~11% excess Si)

Calc.(SiC): C: 29.95%; Si: 70.05%

**Molecular Weight by GPC:** Fig. G6 b

**X-ray Diffraction Pattern:** Fig. G3 a

238
Extraction of the High Molecular Weight Poly(methylsilane) PC-1 From NaCl Crystals Obtained From Synthesis of Oligo(methylsilane). (TS/2/39, PC/8/12, PC/8/17, PC/8/19, PC/8/23)

Extraction of high molecular weight polymer from NaCl crystals where the main reaction product was an oligo(methylsilane).

A 100 mL Schlenk flask was charged with 25.9 g (1.13 mol) of mirror clean Na metal (~ 10 mm in diameter), 90 mL of hexane, 13 mL of THF, and 46.8 mL (51.5 g, 0.45 mol) of MeSiHCl₂. The flask was placed in the ultrasonic bath at 48°C for 16 h. After termination of ultrasonication the solids were filtered and washed three times with 30 mL portions of hexane. The clear filtrate was trap-to-trap distilled yielding 13.9 g (0.32 mol, 71%) of translucent oil, which was soluble in most common organic solvents. The rest of the solids (NaCl and Na) weighted 60.0 g. Out of the 60.0 g of solids 44.0 g of yellow NaCl that contained high molecular weight polymer were placed into a 300 mL round-bottomed flask equipped with a magnetic stir-bar subsequently 200 mL of deoxygenated water (Ar was bubbled for 1 h) was cannulated in very slowly to avoid run-a-way reactions which might be caused by traces of unreacted Na metal. During the water addition the flask contents warmed to about 80°C. The resulting suspension of a fluffy white solid was stirred overnight at room temperature. The solid was filtered and subsequently dried in vacuo. The solid was redissolved in 100 mL of toluene to separate it from any remaining NaCl. After filtration, the filtrate was trap-to-trap
distilled, leaving 1.9 g of a white, pyrophoric solid which was soluble in most common organic solvents.

$^1$H NMR (300 MHz, C$_6$D$_6$): $\delta$ 0.6 ($W_{1/2}$ = 90 Hz, 4.6 H, SiCH$_3$),
4.1 ($W_{1/2}$ = 75 Hz, 1.0 H, SiH, SiH$_2$), CH/SiH = 4.6.

IR (thin film, NaCl, cm$^{-1}$): 2955(s), 2893(s), 2794(w), 2078(vs), 1913(w),
1408(m), 1248(s), 1035(vw), 931(m), 864(vs), 764(vs),
684(vs), 644(s), 587(m).

Ceramic Residue Yield (TGA) (10°C/min., 600°C, Ar): 77% brown ceramic

Analysis: 
C: 23.71%; Si: 63.49%; H: 8.27%; Na: 0.14%; $\Sigma$ = 95.61%
Calc.(MeSiH$_x$)$_{0.65}$(MeSi)$_{0.35}$: C: 27.43%; Si: 64.15%; H: 8.42%

Analysis of Ceramic (1500°C, Ar): C: 27.27%; Si: 65.43%; $\Sigma$ = 92.70%
Calc.(SiC): C: 29.95%; Si: 70.05%

Molecular Weight by GPC: Fig. G6 d

X-ray Diffraction Pattern: Fig. G3 b

Wurtz Coupling Reaction of MeSiHCl$_2$ and 2.05 Na in 7/1 v/v Toluene/THF by

Ultrasonic Activation and Subsequent Cross-Linking of the Oligomer With 0.5 Na.

Synthesis of TS-2. (TS/2/68, 72t, 72h)

The effect of stoichiometric Na on a long reductive coupling reaction of MeSiHCl$_2$ was investigated.

A 300 mL Schlenk flask equipped with an addition funnel containing 64 mL (0.61 mol) of MeSiHCl$_2$ was charged with 29.0 g (1.26 mol) of shiny Na metal (~10 mm in diameter), 105 mL of toluene and 15 mL of THF. The flask was placed in the ultrasonic bath and the chlorosilane was added dropwise over a period of 1.5
h. The mixture was ultrasonicated at 25°C for 40 h. After termination of ultrasonication the solids were washed three times with 50 mL portions of toluene and the washings, together with yellow solution, were cannulated into a thick-walled centrifuge bottle and centrifuged for 1 h. The yellow supernatant solution was trap-to-trap distilled yielding 17.1 g (0.39 mol, 64%) of yellow oil, soluble in most common organic solvents. The oil (17.0 g) was redissolved in 81 mL of toluene and 12 mL of THF. The solution then was cannulated into 250 mL Schlenk flask containing 4.4 g (0.19 mol) of mirror clean Na. The flask was placed in the ultrasonic bath at 25°C for 18 h. After termination of ultrasonication, the solids were washed three times with 50 mL portions of toluene and the washings, together with yellow-orange solution, were cannulated into a thick-walled centrifuge bottle and centrifuged for 1 h. The yellow-orange supernatant solution was trap-to-trap distilled yielding 13.2 g (0.30 mol, 77%) of an orange solid, which was pyrophoric (when compressed or in a heap, but not when spread out) and soluble in toluene. Out of the toluene soluble fraction (TS-2T) about 80% by weight of it was soluble in hexane (TS-2H). The orange solid, upon exposure to daylight for 1 h became green in color. No melting was observed during pyrolysis.

$^1$H NMR (300 MHz, C$_6$D$_6$): δ 0.45 ($W_{1/2} = 83$ Hz, 9.8 H, SiCH$_3$);

4.2 ($W_{1/2} = 68$ Hz, 1.0 H, SiH, SiH$_2$), CH/SiH = 9.8.

IR (thin film, NaCl, cm$^{-1}$): 2953(s), 2889(s), 2790(w), 2060(s), 1407(m),
1243(m), 1032(w), 932(w), 864(vs), 760(vs), 680(vs), 638(s).

Ceramic Residue Yield (TGA): 90%

Analysis:  
C: 28.54%; H: 7.98%; Na: 1.45%

Calc. (MeSiH\textsubscript{x})\textsubscript{0.31} (MeSi)\textsubscript{0.69}: C: 27.66%; H: 7.66%

-hexane extracted polymer (TS-2H) fraction contains only 0.096% Na

Analysis of ceramics:

(1500°C, Ar): C: 27.07%; Si: 70.92%; Na: 0.055%; \(\sum = 98.04\%\)

(1000°C, Ar): C: 24.69%; Si: 67.51%; Na: 0.68%; \(\sum = 92.88\%\)

Calc. (SiC): C: 29.95%; Si: 70.05%

Analysis of ceramics derived (1500°C, Ar) from:

toluene extracted fraction (TS-2T): C: 28.30%; Si: 63.27%; \(\sum = 91.57\%\)

hexane extracted fraction (TS-2H): C: 29.34%; Si: 66.04%; \(\sum = 95.38\%\)

Calc. (SiC): C: 29.95%; Si: 70.05%

Molecular Weight by GPC: Fig. G7

X-ray Diffraction Pattern (TS-2T): Fig. G8 b

X-ray Diffraction Pattern (TS-2H): Fig. G8 a

Stoichiometric Na even after 40 h of ultrasonication affords an oily product which after additional reaction with Na affords high molecular weight PMS.

Extended Reaction Time Experiment of MeSiHCl\textsubscript{2} and 2.5 Na in Refluxing 7/1 v/v Toluene/THF. (TS/2/73)

The effect of long refluxing on reductive coupling reaction.

A 300 mL Schlenk flask equipped with a reflux condenser and a magnetic stir-bar was charged with 11.5 g (0.50 mol) of mirror clean Na metal (~ 10 mm in
diameter), 40 mL of toluene, 6 mL of THF, and 20.8 mL (22.88 g, 0.20 mol) of MeSiHCl₂. The flask was placed in a 120°C constant temperature bath for 40 h. After cooling to room temperature, the reaction mixture was washed with three 40 mL portions of toluene and the washings, together with the yellow-orange solution were cannulated into a thick-walled centrifuge bottle and centrifuged for 1 h. The clear yellow-orange supernatant solution was trap-to-trap distilled yielding 0.40 g (4.5%) of tacky, yellow-orange solid, which was soluble in most common organic solvents. The insoluble solids weighed 33.90 g.

¹H NMR (300 MHz, C₆D₆): δ 0.5 (W₁/₂ = 86 Hz, 10.8 H, SiCH₃), 4.2 (W₁/₂ = 86 Hz, 1.0 H, SiH, SiH₂); poly(THF) impurity: 1.4 (W₁/₂ = 60 Hz, 0.85 H, CH₂), 2.0 (W₁/₂ = 86 Hz, 0.38 H, CH₂).

IR (thin film, NaCl, cm⁻¹): 2951(m), 2888(s), 2790(w), 2058(s), 1451(m), 1242(m), 1012(w), 908(vw), 868(vs), 789(vs), 762(vs), 681(vs), 644(s).

Prolonged refluxing yields mostly insoluble gels with poly(THF) impurity.
Recommended Procedure for the Preparation of Poly(methylsilane) (TS-2) by Reaction of Oligo(methylsilane) With 0.5 Na in 7/1 v/v Toluene/THF Using Ultrasonic Activation and Subsequent Quenching of the Polymer with Mel (PC/8/42, 55; TS/3/22, 39)

Crosslinking reaction of OMS by Na was explored.

A 250 mL Schlenk flask was charged with 14.3 g (0.325 mol) of oligo(methylsilane) (CH/SiH = 3.6) clear oil, 3.7 g (0.161 mol) of shiny Na shot, and 10 mL of THF and 75 mL toluene. The flask was placed in the ultrasonic bath at 25°C for 20 h (after about 1.5 h clear solution became yellow-orange). After termination of ultrasonication, the solids were washed three times with 50 mL portions of toluene and the washings, together with yellow-orange solution, were cannulated into a thick-walled centrifuge bottle and centrifuged for 3 h. The yellow-orange supernatant solution was trap-to-trap distilled yielding 8.5 g (0.19 mol, 60%) of an orange solid, which was soluble in toluene, the rest of the polymer was an insoluble gel.

\(^1\text{H NMR}\) (300 MHz, C\(_6\)D\(_6\)): δ 0.45 (W\(_{1/2}\) = 90 Hz, 13 H, SiCH\(_3\)), 4.2 (W\(_{1/2}\) = 70 Hz, 1.0 H, SiH, SiH\(_2\)), CH/SiH = 13.

\(\text{IR (thin film, NaCl, cm}^{-1}\): 2951(m), 2889(s), 2057(s), 1405(m), 1242(s), 1032(m), 930(w), 866(vs), 760(vs), 681(vs), 518(w).

Analysis: Na: 1.72%

Ceramic Residue Yield (TGA): 88%

Another reaction (PC/8/42) where the same ratio of oligomer to Na was
used, after 4.5 h of ultrasonication at 30°C in a 7/1 v/v hexane/THF yielded 98% of yellow-orange solid product which was soluble in hexane and toluene.

\[ ^1H \text{ NMR (300 MHz, C}_6\text{D}_6) \delta 0.5 (W_{1/2} = 90 \text{ Hz}, 6.0 \text{ H, SiCH}_3); \]

\[ 4.1 (W_{1/2} = 105 \text{ Hz}, 1.0 \text{ H, SiH, SiH}_2), \text{ CH/SiH = 6.0.} \]

**Ceramic Residue Yield (TGA): 53%**

Another reaction (PC/8/60) where the same ratio of oligomer to Na was used, after 6.5 h of ultrasonication at 19°C in a 7/1 v/v toluene/THF yielded 100% of yellow-orange solid product (containing 1.09 % Na) which was soluble in hexane, toluene, and benzene.

\[ ^1H \text{ NMR (300 MHz, C}_6\text{D}_6) \delta 0.5 (W_{1/2} = 90 \text{ Hz}, 6.1 \text{ H, SiCH}_3); \]

\[ 4.1 (W_{1/2} = 90 \text{ Hz}, 1.0 \text{ H, SiH, SiH}_2), \text{ CH/SiH = 6.1.} \]

**Ceramic Residue Yield (TGA): 83%**

Another experiment (PC/8/55) where the same ratio of oligomer to Na was used, after 17.5 h of ultrasonication at 30°C in a 7/1 v/v hexane/THF yielded 84% of yellow-orange solid product which was soluble in hexane and toluene. The rest of the product was insoluble fully crosslinked polysilane.

\[ ^1H \text{ NMR (300 MHz, C}_6\text{D}_6) \delta 0.6 (W_{1/2} = 75 \text{ Hz}, 8.3 \text{ H, SiCH}_3); \]

\[ 4.1 (W_{1/2} = 90 \text{ Hz}, 1.0 \text{ H, SiH, SiH}_2), \text{ CH/SiH = 8.3.} \]

**Ceramic Residue Yield (TGA): 87%**

**Quenching of The Living Polymer With MeI.**

A 100 mL Schlenk flask was charged with 2.35 g (0.053 mol) of poly(methylsilane) (CH/SiH = 13) yellow-orange solid and 50 mL toluene. The flask then was charged with 5.0 mL of MeI and the solution was stirred for 0.5 h at
room temperature. The solution and the fine dispersion of NaI, together with 3 20 mL toluene washings were cannulated into a thick-walled centrifuge bottle and centrifuged for 1 h. The clear supernatant solution was trap-to-trap distilled yielding 2.30 g (0.052 mol, 99%) of a pyrophoric (when compressed or in a heap, but not when spread out) white solid, which was soluble in toluene. The amount of NaI was less < 1 mg. The polymer did not show any reaction with ViMe₂SiCl or any melting behavior upon pyrolysis.

**¹H NMR** (300 MHz, C₆D₆): δ 0.45 (W₁/₂ = 90 Hz, 10 H, SiCH₃);
4.2 (W₁/₂ = 70 Hz, 1.0 H, SiH, SiH₂), CH/SiH = 10.

**IR** (thin film, NaCl, cm⁻¹): 2951(m), 2888(s), 2057(s), 1406(m), 1242(s), 1032(w), 930(w), 867(vs), 760(vs), 682(vs), 640(s).

**Analysis:**
C: 23.61%; H: 7.01%; Si: 63.55%; Na: 1.11%; ∑ = 95.28%

Calc. (MeSiHₓ)₀.₃₀(MeSi)₀.₇₀: C: 27.71%; H: 7.62%; Si: 64.67%

**Analysis of Ceramics**
(1000°C, Ar): C: 23.67%; H: < 0.5%; Si: 73.34%; Na: 0.45%; ∑ = 97.46%
(1500°C, Ar): C: 25.64%; H: < 0.5%; Si: 72.77%; Na: < 0.10%; ∑ = 98.51%
Calc. (SiC): C: 29.95%; Si: 70.05%

**Ceramic Residue Yield (TGA):** 79%

**Molecular Weight by GPC:** Fig. E7 a

Na as a crosslinking agent affords after quenching with MeI a high recovery of a soluble product, high molecular weight product, which gives a high ceramic residue yield on pyrolysis.
Blend of Oligo(methylsilane) and Ploy(methylsilane) with BHT to Prevent Their Oxidation Upon Exposure to Air. (TS/2/48, 57)

A 50 mL flask equipped in a magnetic stir-bar was charged with 1.25 g (0.0284 mol) of poly(methylsilane) (TS-1) (CH/SiH = 6.0), 0.053 g (0.24 mmol) of BHT, and 20 mL toluene. The solution was stirred for 2 h and then it was trap-to-trap distilled leaving 1.30 g of white powder. The polymer which was originally pyrophoric was now stable to air oxidation.

**IR (after exposure to air)**

(thin film, NaCl, cm⁻¹): 2949(s), 2887(s), 2057(s), 1406(m), 1244(s),

930(s), 867(vs), 774(vs), 688(vs) (note the absence of Si-O-Si).

**Ceramic Residue Yield (TGA): 74%**

A 50 mL flask equipped in a magnetic stir-bar was charged with 1.00 g (0.0227 mol) of oligo(methylsilane) (CH/SiH = 3.6) clear oil, 0.050 g (0.23 mmol) of BHT, and 20 mL toluene. The solution was stirred for 2 h and then it was trap-to-trap distilled leaving 1.05 g of white oil. The polymer which was originally very air sensitive was now stable to air oxidation.

**IR (after exposure to air)**

(thin film, NaCl, cm⁻¹): 2957(s), 2894(s), 2107(vs), 1410(m), 1248(s), 931(s),

862(vs), 769(vs), 685(vs), 587(s) (note the absence of Si-O-Si).
Control Experiment of Oligo(methylsilane) Ultrasonication in 7/1 v/v

Hexane/THF. (PC/8/37)

The effect of ultrasonication on OMS was examined.

A 50 mL Schlenk flask was charged with 0.64 g (0.015 mol) of oligo(methylsilane) (CH/SiH = 3.4) clear oil, 14 mL of hexane and 2 mL of THF. The solution was placed in the ultrasonic bath at 28°C for 89.5 h. After termination of ultrasonication the solution was trap-to-trap distilled leaving 0.63 g (0.014 mol, 98%) of white oil.

$^1$H NMR (300 MHz, C$_6$D$_6$): $\delta$ 0.5 ($W_{1/2} = 105$ Hz, 3.5 H, SiCH$_3$),

3.9, 4.0 ($W_{1/2} = 75$ Hz, 1.0 H, SiH, SiH$_2$),

CH/SiH = 3.5.

IR (thin film, NaCl, cm$^{-1}$): 2956(s), 2893(s), 2794(w), 2107(vs), 1918(w),

1410(s), 1247(s), 1035(w), 931(s), 876(vs), 769(vs),

686(vs), 587(s).

Ultrasonication does not have any visible effect on OMS alone.

Reaction of Oligo(methylsilane) With 15 mol% NaH in THF and Using Ultrasonic Activation. (PC/8/54; PC/8/41)

A 50 mL centrifuge tube was charged with 0.87 g (0.020 mol) of oligo(methylsilane) clear oil and 0.085 g (0.0035 mol) of NaH, and 40 mL of THF. The tube was placed in the ultrasonic bath at 27°C for 5 h. After termination of ultrasonication, the solid phase present and the yellow-orange solution were
centrifuged for 1 h. The yellow-orange supernatant solution was trap-to-trap distilled leaving 0.73 g (0.016 mol, 84%) of yellow-orange solid which was pyrophoric in air and soluble in most common organic solvents.

$^1$H NMR (300 MHz, C$_6$D$_6$): $\delta$ 0.5 ($W_{1/2} = 60$ Hz, 7.9 H, SiCH$_3$),

4.1, 4.2 ($W_{1/2} = 90$ Hz, 1.0 H, SiH, SiH$_2$),

CH/SiH = 7.9.

IR (thin film, NaCl, cm$^{-1}$): 2953(s), 2889(s), 2790(w), 2064(vs), 1895(w),

1456(w), 1407(m), 1268(w), 1243(s), 1059(s), 930(m),

868(vs), 789(vs), 685(vs), 642(s), 585(w).

Ceramic Residue Yield (TGA) (10°C/min., 1000°C, Ar, 3 hr.): 53%

Molecular Weight by GPC: Fig. G17 a, G18 d

Wurtz Coupling Reaction of MeSiHCl$_2$ and 2.5 Na in THF by Ultrasonic

Activation. (PC/3/22, 63; PC/8/45, 46)

Experiment by Wood$^{36}$ was repeated using ultrasonication activation.

A 100 mL Schlenk tube was charged with 7.3 g (0.32 mol) of mirror clean Na metal (~ 10 mm in diameter), 30 mL of THF and 13 mL (14.3 g, 0.124 mol) of MeSiHCl$_2$. The flask was placed in the ultrasonic bath at 28°C for 93 h. After termination of ultrasonication the solids were washed three times with 20 mL portions of hexane and the washings, together with blue solution, were cannulated into a thick-walled centrifuge bottle and were centrifuged for 1 h. After centrifuging, the solution became clear and then the supernatant solution was trap-
to-trap distilled leaving 3.2 g (0.073 mol, 59%) of white solid, which was soluble
in most common organic solvents.

\[ ^1H \text{NMR} \ (300 \text{ MHz, } C_6D_6): \delta 0.6 \ (W_{1/2} = 120 \text{ Hz, } 5.5 \text{ H, SiCH}_3), \ 4.1 \ (W_{1/2} =
90 \text{ Hz, 1.0 H, SiH, SiH}_2); \text{poly(THF) impurity 1.7, 3.3}
(0.82 H, 0.45 H respectively, CH}_2). \]

\[ \text{IR (thin film, NaCl, cm}^{-1})): \ 2954(s), 2891(s), 2792(w), 2100(vs), 1914(w),
1408(s), 1247(s), 1098(m), 930(s), 864(vs), 766(vs),
684(vs), 588(m), 492(m). \]

\[ \text{Ceramic Residue Yield (TGA): 48%} \]

\[ \text{Analysis: C: 30.04%; H: 7.91% (carbon rich probably due to some poly(THF))} \]

\[ \text{Calc. (MeSiH}_x\text{)}_{0.54}(\text{MeSi})_{0.46}: \text{C: 28.16%; H: 7.47%} \]

\[ \text{Molecular Weight by GPC: Fig. G11 c} \]

Poly(methylsilane) was obtained with a large poly(THF) impurity.

\[ \text{Wurtz Coupling Reaction of MeSiHCl}_2 \text{ and 2.5 Na in Refluxing THF.}^{36} \]

\[ \text{(PC/8/50; TGW-VIII-39)}^{36} \]

The synthesis of poly(methylsilane) according to Wood\textsuperscript{36} was performed.

A 250 mL Schlenk flask equipped with a magnetic stir-bar and a reflux
condenser was charged with 7.3 g (0.32 mol) of mirror clean Na metal (\~10 mm
in diameter), 30 mL of THF and 13 mL (0.124 mol) of MeSiHCl\textsubscript{2}. The reaction
mixture was stirred for 16 h at room temperature and was heated at reflux for 48 h.
After cooling to room temperature, the solids were washed three times with 20 mL
portions of hexane and the washings, together with blue solution were cannulated
into a thick-walled centrifuge bottle and centrifuged for 1 h. After centrifuging, the supernatant solution became clear and was trap-to-trap distilled leaving 2.2 g (0.05 mol, 40%) of white solid which was soluble in hexane and toluene.

$^1$H NMR (300 MHz, C$_6$D$_6$): $\delta$H 0.6 ($W_{1/2}$ = 120 Hz, 6.6 H, SiCH$_3$), 4.1 ($W_{1/2}$ = 90 Hz, 1.0 H, SiH, SiH$_2$); poly(THF) impurity 1.7, 3.3 (0.015 H, 0.010 H respectively, CH$_2$).

IR (thin film, NaCl, cm$^{-1}$): 2954(s), 2890(s), 2790(w), 2100(vs), 1913(w), 1453(w), 1408(s), 1246(s), 1079(m), 930(s), 865(vs), 769(vs), 683(vs), 587(m), 490(w).

Ceramic Residue Yield (TGA): 55%

Analysis: C: 26.96%; H: 8.32%

Calc. (MeSiH$_x$)$_{0.48}$(MeSi)$_{0.52}$: C: 28.16%; H: 7.47%

Analysis of Ceramics (1000°C, Ar): C: 25.21%; Si: 64.20%; $\Sigma$ = 89.41%

Calc. (SiC): C: 29.95%; Si: 70.05%

Molecular Weight by GPC: Fig. G11 a

A nearly identical polymer as reported by Wood$^{36}$ was obtained.

Coating of an Alumina Substrate With Poly(methylsilane) (TS-2H), (PC/8/52)

An alumina substrate was pretreated at 1000°C in air for 3 h prior to coating to assure all possible phase changes on its surface. The substrate then was suspended on a wire and submerged into 1 M hexane solution of TS-2H. The substrate was withdrawn using 0.01 mm/s draw rate (using a modified syringe pump). A uniform yellow film was achieved. The coated substrate was pyrolyzed
in Ar starting at room temperature and ramping 5°C/min. to 1000°C and held at that temperate for 3 h. After pyrolysis, a brown film was obtained. The film was mostly uniform based on the SEM analysis and was resistant to the scotch tape test.

**Spinning SiC Fibers From High Molecular Weight Poly(methylsilane) (TS-2H).**

A viscous solution of TS-2H in hexane was prepared in the glove box. A spatula was used to manually pull 2-3 cm fibers. The fibers were directly (not requiring curing step) pyrolyzed in an open tube furnace in Ar at a rate of 10°C/min. to 1000°C where they were kept for 3 h. After pyrolysis, the black fibers were between 1-2 cm in length.

**Preparation of Monolithic SiC From TS-2T.**

Dry powder of TS-2T was compressed in a IR KBr press. The yellow-orange pellet (ρ = 0.96 g/cc) was placed in the furnace which was programmed with heating rate of 10°C/min. 3 h of dwell at 1000°C (in argon). After pyrolysis, the pellet (ρ = 2.27 g/cc) had shrunk 70% by volume but retained its shape without any signs of melting. Vickers microhardness of the monolith was 2400 HV.
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257


Chapter Two

Applications of Poly(methyldisilane) and Other Polymeric Ceramic Precursors

to in situ Preparation of Metal Matrix Composites and Cermet
Introduction

A metal matrix composite (MMC) is a metallic material reinforced with a continuous or particulate ceramic phase (10 - 60 volume%). A graphical depiction of a MMC is presented in Figure 1.

![Diagram](image)

**Figure 1** Metal Matrix Composite

As early as in ancient Egypt the principle of reinforced materials was utilized in strengthening bricks with straw. More recently, namely in the 1960's, MMCs were introduced as light weight alloys strengthened with fibers. Early applications of MMCs were limited mainly to military aircraft, where the enhanced material properties outweighed their high cost. Within the MMC family there are cermets which usually contain more ceramic filler (15 - 85 volume%) than do MMCs. These cermets are usually used for applications requiring wear resistance such as cutting tools, rocket nozzles, or furnace fixtures.

Recently, national programs in Japan and the US have contributed to the development of MMCs for civilian applications.\(^1\) Reduced material and
fabrication costs, as well as progress in the development of near net-shape MMCs (part adequate for immediate use without requiring any additional machining), has contributed to recent interest in MMCs. A good deal of attention was directed towards automotive applications and especially components such as driveshafts, brake rotors, engine blocks, cylinder liners, connecting rods, or pistons.\(^2\) Art Metals Co. is already producing reinforced pistons for a Toyota light diesel engine.\(^3\) Honda recently has introduced a cylinder liner reinforced with 12% aluminum, 9% carbon fiber reinforced Al-12.7% Si MMC.\(^4\) As the manufacturing processes of ceramic reinforcement and MMCs become cost effective, more MMCs will be visible in civilian applications.

MMCs offer a competitive advantage over conventional metallic systems. One such advantage is in the anisotropic character of the composite, which may be utilized in the efficient design and fabrication of structures. The concept of anisotropic MMCs will be addressed \textit{vide infra}. Another advantage of MMCs (cermets) lies in their capacity for being tailored for an application requiring strength, stiffness or thermal stability. It is not uncommon to observe a considerable increase in fatigue strength, stress rupture, or creep as well a 40% weight savings for a specific structure.\(^5\) The most obvious potential advantage of MMCs over common materials is in their toughness, retention of strength at high temperatures, and their resistance to severe environments.\(^5\) Discontinuously reinforced MMCs generally have an inherent isotropy, are easier to fabricate, and
generally are of lower cost than the continuous fiber strengthened materials.

The common methods for the fabrication of MMCs are: powder metallurgy (P/M) methods,\textsuperscript{6} liquid metal infiltration,\textsuperscript{7} cospraying,\textsuperscript{8} liquid metallurgy methods,\textsuperscript{9} semi-solid slurry processing,\textsuperscript{10} plasma spraying in conjunction with diffusion-bonding,\textsuperscript{11} and electroforming.\textsuperscript{12} Powder metallurgy, although more costly than commonly used casting, overcomes some difficulties inherent to the casting process; these include problems of dispersion control, and the separation of dispersoid from the matrix resulting from density differences between the metal matrix and the ceramic filler.

In conventional powder metallurgy (P/M) of MMCs, mixtures of metal and ceramic powders are utilized. Since high interparticle friction is introduced during powder mixing as a result of differences in the shape, size and coefficient of friction of the mixed materials, it is, therefore, necessary to use polymers as binders and lubricants. The amount of polymer, depending upon application, may vary from 2 wt\% in simple compression molding to 30 wt\% or higher in injection molding applications. It is essential to use polymeric lubricants, especially in injection molding,\textsuperscript{13a} extrusion,\textsuperscript{13b} or slip casting,\textsuperscript{13c} of cermet powder mixes to minimize die wear and to increase the flowability and packing of powders.\textsuperscript{13} Commercially, organic polymers such as polystyrene, Acrawax\textsuperscript{®}, stearate salts,\textsuperscript{14} or microcrystalline cellulose (Avicel\textsuperscript{®} PH-105)\textsuperscript{15} are used to improve the flow and packing properties of metal powders. Currently, in the commercial preparation of
ceramic parts by powder processing, organic polymers (e.g., poly(vinyl alcchole), poly(vinyl butyral), etc.) are being used as binders for SiC or Si₃N₄ powders.¹⁶

The following prerequisites usually are met by commercial organic lubricant/binders: a low melting temperature (150-200°C), chemical inertness, and a low temperature for complete decomposition (400°C). Before the sintering of the molded part, the organic binder must be removed by means of slow heating and gradual evacuation of volatiles, a process which is costly, complex, and very time-consuming (Fig. 2). The use of an organic binder brings some disadvantages: (1) evolution of volatiles due to binder burnout during the firing of the ceramic part will, in the absence of suitable open porosity, cause microstructural flaws (cracks and voids); (2) thermolysis of the organic binder can leave behind carbonaceous residues that could inhibit densification or form detrimental reaction products; (3) the burnout cycles are generally slow and hence costly; (4) manufactured parts have a high rejection rate and are generally of low reliability.
Figure 2 Conventional Powder Metallurgy of MMCs and cermets using organic binders for near net-shape composites.
Preceramic polymers\textsuperscript{17} serve excellently as binders for ceramic powders in the fabrication of shaped ceramic parts. For example, Semen and Loop at the Ethyl Corp. laboratories\textsuperscript{18a} demonstrated strengths of over 650 MPa (94 kpsi) for parts made from submicron SiC particles bonded with an amorphous silicon carbonitride matrix generated by pyrolysis of a polysilazane of the type 
\[(\text{CH}_3\text{Si(H)NH})_a(\text{CH}_3\text{SiN})_b\]_n.\textsuperscript{19} These parts exhibited excellent oxidation resistance and strength retention at temperatures up to 1300°C. More recently Lukacs of Hercules Inc. explored the use of liquid preceramic polymers in about 28 wt%, such as poly(methylvinylsilazane) with a dicumyl peroxide curing agent, as binders for the injection molding of ceramic parts.\textsuperscript{18b} Preceramic polymers, if properly chosen, avoid the problems that are inherent to organic polymers: cracking, deformation, bloating, or large volume shrinkage of the sintered part in the P/M process.

Preceramic polymers suitable for the improved P/M of MMCs must give high ceramic residue yields on pyrolysis, with minimal evolution of volatiles. In 1976, Yajima et al.\textsuperscript{20} described experiments in which a polycarbosilane (the Nicalon\textsuperscript{®} ceramic fiber precursor\textsuperscript{21}) was used as a binder for a Fe/Cr alloy powder. Fabrication by hot pressing to 1100°C gave a Fe/Cr alloy part containing uniformly distributed particles of Cr carbide and silicide (by XRD and TEM). The resulting composite was resistant to oxidation at 1000°C and, as expected, exhibited higher hardness than the base alloy. Yajima's work was not followed up,
most likely because the interest in preceramic polymers was directed towards the preparation of fibers and coatings. More recently, workers at Fujitsu Ltd. explored the use of polysilazanes, polycarbosilanes, and polysilanes as binders for stainless steel (SUS 304) powders and demonstrated that the MMCs made in this way have higher tensile and yield strengths as well as higher hardness than pure SUS 304. Also Seyferth and Czubarow utilized poly(methylsilane) in the preparation of Al and Ti MMCs. The latter work, as well its extension, will be fully described in this chapter.

The main focus of this chapter will be on an improved fabrication method of MMCs using powder metallurgy (P/M). The current process employs preceramic polymers as binders, lubricants, and as a source for in situ prepared reinforcement for MMCs and cermets by P/M. The main difference between this approach and the conventional process lies in the elimination of the debinding step prior to sintering (Fig. 3). Also the current process enables convenient P/M preparation of near net-shape cermets containing a large amount of ceramic phases which do not require the debinding step and further machining after firing. Cermets are very difficult to machine; usually most of the high speed cutting tools are cermets. The current approach should be broadly applicable to P/M production of a large variety of discontinuously reinforced, near net-shape MMCs and cermets.
Figure 3 Improved powder metallurgy of MMC and cermets using ceramic precursor binders for near net-shape composites (Note lack of debinding step).
**Results and Discussion**

The most attention in the MMC field is given to aluminum composites due to their low density, low cost, high durability, and high corrosion resistance. The other metal of choice is titanium which is known to form MMCs that exhibit good specific strength at room and elevated temperatures and have a strong resistance to severe environments. They are especially useful as fan and compressor blades for advanced turbine engines. The use of preceramic polymers with these and other metals for the fabrication of MMCs will be the focus of this chapter.

The experimental procedure for producing MMCs with preceramic binders is quite simple. A 100-mL round-bottomed flask was charged with 2-3 cm$^3$ of the metal powder (generally -325 mesh; the same powder used commercially in P/M) and 3-15 mol% (1-16 wt%) of the polymer (based on silicon when an organosilicon polymer is used) and 30 mL of anhydrous solvent. The resulting suspension of the metal powder in the solvent solution of the polymer was placed in an ultrasonic bath for 20-24 hours. The sonic activation is necessary to clean the surface of the metal particles and to ensure their homogeneous dispersion. Subsequently, the volatiles were removed at reduced pressure on a high-vacuum line with vigorous agitation. The solid residue was dried in vacuo at 50°C overnight and ground to a fine powder using a mortar and pestle or a ball mill (for larger quantities). The pulverized green powder then was sifted through a 270 mesh sieve to remove large agglomerates (Fig. 4). Uniaxial pressing in a
rectangular die with double-action opposing punches at 13.5 kpsi for 1 hour (Fig. 5) and isostatic pressing at 40 kpsi for 10 minutes, usually at room temperature, gave the green bar (3.5 x 1.2 x 0.5 cm). Subsequent heating under argon in a tube furnace to temperatures below the melting point of the metal for ~2 h (temperature ramp rate of 5°C/min) gave the final composite.

The preceramic polymers used in the current study were:

poly(methylsilane) (PMS) which had been cross-linked with (Cp$_2$ZrH$_2$)$_n$ from the prolonged reductive coupling described in the previous chapter;
poly(methylsilane) (PMSII) of composition [(MeSiH)$_{2.3}$(Me$_2$Si)$_{1.0}$]$_n$ cross-linked with 0.5 mol% of (Cp$_2$ZrH$_2$)$_n$; the Nicalon® polycarbosilane (PCS); the Wiseman polysilazane (PSZ), a pollysilane containing methyl, vinyl, and hydrogen substituents (PVS); poly(borazinylamine) (PBA); (CH$_3$)$_3$SiNHTiCl$_3$, a TiN precursor; [6,9-(Me$_2$NH)$_2$B$_{10}$H$_{12}$]$_x$ (DBA), poly(diphenyldimethylcarbosilane) (D-PPMC-1), and poly(diphenylcarbosilane) (D-PCC). The list of these polymers is presented in Table 3 of the experimental section.
Figure 4 Green powder preparation process.
Figure 5 Process of compacting and sintering the green powder; a) application of powder; b) smoothing the powder bed by counter rotating the roller; c) lowering the bottom punch and introducing the top punch; MMC - final product.
Poly(methylsilane) and Other Polymeric Ceramic Precursors Containing Silicon.  
Carbon Nitrogen or Boron as Binders for Ti, Al, Cu, Mo, W, V, and Zr Powders.  

During the heating of the green bodies, there are two main chemical stages:  
(1) pyrolysis of the preceramic polymer to give the amorphous ceramic product  
dispersed in the metal matrix; (2) solid-state reaction of this ceramic with the  
metal powder matrix to give new ceramic phases that are dispersed throughout the  
metal matrix. The ceramic phases which result from such reactions of  
organosilicon polymers with metal powders had been established in earlier studies  
of stoichiometric preceramic polymer/metal powder high-temperature, solid-state  
reactions.\textsuperscript{30a, b}  

The morphology change of the MMC with temperature also is instructive.  
An example of a composite of -325 mesh titanium powder with 10 mol\% (based  
on Si; 9 wt\%) of PMS binder showed the morphology depicted in Figure 6 as it  
was heated in stages from room temperature to 1200\(^{\circ}\)C in argon. Powder X-ray  
diffraction (XRD) examination of the bars heated to 600, 800, and 1200\(^{\circ}\)C showed  
progressive development of crystalline TiC (JCPDS card \# 31-1400) and Ti\(_{5}\)Si\(_{3}\)  
(JCPDS card \# 29-1362) (Fig. 7a, b). At 600\(^{\circ}\)C a composite is present that shows  
Ti particles with their original shapes retained that are "glued" together with an  
amorphous SiC (Fig. 6a). This bar had a density only slightly greater than that of  
the original green body (2.94 vs. 2.89 g/cm\(^{3}\), respectively), exhibiting only 3.6\%
volume shrinkage mostly from the initial binder burnout. It had a large number of voids and was very brittle. At 800°C (Fig. 6b) the number of voids had diminished and, judging from the back scattering electron image, the Ti metal particles had begun to lose their original shape, probably due to surface reaction with the amorphous SiC which occludes the pores. The ceramic phases were becoming more pronounced. At 1200°C (Fig. 6c, d) a composite with minimal flaws (density = 4.2 g/cm³ or 93% of theoretical matrix density) was present that contained relatively well-dispersed ceramic phases, TiC and Ti₅Si₃ (by XRD, energy electron dispersive X-ray (EDX), and transmission electron microscopy (TEM)). The volume shrinkage after firing (at 1200°C) was about 15%, and no other distortions were present. A closer look at the TiC and Ti₅Si₃ phase boundaries by TEM revealed that both grains are very well bound together (Fig. 8). In addition, TiC grains were composed of twin crystals (lying along the (1̅1̅1̅̅̅) plane) as shown by the accompanying selected area diffraction (SAD). It appears that the grain boundary is very sharp without any graded regions. The TiC and Ti₅Si₃ phases exist as cubic (a = 0.433 nm) and hexagonal (a = 0.744 nm and c = 0.514 nm) structures, respectively, and seemed not to have any impurities.
Figure 6 The SEM micrograph of a Ti-PMS composite crosssection pyrolyzed: a) at 600 °C in Ar for 3 h (note the original shape of Ti particles; b) at 800 °C in Ar for 3 h. Backscattering electron image (note the development of ceramic phase between Ti particles).
Figure 6 The SEM micrograph of a Ti-PMS composite crosssection pyrolyzed at 1200°C in Ar for 3 h. c) secondary electron scattering image depicting convex TiC rich grains, d) backscattering electron image with Ti₅Si₃ grains. The EDX patterns confirm the assignment.
Figure 7 X-ray diffraction pattern of Ti/PMS composite pyrolyzed: a) 600°C and b) 1200°C in Ar.
Figure 8 TEM micrograph of (A) TiC and (B) Ti₅Si₃ grains.
A similar morphology vs. temperature study also was carried out on a Ti composite made of -325 mesh Ti particles and 10 mol% (based on Si; 12 wt%) of PCS binder. At 600°C, as in the Ti/PMS case, the Ti particles still assumed their original shape and were "glued" together with an amorphous SiC/C phase (Fig. 9a). This bar had a density slightly lower than that of the original green body (2.78 vs. 2.85 g/cm³, respectively), had a large number of voids, and was very brittle. This lowering of density probably is a result of the PCS behaving, in part, as a conventional organic binder since the ceramic residue yield of untreated PCS is only 65% as opposed to the 82% ceramic residue yield of PMS. Therefore, due to large amounts of micropores created in the pyrolysis of PCS above 600°C pyrolysis, the resulting Ti "sponge" has a lower density than its precursor green body. Finally, at 1200°C (Fig. 9c, d) the density reached 4.1 g/cm³ and total of 32% shrinkage by volume was observed without any other deformations. Based on XRD and SEM, the dispersed ceramic phases are TiC (JCPDS card# 32-1383) and Ti₅Si₃ (JCPDS card# 29-1362) (Fig. 10). The SEM analysis revealed that the volume fraction of the ceramic phases in Ti/PCS MMC is larger than in Ti/PMS MMC (Fig. 11), probably because PCS would yield a larger amount of TiC ceramic. The volume ratio of ceramic phase to metal matrix in the composite in Ti/PCS was about one and hence the composite resembles a cermet. The ceramic phase formation at 1200°C probably is due to the solid state reaction between Ti
and amorphous SiC\textsuperscript{30c} as depicted in equation 1.

$$9\text{Ti} + 3\text{SiC} + \text{C} \rightarrow 4\text{TiC} + \text{Ti}_5\text{Si}_3$$ (1)

In both cases, Ti/PMS and Ti/PCS, the ceramic phase dispersion became more uniform with higher temperature. It appears that the dispersion is governed mostly by the metal particle size and homogeneity of the original powder suspension (typical of the P/M process).
Figure 9 The SEM micrograph of a Ti/PCS composite crosssection pyrolyzed: a) at 600°C in Ar for 3 h (note the original shape of Ti particles; b) at 800°C in Ar for 3 h. Backscattering electron image (note the development of the ceramic phase between Ti particles).
Figure 9 The SEM micrograph of a Ti/PCS composite crosssection pyrolyzed at 1200°C in Ar for 3 h: c) secondary electron scattering image depicting convex TiC rich grains, d) backscattering electron image with Ti₅Si₃ grains. The EDX patterns confirm the assignment.
Figure 10 X-ray diffraction patterns of Ti/PCS composites pyrolyzed at: a) 600°C and b) 1200°C in Ar.
Figure 11 The SEM micrographs depicting crosssections of composites pyrolyzed at 1200°C in Ar: a) Ti/PMS and b) Ti/PCS.
A very intriguing case is an aluminum MMC produced with 10 mol% (16 wt%) of PMS binder. Pyrolysis of the green bar at 550°C in argon yielded an amorphous silicon carbide dispersed in an aluminum matrix. The volume shrinkage on pyrolysis was 10% without any other defects. The ceramic phase appeared to be poorly dispersed in the Al matrix (Fig. 12a). Examination by Vickers microhardness tests showed soft metal regions of 46.8 HV (44 HB) and harder metal/ceramic regions of 75.5 HV (66 HB). Also, the modulus of rupture (tested in four point bending) (MOR) of this composite was 14.15 kpsi, which is when this bar was heated to 1000°C in argon (above the mp. of pure Al, 660°C), it retained its shape and became stronger (MOR = 28.00 kpsi) and harder (75.3 HV) throughout. At that temperature the ceramic phase had dispersed (Fig. 12b), probably as the result of a solid-state reaction that had taken place between SiC and Al (eq. 2).\(^\text{31}\)

\[ 4\text{Al} + 3\text{SiC} \rightarrow \text{Al}_4\text{C}_3 + 3\text{Si} \]  

The XRD analysis showed that besides the aluminum matrix (JCPDS card # 4-787) elemental Si (JCPDS card # 5-565), \(\text{Al}_4\text{C}_3\) (JCPDS card # 11-629), and some \(\text{Al}_2\text{O}_3\) (JCPDS card # 10-173) were present (Fig. 13). So the final result was an aluminum-silicon alloy that contained dispersed \(\text{Al}_4\text{C}_3\) and \(\text{Al}_2\text{O}_3\) ceramic phases.
Figure 12 An optical micrograph of a crosssection of an Al/PMS MMC pyrolyzed at: a) 550°C (darker region hardness: 75.5 HV, lighter region hardness: 46.8 HV) and b) 1000°C in Ar. Note that the darker regions in a) become dispersed at 1000°C.
The $\text{Al}_2\text{O}_3$ is an impurity introduced during processing, probably from partial oxidation of the PMS binder since part of the compacting (uniaxial pressing) was carried out in air. A study of the morphology by TEM indicated that $\text{Al}_2\text{O}_3$ can be in the form of whiskers (Fig. 14), formed in situ, or irregular particles. To avoid $\text{Al}_2\text{O}_3$ formation one may conduct the entire process in inert atmosphere or use antioxidants with PMS. The use of antioxidants was explored by Bryson$^{32}$ who found that a catalytic amount of 2,6-di-tert-butyl-4-methylphenol (BHT) or its derivatives prevent oxidation of highly air-sensitive polysilanes. Indeed, such additives inhibit oxidation of PMS upon air exposure for extended periods of time (Chapter 1). An Al MMC prepared with 10 mol% PMS containing 0.5 wt% BHT yielded much less $\text{Al}_2\text{O}_3$ compared with the unstabilized composite as depicted on XRD (Fig. 13). It was observed that the green body which did not contain any BHT became very warm upon exposure to air. However, when BHT was used, there was no exothermic behavior upon air exposure.
Figure 13 X-ray diffraction patterns of Al/PMS composite pyrolyzed at 1000°C in Ar: a) with BHT and b) without BHT antioxidant (Note the increase in $\text{Al}_2\text{O}_3$ lines).
Figure 14 TEM micrograph of *in situ* formed Al$_2$O$_3$ whiskers.
Further TEM analysis of Al/PMS MMC revealed rhombohedral (a = 0.334 nm and c = 2.499 nm) Al₄C₃ free of any impurities surrounded by the Al metal matrix as shown by the bright field image and the SAD (Fig. 15). The elemental silicon present in the Al matrix exhibited a high density of stacking faults. Because of the very low solubility of Al in Si at room temperature, only a mixture of Al and Si was observed in the regions between the Al matrix and the Si grains (Fig. 16). Also, a very small amount of amorphous SiC in the absence of any other neighboring phase was detected in the Al metal matrix indicating that the reaction (eq. 2) was not complete. Also the pyrolysis of an Al/PMS 7/3 mol ratio powder mix at 1000°C in argon yielded a metal/ceramic powder which showed the β-SiC (JCPDS card# 29-1129) pattern in XRD.
Figure 15 TEM bright field image micrograph of Al₄C₃ surrounded by the Al metal matrix in Al/PMS MMC.
Figure 16 TEM micrograph of elemental Si surrounded by the Al matrix in Al/PMS MMC.
In general, the melting temperatures of the final composite bars were lower than those of the pure metal. However, the aluminum MMC retained its shape without apparent melting up to 1000°C (Fig. 17) and even up to 1300°C. Differential scanning calorimetry indicated some internal melting shortly before the melting point of pure aluminum, which, however, did not compromise the macrostructural integrity of the composite bar (Fig. 18). This lack of apparent melting most probably is a result of the Al₄C₃ dispersoid reinforcement of the MMC. The Al/PMS MMC containing BHT (i.e., yielding minimal Al₂O₃) also exhibited retention of bulk shape at 1000°C in argon. It has been observed by some investigators that the presence of a nonmetallic dispersoid such as Al₄C₃ results in greatly improved high-temperature (550°C) creep behavior, excellent thermal shock resistance and high sound damping capacity in aluminum MMCs.
Figure 17 Al/PMS composite pyrolyzed in argon at: a) 550°C and b) 1000°C.
Figure 18 DSC trace of Al/PMS MMC from 50°C to 1300°C. Note melting point around 660°C.
The copper MMCs also are of commercial interest due to their corrosion resistance and use in combustion chamber walls of advanced rocket engines. The MMC of copper powder and 10 mol% (7.2 wt%) PMS was very brittle. However, when 10 mol% (9.3 wt%) PCS was used as binder, the composite bar was very strong. XRD analysis did not reveal any other crystalline phases besides Cu. Surface analysis by XPS showed the presence of SiC, SiO₂, and SiCₙO_y. The oxide phases probably come from the surface. The Cu blank (not containing any binder) was very soft and its hardness could not be determined, even by the Rockwell superficial hardness with scale 15-T, whereas Cu/PCS 9:1 mol ratio showed 60.5 15-T (52 HB).

Composites of Group 6 metals, due to their high hardness, are of considerable interest to cermets manufacturers. In the current study, metals such as Mo (~40 µ) and W (~12 µ) yielded composites with improved mechanical properties such as hardness at low polymer content. Thus, use of 3 mol% of PCS in the case of W powder of ~12 µm average particle size gave a composite bar with a hardness of 40.2 HRA. Higher (1:9 mol ratio) ratios of polymer to metal yielded soft, grainy, brittle materials of low density and negligible volume shrinkage. However, when smaller particle size metal powders were used, such as <1 µ tungsten powder, the MMC proved to be well sintered even with 10 mol% of PMS as a binder. Improved densities and mechanical properties of the latter MMC are a result of the greater tendency for smaller particles to sinter because of their
high surface area and/or an increased propensity for the metal particles to react with the amorphous ceramic derived from the binder pyrolysis. Based on XRD analysis of Mo MMCs with PMS and PCS, Mo₂C (JCPDS card# 35-787) and Mo₃Si (JCPDS card# 4-814) were recognized in addition to Mo metal (JCPDS card# 4-809). The presence of these phases indicates a solid state reaction involving amorphous SiC and Mo depicted by equation 3.

\[ 5\text{Mo} + \text{SiC} \rightarrow \text{Mo}_2\text{C} + \text{Mo}_3\text{Si} \]  

(3)

XRD analysis of the W (with PCS, PMS, PVS, or PMSII) MMCs revealed the presence of W (JCPDS card# 4-806), W₂C (JCPDS card# 35-776) or W₆C₂.5₄ (JCPDS card# 31-1408), and W₅Si₃ (JCPDS card# 16-261). The recognized phases are a result of a solid state reaction of the W matrix with amorphous SiC/C (eq. 4).

\[ 11\text{W} + 3\text{SiC} \rightarrow 3\text{W}_2\text{C} + \text{W}_5\text{Si}_3 \]  

(4)

The V/PMS compact (9:1 mol ratio), after its pyrolysis at 1500°C in argon, yielded a strong (MOR = 25.4 kpsi) and hard (66.7 HRA (311 HB)) composite. XRD analysis of the V/PMS MMC showed diffraction patterns for the vanadium matrix (JCPDS card# 22-1058), V₂C (JCPDS card# 20-1373), and V₃Si (JCPDS card# 19-1405). The presence of the carbide and silicide is evidence of a solid state reaction of the metal matrix with SiC (eq. 5).

\[ 5\text{V} + \text{SiC} \rightarrow \text{V}_2\text{C} + \text{V}_3\text{Si} \]  

(5)
The Zr/PMS MMC (9:1 mol ratio) compact, after pyrolysis at 1500°C, yielded a composite with MOR = 15.4 kpsi and 64 HRA (264 HB). XRD analysis of the Zr/PMS MMC, pyrolyzed at 1500°C in argon, showed that, besides the Zr metal matrix (JCPDS card# 5-665), ceramic phases, ZrC (JCPDS card# 35-784) and ZrSi (JCPDS card# 9-226), were present (eq. 6).

\[ \text{Zr} + \text{SiC} \rightarrow \text{ZrC} + \text{ZrSi} \]  \hspace{1cm} (6)

Group 4 and 5 metals formed very strong and wear resistance composites when PSZ was applied as binder. PSZ afforded high yield of ceramic residue (84%) upon pyrolysis consisting of Si, C, and N.\(^1\) When PSZ was used as a binder with metal powders it acted as an \textit{in situ} reagent\(^{30a,b}\) which could yield three ceramic phases: metal silicide, carbide, and nitride phases dispersed in the metal matrix. Since PSZ would give more ceramic phases than an SiC precursor (PMS), and if the same mol ratio of both is used, the obtained composite, with PSZ due to its high ceramic content, would resemble a cermet. Indeed, Ti, Zr, and V powders when bound with PSZ afford composites which are very hard and considerably more difficult to machine than composites made with PMS. For example, a Ti/PSZ 9:1 mol ratio composite that had been fired at 1200°C in argon showed hardness of 74 HRA (448 HB) (ingot Ti hardness is 70 - 74 HB). Based on the XRD analysis it was composed of Ti (JCPDS card # 5-682); TiN\(_{0.9}\) (JCPDS card # 31-1403); TiC (JCPDS card # 32-1383); Ti\(_5\)Si\(_3\) (JCPDS card # 8-41) \(\text{(Fig.}\).
19). Usually titanium carbide and nitride are highly desirable phases for conventional cermets. Also, as a result of the polymer-ceramic-metal reaction the volume fraction of ceramic phase in the final cermet was nearly double the starting volume fraction of polymeric precursor. For example, in the Ti/PSZ 9:1 mol ratio composite about 30 volume% of polymer yielded more than about 60 volume% of the ceramic phase as depicted by an SEM micrograph (Fig. 20).

Similarly, the V/PSZ 9:1 mol ratio composite furnished a cermet with a hardness of 57 HRA (167 HB) which was far greater than the hardness of pure V ingot (72 HB). XRD analysis of the V/PSZ composite revealed the presence of V (JCPDS card # 22-1058); VN (JCPDS card # 2-1064); β-V₂N (JCPDS card # 33-1439); V₃Si (JCPDS card # 19-1405) (Fig. 21). The carbon was not accounted for in the XRD analysis, possibly because it was present either as amorphous vanadium carbide or free carbon. The possible solid-state reaction of V and PSZ derived ceramics is shown in equation 7.

\[
11V + 2Si-C-N \rightarrow VN + V₂N + 2V₃Si + 2VC
\] (7)

The use of PSZ as a binder for Group 6 metals gave composites which were poorly sintered, very grainy, and brittle. The Mo and W MMCs also were very soft compared with the respective metal matrix.
Figure 19 The X-ray diffraction pattern of Ti/PSZ 9:1 mol ration composite pyrolyzed at 1200°C in argon
Figure 20 SEM backscattering image of a Ti/PSZ 9:1 mol ratio cermet having more than 60% by volume of ceramic phase (Note the dark regions represent ceramic phases).
Figure 21 The X-ray diffraction pattern of V/PSZ composite pyrolyzed at 1500°C in argon.
In general, denser MMCs were obtained with binders that give higher ceramic residue yields on pyrolysis. The Mo MMCs made with the same mol ratio of 9:1 metal to PMS and PCS had densities of 7.3 and 6.0, respectively. In the case of 9:1 mol ratio of W to PMS or PCS MMCs, the densities were 13.9 g/cm\(^3\) and 9.5 g/cm\(^3\), respectively. However, the shrinkage in the Group 6 metal MMCs was greater with binders whose pyrolysis gives high ceramic residue yields such as PMS (but not PCS). For example, the Mo MMC afforded 15% volume shrinkage when PMS was used as a binder and 0% volume shrinkage when PCS was used. The use of low ceramic-residue-yield binders produced many microvoids compared with high-ceramic yield binders, thus compromising the final MMC density, and resulting in lower shrinkage.

The high-temperature reaction which results in dispersion of ceramic phases throughout the metal matrix can have useful consequences. Taking titanium powder as an example, it was found that when crosslinked PMS (a source of near-stoichiometric SiC) was used as binder, the final product (after heating to 1200° C) had a Brinell hardness of 71HRA (390 HB) (vs 70-74 HB for pure ingot Ti). In contrast, use of the PCS and PVS polymer binders (whose pyrolysis results in an excess of free carbon) gave a final composite much richer in TiC (via the Ti + C reaction) that has a lower hardness (45.6 HRA (132 HB) for the PCS bar and (59.5 HRA (222 HB) for the PVS bar). On the other hand, the composite bars which are richer in TiC, had a higher modulus of rupture (MOR, Appendix A) (344.6 MPa
(49.97 kpsi)) the bar in which PVS was used, 377.2 MPa (54.70 kpsi) for the bar in which PCS was used) than the bar in which PMS was used as binder (203.1 Mpa (29.45 kpsi)). In general, MOR was observed to be inversely proportional to preceramic content and to hardness.

Enhanced resistance to high-temperature oxidation was seen in some cases. In particular, titanium composite bars consolidated using 10 mol% of PMS or PSZ as binder retained their rectangular shape on being heated in air at 1000°C for 50 hours (Fig. 22a, b). Surface oxidation (6% and 11% weight gain, respectively) did occur, but removal of the outer oxide layer left a hard (PMS = 73.1 HRA (421 HB) and PSZ = 76.3 HRA (487 HB)) metallic bar. In comparison, a Ti blank (not containing any binder) in the same heating environment gained 15 wt% and 33% by volume without losing its shape. In contrast, the use of organosilicon polymers as binders whose pyrolysis gives a substantial amount of carbon in addition to SiC, such as PVS, did not result in good oxidation resistance in the final product. A sample made with Ti/PVS in 26:1 mol ratio upon heating to 1000°C for 50 hours totally lost its shape (Fig. 22c) and gained 42% in weight.

Unfortunately, the PMS and PCS binders did not yield ceramics which would protect the Group 6 composites against high temperature oxidation. For example, W/PCS 97:3 and W/PMS 9:1 MMCs were totally oxidized to a yellow powder after exposure to air at 1000°C for 50 h (Fig. 22 d).
Figure 22 Photograph of composites which were exposed to oxidation resistance test of 1000°C for 50 h in air: a) Ti/PMS; b) Ti/PSZ; c) Ti/PVS; d) W/PCS; e) Zr/PVS.
Enhanced resistance to high-temperature oxidation also was seen in the case of the Al/10 mol% PMS composite that had been heated first to 550°C in argon with a 2-h hold and then to 1000°C with a 2-h hold. It survived very well heating in air at 1000°C for 50 h, showing a 2% weight increase, a 10% volume increase, and retaining its original hardness of 75 HV (66 HB) (Fig. 23). This MMC also was corrosion resistant in boiling water. After such treatment for 1 month, a bar (Al/PMS 9:1) that had been heated to 550°C (i.e., no Al₄C₃ formed) showed a 0.1% weight decrease, no change in volume, and undiminished hardness. A bar that had been heated to 1000°C (i.e., containing Al₄C₃), on treatment with boiling water for 1 month, underwent surface corrosion as indicated by 14% weight increase and a 26% volume increase. After removing of the surface layer, the hardness of the bulk body was found to be undiminished.
Figure 23 Al/PMS MMC fired at: a) 1000°C in argon for 3 h and subsequently machined and b) composite of a) fired at 1000°C in air for 50 h.
The prepyrolysis processing, especially compaction, plays an important role in improving the mechanical properties. It was found that, in the case of the Ti MMC with PMS as binder, isopressing at 100°C yielded material with a MOR of 47.50 kpsi as opposed to 29.45 kpsi when the green body was isopressed at ambient temperature. The densities and MORs of the final MMCs also were improved when PSZ was used as a binder for Ti metal powder. The density of the MMC was 2.9 g/cm³ when the sample was isopressed at room temperature and 3.1 g/cm³ when isopressed at room temperature followed by further isopressing at 100°C. The modulus of rupture of the final MMC bar increased from 12.1 kpsi to 16.8 kpsi for ambient temperature isopressing and 100°C isopressing, respectively. The difference in isopressing temperatures also is manifested in percent volume shrinkage between the green body and the resulting MMC. For example, the Al/PMS blend isopressed at ambient temperature exhibited volume shrinkage of 20% while an analogous sample isopressed at 100°C showed only 9% volume shrinkage. Another example is the Ti/PSZ blend where ambient temperature isopressing produced 15% volume shrinkage compared with 11% after 100°C pressing. Isopressing at elevated temperatures helps the metal powder pack better and the polymeric ceramic precursor flow into open pores resulting in diminished free volume and, therefore, higher final densities.

The density of the final product also is dependent on the duration of isostatic pressing. For example, the Ti/PMS blend compressed at 40 kpsi for 2
min or 10 min yields final densities of 4.1 and 3.9 g/cm³ respectively. In the case of the Al/PMS MMC the same difference in pressing time gave final densities of 2.3 and 2.7 g/cm³ respectively. Similar improvements in processing at ambient temperature may be accomplished when a liquid (at room temperature) polymeric precursor such as PVS is used as binder. Overall, the green bodies prepared with PVS were very sound. An example of liquid vs. solid binder is given by a W MMC. Tungsten powder with PMSII binder (solid at room temperature SiC precursor) in 20:1 mol ratio afforded an MMC with 20% shrinkage by volume. However, a W/PVS MMC (liquid binder) in 19:1 mol ratio showed only 1% shrinkage. In both cases, the densities and hardness of the final MMCs were comparable.

Shrinkage also is dependent on metal powder particle size. For example, a W/PMS 9:1 mol ratio MMC in which the average particle size of the W powder was ~12 μm showed almost no shrinkage, while the same binder/polymer ratio of submicron W powder composite showed 20% shrinkage by volume. The higher shrinkage probably results from a higher reactivity of the finer particle size powder with the amorphous ceramic derived from pyrolysis of the ceramic precursor during the densification process (Figs. 6, 9).

The ceramic residue yield of preceramic binder also plays an important role in the volume shrinkage and the density of MMCs. In the case of Ti powder with PMS binder (ceramic residue yield of 82%) or PSZ binder (ceramic residue yield
of 84%) in the same Ti/binder mol ratio the shrinkage was about 15% by volume, while Ti/PCS binder system (ceramic residue yield of 65%) showed shrinkage of 30% by volume. The shrinkage of the Cu MMC varied with the ceramic yield of the binder. For example, use of PCS and PVS as binders for Cu powder, whose ceramic yields are 65% and 59%, respectively, resulted in about 30% volume shrinkage. However, when PMS and DBA (ceramic yields 82% and 73% respectively) were used, the shrinkage was 13% and 7%, respectively. When V metal powder was bound with PMS or PSZ the shrinkage was 18% and 8%, respectively. An MMC of V/PCS, on the other hand, pyrolyzed at the same temperature as the other two MMCs, exhibited 25% shrinkage by volume. Group 6 metals showed a reversed shrinkage dependence on ceramic residue yield, possibly because of poor sintering.

In summary, the shrinkage is dependent on five variables: 1) the shrinkage is inversely proportional to the ceramic residue yield of the ceramic precursor; 2) it is inversely proportional to the particle size of the metal powder; 3) it is directly proportional to the amount of preceramic binder used; 4) it is inversely proportional to the temperature used in the isostatic pressing step; 5) it is dependent on the physical nature of the polymer used as binder. A liquid binder results in less shrinkage than a solid binder. The summary of above results is provided in Appendix B, Table 1.

Polymer-metal compatibility is a very important issue. Not every polymer
gave satisfactory results with a given metal. Which polymer is best and at what loading must be determined empirically. For instance, in the case of aluminum powder, the PMS (ceramic residue yield = 82%) and PBA (ceramic residue yield = 64%) (vide infra) gave excellent results (both are precursors to their stoichiometric ceramics i.e., SiC, BN respectively), but the use of PCS (ceramic residue yield = 65%) and PSZ (ceramic residue yield = 84%) resulted in brittle and porous bodies (Fig. 24a). In any case, a general requirement was found that the ceramic residue yield when the pure polymer is pyrolyzed in argon to 1000°C (TGA) should be above 60%. A number of polymers such as D-PPMC-1 (ceramic residue yield of 14%), D-PCC (ceramic residue yield of 22%), and polystyrene (ceramic residue yield of 0.3%) afforded shapeless, porous, brittle bodies (Fig. 24a). Other deformations may result from use of too low amounts or poor dispersion of the precursor which could cause leakage of metal during sintering (Fig. 24b) or bloating of a pyrolyzed part (Fig. 24c).
Figure 24 Typical deformations of MMC derived from P/M process; a) brittle sponge (Al/PCS) or melting (W/polystyrene); b) matrix leakage (Sn/PBA); c) bloating (Fe/PCS).
Precursor to Near-Stoichiometric BN (PBA) as Binder for Ti, Al, Cu, Fe, Ni, and W Metal Powders.

In addition to the DBA binder, use of a precursor for near-stoichiometric BN also was explored. Poly(borazinylamine) (PBA) with its ceramic residue yield of 64%\(^2\) afforded high density and very uniform MMCs with various metals. The general experimental procedure for metal/PBA blends involved suspending -325 mesh metal powders in a solution of PBA in liquid ammonia (dried over sodium metal). After pyrolysis of the compacted green body at atmospheric pressure, high density MMCs were obtained for some metals. For example, aluminum and titanium based MMCs containing PBA as a binder attained densities as high as 2.55 and 4.06 g/cm\(^3\) which corresponded to 95 and 91% of the theoretical matrix density, respectively. Iron, copper, nickel, and tungsten based MMCs attained only ~65% of the theoretical matrix densities.

Another remarkable Al MMC was obtained when PBA was used as a preceramic binder. After pyrolysis at 1000°C, the Al/PBA, 9:1 Al/B mol ratio MMC retained its structural integrity (Fig. 25). The moduli of rupture and modulus of elasticity of this composite measured in 4 point bending (Appendix A) were found to be 14.5 Kpsi and 0.72 Mpsi, respectively, while hardness was found to be 51.2 HV (48 HB). It may be pointed out that the ceramic residue yields of PBA and PCS are about equal. However, in the case of PCS the Al MMC failed to
give a dense body. This observation provides further evidence that metal-ceramic compatibility is sometimes more important than the ceramic residue yield.

The XRD of a Al/PBA MMC pyrolyzed at 500°C shows the diffraction pattern for aluminum metal (JCPDS card # 4-787) and even aluminum nitride (JCPDS card # 25-1495). The presence of aluminum nitride suggests nitridation of aluminum by amorphous boron nitride (eq. 8). The resulting elemental boron and aluminum boride species were amorphous at this temperature.

$$4\text{Al} + \text{BN} \rightarrow 3\text{AlN} + \text{B} + \text{AlB}_2 \quad (8)$$

Samples heated at 1000°C, exhibited diffraction peaks due to elemental boron (JCPDS card # 17-788) and aluminum boride (JCPDS card # 9-154) in addition to the peaks due to Al and AlN (Fig. 26). The XPS of Al/PBA pyrolyzed at 1000°C did not exhibit boron or nitrogen peaks suggesting that the boron containing species are not on the surface but beneath the metal oxide layers.
Figure 25 Al/PBA MMC fired in argon at 1000°C and machined for fatigue testing.
Figure 26 X-ray diffraction pattern of Al/PBA MMC fired at 1000°C in Ar.
The XRD of a Ti/PBA MMC pyrolyzed at 1200°C showed diffraction peaks due to titanium nitride (JCPDS card # 38-1420) and titanium boride (JCPDS card # 5-700) in addition to titanium (JCPDS card # 5-682) (Fig. 27) of the matrix (eq. 9).

\[ 2\text{Ti} + \text{BN} \rightarrow \text{TiN} + \text{TiB} \quad (9) \]

Aluminum and titanium particles coated with poly(borazinylamine) also were subjected to a slightly different thermal treatment to determine the effect of evolving PBA pyrolysis products on MMC formation. The coated particles were first pyrolyzed at 500°C in an argon atmosphere to complete the weight loss and then the green body was fabricated and sintered at high temperature. This procedure offers no advantages since in situ pyrolysis furnishes MMCs of higher density than those obtained from such prepyrolyzed starting materials (Ti/PBA: 4.1 vs. 3.5 g/cm³; Al/PBA: 2.6 vs. 2.3 g/cm³). The X-ray powder diffraction patterns of aluminum and titanium MMCs, PC/7/39/A, PC/7/39/B, and PC/7/40/C prepared by the prepyrolysis routes were identical to those of PC/7/36/A, PC/7/36/B, and PC/7/40/A prepared by in situ weight loss. Thus the in situ weight loss from poly(borazinylamine) during the preparation of MMCs does not affect the structural changes.
Figure 27 X-ray diffraction pattern of Ti/PBA composite fired at 1200 °C in argon.
The XRD of an iron-based MMC heated to 800°C, showed diffraction patterns of iron (JCPDS card # 6-696) and iron boride, Fe$_{23}$B$_6$ (JCPDS card # 34-991). Although no nitrogen-containing species were seen, it is possible that nitrogen is occupying octahedral holes in the iron matrix.\textsuperscript{35} Diffraction peaks due to crystalline Fe$_3$N (JCPDS card # 1-1236) and elemental boron (JCPDS card # 12-377) (Fig. 28) were seen in the X-ray powder diffraction pattern of a sample heated at 1200°C (eq. 10).

$$44\text{Fe} + 7\text{BN} \rightarrow \text{Fe}_{23}\text{B}_6 + 7\text{Fe}_3\text{N} + \text{B} \quad (10)$$

The XPS of Fe/PBA MMC prepared at 1200°C shows Fe 2p3, Fe 3s, Fe 3p, B 1s, and N 1s peaks. There was no evidence of iron borides on the surface. There was only one peak in B 1s window at 192.8 which was assigned to boron oxynitride (Fig. 29a). The N 1s window showed two peaks at 398 and 400 eV which can be assigned to iron nitride and boron oxynitride, respectively (Fig. 29b).

The Fe/PBA composite pyrolyzed at 1200°C had greater density (6.6 g/cm$^3$) compared with 800°C fired MMC (4.8 g/cm$^3$), as well as greater resistance towards rusting than the 800°C counterpart. It has been found by previous investigators that nitridation of steel reduces its susceptibility to corrosion.\textsuperscript{36a} In addition, corrosion also may be suppressed by coating steel with a preceramic polysilazane and subsequently firing it to obtain a ceramic coating.\textsuperscript{36b}
Figure 28 The X-ray diffraction pattern of Fe/PBA pyrolyzed at 1200°C in argon.
Figure 29 XPS 1s windows for Fe/PBA MMC fired at 1200 °C: a) boron; b) nitrogen.
The X-ray diffraction pattern of the copper-based MMC (Cu/PBA 9:1 pyrolyzed at 900°C), showed diffraction peaks due to copper (JCPDS card # 4-836) only. Since copper does not react with nitrogen or ammonia at this temperature\textsuperscript{37} and the only known copper nitride, Cu\textsubscript{3}N, is unstable above 300°C\textsuperscript{38}, it is unlikely that copper nitride is formed. Furthermore, copper borides are generally prepared at much higher temperatures.\textsuperscript{39} Thus the absence of copper boride, copper nitride, and elemental boron suggest that the Cu/PBA composite contains only copper and amorphous boron nitride. Because the identity of the ceramic phase could not be determined by XRD, XPS was utilized to determine the amorphous phases. The XPS analysis suggested that the ceramic phase is amorphous boron nitride, although surface oxide species also were present. The XPS of Cu/PBA exhibited Cu 2p\textsubscript{1}, Cu 2p\textsubscript{3}, Cu 3p, B 1s, and N 1s peaks. The B 1s window contained three peaks at 190.8, 192.0, and 194.0 eV (Fig. 30a) and there were two peaks in the N 1s window at 398.4 and 400 eV (Fig. 30b). The peaks at 190.8 and 194.0 eV correspond to the binding energies of B 1s for boron nitride\textsuperscript{40} and boron oxide,\textsuperscript{41} respectively. The third peak at 192.0 eV most probably is due to boron oxynitride.\textsuperscript{42} This assignment is supported by the presence of two peaks in the N 1s window - the peak at 398.4 eV which is characteristic of nitrides\textsuperscript{40} and the peak at 400 eV due to oxynitride.\textsuperscript{43} A scanning electron micrograph of Cu/PBA MMC showed loosely bonded ceramic grains in a copper matrix. This
morphology is desirable for improving fracture toughness of the composite by dissipating the crack growth energy through the open ceramic-metal interface.\textsuperscript{18a}
Figure 30 XPS 1s window for Cu/PBA MMC fired in Ar at 900°C: a) boron; b) nitrogen.
The X-ray diffraction pattern of W/PBA pyrolyzed at 1500°C showed diffraction peaks due to tungsten boride (JCPDS card # 6-591) and nitride (JCPDS card # 25-1256) which is not surprising since both materials are stable at this temperature (eq. 11).

\[3W + BN \rightarrow W_2B + WN \]  \hspace{1cm} (11)

The XPS of W/PBA did not exhibit boron or nitrogen peaks suggesting that the boron containing species are not on the surface but beneath the metal oxide layers.

The X-ray diffraction of Ni/PBA pyrolyzed at 1200°C showed peaks due to nickel (JCPDS card # 4-850) and nickel boride, Ni₃B, (JCPDS card # 19-834); there was no evidence of the presence of nitrides.

These X-ray diffraction studies thus have shown that the PBA reacts with metals at relatively low temperatures. The resulting MMCs generally contain metal borides and nitrides instead of the originally formed amorphous or crystalline boron nitride. It should be pointed out that the formation of transition metal borides and nitrides has been observed previously in the reaction of metals with \([\text{B}_{10}\text{H}_{12}\text{.diamine}]_x\) polymers at about 1500°C.\(^{30a,b}\) The summary of the MMCs derived from metal powders using PBA as the binder is provided in Appendix B, Table 2.

326
A TiN Precursor as a Binder for Ti and Si$_3$N$_4$ Powders and as a Precursor for a Continuous TiN Thin Films on an Alumina Substrate.

Due to its attractive properties, an increased interest in TiN has promoted numerous research efforts in developing precursors to TiN. Titanium nitride is known for its useful properties such as high hardness, high melting point, chemical inertness and electrical conductivity. There are numerous applications of this material in wear-resistant coatings, solar control windows, low resistance contacts, and in Schottky devices. In recent years, titanium nitride thin film deposition by methods such as sputtering, ion implantation, and MOCVD has been an area of intense research. Low temperature chemical vapor deposition methods at atmospheric pressure have been demonstrated by Fix et al.

There are some reports describing preceramic precursor routes for the preparation of Group 4 metal nitrides with emphasis on titanium nitride involving the preparation of polymers from amido or alkoxy compounds of Group 4 elements. For example, Maya et al. described the ammonolysis of titanium or zirconium tetrakis(dialkylamides) to obtain insoluble polymers. Drake, Hursthouse and coworkers prepared a TiN precursor by reacting TiCl$_4$ with N, N', N'''-trimethylethlenediamine at -78°C. The soluble polymers obtained in the reactions of Ti[N(CH$_3$)$_2$]$_4$ with primary amines have been used by Seyferth and Mignani in the pyrolytic generation of TiN. A rather minor variation of this route which employs Ti[N(C$_3$H$_7$)$_2$]$_4$ instead of Ti[N(CH$_3$)$_2$]$_4$ has been reported.
by Mackenzie and coworkers.\textsuperscript{53} to prepare titanium nitride. Jiang and Rhine\textsuperscript{54a} synthesized polymers by reacting furfuryl alcohol with titanium alkoxides. These polymers require pyrolysis in an ammonia atmosphere in the temperatures range of 800-1100°C to form amorphous titanium nitride and calcining at 1100-1200°C for crystallization. A monomer, FTi[N(SiMe\textsubscript{3})\textsubscript{3}], has also been proposed to form titanium nitride based on thermoanalytical studies.\textsuperscript{54b}

Several TiN films by using preceramic precursor method have been prepared in the past. However, all of them suffered from carbonatious residues. Workers at Toray Industries, Inc. prepared TiN films and fibers from titanium halide or alkoxide infiltrated cyano group-containing polymers and subsequent its pyrolysis in nitrogen at 1200°C.\textsuperscript{55a} Researchers at Central Glass Co., Ltd. used hydrolyzed titanium alkoxide gels to cast films and spin fibers which then after the pyrolysis in ammonia at ≥ 800°C afforded gold-colored TiN.\textsuperscript{55b} Another method of making TiN films was developed when titanium was anodically dissolved in organic electrolyte which gave a viscous solution that could be used for film casting and on pyrolysis afforded TiN.\textsuperscript{56}

The motivation for current study of TiN ceramics stems from their possible application in the automobile industry in devices such as the sodium heat engine (SHE),\textsuperscript{57a} electrically heated catalyst systems,\textsuperscript{57b} and optical coatings.\textsuperscript{57c} The SHE is a thermoelectric device for energy conversion based on a β-alumina solid electrolyte.\textsuperscript{57a} One such device containing titanium nitride films as electrodes,
deposited by magnetron sputtering, was tested by Ford in the late eighties and found to be suitable for high performance SHE devices.\textsuperscript{58} An electrically heated catalyst is required to catalyze the reduction of NOx and oxidation of hydrocarbons and CO in automotive exhaust gases from a cold start. Titanium nitride films deposited on the corderite honeycomb substrate beneath an alumina washcoat containing noble metals can be used to electrically heat the catalyst from the existing battery.\textsuperscript{57b} Considering the volume of automobiles sold in the world (15 million annually in US alone) and the demand for low-emission or zero-emission vehicles, devices such as SHE and an electrically heated catalyst represent important technological advances. For mass-production of such devices, economical methods for the fabrication of components are needed since methods such as sputtering, ion implantation, or MOCVD are uneconomical.

In the current, studies (CH\textsubscript{3})\textsubscript{3}SiNHTiCl\textsubscript{3} was utilized as a binder for production of Ti/TiN MMC and Si\textsubscript{3}N\textsubscript{4}/TiN composites. The thermogravimetric analysis\textsuperscript{27} of (CH\textsubscript{3})\textsubscript{3}SiNHTiCl\textsubscript{3} showed a weight loss of 44% in the 120-200°C range. Further heating resulted in a gradual weight loss of 11% in the 220-550°C and of 7% in the 550-600°C region. The following reactions course can be proposed for the decomposition of (CH\textsubscript{3})\textsubscript{3}SiNHTiCl\textsubscript{3} based on the TGA (eq. 12).

\[
(\text{CH}_3)_3\text{SiNHTiCl}_3 \rightarrow \text{NHTiCl}_2 \rightarrow \text{NTiCl} \rightarrow \text{TiN}
\] (12)

The first step in the decomposition probably proceeds with the elimination of
Me₃SiCl. Loss of Me₃SiCl would result in a weight loss of 45%, which is in good agreement with the weight loss observed in the 120-200°C range. The next two steps require a total weight loss of 29.5%. However, the observed weight loss is 18%. This suggests that the pyrolysis of (CH₃)₃SiNHTiCl₃ will furnish contaminated TiN. Silicon and chlorine contamination has been previously observed in the pyrolysis of Me₃SiAlCl₂.⁵⁹

Since the TGA analysis of (CH₃)₃SiNHTiCl₃ indicates that the yield of ceramics is only 38%, the expected composites would have low densities and would be very porous. Two approaches were used in preparation of Ti/TiN MMC composites. In both cases -325 mesh Ti metal powder was used and a mol ratio of 9:1 of Ti/(CH₃)₃SiNHTiCl₃. In the first case, after the compaction, the green body (density 3.2 g/cm³) was pyrolyzed in argon at a rate of 5°C/min to 200°C (2 h hold) and at the same rate to 900°C (3 h hold). The final MMC was very porous and brittle. It exhibited lower density than the green body (2.4 g/cm³) and experienced 12% volume increase. For the second case, green powder was prepyrolyzed at 300°C, 3 h in argon, where most of the weight loss took place. After compaction, the resulting powder had a density of 3.3 g/cm³ and after pyrolysis at 1200°C for 3 h in Ar it afforded an MMC with density of 4.2 g/cm³ and a 27% reduction in volume. The X-ray powder diffraction pattern of the Ti-TiN body showed diffraction peaks due to metallic titanium and nitrogen-deficient titanium nitride, Ti₂N (JCPDS card # 17-386). The formation of Ti₂N is due to
reaction of TiN with Ti metal.

The second composite comprised of Si₃N₄-TiN where a Si₃N₄/(CH₃)₃SiNH TiCl₃ mixture in 9/1 mol ratio was used. The compacted green body was first pyrolyzed in ammonia at a rate of 5°C/min from room temperature to 200°C (2 h hold) and then at the same rate to 600 °C (2 h hold). The final pyrolysis was effected in argon at a rate of 5°C/min to 1500°C with a 2 h hold. The final composite was not a success, being very porous, deformed, and brittle with a density of only 1.71 g/cm³. The X-ray powder diffraction pattern of the Si₃N₄-TiN composite showed besides lines due to Si₃N₄, lines indicative of TiN (JCPDS card # 38-1420).

(CH₃)₃SiNH TiCl₃ proved to be an excellent precursor for formation of TiN thin films on alumina substrates. This method is convenient and economical and can be scaled up for mass production of films on a variety of substrates.

In this new approach to TiN film preparation, (CH₃)₃SiNH TiCl₃ was dissolved in THF to obtain a 1.0 M solution. An alumina substrate then was dipcoated (only once) at a withdrawal rate of 0.01 mm/s. The coated alumina substrate was transferred to a tube furnace and pyrolyzed in a stream of ammonia (heating rate 5°C/min to 1690°C and 3 h hold at that temperature). The resulting coated substrate was bronze in appearance, passed the "scotch tape test", and was electrically conductive (0.53 kΩ/cm). The thickness of the films was ~1 μm as measured by breaking the coated substrate in the middle and examining the
fracture surface under an electron microscope.

Grazing angle X-ray diffraction of the films (Fig. 31) showed α-alumina peaks from the substrate (JCPDS card # 10-173). The titanium nitride diffraction peaks from the coating were observed at 2θ (in degrees) = 36.86, 42.76, 62.1, 74.0, 78.4, which is in complete agreement with the reported values for TiN (JCPDS card # 38-1420). In addition, there were very weak peaks at 2θ (in degrees) = 28.26, 30.06, and 31.46 which could not be assigned to any well defined phase but probably are due to aluminum oxynitride (JCPDS card # 28-28). The formation of aluminum oxynitride in nitridation of boehmite and titanium oxide has been noted previously. The scanning electron micrographs (Fig. 32) of the films showed that they contain large 7-8 μm grains and small 2-3 μm grains. No microporosity of the grains could be observed under the limits of the resolution of instrument.

The X-ray photoelectron spectra of the film showed Ti(2p), N(1s), C(1s), Si(2s), Si(2p), Al(2s), Al(2p), O(1s), and O(2s) peaks. Sputtering of a 50 Å layer led to removal of peaks due to carbon, silicon and to substantial reduction of the peak intensity of oxygen. This suggests that the carbon and silicon resulted from handling of the sample and are not part of the coating. Surface contamination of the films was observed previously in films deposited by chemical vapor deposition methods. The Ti 2p3/2 and N 1s peaks are observed at 455.3 eV and 397.4
eV, respectively, for TiN. The atomic concentration shows that the ratio of Ti:N is 1:1. The Al 2s and 2p peaks were extremely weak but were observed due to the film porosity.

It thus was possible to grow high quality titanium nitride films on the ceramic substrates from the THF solution of (CH₃)₃SiNHTiCl₃ and subsequent pyrolysis in a stream of ammonia. The simplicity of the method of preparation of the precursor and of the fabrication of films might make it economically feasible to use this method in mass production.
Figure 31 1° grazing angle X-ray diffraction pattern of TiN film on alumina substrate.
Figure 32 SEM micrograph of a TiN thin film on alumina
Conclusion

The novel route for MMC and cermet preparation described here utilizes polymeric ceramic precursors as binders and as a source of ceramics. In general, during *in situ* MMC preparation metals react with amorphous ceramics to yield metal carbides, silicides, nitrides, or borides, depending on the polymer and the metal used.

The properties of the MMCs depend on several factors such as type, particle size and shape of the metal powder, and the volume fraction of dispersoid. The uniformity of dispersion and the wettability of the dispersoid with a metal play an important role in strength of MMCs. In general, most ceramics exhibit poor wettability with molten metals which limits the infiltration process in MMC preparation. By employing ceramic precursors an interface (possibly a graded interface) in the form of metal/nonmetal ceramic is introduced between the metal matrix and the ceramic reinforcer. This interface is a result of a solid state reaction which takes place at higher temperatures between metal and the ceramic phases derived from the pyrolysis of the preceramic binder. For instance, it has been observed in the case of the Al/PMS MMC that besides the Al matrix, elemental Si, Al$_4$C$_3$ and amorphous SiC also are present.

Ceramic precursors offer a possibility for *in situ* alteration of MMC composition. For example, if TiC and TiN are desired as components of a cermet, a polysiilazane may be used as binder for the Ti metal powder. In the Al MMC,
besides Si and Al$_4$C$_3$, some amorphous SiC was found. If one carefully engineers the process, it probably will be possible to minimize the amount of Si and Al$_4$C$_3$ and have mostly SiC as a filler present.

Traditional powder metallurgy of MMCs generally involves hot-pressing for fabrication of dense bodies. Since the current process does not involve hot pressing, high density MMCs were not expected. However, in most of the cases densities were 90% or higher of the theoretical metal matrix density.

It is clear that preceramic polymers serve well as low loss binders for metal powders and provide sound green bodies. It may be expected that future research will lead to the development of metal powder/preceramic polymer formulations suitable for fabrication of near net-shape parts by injection, extrusion, and compression molding. The preceramic polymer binders also serve as the *in situ* source of well-dispersed, discontinuous ceramic reinforcement phases, leading, in favorable cases, to stronger, harder, and more oxidation/corrosion-resistant materials. Preceramic polymers may be especially useful in the fabrication of near net-shape, hard, wear-resistant cermets which could be used directly for cutting tools applications. This new variation of powder metallurgy/metal matrix composite fabrication has good potential in materials applications. However, due to the current high cost of ceramic precursors and the natural reluctance of the designer to undertake new design concept development, the current process will probably not be commercialized in the near future.
Appendix A

The 4 point bending tests was accomplished using screw type Instron 4505.

In addition to the following equations a jig (Fig. 33) was utilized:

![Diagram of 4 point bending sample geometry]

The 4 point bending sample geometry.

\[
MOR = \frac{3PL}{4wh^2} \quad \text{for} \quad a = \frac{L}{4}
\]

\[
MOE = \frac{PL^3}{8wh^3\Delta} \quad \text{where} \quad \Delta = \frac{PL^2}{16wh^3MOE} (3L-L) \quad \text{for} \quad a = \frac{L}{4}
\]


![Sample diagram]

**Figure 33** Four point bending jig used to determine MOR and MOE.
Appendix B

Properties of Pure Metals

<table>
<thead>
<tr>
<th>Metal</th>
<th>Density(a) (g/cm(^3))</th>
<th>Hardness(^b)</th>
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<tbody>
<tr>
<td>Al</td>
<td>2.702</td>
<td>150 HV (99.9% pure)</td>
</tr>
<tr>
<td>Ti</td>
<td>4.5 at 20°C</td>
<td>70-74 HB ingot</td>
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<tr>
<td>Cu</td>
<td>8.92</td>
<td>37 HRB (72 HB) cold drawn</td>
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<tr>
<td>V</td>
<td>5.96</td>
<td>72 HB electron beam ingot</td>
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<tr>
<td>Zr</td>
<td>6.49</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>10.2</td>
<td>~ 350 HV (336 HB) at room temperature</td>
</tr>
<tr>
<td>W</td>
<td>19.35</td>
<td>~ 350 HV (336 HB) at room temperature</td>
</tr>
<tr>
<td>Ni</td>
<td>8.90</td>
<td>64 HV annealed</td>
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<tr>
<td>Fe</td>
<td>7.86</td>
<td>~ 62.5 HV at room temperature</td>
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### Table 1 MMCs Prepared by Using Polymeric Ceramic Precursors as Binders

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<tr>
<th>ID</th>
<th>Metal (-325 mesh)</th>
<th>Preceramic Polymer Binder</th>
<th>Metal/Silicon Mole Ratio</th>
<th>Amount of Binder (wt%)</th>
<th>Green Body Density (g/cm³)</th>
<th>Pyrolysis Program (°C) at 5 °C/min.</th>
<th>MMC Density (g/cm³)</th>
<th>Volume Shrinkage (%)</th>
<th>Crystalline Phase Recognition by XRD and Matched by (JCPDS card #)</th>
<th>Hardness (ksi)</th>
<th>MOR (ksi)</th>
<th>MOE (Mpsi)</th>
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<td>3.5</td>
<td>RT→1200(2 h)</td>
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<td>15</td>
<td>Ti (5-682) TiC (32-1383) Ti₃Si₃ (29-1362)</td>
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<td>29.45</td>
<td>7.05</td>
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<td>PMS</td>
<td>9:1</td>
<td>9.0</td>
<td>2.9</td>
<td>RT→1200(2 h)</td>
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<td>28</td>
<td>Ti (5-682) TiC (31-1400) Ti₃Si₃ (29-1362)</td>
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<td>2.50</td>
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<td>PCS</td>
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<td>12.1</td>
<td>2.9</td>
<td>RT→1200(2 h)</td>
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<td>54.70</td>
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<td>10:0</td>
<td>0</td>
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<td>Pyrolysis Program (°C) at 5° C/min.</td>
<td>Volume Shrinkage (%)</td>
<td>Hardness (HRA)</td>
<td>Crystalline Phase Recognition by XRD and Matched by ICPEDS Card #</td>
<td>MOF (ksi)</td>
<td>MOR (ksi)</td>
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*MOF* indicates the tensile strength of the material in MPa.
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<th>Metal (-325 mesh)</th>
<th>Preceramic Polymer Binder</th>
<th>Metal/Silicon Mole Ratio</th>
<th>Amount of Binder (wt%\textsuperscript{a})</th>
<th>Green\textsuperscript{b} Body Density (g/cm\textsuperscript{3})</th>
<th>Pyrolysis Program (\textdegree C)</th>
<th>Pyrolysis Program (\textdegree C/min)</th>
<th>MMC\textsuperscript{h} Density (g/cm\textsuperscript{3})</th>
<th>Volume Shrinkage (%)\textsuperscript{a}</th>
<th>Crystalline Phase Recognition by XRD</th>
<th>Crystalline Phase Recognition by XRD and Matched by (JCPDS card #)</th>
<th>Hardness\textsuperscript{k} (ksi)</th>
<th>MOR\textsuperscript{i} (ksi)</th>
<th>MOE\textsuperscript{i} (Mpsi)</th>
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a - MOR (Modulus of Rupture); MOE (Modulus of Elasticity); tested in 4-point bending using cross head speed of 0.005 in/min.
b - sample exhibited stress hardening during 4-pt. bending
c - first isopressed for 10 min. at ambient temp. and 40 kpsi and additionally hot pressed at 100°C and 40 kpsi for 5 min.
d - sample exhibited yielding during 4-pt. bending
e - metal/boron mole ratio
f - after uniaxial pressing the sample was isostatically pressed at 100 °C and 40 kpsi for 5 min.
g - sample was deformed
h - bulk density measured with slide calliper
i - (weight of binder)/(weight of binder + weight of metal)
j - (green volume - MMC volume)/(green volume)
k - converted to HB by using ASTM E 140 hardness conversion tables
HRA - Rockwell hardness number A scale (60-kgf load with diamond penetrator)
15-T - Rockwell Superficial hardness number (15-kgf load with 1/16" steel ball penetrator)
15-N - Rockwell Superficial hardness number (15-kgf load with diamond penetrator)
HV - Vickers microhardness number
HB - Brinell hardness number, converted using ASTM E 140 - 88 Standard Hardness Conversion Tables
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<td>W</td>
<td>1.8</td>
<td>10.4</td>
<td>RT→250(2 h)→1500(3 h)</td>
<td>12.1</td>
<td>15</td>
<td>W (4-806), W₃B (6-591), WN (25-1256)</td>
<td>35 HRA (83 HB)</td>
</tr>
</tbody>
</table>

**Key:**

a - amount of binder = (weight of binder)/(weight of binder + weight of metal)
b - bulk density measured with a slide calliper
c - volume shrinkage = (green volume - MMC volume)/(green volume)
d - green powder was prepyrolyzed in argon at 5°C/min: RT→250°C(2h)→500°C(5h)
e - the green body was PC/7/44/A MMC, after 1200°C pyrolysis improved corrosion resistance was observed
f - MMC showed small regions of rust upon exposure to air for several months.
g - too soft for superficial hardness test
h - converted to HB using ASTM E 140-88 Standard Hardness Conversion Tables
HV - Vickers hardness number (100-gf)
HRA - Rockwell hardness number A scale (60-kgf with a diamond penetrator)
HB - Brinell hardness numbers converted to HB using ASTM E 140-88 Standard Hardness Conversion Tables

Table 3 Polymeric Ceramic Precursors Used as Binders for Metal Powders

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>TGA (%)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMS</td>
<td>82</td>
<td>poly(methylsilane) crosslinked with 0.5 mol% ((\text{Cp}_2\text{ZrH}_2)_n)</td>
</tr>
<tr>
<td>PMSII</td>
<td>73</td>
<td>([\text{MeSiH}]_{2.5}(\text{Me}_2\text{Si})_n) crosslinked with 0.5 mol% of ((\text{Cp}_2\text{ZrH}_2)_n)</td>
</tr>
<tr>
<td>PCS</td>
<td>65</td>
<td>polycarbosilane the Nicalon® fiber precursor</td>
</tr>
<tr>
<td>PVS</td>
<td>59</td>
<td>([\text{Me}<em>3\text{Si}]</em>{0.32}(\text{ViSiMe})<em>{1.0}(\text{MeHSi})</em>{0.37}]_n); PVS-200 from Flamel Technologies</td>
</tr>
<tr>
<td>PSZ</td>
<td>84</td>
<td>((\text{MeSiHNH})_n) crosslinked with KH</td>
</tr>
<tr>
<td>DBA</td>
<td>73</td>
<td>([6,9-\text{(Me}<em>2\text{NH})<em>2\text{B}</em>{10}\text{H}</em>{12}]_x)</td>
</tr>
<tr>
<td>PBA</td>
<td>64</td>
<td>poly(borazinylamine)</td>
</tr>
</tbody>
</table>
Experimental

General Comments

All green powder preparations of mixtures of the metal powder and the polymeric ceramic precursor were conducted in an air-free atmosphere using standard Schlenk line and dry-box techniques. Solvents such as toluene were distilled from sodium and ether from sodium/benzophenone and deoxygenated prior to use. Liquid ammonia was dried over sodium metal prior to use. The following -325 mesh powders were purchased from CERAC and were handled in the dry-box at all times: Al (cat. # A-1182; lot # X14720); Ti (cat. # T-1147; lot # X15521); Cu (cat. # C-1133; lot # X14557); Zr (cat. # Z-1026; lot # X14376-1); Mo (cat. # M-2000; lot # 73738-B-1); Fe (cat. # I-1021; lot # X14840); Ni(5μ) (cat. # N-1089; lot # X14815); and Si3N4 (cat. # S-1068; lot # X14860). Johnson Matthey provided -325 mesh V (cat. # 12234; lot # 128C04) and ~12 μm particle W (cat. # 10401; lot # G15C07). Ceramic precursors were prepared according to published procedures: poly(methylsilane) (PMS) which had been cross-linked with (Cp2ZrH2)n24 and PMS from the prolonged reductive coupling as described in the previous chapter, polysilazane (PSZ),19 poly(borazinylamine) (PBA),26 (CH3)3SiNH[TiCl3, a TiN precursor,27 [6,9-(Me2NH)2B10H12]x (DBA),28 Poly(diphenyldimethylcarbosilane) (D-PPMC-1) and poly(diphenylcarbosilane) (D-PCC) were obtained from Solvay Deutschland GmbH. Polysilane containing methyl, vinyl, and hydrogen substituents (PVS) was obtained from Flamel
Technologies, France (PVS-200, lot # SEG 82). The Nicalon® polycarbosilane (PCS) was purchased from Dow Corning Corp., X9-6348, lot# PG110064.

Uniaxial pressing was conducted using a Carver Laboratory Press Model C and isopressing using a HIP press by High Pressure Equipment Co. Inc.. The final pyrolysis took place in a Lindberg tube furnace at 5°C/min. to temperatures specified in Tables 1 and 2.

Thin films were casted by dipcoating using modified syringe pump model 341A made by Sage Instrumants division of Orion Research Inc.

Ultrasonic activation was accomplished using an internally cooled Branson 3200 ultrasonic cleaner operating at 45-56 kHz, 300 W.

X-ray powder diffraction was performed on Rigaku Rotaflex RU-300 diffractometer using Cu Kα (λ = 1.5418 Å) radiation from a rotating anode source (50 kV, 200 mA).

X-ray photoelectron spectra were obtained on a PHI 5100 ESCA instrument with 50Å ion milling.

Scanning electron microscopic studies were carried out on a Hitachi S-530 with HNU systems EDX detector in conjunction with System 5000.

Transmission electron microscopic studies were performed by bright field image, selected area diffraction (SAD), and energy dispersive X-ray spectroscopy (EDXS) using a Philips EM400T TEM and a Noran ultrathin window Micro-Z detector. The TEM specimens were sectioned from MMCs with a low-speed
diamond saw and mechanically ground to ~300 μm. Circular discs of 3 mm in
diameter were core drilled from the ground sections, mechanically ground to ~120
μm, and then dimpled to ~30 μm. The specimens were ion milled with 5 kV Ar⁺
ions at an incident angle of 12° until the perforation was achieved.

Hardness tests were performed on a Rockwell Tester Model 4JR and the
Superficial Model 4JS, both made by Acco Wilson Industry Division. Vickers
microhardness was measured on a Leco DM 400. Between 10-15 hardness
numbers were collected and the average was reported.

Four point bending tests were performed on screw type Instron 4505.
Between 4 - 8 samples were broken in four point bending using the jig (Fig. 33)
and the average was reported.

Preparation of Ti/PMS 9:1 Mol Ratio Green Body. (PC/5/17, 21, 24, 68)

A 100 mL round-bottomed flask was charged with 1.30 g (0.0295 mol) of
PMS (previously crosslinked with 0.5 mol% (Cp₂ZrH₂)ₙ as reported in Chapter 1)
and 12.73 g (0.266 g atom) of -325 mesh Ti metal. Then 20 mL of toluene was
added and the flask was placed in the ultrasonic bath for 18.5 h. The volatiles
were removed, leaving 14.01 g of silver-gray solid. The solid was ground to a fine
powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and
isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed:
5°C/min to 1200°C with a 2 h hold at that temperature. The summary of
properties is given in Table 1.

Preparation of Ti/PMS 9:1 Mol Ratio Green Body by 100°C Isostatic Pressing.

(PG6/5)

A 100 mL round-bottomed flask was charged with 1.30 g (0.0295 mol) of PMS (previously crosslinked with 0.5 mol% (Cp₂ZrH₂)ₙ as reported in Chapter 1) and 12.73 g (0.266 g atom) of -325 mesh Ti metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 18.5 h. The volatiles were removed, leaving 14.01 g of silver-gray solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed first 10 min at 40 kpsi and then for 5 min at 40 kpsi and 100°C. The green bars were pyrolyzed: 5°C/min to 1200°C with a hold for 2 h at that temperature. The summary of properties is given in Table 1.

Preparation of Ti/PCS 9:1 Mol Ratio Green Body. (PC5/30)

A 100 mL round-bottomed flask was charged with 1.00 g (0.0172 mol) of PCS and 7.43 g (0.155 g atom) of -325 mesh Ti metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 24 h. The volatiles were removed, leaving 8.42 g of silver-gray solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and
isostatically pressed for 2 min at 40 kpsi. The green bars were pyrolyzed:
5°C/min to 1200°C with a hold for 2 h at that temperature. The summary of
properties is given in Table 1.

**Preparation of Ti/PVS 26:1 Mol Ratio Green Body.** (ML 13)

A 100 mL round-bottomed flask was charged with 0.5 g (7.2 mmol) of
PVS and 9.0 g (0.189 g atom) of -325 mesh Ti metal. Then 20 mL of toluene was
added and the flask was placed in the ultrasonic bath for 20 h. The volatiles were
removed, leaving 9.5 g of silver-gray solid. The solid was ground to a fine powder
with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically
pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 1200°C
with a hold for 2 h at that temperature. The green body was very brittle and the
MMC showed cracks on the edges. The summary of properties is given in Table
1.

**Preparation of Ti/DBA 9:1 Mol Ratio Green Body.** (ML 14)

A 100 mL round-bottomed flask was charged with 0.44 g (2.1 mmol) of
DBA and 9.0 g (0.189 g atom) of -325 mesh Ti metal. Then 20 mL of toluene was
added and the flask was placed in the ultrasonic bath for 20 h. The volatiles were
removed, leaving 9.44 g of silver-gray solid. The solid was ground to a fine
powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 1200°C with a hold for 2 h at that temperature. The summary of properties is given in Table 1.

Cowurtz Reductive Coupling of 1.0 MeHSiCl₂ and 0.4 Me₂SiCl₂ and 2.5 N₂, and Subsequent Crosslinking With (Cp₂ZrH₂)ₙ: Synthesis of PMSII. (ML 1, 6)

A 200 mL flask was charged with 16.1 g (0.7 mol) of mirror clean sodium metal, 61.25 mL of hexane, 8.75 mL of THF, 23.0 g (0.2 mol, 20.8 mL) of MeHSiCl₂, and 10.3 g (0.08 mol, 9.7 mL) of Me₂SiCl₂. The reaction mixture was ultrasonicated for 16 h and afterwards filtered. The residue was washed twice with 50 mL of hexane and combined with the filtrate. Trap-to-trap distillation left 7.7 g (57% yield) of clear oil. For crosslinking, 7.5 g (158 mmol) of the oil was placed in a 100 mL flask with 177 mg (0.79 mmol) of (Cp₂ZrH₂)ₙ and 50 mL of toluene. The mixture was heated at reflux for 3-4 h. The volatiles were removed by trap-to-trap distillation, leaving 7.7 g of orange solid.

\(^1\)H NMR (C₆D₆, ppm): δ 0.5 (5.8 H, SiCH₃); 4.1 (1 H, SiH).

Ceramic residue yield by TGA: 73% black residue
Preparation of Ti/PMSII 19:1 Mol Ratio Green Body. (ML 21)

A 100 mL round-bottomed flask was charged with 0.48 g (9.9 mmol) of PMSII and 9.0 g (0.189 g atom) of -325 mesh Ti metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 20 h. The volatiles were removed, leaving 9.47 g of silver-gray solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 1200°C with a hold for 2 h at that temperature. The summary of properties is given in Table 1.

Preparation of Ti/PSZ 9:1 Mol Ratio Green Body. (SWK/1/23)

A 100 mL round-bottomed flask was charged with 1.85 g (0.0313 mol) of PSZ and 13.5 g (0.281 g atom) of -325 mesh Ti metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 24 h. The volatiles were removed, leaving 15.3 g of silver-gray solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 1200°C with a hold for 2 h at that temperature. The summary of properties is given in Table 1.
Preparation of Ti/PSZ 9:1 Mol Ratio Green Body and Its Isopressing at 100°C.

(SWK/1/34)

A 100 mL round-bottomed flask was charged with 1.85 g (0.0313 mol) of PSZ and 13.5 g (0.281 g atom) of -325 mesh Ti metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 24 h. The volatiles were removed, leaving 15.3 g of silver-gray solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi and finally isopressed for 5 min at 40 kpsi at 100°C. The green bars were pyrolyzed: 5°C/min to 1200°C with a hold for 2 h at that temperature. The summary of properties is given in Table 1.

Preparation of Ti/PSZ 9:1 Mol Ratio Green Body and Its Isopressing at 100°C.

(SWK/1/42)

A 100 mL round-bottomed flask was charged with 1.23 g (0.0209 mol) of PSZ and 9.0 g (0.188 g atom) of -325 mesh Ti metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 21 h. The volatiles were removed, leaving 10.2 g of silver-gray solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 5 min at 40 kpsi and 100°C. The green bars were pyrolyzed: 5°C/min to 1200°C with a hold for 2 h at that temperature. The
summary of properties is given in Table 1.

**Preparation of Ti/PBA 9:1 Mol Ratio Green Body.** (PC/7/40/A, C)

A 100 mL round-bottomed flask was charged with 0.556 g (17.37 mmol) of PBA and 8.0 g (0.166 g atom) of -325 mesh Ti metal powder. Then 30 mL of sodium dried ammonia was condensed into the reaction flask. After stirring for 30 min, the mixture was allowed to warm up which initiated evaporation of ammonia. The volatiles were removed under vacuum leaving 8.5 g of gray solid. The solid was ground to a fine powder with a mortar and pestle, sifted through 270 mesh sieve, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 250°C held for 2 h and then to 1200°C with a hold for 3 h. The summary of properties is given in Table 2.

**Preparation of Al/PMS 9:1 Mol Ratio Green Body.** (PC/5/31, 39)

A 100 mL round-bottomed flask was charged with 1.15 g (0.026 mol) of PMS (previously crosslinked with 0.5 mol% (Cp₂ZrH₂)ₙ as reported in Chapter 1) and 6.35 g (0.235 g atom) of -325 mesh Al metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 18 h. The volatiles were removed, leaving 7.50 g of silver-gray solid. The solid was ground to a fine
powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green body became very warm upon exposure to air. The green bars were pyrolyzed: 5°C/min to 550°C with a hold for 2 h at that temperature. The summary of properties is given in Table 1.

Preparation of Al/PMS 9:1 Mol Ratio Green Body and Its Isopressing at 100°C.
(PC/6/6)

A 100 mL round-bottomed flask was charged with 1.11 g (0.025 mol) of PMS (previously crosslinked with 0.5 mol% (Cp₂ZrH₂)ₙ as reported in Chapter 1) and 6.13 g (0.23 g atom) of ~325 mesh Al metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 18 h. The volatiles were removed, leaving 7.24 g of silver-gray solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi and finally isopressed for 5 min at 40 kpsi at 100°C. The green body became very warm upon exposure to air. The green bars were pyrolyzed: 5°C/min to 550°C with a hold for 2 h at that temperature. The summary of properties is given in Table 1.
Preparation of Al/PMS (with 0.5 wt% BHT) 9:1 Mol Ratio Green Body. (TS/2/60)

A 200 mL round-bottomed flask was charged with 4.53 g (0.103 mol) of PMS (from the extensive reductive coupling of MeSiHCl₂ with Na as reported in Chapter 1, Section G), 23 mg (0.104 mmol) BHT and 25 g (0.926 g atom) of -325 mesh Al metal. Then 50 mL of toluene was added and the flask was placed in the ultrasonic bath for 16 h. The volatiles were removed, leaving 29.5 g of silver-gray solid. The solid was ground to a fine powder with a mortar and pestle, ball milled for 4 h with 1/4" steel balls, sifted through 270 mesh sieve, uniaxially pressed for 1 h at 8.1 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green body did not become hot upon exposure to air. The green bars were pyrolyzed: 5°C/min to 550°C with a hold for 2 h at that temperature. After pyrolysis at 1000°C MMCs retained their structural integrity.

Preparation of Al/PMSII 20:1 Mol Ratio Green Body. (ML 10)

A 100 mL round-bottomed flask was charged with 0.514 g (10.7 mmol) of PMSII and 6.0 g (0.222 g atom) of -325 mesh Al metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 20 h. The volatiles were removed, leaving 7.50 g of silver-gray solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 550°C with a hold for 2 h at that temperature. The summary of
properties is given in Table 1.

**Preparation of Al/PVS 28:1 Mol Ratio Green Body. (ML 12)**

A 100 mL round-bottomed flask was charged with 0.58 g (8.3 mmol) of PVS and 6.3 g (0.234 g atom) of -325 mesh Al metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 20 h. The volatiles were removed, leaving 6.58 g of silver-gray solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min. at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 550°C with a hold for 2 h at that temperature. The summary of properties is given in Table 1.


A 200 mL round-bottomed flask was charged with 2.964 g (92.62 mmol) of PBA and 24.0 g (0.889 g atom) of -325 mesh Al metal powder. Then 30 mL of sodium dried ammonia was condensed into the reaction flask. After stirring for 30 min., the mixture was allowed to warmup which initiated evaporation of ammonia. The volatiles were removed under vacuum leaving 26.9 g of gray solid. The solid was ball milled for 4 h using 1/4" steel shots, sifted through 270 mesh sieve,
uniaxially pressed for 1 h at 8.5 kpsi, and isostatically pressed for 10 min. at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 250°C held for 2 h and to 500°C with a hold for 3 h (or 1000°C, 3 h). The summary of properties is given in Table 2.

Preparation of Cu/PMS 9:1 Mol Ratio Green Body. (PC/5/57)

A 100 mL round-bottomed flask was charged with 1.4 g (0.32 mol) of PMS (previously crosslinked with 0.5 mol% (Cp₂ZrH₂)ₙ as reported in Chapter 1) and 18.2 g (0.286 g atom) of -325 mesh Cu metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 19 h. The volatiles were removed, leaving 19.6 g of red solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed under 100 g load: 5°C/min to 900°C with a hold for 2 h at that temperature. The summary of properties is given in Table 1.

Preparation of Cu/PCS 9:1 Mol Ratio Green Body. (PC/5/58/A)

A 100 mL round-bottomed flask was charged with 1.86 g (0.032 mol) of PCS and 18.19 g (0.286 g atom) of -325 mesh Cu metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 18 h. The volatiles
were removed, leaving 20.0 g of red solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 900°C with a hold for 2 h at that temperature. The summary of properties is given in Table 1.

**Preparation of Cu/PVS 22:1 Mol Ratio Green Body.** (ML 5)

A 100 mL round-bottomed flask was charged with 1.6 g (0.0225 mol) of PVS and 32.0 g (0.504 g atom) of -325 mesh Cu metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 20 h. The volatiles were removed, leaving 33.6 g of red solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 900°C with a hold for 2 h at that temperature. The summary of properties is given in Table 1.

**Preparation of Cu/DBA 9:1 MolRatio Green Body.** (ML 18)

A 100 mL round-bottomed flask was charged with 0.66 g (3.15 mmol) of DBA and 18.0 g (0.283 g atom) of -325 mesh Cu metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 20 h. The volatiles
were removed, leaving 18.6 g of red solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 900°C with a hold for 2 h at that temperature. The final MMC was full of channels, probably a result of binder burnout. The summary of properties is given in Table 1.

**Preparation of Cu/PMSII 19:1 Mol Ratio Green Body. (ML 19)**

A 100 mL round-bottomed flask was charged with 0.72 g (14.9 mmol) of PMSII and 18.0 g (0.283 g atom) of -325 mesh Cu metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 20 h. The volatiles were removed, leaving 18.7 g of red solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 900°C with a hold for 2 h at that temperature. The summary of properties is given in Table 1.

**Preparation of Cu/PBA 9:1 Mol Ratio Green Body. (PC/7/43, CKN/1/5/A)**

A 100 mL round-bottomed flask was charged with 1.05 g (32.81 mmol) of PBA and 20.0 g (0.315 g atom) of -325 mesh Cu metal powder. Then 30 mL of
sodium dried ammonia was condensed into the reaction flask. After stirring for 30 min, the mixture was allowed to warmup which initiated evaporation of ammonia. The volatiles were removed under vacuum leaving 21.0 g of red solid. The solid was ground to a fine powder with a mortar and pestle, sifted through 270 mesh sieve, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 250°C held for 2 h and then to 900°C with a hold for 3 h. The summary of properties is given in Table 2.

Preparation of Zr/PMS 9:1 Mol Ratio Green Body. (PC/5/71)

A 100 mL round-bottomed flask was charged with 0.70 g (0.16 mol) of PMS (previously crosslinked with 0.5 mol% \((\text{Cp}_2\text{ZrH}_2)_n\) as reported in Chapter 1) and 13.0 g (0.142 g atom) of -325 mesh Zr metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 23.5 h. The volatiles were removed, leaving 13.7 g of gray solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 1500°C with a hold for 2 h at that temperature. The summary of properties is given in Table 1.
Preparation of Zr/PCS 9:1 Mol Ratio Green Body. (PC/6/4)

A 100 mL round-bottomed flask was charged with 0.922 g (0.0159 mol) of PCS and 13.0 g (0.142 g atom) of -325 mesh Zr metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 17.5 h. The volatiles were removed, leaving 13.9 g of gray solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 1500°C with a hold for 2 h at that temperature. The summary of properties is given in Table 1.

Preparation of Zr/PSZ 9:1 Mol Ratio Green Body. (SWK/1/22z)

A 100 mL round-bottomed flask was charged with 2.17 g (0.0369 mol) of PSZ and 19.5 g (0.214 g atom) of -325 mesh Zr metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 23 h. The volatiles were removed, leaving 21.6 g of gray solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 1500°C with a hold for 2 h at that temperature. The summary of properties is given in Table 1.
Preparation of Zr/PVS 18:1 Mol Ratio Green Body. (ML 25)

A 100 mL round-bottomed flask was charged with 0.52 g (7.5 mmol) of PVS and 13.0 g (0.142 g atom) of -325 mesh Zr metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 20 h. The volatiles were removed, leaving 13.52 g of gray solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 1500°C with a hold for 2 h at that temperature. The summary of properties is given in Table 1.

Preparation of V/PMS 9:1 Mol Ratio Green Body. (PC/5/72)

A 100 mL round-bottomed flask was charged with 1.15 g (0.0261 mol) of PMS (previously crosslinked with 0.5 mol% (Cp₂ZrH₂)ₙ as reported in Chapter 1) and 12.0 g (0.235 g atom) of -325 mesh V metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 23.5 h. The volatiles were removed, leaving 13.15 g of gray solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 1500°C with a hold for 2 h at that temperature. After a long exposure to air the MMC became green on the surface. The summary of properties is given
in Table 1.

**Preparation of V/PCS 9:1 Mol Ratio Green Body.** *(PC/5/74)*

A 100 mL round-bottomed flask was charged with 1.52 g (0.0262 mol) of PCS and 12.0 g (0.235 g atom) of -325 mesh V metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 16.5 h. The volatiles were removed, leaving 13.52 g of gray solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 1500°C with a hold for 2 h at that temperature. After a long exposure to air the MMC became green on the surface. The summary of properties is given in Table 1.

**Preparation of V/PVS 18:1 Mol Ratio Green Body.** *(ML 26)*

A 100 mL round-bottomed flask was charged with 0.86 g (0.0124 mol) of PVS and 12.0 g (0.235 g atom) of -325 mesh V metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 20 h. The volatiles were removed, leaving 12.86 g of gray solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to
1200°C with a hold for 2 h at that temperature. After a long exposure to air the MMC became green on the surface. The summary of properties is given in Table 1.

**Preparation of V/DBA 9:1 Mol Ratio Green Body.** (ML 28)

A 100 mL round-bottomed flask was charged with 0.55 g (2.62 mmol) of DBA and 12.0 g (0.235 g atom) of -325 mesh V metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 20 h. The volatiles were removed, leaving 12.55 g of gray solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 1500°C with a hold for 2 h at that temperature. After a long exposure to air the MMC became green on the surface. The summary of properties is given in Table 1.

**Preparation of V/PSZ 9:1 Mol Ratio Green Body.** (SWK/1/22v)

A 100 mL round-bottomed flask was charged with 1.33 g (0.0260 mol) of PSZ and 11.9 g (0.233 g atom) of -325 mesh V metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 23 h. The volatiles were removed, leaving 13.2 g of gray solid. The solid was ground to a fine powder with
a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 1500°C with a hold for 2 h at that temperature. After a long exposure to air the MMC became green on the surface. The summary of properties is given in Table 1.

**Preparation of Mo/PMS 9:1 Mol Ratio Green Body.** (PC/5/70)

A 100 mL round-bottomed flask was charged with 1.02 g (0.0227 mol) of PMS (previously crosslinked with 0.5 mol% (Cp₂ZrH₂)n as reported in Chapter 1) and 20.0 g (0.208 g atom) of -325 mesh Mo metal. Then 40 mL of toluene was added and the flask was placed in the ultrasonic bath for 21.5 h. The volatiles were removed, leaving 21.0 g of gray solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 1500°C with a hold for 2 h at that temperature. The summary of properties is given in Table 1.

**Preparation of Mo/PCS 9:1 Mol Ratio Green Body.** (SWK/1/1)

A 100 mL round-bottomed flask was charged with 2.03 g (0.0347 mol) of PCS and 30.0 g (0.312 g atom) of -325 mesh Mo metal. Then 40 mL of toluene
was added and the flask was placed in the ultrasonic bath for 23 h. The volatiles were removed, leaving 32.0 g of gray solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 1500°C with a hold for 2 h at that temperature. The summary of properties is given in Table 1.

Preparation of Mo/PSZ 9:1 Mol Ratio Green Body. (SWK/1/20)

A 100 mL round-bottomed flask was charged with 2.06 g (0.0347 mol) of PSZ and 30.0 g (0.312 g atom) of -325 mesh Mo metal. Then 40 mL of toluene was added and the flask was placed in the ultrasonic bath for 22 h. The volatiles were removed, leaving 32.0 g of gray solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 1500°C with a hold for 2 h at that temperature. The summary of properties is given in Table 1.

Preparation of W/PMS 9:1 Mol Ratio Green Body. (PC/5/63)

A 100 mL round-bottomed flask was charged with 1.0 g (0.0227 mol) of PMS (previously crosslinked with 0.5 mol% (Cp₂ZrH₂)ₙ as reported in Chapter 1)
and 37.6 g (0.204 g atom) of ~12 μm particle size W metal. Then 30 mL of toluene was added and the flask was placed in the ultrasonic bath for 19 h. The volatiles were removed, leaving 38.6 g of gray solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 1500°C with a hold for 2 h at that temperature. The summary of properties is given in Table 1.

**Preparation of W/PCS 9:1 Mol Ratio Green Body** (PC/565)

A 100 mL round-bottomed flask was charged with 1.0 g (0.0172 mol) of PCS and 28.4 g (0.154 g atom) of ~12 μm particle size W metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 15.5 h. The volatiles were removed, leaving 29.4 g of gray solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 1500°C with a hold for 2 h at that temperature. The summary of properties is given in Table 1.
Preparation of W/PCS 9:3 Mol Ratio Green Body. (PC/5/69)

A 100 mL round-bottomed flask was charged with 0.5 g (0.0113 mol) of PCS and 51.2 g (0.278 g atom) of 12 μm particle size W metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 20 h. The volatiles were removed, leaving 51.7 g of gray solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 1500°C with a hold for 2 h at that temperature. The summary of properties is given in Table 1. The blank powder (without binder) failed since powder did not hold together.

Preparation of W(<1μ)/PMS 9:1 Mol Ratio Green Body. (PC/7/67)

A 100 mL round-bottomed flask was charged with 0.5 g (0.0114 mol) of PMS (previously crosslinked with 0.5 mol% Cp₂ZrH₂)n as reported in Chapter 1 and 18.8 g (0.102 g atom) of <1 μm particle size W metal. Then 30 mL of toluene was added and the flask was placed in the ultrasonic bath for 23.5 h. The volatiles were removed, leaving 19.3 g of gray solid. The solid was ground to a fine powder with a mortar and pestle, sifted through 270 mesh sieve, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 250°C with a hold for 2 h then at the same rate to 1500°C with a hold for 3 h at that temperature. The summary of properties is
given in Table 1.

Preparation of W/PVS 19:1 Mol Ratio Green Body. (ML 4)

A 100 mL round-bottomed flask was charged with 1.21 g (0.0173 mol) of PVS and 60.0 g (0.326 g atom) of ~12 μm particle size W metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 20 h. The volatiles were removed, leaving 61.2 g of gray solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 1500°C with a hold for 2 h. The summary of properties is given in Table 1.

Preparation of W/PMSII 20:1 Mol Ratio Green Body. (ML 9)

A 100 mL round-bottomed flask was charged with 0.52 g (0.0109 mol) of PMSII and 40.0 g (0.218 g atom) of ~12 μm particle size W metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 20 h. The volatiles were removed, leaving 40.5 g of gray solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min. at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 1500°C with a hold for 2 h at that temperature. The summary of
properties is given in Table 1.

**Preparation of W/PSZ 9:1 Mol Ratio Green Body.** (SWK/1/18)

A 100 mL round-bottomed flask was charged with 2.04 g (0.0344 mol) of PSZ and 57.0 g (0.310 g atom) of ~12 μm particle size W metal. Then 20 mL of toluene was added and the flask was placed in the ultrasonic bath for 21 h. The volatiles were removed, leaving 59.0 g of gray solid. The solid was ground to a fine powder with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 1500°C with a hold for 2 h at that temperature. The summary of properties is given in Table 1.

**Preparation of W/PBA 9:1 Mol Ratio Green Body.** (PC/7/65, CKN/1/11/A)

A 100 mL round-bottomed flask was charged with 0.18 g (5.63 mmol) of PBA and 10.0 g (0.054 g atom) of -325 mesh W metal powder. Then 30 mL of sodium dried ammonia was condensed into the reaction flask. After stirring for 30 min, the mixture was allowed to warm up which initiated evaporation of ammonia. The volatiles were removed under vacuum leaving 10.15 g of gray solid. The solid was ground to a fine powder with a mortar and pestle, sifted through 270 mesh sieve, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min.
at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 250°C held for 2 h and then to 1500°C with a hold for 3 h. The summary of properties is given in Table 2.

Preparation of Fe/PBA 9:1 Mol Ratio Green Body. (PC/7/44, CKN/1/3/C)

A 100 mL round-bottomed flask was charged with 0.477 g (14.91 mmol) of PBA and 8.0 g (0.143 g atom) of -325 mesh Fe metal powder. Then 30 mL of sodium dried ammonia was condensed into the reaction flask. After stirring for 30 min., the mixture was allowed to warm up which initiated evaporation of ammonia. The volatiles were removed under vacuum leaving 8.45 g of gray solid. The solid was ground to a fine powder with a mortar and pestle, sifted through 270 mesh sieve, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 250°C held for 2 h and then to 800°C with a hold for 3 h (or later 1200°C, 3 h). The summary of properties is given in Table 2.

Preparation of Ni/PBA 9:1 Mol Ratio Green Body. (PC/7/46, CKN/1/5/B)

A 100 mL round-bottomed flask was charged with 0.91 g (28.44 mmol) of PBA and 16.0 g (0.271 g atom) of -325 mesh Ni metal powder. Then 30 mL of sodium dried ammonia was condensed into the reaction flask. After stirring for 30
min, the mixture was allowed to warm up which initiated evaporation of ammonia. The volatiles were removed under vacuum leaving 17.0 g of gray solid. The solid was ground to a fine powder with a mortar and pestle, sifted through 270 mesh sieve, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min at 40 kpsi. The green bars were pyrolyzed: 5°C/min to 250°C held for 2 h and then to 1000°C with a hold for 3 h. The summary of properties is given in Table 2.

Oxidation Resistance Study of Some MMCs.

The following MMCs (Table 4) were placed in a furnace that was open to the air at 1000°C for 50 h.

<table>
<thead>
<tr>
<th>ID</th>
<th>Metal</th>
<th>Binder</th>
<th>Metal/Binder mol ratio</th>
<th>Volume before heating (cm³)</th>
<th>Weight before heating (g)</th>
<th>Volume after heating (cm³)</th>
<th>Weight after heating (g)</th>
<th>Hardness after heating</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC/6/5</td>
<td>Ti</td>
<td>PMS</td>
<td>9:1</td>
<td>0.365</td>
<td>1.6438</td>
<td>0.448</td>
<td>1.7434</td>
<td>73 HRA (421 HB)</td>
</tr>
<tr>
<td>SWK/1/38</td>
<td>Ti</td>
<td>PBSN</td>
<td>99:1</td>
<td>0.377</td>
<td>1.5100</td>
<td>0.482</td>
<td>1.7963</td>
<td>67 30-N</td>
</tr>
<tr>
<td>SWK/1/34</td>
<td>Ti</td>
<td>PSZ</td>
<td>9:1</td>
<td>0.233</td>
<td>0.9630</td>
<td>0.275</td>
<td>1.0704</td>
<td>69 30-N</td>
</tr>
<tr>
<td>ML 13</td>
<td>Ti</td>
<td>PVS</td>
<td>26:1</td>
<td>0.271</td>
<td>1.1075</td>
<td>lost shape</td>
<td>1.5757</td>
<td></td>
</tr>
<tr>
<td>PC/8/13/B</td>
<td>Ti</td>
<td>blank</td>
<td>10:0</td>
<td>0.185</td>
<td>0.7711</td>
<td>0.247</td>
<td>0.8880</td>
<td>67 HRA (311 HB)</td>
</tr>
<tr>
<td>PC/5/67</td>
<td>Al</td>
<td>?PMS</td>
<td>9:1</td>
<td>0.142</td>
<td>0.3255</td>
<td>0.157</td>
<td>0.3298</td>
<td>75 HV (66 HB)</td>
</tr>
<tr>
<td>ML 25</td>
<td>Zr</td>
<td>PVS</td>
<td>18:1</td>
<td>0.259</td>
<td>1.4560</td>
<td>degraded</td>
<td>1.9497</td>
<td></td>
</tr>
<tr>
<td>PC/5/69</td>
<td>W</td>
<td>PCS</td>
<td>97:3</td>
<td>0.259</td>
<td>1.4560</td>
<td>degraded into yellow powder</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Key:
a - hardness tested after removing the oxide layer; converted to HB using ASTM E 140 conversion tables. See Table 1 for initial hardness.
30-N - Rockwell Superficial hardness number (30-kgf load, diamond penetrator).
HRA - Rockwell hardness number A scale (60-kgf load, diamond penetrator)
HB - Brinell hardness number
b - metal/silicon mol ratio

PC/6/5 retained its shape and gained 6 wt% and 22% by volume. The oxide layer was only on the surface and was easily peeled off. SWK/1/38 retained its shape and gained 19 wt% and 27% by volume. The oxide layer was only on the surface and was easily peeled off. SWK/1/34 retained its shape and gained 11 wt% and 18% by volume. The oxide layer was only on the surface and was easily peeled off. ML 25 did not retain its shape, a ceramic shell formed around the bar (Fig. 6). The MMC gained 34% by weight. PC/8/13 retained its shape and gained 15 wt% and 33% by volume. The oxide layer was only on the surface and was easily peeled off. PC/5/67 retained its shape and gained 2 wt% and 10% by volume.

Corrosion Resistance Test for Al/PMS Containing Al₄C₃ Dispersoid. (PC/6/59)

A 100 mL round-bottomed flask was charged with 50 mL of HPLC grade water and a 0.1787 g (0.0661 cm³) of Al/PMS 9/1 pyrolyzed at 1000°C MMC bar. Above the surface of the water another sample 0.1833 g (0.0718 cm³) of the same MMC was suspended on a Pt wire. The water in the flask then was heated to
reflux for 762 h. The water became murky with neutral pH. The sample which had been immersed in boiling water experienced a 12 wt% gain and a 27% volume increase (0.2010 g, 0.0842 cm³). After the oxide layer, had been removed, it showed a hardness of 60.9 HV. The second sample, which had been exposed to water vapors, showed a 14 wt% gain and a 26% volume increase (0.2090 g, 0.0907 cm³), and a hardness of 69.4 HV after removal of the surface layer.

Preparation of Si₃N₄-TiN Composite with (CH₃)₃SiNHTiCl₃ as a Binder.

(PC/7/68, CKN/1/11/B)

A 100 mL flask was charged with 10.0 g (71.4 mmol) of Si₃N₄ (<1μ) powder, 2.0 g (8.26 mmol) of (CH₃)₃SiNHTiCl₃, and dichloromethane (~40 mL). The solvent was removed with vigorous stirring in vacuum and the residual solid was ground with a mortar and pestle, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min. at 40 kpsi. The green body was placed in the furnace and the temperature was raised at a rate 5°C/min. to 200°C in argon (hold 2 h), to 600°C in ammonia (hold 2 h), and to 1500°C in argon (hold 2 h). The X-ray powder diffraction pattern showed lines due to β-Si₃N₄, α-Si₃N₄, Si, and TiN. The density of the composite was 1.71 g/cm³. The silicon in the composite body originated from the decomposition of silicon nitride (a sample of CERAC Si₃N₄ showed β-Si₃N₄, α-Si₃N₄, and Si after heating at 1500°C in argon).
Preparation of Ti-TiN Composite With (CH$_3$)$_3$SiNHTiCl$_3$ as a Binder. (PC/7/48, 68; CKN/1/6/A)

A 100 mL flask was charged with 8.0 g (0.167 mol) of Ti powder, 2.0 g (8.25 mmol) of (CH$_3$)$_3$SiNHTiCl$_3$, and 50 mL of dichloromethane. After the solvent was removed in vacuum with vigorous stirring, the powder was ground with a mortar and pestle, sifted through a 270 mesh sieve, uniaxially pressed for 1 h at 13.5 kpsi, and isostatically pressed for 10 min. at 40 kpsi. The powder then was used to fabricate a MMC by firing the green body at 200°C in argon (hold 2 h), followed by heating in ammonia at 600°C (hold 2 h) and argon at 1000°C (hold 2 h). The rate of heating was 5°/min. The X-ray powder diffraction pattern of the resulting body showed peaks due to Ti and Ti$_2$N. The density of the composite was 2.2 g/cm$^3$.

Preparation of a TiN Thin Film on an Alumina Substrate Using the (CH$_3$)$_3$SiNHTiCl$_3$ Precursor. (PC/8/51, 56)

In the glove box, a 20 mL test tube was charged with 3.03 g (12.5 mmol) of (CH$_3$)$_3$SiNHTiCl$_3$ and 12.5 mL of THF to obtain a 1.0 M solution. An alumina substrate (previously heat treated in air at 1000°C) of size 15 x 1 x 80 mm was suspended on a wire and submerged in to the 1.0 M solution. It was then withdrawn at a rate of 0.01 mm/s (using a modified syringe pump). The coated alumina substrate then was transferred to a tube furnace and pyrolyzed in an
ammonia atmosphere (heating rate $5^\circ$C/min to 1000$^\circ$C with a hold for 3 h). The resulting coated substrate was bronze in appearance, passed the "scotch tape test", and was electrically conductive (0.53 kΩ/cm). The thickness of the film was ~1 μm as measured by breaking the coated substrate in the middle and examining the fracture surface under a microscope.
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Chapter Three

Application of Poly(methylsilane) and Nicalon® Polycarbosilane Precursors as Binders for Metal/Ceramic Powders in Preparation of Functionally Graded Materials
Introduction

The concept of Functionally Graded Materials (FGM's) was proposed\(^1\) in the last decade as a means of preparing thermal barrier materials suitable for use in aeronautics (hypersonic aircraft skins), fusion reactors, and space transportation systems. An FGM is an anisotropic composite material in which a continuous change in microstructure from low modulus (usually metal) to high modulus (usually ceramic) domains results in a gradient of properties (Fig. 1). An abrupt transition in material composition from pure ceramic to pure metal due to the low coefficient of thermal expansion of the ceramic and relatively high thermal expansion coefficient of the metal (Fig. 2)\(^2\) results in severe thermal stress which encourages the propagation of interfacial cracks. A well-controlled interlayer may relieve stress acting across the bonded interface and may thus prevent crack formation. This technique is especially applicable within materials which exhibit thermal-expansion mismatch (Fig. 2).
Figure 1 Thermal expansion coefficients.²
Depending on the application of the FGM, the gradient can be created in a single step, in a continuous or in a stepwise fashion (Fig. 1). The single step gradient is comprised of a uniform mixture of metal and ceramic sandwiched between pure ceramic and metal layers. In a continuous gradient the mixtures of metal/ceramic blends gradually vary from ceramic-rich to metal-rich layers. The stepwise gradients are achieved by steps in composition of ceramic-rich to metal-rich layers (Fig. 2).\textsuperscript{1a}

\begin{figure}[h]
\centering
\includegraphics[width=\columnwidth]{gradient_types.png}
\caption{Functionally Graded Material (FGM); M - metal, C - ceramic.}
\end{figure}

The interest in the field of FGMs is constantly growing. In 1987 Japan initiated a national project under the auspices of the Science and Technology Agency of the Japanese Government. This project, involved about 30 industrial
and academic organizations which explored the basic science and engineering of FGMs. In 1993, a second phase of this project was launched with a focus on energy conversion materials with FGM structures. Recently, MIT's Materials Processing Center, in conjunction with the Office of Naval Research, organized a workshop devoted to FGMs where researchers from the U.S., Japan, and Europe discussed the recent advances in this field.

The application of FGMs can be found wherever corrosion, wear, and heat-blocking are required such as the fuselage of a hypersonic plane which, due to aerodynamic heating, may experience temperatures of up to 1700°C. Ceramic tails, traditionally used for this purpose, tend to debond at the metal-ceramic interface as a result of thermal stress. Other applications of FGMs also may be found in biotechnology for bone implants, e.g., Ti/hydroxyapatite FGM.

The notion of FGMs is not very recent in the field of biology. For centuries the concept of transition from a ductile (low modulus) to stiff (high modulus) material has been employed in living organisms in a variety of connective tissues (i.e. ligaments or a tendon), blood vessels (i.e., aorta), bones, or dentine.

The FGM preparation methods include: various powder metallurgy (P/M) techniques, plasma spray techniques, chemical vapor deposition, self-propagating high temperature synthesis (SHS), as well as magnetron sputtering, physical vapor deposition, dynamic ion mixing, chemical vapor infiltration, and reaction bonding. Powder metallurgy processes, due to their speed, simplicity,
and economy, are employed mostly for FGMs that are composed of layers (plies) with a thickness in the order of millimeters. The powder techniques generally are divided into dry and wet processes.

An FGM is prepared by dry powder metallurgy in a number of ways. In one of these, dry powders such as Al, Si, and ZrO₂₁² or SiC, C, ZrO₂, and TiC¹³ are deposited by thermal spraying and subsequently compacted by cold isostatic pressing (CIP) prior to sintering. Another dry P/M process of FGM preparation includes sintering of a powder compact at high temperature (1500°C) and isostatic pressure (HIP) (12.5 MPa).¹⁴

In wet P/M most of the powder processes require binders. For example, injection molded Fe-Co alloy/stainless steel (SUS 304) FGM required 7.11 wt% of an organic binder (such as poly(vinyl acetate) or polyethylene) which had to be removed in vacuum at 350°C prior to sintering.¹⁵ Another process for the preparation of functionally gradient materials utilizes a suspension of metal and ceramic powders in water and is analogous to the packing of a liquid chromatography column. The gradual variation in suspension composition from metal-rich to ceramic-rich gives the gradient. In the final step, solid/liquid separation is carried out and the resulting cake is dried at 100°C in vacuum.¹⁶

Niino and coworkers³ have extensively explored the thin sheet laminating process which involves the preparation of a slurry and the subsequent use of a doctor blade technique for preparation of thin sheets. These sheets may vary in
thickness from tens of microns to about 2 mm. They then are overlayed and uniaxially pressed in a way to give the final composition gradient (Fig. 3). The green laminate preform requires a debinding (dewaxing) step prior to sintering which involves heating the green FGM to 500°C with an air pressure of 0.5 MPa.

In both wet and dry P/M, the shrinkage of the laminate layers may cause deformation in the final product. The shrinkage control of individual layers of the FGM composite is important, especially when powders of various particle sizes are used. If shrinkage is not addressed, total warpage of the FGM composite takes place. It is essential to make all the layers of the laminate shrink equally during sintering to avoid deformations of the final part. Niino and coworkers\textsuperscript{3} showed that when 0.03 μ particle size ZrO\textsubscript{2} is blended with Ni (4 μ) powder, the percent shrinkage increases with an increase in volume fraction of ZrO\textsubscript{2}; however, the reverse is the case when 15 μ particles of ZrO\textsubscript{2} are employed. It also was observed that the volume shrinkage ratio was nearly equal to the volume fraction of organic binder in the green body. Therefore, successfully controlled shrinkage requires the incorporation of a mixture of different sized ZrO\textsubscript{2} particles in conventional P/M preparation of FGMs. In general, the shrinkage of parts prepared from powders depends on powder characteristics such as size, shape, and size distribution.\textsuperscript{17}
Figure 3 Preparation of FGMs by thin sheet lamination process.⁴
In the preparation of FGMs by powder metallurgy to data only organic binders have been utilized; there is no precedent in the literature of using preceramic polymers as binders for the fabrication of FGM's. Recently, it has been shown that preceramic polymers serve excellently as binders for ceramic powders in the fabrication of shaped ceramic parts. When the part is sintered, pyrolysis of the preceramic polymer occurs with minimal evolution of gases to give a high yield of ceramic residue, which is retained in the part. Chapter 2 reports many examples of the use of preceramic polymers as binders for metal powders for the in situ fabrication of metal matrix composites (MMCs). In both cases, the utilization of a preceramic polymer does not require the debinding step and the preceramic polymer also acts as an in situ source of ceramics.

The subject of this chapter is an improved powder metallurgy technique for FGM preparation. This novel approach to the preparation of FGM materials involves the use of preceramic polymers as binders for metal/ceramic powder blends and provides shrinkage control of each individual layer. The preliminary results of this technique as applied to two thermal-expansion mismatched systems, Cu/SiC FGMs and Al/SiC FGMs, will be discussed.
Results and Discussion

Two FGM systems; Cu/SiC and Al/SiC, were prepared using ceramic precursors as binders. The Al/SiC FGM is of interest for possible aerospace application because of its light weight and high durability. The Cu/SiC FGM, on the other hand, may find its use in dynamic seal applications, as in mechanical face seals where corrosion resistance and good heat transfer ability are required.

The P/M FGM preparation process using preceramic binders is much simpler than the conventional P/M techniques (Fig. 4). The green powder preparation is similar to the one described in Chapter 2 where, in addition to metal powder and preceramic binder, a ceramic filler such as SiC is used for ceramic-rich plies. Once the powder premix has been prepared, the FGM preparation process involves a sequential formation of two dimensional powder layers of varying metal/ceramic ratios containing constant or varying amounts of preceramic polymeric binder to yield a three dimensional FGM structure as depicted in Figure 4. Each layer begins with a thin distribution of powder spread over the surface of the powder bed. A retractable punch that supports the powder bed is then lowered so that the next powder layer may be introduced (Fig. 5). This layer-by-layer process is repeated until the final ceramic/polymer layer is applied (Fig. 4). Uniaxial and isostatic pressing then follow. Finally, the heat treatment/sintering (not involving debinding) is administered.
Figure 4 The process of FGM preparation using ceramic precursors as binders. a - deposition of green powder; b - smoothing of the powder bed by counter rotating the roller; c - lowering the powder bed for the next green powder composition; d - introducing the top punch; e - uniaxial pressing; f - the final product - FGM.
Figure 5 Schema of a rectangular die used for FGM preparation.

The thickness of the FGM plies is controlled by the position of the powder bed punch. Two kinds of supports were used for the powder bed punch (Fig. 5). One support was made of a magnet permanently welded to the die which kept the ferromagnetic punch from sliding out of the die cavity (Fig. 6a). This setting is especially useful for overlaying nonmagnetic powders. The other support consisted of an adjustable jack placed under the powder bed punch (Fig. 6b).

Two types of Cu/SiC FGM have been prepared, one having a Cu powder substrate and the other having a solid 1/8" Oxygen Free Copper (OFC) grade Cu piece. In both cases, a commercially available polycarbobisilane (PCS) (the
precursor to Nicalon® fibers) was used as binder, a source of ceramic, and as sintering agent for the SiC filler²¹ (due to presence of excess carbon after the pyrolysis).
Figure 6 Rectangular dies for FGM preparation; a) powder bed punch supported with a magnet, b) powder bed punch supported with a jack.
When the Cu/SiC FGM is built up from a solid Cu metal base, the first powder layer comprises -325 mesh Cu metal powder and PCS while the last one contains the SiC and the PCS binder. The layers are compacted as shown in Figure 4. Uniaxial pressing, isostatic pressing and heat treatment then follow. The solid Cu base requires a mild surface oxidation of the Cu surface to promote sintering of the Cu/PCS powder premix. The surface oxidation was accomplished by extensive polishing of the substrate on 4000 grit SiC paper in air using water as a coolant. In both cases the pyrolysis at 900°C with a 3 h hold at that temperature in Ar was conducted under a constant uniaxial 200 g load to prevent any deformation.

Figures 7 depicts the cross-sectional area of the Cu/SiC FGM made from the Cu powder substrate and 6 other layers gradually changing in composition from Cu-rich to SiC-rich (Table 1). It appears that good adhesion was achieved between all of the layers (Fig. 7b). The first two plies after the pure Cu layer were composed of Cu powder mixed with a PCS binder in the absence SiC filler in 95:5 and 9:1 mol ratio, respectively. All subsequent plies contained SiC filler.
### Table 1  Cu/PCS/SiC Powder Mixes with Constant PCS Content

<table>
<thead>
<tr>
<th>Mix No.</th>
<th>PCS&lt;sub&gt;a&lt;/sub&gt;/SiC(&lt;1μ)/Cu mol ratio</th>
<th>Nicalon&lt;sup&gt;®&lt;/sup&gt; PCS Precursor wt%</th>
<th>SiC (&lt;1μ) wt%</th>
<th>Cu (-325 mesh) wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0:0:100</td>
<td>pure Cu powder</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>5:0:95</td>
<td>4.6</td>
<td>0</td>
<td>95.4</td>
</tr>
<tr>
<td>3</td>
<td>10:0:90</td>
<td>9.2</td>
<td>0</td>
<td>90.8</td>
</tr>
<tr>
<td>4</td>
<td>10:10:80</td>
<td>9.6</td>
<td>6.6</td>
<td>83.8</td>
</tr>
<tr>
<td>5</td>
<td>10:20:70</td>
<td>10.0</td>
<td>13.7</td>
<td>76.3</td>
</tr>
<tr>
<td>6</td>
<td>10:50:40</td>
<td>11.3</td>
<td>39.1</td>
<td>49.6</td>
</tr>
<tr>
<td>7</td>
<td>10:90:0</td>
<td>12.7</td>
<td>87.3</td>
<td>0</td>
</tr>
</tbody>
</table>

a - based on Si

**Figure 8a** shows a cross-section of solid Cu coated with SiC having an intermediate layer (single step gradient) of Cu and PCS in 9:1 mole ratio. The intermediate layer appears to be well sintered to the solid Cu plate. **Figure 8b** depicts a birds eye view of the Cu plate which has a very well bonded SiC patch (withstands attempted removal with a sharp object and a scotch tape test). Direct deposition of SiC/PCS in 9:1 mole ratio powder on solid Cu also was accomplished (Fig. 8c); however, gradientless deposition of SiC yields a much weaker coat than the one with even a single step gradient. It appears that Cu from the solid substrate partly infiltrates the SiC face creating a self-generated gradient (Fig. 8c).
Table 2 Cu/PCS/SiC Powder Mixes for the Solid Substrate

<table>
<thead>
<tr>
<th>Mix No.</th>
<th>PCS³/SiC/Cu mole ratio</th>
<th>Nicalon$^r$ PCS wt%</th>
<th>SiC (-600 mesh) wt%</th>
<th>Cu (-325 mesh) powder wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10:0:90</td>
<td>9.2</td>
<td>0</td>
<td>90.8</td>
</tr>
<tr>
<td>2</td>
<td>10:90:0</td>
<td>12.5</td>
<td><strong>85.8% SiC; 1.7% B</strong>$^{21}$</td>
<td>0</td>
</tr>
</tbody>
</table>

a - based on Si

Figure 7a SEM micrograph of a crosssectional area of Cu/SiC FGM prepared using powder substrates and SiC particle size of <1μ. The mix numbers correspond to Table 1.
Figure 7b SEM micrograph of a two ply interface from the FGM in fig. 7 a). The mix numbers correspond to Table 1.
Figure 8 SEM micrograph of a crosssectional area of Cu/SiC FGM prepared from the solid substrate and -600 mesh SiC: a) having a single step gradient; b) bird's eye view of a bulk composite in a). The mix numbers correspond to Table 2.
**Figure 8** SEM micrograph of a crossectional area of Cu/SiC FGM prepared from the solid substrate and -600 mesh SiC: c) directly deposited SiC/PCS powder onto Cu solid substrate. The mix numbers correspond to **Table 2**.

An Al/SiC FGM was prepared using Al powder, poly(methylsilane) (PMS) crosslinked with \((\text{C}_2\text{ZrH}_2)_m\) and SiC as filler (**Table 3**). Its pyrolysis in Ar at 550°C with a 2 h hold at that temperature followed (**Fig. 9a**) by pyrolysis at 1000°C with a 3 h hold yielded a composite with retained bulk structural integrity. **Figure 9b** depicts the cross-sectional area of the four laminate
composite material pyrolyzed in Ar at 1000°C. The composite appears to be strong, well-bonded between layers, and nearly fully dense at the SiC side. Several different Al/SiC symmetrical FGM composite configurations also were explored. Two sandwich geometries were made, one having pure Al on both outer faces and gradually changing in composition to SiC rich in the middle of the composite after its pyrolysis at 250°C for 1 h and 550°C for 5 h (Fig. 10a). The other sandwich was made with a SiC faces on the outside and a gradual change to Al rich domains towards the middle after its pyrolysis at 1000°C for 3 h (Fig. 10b).

### Table 3 Al/PMS/SiC Powder Mixes

| Mix No. | PMS<sup>a</sup>/SiC/Al mole ratio | PMS<sup>23</sup> wt% | SiC (<1μ) wt% | Al (-325 mash powder wt%)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0:0:100</td>
<td>pure Al powder</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>10:0:90</td>
<td>15.3</td>
<td>0</td>
<td>84.7</td>
</tr>
<tr>
<td>3</td>
<td>10:10:80</td>
<td>14.6</td>
<td>13.4</td>
<td>72.0</td>
</tr>
<tr>
<td>4</td>
<td>10:20:70</td>
<td>14.0</td>
<td>25.7</td>
<td>60.3</td>
</tr>
<tr>
<td>5</td>
<td>10:50:40</td>
<td>12.5</td>
<td>56.8</td>
<td>30.7</td>
</tr>
<tr>
<td>6</td>
<td>10:90:0</td>
<td>12.7 (PCS)</td>
<td>87.3</td>
<td>0</td>
</tr>
</tbody>
</table>

<sup>a</sup> - based on Si

406
Figure 9 Optical micrograph of a cross-sectional area of a Al/SiC FGM; a) pyrolyzed at 550°C and b) 1000°C. Mix numbers correspond to Table 3.
**Figure 10** Optical micrograph of a crosssectional area of a sandwich A/SiC FGM: a) pyrolyzed at 550°C with Al outer skins and b) pyrolyzed at 1000°C with SiC outer skins. The mix numbers correspond to **Table 3**.
It was observed that percent shrinkage of ceramic/preceramic polymer parts is nearly linearly related to weight percent of preceramic polymer (Fig. 11). The density, on the other hand, is about constant. This relationship was demonstrated by employing submicron SiC powder and Co$_2$(CO)$_8$ crosslinked$^{24}$ polycarbosilane (Nicalon$^\text{®}$ precursor) in various amounts (Fig. 11). An average density of 2.58 g/cm$^3$ was obtained.

![Shrinkage Control by Ceramic Precursors](image)

**Figure 11** Shrinkage control by ceramic precursors; % volume shrinkage vs. wt% of PCS.

Shrinkage control in FGM composites is an essential feature in their preparation process, especially when powders of different particle size are joined by a gradient
as in the case of Cu (~10 μ) and SiC (< 1 μ). It has been observed that with a constant amount of binder the highest shrinkage takes place on the Cu side and lowest on the SiC side. This shrinkage is well visible on a crossectional view of a sandwich composite (Fig. 12a). It appears that if the amount of polymeric ceramic precursor is continuously increasing from the higher shrinkage domain (Cu) to the lower shrinkage domain (SiC), the deformation due to shrinkage would be reversed. An example of such shrinkage control is portrayed by a symmetrical sandwich composite of SiC and Cu, crossectional view of which is depicted in Fig. 12b. The current shrinkage control mechanism does not require incorporating various sizes of ceramic particles as is conventionally practiced.  

### Table 4: Cu/PCS/SiC Powder Mixes with Varying PCS Content

<table>
<thead>
<tr>
<th>Mix No.</th>
<th>PCS&lt;sup&gt;a&lt;/sup&gt;/SiC (1&lt;μ)/Cu mol ratio</th>
<th>Nicalon&lt;sup&gt;b&lt;/sup&gt; PCS&lt;sup&gt;b&lt;/sup&gt; wt%</th>
<th>SiC (&lt;1μ) wt%</th>
<th>Cu (-325 mesh) powder wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0:0:100</td>
<td></td>
<td></td>
<td>pure Cu powder</td>
</tr>
<tr>
<td>2</td>
<td>8:20:72</td>
<td>7.8</td>
<td>13.7</td>
<td>78.5</td>
</tr>
<tr>
<td>3</td>
<td>14:36:50</td>
<td>15.4</td>
<td>26.9</td>
<td>57.7</td>
</tr>
<tr>
<td>4</td>
<td>19:52:29</td>
<td>22.7</td>
<td>39.6</td>
<td>37.7</td>
</tr>
<tr>
<td>5</td>
<td>24:62:14</td>
<td>29.6</td>
<td>51.9</td>
<td>18.5</td>
</tr>
<tr>
<td>6</td>
<td>31:69:0</td>
<td>40.0</td>
<td>60.0</td>
<td>0</td>
</tr>
</tbody>
</table>

*a - based on Si  
b - crosslinked with Co<sub>2</sub>(CO)<sub>8</sub><sup>24</sup>
Figure 12 Optical micrographs of cross-sectional area of Cu/SiC sandwich FGM composites. The following layers (mix numbers) were overlayed: a) 7, 6, 5, 4, 3, 1, 3, 4, 5, 6, 7 (Table 1); b) 6, 5, 4, 3, 2, 1, 2, 3, 4, 5, 6 (Table 4).
Conclusion

Polymeric ceramic precursors prove to be very effective substitutes for organic fillers in the preparation of FGMs. This novel process of FGM preparation avoids the debinding step (removal of organic binder) used in conventional wet P/M. It also introduces a means for shrinkage control by blending various amounts of a polymeric ceramic precursor into individual FGM layers. Based on the findings described in Chapter 2 shrinkage may also be controlled through incorporation of precursors which give various ceramic residue yields on pyrolysis (i.e., shrinkage is inversely proportional to ceramic residue yield), or gradually changing the nature of the polymeric binder used (i.e., a liquid binder results in less shrinkage than a solid binder). The current FGM process may further be extended to rapid prototyping applications such as 3-D printing.25
Experimental

General Comments

All green powder preparations of metal and polymeric ceramic precursors were conducted in an air-free atmosphere using standard Schlenk line and dry-box techniques. Toluene was distilled from sodium under Ar flow. Metal powders were purchased from CERAC and were handled in the dry-box at all times: Al (cat. # A-1182; lot # X14720) and Cu (cat. # C-1133; lot # X14557). SiC powders were obtained from: CERAC ((<μ); cat. # S-2022; lot # X15459) and City Chemical Corp. NY, 600 mesh.

Nicalon® polycarbosilane (PCS) was purchased from Dow Corning Co., X9-6348, lot# PG 110064. Ceramic precursors were prepared using published procedures: PCS crosslinked with Co₂(CO)₈²⁴ and PMS²³ from Chapter 1. The particle size distribution of Al, Cu, and SiC (all from CERAC) is given on Fig. 13.
Figure 13 Particle size distribution of Al, Cu, SiC powders used for FGM preparation.
Preparation of Cu/SiC FGM by Using Powder Cu Substrate.

The following powder mixes were prepared:

**Table 5 (constant amount of polymeric precursor)**

<table>
<thead>
<tr>
<th>Mix No.</th>
<th>PCS&lt;sup&gt;3&lt;/sup&gt;/SiC(&lt;μ)/Cu mol ratio</th>
<th>Nicalon® PCS Precursor wt (g)</th>
<th>SiC (&lt;1μ) weight (g)</th>
<th>Cu (-325 mesh) weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0:0:100</td>
<td>pure Cu powder</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>5:0:95</td>
<td>0.96</td>
<td>0</td>
<td>20.00</td>
</tr>
<tr>
<td>3</td>
<td>10:0:90</td>
<td>2.03</td>
<td>0</td>
<td>20.00</td>
</tr>
<tr>
<td>4</td>
<td>10:10:80</td>
<td>1.00</td>
<td>0.69</td>
<td>8.76</td>
</tr>
<tr>
<td>5</td>
<td>10:20:70</td>
<td>1.00</td>
<td>1.38</td>
<td>7.66</td>
</tr>
<tr>
<td>6</td>
<td>10:50:40</td>
<td>1.50</td>
<td>5.20</td>
<td>6.60</td>
</tr>
<tr>
<td>7</td>
<td>10:90:0</td>
<td>0.87</td>
<td>6.00</td>
<td>0</td>
</tr>
</tbody>
</table>

a - based on Si

**Table 6 (gradual increase of polymeric precursor from Cu to SiC)**

<table>
<thead>
<tr>
<th>Mix No.</th>
<th>PCS&lt;sup&gt;3&lt;/sup&gt;/SiC (1&lt;μ)/Cu mol ratio</th>
<th>Nicalon® PCS&lt;sup&gt;b&lt;/sup&gt; weight (g)</th>
<th>SiC (&lt;1μ) weight (g)</th>
<th>Cu (-325 mesh) weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0:0:100</td>
<td>pure Cu powder</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>8:20:72</td>
<td>0.08</td>
<td>0.14</td>
<td>0.80</td>
</tr>
<tr>
<td>3</td>
<td>14:36:50</td>
<td>0.16</td>
<td>0.28</td>
<td>0.60</td>
</tr>
<tr>
<td>4</td>
<td>19:52:29</td>
<td>0.24</td>
<td>0.42</td>
<td>0.40</td>
</tr>
<tr>
<td>5</td>
<td>24:62:14</td>
<td>0.32</td>
<td>0.56</td>
<td>0.20</td>
</tr>
<tr>
<td>6</td>
<td>31:69:0</td>
<td>0.40</td>
<td>0.60</td>
<td>0</td>
</tr>
</tbody>
</table>

a - based on Si
b - crosslinked with Co<sub>2</sub>(CO)<sub>8</sub>
The dry mixes were suspended in toluene and ultrasonic activation was used to maintain dispersion and the cleanliness of the surface of metal powder. After overnight sonication, the solvent was removed in vacuum. The resulting powder was dried, pulverized in a mortar and pestle and passed through the 270 mesh sieve to assure a uniform particle size distribution. The powders then were compacted in a manner shown on Fig. 4. The layers were compressed uniaxially in a die at 13.5 kpsi for 1 h. The green FGM compact was ejected from the die and isostatically pressed at 40 kpsi for 10 min and subsequently was fired in the furnace in argon at a rate of 5°C/min. to 250°C with a 2 h hold and 5°C/min. to, 900°C with a 3 h hold at that temperature. The entire pyrolysis was conducted under a uniaxial load of 200 g.

Preparation of Cu/SiC FGM by Using a Solid Cu Substrate.

The following powder mixes were prepared:

**Table 7**

<table>
<thead>
<tr>
<th>Mix No.</th>
<th>PCS³/SiC/Cu mole ratio</th>
<th>Nicalon® PCS weight (g)</th>
<th>SiC(-600 mesh) weight (g)</th>
<th>Cu (-325 mesh) weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10:0:90</td>
<td>2.03</td>
<td>0</td>
<td>20.0</td>
</tr>
<tr>
<td>2</td>
<td>10:90:0</td>
<td>0.87</td>
<td>6.0 SiC; 0.12 B²¹</td>
<td>0</td>
</tr>
</tbody>
</table>

a - based on Si

416
The mixes were prepared as described in the first experiment. The powders were deposited (in sequence: No.1, No. 2) on a solid (OFC) Cu plate (1.25 x 3.78 x 0.15 cm), the surface of which previously had been oxidized by extensive (15 min) polishing of the substrate on 4000 grit SiC paper in air using water as a coolant. The pressing and pyrolysis were conducted as described in the first experiment.

**Preparation of Al/SiC FGM by Using a Powder Al Substrate.**

The following powder mixes were prepared:

**Table 8**

<table>
<thead>
<tr>
<th>Mix No.</th>
<th>PMS(^a)/SiC/Al mole ratio</th>
<th>PMS(^{23}) weight (g)</th>
<th>SiC (&lt;1(\mu)) weight (g)</th>
<th>Al (-325 mesh) powder weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0:0:100</td>
<td>1.10</td>
<td>0</td>
<td>pure Al powder</td>
</tr>
<tr>
<td>2</td>
<td>10:0:90</td>
<td>0.92</td>
<td>0.84</td>
<td>4.52</td>
</tr>
<tr>
<td>3</td>
<td>10:10:80</td>
<td>0.71</td>
<td>1.30</td>
<td>3.05</td>
</tr>
<tr>
<td>4</td>
<td>10:20:70</td>
<td>0.50</td>
<td>2.28</td>
<td>1.23</td>
</tr>
<tr>
<td>5</td>
<td>10:50:40</td>
<td>0.87 (PCS)</td>
<td>6.0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>10:90:0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) - based on Si

The preparation and compaction of mixes were performed as described in the first experiment. The pyrolysis was effected at 5\(^\circ\)C/min. with a 2 h hold at 250\(^\circ\)C, further pyrolysis at 5\(^\circ\)C/min. with a 3 h hold at 550\(^\circ\)C. The final pyrolysis took place at 1000\(^\circ\)C for 3 h, at which temperature no outward signs of melting
were observed.

**Shrinkage Experiment Using Crosslinked PCS Precursor and SiC filler.**

Blends of PCS crosslinked with 1.0 mol% Co$_2$(CO)$_8$ as depicted in Table 9. The powders were suspended in toluene and ultrasonicated overnight. After removal of volatiles, the powders were pulverized in a mortar and pestle and uniaxially compacted at 90 kpsi for 1 h and isostatically at 40 kpsi for 10 min. Green bodies were pyrolyzed at 5°C/min to 250°C with a 2 h hold and further at the same rate to 1500°C with a 3 h hold at that temperature. The volumes and weights of the compacts before and after the pyrolysis are given in Table 9.

Table 9

<table>
<thead>
<tr>
<th>Mix No.</th>
<th>PCS/SiC wt ratio</th>
<th>PCS weight (g)</th>
<th>SiC weight (g)</th>
<th>Green body weight (g) volume$^a$ (cm$^3$)</th>
<th>Ceramic body weight (g) volume$^b$ (cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>2.86</td>
<td>2.86 (g) 1.00 (cc)</td>
<td>2.81 (g) 1.00 (cc)</td>
</tr>
<tr>
<td>2</td>
<td>2:8</td>
<td>0.4</td>
<td>1.6</td>
<td>1.8415 (g) 0.83 (cc)</td>
<td>1.7235 (g) 0.60 (cc)</td>
</tr>
<tr>
<td>3</td>
<td>4:6</td>
<td>0.8</td>
<td>1.2</td>
<td>1.6590 (g) 0.91 (cc)</td>
<td>1.4606 (g) 0.60 (cc)</td>
</tr>
<tr>
<td>4</td>
<td>6:4</td>
<td>1.2</td>
<td>0.8</td>
<td>1.4064 (g) 0.94 (cc)</td>
<td>1.1785 (g) 0.50 (cc)</td>
</tr>
<tr>
<td>5</td>
<td>10:0</td>
<td>1.1</td>
<td>0</td>
<td>1.1000 (g) 1.04 (cc)</td>
<td>0.8565 (g) 0.35 (cc)</td>
</tr>
</tbody>
</table>

$^a$ - volume measured with a calliper  
$^b$ - Archimedes volume, measured by displacement of isopropanol  
% shrinkage = (green volume - final volume)/(green volume)
References


d) "The Application of Combustion Synthesis in the In-Situ Production of Functionally-Graded Materials (FGM)," Feng, H. J.; Moore, J. J. In-Situ
Composites, Singh, M., ed. (TMS, 1993).


Acknowledgement

There is a whole army of people whom I would like to acknowledge for making this thesis a reality. First and foremost, I would like to extend my deepest gratitude to Professor Dietmar Seyferth for the opportunity to work in his group. I would like to thank him for his enthusiastic support and for giving me the flexibility and independence to explore the uniqueness of the fascinating preceramic poly(methylsilane) system. I am also indebted to: Dr. Wendell E. Rhine for his helpful advice and useful discussions, as well as for proofreading part of this thesis, Dr. Chaitanya K. Narula for collaboration on the PBA MMCs and TiN thin films and very helpful tips and coaching for job interviews. CKN, I still don't know how you could accomplish so much without a visual catalysis (perhaps your constant newspaper reading had something to do with it). A great thanks should also go to Professor Hee-Gweon Woo (the "Sea King") for his guidance in the field of polysilanes and showing me the application of various NMR techniques. My unlimited gratitude goes to Mr. Toshiya Sugimoto (スキ モ ト トシヤ) the Nippon no Kagakusha of Sekisui Chemical Co., Ltd. for his devoted help with the photochlorination reactions as well as for the synthesis of TS-1 poly(methylsilane) (the Sugimoto polymer). Toshiya, I don't know how you could have done such a superb job and hard hataraki (work) after all the parties you went to! I guess the idea of "low tech high end" really works. I would like to recognize Dr. Michael Leise and Mr. Shane W. Kraska for their help with
the MMC project and especially SWK for his persistence at polishing these PSZ cermets, I hope all your fingers grew back properly. I would also like to thank SWK for being my labmate and putting up with me, for helpful discussions, and for doing dishes! My great appreciation also goes to Dr. David Son for his collaboration on the WC project, and to Dr. James P. Gardener and Dr. T. Craig Masterman for their unforgettable help and encouragement with my oral exam. Other Seyferth group members should also be recognized: Christine A. Sobon, Jennifer L. Robison, David Workman, David Lindquist, Lea A. Anderson, Lars Wesemann, Nathan Bryson, Pierre Naudin (great French parties), Fernando Villafañe, and Bruno Boury, Tao Wang, Frank Richter, and Manfred Döring, Ralf Wyrwa, Tsuyoshi Kugita, and Judy Little and Terry King.

The MIT library staff and especially John Mess (the traffic officer for the chemical information superhighway) and William A. Mayer for his speedy interlibrary services, all deserve my special thanks. In addition, I received help from the MIT's Center for Materials Science and Engineering (CMSE) metallography lab staff: Pat Kearney and Yin Lin Xie (the lady of perpetual help); the MIT's Ceramics Processing Research Lab (CPRL) support staff: John A. Centorino and Lenny Rigione need to be recognized for their help with isopressing and SEM as well as their advice on powder processing. Bob Di Giacomo must be acknowledged for all the rush and unusual glass blowing jobs he performed over the years, Dr. Mary Chen for her help with four-point-bending tests and Dr.
Richard Pober for letting me use his 4-pt. bending jig. Great thanks also goes to the entire Spec Lab staff: Jim Simms, Jeanne Owens, Debbie Western, and Ed Takach, and the Chemistry Department machine shop staff: Johnny Annese (great Christmas parties), Murray Somerville, Tony Cieri, Ed Udas, as well as the CMSE X-ray diffraction facility especially Joe A. Adario and Peter Klouman.

The Center for Advanced Materials of University of Massachusetts at Lowell should be acknowledged for the TEM analysis of various MMC and cermet composites. In particular, I would like to thank Prof. Changmo Sung, Mr. Ju-Hwan Choi, Dr. H. Fred Chen, and Dr. Kyeongsoon Park, for their hard work in preparing and analyzing TEM samples of Al/PMS and Ti/PMS composites.

I would also like to acknowledge my mentors in my undergraduate years: Prof. Emeritus. Hassan S. El Khadem, Dr. Horace S. Isbell, and Dr. Milton Harris for teaching me the research-mentship; and Dr. Robert S. Roth and Dr. Joseph Ritter of NIST who initiated my interest in the field of ceramic precursors.

Finally, I would like to greatly acknowledge my parents for their love and understanding and Ken and Fran Valentine for their love and support. My lovely wife Danuta deserves much credit for her great moral support and for being with me every step of the way in this endeavor.
Biographical Sketch

The author was born in Warsaw, Poland, on March 27, 1967 to Nonna and Włodzimierz Czubarow. After completing his elementary education, Paweł entered Liceum Jana Zanoyskiego in Warsaw. During this time he was a member of "Gibbon" theater ensemble and also participated in the Polish-Bulgarian movie production, based on W. Łoziński's story "Oko proroka" and directed by P. Komorowski. At the age of 17, he arrived in Washington, DC, where he stayed for the next 6 years. In Washington he graduated from Woodrow Wilson Senior High School and entered the undergraduate chemistry program at The American University. While at A.U., he conducted research in carbohydrate chemistry under the direction of Prof. Hassan S. El Khadem and Dr. Horace S. Isbell, as well as research at NIST (NBS) in the field of solid state chemistry under the supervision of Dr. Robert S. Roth and Dr. Joseph Ritter. In May 1990, he received a B.S. degree in chemistry and B.A. degree in physics, magna cum laude from A.U. In the summer of 1990, he entered the Ph.D. program at the Department of Chemistry at MIT and joined the research group of Prof. Dietmar Seyferth. In the first year at MIT, he completed the core curriculum of the Polymer Science and Technology Program as a Dow Chemical fellow and later continued the investigations on poly(methylsilane). In 1995, he will join Raychem Corporation as a staff scientist.