

**SYNTHESIS AND CHARACTERIZATION OF NITRILE CONTAINING
POLYSILOXANES AND THEIR CORRESPONDING NETWORKS AS
AIRCRAFT SEALANT MATERIALS**

by

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SYNTHESIS AND CHARACTERIZATION OF NITRILE CONTAINING POLYSILOXANES AND THEIR CORRESPONDING NETWORKS AS AIRCRAFT SEALANT MATERIALS

Jennifer K. Hoyt

Abstract

Polysiloxane networks have excellent oxidative and good UV environmental stability, flexibility at low temperatures, and thermal stability at higher temperatures. This wide service temperature range makes these materials a candidate class of materials for high performance adhesives and sealants, and in particular for applications on high speed aircraft. Polar polysiloxane networks were prepared with cyanopropyl substituents to lower any propensity for the materials to swell in hydrocarbon fuels and to improve adhesion to metal substrates. 1,3,5,7-tetramethyl,1,3,5,7-tetrahydrocyclotetrasiloxane (D₄H) was hydrosilated with allyl cyanide to yield the corresponding 3-cyanopropylmethylcyclotetrasiloxane monomer (D₄CN). Controlled molecular weight oligomers with vinyl termination were prepared in equilibrium reactions using a basic catalyst. These oligomers were then crosslinked with various hydride functional crosslinking reagents to yield model networks for mechanical and adhesion studies. The network properties of nonpolar polydimethylsiloxane (PDMS), polar poly[methyl(3,3,3-trifluoropropyl)siloxane] (PMTFPS), and the novel polar poly(3-cyanopropylmethylsiloxane) (PCPMS) were investigated as a function of sidechain chemical structures. Effects of increasing crosslink density were investigated for the PDMS networks by adding a difunctional siloxane dimer with vinyl groups. Moduli and tensile strengths increased while percent elongation decreased as the crosslink density was increased. All networks were thermally stable above 300°C in both air and N₂ (when heated at a rate of 10°C/min.) and exhibited T_gs lower than -55°C. The polar networks swelled to a much lesser extent (at least one order of magnitude) than the nonpolar networks in hydrocarbons and Jet fuel. Cohesive failure was observed for the polar networks via metal to metal (Al foil substrate to Al and Ti adherends) 180° peel test. The PCPMS elastomers had average load values twice those of the PDMS networks independent of crosslink density.

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DEDICATION

Most of all, my sincere gratitude goes out to my friends and family whose love and support have helped me to succeed and be as happy as I am today.

To my love and best friend, Chris, who made me believe that everything would work out, and who is the source of my present and eternal happiness; & of course N. P.

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ABBREVIATIONS

D ₃	1,1,3,3,5,5-hexamethylcyclotrisiloxane or hexamethylcyclotrisiloxane
D ₄	1,1,3,3,5,5,7,7-octamethylcyclotetrasiloxane or octamethylcyclotetrasiloxane
D ₅	1,1,3,3,5,5,7,7,9,9-decamethylcyclopentasiloxane or decamethylcyclopentasiloxane
D ₃ CN	1,3,5-tris(3-cyanopropyl)-1,3,5-trimethylcyclotrisiloxane or 3-cyanopropylmethylcyclotrisiloxane
D ₄ CN	1,3,5,7-tetrakis(3-cyanopropyl)-1,3,5,7-tetramethylcyclotetrasiloxane or 3-cyanopropylmethylcyclotetrasiloxane
D _x CN	cyclic poly(3-cyanopropylmethylcyclosiloxane)s
D ₄ H	1,3,5,7-tetrahydro-1,3,5,7-tetramethylcyclotetrasiloxane or hydromethylcyclotetrasiloxane
D ₄ (CN) ₂ H ₂	1,3,5,7-tetramethyl-1,3-dihydro-5,7-di(3-cyanopropyl)-cyclotetrasiloxane
D ₄ CNH ₃	1,3,5,7-tetramethyl-1,3,5-trihydro-7-(3-cyanopropyl)-cyclotetrasiloxane
DSC	differential scanning calorimetry
FTIR	Fourier Transform Infrared Spectroscopy
GPC	gel permeation chromatography
NMR	nuclear magnetic resonance
PDMS	polydimethylsiloxane
PCPMS	poly(3-cyanopropylmethylsiloxane)
PMTFPS	poly[methyl(3,3,3-trifluoropropyl)siloxane]
TMAH	tetramethylammonium hydroxide

TABLE OF CONTENTS

Chapter 1:	Introduction.....	1
Chapter 2:	Literature Review.....	5
	2.1 Introduction to Organosiloxanes and Their Applications.....	5
	2.1.1 The Siloxane Bond and its Effect on Organosiloxanes.....	12
	2.1.2 Synthesis of Organochlorosilanes.....	17
	2.1.3 Cyclic and Linear Polyorganosiloxane Precursors.....	22
	2.1.4 Anionic Ring Opening Equilibration.....	23
	2.1.5 Hydrosilation of Vinyl Terminated Polyorganosiloxanes.....	33
	2.2 PDMS Network and Sealant Studies.....	38
	2.2.1 Tensile and Thermal Studies.....	39
	2.2.2 Swelling Resistance of Siloxanes and PMTFPS.....	47
	2.2.3 Adhesion Studies.....	53
	2.3 Introduction to Integral Fuel Tank and Aerospace Sealants.....	60
	2.4 Introduction to Nitrile Containing Organosiloxanes and PCPMS.....	64
Chapter 3:	Experimental.....	67
	3.1 Reagents and Purification Procedures.....	67
	3.2 Synthesis of Siloxane Oligomers and Cyclics.....	68
	3.2.1 Synthesis of Tetramethylammonium Disiloxanolate Catalyst.....	68
	3.2.2 Synthesis of Polydimethylsiloxane (PDMS).....	68
	3.2.3 Synthesis of 3-Cyanopropylmethylcyclotetrasiloxane (D ₄ CN).....	72
	3.2.4 Synthesis of D ₄ CNH ₃ and D ₄ (CN) ₂ H ₂ Cyclics.....	74
	3.2.5 Synthesis of Divinyl Terminated Poly(3-cyanopropyl- methylsiloxane) (DV-PCPMS).....	74
	3.2.6 Synthesis of Hexavinyl Terminated Poly(3-cyanopropyl- methylsiloxane) (HV-PCPMS).....	76
	3.3 Preparation of Networks.....	78
	3.3.1 Hydrosilation Curing to Form PDMS Networks.....	78
	3.3.2 PDMS Networks with Varying Crosslink Density.....	82
	3.3.3 Hydrosilation Curing to Form PMTFPS Networks.....	82
	3.3.4 Hydrosilation Curing to Form DV-PCPMS Networks.....	87
	3.3.5 Hydrosilation Curing to Form HV-PCPMS Networks.....	87
	3.4 Characterization Methods for Monitoring Reactions and Purity of Reagents.....	90
	3.4.1 Gel Permeation Chromatography.....	90
	3.4.2 Fourier Transform Infrared Spectroscopy.....	90
	3.4.3 ¹ H, ¹³ C, ²⁹ Si Nuclear Magnetic Resonance Spectroscopy.....	91
	3.5 Characterization of Polymers and Networks.....	91
	3.5.1 Tensile Properties:%Elongation, Strength,and Modulus.....	91
	3.5.2 Thermal Properties.....	93
	3.5.2.1 Thermogravimetric Analysis.....	93

	3.5.2.2 Differential Scanning Calorimetry.....	93
	3.5.3 Network Solvent Resistance.....	93
	3.5.4 Adhesion Analysis: 180° Peel Test.....	94
Chapter 4	Results and Discussion.....	98
	4.1 Synthetic Plan and Overview of Organosiloxanes and Their Corresponding Networks with Sidechain Chemical Structures of Varying Polarity.....	98
	4.2 Synthesis and Characterization of Novel Polar Nitrile Containing Cyclics and Polyorganosiloxanes.....	100
	4.2.1 D ₄ CN via Hydrosilation of D ₄ H.....	100
	4.2.2 D ₄ CN Monitored via FTIR.....	101
	4.2.3 D ₄ CNH ₃ and D ₄ (CN) ₂ H ₂ via Modification of D ₄ H.....	101
	4.2.4 D ₄ (CN) _x H _x Monitored and Characterized via ¹ H NMR..	103
	4.2.5 Equilibration of DV-PCPMS and HV-PCPMS.....	106
	4.2.6 PCPMS Molecular Weight Control & Characterization..	109
	4.3 Preparation and Characterization of the Nonpolar, Control Polyorganosiloxane PDMS.....	115
	4.3.1 Equilibration of PDMS.....	115
	4.3.2 PDMS Molecular Weight Control and Characterization..	117
	4.4 Preparation and Characterization of Networks.....	121
	4.4.1 Polar, Novel DV-PCPMS and HV-PCPMS Networks...	121
	4.4.2 PMTFPS Networks.....	124
	4.4.3 Nonpolar, Control PDMS Networks.....	124
	4.4.4 PDMS with Varied Weight % Hard Segment.....	125
	4.4.5 Monitoring Hydrosilation Cures via FTIR.....	126
	4.5 Network Properties.....	126
	4.5.1 Tensile Properties.....	128
	4.5.1.1 Tensile Strength.....	129
	4.5.1.2 Modulus.....	131
	4.5.1.3 Percent Elongation.....	131
	4.5.1.4 Tensile Properties for PDMS with Varied Hard Segment Contents.....	134
	4.5.2 Thermal Properties.....	134
	4.5.2.1 Thermogravimetric Analysis.....	136
	4.5.2.2 Differential Scanning Calorimetry.....	139
	4.5.3 Swelling Properties.....	141
	4.5.4 Adhesive Properties.....	144
Chapter 5	Conclusions.....	148
	5.1 Polymer and Network Synthesis Conclusions.....	148
	5.2 Comparative Network Overview.....	149
Chapter 6	Recommendations for Further Work.....	151

LIST OF FIGURES

1.1	Network series of increasing polarity.....	3
2.1	Mechanisms for acid and base catalysed condensation reactions.....	24
2.2	Mechanism for the anionic ring-opening polymerization of a cyclic siloxane trimer.....	26
2.3	Mechanism for the anionic ring-opening polymerization of a cyclic siloxane tetramer.....	30
2.4	Proposed mechanism for a catalytic cycle for Platinum catalysed hydrosilation..	36
3.1	Apparatus diagram for preparing tetramethylammonium siloxanolate catalyst....	69
3.2	Mechanism for synthesis of tetramethylammonium siloxanolate catalyst.....	70
3.3	Mechanism for equilibration of PDMS.....	71
3.4	Synthesis of D ₄ CN cyclics via hydrosilation.....	73
3.5	Synthesis of D ₄ CNH ₃ and D ₄ (CN) ₂ H ₂ cyclics via hydrosilation.....	75
3.6	Equilibration of DV-PCPMS.....	77
3.7	Equilibration of HV-PCPMS.....	79
3.8	Hydrosilation of DV-PDMS.....	81
3.9	Hydrosilation of DV-PDMS with varied weight % hard segment.....	83
3.10	Hydrosilation of DV-PMTFPS.....	86
3.11	Hydrosilation of DV-PCPMS.....	88
3.12	Hydrosilation of HV-PCPMS.....	89
3.13	Picture of sample in Minimat during tensile test and example of data obtained..	92
3.14	Picture of drawdown preparation for 180° adhesive peel test.....	95
3.15	Picture of adherends bonded to substrates for 180° peel test.....	96
3.16	Picture of sample in Instron during 180° peel test & example of data obtained..	97
4.1	Synthesis of D ₄ CN monitored via FTIR.....	102
4.2	¹ H NMR for monitoring the modification of D ₄ H.....	104
4.3	¹ H NMR for D ₄ CNH ₃ after distillations.....	105
4.4	¹ H NMR for D ₄ (CN) ₂ H ₂ after distillations.....	107
4.5	GPC of a 35,200 g/mole PCPMS at equilibrium.....	110
4.6	¹ H NMR for 25,200 g/mole HV-PCPMS.....	112
4.6 B	¹³ C NMR for 35,000 g/mole HV-PCPMS.....	113

4.6 C	^{29}Si NMR for 35,000 g/mole HV-PCPMS.....	114
4.7	GPC of PDMS at equilibrium.....	118
4.8	^1H NMR of 1900 g/mole PDMS.....	120
4.9	FTIR spectral series depicting the progression of a network formation reaction using an 8850 g/mole HV-PCPMS crosslinked with $\text{D}_4(\text{CN})_2\text{H}_2$	127

LIST OF TABLES

1.1	Series of polymers with tailored repeat units.....	4
2.1	Structural units of the polyorganosiloxanes.....	6
2.2	Major discoveries in the silicone project before 1950 ⁷	10
2.3	Silicone applications ⁷	13
2.4	Interatomic distances and valence angles of siloxane and related bonds ^(1,2,11)	18
2.5	Bond strengths of siloxanes and related bonds ¹	19
2.6	Considerations required for choosing a good sealant.....	40
2.7	Summary of sealant properties for silicones.....	41
2.8	Characteristic thermal aging properties of an extremely high-temperature RTV siloxane sealant ⁸⁹	43
2.9	Improvements of tensile properties of siloxane sealants since the 1950's.....	45
2.10	Swelling data for PDMS rubber relative to those of other common organic rubbers ⁵	50
2.11	Swelling data for a PMTFPS network ¹¹⁷	52
2.12	180° peel strength of silicone PSA on various substrates ⁸⁹	57
2.13	Effect of temperature on 180° peel strength.....	58
2.14	Physical properties of integral fuel tank sealants.....	62
3.1	Varied weight % hard segments for PDMS networks.....	84
3.2	Calculations for varied weight % hard segments for PDMS.....	85
4.1	Series of polymers with tailored repeat units and corresponding weight % hard segments.....	122
4.2	Tensile strength at break (MPa) data for networks.....	130
4.3	Moduli (MPa) data for networks.....	132
4.4	Percent elongation (%) data for networks.....	133
4.5	Tensile properties for 5K PDMS with varied weight % hard segments.....	135
4.6	Thermogravimetric analysis data for networks in N ₂	137
4.7	Thermogravimetric analysis data for networks in N ₂ and air.....	138
4.8	Differential scanning calorimetric data(2nd heat scans) for networks in N ₂	140
4.9	Network solvent resistance.....	143
4.10	Networks' adhesion to metal adherends (Ti, Al).....	146

Chapter 1

INTRODUCTION

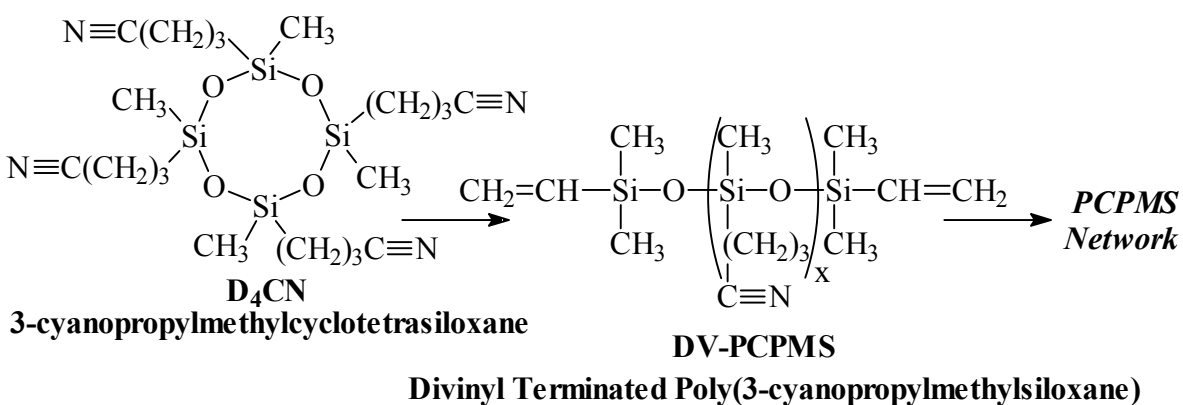
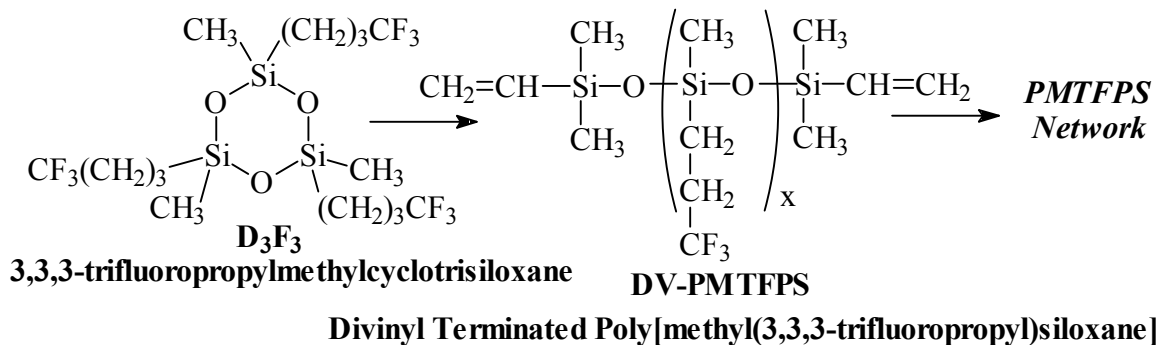
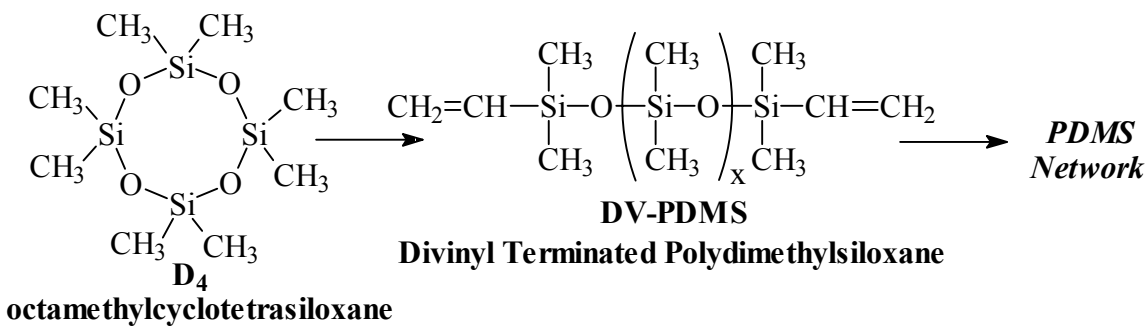
Polysiloxane networks have excellent oxidative stability, flexibility at low temperatures, and thermal stability at higher temperatures.¹ This allows for good UV environmental stability and a wide temperature use range making these materials candidate precursors for aircraft sealants and adhesives. To obtain maximum fuel capacity, internal cavities in the wings and various parts of the aircraft typically too small or geometrically complex for fitting bladder cells are used for fuel tanks. Elastomeric sealants are applied to all discontinuous surfaces of the fuel tanks. Aircraft integral fuel tank sealants also require excellent chemical/fuel resistance and adhesion to metal substrates. While nonpolar polydimethylsiloxane (PDMS) networks have been extensively studied, and poly[methyl(3,3,3-trifluoropropyl)siloxane] (PMTFPS) networks represent the current area of study for polar organosiloxane sealants in industry; more polar poly(3-cyanopropylmethylsiloxane) (PCPMS) networks are described herein and their mechanical and adhesive properties are compared to those of PDMS and PMTFPS networks.

Polar polysiloxane thermosets with cyanopropyl substituents were prepared to lower any propensity for the networks to swell in hydrocarbon fuels, and to improve adhesion to metal substrates. 1,3,5,7-tetramethyl-1,3,5,7-tetrahydrocyclotetrasiloxane monomer (D₄H) was hydrosilated with allyl cyanide in toluene using a platinum catalyst complexed with divinyltetramethyldisiloxane (Karstedt's catalyst) to give the corresponding 3-cyanopropylmethylcyclotetrasiloxane monomer (D₄CN). Controlled molecular weight vinyl terminated polymers were prepared in equilibration reactions using a lithium siloxanolate catalyst, and then crosslinked with novel, polar trihydride and dihydride functional respective crosslinking reagents [1,3,5,7-tetramethyl-1,3,5-trihydro,7-cyanopropyl-cyclotetrasiloxane (D₄CNH₃) and 1,3,5,7-tetramethyl-1,3-dihydro,5,7-cyanopropyl-cyclotetrasiloxane (D₄(CN)₂H₂)] to yield model networks for mechanical and adhesion studies.

Organosiloxane networks with sidechains of varying polarity: nonpolar polydimethylsiloxane (PDMS), moderately polar poly[methyl(3,3,3-trifluoropropyl)siloxane] (PMTFPS), and polar poly(3-cyanopropylmethylsiloxane) (PCPMS), were prepared (Figure 1.1). Divinyl terminated polydimethylsiloxane (with an average number of 25, 62, and 235 repeat units), and both divinyl and hexavinyl terminated poly(3-cyanopropylmethylsiloxane) (with an average number of 61, 77, and 298, and 68, 197, and 275 repeat units, respectively) have been synthesized and freed of their remaining cyclics. Divinyl terminated poly[methyl(3,3,3-trifluoropropyl)siloxanes] (with 26 and 261 repeat units) were obtained from the Dow Corning Corp. (Table 1.1). All polymers were hydrosilated at 90°C with Karstedt's catalyst and stoichiometric amounts of hydride functional crosslinking reagents (two-component addition cure) and fully characterized. A 5000 g/mole PDMS oligomer was also incorporated with varied amounts of added 1,3-divinyltetramethyldisiloxane to study the effects of increasing crosslink density. Tensile and thermal properties, solvent resistance, and adhesive properties (180° peel) were investigated.

Figure 1.1

Network Series of Increasing Polarity



Increasing
Polarity

Table 1.1
Series of Polymers with Tailored Repeat Units

Polymer	# of Repeat Units	M _n (g/mole) via ¹ H NMR	Target M _n (g/mole)
2K PDMS	25	1900	1700
5K PDMS	62	4700	4250
17K PDMS	235	17,500	17,200
4K PMTFPS	26	4200	NA
40K PMTFPS	261	41,050	NA
8K DV-PCPMS	61	7900	5000
10K DV-PCPMS	77	10,000	10,000
38K DV-PCPMS	298	38,000	33,260
9K HV-PCPMS	68	8850	5000
25K HV-PCPMS	197	25,200	17,300
35K HV-PCPMS	275	35,200 (too many extractions)	17,300

Chapter 2

Literature Review

2.1 Introduction to Organosiloxanes and Their Applications

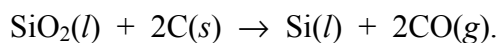
The terms siloxane, silicone, and organosiloxane are often used inconsistently; although they are used with the same intentions to describe compounds containing the siloxane bond. Silicones represent either monomeric or polymeric organosilicon compounds containing Si-C bonds and/or Si-O-Si bonds. The term “silicone” is generally associated with technical, polymeric products, while “siloxane” is generally more useful for scientific nomenclature. A silicon atom in an organosiloxane may be bonded to one (trifunctional T), two (difunctional D), three (monofunctional M), or no (quadrifunctional Q) organic groups, while the remaining valences are filled by oxygens. A nonfunctional organosilicon compound is formed when all four silicon valences are occupied by organic groups, e.g. R_4Si . Table 2.1 depicts how the functionality (and terminology) of the siloxane units are commonly described. Organosiloxane units are represented by n values of 1 to 3, while the oxygen atom serves as a link between two silicon atoms, where the general formula for the series is $R_nSiO_{(4-n)/2}$ (Table 2.1). Interesting properties of organosiloxanes arise from their dual intermediate nature between inorganic (silicates) and organic (organic polymers) compounds.¹

More than 90% of the earth's crust is comprised of silica and silicates which are the inorganic silicon compounds containing the siloxane bond. These have made a major impact on both human life and nature.² Although silicon is the second most abundant element in the earth's crust and silica is forty times more abundant than carbon, its concentration in living organisms is about 800 times less than carbon due to its size. The silicon atom, being about twice the size of a carbon atom, forms only single bonds which are longer and weaker than most carbon bonds.³ Silicon atoms form single bonds with oxygen rather than double bonds, allowing them to build up crystalline silicates or polymerize into stable endproducts, while carbon compounds degrade with oxygen to form monomeric double bonds with oxygen to the gaseous carbon dioxide.¹

Table 2.1Structural Units of the Polyorganosiloxanes¹

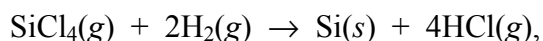
Structural Formula	Composition	Functionality	Symbol
$\text{R}_3\text{Si-O-}$	$\text{R}_3\text{SiO}_{1/2}$	monofunctional	M
$\begin{array}{c} \text{R} \\ \\ \text{---O---Si---O---} \\ \\ \text{R} \end{array}$	$\text{R}_2\text{SiO}_{2/2}$	difunctional	D
$\begin{array}{c} \text{R} \\ \\ \text{---O---Si---O---} \\ \\ \text{O} \\ \end{array}$	$\text{RsiO}_{3/2}$	trifunctional	T
$\begin{array}{c} \\ \text{O} \\ \\ \text{---O---Si---O---} \\ \\ \text{O} \\ \end{array}$	$\text{SiO}_{4/2}$	tetrafunctional or quadri-functional	Q

Siloxanes do not occur in nature, rather they are synthetically produced from silicon and a variety of other silicate minerals. Silicon is isolated by the reduction of molten silicon dioxide with carbon at high temperature:



Natural silicates served man for thousands of years as hydraulic cements, glasses, and ceramic products.¹ One of the more familiar products of silica is silica glass or quartz glass which is formed by melting silica at $\sim 1600^\circ\text{C}$. Many Si-O bonds are broken in the melt, and then reformed after quenching in an ordered fashion to an amorphous solid glass. Another common example of a silicate was a popular thermal insulation material until the last decade known as asbestos. This is a general term applied to a group of fibrous silicate minerals. It served well in high temperature applications where the excellent chemical stability of the silicate was required until the last decade when it was discovered that tiny asbestos fibers readily penetrate the lungs and digestive tracts of humans.

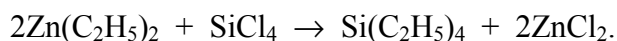
Elemental, crystalline silicon, a semiconductor, is a gray metallic-looking solid with a melting point of 1410°C . It is used for the production of electronic devices, transistors, and solar cells (when extremely pure). To purify the $\text{Si}(l)$, it is treated with Cl_2 to give SiCl_4 , a volatile liquid, which is then purified by fractional distillation and reduced to elemental $\text{Si}(s)$ by H_2 :



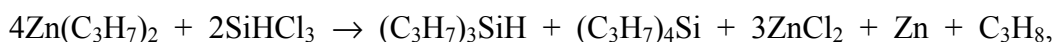
and even further purified by zone refining.⁴

Once silicon has been isolated, it may be converted into methylchlorosilanes, which are then used to synthesize various organosiloxanes and polyorganosiloxanes (as discussed in section 2.1.2). The resultant organosilicon products have viscosities ranging from water thin through heavy oil-like fluids to greases, gels, rubbers, and solid resins, depending on the length of the siloxane backbone, $(-\text{O}-\text{Si}-\text{O})_n$, and the type of organic substituents which fill the remaining valences of the silicon atoms beyond the attached oxygen atoms.⁵ Properties of polyorganosiloxanes and their corresponding crosslinked networks depend on the types of endgroups and pendent substituents on the polysiloxane and on the crosslink density of the networks.

Dumas was the first to propose the existence of organosiloxanes in 1840.⁶ Friedel and Crafts (1863 – 1880), and later Ladenburg, prepared tetraethylsilane, the first organosilane compound, by heating diethylzinc with silicon tetrachloride in sealed tubes to ~ 160°C:



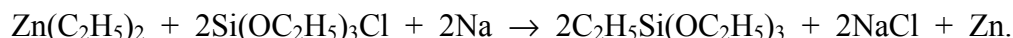
Later, in 1884, Pape reacted trichlorosilane with dipropylzinc:



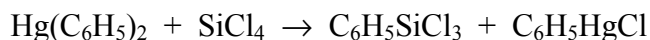
and in 1885, Polis was successful in using the Wurtz reaction to synthesize aromatic derivatives of silicon:



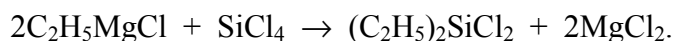
such as tetraphenylsilane, tetratolylsilane, and tetrabenzylsilane. Ladenburg and Friedel also discovered methods for the partial alkylation of silicon compounds, alkylalkoxysilanes, by reacting diethylzinc with triethoxychlorosilane and metallic sodium without sealed tubes, and postulated by:



Ladenburg was also successful in synthesizing phenylchlorosilanes by reacting diphenylmercury with silicon tetrachloride at 300°C in sealed tubes:



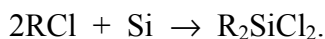
Although the above authors and others such as Wöhler⁵ experimented in the area of siloxanes over one hundred years ago (1843), it is agreed that the foundations of organosiloxane chemistry were based on Kipping's work from 1899-1944 at the University College, Nottingham, UK. His work focused on non-polymeric compounds, and he likely did not see the potential for commercial success, since he reputedly regarded the frequently encountered resinous polyorganosiloxane materials as troublesome. In the middle 1940's silicones were introduced to the public on a limited commercial basis.⁶ Kipping and Dilthey, separately and simultaneously in 1904, utilized the Grignard reaction successfully for the synthesis of organosiloxanes:



The intermolecular condensation of silanediols and silanetriols to polyorganosiloxanes was also discovered by Kipping after partially alkyl-substituted silanes containing hydrolyzable functional groups to make silanols were available. Both Kipping and Stock

recognized the intermediate chemistry as routes to the silicones and the fascinating differences between classical organic chemistry and silicon chemistry.¹

During the late 1930's, a major change in the emphasis of organosiloxane chemistry from monomeric products to technically useful polymeric organosiloxane materials was made in the search for heat-resistant electrical insulating materials. Silicon resins were developed through the research efforts at Corning Glass Works (USA) and the General Electric Co. (USA).⁶ Dr. J. F. Hyde developed a resinous electrical insulating varnish in 1930 at the Corning Glass Works, the first practical silicone product. The merger of Corning Glass Works and the Dow Chemical Company combined the experience of both companies to explore the organic chemistry required for the production of silicones. Also during this same era, Dr. E. G. Rochow (and W. J. Patnode)¹ from the General Electric Co. discovered the process for the production of chlorosilanes known as the "Direct Process" (discussed in section 2.1.2):



This led to the economical large scale production of silicones.⁵ A Russian group, B. N. Dolgov and K. A. Adrianov, also investigated the synthesis of polyorganosiloxanes.¹

Silicone manufacturing was started in 1943 by the Dow Corning Corp. of Midland, Michigan and in 1946 by the General Electric Co. of Waterford, New York in an energetic drive to produce silicones for military applications during World War II.⁶ The Dow Corning Corp. produced viscous, silicone fluids with a wide service temperature range as both damping fluids in sensitive aircraft instruments, and as anti-foam agents in the lubricating oils for aircraft engines. They also produced silicone greases for military use as moisture-proof sealing compounds in the spark plug wells of aircraft engines. These also retained their electrical insulating properties and viscosity over a wide service temperature range from the hottest engine temperatures and below 0°C. At General Electric, M. C. Agens applied for the first silicone rubber patent.⁵ Table 2.2 outlines several of the major discoveries in siloxane chemistry before 1950.⁷

It is apparent that the search for heat-resistant polymeric materials led to a material which not only had countless other technical applications; but had actually encompassed a whole new breed of chemistry and the birth of many new international companies specializing in organosiloxanes. After the war, Union Carbide of Long

Table 2.2Major Discoveries in the Silicone Project Before 1950^{a7}

No.	Description	Discoverer(s) ^b	Year ^c	Project Size ^d
1	Methyl silicone resins	Rochow	1938	0.5
2	Direct process for methylchlorosilanes	Rochow	1940	3
3	Contact masses for direct process	Patnode and Rochow	1940	3
4	Silicone surfaces	Patnode	1940	3
5	Direct processes for phenylchlorosilanes	Rochow and Gilliam	1941	11
6	Controlled preparations of oils	Patnode	1942	16
7	Silicone rubber	Agens	1942	16
8	Preparation of methyl silicone gum	Wright	1943	25
9	Cross-linking of gum	Wright and Oliver	1943	25
10	Cross-linking with vinyl groups	Marsden	1944	34

^a U.S. patents were granted on all these discoveries. Other discoveries are covered in later chapters of this source. The use of *discovery* instead of *invention* is defended in Chapter 5 of this source.

^b All discoverers had joined the Chemistry Section by August 1, 1939, W. F. Gilliam being the last to arrive. Among the discoverers listed, four of seven had been awarded PhD.s.

^c The choice of year could be argued in some cases.

^d Project size measured by estimated man-years of research effort during year on left. Data compiled by Arthur E. Newkirk and taken from CRDA.

Beach, West Virginia (1957) and the Stauffer Chemical Co. of Adrian, Michigan (1965) each started their own silicone divisions. International silicone companies also sprouted up in the German Federal Republic (1952, Farbenfabriken Bayer AG of Leverkusen and 1951, Wacker-Chemie of Munich), East Germany (Chemie-Werke, Nünchritz), France (Rhône Poulenc, and Société Industrielle des Silicones et des Produits Chimiques du Silicium (S.I.S.S.)), Great Britain (Chemical Industries and Midland Silicones), Belgium (Union Chimique Belge), Japan (Shin Etsu Chemical Industry Co., the Tokyo Shibaura Electrical Co. Ltd., Fuji Kobunshi Kogyo, and Toray Silicone), and also in the U.S.S.R. and Czechoslovakia.¹

After just a few decades, the silicone industry has grown to well over a billion dollar industry due to the unique properties of silicones. These include their outstanding resistance to aging and weathering (against heat, light, oxygen, and water), their unusual surface properties (water repellancy), and their ability to maintain desirable physical properties over a wide service temperature range (well below 0°C and up to ~ 390°C) as well as their being nontoxic.¹⁰ There are numerous sources which describe the applications of silicones, and Volumes I and II of "Silicones"^(8,9) describe many of them. Silicone rubbers as room temperature vulcanizates (RTVs) or heat curable types are used for medical applications including prosthetic devices and artificial organs, contraceptive devices, implant capsules, contact lenses, linings for dentures, and hairpieces. Other RTV applications include mold making, membrane separation processes, printing and recording media, explosives and propellants, sealants and gaskets, adhesion promoters-primers, and more including fluoroelastomers. Electrical molding resins and functional siloxane fluids are used for general molding, semiconductor applications, in tape compositions, electronic applications, additives, and in silicon-containing copolymers. Lubricant and grease compositions are used as functional fluids including dielectric fluids, fire resistant hydraulic fluids, brake fluids, and others.⁸ Siloxanes are commonly used as coatings for baking pans and utensils, paper coatings-release, in pressure sensitive-controlled release compositions, silicone-organic resin coatings, coated plastics and other coatings, and as paint additives. Printing, photocopy and magnetic tape applications include printing inks-additives, magnetic tapes, and vesicular films. Siloxanes are used in urethane foams which are flexible, highly resilient, or rigid, froth,

and are flame retardant. Isocyanurate foams, phenolic foams, and other cellular plastic products are coupled with siloxane materials. Siloxanes are used in textile applications such as thread, carpet backing, fibers for fill, water-repellent treatments, processing aids, leather coatings, and others. Common consumer products such as personal care products and polish formulations have been improved by incorporating siloxanes. Finally, antifoam agents, plastics additives and other artifacts including encapsulants and food additives, explosives, composites, and tire mold release agents, etc. are all based on siloxanes.⁹ A list of technical applications for silicones are also presented in Table 2.3.⁷ Today, silicone materials, mostly methyl- substituted, are produced in the forms of rubber (~ 50%), liquids (~ 40%), and the rest as resins on a scale of 475,000 metric tons per year, which corresponds to ~ \$3,500,000,000.¹⁰

2.1.1 The Siloxane Bond and its Effect on Organosiloxanes

The silicon-oxygen bond, Si-O, is one of the most thermodynamically stable bonds, so much so, that SiO₂ itself was thought to be an element until Antoine Lavoisier dissolved it with HF to produce SiF₄ in 1807. This reaction also produces H₂SiF₆ and when neutralized with KOH yields K₂SiF₆. Later, in 1823, Jöns Jacob Berzelius first made silicon a useful element for further research by the action of potassium metal on K₂SiF₆. He reacted silicon in this form in a stream of chlorine gas to make SiCl₄, which is now an essential starting material for the commercial production of siloxanes. In 1830, he was the first to introduce the terms *polymer*, *crystalline polysiloxane* (giant silica molecule), and *glassy, amorphous polysiloxane* (vitreous silica). He also introduced the terms “catalyst”, “isomer”, and “protein”; and even synthesized a polymer in his laboratory in 1847! The work of Friedrich Wöhler, C. Friedel, and J. M. Crafts (section 2.1) followed Berzelius’.⁷

Interesting properties of the siloxane bond are brought to mind when recalling the comparison of carbon forming gaseous CO₂ rather than solid, crystalline SiO₂. Silicon dioxide, SiO₂, free or combined, exists in as many as 22 forms (phase modifications, all with the same composition but different structures) with the most prevalent being quartz, vitreous (glassy) silica, or hydrated SiO₂ which belongs to the silicic acids family. A

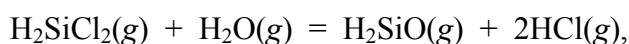
Table 2.3Silicone Applications⁷

Automotive	Electrical/Electronic
Wire insulation Transmission seals Spark-plug boots Special lubricants Hydraulic bumpers Truck hose	Motor and transformer insulation Wire and cable insulation Circuit board laminates Telephone wire connectors Transistor encapsulants Circuit encapsulants Television insulation Rubber tapes (adhesive)
Paper	Rubber
Antistick surfaces Process defoamers	Tire release coatings
Military/Aerospace	Textiles
Aircraft seals Firewall insulation Special lubricants Heat shields	Water repellents Fabric softeners Dyeing-process defoamers
Consumer Products	Food
RTV sealants Tile grout Shoe water repellents Eye-glass tissues Lubricant sprays	Coffee defoamers Bread pan coatings Milk-carton release coatings Cooking-process defoamers
Chemical Specialties and Cosmetics	Construction
Auto and furniture polish Antiperspirants Hair sprays Hand creams Bath oils Foaming agents	Window and building sealants Roof coatings Masonry water repellents Weather-durable paints Heat-resistant paints
Plastic Tooling	
Furniture molding Vinyl shoe molding Jewelry molding	

Note. This list was not intended to be complete. Even in 1954 Rob Roy McGregor in Chapter 4 of his *Silicones and Their Uses* (McGraw-Hill, New York) showed that silicones were being used by 20 industries in a total of 425 ways!

crystal of silica is a giant molecule, unlike the small CO₂ gas molecules where each carbon bonds to 2 oxygens.⁷ Carbon, with 4 valence electrons, can have 4 tetrahedral sp³ bonds where each bond angle is ~ 109°. It also has the ability to double bond with 2 oxygens (with sp² hybridized) yielding carbon dioxide, O=C=O, having a bond angle of 180°. In silica structures every oxygen atom bonds to two silicon atoms.¹

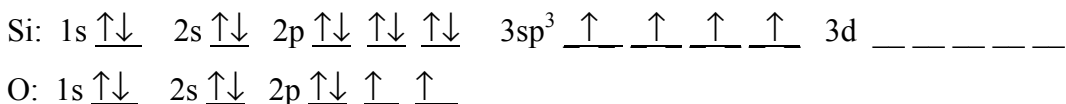
Si-O and Si-C double bonds do not appear in stable compounds. Silicon does not typically form double bonds. Although Stock claims to have isolated “pro-siloxane”, H₂Si=O, its existence has never been experimentally proven. Its formation would require too great a tetrahedral distortion. Stock’s reaction:



where the reactants were mixed at low pressure and room temperature, led him to propose the formation of pro-siloxane due to a pressure increase and the formation of 2 moles of HCl. He proposed that H₂SiO reacted quickly to form the (H₂SiO)₆(l) since the unstable Si-O double bond reverted to the more favorable Si-O-Si bridges and that the H₂SiO molecule existed as a gaseous intermediate.

Stock’s proposal of the “pro-siloxane” prompted further investigations leading to surprising discoveries about the siloxane bond. The interatomic distance of Si-O and valence angle of Si-O-Si are respectively smaller and wider than one would predict.⁷ Once SiO₂ is broken down, one can imagine the formation of a polymer by replacing 2 of the 4 original oxygens bonded to the silicon with organic groups, most commonly methyls, to give a (Si-O-Si)_x backbone or polydimethylsiloxane chain, PDMS, where silicon always has 4 covalent bonds. This would lead to the belief that each silicon in PDMS is sp³ tetrahedrally hybridized with bonds angles of ~ 109°. However this is not the case.¹

Silicon (1s²2s²2p⁶3s²3p²) and oxygen (1s²2s²2p⁴) have the following valence states in neutral molecules:



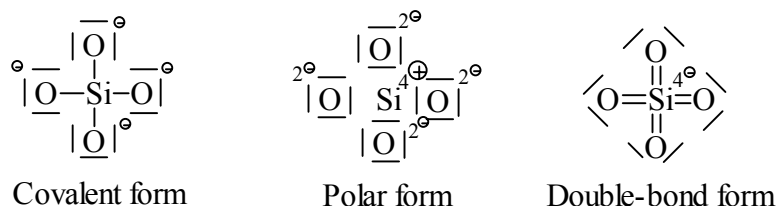
Oxygen has lone pairs of electrons in its p orbitals which can overlap with the 3sp³ orbitals and also the empty d_{x²-y²} and d_{z²} orbitals of silicon to form σ (single) bonds. The unshared p electrons of oxygen can also overlap with the empty 3d_{xz}, 3d_{yz}, and 3d_{xy}

orbitals of silicon giving rise to an additional π interaction named $p_\pi - d_\pi$ or $(p \rightarrow d)_\pi$ conjugation. A traditional $p_\pi - p_\pi$ double bond restricts rotation around the σ bond, where the $p_\pi - d_\pi$ type does not. This additional $p_\pi - d_\pi$ interaction is what gives the Si-O bond its partial double bond or partially “ionic” character, along with its shorter than expected Si-O bond length and the larger than expected (Si-O-Si) bond angle.²

The vast majority of organosiloxanes have Si-O bond lengths of $1.64 \pm 0.03 \text{ \AA}$; while the interatomic bond length of Si-O is 1.83 \AA , calculated from the addition ($1.17 \text{ \AA} + 0.66 \text{ \AA}$) of the silicon and oxygen atomic radii. This 0.2 \AA shorter than expected bond can be explained by both its substantial ionic character of approximately 40%, and also by its partial double bond character. The bond length can be altered by the electronegativity of attached organic groups. Electron accepting substituents on the silicon atom lower the energy of the 3d orbitals; metal atoms on the oxygen atom increase its effective negative charge. These situations tend, respectively, to raise or decrease the double bond character of the Si-O bond. Most organosiloxane compounds are ionized to extents of 40 – 50% with bond orders between 1.2 – 1.5.² With electronegativity values of 1.8 for Si and 3.5 for O, the ionic character of the Si-O bond was first calculated by Pauling as about 50%. Hannay improved on his calculation using:

$$\text{Polar bond contribution, \%} = 16(X_A - X_B) + 3.5(X_A - X_B)^2,$$

where $|X_A - X_B|$ is the absolute difference of the electronegativity of the pair of atoms (1.7 for Si and O). This equation reduced the polarity of the Si-O bond down to about 38%. The following polar and covalent bond resonance contributions for SiO_4 have been proposed to reconcile the calculated and measured radii of the Si-O bond length, as the three following limiting bond types:



This resonance bond system supports Pauling’s postulate which requires the electric charge on each atom in stable molecules or crystals to approach zero, where the charge on the Si atom is 4 in the polar form and 0 in the covalent form.¹ This partial double

bond character now leads to the discussion of the wide bond angles.

The bond angle for Si-O-Si in organosiloxane compounds varies widely between 105° and 180° , and between 125° and 180° for silicates. In almost every case it greatly exceeds the expected valence angle of oxygen in an sp^3 hybridized bond which is $\sim 109^\circ$. This further supports the evidence for $p_\pi - d_\pi$ bonding where the five, orthogonal, diffuse 3d orbitals allow π bond formation with any valence angle of oxygen. As the Si-O-Si bond angle increases, the Si-O bond distance decreases by about $0.02 - 0.03 \text{ \AA}$ for every 10° .² The bond lengths and valence angles of PDMS are remarkably constant at about 1.645 \AA for Si-O and about 1.88 \AA for the Si-C bonds. Approximately 130° is observed for both the Si-O-Si and C-Si-C bond angles. Since the silicates have more stringent symmetry requirements than the liquid silicones, they generally have lower valence angles than 130° .¹

The average single-bond energies of organosiloxanes are defined as the heat of formation of gas AB_n from its elements at 0°K , and measure the strength of a bond A-B. A number of authors have calculated the value for the Si-O bond energy using a variety of methods with results ranging from $101 - 117 \text{ kcal/mol}$, although Pauling's thermochemical data will be presented here for consistency. The stability of the siloxane bond, Si-O (88.2 kcal/mol), is second only to Si-F (129.3 kcal/mol). It has greater heats of formation than less polar bonds such as C-O (84.0 kcal/mol), Si-C (69.3 kcal/mol), and C-C (83.1 kcal/mol)¹ and than more polar bonds such as Cl-O, Sn-O, and Pb-O.² This also supports evidence of its $p_\pi - d_\pi$ bonding; although this thermochemical data does not explain why the Si-O bond is more sensitive to heterolytic cleavage than the C-C bond.¹

The complex bonding involved in organosiloxanes and polyorganosiloxanes leads to their unique and favorable properties. The longer Si-O bond length, 1.64 \AA (of PDMS), allows for wider valence angles around the Si-O-Si bond, which leads to higher flexibility along the siloxane polymer chains. Therefore PDMS has flexibility at very low temperatures and a glass transition temperature, T_g , of -127°C . The fact that the Si-O bond length is shorter than the expected 1.83 \AA , as a result of its partial double bond character from the $p_\pi - d_\pi$ interaction, leads to a very stable bond (88.2 kcal/mol , second only to Si-F, 129.3 kcal/mol). Therefore it has stability at very high temperatures ($300^\circ - 400^\circ\text{C}$). The Si-O bond also results in very weatherable materials, since it is not affected

by ozone and does not absorb in the near ultraviolet region.¹ Tables 2.4 and 2.5 are comprehensive lists of interatomic distances, valence angles, and bond strengths for siloxane and related bonds.^(1,2)

2.1.2 Synthesis of Organochlorosilanes

This study is based on the synthesis of polyorganosiloxanes and their corresponding networks. The cyclic organosiloxanes such as hexamethylcyclotri-siloxane, D₃, or octamethylcyclotetrasiloxane, D₄, used to synthesize polydimethyl-siloxane, PDMS, are commonly referred to as monomers. The cyclic and linear siloxane precursors for polyorganosiloxanes are synthesized from organohalosilanes.⁷ Commercially, chlorosilanes are synthesized from Si (derived from SiO₂).⁶

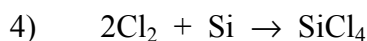
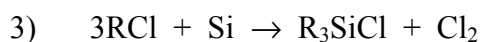
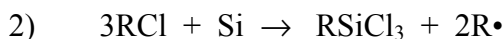


These are then hydrolyzed to yield unstable organosilanols which readily condense into the desired linear and cyclic organosiloxane precursors. The direct, Grignard, olefin addition, and redistribution processes are important commercial processes for synthesizing chlorosilanes and organochlorosilanes.⁶

The direct process or direct synthesis describes the reactions of organic halides with silicon, and was first patented by E. G. Rochow and referred to as the “Rochow synthesis”.¹ Chlorosilanes (Cl being the most common halogen) are synthesized in this manner directly by reacting elemental silicon with alkyl or aryl chlorides, and is ideally described with one diorganochlorosilane product by⁷



A mixture of organochlorosilane products are produced in practice as other side reactions occur simultaneously which are



The organic free radicals produced in the reaction either react further or decompose.¹ Since silicon reacts sluggishly with organic halides, a copper catalyst is normally used. Maximum contact with the surface area of the metallic silicon is obtained by sintering a finely ground mixture of the two metals at ~ 1000°C in H₂ to produce a superficial alloy.

Table 2.4

Interatomic Distances and Valence Angles
for Siloxane and Related Bonds¹

Measured and Calculated Si-O Interatomic Distances (Å)					
Covalent radius Si = 1.17Å O = 0.66Å	Measured	Calculated sum of:		as covalent-polar resonance bond	as covalent-polar- double resonance bond
		Ionic radii	Atomic radii		
Forms of SiO ₂	1.60	1.71	1.83	1.67	1.63
Polydimethylsiloxanes	1.64				

Bond	Mean Distance (Å)
Si-O in PDMS	1.645
Si-O in quartz	1.61
Si-O in glass	1.60
Si-C in PDMS	1.88
Si-O in D ₃	1.66
Si-C in D ₃	1.88
Si-O in D ₄	1.65
Si-C in D ₄	1.92

Valence Angle (deg) ^(1,2)			Bond Rotational Barriers ¹¹	
Compound	Si-O-Si	O-Si-O	Bond	Energy (kcal/mol)
D ₃	125 ± 5	115 ± 5	Si-O	< 0.8
D ₄	142.5	109	C-O	11.3
Polydimethyl siloxane	130 ± 10	130 ± 10	Si-CH ₃	6.7
			C-CH ₃	15.1

Table 2.5Bond Strengths of Siloxanes and Related Bonds¹

Single Bond Energies		
Bond	Data according to Pauling (kcal/mol)	Other Authors
Si-O	88.2	106 ⁶¹ ; 117 ¹⁹¹ ; 101-102 ¹⁸⁷
C-O	84.0	80.9 ⁶¹
Si-C	69.3	75.0 ⁶¹ ; 64 ¹⁹¹ ; 52-76 ¹⁸⁸
Si-Si	42.2	51.3 ¹⁶⁷
C-C	83.1	84.9 ⁶¹
Si-H	70.4	79.9 ¹⁶⁷
C-H	98.8	98.1 ⁶¹
Si-F	129.3	147.4 ¹⁶⁷
C-F	105.4	102 ⁶¹
Si-Cl	85.7	90.3 ¹⁶⁷
C-Cl	78.5	77.9 ⁶¹

⁶¹Gilman and Dunn figures are based in their interest for a comparison of silicon and carbon chemistry.

¹⁹¹New calculations by Thompson from the heat of combustion of siloxanes.

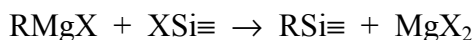
¹⁸⁷Heats of combustion of organooxysilanes and siloxanes by Tanaka and Watase

¹⁸⁸Heats of combustion of silanes by Tannenbaum

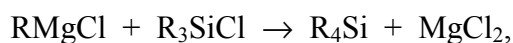
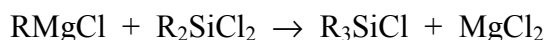
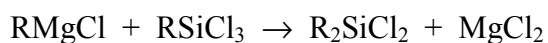
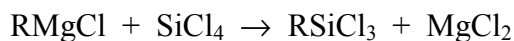
¹⁶⁷Skinner's evaluation of the dissociation energies of diatomic molecules on the basis of spectroscopic data.

This may also be achieved by heating a mixture of silicon and cuprous chloride at 200 – 400°C. Methyl chloride is passed through the silicon and copper catalyst mixture at about 250 – 280°C, and the desired organochlorosilanes are then separated by fractional distillation. The reactions involved in the direct process are quite complex and not well understood. Compared to the Grignard process, it is not very versatile since yields for organochlorosilanes besides phenyl and methylchlorosilanes are unacceptably low. However, since methylchlorosilanes are the most widely used chlorosilanes for the manufacture of commercial silicones, it remains the dominant commercial process.⁶

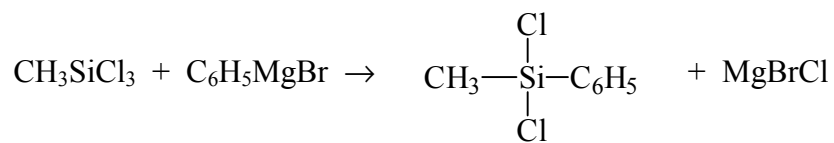
The Grignard process utilizes organomagnesium compounds to transfer organic groups to silicon.



First, the Grignard reagent is prepared by the addition of an alkyl halide (most commonly Cl) or aryl halide (commonly Br) to a suspension of magnesium in an ether (commonly diethyl ether). The second step involves treatment of the ethereal solution with silicon tetrachloride (other halides and salicylic acid esters can also be employed). This is an exothermic reaction and requires concurrent cooling. A series of products arise from the following reaction sequence:

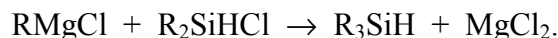
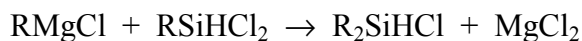
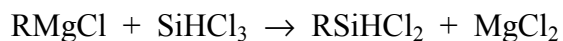


where the magnesium chloride precipitate is filtered and the solvent is removed to yield a mixture of various organochlorosilanes. The products may be separated by fractional distillation, although the diorganodichlorosilane is the major product since steric effects retard the introduction of further organic groups. The Grignard process is more versatile than the direct process, since it allows for the possibility of forming mixed organochlorosilanes.

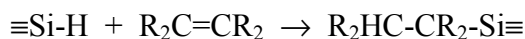


These reactions may also be used for the preparation of organo-H-chlorosilanes since

Grignard reagents generally do not affect silicon-hydrogen bonds:



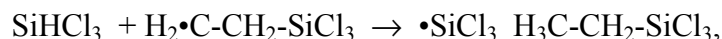
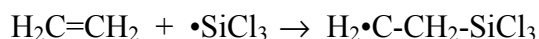
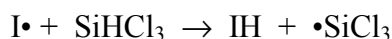
The olefin addition process adds compounds containing Si-H bonds to olefins.



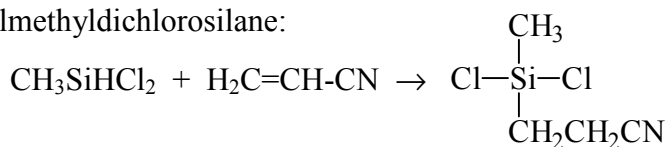
This may also be used to synthesize unsaturated silanes from alkynes



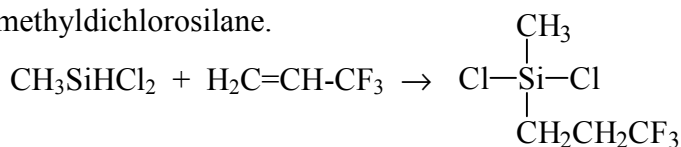
It can be carried out without catalysts at 200 – 400°C, or with catalysts (organic peroxides) at 40 – 75°C. This involves a free radical mechanism, as shown in the following examples for the synthesis of ethyltrichlorosilane from trichlorosilane and ethylene:



where I• is the initiator radical. It is useful for the synthesis of organofunctional silanes such as β-cyanoethylmethyldichlorosilane:

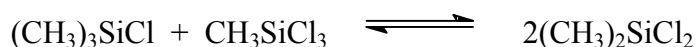


or γ-trifluoropropylmethyldichlorosilane.



Although the olefin addition process yields one major product (rather than a mixture with very similar boiling points), and is economically attractive, it cannot be used to prepare methylchlorosilanes which are primarily used for the manufacturing of silicones.⁶

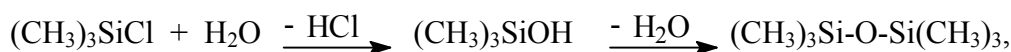
The redistribution process involves the exchange of various substituents on the silicon atoms for one another under appropriate conditions. A practical example is the synthesis of dimethyldichlorosilane by reacting a mixture of trimethylchlorosilane with methyltrichlorosilane.



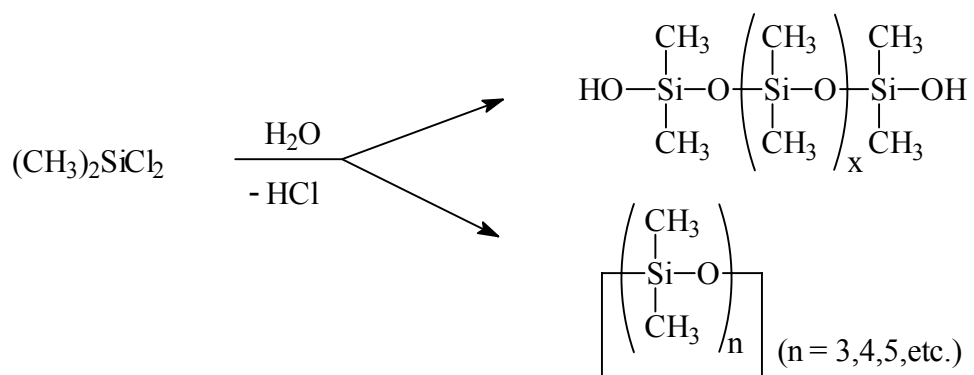
This is conducted in the presence of aluminum chloride between 200 – 400°C. The redistribution process is a useful method of converting chlorosilane by-products into more useful materials.

2.1.3 Cyclic and Linear Polyorganosiloxane Precursors

The cyclic and linear organosiloxane precursors for polyorganosiloxanes are synthesized by hydrolysis of the organochlorosilanes to give unstable organosilanols which spontaneously condense to form water and siloxanes. The type of siloxane formed depends on the functionality of the halosilane and the reaction conditions. The hydrolysis of trimethylchlorosilane reacts to form the dimer, hexamethyldisiloxane.

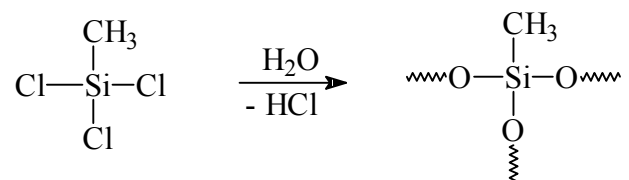


This can act as an endcapping reagent and be used to control molecular weights of polyorganosiloxanes. The hydrolysis of the difunctional halosilane, dimethyldichlorosilane leads to a mixture of linear and cyclic oligomers:



where the percentages of the linear and cyclic siloxanes produced depend on the reaction conditions. When hydrolysis is carried out exclusively with water, yields of 50 – 80% of linear polydimethylsiloxane- α,ω -diols and 50 – 20% polydimethylcyclosiloxanes are obtained. The oligomeric portion of cyclosiloxanes is increased to ~ 70% when hydrolysis is carried out using 6N HCl instead of water.¹ By contrast, when 50 – 85% sulfuric acid is present during the hydrolysis, high molecular weight linear polymers are preferentially formed with only a small percentage of cyclosiloxanes. If the preferential formation of lower cyclosiloxanes is desired, then hydrolysis with water is carried out interfacially in the presence of solvents such as toluene, xylene, or diethyl ether. Intramolecular condensation is favored over intermolecular condensation due to the

reduction in concentration of the organochlorosilanes in the aqueous phase. Since the cyclosiloxane products are soluble in the organic phase, they are protected from the attack of the aqueous HCl acid. Finally, hydrolysis of the trifunctional, methyltrichlorosilane, yields highly crosslinked gel-like or powdery polymers:



The linear silanol and cyclosiloxane products of the hydrolysis reactions described above may be catalysed by either acids or bases (Figure 2.1). When organochlorosilanes are hydrolysed (in the absence of an organic solvent), the acidic HCl yielded typically acts as the catalyst leading to rapid condensation.⁶

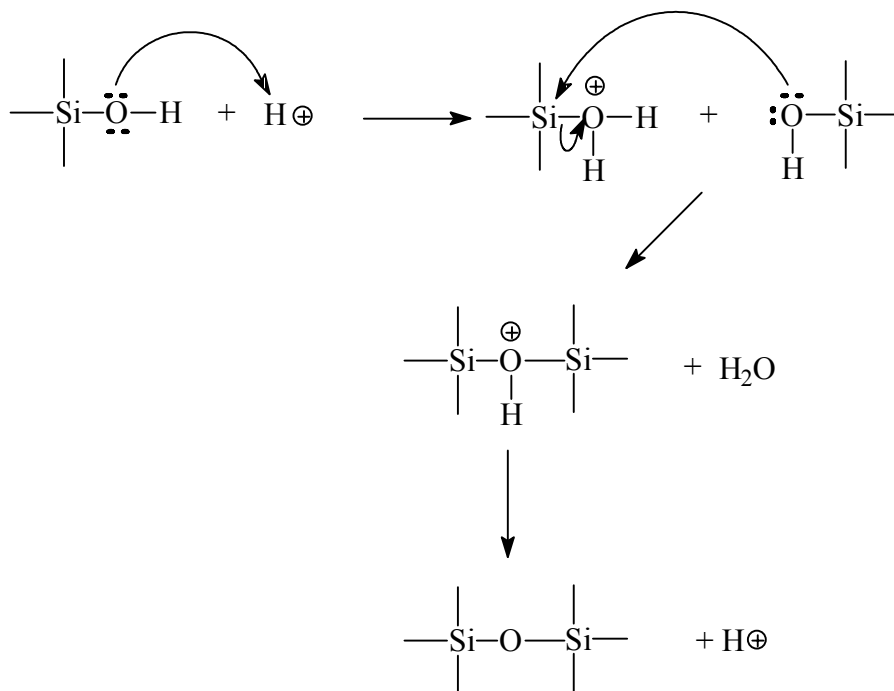
2.1.4 Anionic Ring Opening Equilibration

The synthesis and characterization of polyorganosiloxanes have been extensively investigated and many excellent references are available today.^(1,2,6,7,10-22) Polyorganosiloxanes are typically synthesized by either the hydrolysis of bifunctional silanes or via ring opening polymerizations of lower cyclic siloxanes. Most commonly, D₃ or D₄ may be polymerized into high molecular weight polyorganosiloxanes by cleaving the Si-O bond and reforming new siloxane bonds. These types of polymerizations may be done using acidic or basic catalysts. For anionic polymerizations, activation energies increase as the ring strain of the cyclic siloxane monomers decrease. Cyclic trimer siloxanes are less stable due to a larger degree of ring strain, and have lower activation energies for ring-opening, $\sim 16.5 \pm 1.0$ kcal/mole, as compared to more stable cyclic siloxanes having greater than 3 siloxane units which have activation energies of $\sim 19.5 \pm 1.0$ kcal/mole. This difference in activation energies of ~ 3 kcal/mole is about equal to the energy value for the ring strain in cyclic siloxanes with 3 units.² Polymerizations of cyclic siloxane trimers ($\Delta H = \text{exothermic}$) are enthalpically driven, whereas polymerizations of higher cyclics (most commonly D₄ with $\Delta H \cong 0$) are entropically controlled equilibrations.²¹ A brief description of the ring-opening polymerization of the cyclic siloxane trimer follows. Since the syntheses for the study

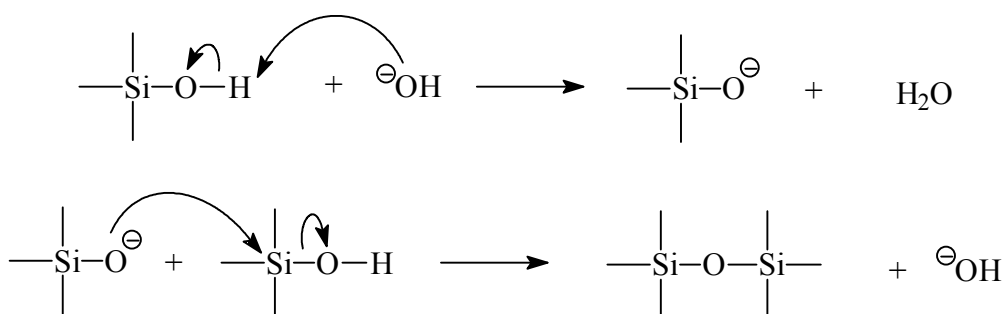
Figure 2.1

Mechanisms for Acid and Base Catalysed Condensation Reactions

Acid Catalysed Condensation



Base Catalysed Condensation



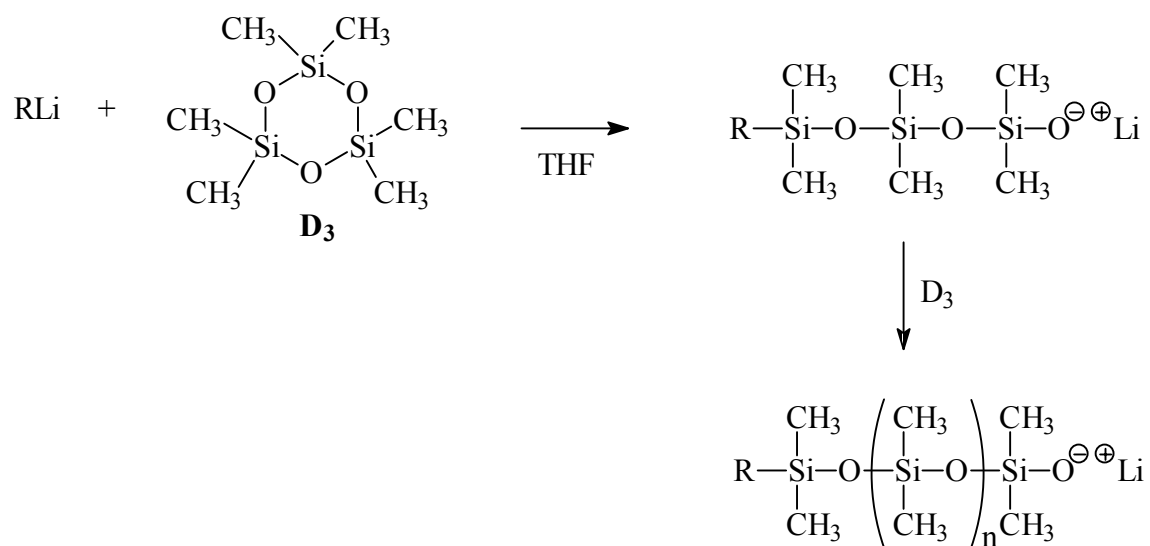
herein focus on base catalysed ring opening equilibrations of cyclic siloxane tetramers, those processes will be described in greater detail.

Cyclic siloxane trimers generally require a basic initiator such as an organolithium. Typically, these reactions are conducted in hydrocarbon solvents with limited amounts of a polar solvent such as THF to yield lithium siloxanolate reactive centers. Polar solvents in modest concentrations ($\sim 10 - 20$ volume %) are required to promote sufficient reactivity for propagation by solvating the tight lithium siloxanolate ion pairs. Too high a concentration of THF may promote equilibration since the partially ionic Si-O-Si backbone of the growing chains would then be susceptible to attack by the highly solvated lithium siloxanolate. The cyclic trimer has an exothermic heat of polymerization and behaves as a living polymerization where the degree of polymerization increases with conversion. The lithium siloxanolate centers continue to propagate by attacking the electropositive silicon atoms of D_3 monomers (ring-opening) until the anions are quenched with the desired endcapping reagent (Figure 2.2). Under appropriate conditions, it is possible to obtain $\sim 100\%$ conversion of a polyorganosiloxane with a narrow molecular weight distribution, $M_w/M_n \cong 1.1$.⁽¹⁴⁻¹⁹⁾

PDMS is commonly manufactured using the more stable D_4 tetramer since it is a less expensive and more readily available monomer than D_3 . While D_3 has a ring strain of about 3.2 kcal/mole (12 – 15 kJ/mole), D_4 has essentially no ring strain.^(1,2,14,15) Since the activation energy for ring opening D_4 is higher than for D_3 , it requires more basic reactive centers than the tightly associated lithium siloxanolate (for D_3) for its ring-opening polymerization.^(2,14,15) The ring-opening polymerization of D_4 is entropically driven, $\Delta S \cong +6.7$ J/mole $^\circ$ K. It can be envisioned that this stable tetramer opens to form a large number of highly flexible chains with greater degrees of freedom than the ring due to the large silicon atoms and long Si-O bonds along the siloxane backbone. This positive entropy for polymerization is unusual since most monomers are more disordered than their corresponding polymers.²² A thermodynamic equilibrium is established between the rings and the chains for the polymerization of cyclic siloxanes with greater than three units, and the position of the equilibrium depends on the types of sidechain chemical structures on the silicon atoms. Another interesting feature of this polymerization is that oligomers with controlled average molecular weights can be

Figure 2.2

Mechanism for the Anionic Ring-Opening Polymerization of a Cyclic Siloxane Trimer



prepared when D₄ is polymerized in the presence of a small linear M type (monofunctional) siloxane endcapping reagent. The mechanism for the polymerization of D₄ is complex after initiation due to the number of reaction pathways which the reactive centers may take.

Since the Si-O bond is resistant to homolytic cleavage, either a cationic or anionic catalyst is required to heterolytically cleave the Si-O bond to form the ionic active centers, R₃Si-O⁻, necessary for propagation. Polymerizations will reach an equilibrium between the linear (PDMS or siloxanolate) chains formed and small cyclics (mostly D₃ – D₅) at a rate dependent upon the base strength of the catalyst.^(2,17a) The specific catalyst chosen is based on the types of sidechain chemical structures on the silicon atoms of the monomer, and the endgroups of the endcapping reagent. Generally, when these groups are susceptible to attack by acid, a basic catalyst is chosen and vice versa.¹⁹ The initiation step involves attack of the base on the electropositive silicon atom in the cyclic siloxane tetramer to yield reactive siloxanolate centers, ≡Si-O⁻. The reactivity of common bases (listed below) towards lower cyclic and linear siloxanes was found to be greatest for strained difunctional (D type units) siloxanes, and least reactive towards unstrained monofunctional (M type units):



This phenomenon illustrates how the reactivity of the siloxane bond towards base increases with the number of electronegative oxygen atoms which effectively increase the positive character of the silicon atom.^(23,24) It also supports the observation that D₄ requires a stronger base than D₃ for ring-opening polymerization, and how an MM type linear siloxane will function as an effective endcapping reagent (discussed below).

The most active anionic catalysts include hydroxides, alcoholates, phenolates, silanolates or siloxanolates, mercaptides of the alkali metals, quaternary ammonium and phosphonium bases and their siloxanolates, organo -lithium, -sodium, and -potassium compounds, hydrocarbon radicals (R•) or RM type compounds.² Many catalysts have been extensively studied^(1,2,11,17a,25), although those commonly used for the anionic ring opening of the stable, cyclic tetramer D₄, will be focused on here.

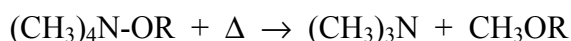
The polymerization of D₄ with strong bases to yield polydimethylsiloxanes was carried out to investigate the nature of the silicon-oxygen-alkali bond.²⁵ The alkali metal

hydroxides (commonly anhydrous KOH) which are more basic than the organolithiums are frequently chosen for the ring-opening of D₄, and polymerization temperatures of about 140 – 160°C are normally used.^(15,25) Both the solubility in D₄ and reactivity of the alkali metal hydroxides depend on the size of the cation. It was found that cesium hydroxide dissolves below 100°C, potassium hydroxide at ~ 150°C, and the weaker sodium and lithium hydroxide bases do not dissolve, even above 150°C. Polymerization temperatures can be decreased and reactivity of the base increases with the size of the cation as:

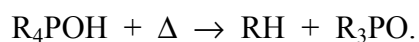


where tetramethylammonium^(2,25,26) and tetrabutylphosphonium^(2,25,28) siloxanates react at similar rates to cesium siloxanates.

Thermally labile catalysts^(2,20,25-30) such as quaternary ammonium (R₄NOH) and phosphonium hydroxides (R₄POH) are an excellent choice due to their transient nature. Since they decompose when heated (above 100°C) into inert, volatile products which can be distilled after the reaction, extra steps (required for alkali metal hydroxides) of washing or neutralizing the solution are eliminated.^(2,20) The tetramethylammonium siloxanolate decomposes slowly above ~ 90°C and quickly above 130°C to yield methanol (or trimethoxysilane) and trimethylamine (activation energy of ~ 42 kcal/mole):



where R = H or (-Si(CH₃)₂O)-_n.^(25,29) The quaternary phosphonium siloxanates degrade at a slightly lower temperature of ~ 110°C to yield gaseous hydrocarbons and triorganylphosphine oxides²⁸:



The activation energy for opening D₄ (when run between 60 – 100°C) is reported as ~ 20.0 kcal/mole when catalysed with tetramethylammonium hydroxide and as ~ 19.0 kcal/mole when using tetrabutylphosphonium hydroxide.^(2,29) While other labile catalysts have been investigated, it should be noted here that their reactivity is too great to catalyse the ring-opening polymerizations of cyclic siloxane trimers. They are mainly used to equilibrate D₄ since only very low yields of linear polyorganosiloxanes are obtained with strained and/or polar cyclic siloxanes.³⁰ For this study, tetramethylammonium hydroxide

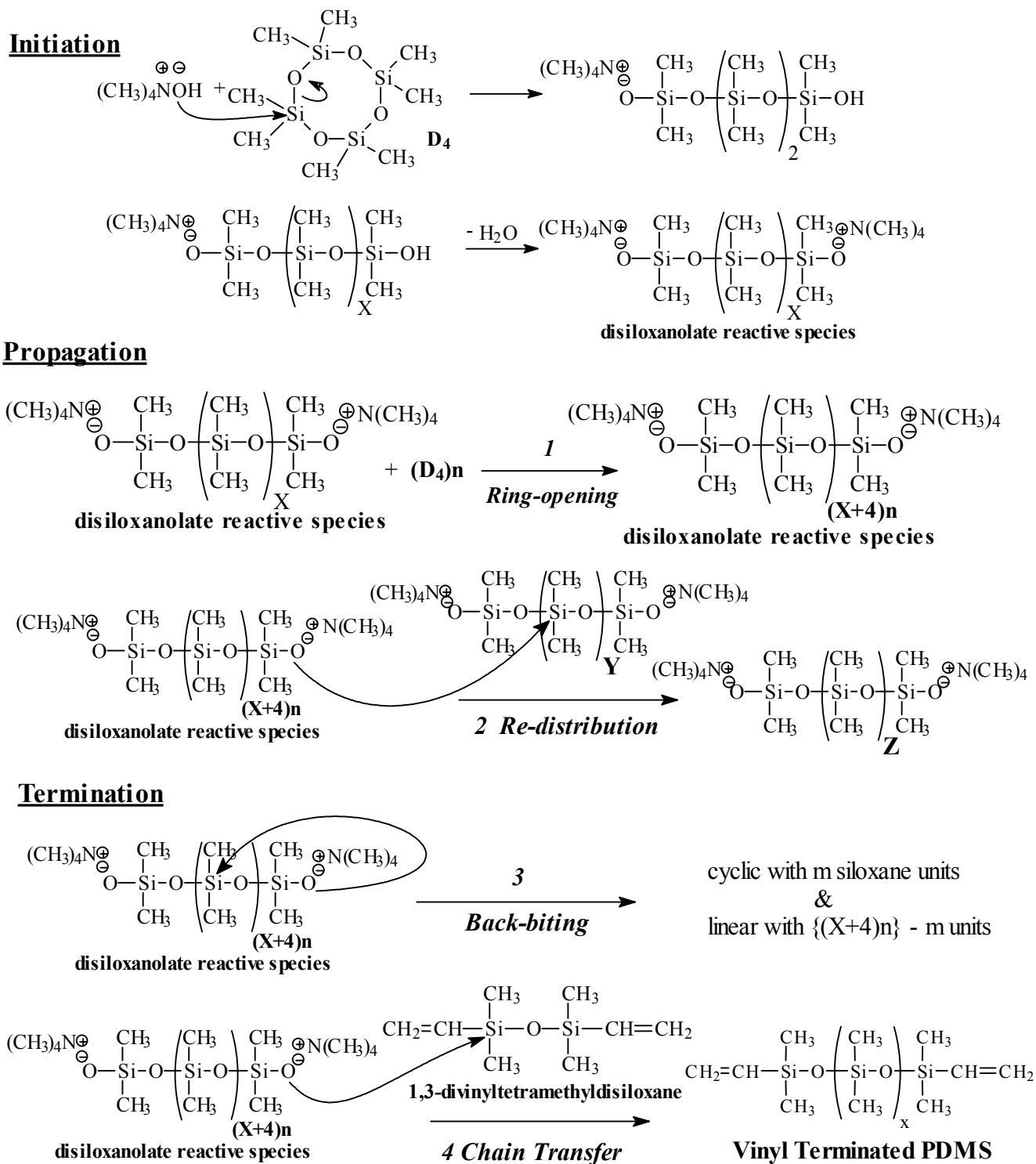
was the basic catalyst chosen for the equilibration of D₄ in the bulk (no solvent) to yield PDMS, and will be used in the following discussion and figures for the mechanism.

Once all of the base has completely reacted during the initiation step to yield tetramethylammonium siloxanolate reactive centers and silanol groups, the silanols can react by several pathways. The silanol groups can condense and evolve water by reacting with another silanol endgroup, can attack its own chain, or can attack another growing chain. (Figures 2.3 and 3.2).³¹ A moisture free catalyst is typically desired for the equilibrations of high molecular weight polymers since water (which will react to form silanols) is a known impurity which decreases the molecular weight.^{17a} Once a moisture free system is established, propagation of the D₄ proceeds with a large initial increase in the molecular weight and the viscosity of the solution.²³ Kantor's study suggests that the propagation step initially results in successive additions of discrete tetrameric dimethylsiloxane increments via siloxanolate chains attacking D₄ cyclics.^(23,32) This quick and steady increase in molecular weight typically occurs until about 60 – 70% conversion of the cyclics to linear chains, whereupon the molecular weight begins to decrease by a series of redistribution reactions and an equilibrium plateau is observed.¹⁵ Grubb and Osthoff demonstrated the kinetics of the equilibration of D₄ in the presence of hexamethyldisiloxane to be first order with respect to D₄ and to have a square root dependence on either KOH or its siloxanolate. This study was conducted by monitoring the vapor pressure above the equilibration mixtures and comparing them to known concentrations of D₄ and polymer.¹¹

A small dimeric unit (typically hexamethyldisiloxane) may be introduced at the beginning of the polymerization to serve as a chain transfer reagent and effectively endcap the siloxane chains. The siloxane bond was previously described as having partial ionic character, while a Si-C bond is mostly covalent. The siloxanolate reactive species attacks the siloxane bond of the dimer and will not react with the Si-C bond at the end of the chain under normal equilibration conditions. Controlled molecular weight polymers are therefore predicted by the molar concentration ratio of D₄ to the endcapping reagent, taking into account the equilibrium concentration of cyclics.¹⁵ In this study 1,3-divinyltetramethyldisiloxane was used as the endcapping reagent since vinyl terminated oligomers of controlled molecular weights were desired.

Figure 2.3

Mechanism for the Anionic Ring-Opening Polymerization of a Cyclic Siloxane Tetramer



The propagation mechanism first involves attack of the siloxanolate anion on: 1) the electropositive silicon atom of a cyclic tetramer (*ring-opening*) followed by a series of redistribution reactions involving the attack of the siloxanolate anion on: 2) the silicon atom of a growing chain (*re-distribution*) 3) a silicon atom within its own chain to form a new cyclic (*backbiting*) or 4) the silicon atom in the dimeric endcapping reagent (*chain transfer*) (Figure 2.3). After the initial increase in molecular weight of the linear siloxane chains, steps 2 through 4 (which only affect the longer chains) become increasingly important until an equilibrium between the rings and chains is established. Steps 3 and 4 are included in this discussion of propagation because they are included in the breaking and remaking of siloxane bonds, but they are actually termination steps. Step 3, backbiting is depolymerization, since the chain attacks itself and must shorten in length since it also forms a new cyclic. As mentioned above (step 4) chain transfer attacks the dimer and forms a new Si-C bond, which is essentially non-reactive towards the ionic reactive species. The chain is hence terminated once both ends are endcapped by this monofunctional dimer. The reaction is terminated by removing the reactive species once equilibrium is confirmed so that further depolymerization will not occur. In this case, the transient catalyst (described above) tetramethylammonium siloxanolate is decomposed by heating the solution above 130°C and bubbling N₂ through to remove the inert, volatile decomposition products. Therefore, it is important to follow the reaction to establish when thermodynamic equilibrium is attained (where the concentrations of the small cyclics and linear chains remains constant), to avoid removal of the reactive species too early during the equilibration.

Gel Permeation Chromatography, GPC, is one of the most common methods today for monitoring equilibration since the concentrations of small cyclics and the Gaussian distribution of linear chains can be established. GPC separates molecules based on their hydrodynamic volumes in a solvent by passing them through porous, polymeric beads. The larger molecules (linear chains) pass through the column first since they will not fit in the tiny pores inside the beads and therefore travel a shorter path.³³ This method for monitoring equilibrations of D₄ was first established by Brown and Slusarczuk.³⁴ The concentration of cyclics present at equilibrium generally does not depend on the target molecular weight of the newly formed chains, and is typically ~ 17% for PDMS.^(15,35,36)

Knowing how the equilibrium conditions are affected by the starting conditions (type of monomer, etc.) is obviously of substantial importance for defining the appropriate conditions which will favor the highest yield of the polymer.³⁷

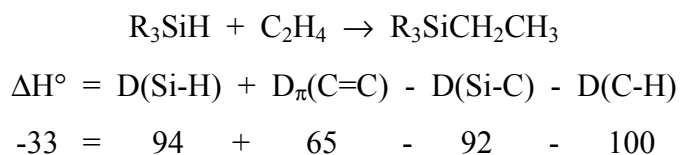
The work by Brown and Slusarczuk was used as the basis for extensive studies of the cyclic populations in equilibrated polymeric systems. Semlyen and coworkers made use of Jacobson and Stockmayer's equilibrium theory of macrocyclization³⁸ by relating the concentration of cyclics present at equilibrium to the statistical conformations of their respective open chains.^{17a} Jacobson and Stockmayer's theory showed that the concentration of cyclics increases with dilution, and 100% cyclics will result beyond a critical dilution.³⁸ Later, this theory was revised by Semlyen and Flory³⁹ who accounted for the larger than predicted amounts of unstrained cyclics D_4 and D_5 present at equilibrium. The rotational isomeric state theory of Flory, Crescenzi, and Mark has been used to interpret the conformation dependent properties of many synthetic polymers.^(35,36) The focus of this study involves the equilibrations of siloxanes with substituents of varied polarity which may be a major determiner of the concentration of cyclics remaining at equilibrium.

The percentage of cyclics remaining at equilibrium depends on both the size of the monomer, and also the size and polarity of the groups substituted on the silicon atoms of that monomer. The concentration of cyclics at equilibrium does not depend on the target M_n , although there is strong dependence on the type of monomer being equilibrated. A study supporting this was conducted by Wright and Semlyen.⁴⁰ They equilibrated a series of substituted R-methylcyclotetrasiloxanes, where R = H-, CH_3 -, CH_3CH_2 -, $CH_3CH_2CH_2$ -, and $CF_3CH_2CH_2$ - in the presence of base. None of the cyclic monomers in that study were strained. The only difference in the polymerizations was that the hydrogenmethyltetracyclosiloxane was equilibrated at a lower temperature (273 K) than the others (383 K). The cyclization data from that study corresponded to earlier work using intrinsic viscosities.^{17a} The percentage of small cyclics ($x = 3 - 6$) at equilibrium increased with the size and polarity of the substituent on the monomer as: R = H- (~ 6%), CH_3 - (~ 12%), CH_3CH_2 - (~ 20%), $CH_3CH_2CH_2$ - (~ 30%), and $CF_3CH_2CH_2$ - (~ 78%). This data suggested that as the size and/or polarity of the substituent on the monomer was increased, the conformational freedom of the resultant polysiloxane chains

decreased. This in turn led to a shift in the equilibrium toward increased concentrations of cyclics.^(40,41) This phenomenon will be discussed in this study when comparing the equilibrations of D₄ and D₄CN.

2.1.5 Hydrosilation of Vinyl Terminated Polyorganosiloxanes

Hydrosilation (or hydrosilylation) reactions involve the addition of a silicon-hydrogen bond across a carbon-carbon double bond (typically). This is most commonly catalysed by platinum catalysts or transition metal salts, although it may occur thermally or photochemically.¹⁰ This exothermic reaction forms new C-C σ -bonds from C=C π -bonds, with a $\Delta H^\circ = -33$ kcal/mole^(42,43):

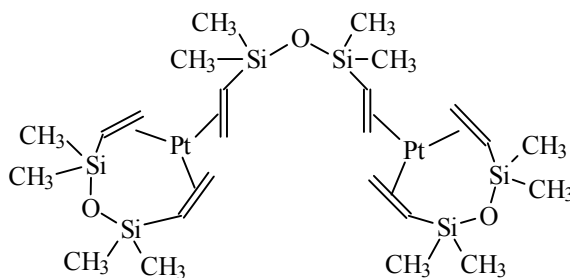


One technologically important feature of this reaction is that two molecules react to form a third molecule free of any by-products. It can yield crosslinked networks which are dimensionally stable without problems which generally arise from volatiles. One-component polysiloxane crosslinking reactions (condensation/displacement cures) generally cure upon contact with air, and release small volatile molecules such as water, methanol, or acetic acid. The hydrosilation reactions are referred to as two-component addition cure reactions. The first component is typically the vinyl containing component and catalyst mixture, while the second component is the hydride functional crosslinking reagent.⁽⁴⁴⁻⁴⁷⁾

The most common Pt catalysts are H₂PtCl₆ (Speier's catalyst), a homogeneous chloroplatinic acid catalyst in isopropanol with its active species being Pt(II)⁴⁸, and Pt⁰·1.5[(CH₂=CH(CH₃)₂Si)₂O] with a 2.1 – 2.4 weight % Pt conc. (Karstedt's catalyst), a complex of 1,3-divinyltetramethyldisiloxane with the active species being Pt(0).^(49,50) Speier's catalyst (introduced in the 1950's at Dow Corning) can result in long induction periods, solubility problems, and, being an acid, it can yield ring rearrangements. Karstedt's catalyst (introduced in the 1970's at GE)⁽⁵¹⁻⁵³⁾ can be used to overcome many of these problems. For example, Dvornic and Gerov compared the reactivities of Speier's and Karstedt's catalyst in an effort to synthesize high molecular weight polymers

(poly[(1,1,3,3-tetramethyldisiloxanyl)ethylene]) via hydrosilation of 1,3-dihydrotetramethyldisiloxane with 1,3-divinyldisiloxane. They found that Speier's catalyst generates HCl which attacked the growing polymers and caused desilation at the Si-C bonds. They could only obtain oligomers with Speier's catalyst, while Karstedt's catalyst enabled the hydrosilation reaction to proceed unobstructed and resulted in high molecular weight polymers.⁵⁴ Other interesting studies comparing Speier's and Karstedt's catalysts found that Speier's catalyst was less reactive, and it could produce yellow/brown products whereas Karstedt's did not under similar reaction conditions.^(55,56)

There are many excellent reviews for reactions employing Speier's homogeneous catalyst.⁽⁵⁷⁻⁶¹⁾ The focus herein will remain on Karstedt's catalyst⁽⁶²⁻⁶⁷⁾, although other interesting platinum catalysts do exist.^(68,69) Karstedt's catalyst has three vinyl siloxane groups bound to a neutral platinum (Pt(0)) and is highly reactive. Each Pt atom is capable of catalyzing several thousand cycles per minute. It was first synthesized in the 1970's by Willing of Dow Corning and Karstedt of G. E. by reacting chloroplatinic acid with 1,3-divinyldisiloxane to make silicone soluble platinum complexes:^(62,66)

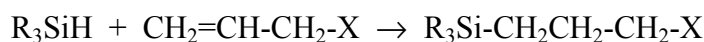


In general, a 1:1 ratio of vinyl:silane equivalents are reacted with Karstedt's catalyst at ppm levels due to its high reactivity.^{70a} Care must be taken to maintain an environment free of other carbon-carbon double bonded species which are not in the proposed reaction. It will strongly bind to compounds such as phosphines, amines and a variety of sulfur-containing compounds, which will form a catalytically inactive Pt species rendering it unreactive towards the desired reaction. Reaction temperatures can vary from less than 50°C (Room Temperature Vulcanizing (RTV)), between 50°C – 130°C (Low Temperature Vulcanizing (LTV)), and above 130°C (High Temperature

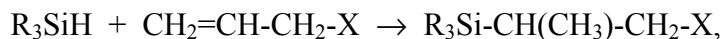
Vulcanizing (HTV)).⁷¹ Karstedt's catalyst was chosen for all hydrosilation reactions in this study and was not used above 95°C since degradation has been reported to occur above 100°C.⁷⁰ The mechanism for the hydrosilation process is not well understood. However, Figure 2.4 represents a proposed mechanism for a platinum catalysed hydrosilation cycle.^(60,66,67,72)

Hydrosilation is typically used to form new C-C σ -bonds from C=C bonds, although other double bonds such as C=O, C=N, or even alkynes have been reported to react with silane in the presence of a catalyst. Reagents in hydrosilation reactions should be free of impurities and moisture. There are five main side reactions associated with hydrosilation reactions.¹⁰

1. α and β addition of the silane to the alkene:
 - a. β - or anti-Markovnikov addition (normal addition):

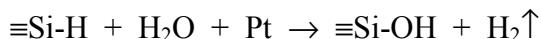


- b. α - or Markovnikov addition (reverse addition):



where the reverse addition product generally yields 0 – 20% of the product, and the ratio of α to β products depends on the structures of the silane, alkene, and catalyst employed in the reaction.

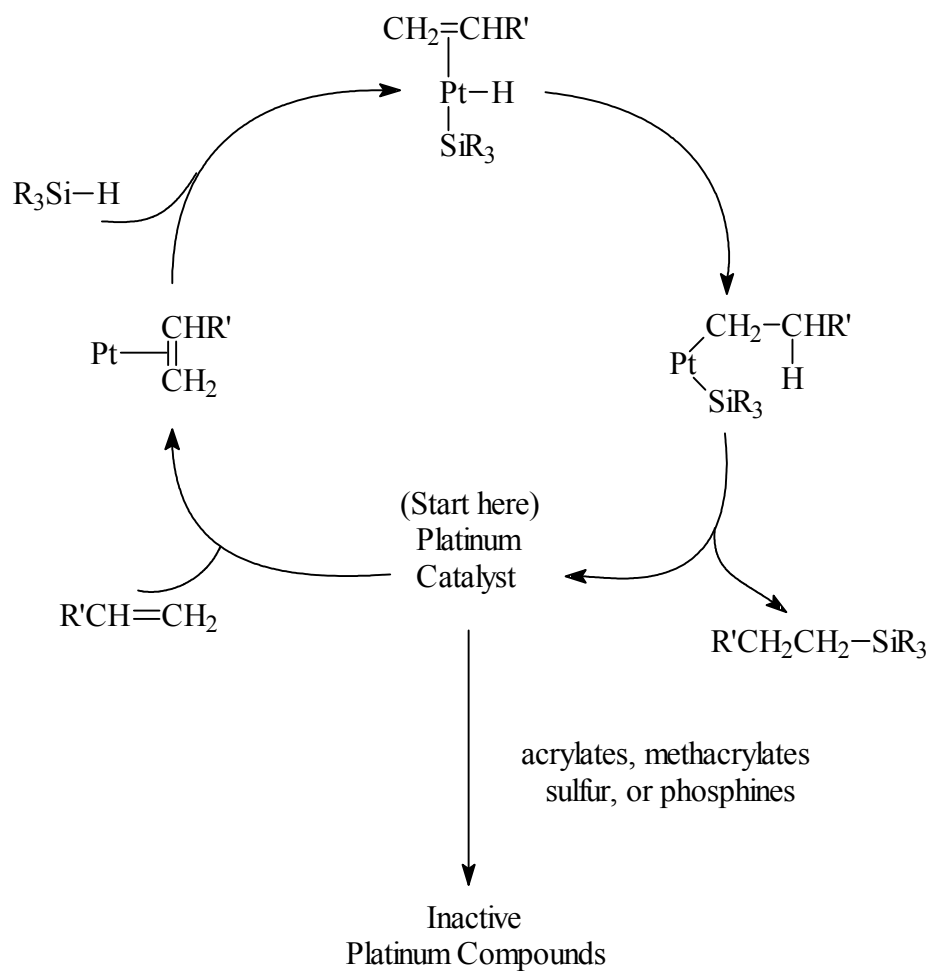
2. Isomerization of the alkene (typically internal alkenes) when the silane is added too slowly.
3. Reaction of the silane with protic species, especially alcohols or water (for hydrosilations with α,ω -dihydrosiloxanes). Side reactions may occur in the presence of protic solvents or with the alcohols present in hexachloroplatinic acid (Speier's catalyst). This side reaction is most noted when the concentration of the (desired) reactive silane is low.¹⁰

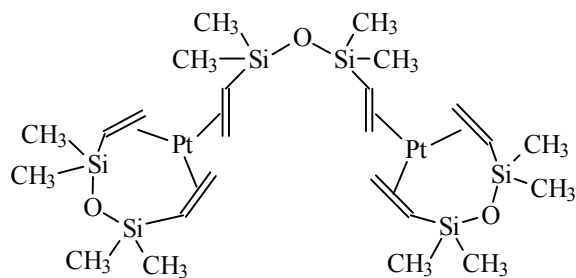


Macosko and Benjamin have qualitatively confirmed this side reaction by detecting the evolution of H_2 . Using FTIR, they quantitatively found that this side reaction occurred at a much slower rate (relative to the addition reaction between the C=C double bond and silane) and it typically consumes about 5 – 10% (confirmed by sol-fraction tests) of the Si-H.⁷³ Gorshov and co-workers found that less Si-H was consumed when hydrosilating

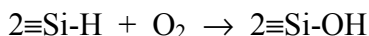
Figure 2.4

Proposed Mechanism for a Catalytic Cycle for Platinum Catalysed Hydrosilation

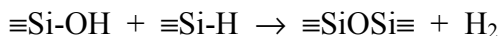
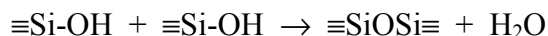


$$\text{CH}_2=\text{CH}-\text{Si}(\text{CH}_3)_2-\text{O}-\text{Si}(\text{CH}_3)_2-\text{CH}=\text{CH}_2 + \text{H}_2\text{PtCl}_6 \rightarrow \text{Karstedt's Catalyst:}$$


systems were heated in a press rather than in an air oven, leading them to surmise that side reactions also involving air (and moisture above) occur.⁷⁴



Both Hickey and Gorshov's group found that side reactions between the silane and resultant silanols can occur.



However, the rates are so slow that generally all Si-H is consumed before this happens.^(74,75) Although excess Si-H is sometimes suggested to ensure a fully cured system, it has been found that this excess can be disadvantageous. Quan explored the properties of postcured crosslinked siloxane networks, and showed that the presence of excess Si-H in networks could undergo further reactions with moisture and resulted in significant changes in the networks. This was clear at elevated temperatures, $\sim 150^\circ\text{C}$, in air (and slowly at lower temperatures), and could potentially affect the networks' long-term aging properties.⁷⁶

4. Disproportionation of the hydrosiloxane during hydrosilation has been reported. Chain branching reactions leading to the formation of small amounts of high molecular weight side product have been found when using Speier's catalyst in reactions with α,ω -dihydrosiloxanes.¹⁰

5. Metal-catalysed Si-C bond cleavage can occur at elevated temperatures when using platinum metals and some of its derivatives.¹⁰

There are many interesting reviews available which include hydrosilations of PDMS polymers with vinyl functional groups (either on the ends or along the chain) to yield networks. Hydrosilation reactions can yield model networks when both pendant and terminal vinyl groups are systematically reacted, which lead to materials for investigating theories of rubber elasticity. Macosko, Benjamin, and Saam have investigated hydrosilation side reactions, and also hydrosilated vinyl terminated PDMS polymers to yield networks for testing several theoretical relations for the small strain modulus of rubber.^(73,77,78) Valles and Macosko have done similar studies while using FTIR for the kinetic study of hydrosilation reactions of PDMS.⁷⁸

Sharaf, Mark, and Alshamsi have studied the small-strain moduli of PDMS networks (in the absence of hydrosilation side reactions) with high functionality crosslinks. These networks were prepared by hydrosilating vinyl terminated PDMS chains with highly functional (with Si-H units) PDMS oligomers.^(79,80) They found the networks at small strains had elongation moduli which greatly exceeded values predicted by the Flory-Erman theory. They believed this was due to both network imperfections and the role which short chains between crosslinks along the junction precursor play (which can also act as short network chains). These short chains between the silane functional sites gave the network a bimodal character and offered an explanation for departure from the expected values. The ultimate network properties improved with the bimodal networks as the short chains limited the extensibility, while the longer chains retarded the rupture process. Their studies offer examples of the wide applicability of the theories of elasticity for elastomeric PDMS networks.⁽⁷⁹⁻⁸¹⁾ Several other excellent references involving the hydrosilation of PDMS⁽⁸²⁻⁸⁷⁾, and also a method for the preparation of higher molecular weight hindered amine light stabilizers (HALS) via hydrosilation exist.⁸⁸

In summary, the hydrosilation mechanism for yielding functional monomers or model networks has been an excellent versatile route for producing a wide range of products with varied properties. Its only drawback is that it can only be used in two-component addition reactions (two-pack). One-pack formulations are generally more convenient since no mixing is required, and thus hydrosilation formulations via encapsulation of the platinum catalyst are under investigation.⁶⁸ Ideally, this system will be one where the “capsule” is impermeable to reactants at room temperature, and would not release the platinum (via breaking down or melting) until the desired crosslinking temperature.

2.2 PDMS Network and Sealant Studies

The primary function of a sealant is to seal holes and gaps between other engineering materials, while the secondary requirement is to adhere to the corresponding substrates (adhesive sealants).⁸⁹ Siloxanes are the choice materials for sealing applications in the world market today since they offer good combinations of physical

strength, cure rate, performance over a wide service temperature range, adhesion, sealability and weatherability.⁴⁷ Their drawbacks include “dirt-pickup”, low tear strength and sometimes “nonpaintability” and high prices.⁸⁹ The focus of this study is to compare a series of polyorganosiloxane networks based on the polarity of their substituents along the siloxane backbone and the length of these chains. A novel nitrile containing polyorganosiloxane (PCPMS) network will be introduced as a potential sealant, more specifically for aircraft applications such as fuel tanks. Although pure PDMS polymers and their networks are not generally used for this purpose due to their high propensity for swelling in hydrocarbon fuels, they are important as a comparison. PDMS is by far the most widely studied polysiloxane, making it a good control material to improve upon. The general network properties required for a good sealant (Table 2.6)⁴⁷ include good tensile, thermal, swelling, and adhesive properties. A summary of specific properties of siloxane sealants is also provided (Table 2.7).⁴⁷ The major market for silicone sealants include structural glazing, construction, consumer household products, highway, aerospace, fuel containment, appliance, industrial, and specialty areas.⁸⁹ Section 2.3.1 will focus primarily on requirements for fuel tank sealants.

2.2.1 Tensile and Thermal Properties

Tensile properties for the networks include strength, modulus, and percent elongation at break. Tensile strength is the maximum load or force per unit cross-sectional area within a sample’s gauge length, and is the maximum strength at break.⁸⁹ For silicone rubbers, their ultimate tensile strengths generally range from a few hundred to ~1500 psi (~ 1 – 10 MPa).⁵ Siloxanes generally have lower tensile strengths at room temperature than other organic polymers.¹ For rubbers, the moduli reported are the stress required to produce a certain elongation (a measure of the stiffness).^(5,89) Young’s modulus is the initial ratio of the stress to the strain produced in a sample that is elastically deformed. Elongation at break is the fractional increase in the sample’s length when stressed in tension to rupture, and often expressed as percent elongation (the elongation of the original gage length expressed as a percentage).⁸⁹ Ultimate elongations of silicone rubbers depend on the type of siloxane network being tested and the process

Table 2.6

Considerations Required for Choosing a Good Sealant

Checklist for Sealant Selection⁴⁷

Joint movement needed

Minimum joint width

Strength needed

Chemical environment

Temperatures to be experienced in service

Temperatures at time of application

Intensity of sun and weather the sealant will see

Longevity

General climate at application time

Materials cost – initial and lifetime

Installation cost

Other considerations:

 Fungicides

 Radiation resistance

 Insulating or conductive

 Color

 Intrusion or abrasion resistance

 Cure rate

 Below-grade or continuous water immersion

 Accessibility of joint

 Priming

 Special cleaning

 Dryness

 Other restrictions

Table 2.7Summary of Sealant Properties for Silicones^{a47}

Properties	Silicones	
	One Part	Two Part
Movement ability in % of joint width (recommended maximum joint movement)	±25% to +100% to -50%	±12.5% to ±50%
Life Expectancy, years ^b	10 – 50	10 – 50
Servic temperature range: °F (°C)	-65 to +400 (-54 to +200)	-65 to +400 (-54 to +200)
Recommended application temp. range, °F ^c	-20 to +160	-20 to +160
Cure time to a tack-free condition, hour	1 – 3	0.5 – 2
Cure time ^d to specified performance, days	5 – 14	0.25 – 3
Shrinkage, %	0 – 5	0 – 5
Hardness, old (5 yr), a scale at 75°F	15 – 40	15 – 40
Resistance to extrusion at low temp.	low	low
Primer required for sealant bond to:		
Masonry	no	yes
Metal	...	no
Glass	no	no

a: Data from manufacturer's data sheets: U. S.-made sealants are generally considered.

b: Affected by conditions of exposure.

c: Some sealants may require heating in low temperatures.

d: Affected by temperature and humidity.

(and possibly postcure) used to cure it. This can be as high as over 1000% for certain siloxane networks.⁵

The tensile properties of siloxane rubbers do not depend on temperature as strongly as most other organic polymers. Siloxanes are also known for their chemical stability at high temperatures and for their low-temperature flexibility (low T_g s). As discussed earlier, these excellent properties are a result of the long siloxane bonds coupled with low energy barriers for rotation, and strong partial ionic character of siloxane bonds.^(1,7) Polydimethylsiloxanes have a T_g of -123°C , and can be heated in air for one year or more between $160 - 205^\circ\text{C}$ without significant changes in their properties.¹ They can also maintain their tensile properties at higher temperatures (between $205 - 345^\circ\text{C}$) for short periods ranging from several hours to months.¹ Their superiority over most organic materials is clear at higher temperatures since organic polymers would degrade and decrease in strength if heated for weeks at 125°C .¹ Table 2.8 shows the thermal aging properties of a representative RTV silicone sealant.⁸⁹ Another interesting property which both PDMS liquids and solids possess is their ability to significantly lower fire hazards when burned. An inorganic silicon surface layer can form during burning, which reduces the burning and heat release rates. This makes siloxanes good candidates to replace polychlorinated biphenyls (PCBs, environmental hazards) in fluid-filled transformers, or for applications as fabric coatings and cable insulation where fire safety is an issue.^{70b}

Siloxanes also have excellent weatherability against UV radiation and ozone.¹ These properties are attributed to the inorganic character of the siloxane backbone which does not absorb UV radiation. Their lack of unsaturation is one reason for this.⁸⁹ Siloxanes surpass most organic-type sealants in ozone resistance by maintaining their performance after 50,000 hours in an ozone rich atmosphere. Silicone sealants are even used to seal the test chambers of “weather simulating” machines. Siloxanes are capable of surviving 6000 – 20,000 hours in a weatherometer with almost no change in properties relative to typical organic sealants which survive only 500 – 1000 hours of exposure. This inherent inertness is one factor which allows siloxanes to excel in outdoor applications.^(46,47) It should be noted that because silicone sealants are transparent to UV radiation, the underlying surfaces will not be protected from sunlight. If this surface is

Table 2.8

The Thermal Aging Properties of an Extremely High-Temperature RTV Siloxane Sealant

Property	Original Properties	After 168 h at 250°C	After 168 h at 315°C	After 336 h at 315°C
Shore A, hardness	33	28	45	65
Tensile Strength, MPa (psi)	2.4 (350)	2.7 (390)	2.9 (420)	3.3 (475)
Elongation, %	400	540	300	180

susceptible to attack, it may degrade and the sealant/substrate bond can fail. In this case, either the surface must be protected or a filled silicone sealant should be used.⁴⁷

The various types of silicone sealants available commercially cover a wide range of tensile properties (ASTM D412). They typically have tensile strengths between ~ 0.7 MPa – 7 MPa (~ 100 – 1000 psi), moduli at 100% extension from <0.35 MPa – 3.5 MPa (<50 - 500 psi), and ultimate elongations 50% - 1200%. Since the tensile properties of siloxane networks depend on the molecular weights of the precursors and crosslink densities, a siloxane sealant can be tailored to a desired application without affecting other properties such as weatherability or thermal stability. Silica fillers are often used to improve the mechanical properties of siloxanes, without affecting their T_g . Natural rubbers and other elastomers experience an increase in their T_g as filler is added. The mechanical behavior of filled siloxane elastomers depend strongly on the nature of the filler particles.¹⁰ A non-filled crosslinked PDMS elastomer has a tensile strength of about 20 psi, although when $\sim 15\%$ of a highly functional silica filler is added, a 30-fold increase (tensile strength >600 psi) is observed.⁴⁶ Significant improvements on the tensile strengths and elongations of siloxane sealants have been made since the 1950's (Table 2.9).

Sealants can be categorized in terms of high or low strength materials. High strength sealants are used in aerospace applications. Low strength (extremely high elongation) sealants are used in the construction industry where low-modulus sealants require long-term adhesion to concrete in building and expansion joints.⁸⁹ Siloxane sealants may also be defined as high, medium, or low modulus materials. Generally, high modulus sealants are required for adhesive applications, medium modulus sealants are used for general sealing and glazing, while low modulus sealants (with very high elongation) are used for applications such as expansion or highway joints.⁴⁶

Klosowski and Shisler have studied the tensile properties of various sealants to determine whether they are the same when stressed in both tension and shear. They stressed the sealants in the tension mode and two shear modes (longitudinal and transverse). The silicone sealants had approximately the same shear stresses in both directions and much lower stress values than in the tension mode at the same elongation. They found that silicone sealants had higher elongations and performed better when

Table 2.9

Improvements of Siloxane Sealants Since the 1950's

Physical Properties of the Early Two-Component RTV Silicone Sealants⁸⁹

<u>Property:</u>	<u>Value:</u>
Shore A, hardness.....	15 – 70
Tensile Strength, MPa (psi).....	0.7 – 6.2 (100 – 900)
Elongation, %.....	80 – 200

Typical Strength and Elongation Properties of RTV Silicone Adhesive Sealants⁸⁹

<u>Property:</u>	<u>Low Strength</u>	<u>Medium Strength</u>	<u>High Strength</u>
Shore A, hardness.....	10 – 30	20 – 70	25 – 60
Tensile Strength, MPa.....	0.7 – 1.7	1.7 – 4.1	4.1 – 8.3
(psi).....	(100 – 250)	(250 – 600)	(600 – 1200)
Elongation, %.....	100 – 1200	80 – 700	300 – 1000
Tear Strength, kN/m.....	1.75 – 5.3	3.5 – 14	14 – 22/44

pulled in shear. They then calculated the allowable shear movements for the sealants together with the tensile modulus properties.⁹⁰

Many reviews on tensile properties of PDMS networks are available.^(62,73,78-83,90-102) These materials have also been used as models to test and extend the theories of rubber elasticity. Affine and phantom networks are the two hypothetical networks used to describe the Gaussian theories of rubber elasticity. Phantom networks represent free movement of chains which are not restricted by their neighboring chains, as if the chains could pass through one another during movement. The chains in affine networks are assumed to be restricted by their neighboring chains, where network junction sites are firmly embedded in the network. Model networks have network chain dimensions which are said to change affinely (linearly) with macroscopic changes in the sample dimensions. Linear changes are not observed when considering phantom networks with random crosslink sites.⁷⁹ Opperman and Rehage studied the equilibrium moduli of PDMS networks having comb-like crosslinks.⁹¹ They found that networks with high branching densities had moduli three times greater than calculated from the theory of phantom networks. Also, the moduli decreased with decrease in the degree of branching and approached the expected value calculated from the phantom theory. This explained a transition between the phantom and affine limits of more complex comb-like networks differing from networks with tetrafunctional junctions.⁹¹ Another study on the equilibrium tensile behavior of model silicone networks having high junction functionality was done by Meyers and Merrill.⁹² They found that the stress-strain behavior of highly functional PDMS networks differed from calculations using Flory's theory of rubber elasticity. Good agreement with the experimental data was found using the small-strain theory of Langley and Graessley.⁹² Other recent studies of the elastic moduli and equilibrium swelling of PDMS networks imply that trapped entanglements are formed by the introduction of crosslinks, which influence the moduli considerably.^(93,94) Theories of rubber elasticity were also studied by Wang⁸² and by Bontems⁶² using PDMS networks.

Macosko^(73,78,83,95,96) and Mark^(79,97) have designed model PDMS networks to study how the networks behave under load and to test theories of rubber elasticity. These studies were extended further by Mark who investigated networks prepared from

mixtures of short and long PDMS chains. These had bimodal distributions of chain lengths between crosslink sites.⁽⁹⁸⁻¹⁰⁰⁾ These bimodal networks had improved network properties relative to monomodal networks and were used to describe the constrained junction theory. According to this theory, the affine modulus of real networks lies between the affine and phantom limits, even in the undeformed isotropic state.⁸⁰ The short chains were important in that they limited chain extensibility (imparting strength), and the long chains were reported to inhibit the growth of “rupture nuclei” making higher elongations possible.⁹⁸ These bimodal networks increased the ultimate strength of the PDMS networks without the usual corresponding decrease in maximum elongation. Short PDMS chains (220 g/mole) were systematically added to longer PDMS chains ($M_n \sim 18,500$ g/mole). This short chain reinforcing effect led to an increase in E_r (energy required for rupture) by a factor of ~ 5 as the amount of short chains was increased from 0 to 90 mole %. A 90 mole % increase of short chains corresponded to only a 9.7 weight % increase. The samples generally broke at 80% elongation.⁹⁹ In another study by Mark, PDMS oligomers with M_n s of 1100 g/mole and 18,500 g/mole were used to prepare bimodal networks.⁹⁸ These samples also had typical % elongations of $\sim 80\%$.⁹⁸ This was an important discovery both theoretically and technologically, in order to achieve ultimate properties significantly better than those of the most commonly studied monomodal networks.¹⁰⁰ Yanyo studied tear energies of siloxane elastomers using bimodal PDMS networks (of 20,500 g/mole and 930 g/mole).¹⁰¹ This bimodal network was prepared as a blend to have the same average M_n as a monomodal PDMS network prepared from a 6800 g/mole PDMS which they compared it to. Evidence of enhanced tensile strength was found which supported Mark’s work. In fact, these bimodal networks ($T_0 = 50$ N/m) had 70% higher tearing strengths (T_0) relative to the monomodal networks ($T_0 = 30$ N/m) at threshold conditions.¹⁰¹ Sharaf studied the small-strain moduli of elastomeric PDMS networks formed with highly functional precursors.⁽⁷⁹⁻⁸¹⁾ He performed similar experiments using bimodal PDMS networks with Mark.¹⁰²

2.2.2 Swelling Resistance and PMTFPS

The goal of this study was to synthesize a novel, polar network and compare it to the well studied, nonpolar PDMS and increasingly industrially important, polar PMTFPS

elastomers. The Dow Corning Corp. has been investigating fluoroelsilicone elastomers for some time, and has graciously donated all of the fluorine containing siloxane materials for this study. One current area of industrial interest, fluorine containing elastomers and PMTFPS elastomers, will be included here since they have a major advantage over PDMS in their excellent resistance to swelling in particular solvents. Nitrile containing siloxanes have only been sparingly studied, and will be discussed in section 2.4 (nitrile containing organosiloxanes).

The swelling of networks by diluents is related to intermolecular or cohesive forces of the polymers. Generally, noncrystalline polymers swell in solvents having the most similar solubility parameter (δ) in solvents where specific interactions exist.¹⁰³ In the 1940's, Gee's investigations of the swelling of natural rubber led him to propose that maximum swelling occurs in a solvent of the same Hildebrand solubility parameter (δ) as the polymer.^(104,105) Similar studies were applied to siloxanes by Yerrick and Beck.¹⁰³ They placed PDMS elastomers in several solvents with varied solubility parameters to find the solubility parameter of the elastomers. The solubility parameter of the solvent which swelled the network to the highest extent was then used to describe the approximate δ value for the elastomer. They characterized PDMS [$\delta = 7.5 \text{ (cal cm}^{-3})^{1/2}$] and PMTFPS [$\delta = 9.6 \text{ (cal cm}^{-3})^{1/2}$] using this method. Recently, similar solubility parameters were reported for PDMS [$\delta = 7.6 \text{ (cal cm}^{-3})^{1/2}$] and PMTFPS [$\delta = 8.8 \text{ (cal cm}^{-3})^{1/2}$] using the Flory-Erman constrained junction theory.⁽¹⁰⁶⁻¹⁰⁸⁾ The δ values for copolymers of poly(dimethylsiloxane-co-methyl- γ -cyanopropylsiloxane) varied between 7.5 – 11 $\text{(cal cm}^{-3})^{1/2}$ depending on the concentration of the cyanopropyl groups.¹⁰⁹

Copolymers containing crystalline blocks typically offer greater solvent resistance relative to completely amorphous polymers. This was illustrated by Razzono who compared block versus random copolymers of diphenyl and methyltrifluoropropyl siloxanes. A silica filled block copolymer, poly(diphenylsiloxane-b-methyltrifluoropropyl-b-diphenylsiloxane) with 80% methyltrifluoropropylsiloxane, swelled to 39 volume % in toluene, whereas the same bulk composition random copolymer swelled to 139 volume %.¹¹⁰

Siloxanes are known for their hydrophobic nature. They are even resistant against steam up to 30 psi, but when siloxane rubber is exposed to steam at very high

temperatures for prolonged periods it may be destroyed. PDMS elastomers should be freed of all acidic or basic residues and peroxide catalysts to be used at high temperatures since the Si-O bond is susceptible to attack by either acids or bases, and the pendent groups are susceptible to oxidative damage. Platinum catalyzed addition cures are preferred over the peroxide cures when the elastomer will be subjected to water or steam in their applications, since they are generally free of an acid or base; and do not produce byproducts. Moisture, sunlight, ozone, oxygen, bacteria, fungi, and soil chemicals do not affect the material properties of the siloxane elastomer substantially.⁵ PDMS and polymethylphenylsiloxane elastomers are resistant to mineral oils to a greater extent than polychloroprene at higher temperatures. Siloxane rubbers do not perform well in aromatic oils, especially above 150°C. The extent of swelling also decreases with increasing network molecular weight (precursors). Certain additives such as fillers may also be added to improve swelling properties.¹ When solvent resistance is a concern, fillers are important to obtain a tighter network.⁵ In general, polar siloxane elastomers are resistant to nonpolar fuels and hydrocarbons. By contrast, nonpolar siloxanes swell to much greater extents in organic solvents such as gasoline, aliphatic, and aromatic hydrocarbons, and chlorinated hydrocarbons.¹¹¹ Table 2.10 represents swelling data for some common elastomers in a variety of deleterious solvents.⁵

Siloxanes modified by special substituents have unique solvent resistance properties. Organofunctional siloxanes with polar substituents exhibit much lower swelling in gasoline, benzene, and nonpolar solvents. Silicone elastomers prepared from oligomers where poly- γ -trifluoropropyl¹¹², β -cyanoethyl, and γ -cyanopropyl¹¹³ groups partially replace some methyl groups of dimethylsiloxanes have been found to generally improved solvent resistance.¹ Fluoroelastomers such as Viton[®] (a fluorine containing hydrocarbon, polyvinylidene fluoride) and nitrile containing siloxanes exhibit less swelling in common technical lubricants and fuels, although their heat stability is somewhat inferior to PDMS elastomers.⁽¹¹⁴⁻¹¹⁶⁾

Fluorine containing siloxanes are the result of partial or complete replacement of methyl groups in PDMS by fluorine containing side groups. They exhibit decreased solubility and surface activity in most nonpolar solvents due to the electronegative

Table 2.10

Swelling Data for PDMS Rubber Relative to Those of Other Common Organic Rubbers

Silicone Rubber Compared With Other Synthetic Rubbers in Their Resistance to Some Common Deleterious Fluids⁵

(Values are expressed as % volume swell after 3-day immersion)

Solvent	Temp. (°C)	MQ	FVMQ	Nitrile Rubber	Acrylate Rubber	Neoprene®	Viton B®
Organic							
Acetone	all 25°C	15	181	130	250	40	300
Benzene		175	27	100	350	290	12
70/30 Isooctane/Toluene		200	22	22	40	75	2
Ethyl acetate		175	140	105	250	60	280
Methylene chloride		150	150	300	300	150	25
Ionorganic							
Hydrochloric acid (conc.)	25	5	8	11	det.	4	1
Nitric acid (conc.)	25	-10	4	det.	det.	det.	4
Sulfuric acid (conc.)	25	det.	det.	det.	det.	det.	4
Sodium hydroxide (50%)	25	-1	1	0	det.	2	0
Steam	149	+2	-2	-	-	-	-
Functional							
ASTM Oil #3	149	49	4	10	16	-	3
MIL-L-7807 Lubricant	204	31	13	-	-	-	10
OS-45 Hydraulic fluid	204	80	13	-	-	-	3

Adapted from the Vanderbilt Rubber Handbook 11th Edition, p. 200.

MQ = Dimethyl Silicone Rubber

FVMQ = Fluorine Containing Vinyl-Methyl Silicone Rubber

Viton B® = DuPont Fluorocarbon Elastomer, a terpolymer polymerized using vinylidene, hexafluoropropylene, and tetrafluoroethylene

fluorine atoms (relative to hydrogen), strong CF bonds, and greater inaccessibility of the polymer backbone. The fluorosiloxane terminology refers to CF₃ groups on a siloxane chain, not Si-F bonds which are unstable. The CF₃ groups placed directly on a siloxane chain would also be hydrolytically and thermally unstable. A hydrocarbon spacer is required, and the substituent is usually -CH₂CH₂CF₃. PMTFPS was originally introduced in the 1950s and remains the most widely available fluorosiloxane due to its excellent solvent resistance and good thermal stability. The precursor is typically synthesized via hydrosilation of 3,3,3-trifluoropropene with dichloromethylsilane using a platinum catalyst (either Speier's or Karstedt's catalyst described above).¹¹⁷



PMTFPS is synthesized by hydrolysis of the resultant silane, methyl(3,3,3-trifluoropropyl)dichlorosilane, followed by condensation of the newly formed silanol oligomers. Ring opening polymerizations of the cyclic trimer with methyl(3,3,3-trifluoropropyl) groups are used when high molecular weights are desired, due to their living anionic nature.¹¹⁷ The corresponding cyclic tetramer is too stable for ring-opening, and typically yields only ~18% polymer (82% cyclics) at equilibrium when opened with KOH at 383K. This equilibrium, which lies preferentially towards the cyclics side, is due to the larger and more polar nature of the 3,3,3-trifluoropropyl substituents. PMTFPS networks can be produced by hydrosilation additions, condensation reactions, peroxide induced free radical reactions, or in some cases UV initiated reactions. Hydrosilation cures of vinyl containing PMTFPS are ideal in that no by-products are formed and void-free networks are produced.¹¹⁷

PMTFPS elastomers have T_gs of ~ -75°C with no low-temperature crystallization (PDMS crystallizes at ~ -40°C). This 50°C higher T_g value for PMTFPS relative to -123°C for PDMS is attributed to the much more bulky trifluoropropyl groups. These materials are thermally stable up to 200°C for 1350 hours with a 40% reduction in tensile strength, 15% reduction in elongation and a two-point reduction in durometer hardness.¹¹⁷ They are best recognized for their excellent solvent resistance against jet fuels, hydrocarbons, and oils, etc. (Table 2.11) whereas higher swelling is found in the presence of ketones and esters.¹¹⁷

Table 2.11

Swelling Data for a PMTFPS Network.

Fluid and Chemical Resistance (ASTM D 471)¹¹⁷

Fluid	Immersion Conditions	Hardness Change (points)	Volume Change (%)
ASTM No. 1 oil	3 days/150°C	-5	0
Crude oil 7 API	14 days/135°C	-10	+5
JP-4 fuel	3 days/25°C	-5	+10
ASTM Ref. Fuel B	3 days/65°C	-5	+20
Benzene	7 days/25°C	-5	+25
Carbon tetrachloride	7 days/25°C	-5	+20
Methanol	14 days/25°C	-10	+4
Ethanol	7 days/25°C	0	+5
Hydrochloric acid (10%)	7 days/25°C	-5	0
Nitric acid (70%)	7 days/25°C	0	+5
Sodium hydroxide (50%)	7 days/25°C	-5	0

Elastomers prepared from vinyl terminated fluorosiloxanes are generally more solvent resistant than elastomers prepared from vinyl terminated dimethylsiloxanes (with a few exceptions). Some exceptions are mentioned here. When immersed in acetone at room temperature for 7 days, a PDMS network swelled 15 volume %, relative to 180% for a fluorosiloxane network. Other solvents which swell fluorosiloxane networks include ammonia, ammonium hydroxide, ethylene oxide, monoethanolamine, glacial acetic acid, ethyl and methyl alcohol, and certain hydraulic fluids such as Skydrol[®] (a phosphate ester fire resistant aircraft hydraulic fluid).⁵ Fluoroelastomers are often blended with dimethylsiloxane to improve some of the properties which PMTFPS lacks relative to PDMS elastomers. Swelling of this type of hybrid network was, however, unacceptably high in fuels. Gentle received a patent on a blend of a fluorocarbon elastomer modified by amorphous polydiorganosiloxane resins, and found high solvent resistance and low fuel permeability. These fluoroelastomers were Tecnoflon[®] poly-fluorinated ethers and Viton A[®] (vinylidene fluoride, hexafluoropropylene dipolymer).¹¹⁸

The maximum swelling ratio (Q_M) can be related to elastic moduli as a linear function.¹⁰ Many good reviews are available on relating equilibrium swelling properties to the elastic moduli of model PDMS networks. Trapped entanglements caused by crosslinking increase the modulus considerably.^(91-94,98,119)

Solvent extractions can be used to determine sol fractions of cured networks. This entails extracting the network with a solvent for the precursor polymer, removing the network from the solvent and drying it. Any difference in weight is considered the sol-fraction.^(62,73,120,121)

2.2.3 Adhesion Studies

Sealants are materials used to prevent leaks and adhesives are used for holding substrates together, but their chemical compositions can be similar. Adhesives can be high tensile and shear strength replacements for mechanical fasteners in load-bearing applications. Sealants can have lower strengths and increased flexibility as long as they prevent the passage or entry of designated gases and liquids. For most sealant applications good adhesion to the substrate is important for maintaining a good seal. A sealant should first flow and fill voids, and thereby conform completely to surface

irregularities.⁸⁹ This study focuses on novel, polar PCPMS networks as potential fuel tank sealants. Good adhesion to metal adherends should be coupled with good fuel resistance and a wide service temperature range.

One fundamental property of an adhesive is its failure mode, either adhesive or cohesive. A bond that fails adhesively is undesirable since it occurs between the adhesive and substrate. Cohesive failure within the adhesive is normally desirable since the adhesive does not separate from the substrate. One notable exception is that adhesive failure is frequently the desired failure mode for pressure sensitive adhesives (PSAs). An example is the “Post It Note[®]” which has weak adhesive bond strength and may be removed easily from the substrate.⁸⁹ If a sealant separates from the substrate adhesively, deleterious liquids may easily penetrate through the weak interface until total leakage occurs.⁴⁷

Another important consideration is to optimize the adhesion of the specific substrate for the application. Primers may be used on substrates to improve adhesion of sealants. For aerospace applications, corrosion inhibiting primers such as phosphoric acid anodization or etching treatments may be used. These methods grow a small, porous oxide layer on the substrate which is tenaciously adherent to the metal. This oxide layer, which is present on aluminum and titanium adherends used for fuel tanks, contains polar hydroxyl groups which are more likely to bond strongly to sealants prepared with polar substituents along the polymer backbone.⁸⁹ Silane functional adhesion promoters are also often used with vinyl functional siloxanes, since these are often compatible with both the substrate and resinous sealant.⁸⁹

Another route to improving adhesion to metal surfaces is to optimize the surface preparation of the substrates. Improvements in adhesion can often be invoked by mechanically abrading metal surfaces. Roughness, with depths on the order of tens of nanometers, can be beneficial. When abrasion is coupled with a chemically compatible substrate, even greater improvements can be obtained. When polar interactions are coupled with the small but real van der Waals forces, along with chemical bonds from adhesion promoters, the surface makes an ideal substrate.¹²² It is for this reason that the novel polar PCPMS elastomers should make good adhesive-sealants.

Sealant repair can also be important. This requires that the old sealant must be removed and replaced. Many organic sealants have similar adhesion to the joint as the old sealant. Although, for siloxane sealants, it is difficult to obtain good adhesion with anything other than a siloxane, even if a primer is used. The adhesion rule for remedial sealant is that any sealant can follow an organic sealant, but a siloxane should be replaced only with a siloxane.⁴⁷ The type of substrate and cure should also be considered for good adhesion. It is much more difficult to remove a siloxane sealant from a porous substrate than from a non-porous, smooth one. One component acid liberating (acetoxo) sealants adhere well to glass and many aluminums, but should not be used on porous cementitious substances because a thin powdery film of $\text{Ca}(\text{OCOCH}_3)_2$ may form resulting in adhesion failure. Cementitious substances may be used with either neutral or base-liberating sealants with no loss of adhesion over time.⁴⁶

One common method for assigning an adhesion value to a sealant and determining its failure mode is the 180° peel test. Timberlake investigated the adhesive properties of moisture cured sealants using a silane modified polyether by means of a 180° peel test.¹²³ The polymer backbone was a polyoxypropylene with methylmethoxysilane endgroups and was cured with moisture in the presence of catalysts to yield a flexible polyether connected with siloxane bonds. The sealant showed excellent weatherability, little change in properties after 4 years, and good adhesion to substrates including aluminum, mortar, and stone. The peel adhesion values in N/m on different substrates were ~ 0.39 N/m on aluminum, ~ 0.98 N/m on stainless steel, ~ 0.49 N/m on granite, ~1.01 N/m on mortar, ~ 1.01 N/m on plywood, ~ 0.98 N/m on a PVC plate (or 4.0, 10.0, 5.0, 10.3, 10.3, 10.0 (kg/cm)).¹²³ This adhesion was maintained, and after several years the failure was still cohesive. This was important to prevent the formation of cracks between the building and sealant which would lead to air and moisture movement.¹²³

Gent compared peel tests at different angles and found higher adhesion values for the 180° peel than for 90° peel tests.¹²⁴ He attributed this phenomenon to plastic yielding of the adherend and partly to greater dissipation of energy within the adhesive.¹²⁴ A variation of the peel test was adapted by Andrews. This modified peel test differed from the conventional test in that a spring was inserted between the test machine cross-

head and the peeling strip to simulate a compliant adherend. This was done to eliminate the problem of oscillating peel force. The objective was to provide a test for measuring adhesion of polymeric adhesives (and wound dressings) to human skin.¹²⁵ Another common method used for adhesion testing is the JKR test. The JKR theory developed by Johnson, Kendal, and Roberts is a continuum mechanical model to test adhesive forces at the interface of two elastomers. The JKR experimental apparatus developed by Chaudhury has made adhesion studies on hemispherical elastomeric drops possible. Small droplets of PDMS resins were placed on microscopic slides to cure. A video camera is used to measure the contact area of the elastomeric resin on the surface, and then a load is applied at the contact interface and recorded. Choi investigated PDMS elastomers using this method, and found it to be imperfect since it assumed an idealized linear elastic response.¹²⁶

Most adhesion studies for PDMS elastomers have been done on pressure sensitive adhesive formulations (PSAs) since many PSA siloxane adhesives are available commercially. So far, only high-performance acrylic PSAs match the wide service temperature range of siloxane PSAs. Although acrylics tend to have higher peel strengths than siloxane PSAs, they are inferior at temperatures outside the 0 – 100°C range. Siloxane PSAs may be formed using either a combination of a condensation and radical polymerization or an addition cure. Platinum catalyzed addition siloxanes used as PSAs are advantageous in that they may be cured at much lower temperatures, 80 – 100°C (relative to 130° peroxide catalyzed cures). Additives need to be considered with Pt catalyzed additions since some may inhibit or prevent the curing reaction. An under-cured PSA will yield lower adhesion, tack, and cohesive strength. The ratio of vinyl to silane hydrosilation components affects the final properties of the adhesive. Typical adhesion values for a siloxane PSA are based on 180° peel tests and vary with contact time and the type of substrate to which it is bonded. Adhesion of siloxanes can increase over time with lower surface energy substrates such as LDPE, HDPE, UHMWPE, PP, PVC, PS (white), and ABS (black) (Table 2.12).⁸⁹ The thickness of the adhesive also influences both the tack and adhesion. Increasing temperature also affects the 180° peel strength for many elastomers including siloxane PSAs in an adverse manner (Table 2.13).⁸⁹

Table 2.12180° Peel Strength of Silicone PSA on Various Substrates⁸⁹

Substrate(s)	Immediate N/m	2 days N/m	7 days N/m	14 days N/m
LDPE	190	220	245	285
HDPE	195	245	270	245
UHMWPE	150	190	180	205
PP	185	295	283	290
PVC	130	170	190	195
PS, white	230	300	270	300
PVDF	305	360	320	310
Polycarbonate	310	310	290	295
Acrylic	285	290	265	265
ABS, black	225	315	305	320
Polyurethane, 60 shore D	175	230	245	290
Nylon 101	295	315	290	305
Stainless steel	300	315	305	365

Note: These data are based on 38 μm (1.5 mil) adhesive films cured with 2.0% benzoyl peroxide on 25 μm (1 mil) polypyromelitimide film. LDPE, low-density polyethylene; HDPE, high-density poly-ethylene; UHMWPE, ultrahigh molecular weight polyethylene; PP, polypropylene; PVC, polyvinylchloride; PS, polystyrene; PVDF, polyvinylidene fluoride; ABS, acrylonitrile-butadiene-styrene.

Table 2.13Effect of Temperature on 180° Peel Strength⁸⁹

Temperature (°C)	180° peel strength (N/m)
-73	2109
-50	1607
0	465
50	291
100	111
150	54
200	52
250	25

Note: These data were obtained on 25 μm (1 mil) polypyromelitimide film coated with 38 μm (1.5 mil) adhesive, laminated to stainless steel.

Siloxane PSAs formed via platinum catalyzed addition cures using vinyl and hydride terminated PDMS fluids with a variety of multifunctional vinyl crosslinking reagents were investigated by Lin.⁸² The adhesive properties were evaluated as a function of varied addition cure formulations. Adhesive data were obtained using 180° peel test on clean steel plates with consistent adhesive thickness, and a peel rate of 12"/minute. They found that a ratio of 0.98 SiH/Si-vinyl gave high adhesion although weak cohesive strength. The best peel adhesion was found using a ratio of 1.28 silane to vinyl. As this ratio was increased the peel and tack properties decreased. A ratio of 14.7 yielded cured adhesives which no longer had sufficient structural integrity and left residues on steel and glass substrates. The adhesion data using a MDTQ crosslinking reagent at various ratios of Si-H/Si-vinyl were: 0.984 ~ 557 N/m; 1.28 ~ 426 N/m; 4.93 ~ 306 N/m; 9.85 ~ 284N/m; 14.7 < 109 N/m (or 51, 39, 28, 26, <10 oz./in.). The average supportable loads decreased with the different crosslinking reagents, with $M_{0.648}M^{vi}_{0.076}Q$, $M_{0.678}M^{vi}_{0.114}Q > M_{0.59}D^{vi}_{0.13}T_{0.51}Q_{0.49} > M^{vi}D_{175.9}D^{vi}_6M^{vi}$. Overall, the smaller, high functionality vinyl crosslinking reagents yielded PSAs having greater adhesion than those formed with the larger, linear polymer crosslinking reagent.⁸²

Another interesting study on adhesion of PDMS networks formed by addition cures was done by Gent.¹²⁰ PDMS networks were formed by endlinking PDMS chains with M_n s of 11,500, 22,500, and 36,000 g/mole using tetrakisdimethylsiloxysilane as the crosslinking reagent. A second uncured resin layer was then cast onto the first fully cured network layer. The new PDMS chains rapidly interdiffused into the surface of the lower layer. Molecular loops “entanglements” were formed by their endgroups looping around the bottom crosslinked layer and crosslinking with themselves. The energy required to separate layers formed in this manner was measured under threshold conditions (low rates, high temperatures, and some in the swollen state). The work of detachment varied from 15 – 25 J/m², which was ~ one-half the work of fracture for the layers. The work of detachment increased with increasing densities of interlinking, and with increasing M_n s in either layer using the PDMS precursors having M_n s of 22,500 and 36,000 g/mole. When two fully cured PDMS network layers were placed on top of one another and not interlinked (held together only by van der Waals forces), the work of detachment was found to be only 70 mJ/m².¹²⁰ Chiang also studied adhesion properties

of UV-curable PDMS urethane acrylate networks.¹²⁷ He found that the excellent adhesive properties of this elastomer to glass was attributed to the similar structures of the PDMS soft segments and glass.

2.3 Introduction to Integral Fuel Tank and Aerospace Sealants

Three basic functions which a sealant must perform are filling the space to create a seal, forming an impervious barrier to fluid flow, and maintaining the seal in the operating environment.⁸⁹ Sealants for aircraft fuel tanks experience harsher environmental conditions than those of most other sealants. Thus, new sealant materials with an inherently wider service temperature use range, greater chemical stability, and a longer operational life than most state-of-the-art elastomers commercially available are needed.¹²⁸ Fuel resistance, stability at very high and sub-zero temperatures, and good adhesion to metal substrates are key requirements in aircraft applications such as integral fuel tanks. Titanium integral fuel tanks have complicated structures and a myriad of possible leakage points making good adhesion essential.¹²⁹ Siloxanes have played a key role in the aerospace industry due to their extreme resistance to both high and low temperatures. Siloxane elastomers are used in coatings for rocket fuel valves, supply cables, and silo doors for protection from rocket blast.⁵ In the 1970's, the fluorosilicones and nitrilesilicones were investigated, although only the fluorosilicones were available commercially.¹³⁰ Currently, materials including cyanosilicones, fluoroalkylarylene-siloxanylenes (FASIL), phosphonitrilic fluoroelastomers (PNF), tetrafluoroethylene oxide phenylquinoxaline elastomers (FEX), and perfluoroalkylethers are being investigated as possible "advanced sealants" for aerospace applications. These are materials expected to survive much more harsh environmental and temperature conditions.⁸⁹

Integral fuel tanks are placed in internal cavities in the wings and other parts of aircraft in order to obtain maximum fuel capacity by maximizing space and reducing extra weight from bladder cells. Heavy bladder cells are eliminated since the shapes of integral tanks are either too small or geometrically complex. Elastomeric sealants are applied to all discontinuous integral tank surfaces such as seams, joints, and fasteners to prevent fuel leakage. Various sealants have different primary functions. A filleting sealant is applied in thicker sections and cannot tolerate large amounts of solvents and

shrinkage. Both faying sealants and fill and drain sealants (or channel sealants) are applied as thin films which consist of solutions of compounded elastomers. Filleting sealants are the most common since they are used in high temperature applications and may be converted into either faying or fill and drain sealants. A filleting sealant is applied as a caulk which cures directly on the titanium substrate. This means it needs to adhere to either a clean titanium substrate to prevent leaks or to an old sealant which has already been exposed to fuel when repairing a leak.¹²⁹

Integral fuel tanks of subsonic aircraft (the KC-135 and B-52) have been sealed using polysulfides. These only performed well at moderate temperatures and did not survive above 250°F. Supersonic aircraft, which experience speeds in the Mach 2-3 range require sealants stable in hydrocarbon fuels between 300 – 600°F. The only elastomers used at this time commercially are polyesters and fluorosilicones. Although polyesters were used in the F-111, they were only stable to 400°F.¹²⁹ Fluorosilicones exhibited long term stability at 450°F, and performed twice as well as the polyesters in the 300 – 600°F range.¹²⁹ This is still unacceptable for Mach 3 aircraft, and new materials are needed. Anspanch investigated potential filleting sealants using a fluorocarbon/fluorosilicone hybrid, hydrofluorocarbons, polyimides, and perfluoroethers.¹²⁹ A dynamic sealant tester was used as a fatigue test which had a titanium cup attached to a titanium plate by a fillet of sealant. Stresses similar to those which an actual integral tank would experience were then imposed on their titanium sample using the proposed materials. The results were compared to those obtained on commercial materials (Table 2.14).¹²⁹

Several high-performance military aircraft integral fuel tanks are sealed with various fluorosilicone sealants, both non-curing and cured elastomers. McDonnell Douglas Corporation used Dow Corning's fluorosilicones to successfully repair four "chronic-leakers".¹³¹ PMTFPS viscous fluids (non-curing) were used to seal integral fuel tanks in the wings of the F-4 Phantom fighter-bomber, replacing a polysulfide sealant.¹³¹ No liners or bladders, due to their large size, are used with integral fuel tanks in fixed sections of the wings. This makes the use of joint sealing vital. Fluorosiloxanes are also used on many doors and access hatches since dripping oil or spilled fuel will swell many

Table 2.14
Physical Properties of Integral Fuel Tank Sealants

Physical properties of sealant materials¹³⁰

Property	Commercial		AFML developments		
	PE	FS	FCS-210	AFML-FC	PI
Tensile strength, psi	940	760	255	1100	6700
Elongation, %	170	400	625	1130	75
Tear strength, ppit	93	34	104	190	--
Adhesion	Fair	Poor	Good	Good	Excellent
Thermal stability °F in fuel	400	450	500	550	450
Low-temperature flexibility, °F	-65	-70	-50	-65	-40
Compatibility toward titanium	V. G.	V. G.	V. G.	Fair	V. G.

PE, Polyester; FS, Fluorosilicone;

FCS-210, Fluorosilicone/Fluorocarbon Hybrid;

AFML-FC, AFML Fluorocarbon; PI, Polyimide

organic elastomers. A fluorosiloxane RTV sealant was gunned into channels around the engine on the Lockheed C-141 jet transport.¹³¹ Waxed (non-stick) cowling doors were then closed on this cured sealant. A perfectly fitted-seal on the door was thereby formed within 24 hours. The Boeing Chinook helicopter uses seals extruded or molded from heat-cured fluorosiloxanes in a variety of applications.¹³¹ These were also used in U. S. military aircraft, being the only fuel-resistant elastomer remaining flexible at -65°F . Finally, the Douglas DC-8 jet aircraft, used molded fluorosiloxane rubber O-rings for 10 years, and maintained an almost perfect performance record.¹³¹

Another review on filleting sealants using fluorosiloxane elastomers was done by Rosenberg.¹²⁸ The emphasis was on the fluorine-containing polymer, fluoroalkylarylene-siloxanylene, FASIL, along with their new thermally and chemically resistant viscoelastic alkarylene- and arylenopolysiloxanylene polymers. These offered potential as both filleting or channel type sealants having a wide service temperature range, and being thermally stable for long periods. The goal was to synthesize an elastomer serviceable between -54°C and 232°C with long-term performance. These workers found that at least 30% fluorine content was necessary in the polymers to obtain the desired solvent resistance. Of all polymers evaluated, FASIL exhibited the best overall combination of physical, chemical, and mechanical properties as a fuel resistant sealant, and was readily synthesized from commercially available materials. Its major benefits offered long term stability up to 260°C , low-temperature flexibility at -54°C , and excellent adhesion to Al and Ti. It was nonhydrolyzable and exhibited high resistance to JP-4 fuel.¹²⁸

Other fluorosiloxanes are patented as aerospace sealants. Griffin proposed that the addition of irregularly shaped and sharp edged vulcanized rubber particles to an uncured elastomeric mastic would prevent gap extrusion and premature failure of the integral fuel tank sealant.¹³² Ideal fuel resistant elastomers for this application included PMTFPS, FASIL, polyurethane, poly(fluoroalkoxy phosphazene), and poly[ethylcyano(methyl)-siloxane elastomers. This method was found to be much more effective in preventing premature failure of the sealants than the method of an older patent¹³² which used (smooth) plastic spheres incorporated into the elastomers.^(133,134) Recently, another interesting sealant was developed to protect shuttle experiments from moisture.¹³⁵ Pelseal[®] Technologies, LLC, Newtown, PA, developed the fluoroelastomer

sealant, Pelseal 2077, which played a critical role in space shuttle experiments. This sealant was on board with John Glenn during the October 1998 STS95 space shuttle mission. It was used to protect thermoelectric devices from moisture in a refrigerated incubator module where very temperature-sensitive protein crystals were grown. The crystals seemed to grow larger and more freely in the weightless space environment. They will be used in hopes of fighting diseases like AIDS, cancer, diabetes, sickle cell anemia, and rheumatoid arthritis by unlocking further secrets of the proteins' molecular structures. Pelseal 2077 is a VITON[®] fluoroelastomer one-part sealant caulk which can withstand temperatures between 40 and 400°C, is impervious to sunlight, ozone, UV radiation, and is resistant to ~ 750 corrosive liquids and chemicals. It is also used industrially where resistance to harsh environmental conditions is crucial.¹³⁵

2.4 Introduction to Nitrile Containing Organosiloxanes

Novel PCPMS nitrile containing siloxane networks have been prepared for this study as potential integral fuel tank sealants having properties associated with siloxanes such as excellent weatherability, high temperature stability, and low temperature flexibility. The polar nature of the 3-cyanopropyl- substituents also increases the networks resistance toward hydrocarbon jet fuels and exhibits potential for improving adhesion to metal substrates. The PCPMS polymers are expected to be more polar than PMTFPS polymers because the Taft polar substituent constant σ^* for $-\text{CH}_2\text{CN}$ of 1.30 is substantially larger than that for $-\text{CH}_2\text{CF}_3$ of 0.92.¹³⁶ To date, no siloxane network having a 3-cyanopropyl- group substituted on every silicon atom of the siloxane backbone has been prepared as described herein. Variations of nitrile containing siloxanes and similar homopolymers using different synthetic routes have been investigated and will be reviewed here.

Nitrile containing siloxanes are generally prepared by an addition reaction of unsaturated nitriles with silane functional groups of a polyorganosiloxane. The strongly electron withdrawing $-\text{CN}$ group in the α - position weakens the Si-C bond as do α -carbonyl or β -halogen substituents. Since boiling water easily splits off a cyanomethyl-group from a $\text{CNCH}_2(\text{CH}_3)_3\text{Si}$ molecule,¹³⁷ neither cyanomethyl- nor α -cyanoethyl-groups are desired on a siloxane chain. Acrylonitrile was generally the unsaturated nitrile

of choice to yield β -cyanoethyl- substituents, although a small percentage of the reverse addition product will yield the unstable α -cyanoethyl- groups. This reaction may also be promoted by radical or ionic catalysts, and catalysts based on amines favor higher yields of the β -cyanoethyl- substituents.¹ Addition reactions of silanes with allyl or methallyl cyanide using a platinum-on-alumina catalyst have yielded 80–90% γ -cyanopropylsilanes.¹³⁸ Siloxanes with β -cyanoethyl and γ -cyanopropyl substituents are susceptible to saponification of the nitrile group by hydrolysis



but not cleavage of the Si-C bond.¹³⁹

Thermal stabilities of nitrile containing siloxanes depend on the position of the cyano group on the alkyl radical, whereas β -functional, α -cyanoethyl- groups are strongly susceptible to β -decomposition. When siloxanes with nitrile groups substituted in various ways were heated to 250°C for 100 hours, the following percentages of carbon contents were found (by comparison with the theoretical amounts)¹¹³:

Substituent	C(%)
α -Cyanoethyl-	<1
β -Cyanoethyl-	88.3
β -Cyanopropyl-	75.6
γ -Cyanopropyl-	94.4

Both β -cyanoethyl- and γ -cyanopropyl- siloxanes have been used to decrease swelling of siloxane elastomers¹¹³, and β -cyanoethyl- siloxane oils have been used to increase the dielectric constants.¹ Polyorganosiloxanes with a portion of the silicon atoms along the chain substituted with 2-cyanopropyl- have proven to be resistant against aliphatic and aromatic hydrocarbons, but soluble in polar solvents including alcohols, ketones, and ethers.¹⁴⁰ The siloxanes having a portion of 3-cyanopropyl- substituents are currently being investigated as “advanced sealants” as mentioned earlier.⁸⁹

My co-workers have prepared polysiloxane homopolymers with pendent 3-cyanopropyl groups⁽¹⁴¹⁻¹⁴⁶⁾, and another group has prepared them with 2-cyanoethyl groups.¹⁴⁷ Previous synthetic routes for preparing PCPMS oligomers included equilibrations of the D₄CN monomer using triflic acid^(143,145), a basic siloxanolate catalyst

prepared from an anhydrous equilibration of tetramethylammonium hydroxide with D_4CN ^(144,146), and a dilithium diphenylsilane-diolate catalyst^(142,147). These nitrile containing siloxanes were primarily prepared as sealant and adhesive materials.⁽¹⁴³⁻¹⁴⁷⁾ PDMS-PCPMS-PDMS triblock copolymers were investigated for use as suspension stabilizers for siloxane magnetic fluids which have been proposed as internal tamponades for retinal detachment surgery. The 3-cyanopropyl group has an affinity for metal atoms or ions and has been found to stabilize nanometer size $\gamma\text{-Fe}_2\text{O}_3$ and cobalt particles in D_4 or hexane.^(142,147)

Polyorganosiloxane thermosets with pendent nitrile substituents have also been used as polar stationary phase materials in gas and liquid chromatographic columns. Their polarity and propensity for hydrogen bonding allows for separation of positional and stereoisomers such as methyl esters of fatty acids and monoglycerides.⁽¹⁴⁸⁻¹⁵²⁾ These polar networks have also been explored as components of polar membranes, and for the detection and titration of alkali metal and alkaline-earth metal cations in solutions where the nitrile group serves as a complexation site for electropositive constituents.¹⁵³ Other interesting reviews on chromatography using PCPMS as stationary phases are available.^(154,155) PCPMS has also been used in studies where differences in polarities of various polymer coatings are important. PCPMS was compared with several other polymers of varied polarity which were all coated on a transducer and exposed to varying organic gases to help in developing capacitive chemical sensors in CMOS technology.¹⁵⁶ Modified polyorganosiloxanes, including PCPMS, were spray-deposited on quartz microbalance oscillators, and their partition coefficients were determined to help explain different molecular interactions between dissolved organic molecules and the polyorganosiloxane functional groups.¹⁵⁷

Chapter 3

EXPERIMENTAL

3.1 Reagents and Purification Procedures

Octamethylcyclotetrasiloxane (D_4 , $C_8H_{24}O_4Si_4$, FW 296.61, b.p. 175-6°C, d 0.956) from mixed cyclics ($D_3 - D_5$) was dried over calcium hydride powder under a N_2 atmosphere and fractionally distilled under a N_2 atmosphere and collected at $\sim 45^\circ C/0.5-1$ torr. 1,3,5,7-tetramethyl,1,3,5,7-tetrahydrocyclotetrasiloxane (D_4H , $C_4H_{16}O_4Si_4$, FW 240.51, m.p. $-69^\circ C$, b.p. $134-5^\circ C$, d 0.9912) was used as received. The D_4 and D_4H were both kindly supplied by the Dow Corning Corp. The poly[methyl(3,3,3-trifluoropropyl)siloxane] polymers (PMTFPS) and the fluorine containing crosslinking reagent were also supplied by the Dow Corning Corp. and used as received. A platinum-divinyltetramethyldisiloxane complex in xylene (Karstedt's catalyst, $Pt^0 \cdot 1.5[(CH_2=CH(CH_3)_2Si]_2O$), 2.1-2.4 weight % Pt conc.) and tetrakis(dimethylsiloxy)silane ($C_8H_{28}O_4Si_5$, FW 328.73, b.p. 188-190°C, d 0.886) were purchased from Gelest, Inc and used as received. Trivinylchlorosilane (Gelest) (C_6H_9ClSi , FW 144.67, b.p. 128-9°C, d 0.9343) and chlorodimethylvinylsilane (Aldrich, 97%) (C_4H_9ClSi , FW 120.66, b.p. 82-83°C, d 0.874) were treated with anhydrous K_2CO_3 for an hour to remove hydrochloric acid, a common impurity in chlorosilanes, then distilled under a N_2 atmosphere just prior to use. Since chlorosilanes can degrade rubber septa, they were stored in septum capped flasks for a maximum of a week. Tetramethylammonium hydroxide pentahydrate (Aldrich, 99%) ($TMAH \cdot 5H_2O$, $(CH_3)_4NOH \cdot 5H_2O$, FW 181.23, m.p. 65-68°C) was stored in a dessicator and was used as received. Lithium hydroxide (Aldrich, 99.5%) ($LiOH$, FW 23.95) was ground to a fine powder under N_2 and stored in a dessicator until used. Allyl cyanide (Aldrich, 98%) ($H_2C=CHCH_2CN$, FW 67.09, b.p. 116-121°C, d 0.834), dried at room temperature with 4Å molecular sieves (activated at 200°C / 0.5-1 torr. for 48 hours), and 1,3-divinyltetramethyldisiloxane (Gelest, Inc.) ($C_8H_{18}OSi_2$, FW 186.4, m.p. $-99^\circ C$, b.p. $139^\circ C$, d 0.811) were distilled under N_2 prior to use. Toluene (Fisher) ($C_6H_5CH_3$, FW 92.14, b.p. 110.6°C, d 0.867) was washed twice with concentrated sulfuric acid at room temperature, and several times with water until

neutral, predried with anhydrous magnesium sulfate, dried overnight with calcium hydride powder, and then distilled.

3.2 Synthesis of Siloxane Oligomers and Cyclics

3.2.1 Synthesis of Tetramethylammonium Disiloxanolate Catalyst

For a typical reaction, 13.7g (0.046 mole) octamethylcyclotetrasiloxane (D_4) and 0.685g (0.0038 mole) tetramethylammonium hydroxide pentahydrate ($TMAH \cdot 5H_2O$) were added to a flask equipped with an overhead mechanical stirrer and an attached Dean Stark trap with condenser linked to a drying tube (Figure 3.1).^(11,20) This represents a 5 weight % ($TMAH \cdot 5H_2O$) solution. The mixture was reacted by heating in an 80°C silicone oil bath for 24 hours under a rapid stream of nitrogen bubbling through the reaction mixture to help in removing the condensed water and water of hydration (Figure 3.2). The ($TMAH \cdot 5H_2O$) is initially insoluble in D_4 , but above 70°C it begins to melt and dissolves gradually as it reacts with D_4 . The solution becomes homogeneous within about 2 hours. After 24 hours, a few drops of water collect in the Dean Stark trap. After this 24h reaction period, the mixture was cooled to room temperature, then diluted with either 15 mL of dried D_4 or 15 mL of purified THF to yield an approximately 50% wt./volume catalyst solution. This transparent solution was then transferred to a pre-dried, septum-capped brown bottle via syringe and stored in a desiccator until use.

3.2.2 Synthesis of Polydimethylsiloxane (PDMS)

For a typical synthesis of 175 g polymer with a target M_n of 4250 g/mole PDMS (55 repeat units), 6.5 g (0.035 mole) 1,3-divinyltetramethyldisiloxane and 168.5 g (0.568 mol.) purified D_4 were added via syringe to a flame-dried tared flask and stirbar capped with a septum. The transparent solution was purged with N_2 while the septum was secured with a copper wire, and then heated in a silicone oil bath to 80°C while stirring. Once the solution reached 80°C, 2.1 mL of the tetramethylammonium disiloxanolate catalyst solution described above was added via syringe. The mixture was then equilibrated for approximately 48 hours (Figure 3.3). The solution initially became cloudy and an increase in viscosity was observed during the first few hours due to the fast propagation and initial large increase in molecular weight. After 48 hours, gel

Figure 3.1

Diagram of Apparatus for Preparing Tetramethylammonium Siloxanolate Catalyst

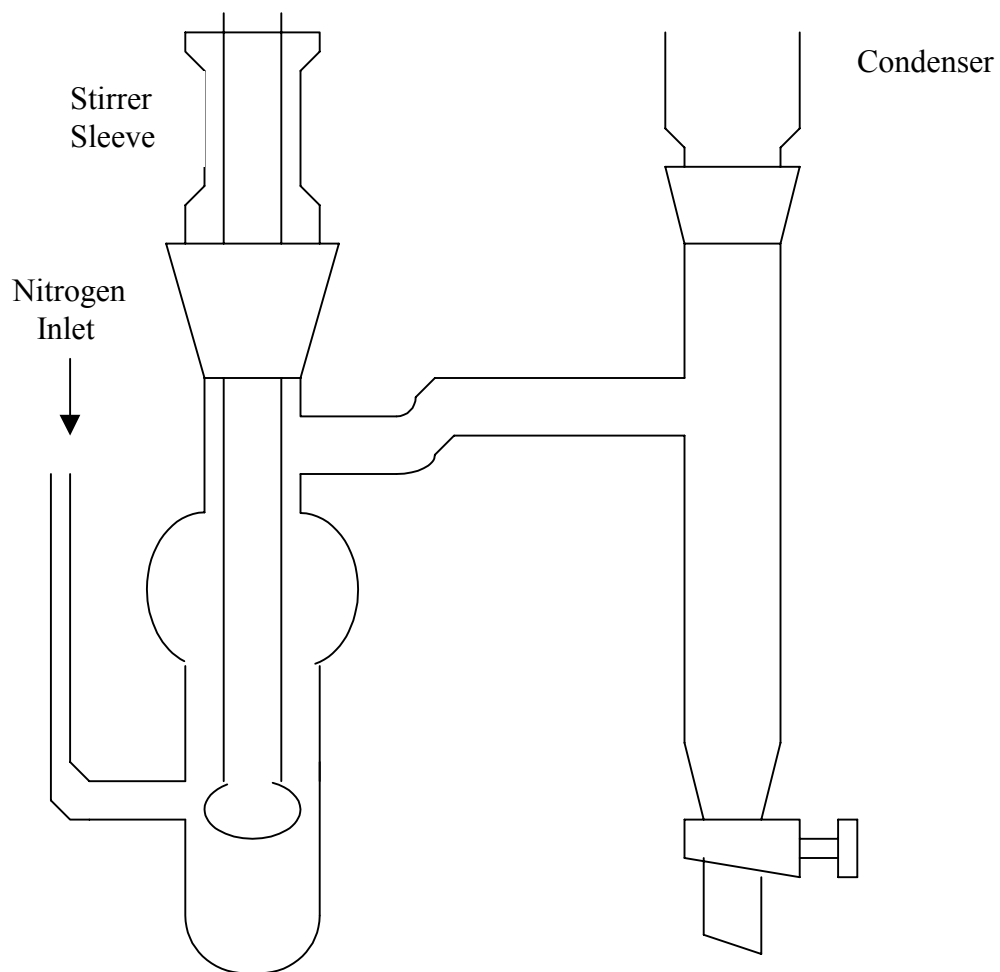
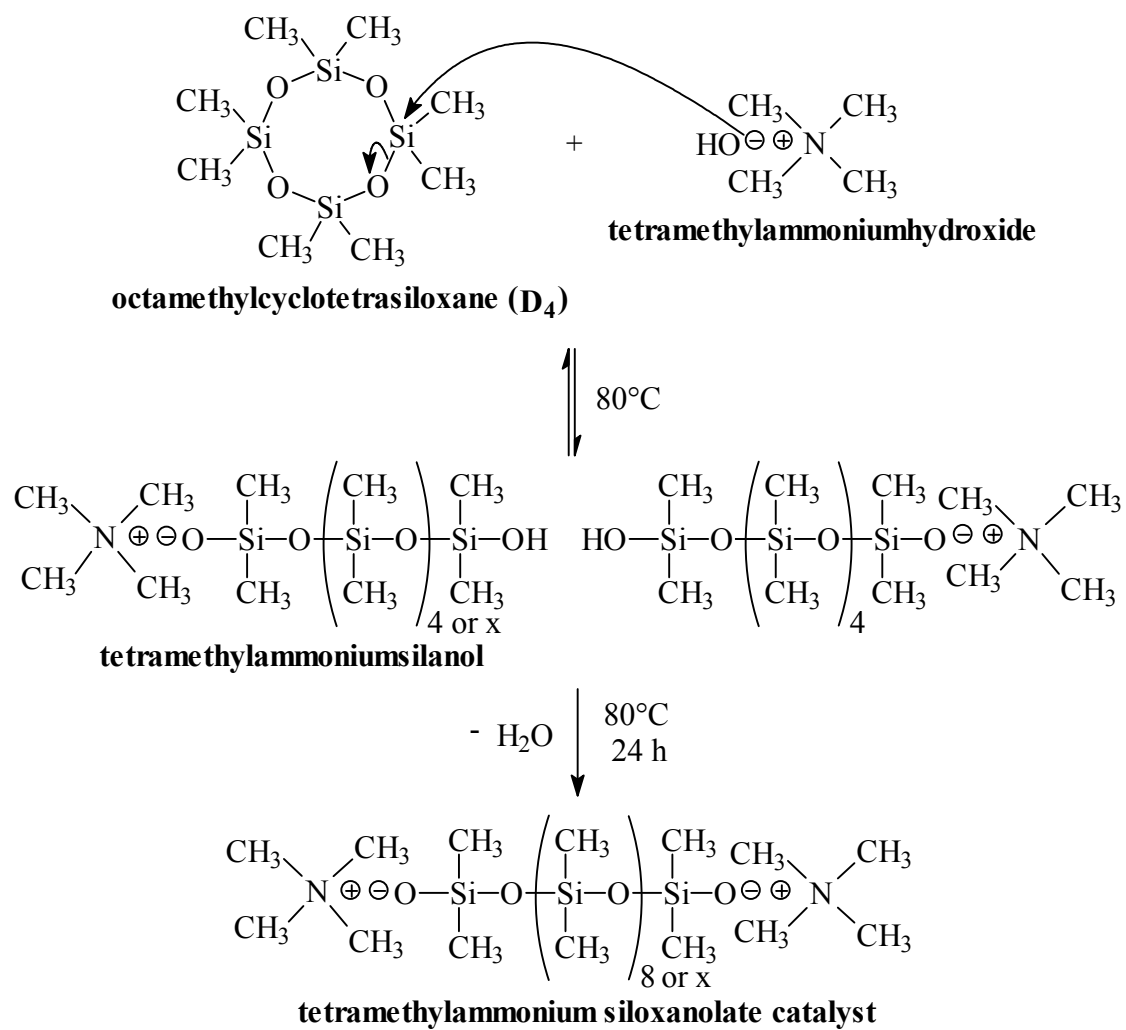


Figure 3.2

Mechanism for Synthesis of Tetramethylammonium Siloxanolate Catalyst

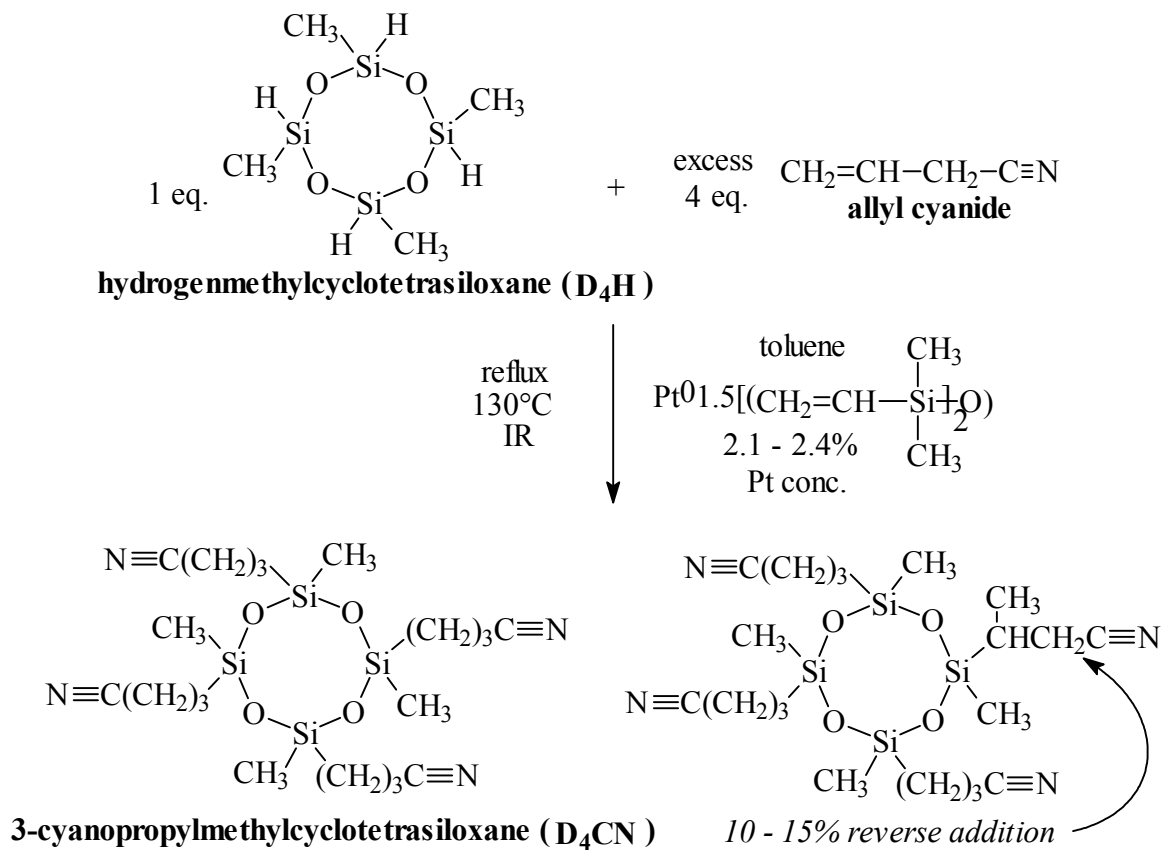


permeation chromatography (GPC) was used to confirm the linear chain/cyclic distribution of molecular weights typical for PDMS (~ 85% linear/15% cyclic). The tetramethylammonium siloxanolate catalyst was removed from the polymer/cyclic mixture by bubbling N₂ through the solution over a 4 – 8 hour period at 135°C. Base removal was confirmed using litmus paper. The small cyclics were then distilled off under vacuum 130°C / 0.5 – 1 torr.

3.3.3 Synthesis of 3-Cyanopropylmethylcyclotetrasiloxane (D₄CN)

A flame-dried two-necked flask was fitted with a rubber septum, condenser, and drying tube filled with Drierite and purged with N₂. For a typical synthesis of 3-cyanopropylmethylcyclotetrasiloxane¹⁴² (D₄CN, FW 508.871), 115 mL (0.474 mole) distilled D₄H, 225 mL (2.80 mole) purified allyl cyanide, and 200 mL purified toluene were charged to the flask. A 50% excess over 4 equivalents of allyl cyanide per mole D₄H was added to ensure complete substitution of hydride functional groups on D₄H by 3-cyanopropyl substituents. Toluene provided a heat sink for this exothermic hydrosilation. A sample of this solution was taken for Fourier Transform Infrared Spectroscopy (FTIR) to represent the mixture with the hydride functionality present before initiation. The catalytic platinum-divinyltetramethyldisiloxane complex in xylene (Karstedt's catalyst) (0.64 mL, ~0.0144 g Pt) was added, then the solution was heated in a silicone oil bath to 130°C and refluxed (Figure 3.4). An observed exotherm begins around 70 - 100°C. Samples were taken every few hours to monitor by FTIR the disappearance of the hydride functional group. Typically, this process is complete within ~ 24 hours. After complete substitution of the hydride groups by 3-cyanopropyl substituents, the excess allyl cyanide and toluene were distilled off under N₂ at 150°C. Final traces of excess reagents were removed under vacuum at 70°C / 0.5 – 1 torr. ¹H NMR showed about 10 – 15% of the reverse addition product from Markovnikov type addition, leading to a small number of 2-cyanoisopropyl substituents. The crude D₄CN was then purified by distillation in an insulated heating mantle under vacuum at 260°C – 270°C/0.5 – 1 torr to yield ~190g (~ 80% yield) of the transparent, slightly yellow monomer. ¹H NMR (CDCl₃) shows peaks for methyl protons (~ 0.12 ppm), protons on the 3-cyanopropyl groups (~0.7ppm, ~1.68 ppm, and ~2.38 ppm), and methyl

Figure 3.4

Synthesis of D₄CN Cyclics via Hydrosilation

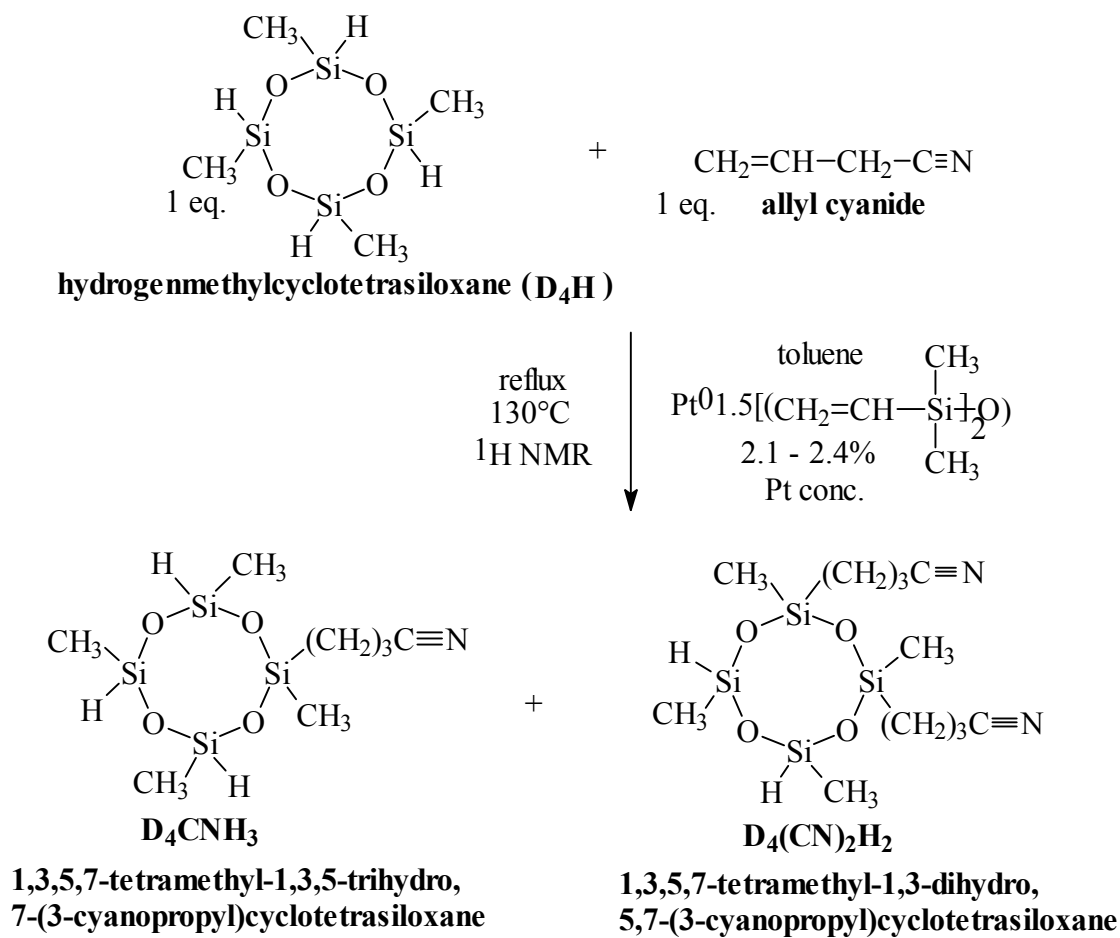
protons on the 2-cyanoisopropylmethyl groups (~ 1.1 ppm).

3.2.4 Synthesis of D_4CNH_3 and $D_4(CN)_2H_2$ Cyclics

The 1,3,5,7-tetramethyl-1,3,5-trihydro-7-(3-cyanopropyl)-cyclotetrasiloxane (D_4CNH_3 , FW 307.60) and 1,3,5,7-tetramethyl-1,3-dihydro-5,7-di(3-cyanopropyl)cyclotetrasiloxane ($D_4(CN)_2H_2$, FW 374.69) cyclics were synthesized in a manner similar to that of the D_4CN cyclic monomer; although a 1:1 molar ratio of allyl cyanide: D_4H (rather than a 50% excess of 4:1) was used for the partial addition of 3-cyanopropyl substituents onto D_4H . A typical synthesis of the hydride functional, polar cyclics involved the addition of 157.8 mL (0.650 mole) purified D_4H , 52.3 mL (0.650 mole) purified allyl cyanide, and 210 mL of purified toluene to the same setup described for the synthesis of D_4CN . A sample of this mixture was removed before initiation for 1H NMR to represent the vinyl protons present on allyl cyanide. The Karstedt's catalyst (0.5 mL, ~0.01125 g Pt) was added and the solution was then heated to reflux at 130°C in a silicone oil bath (Figure 3.5). Samples were taken for 1H NMR analysis hourly after initiation (observed by an exotherm at ~70°C). A typical reaction refluxed for 2-6 hours whereupon 1H NMR confirmed the disappearance of the vinyl protons from allyl cyanide, and the marked appearance of methylene protons characteristic of 3-cyanopropyl substituents on the modified D_4 cyclic. After completion of the hydrosilation, excess toluene was removed as described above from D_4CN . The polar (tri- and di-) hydride-functional D_4CNH_3 and $D_4(CN)_2H_2$ cyclics, were recovered by fractional vacuum distillation at 83°C – 90°C and 130°C – 140°C/0.5 – 1 torr (~90 g and 40 g), respectively.

3.2.5 Synthesis of Divinyl Terminated Poly(3-cyanopropylmethylsiloxane) (DV-PCPMS)

A dry three-neck flask was fitted with a mechanical stirrer and N_2 purge. For a typical synthesis of 389.0 g of a target M_n of 33,260 g/mole (260 repeat units) divinyl terminated poly(3-cyanopropylmethylsiloxane) (DV-PCPMS) not including cyclics, 518.67 g (1.02 mole) purified D_4CN ($518.67 \text{ g} * 0.75\% = 389.0 \text{ g}/33,261 \text{ g/mole}$ to make 0.0117 mole polymer chains) and 0.5602 g (0.0234 mole) of finely ground (under Ar)

Figure 3.5Synthesis of D_4CNH_3 and $D_4(CN)_2H_2$ Cyclics via Hydrosilation

LiOH were added to the flask and allowed to equilibrate in a 140°C silicone oil bath for 72 hours. The LiOH is initially insoluble in the D₄CN, but gradually forms a translucent mixture after reaction for ~ 24 hours. The reaction mixture was cooled to at least 10°C below the boiling point of the selected quenching agent. The equilibrated oligomer was quenched with 6.46 mL (0.0468 mole, a 100 mole % excess relative to lithium disiloxanolate end groups) chlorodimethylvinylsilane at 70°C, whereupon a thick white/yellow solution was observed, indicative of the LiCl byproduct from a fast endcapping reaction (Figure 3.6). This mixture was allowed to stir rapidly under N₂ for an additional 10 minutes to ensure complete endcapping, and the excess quencher was removed under vacuum at 80°C/0.5 – 1 torr. GPC confirmed the 74% linear/26% cyclic molecular weight distribution typical for poly(3-cyanopropylmethylsiloxane). The resultant polymer was diluted with ~100 - 200 mL of chloroform, and the cyclics (and low molecular weight oligomers) were removed by four extractions with ~500 mL each of a 95%ethanol/5%H₂O mixture, and then further washed twice with ~500 mL of water to remove LiCl (which removes the slight opaque appearance) to yield ~325 g (84% yield) of slightly yellow, transparent, viscous DV-PCPMS.

3.2.6 Synthesis of Hexavinyl Terminated Poly(3-cyanopropylmethylsiloxane) (HV-PCPMS)

The HV-PCPMS was prepared by a similar procedure to the one used to prepare DV-PCPMS up until the point of quenching (terminating) the equilibration. A typical synthesis of 300.0 g of a target M_n of 17,300 g/mole (136 repeat units) HV-PCPMS not including cyclics is provided below. Purified D₄CN (400.0 g, 0.786 mole) (or 400.0 g * 0.75 = 300.0 g/17,300 g/mole to make 0.0173 mole polymer chains) and 0.831 g (0.0347 mole) of finely ground (under Ar) LiOH were added to the flask with mechanical stirring and a fast N₂ purge and allowed to equilibrate for 72 hours at 140°C. After 72 hours, the lithium disiloxanolate chains and small cyclics (mostly D₃CN – D₅CN) had reached thermodynamic equilibrium. The reaction was cooled to 100°C (30°C below the b.p. of the trivinylchlorosilane quenching reagent) and the solution was quenched with 10.72 mL (0.0692 mole, a 100% excess over the number of moles of lithium disiloxanolate

endgroups) trivinylchlorosilane, whereupon a thick white/yellow solution was observed, indicative of the LiCl byproduct from a fast endcapping reaction (Figure 3.7). This mixture was allowed to stir rapidly under N₂ for an additional 10 minutes to ensure complete endcapping, and the excess quencher was removed under vacuum at 130°C / 0.5 – 1 torr. The resultant polymer was diluted with ~100 - 200 mL of chloroform, and the remaining cyclics (and low molecular weight oligomers) were removed by four extractions with ~500 mL each of a 95%ethanol/5%H₂O mixture, and then further washed twice with ~500 mL of water to remove LiCl (which removes the slight opaque appearance), to yield ~250 g (83% yield) of slightly yellow, transparent, viscous HV-PCPMS.

3.3 Preparation of Networks

3.3.1 Hydrosilation Curing to form PDMS Networks

The amounts of Karstedt's catalyst used were adjusted to the achieve reasonable reaction rates for each of the chemical structures in the study. The 4K and 40K PTFPMS required 0.2 and 2.0 grams catalyst per mole vinyl group, respectively. All PCPMS oligomers required catalyst amounts on the order of 20.0 grams with the exception of the 9K HV-PCPMS which required only 10.0 grams of catalyst per equivalent of vinyl groups. All of the nonpolar PDMS oligomers required only 0.2 grams of catalyst per equivalent of vinyl groups, with the exception of the 2K PDMS which only required 0.1 grams catalyst per mole vinyl group.

The lower amounts of catalyst required for PDMS resins required catalyst dilutions and thus stock solutions were prepared. For example, a resin mixture of 10 g of 4700 g/mole PDMS required 8.5×10^{-5} g (0.02 g catalyst/equivalent vinyl), which was too small to weigh accurately. Therefore, Karstedt's catalyst was diluted with the PDMS oligomers having the same M_n which was to be used for crosslinking. The Karstedt's catalyst/PDMS stock solutions were prepared in 1 gram amounts by using the following equations for dilution. First, the grams of catalyst solution required per gram of polymer

were calculated by the following equation:

$$\left(\frac{1}{\text{equivalent weight}} \right) \left(\frac{\text{g catalyst solution}}{\text{equivalent}} \right) = \left(\frac{\text{g catalyst solution}}{\text{g polymer}} \right)$$

A known amount of catalyst solution (one drop for each separate stock solution) was weighed and diluted to 1 gram with the desired PDMS oligomer. The stock solutions were used to charge the catalyst to the respective PDMS resin compositions to achieve the catalyst concentrations noted above.

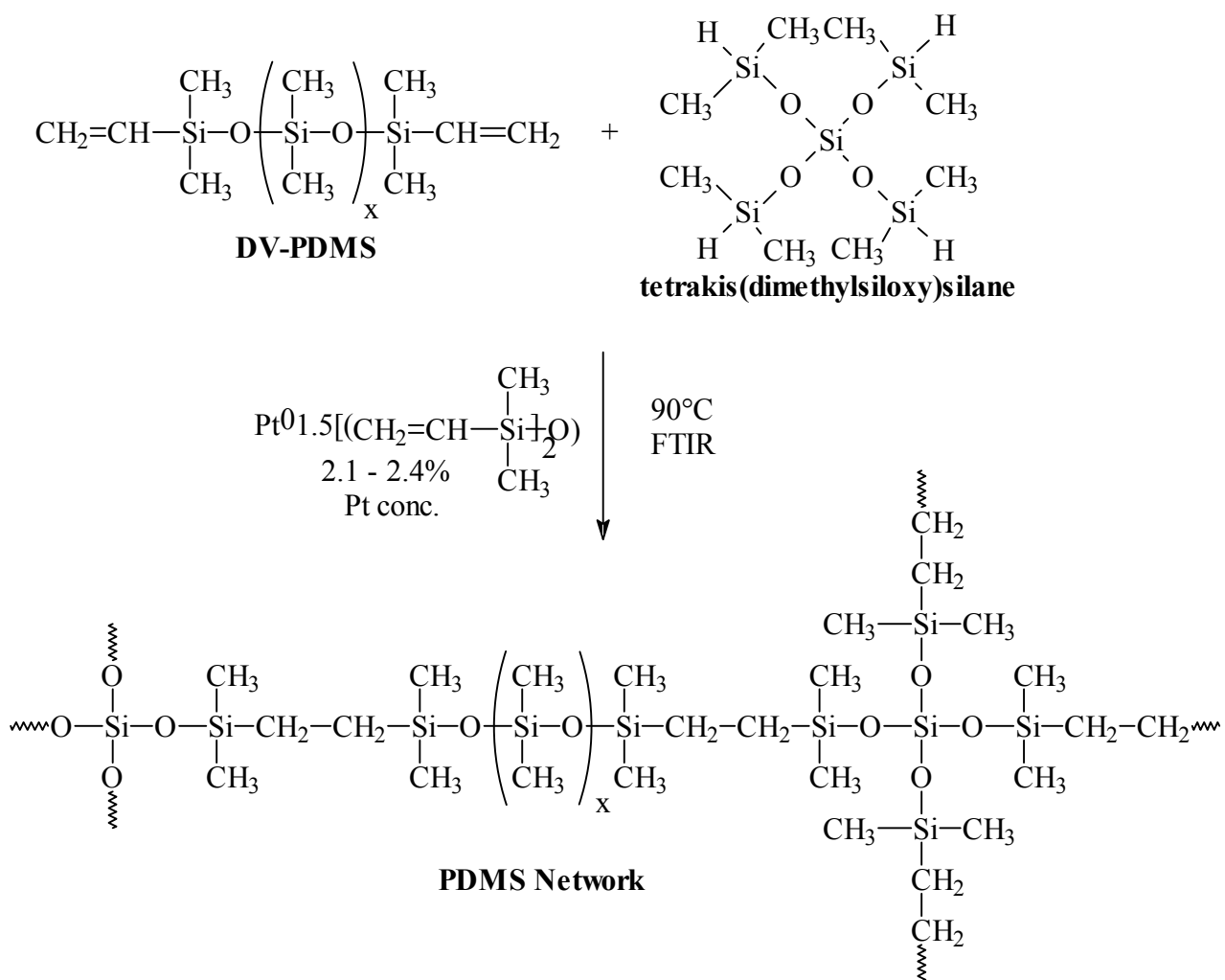
For the particular example noted above, every 1 gram of 4700 g/mole PDMS to be crosslinked required 0.002 g of PDMS/Karstedt's catalyst stock solution which was equivalent to 0.02 g catalyst solution/equivalent vinyl. Thus, for 10 g of the 4700 g/mole PDMS oligomer, $(10)(0.002) = 0.02$ g of this PDMS/Karstedt's stock solution was used. This dilution method provides a miscible catalyst solution ready to add to the respective oligomer in an accurate manner.

Ten grams of 1900 g/mole (25 repeat units) PDMS (1.05×10^{-2} equivalents vinyl) and Karstedt's catalyst (2.1×10^{-4} g, 0.02 g catalyst/equivalent vinyl) were mixed thoroughly; tetrakis(dimethylsiloxy)silane (0.875 g, 1.05×10^{-2} equivalents Si-H) was then added to the polymer/catalyst solution and mixed thoroughly (Figure 3.8). The mixture was poured into a polystyrene weighing dish (mold) and cured at 90°C for 2-4 hours until FTIR confirmed the disappearance of $\equiv\text{Si-H}$ at $\sim 2170\text{cm}^{-1}$ to yield a transparent network with 8 weight % hard segment. Mixing of all reagents must be thorough to ensure homogeneous, completely cured, and transparent networks.

Ten grams of 4700 g/mole (62 repeat units) PDMS (4.26×10^{-3} equivalents vinyl) and Karstedt's catalyst (8.5×10^{-5} g, 0.02 g catalyst/equivalent vinyl) were mixed thoroughly; tetrakis(dimethylsiloxy)silane (0.350 g, 4.26×10^{-3} equivalents Si-H) was then added to the polymer/catalyst solution and mixed thoroughly. The mixture was poured into a polystyrene weighing dish (mold) and cured at 90°C for 2-4 hours until FTIR confirmed the disappearance of $\equiv\text{Si-H}$ at $\sim 2170\text{cm}^{-1}$ to yield a transparent network with 3.4 weight % hard segment.

Ten grams of 17,500 g/mole (235 repeat units) PDMS (1.14×10^{-3} equivalents vinyl) and Karstedt's catalyst (2.2×10^{-6} g, 0.02 g catalyst/equivalent vinyl) were mixed thoroughly; tetrakis(dimethylsiloxy)silane (0.093 g, 1.14×10^{-3} equivalents Si-H) was then

Figure 3.8
Hydrosilation of DV-PDMS



added to the polymer/catalyst solution and mixed thoroughly. The mixture was poured into a polystyrene weighing dish (mold) and cured at 90°C 2-4 hours until FTIR confirmed the disappearance of $\equiv\text{Si-H}$ at $\sim 2170\text{cm}^{-1}$ to yield a transparent network with 0.9 weight % hard segment.

3.3.2 PDMS Networks with Varying Crosslink Density

Transparent networks having 3.2, 9.3, 19.6, 34.4, and 57.7 weight % hard segment (crosslinking reagent plus siloxane dimer) were prepared by incorporating systematically varied amounts of 1,3-divinyltetramethyldisiloxane dimer along with a 5000 g/mole PDMS oligomer and crosslinking with tetrakis(dimethylsiloxy)silane (Figure 3.9 and Tables 3.1 and 3.2). For example, a network with 3.2 weight % hard segment was prepared by mixing 5.0 g PDMS (0.002 mole vinyl) with 0.0001 g (0.05 g catalyst/mole vinyl) Karstedt's catalyst with no additional dimer, and then mixed with 0.1644 g (0.002 mole Si-H) tetrakis(dimethylsiloxy)silane and cured as described in section 3.3.1. A network with 9.3 weight % hard segment was prepared by thoroughly mixing 5.0 g DV-PDMS (0.002 mole vinyl) with 0.1864 g (0.002 mole vinyl) 1,3-divinyltetramethyldisiloxane and 0.0002 g (0.05 g catalyst/mole vinyl) Karstedt's catalyst, and then mixed with 0.329 g (0.004 mole Si-H) tetrakis(dimethylsiloxy)silane and cured as described in section 3.3.1. The remaining networks in the series were prepared in a similar manner.

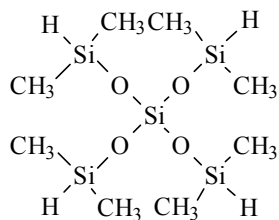
3.3.3 Hydrosilation Curing to Form PMTFPS Networks

Poly[methyl(3,3,3-trifluoropropyl)siloxane] (PMTFPS) networks were prepared from 4200 g/mole (26 repeat units) and 41,050 g/mole (261 repeat units, viscous) PMTFPS vinyl terminated polymers. They were hydrosilated with the kindly supplied fluorinated crosslinking reagent from the Dow Corning Corp. using 0.20 and 2.0 g Karstedt's catalyst/mole vinyl respectively and cured in the same manner as described in section 3.3.4. Stoichiometric amounts of Si-H to vinyl groups were reacted to yield the respective transparent networks with 8 and 0.9 weight % hard segments (% hard segment corresponds to the weight percentage of crosslinking reagent) (Figure 3.10). These reactions were also monitored for the disappearance of the $\equiv\text{Si-H}$ group at $\sim 2170\text{ cm}^{-1}$.

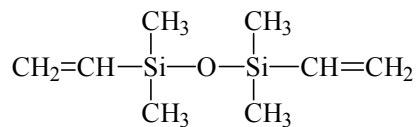
Table 3.1
Varied Weight % Hard Segments for PDMS Networks

HARD Segment		SOFT Segment	Weight % Hard Segment
Crosslinking Reagent (eq.)	Dimer (eq.)	PDMS (5000 g/mole) (eq.)	
2	0	2	3.2
2	1	1	9.3
2	1.5	0.50	19.6
2	1.75	0.25	34.4
2	1.9	0.10	57.7

tetrakis(dimethylsiloxy)silane
crosslinking reagent



1,3-divinyltetramethyldisiloxane
dimer



PDMS

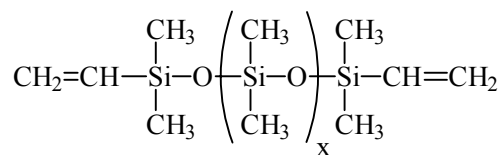


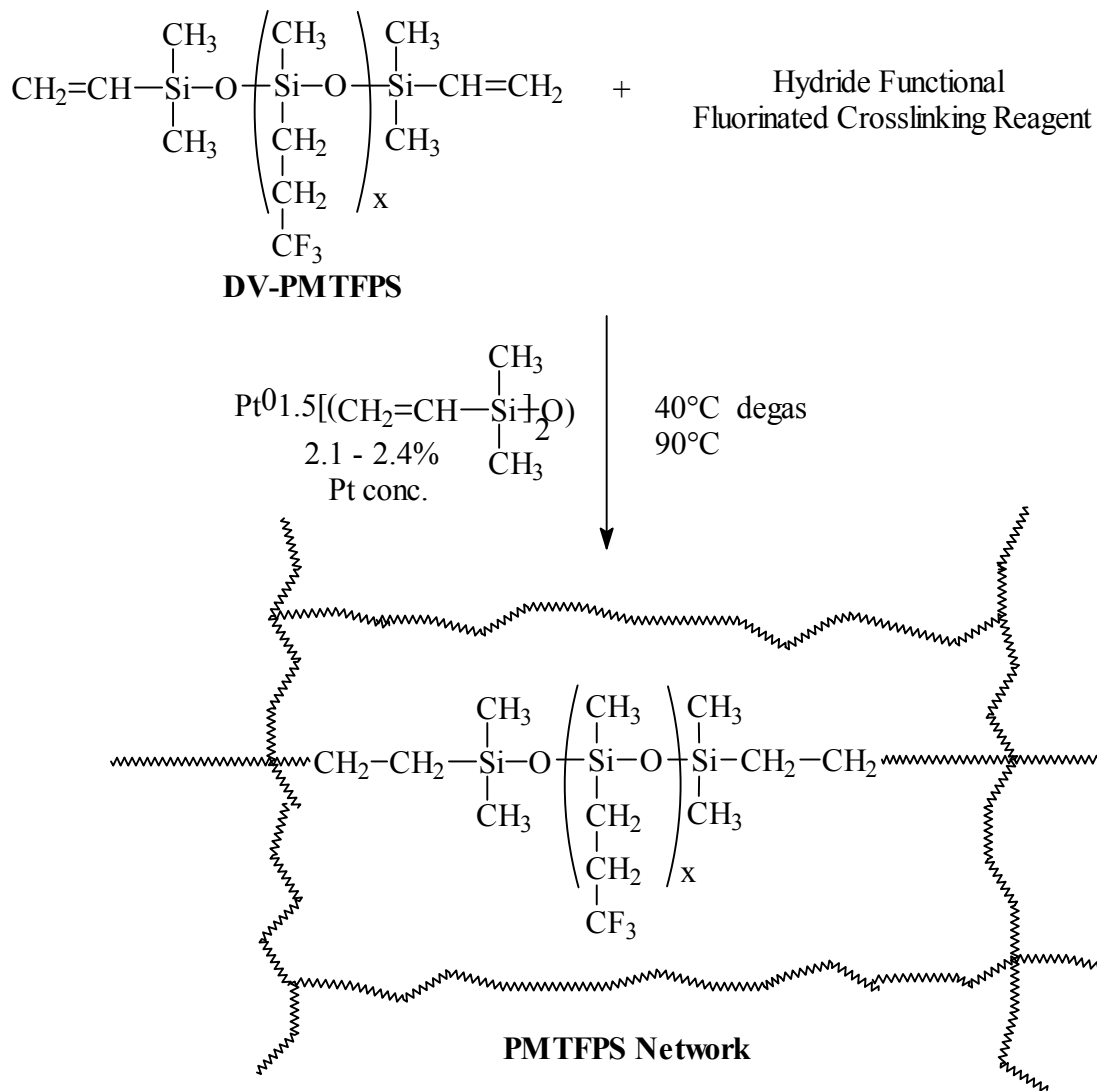
Table 3.2

Calculations for Varied Weight % Hard Segments for PDMS

tetrakis(dimethylsiloxy)silane
crosslinker (XL)1,3-divinyltetramethyldisiloxane
dimerPDMS
polymer

HARD		SOFT	Weight % Hard Segment Calculation (HARD/TOTAL)(100%)	HS %
XL 82.2 g/eq. silane	Dimer 93.2 g/eq. vinyl	PDMS 2498 g/eq. vinyl		
$(2\text{eq.})(82.2) = 164.4$	$(0\text{eq.})(93.2) = 0$	$(2\text{eq.})(2498) = 4996$	$\frac{164.4}{4996 + 164.4}$	3.2%
$(2\text{eq.})(82.2) = 164.4$	$(1\text{eq.})(93.2) = 93.2$	$(1\text{eq.})(2498) = 2498$	$\frac{164.4 + 93.2}{2498 + 164.4 + 93.2}$	9.3%
$(2\text{eq.})(82.2) = 164.4$	$(1.5\text{eq.})(93.2) = 139.8$	$(0.5\text{eq.})(2498) = 1249$	$\frac{164.4 + 139.8}{1249 + 164.4 + 139.8}$	19.6%
$(2\text{eq.})(82.2) = 164.4$	$(1.75\text{eq.})(93.2) = 163.1$	$(0.25\text{eq.})(2498) = 625$	$\frac{164.4 + 163.1}{625 + 164.4 + 163.1}$	34.4%
$(2\text{eq.})(82.2) = 164.4$	$(1.9\text{eq.})(93.2) = 177.1$	$(0.1\text{eq.})(2498) = 250$	$\frac{164.4 + 177.1}{250 + 164.4 + 177.1}$	57.7%

Figure 3.10
Hydrosilation of DV-PMTFPS



3.3.4 Hydrosilation Curing to Form Poly(3-cyanopropylmethyl)siloxane Networks Incorporating DV-PCPMS

For a typical preparation of a transparent network from a 7900 g/mole (61 repeat units) DV-PCPMS, 30.0 grams of DV-PCPMS (7.6×10^{-3} mole vinyl) and 0.152 g Karstedt's catalyst (20.0 g catalyst/mole vinyl) were mixed with a mechanical stirrer while degassing in a three-neck flask. D_4CNH_3 (0.78 g, 7.6×10^{-3} mole Si-H), the polar, trihydride functional crosslinking reagent, was added to the polymer/catalyst solution while stirring and degassing under vacuum. The solution was poured into a polystyrene weighing dish (mold) and cured in a vacuum oven at 40°C for 2 hours, then for an additional 24 – 48 hours at 90°C until FTIR confirmed the disappearance of Si-H at $\sim 2170 \text{ cm}^{-1}$ (Figure 3.11). The resultant network had 2.5 weight % hard segment calculated on the basis of the crosslinking reagent comprising the hard segment. Similarly, a network having 2 weight % hard segment was formed from a 10,000 g/mole (77 repeat units) DV-PCPMS (30.0 g, 0.006 mole vinyl) and D_4CNH_3 (0.615 g, 0.006 mole Si-H) using 0.12 g Karstedt's catalyst (20.0 g catalyst/mole vinyl).

3.3.5 Hydrosilation Curing to Form Poly(3-cyanopropylmethyl)siloxane Networks Incorporating HV-PCPMS

For a typical preparation of a transparent network from a 8850 g/mole (68 repeat units) HV-PCPMS, 30.0 grams of HV-PCPMS (0.0203 mole vinyl) and 0.407 g Karstedt's catalyst (20.0 g catalyst/mole vinyl) were mixed with a mechanical stirrer while degassing in a three-neck flask. $D_4(CN)_2H_2$ (3.80 g, 0.0203 mole Si-H), the polar, dihydride crosslinking reagent was added to the polymer/catalyst solution while stirring and degassing under vacuum. The solution was poured into a polystyrene weighing dish (mold) and cured in a vacuum oven at 40°C for 2 hours, followed by an additional 24 – 48 hours at 90°C until FTIR confirmed the disappearance of Si-H at $\sim 2170 \text{ cm}^{-1}$ (Figure 3.12). The resultant network contained 11 weight % hard segment. Similarly, a network having 4.3 weight % hard segment was formed from a 25,200 g/mole (197 repeat units) HV-PCPMS (30.0 g, 0.00752 mole vinyl) and $D_4(CN)_2H_2$ (1.41 g, 0.00752 mole Si-H) using 0.150 g Karstedt's catalyst (20.0 g catalyst/mole vinyl). Also, a network having 3.1 weight % hard segment was formed from a 35,200 g/mole (275 repeat units) HV-

PCPMS (30.0 g, 0.0051 mole vinyl) and $D_4(CN)_2H_2$ (0.955 g, 0.0051 mole Si-H) using 0.1023 g Karstedt's catalyst (20.0 g catalyst/mole vinyl).

3.4 Characterization Methods for Monitoring Reactions and Purity of Reagents

3.4.1 Gel Permeation Chromatography

Molecular weight distributions of polymer chains/small cyclics compositions at equilibrium and final polymers after removal of cyclics, were obtained on a Waters 2690 Alliance gel permeation chromatograph (GPC) instrument calibrated with polysiloxane standards using an RI detector, a styragel column set (100-500- 10^3 - 10^4 Å), and a chloroform mobile phase operating at 1ml/min and 30°C. Samples were prepared by dissolving 30 – 40 mg of sample in 10 mL HPLC grade chloroform, and then filtering through a 4.5 μ filter before loading into the GPC autosampler. All GPC results were kindly acquired by Dr. Q. Ji and Dr. H. K. Shobha.

3.4.2 Fourier Transform Infrared Spectroscopy

Hydrosilation reactions were monitored for the disappearance of $\equiv Si-H$ via Fourier Transform Infrared Spectroscopy (FTIR) on a Midac GRAMS/32 model M2004 FTIR instrument. For monitoring the syntheses of D_4CN , D_4CNH_3 , and $D_4(CN)_2H_2$ cyclics, samples were prepared by placing one to two drops of solution on NaCl salt plates. For all hydrosilation cure reactions using PDMS, PMTFPS, DV-PCPMS, and HV-PCPMS, samples were prepared by placing one to two drops of the uncured resin mixture on NaCl salt plates. The samples were cured in an oven at 90°C, then removed from the oven briefly at hourly intervals for scanning. The FTIR samples for the 180° peel adhesion tests were prepared by scraping a thin piece of the network with a razor and placing it between NaCl salt plates. Transmission data were obtained by acquiring 8 scans with a resolution of 8 cm^{-1} at room temperature from 4000 cm^{-1} to 900 cm^{-1} with background subtraction for each analysis.

3.4.3 ^1H , ^{13}C , and ^{29}Si Nuclear Magnetic Resonance Spectroscopy

Proton (^1H), Carbon (^{13}C), and Silicon (^{29}Si) Nuclear Magnetic Resonance Spectroscopy (NMR) are powerful characterization tools which were employed to provide data monitoring hydrosilation reactions, number average molecular weights (M_n), characterizing cyclic products based on ratios of hydride functionality: 3-cyanopropyl substituents, and confirming the degree of endcapping of polymer products.

^1H NMR was obtained on a Varian Unity 400 NMR spectrometer operating at 399.9 MHz with a spectral width of 5000 Hz, 22° pulse with a width of 25 μsec and 64 scans with $\pm 2\%$ error. The samples were prepared by dissolving ~ 100 mg of sample in 0.9 mL deuterated chloroform (CDCl_3). Polymer M_n 's were calculated from endgroup analyses, by ratioing the area of one proton in a repeat unit to the area of one proton on a vinyl endgroup. The structures of D_4CNH_3 and $\text{D}_4(\text{CN})_2\text{H}_2$ were also characterized via ^1H NMR.

For ^{13}C NMR, the instrument was operated at 100.6 MHz with a sweep width of 25000.0 Hz and a 90° pulse angle with a relaxation delay of 6 sec and ~ 500 scans with $\pm 5\%$ error at most. For ^{29}Si NMR, the instrument was operated at 79.46 MHz with a sweep width of 25000.0 Hz, 45° angle with a relaxation delay of 11.2 sec. and inverse gated decoupling was used with ~ 500 scans with $\pm 5\%$ error at most. Polymer samples for both ^{13}C and ^{29}Si NMR were prepared by dissolving 0.630 g of polymer in 2.4 mL CDCl_3 , and doping with 0.0519 g tris(acetylacetonato)chromium (III), $\text{Cr}(\text{acac})_3$, to decrease spin-lattice relaxation times (T_1). The relaxation delay time in quantitative ^{13}C and ^{29}Si NMR was set to five times T_1 for each sample. Confirmation of complete endcapping and to assure that no silanol groups were present, ^{13}C , and ^{29}Si NMR were also obtained on a Varian Unity 400 NMR spectrometer. Quantitative ^{13}C and ^{29}Si NMR were kindly obtained by Mr. Tom Glass.

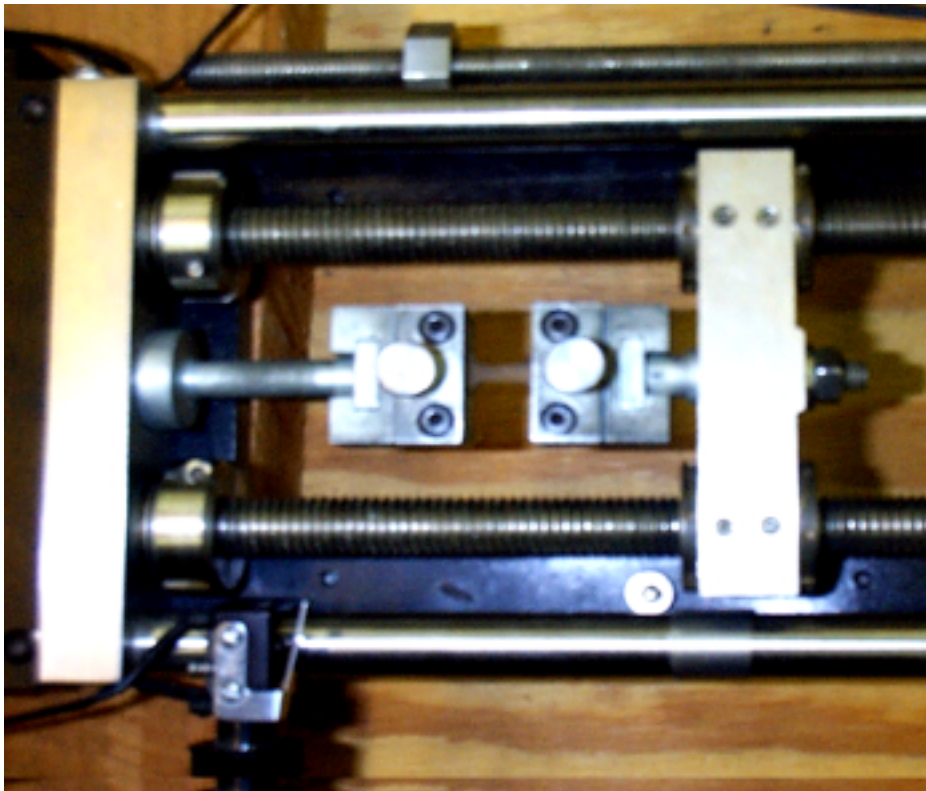
3.5 Characterization of Polymers and Networks

3.5.1 Tensile Properties: % Elongation, Strength, and Young's Modulus


Tensile measurements (ASTM D 412) were conducted on networks using a Polymer Laboratories Miniature Materials Tester at a rate of 2mm/min at 25°C (Figure 3.13). Dogbone samples were cut from 2 mm thick network films with a die with

Figure 3.13

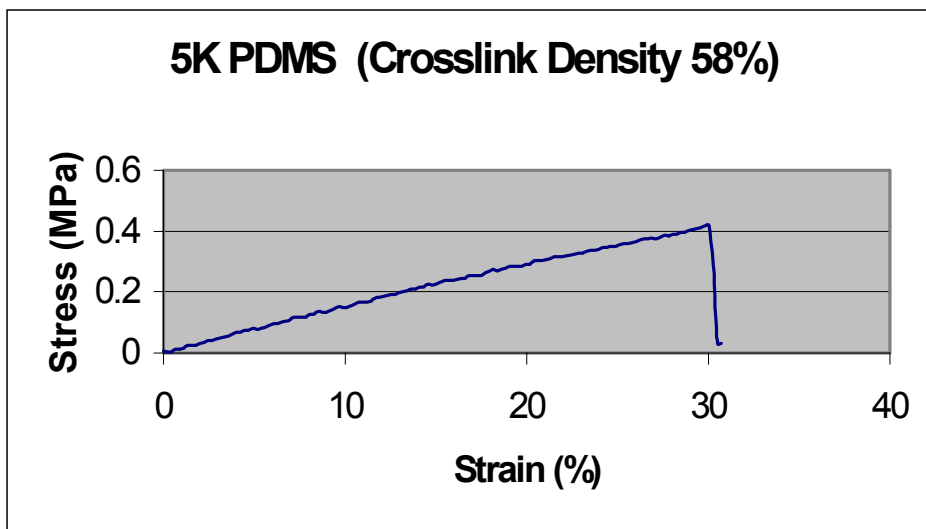
Picture of Sample in Minimat During Tensile Test and Example of Data Obtained



Pull Rate =
2 mm/min



Gauge
Dimensions ~
10 x 2 x 1 (mm)



Modulus
1.4 MPa

Elongation
30%

Strength
0.4 MPa

approximate gauge dimensions of 10x2.6 mm. The tensile data provided % elongation, strength, and Young's modulus for all networks.

3.5.2 Thermal Properties

3.5.2.1 Thermogravimetric Analysis

The thermal properties of all networks were investigated via thermogravimetric analyses (TGA) to measure the temperature at which 5% weight loss of the networks occurred, and to analyze the weight % char yield at 800°C. TGAs were conducted with a Pyris 1 Perkin-Elmer instrument at a heating rate of 10°C/minute. TGA samples sizes of 5 – 10 mg were cut from the network films and heated from 25°C to ~900°C in both air and nitrogen environments.

3.5.2.2 Differential Scanning Calorimetry

The glass transition temperatures (T_g s) were determined for all polymers and networks via differential scanning calorimetry (DSC) by taking the midpoint of the transition. Subambient DSCs were conducted with a Pyris 1 Perkin-Elmer instrument at a heating rate of 10°C/minute. Sample sizes between 5 – 10 mg were used for all polymers and networks in DSC pans with lids. Samples were heated from -150°C to 25°C, quench cooled at “500°C/minute”, then the second heating cycle was done at 10°C/minute. All reported data are from the second heating scans.

3.5.3 Network Solvent Resistance

Assessment of network solvent resistance was determined by performing swelling tests (ASTM D 471) on cured networks at 25°C in Jet A jet fuel, water, chloroform, and Reference Fuels B and C (73/30 and 50/50 v/v mixtures of isooctane/toluene, respectively). Jet A jet fuel was purchased from the Blacksburg airport, isooctane (Aldrich HPLC grade), toluene and chloroform (Fisher), and deionized water were all used as received. Sample sizes between ~0.1 – 0.2 g were cut from their respective networks, and weighed in a scintillation vial, M_1 . Three samples for each network were swollen in each of the solvents for 7 days at ambient temperature out of direct sunlight. The samples were then removed from the solvent, quickly blotted dry with a Kimwipe[®],

and reweighed, M_2 . The percent change in mass was calculated after swelling for 7 days by: $[\{(M_2 - M_1)/M_1\} \times 100\%]$. It should be noted that this does not directly relate to volume swelling % comparison of the liquids due to different solvent densities.

3.5.4 Adhesion Analysis: 180° Peel Test

Adhesive strengths of cured networks were tested using 180° metal to metal peel tests (ASTM D 903), and conducted on a model 1123 Instron 5500R using a 200lb reversible load cell and a rate of 6in/min at 25°C. The adherends, Al(7075-T6) and TiAl₄V₆ panels (1x8x0.125”), were used in conjunction with Al (1100 grade) foil (2 mil thick) substrates. Adherend surfaces were prepared with a soapy water and scotchbrite® scrub to remove any oily residues, then with a solvent cleansing (scotch brite® pad with acetone), mechanical abrasion (scuffed with coarse grain sandpaper), followed by a second solvent rinse (methyl ethyl ketone and acetone); and were allowed to condition in a 100°C oven for a minimum of 60 minutes to ensure removal of residual solvent and water. The substrates were prepared similarly except without the initial soap water treatment. Consistent sealant drawdown thicknesses of 10-15 mils (measured with a caliper) were achieved using a 19 mil (wet thickness) drawdown rod. After the uncured resin mixtures were drawn down onto the aluminum foil substrate, the adherend panels were placed on top of the resin (Figure 3.14). The entire sheet was placed into an oven at 90°C until FTIR confirmed the disappearance of any hydride functional groups. Once cured, the sheet was removed from the oven and a roller type razor was employed to cut precisely along the edges of the substrates, leaving one inch adherends bonded to one inch pieces of foil substrates (Figure 3.15). The extra tab of foil and adherend were clamped at opposite ends of the Instron and separated at a 180° peel angle at a rate of 6"/minute (Figure 3.16).

Figure 3.14

Picture of Drawdown Preparation for 180° Adhesive Peel Test

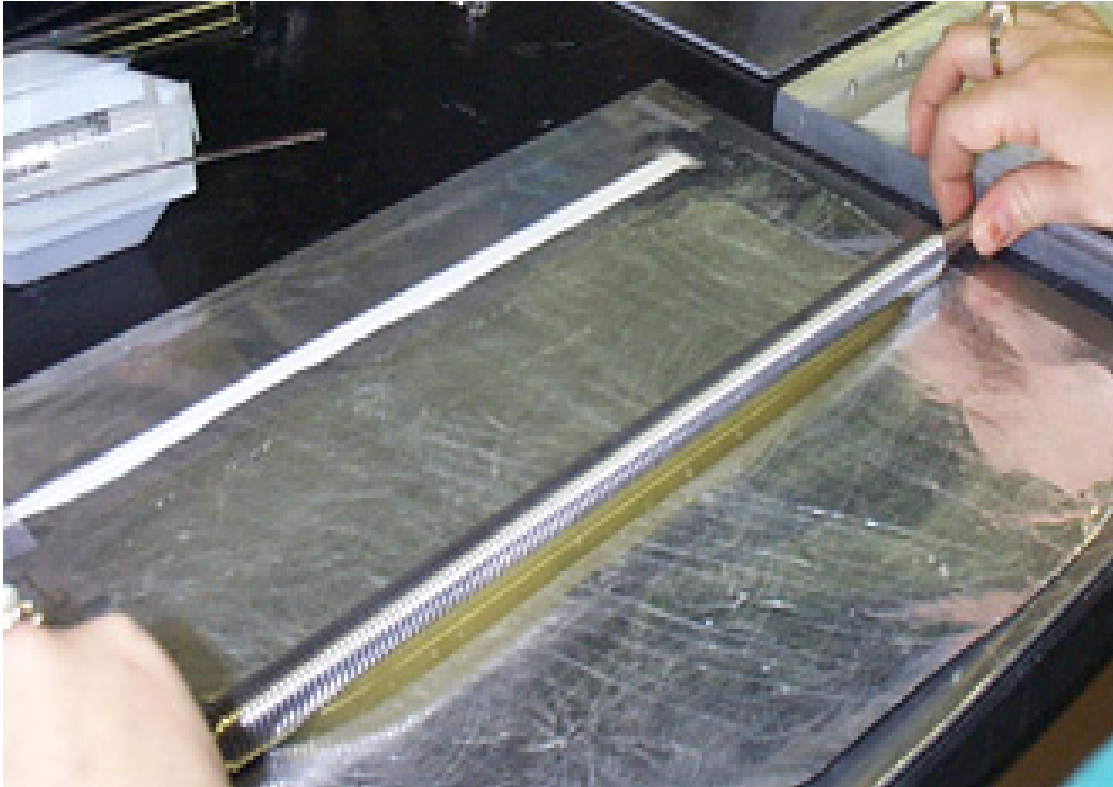


Figure 3.15

Picture of Adherends Bonded to Substrates for 180° Peel Test

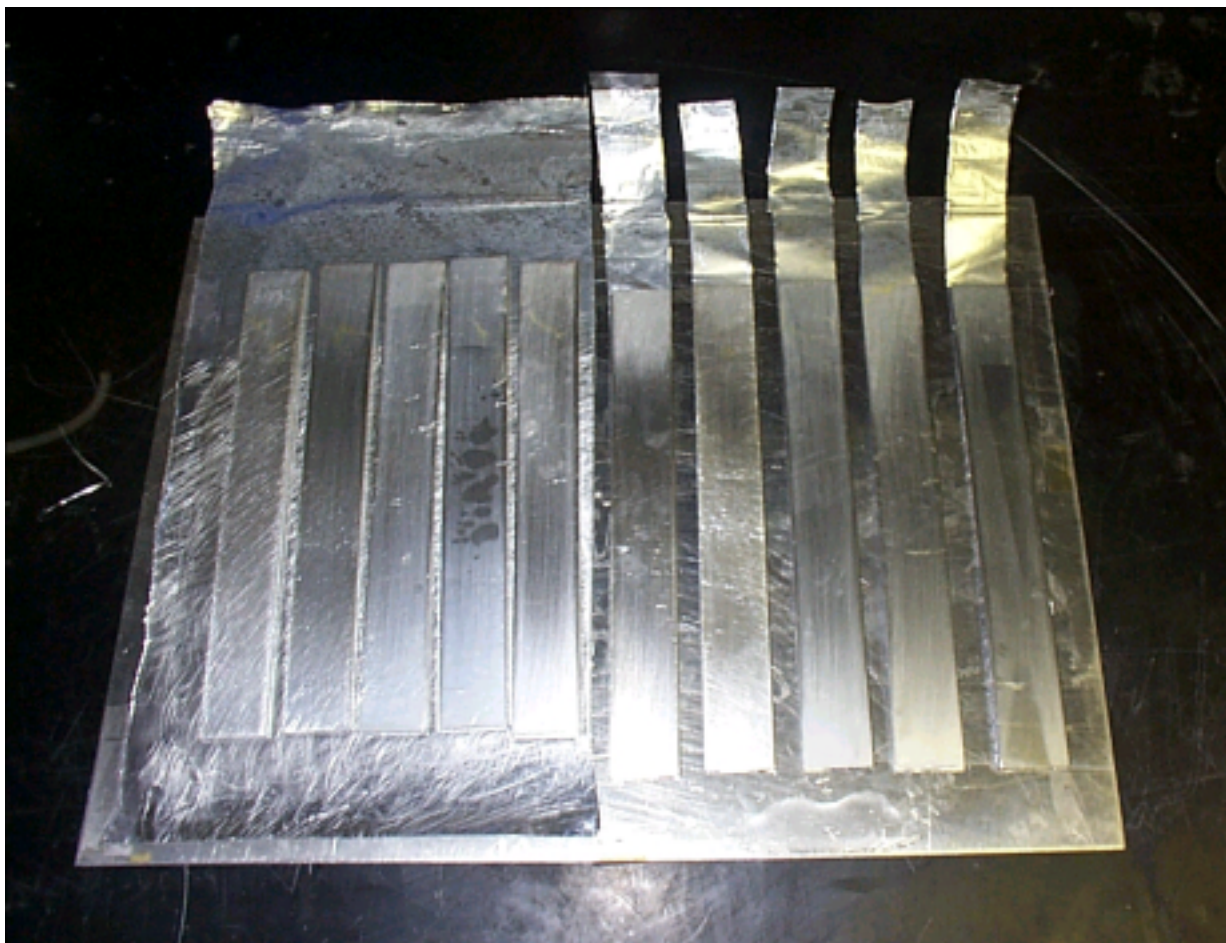
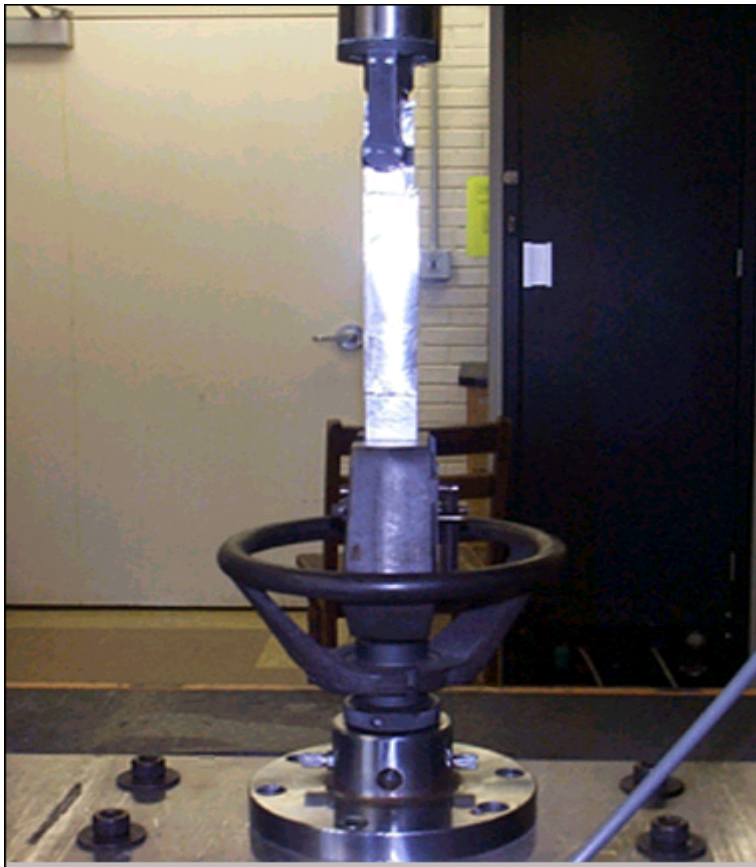
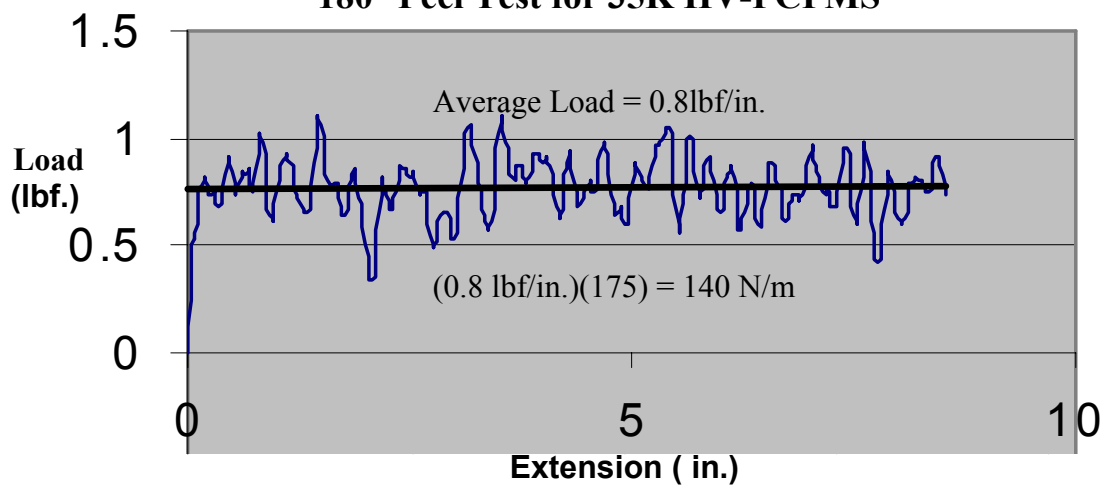


Figure 3.16

Picture of Sample in Instron During 180° Peel Test and Example of Data Obtained



**ASTM D 903
180° Peel Test for 35K HV-PCPMS**



Chapter 4

RESULTS AND DISCUSSION

4.1 Synthetic Plan and Overview of Organosiloxanes and Their Corresponding Networks with Sidechain Chemical Structures of Varying Polarity

The synthetic plan was to form polar polyorganosiloxane networks from vinyl terminated PCPMS oligomers, and compare their network properties as sealant materials to previously studied networks formed from vinyl terminated PMTFPS and vinyl terminated nonpolar PDMS oligomers (Figure 1.1). The polar PCPMS networks are of particular interest in this study, while the PMTFPS networks serve as an industrial comparison and the PDMS networks serve as the nonpolar control for sealant materials. Each oligomer series with varying sidechain chemical structures was synthesized with tailored numbers of repeat units to yield comparative networks with similar weight % hard segments.

Polar polyorganosiloxanes (PMTFPS) are under investigation industrially for aircraft fuel tank sealants. They offer many attractive properties such as thermo-oxidative stability at high temperatures, low temperature flexibility, solvent resistance, and reasonable adhesion to metals.¹²⁸ By contrast, the nonpolar PDMS networks also have excellent properties, but have a much higher propensity to swell in nonpolar, hydrocarbon fuels. The polar 3-cyanopropyl substituents of the PCPMS networks make them resistant to solvents, especially hydrocarbons such as those used in jet fuels. The nitrile group on the 3-cyanopropyl substituent can function as an electron pair donor, which is expected to greatly improve adhesion to hydroxyl groups in oxide surface layers on metal adherends. In the past, thermoset polyorganosiloxanes with pendent nitrile substituents have been used as polar stationary phase materials for gas and liquid chromatography.⁽¹⁴⁸⁻¹⁵²⁾ Networks having pendant nitrile groups have also been explored as components of polar membranes, and for the detection and titration of alkali metal and alkaline-earth metal cations in solutions; where the nitrile group serves as a complexation site for electropositive constituents.¹⁵³

“Advanced sealants” require high temperature fault tolerance, and good adhesion to metals and advanced composites. Examples which have been investigated include: cyanosilicones, fluoroalkylarylenesiloxanylene (FASIL), fluoroelastomers, tetrafluoroethylene oxide phenylquinoxaline elastomers, and perfluoroalkyl ethers.⁸⁹ They have been proposed as sealant materials in harsh environments for aerospace applications such as on fuel tanks, and as channel sealants. The cyanosilicones were found to be resistant to hot hydrocarbon fuels but soluble in polar solvents, (alcohols, ketones, and ethers).¹⁴⁰ They differ from the PCPMS networks in this study in that they do not have 3-cyanopropyl substituents attached to every silicon atom on the siloxane backbone.⁸⁹ These are made by the catalytic addition of an unsaturated nitrile (allyl cyanide) to methylhydrogen polysiloxanes and have random, 3-cyanopropyl, methyl, and hydroxyl substituents (formed by subsequent hydrolysis) on one side of the siloxane backbone. The hydroxyl groups will form the crosslink sites along the chain, rather than at the endgroups as in this study.⁸⁹

In this study, the D₄CN monomer was synthesized from cyclic hydrogenmethylsiloxanes (mostly D₄H) by complete hydrosilation with allyl cyanide in the presence of toluene and Karstedt’s catalyst (Figure 3.4). Purified D₄CN was subsequently equilibrated with LiOH at 140°C, and molecular weights were controlled by adding one mole of base per desired mole of endgroups (2 per chain). Once equilibrated these oligomers were terminated with either a vinyl or trivinyl functional silane quenching reagent to yield either DV-PCPMS or HV-PCPMS (Figure 3.6 and 3.7) as network precursors (Table 1.1). Polar, hydride functional, crosslinking cyclics were required to crosslink the polar DV-PCPMS and HV-PCPMS polymers. Complete hydrosilation of D₄H was used to synthesize D₄CN, the starting material or monomer for PCPMS. Partial hydrosilation, or modification of D₄H was employed to synthesize the tri- and di- hydride functional, polar crosslinking reagents D₄CNH₃ and D₄(CN)₂H₂, respectively (Figure 3.5). Novel, polar, PCPMS networks were formed via two-component addition cure reactions by hydrosilating stoichiometric amounts of vinyl endgroups with ≡Si-H functional groups of D₄(CN)₂H₂ or D₄CNH₃ polar crosslinking reagents (Figures 3.11 and 3.12). The synthesis of the monomers, oligomers, and

crosslinking reagents will be discussed in Section 4.2 and 4.3. Network synthesis will be described in Section 4.4.

The tensile, thermal, swelling and adhesive properties of the three series of networks, PCPMS, PMTFPS, and PDMS, were compared in order to evaluate their potential as sealant materials. The novel, polar, PCPMS networks exhibit excellent thermal stability, low temperature flexibility, excellent resistance to hydrocarbon fuels, and good adhesion to metal substrates. These properties will be discussed in section 4.5 “Network Properties”.

4.2 Synthesis and Characterization of Novel Polar Nitrile Containing Cyclics and Polyorganosiloxanes

4.2.1 D₄CN via Hydrosilation of D₄H

The cyclic species, D_xCN (x = 3 - 6), are cyclic monomers having each silicon atom substituted with one methyl and one 3-cyanopropyl substituent. They may be prepared by hydrolysis of dichlorosilane, reaction of dichlorosilane with zinc oxide or sodium bicarbonate, or hydrosilation with allyl cyanide.¹⁴² In this study, complete hydrosilation of the D₄H cyclic tetramer by addition of the silane, ≡Si-H, across the double bonds of the vinyl groups of allyl cyanide was conducted. This method provides a one-step synthetic route and avoids possible side reactions with the nitrile group since acid byproducts are not involved. Moreover, the D₄H is easy to distill and this leads to excellent yields of D₄CN. The D₄CN product can be fractionally distilled under vacuum, whereas larger cyclics resulting from other synthetic methods cannot be easily purified. A 40% excess of 4 equivalents of allyl cyanide in toluene (acting as a heat sink) was added to D₄H in the presence of platinum(0) complexed with 1,3-divinyltetramethyldisiloxane in xylene (Karstedt's catalyst) to ensure complete addition of the ≡Si-H on the D₄H tetramer across the vinyl groups of the allyl cyanide. Karstedt's catalyst was not only chosen on the basis of the vinyl groups being miscible with the allyl cyanide, but also to avoid ring rearrangements with H₂PtCl₆. Speier's catalyst's is a homogeneous chloroplatinic acid catalyst in isopropanol with its active species being Pt(II).⁴⁸ Karstedt's catalyst is a complex of divinyltetramethyldisiloxane with the active

species being Pt(0).⁴⁹ About 10 - 15% of additions occurred in the reverse manner or Markovnikov¹⁰ type giving 2,2-cyanoisopropylmethyl type substituents. It is worth noting that allyl cyanide addition to dichloromethylsilane yields essentially 100% of the normal addition product, and would thus yield a correspondingly “purer” oligomer. However, the synthetic route used herein provides a much greater yield of the tetracyclic monomer.

4.2.2 D₄CN Monitored via FTIR

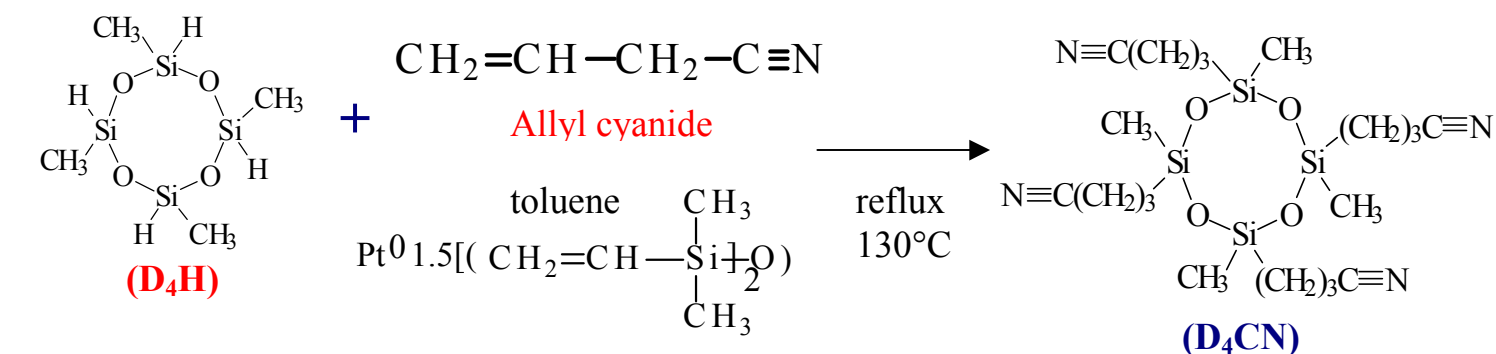
The complete hydrosilation or replacement of silane functional groups with 3-cyanopropyl substituents was followed via FTIR (Figure 4.1). The characteristic peak for ≡Si-H (stretching) is at ~ 2170 cm⁻¹ and that for -CN (stretching) is at ~ 2247 cm⁻¹. The spectrum for the “initial reaction mixture” does not contain catalyst. After the Karstedt’s catalyst was added to the solution and it was brought to reflux at 130°C, samples were taken every hour until the “final product” spectrum was observed where the characteristic peak for the silane functional group (~ 2170 cm⁻¹) had completely disappeared. The typical time for the hydrosilation to be complete was about 24 hours.

Once FTIR confirmed the disappearance of the silane functional groups from the D₄H cyclics, the excess allyl cyanide and toluene were removed by vacuum distillation at 260° - 270°C/0.5 - 1 torr. The crude D₄CN was then purified by high temperature vacuum distillation and the structure was confirmed by ¹H NMR.

4.2.3 D₄CNH₃ and D₄(CN)₂H₂ via Modification of D₄H

Polar, hydride, functional crosslinking reagents were required for crosslinking the polar PCPMS polymers since the nonpolar crosslinking reagent, tetrakis(dimethylsiloxy)silane used for crosslinking PDMS was not miscible with PCPMS. Cyclics, D₄CNH₃ and D₄(CN)₂H₂, were successfully synthesized to meet the miscibility requirements with PCPMS by only modifying the D₄H cyclics with partial hydrosilation with allyl cyanide. Synthesis of the crosslinking cyclics was similar to that for the synthesis of D₄CN. Rather than adding an excess of allyl cyanide to the D₄H, only one mole of allyl cyanide was added for every one mole of D₄H. This reaction was

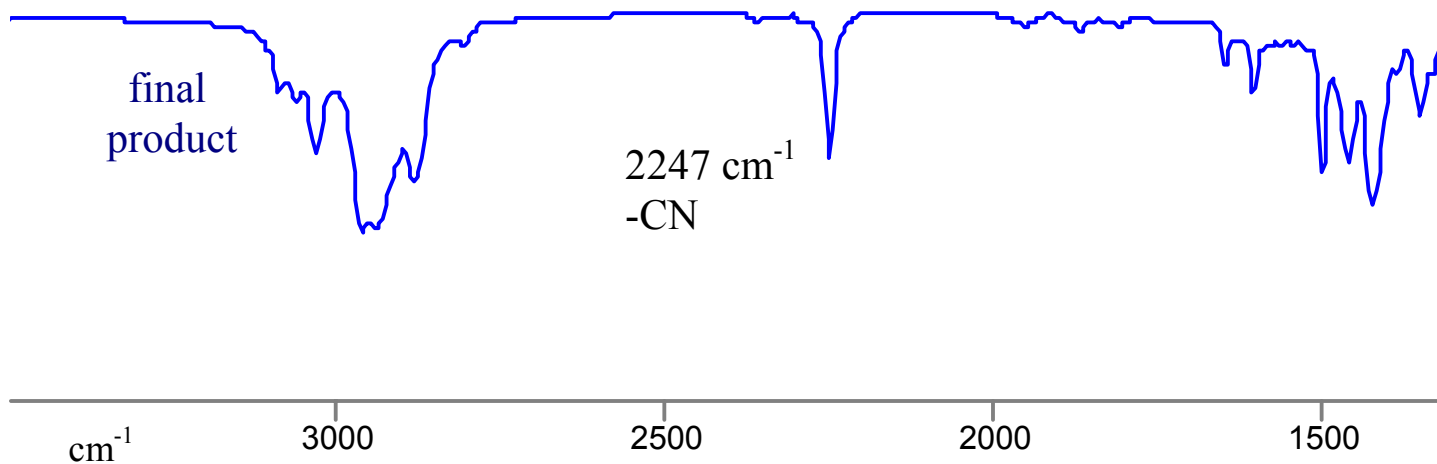
Figure 4.1

Synthesis of D₄CN monitored via FTIR

initial
reaction
mixture

2247 cm^{-1}
-CN

2170 cm^{-1}
-Si-H



conducted in purified toluene as a heat sink and Karstedt's catalyst. The hydrosilation produced a mixture of addition products which were separated by fractional vacuum distillation. The majority of the product rings were substituted once $\sim 55\%$ or twice $\sim 35\%$ by 3-cyanopropyl substituents.

4.2.4 $D_x(CN)_xH_x$ Monitored and Characterized via 1H NMR

Since the modification of D_4H was not intended to replace all of the silane functional groups, FTIR was not employed to observe the complete disappearance of the $\equiv Si-H$ group. Rather than FTIR, 1H NMR was used to monitor 3 changes during the reaction: 1) the disappearance of the vinyl protons from allyl cyanide, 2) the appearance of methylene protons from the newly substituted 3-cyanopropyl groups on the D_4H ring, and 3) the decrease of the integral area of the protons on the D_4H cyclic (Figure 4.2). During the initial \sim one to three hours, most of the vinyl protons (peak **d**) at ~ 5.5 ppm gradually disappear, while the newly substituted methylene protons on the 3-cyanopropyl groups (peaks **a** and **b**) at ~ 0.8 and 1.8 ppm, respectively, appear. The integral corresponding to the hydrogens on the silicon atoms of D_4H (peak **c**) at ~ 4.8 ppm decreases as expected during this period (this will be further discussed in characterization of the fractionated product mixture). The time required for the reaction to go to completion varies from about 2 - 12 hours. The reasons for the variation in reaction time are not clear. The purification procedure for this reaction mixture was similar to that for D_4CN . The crude cyclic mixture was separated into its different boiling fractions by vacuum distillation in an insulated heating mantle. A lower boiling fraction was collected at $83^\circ C - 90^\circ C/0.5 - 1$ torr, and a second higher boiling fraction was collected at $130^\circ C - 140^\circ C/0.5 - 1$ torr.

1H NMR was used to characterize both fractions in terms of the relative amounts of $\equiv Si-H$ and 3-cyanopropyl substituted units (Figures 4.3 and 4.4). The integral area for the two β -methylene protons (peak **a**) at ~ 1.8 ppm was set to 2.00 as a reference corresponding to one 3-cyanopropyl substituted unit. Peak **b** at ~ 4.8 ppm corresponds to the hydrogens remaining on the silicon atoms. In Figure 4.3, the integral area of peak **b** is ~ 3 . So, for every one 3-cyanopropyl substituent present on the ring, there are 3 remaining silane hydrogen atoms. This corresponds to the molecular formula, D_4CNH_3 ,

Figure 4.2

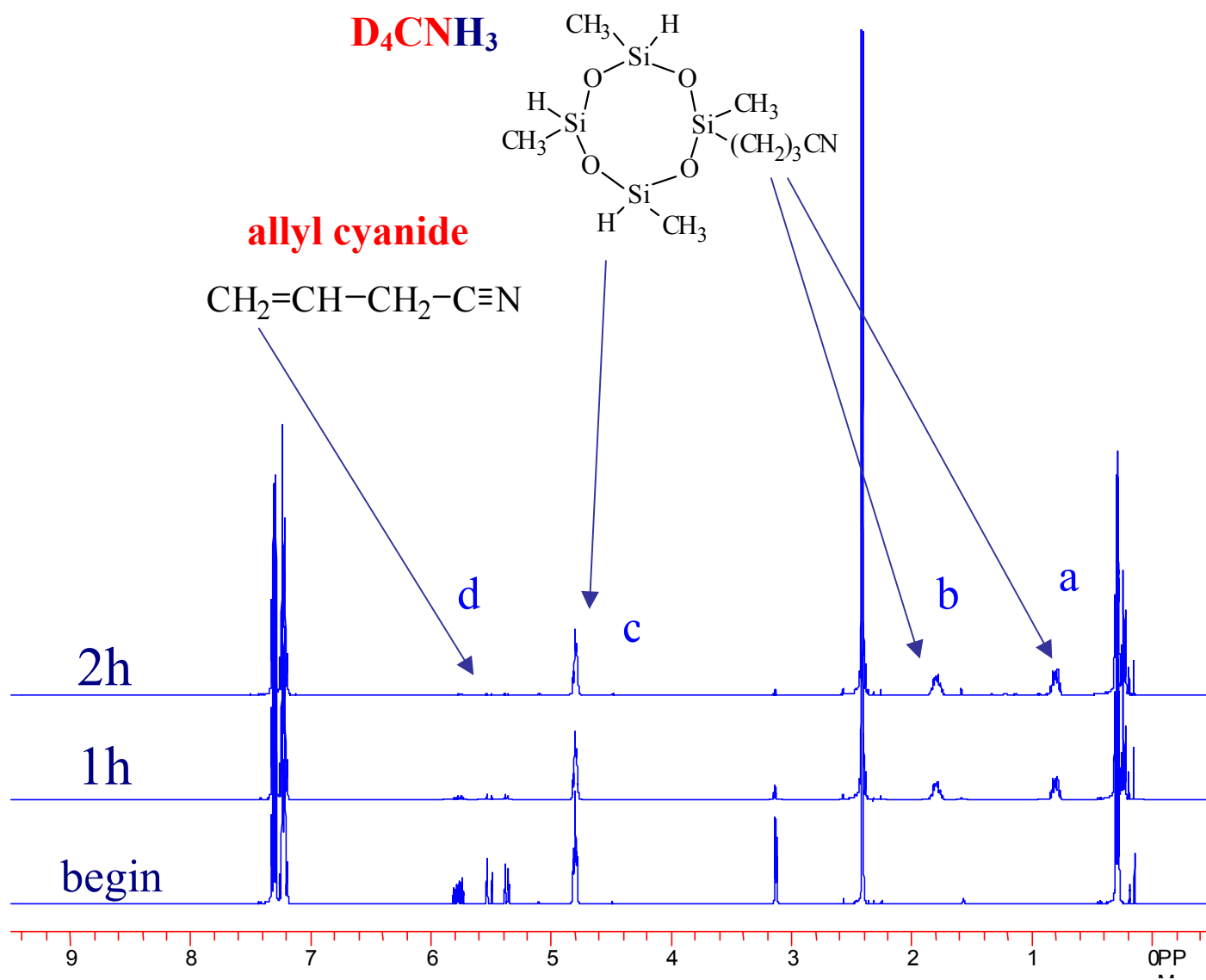
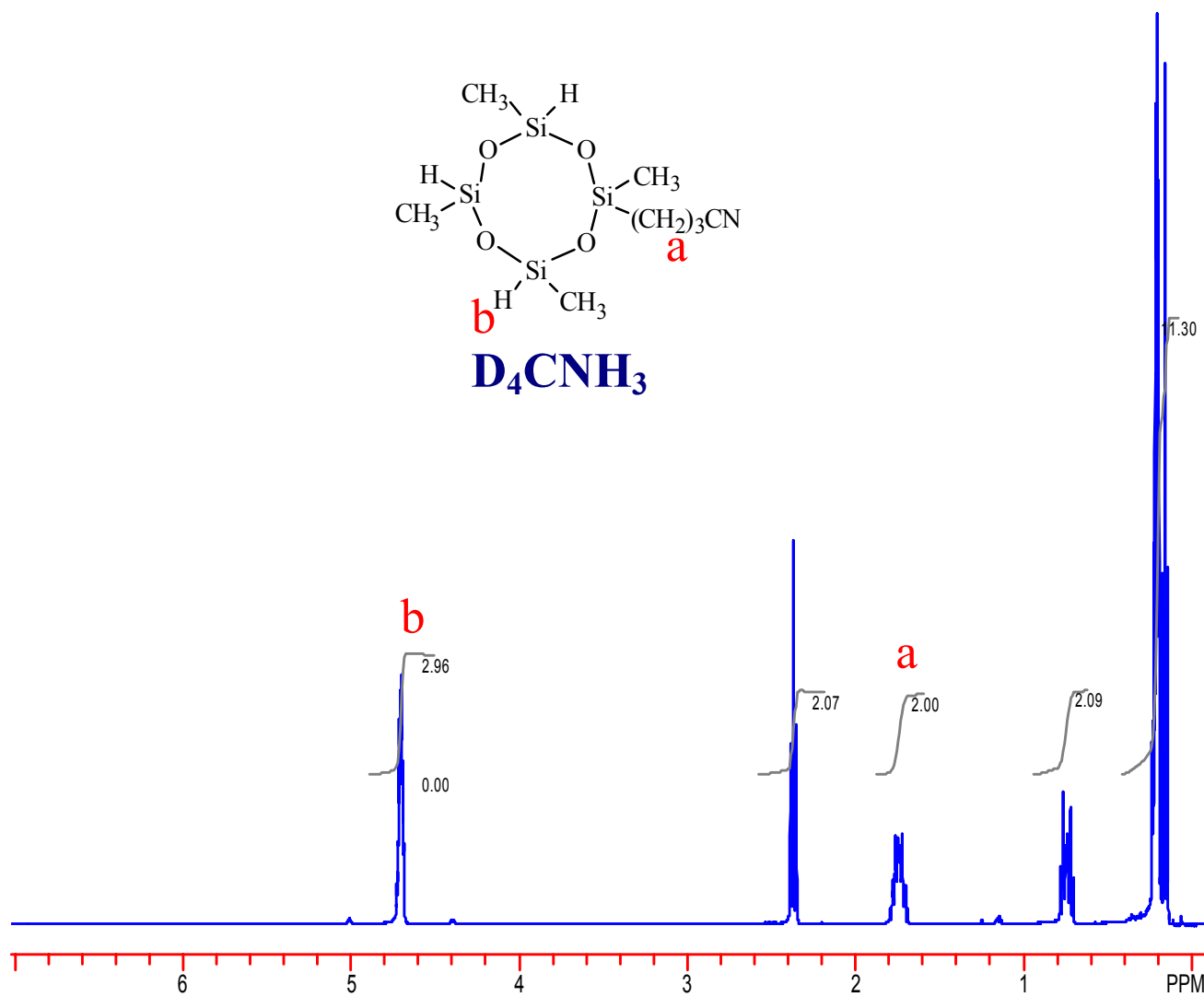
 ^1H NMR for Monitoring the Modification of D_4H 

Figure 4.3

 ^1H NMR for D_4CNH_3 After Distillations

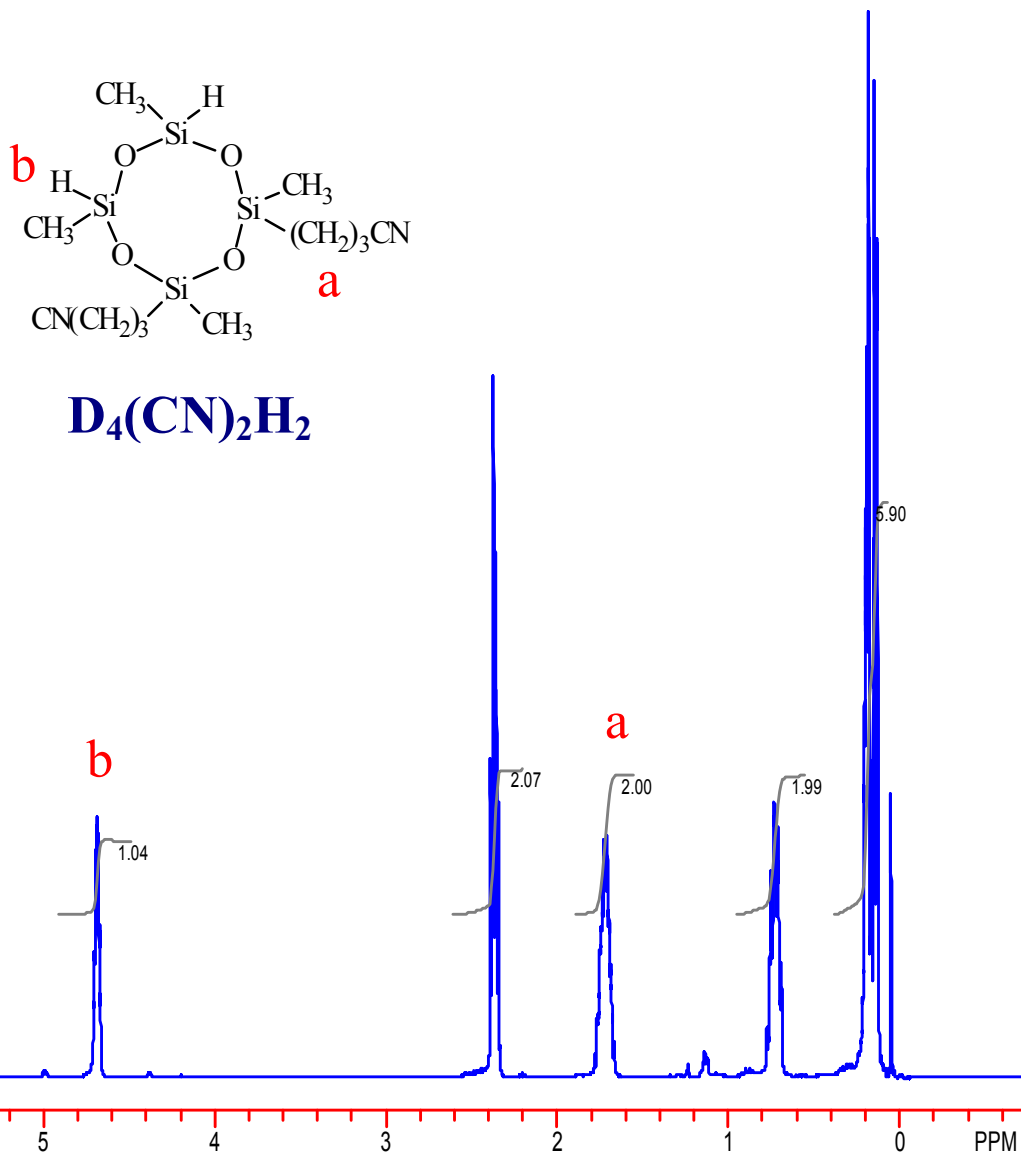
a polar, tri-hydride functional, cyclic crosslinking reagent. The integral area of peak **b** in Figure 4.4 is ~ 1 , thus for every one 3-cyanopropyl substituent, there is one remaining silane hydrogen atom. This represents the molecular formula, $D_4(CN)_2H_2$, a polar, dihydride functional crosslinking reagent which may be used for the hydrosilation of polar polymers with a functionality of three or more.

4.2.5 Equilibration of DV-PCPMS and HV-PCPMS

Polyorganosiloxanes with one methyl- and one 3-cyanopropyl- substituent on each silicon atom along the siloxane backbone, PCPMS, have been synthesized with tailored average numbers of repeat units to make comparisons with the other polymer systems. Two series of these materials were prepared by terminating the oligomers with either vinyltrichlorosilane or trivinylchlorosilane to yield divinyl (DV) and hexavinyl (HV) functional PCPMS oligomers. The polar, monomeric precursor described in section 4.2.1, D_4CN , was equilibrated in the presence of LiOH. Rather than equilibrating in the presence of an endcapping or chain transfer reagent (as in the case of PDMS described herein), molecular weight was controlled by using one mole of LiOH for every desired mole of endgroup (2 per chain). The larger and more polar 3-cyanopropyl (than methyl on D_4) substituents present on the D_4CN rings result in an equilibrium which lies further towards the side of the cyclics (compared to the equilibrium for PDMS and its cyclics). The progress of the equilibrations was monitored by GPC, and the molecular weights, M_n , of the final polymer products were characterized using 1H NMR.

The Si-O bond in the D_4CN monomer is more reactive towards base than in D_4 , and correspondingly reacts slower than D_4 in the presence of acid. Therefore a basic initiator was employed for these equilibrations. The equilibration method used for the PCPMS oligomers was flexible in that it allowed for a variety of termination reactions to afford multiple types of functional endgroups. LiOH, as opposed to KOH, was used to avoid side reactions caused by the stronger base. In the presence of KOH, the reaction mixture darkened rapidly, whereas the LiOH yielded transparent almost colorless oligomers. Likewise, attempts to synthesize a siloxanolate catalyst from D_4CN and tetramethylammonium hydroxide (similar to that described herein for equilibrating

Figure 4.4

 ^1H NMR for $\text{D}_4(\text{CN})_2\text{H}_2$ After Distillations

PDMS), yielded very dark colored catalyst mixtures and subsequent colored oligomers. The finely ground LiOH powder was initially heterogeneous in the reaction mixture, and gradually became homogeneous as it reacted at 140°C. When the mixture became transparent it was allowed to equilibrate for an additional 48 hours. Since the LiOH equilibration was conducted at 140°C, water from the condensation of lithium silanols distilled off and was removed with a strong nitrogen purge through the solution. Although LiOH, where Li is a very small cation, is too tightly associated to open the stable tetramer D₄ at a reasonable rate,²⁵ it is reactive enough to equilibrate D₄CN to produce transparent PCPMS polymers effectively within ~ 48h. The LiOH initiator in D₄CN was also advantageous in that it eliminated any need to first synthesize a separate disiloxanolate catalyst.

The rate of polymerization also depends on the type of the sidechain chemical structures on the cyclic monomer. The following example describes how the polymerization rates of four different monomers of varying polarity greatly differ when each is catalysed by potassium siloxanolate.^(2,10) When a 3,3,3-trifluoropropylmethylsiloxy group on a cyclic siloxane is polymerized, rather than a dimethylsiloxy group from D₄, the polymerization rate is increased by 1.5 times, and when a methyl,phenylsiloxy group is present, the rate increases by 4 times. A dramatic increase in the rate of polymerization is observed when cyclic siloxanes with either a γ -cyanopropylmethylsiloxy or β -cyanoethylmethylsiloxy groups, the rate increases by 440 and 630 times, respectively.^(2,10) The monomer, D₄CN, used in this study, has electron accepting substituents, which effectively pull electron density away from the electropositive D type silicon atom, thereby increasing its effective positive charge and facilitating its attack by base.

For the equilibration of D₄CN with LiOH, the lithium siloxanolate reactive species may attack an electropositive silicon atom of a D₄CN ring (*ring-opening*), or it may attack itself or another growing linear lithium disiloxanolate chain (*backbiting or redistribution*) (Figures 3.6, and 3.7). Here, the equilibration is not done in the presence of a small linear endcapping M type siloxane reagent. Therefore, *chain transfer* with an endcapping reagent (as with PDMS, see Figure 3.3 in section 4.3.2) does not occur.

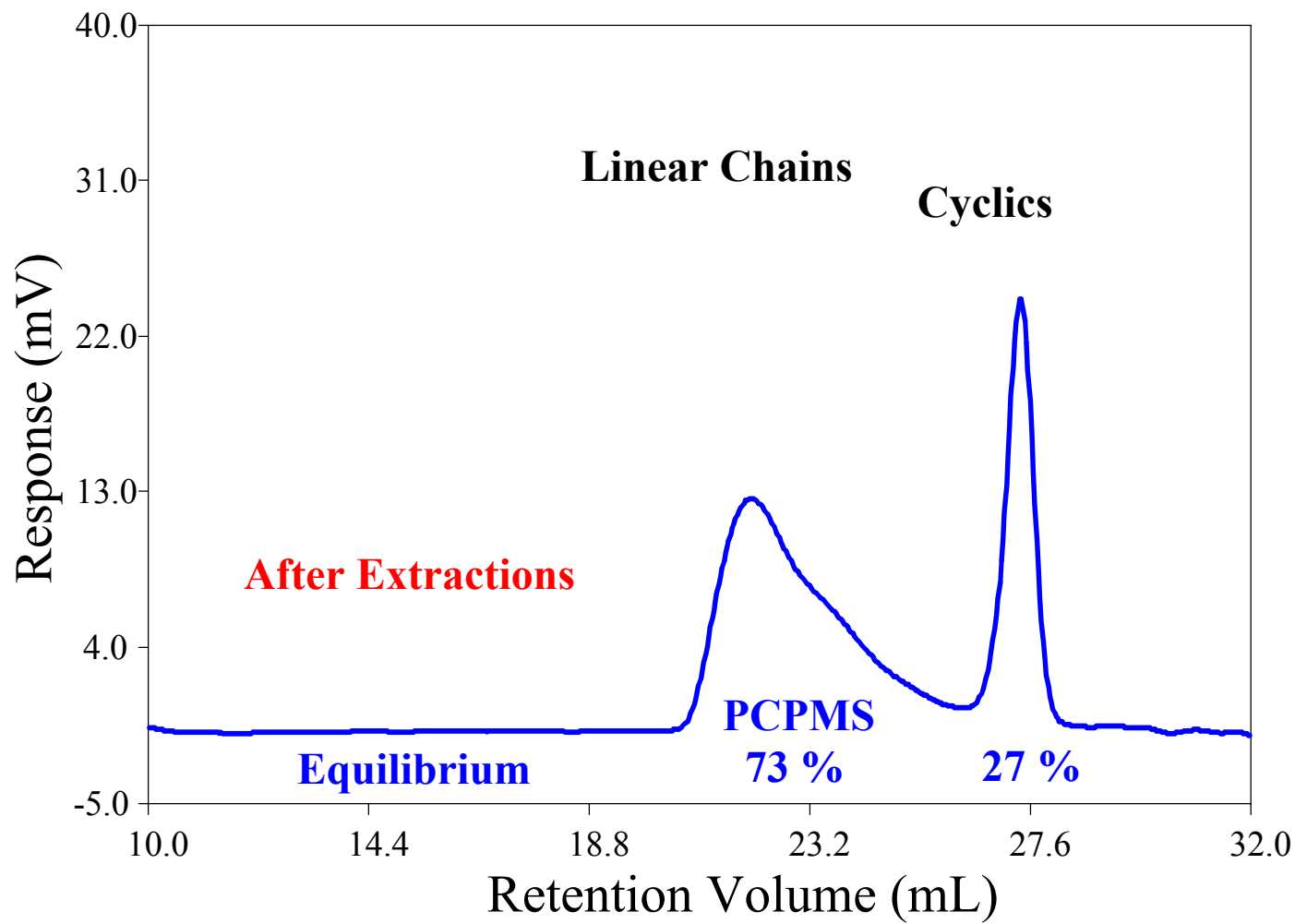
4.2.6 PCPMS Molecular Weight Control and Characterization

In these equilibrations, the LiOH typically requires about 6 - 24 hours (depending on the speed of the mechanical stirrer) to completely dissolve in the D₄CN, after which it takes about 48 hours to reach equilibrium. At equilibrium the concentration of linear chains and small cyclics (mostly D₃CN - D₅CN) remain constant. The reaction was followed by GPC (Figure 4.5). The **equilibrium** curve represents 73% lithium siloxanolate chains in equilibrium with 27% small cyclics. The larger and more polar substituents on the D₄CN monomer cause the equilibrium to lie further toward the small cyclics than in the case of PDMS, which has between ~ 10 - 15% small cyclics at equilibrium. Intrinsic viscosity data confirm that as the size of the substituent on the cyclic monomer increases, the conformational freedom of the organosiloxane chain decreases, thereby pushing the equilibrium further toward the small cyclics at equilibrium.¹⁷ Once equilibration of the lithium disiloxanolate chains with cyclics was achieved, the temperature of the solution was lowered to at least 10°C below the boiling point of the chosen quenching reagent. A 100% excess of the quenching reagent was added at equilibrium to ensure complete endcapping. The siloxanolate oxygens at both ends of the chains attack the electropositive silicon atom of the quenching reagent (either chlorodimethylvinylsilane or trichlorovinylsilane) in an S_N2 reaction to produce endcapped DV-PCPMS or HV-PCPMS chains and LiCl.

Any LiCl which gave the PCPMS a translucent appearance was removed after cyclics extraction by subsequent H₂O washings until the oligomer solutions were transparent. Since the molecular weights and boiling points of the cyclics in this case are much higher than for PDMS cyclics, these cyclics cannot be removed by distillation. Extraction with an 80% ethanol/20% H₂O solvent mixture was effective in preferentially removing the cyclics (Figure 4.5). Very low molecular weight linear chains were also extracted in this process making PCPMS oligomers with target average numbers of repeat units lower than 50 difficult to purify. The broader GPC curve for the **equilibrium** mixture in Figure 4.5 has a shoulder representing lower molecular weight species which are not present in the **after extractions** curve. The latter curve, without the shoulder, demonstrates the removal of some lower molecular weight oligomers. It has a much narrower shape which is characteristic of a lower polydispersity polymer.

Figure 4.5

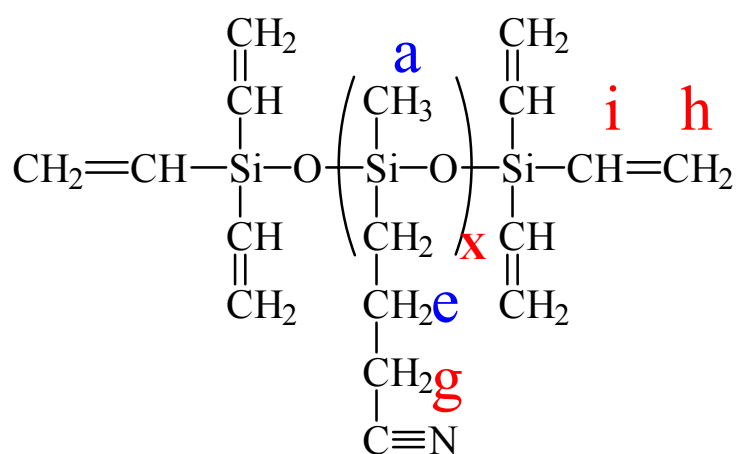
GPC of a 35,200 g/mole DV-PCPMS at Equilibrium



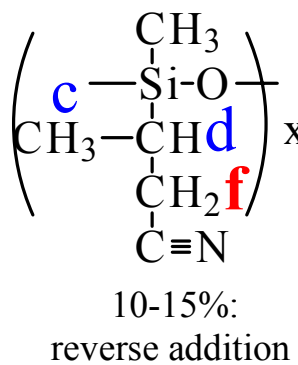
The number average molecular weights, M_n , for all oligomers were determined by ^1H NMR as opposed to GPC due to the absence of narrow distribution PCPMS GPC standards. The low signal in the GPC viscosity detector (due to low polymer viscosities) made application of the “universal calibration” procedure not feasible. A series of DV-PCPMS and HV-PCPMS polymers were prepared with tailored average numbers of repeat units, purified to remove cyclics, and their M_n s were characterized using ^1H NMR (Table 1.1). All of the M_n s achieved were slightly higher than the targeted values, undoubtedly due to the cyclic extraction process. Figure 4.6 represents a ^1H NMR spectrum for a 25,000 g/mole HV-PCPMS. The red letter labels on the peaks for different types of protons represent those used in the M_n calculation. M_n s were determined by the ratios of the integral areas of protons in a repeat unit to the integral areas of protons on endgroups. The integral area of peak **g** at ~ 2.4 ppm corresponds to the number of β -methylene protons on the 3-cyanopropyl groups on units formed via the normal addition reaction. Peak **f** at ~ 2.22 ppm must also be taken into account since this corresponds to the β -methylene protons of the reverse addition product. The total integral area of the two, 2.19, was divided by 2 to arrive at an approximate integral area of 1.095 corresponding to the number of internal siloxane units. The sum of the integral areas of peaks **h,i** at $\sim 5.8 - 6.2$ ppm equal 0.10 and corresponds to 18 vinyl protons on the endgroups of a polymer chain. The integral area of one proton on an endgroup equals 0.005556. Therefore, there are $1.095/0.005556$, or an average of 197 repeat units for this HV-PCPMS. The internal molecular weight of a repeat unit is 127 g/repeat unit for PCPMS polymers. Therefore this corresponds to approximately a 25,000 g/mole polymer, and adding on the endcapper’s molecular weight yields an M_n of 25,234 g/mole.

^1H NMR was also used to analyze the relative amount of direct versus reverse addition products on the oligomer. The data revealed $\sim 10 - 15\%$ reverse substitution. This percentage of reverse substitution unit structures for the most part originated from the addition reaction in forming the D_4CN monomer. The ^{13}C NMR and ^{29}Si NMR spectra for a 35,000 g/mole HV-PCPMS are represented in Figures 4.6B and 4.6C.

Figure 4.6

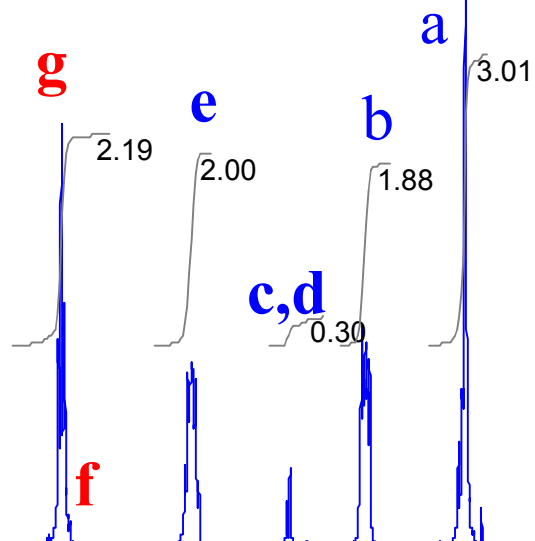
 ^1H NMR for 25,200 g/mole HV-PCPMS

HV-PCPMS



$$(197 \text{ RU})(127 \text{ g/mole}) = 25,000 \text{ g/mol}$$

h,i
0.10



7 6 5 4 3 2 1 PPM

Figure 4.6 B

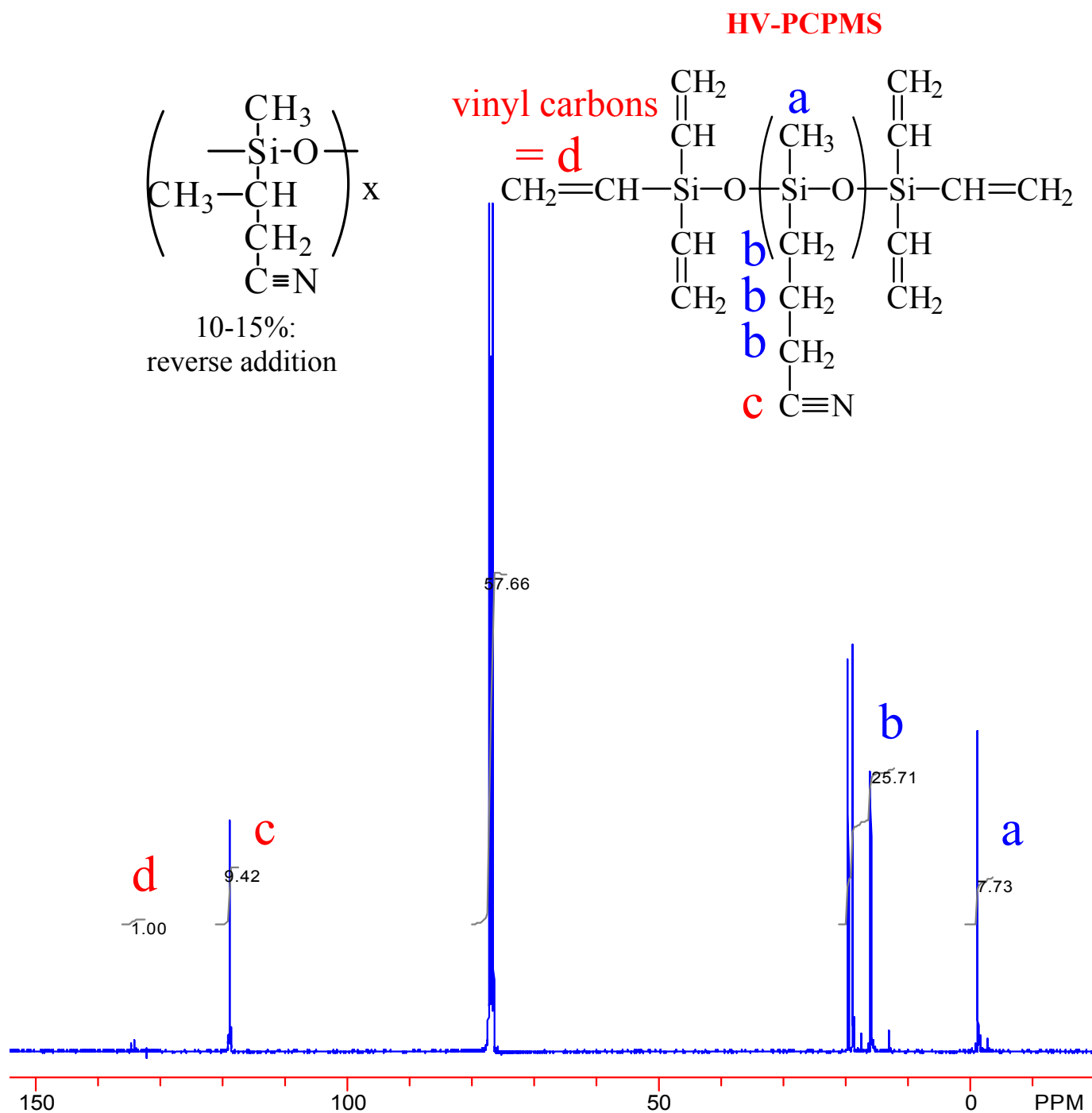
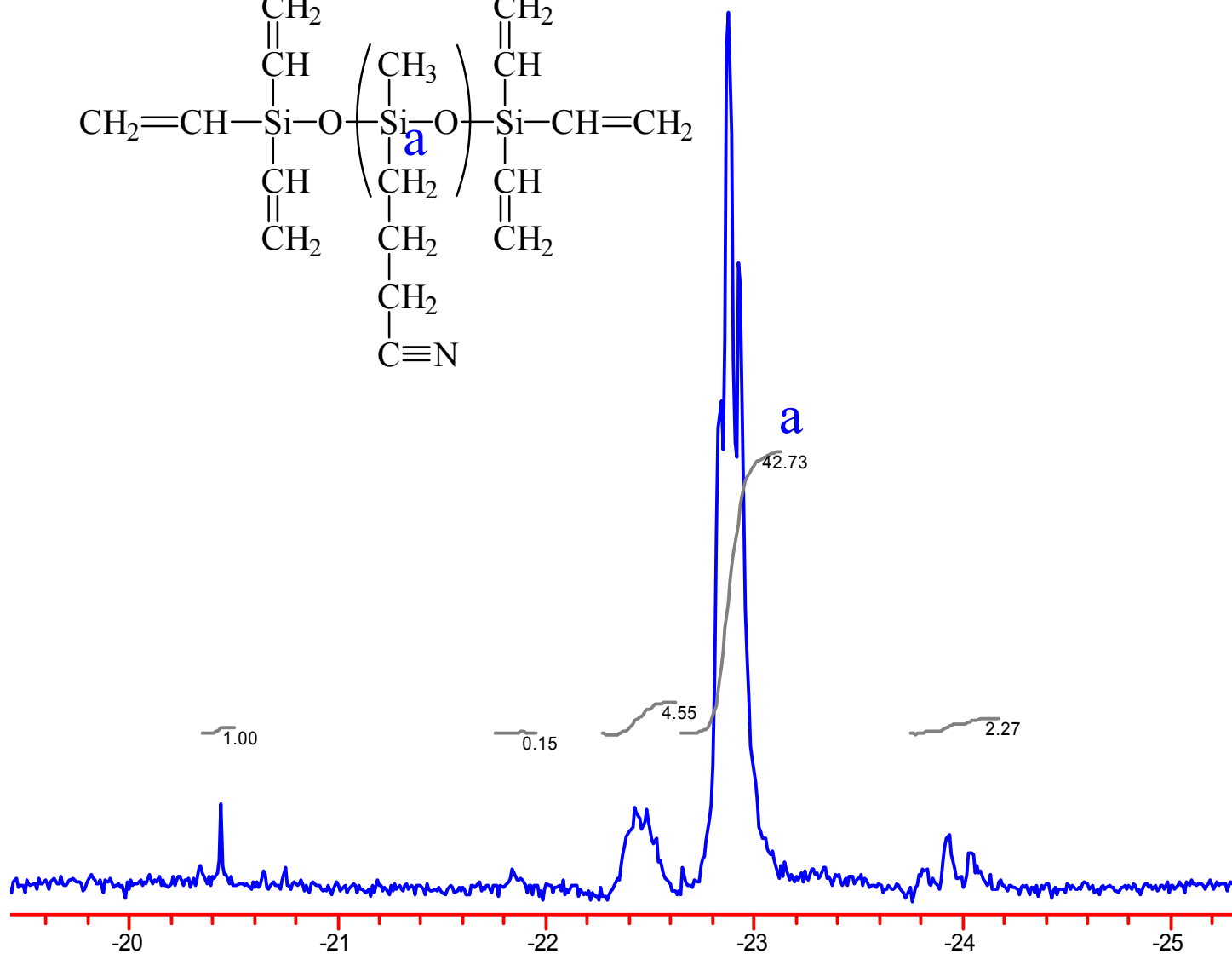
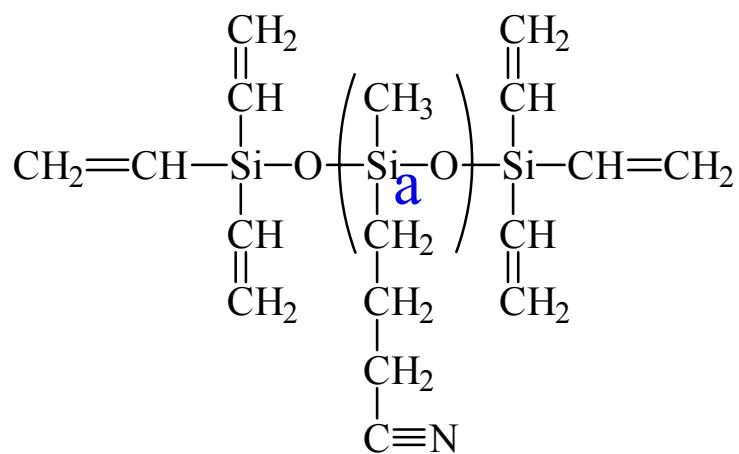
 ^{13}C NMR for a 35,000 g/mole HV-PCPMS

Figure 4.6 C

 ^{29}Si NMR for a 35,000 g/mole HV-PCPMS

HV-PCPMS



4.3 Preparation and Characterization of the Nonpolar, Control PDMS

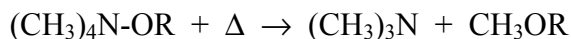
The synthesis and characterization of PDMS polymers and networks has been the focus of both academic and industrial interest, and many excellent references are available in the literature today.^(1,2,6,7,10-22) Thus, PDMS represents an excellent control material for comparing properties of polyorganosiloxanes. A series of divinyl terminated PDMS polymers were synthesized with tailored average numbers of repeat units, subsequently crosslinked via a two-component addition cure, and their corresponding networks were characterized as potential sealant materials. The PDMS materials series represents the nonpolar networks in this study. These chains are known to form helical structures, with the hydrophobic methyl- substituents protruding outwards.¹

4.3.1 Equilibration of PDMS

A moisture free, preformed polysiloxanolate catalyst was used to synthesize controlled molecular weight PDMS oligomers using an equilibration procedure in the presence of an endcapping reagent. Tetramethylammonium disiloxanolate has been proven to be an effective catalyst for the equilibration of PDMS due to its reactivity, solubility, and transient nature.²⁰ The activities of tetramethylammonium and tetrabutylphosphonium siloxanolates in bulk equilibrations of D₄ exhibit reactivities close to that of cesium siloxanolates. For a series of cations, the alkali metal hydroxides and siloxanolates of Cs were found to be the most reactive, i.e., Cs > Rb > K > Na > Li.²⁵ Increasing the cations' ionic radius allows for greater donor action of the oxygen atom in the base, (less tight associations with the siloxanolate active species), therefore leading to higher reactivities.¹

The tetramethylammonium disiloxanolate catalyst used in this research for the equilibrations of PDMS was prepared by charging tetramethylammonium hydroxide pentahydrate into D₄ under a rapid stream of N₂ and reacting it at 80°C. Tetramethylammonium hydroxide becomes increasingly soluble ~ 65 – 70°C as it begins to react with D₄.¹¹ The 80°C reaction temperature was convenient since the catalyst decomposes slowly around 90°C and quickly above 130°C.²⁰ After the equilibration is complete, this catalyst can be decomposed in situ to volatile and inert products. Thus, no additional neutralization or catalyst removal steps are required. Tetramethylammonium

siloxanolate decomposes into methanol or methoxysiloxane and trimethylamine with the decomposition reaction's activation energy being 42 kcal/mole²:



where R = H or (-Si(CH₃)₂O-)n.

Synthesis of the tetramethylammonium disiloxanolate catalyst proceeded by reaction of the hydroxide ion with the electropositive silicon atom of the D₄ cyclic tetramer and opened the ring. The resultant silanols dimerized to condense and evolve H₂O. Following the redistribution reaction, an equilibrium between linear tetramethylammonium siloxanolate chains and small cyclics was established (Figure 3.2). The reaction mixture was slightly hazy during the first few hours, but became translucent by the end of the 24 hour reaction period. The nitrogen stream was bubbled through the reactor at a fast rate to remove the water of condensation. After cooling to ambient temperature, this viscous, translucent catalyst was diluted by 50 volume % of anhydrous D₄. It was then directly transferred to either a reaction or to a predried, septum-capped brown bottle and stored in a dessicator until used.

A series of PDMS polymers were synthesized with average numbers of repeat units similar to those prepared for the polar polymers in this study. The objective was to compare average chain lengths rather than M_ns. Equilibrations of the stable tetramer D₄ are entropically driven since the heat of polymerization is near zero. This requires a more reactive catalyst than that used to ring open a strained D₃ cyclic which is enthalpically driven. The tetramethylammonium disiloxanolate catalyst described above was used to open the D₄ cyclic tetramer in bulk in the presence of a difunctional endcapping or chain transfer reagent, 1,3-divinyltetramethyldisiloxane, to control the molecular weights of the polymers. At equilibrium, both cyclics (primarily D₃ - D₅) and linear chains exist.

Since ΔH of polymerization is nearly zero^(22,21), heat must be supplied to the system to open the relatively stable, unstrained D₄ tetramer at a reasonable reaction rate. The polymerization is entropically driven, ΔS = + 6.7 J/mole-°K. Highly flexible chains with large degrees of freedom due to the large size of the silicon atoms (and longer Si-O bonds) in the polymer backbone result from these equilibrations. A positive ΔS is rare for monomers in this size range since most monomers are more disordered than their corresponding polymers.²² Generally, changes in reaction temperature do not affect

polymer yield or molecular weights for the equilibration of D₄ in the bulk. The reaction temperature is chosen based on the structure of the cyclic monomer and concentration and activity of the catalyst. The activation energy for equilibration of D₄ catalyzed by tetramethylammonium disiloxanolate is reported to be 20.0 kcal/mole.² For anionic polymerizations of cyclic siloxanes, the activation energies decrease with an increase in strain of the cyclic monomer. The activation energies for unstrained siloxanes with more than 3 siloxane units are $\sim 19.5 \pm 1.5$ kcal/mole, and those with 3 siloxane units are $\sim 16.5 \pm 1.0$ kcal/mole. The 3 kcal/mole difference is about equal to the strain energy for the 3 siloxane unit cyclics.

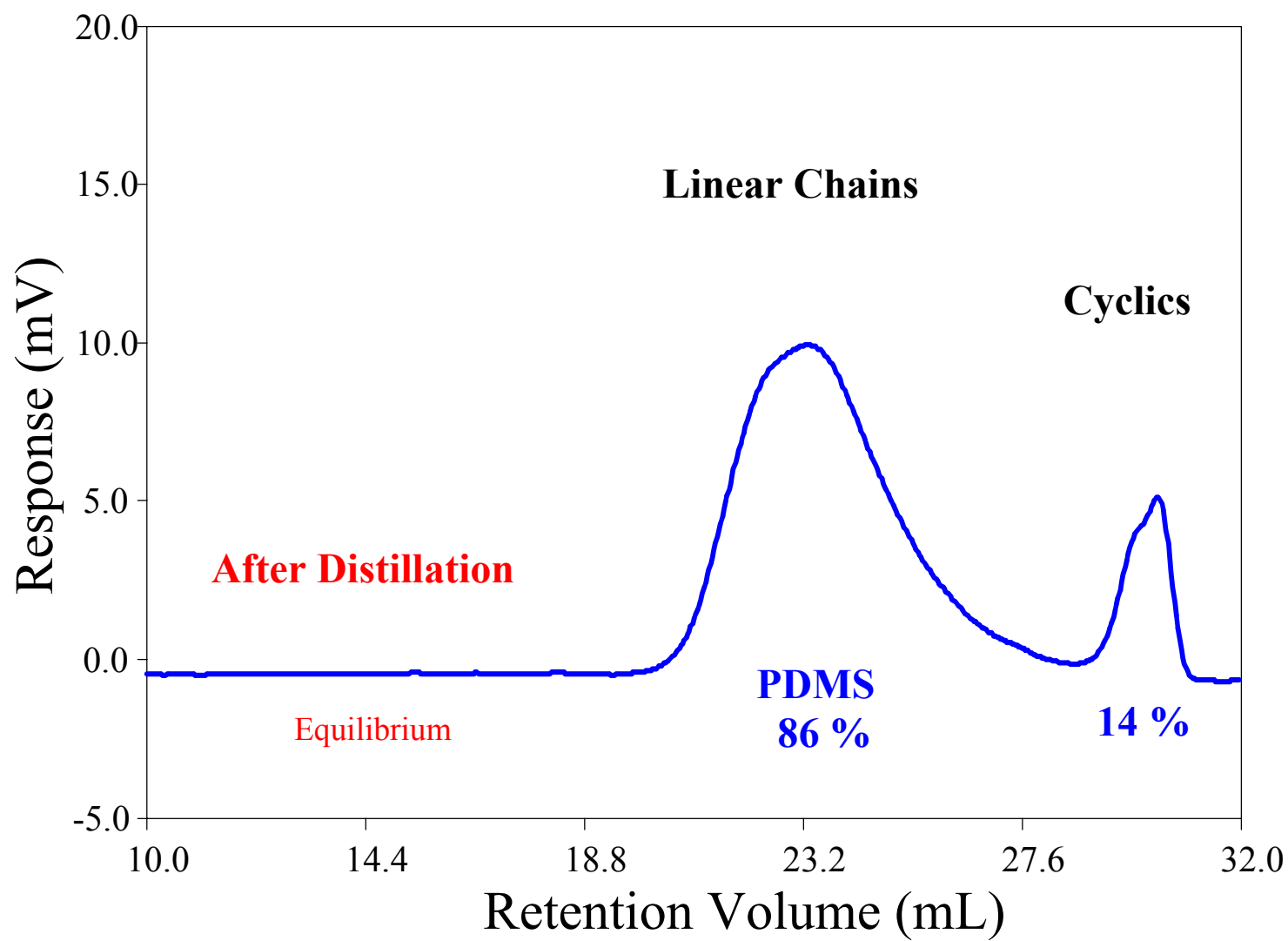
4.3.2 PDMS Molecular Weight Control and Characterization

The active species, R₃Si-O⁻, of the tetramethylammonium disiloxanolate catalyst attacks the electropositive Si atom in the D₄ tetramer, opens the ring, and gives rise to new active centers. The active species react via three different pathways to redistribute the siloxanes. The negatively charged oxygen active species can attack: (1) a cyclic tetramer, *ring-opening*, (2) a linear chain, or a siloxane bond in its own chain, *redistribution and backbiting*, or (3) an endcapping molecule, *chain transfer* (Figure 3.3). The ring-opening occurs very quickly, and a large increase in molecular weight is observed at early conversion. At 60 - 70% conversion, redistribution and chain transfer become prominent and the molecular weight begins to decrease due to these pathways.¹⁵ After ~ 48 hours, a ring/chain equilibrium is established comprised of about 85% chains existing as a gaussian distribution of molecular weights, and about 15% of small cyclics. This was confirmed via GPC (Figure 4.7). Since the larger polymer chains elute first, they are represented by the left curve in the chromatogram. The smaller cyclics take more time to pass through the pores, thereby eluting from the column last. The percentage of small cyclics were obtained by dividing the area under the curve representing the small cyclics by the total area under the RI curve (*equilibrium* curve in Figure 4.7). As mentioned earlier in the section on the synthesis of PCPMS, the amount of small cyclics remaining at equilibrium depends on the size and polarity of substituents.

The tetramethylammonium disiloxanolate transient catalyst decomposes above 130°C. A nitrogen purge is bubbled through the polymer/cyclic solution (at 130°C) after

Figure 4.7

GPC of a 5K PDMS at Equilibrium



an approximate 85/15 % chains/cyclics equilibrium is established (via GPC, usually after about 48 hours) to remove the catalyst. Cyclics were then removed from the mixture without further redistribution reactions. PDMS free of cyclics is represented by the **after distillation** curve in Figure 4.7. The average molecular weights (M_w) were not obtained via GPC since the viscosity detector would not differentiate the PDMS polymers from the baseline sufficiently to obtain accurate results (due to the very low viscosities of the target molecular weights).

^1H NMR was used to characterize the number average molecular weights (M_n s) of the polymers (Table 1.1). The MM type linear disiloxane endcapper, 1,3-divinyltetramethyldisiloxane, has a $\equiv\text{Si-O-Si}\equiv$ bond which can be cleaved, but also has two $\equiv\text{Si-C}$ bonds which are stable under the equilibration conditions. This can effectively endcap the polymer chains with vinyl groups and control their molecular weight by the molar ratio of D_4 to endcapping reagent. Each mol of D_4 corresponds to four repeat units and each mol of endcapper will endcap one PDMS chain. Therefore, a 24 average repeat unit PDMS chain requires a molar ratio of D_4 to endcapper of 6 to 1. PDMS polymers having average numbers of repeat units of 25, 62, and 235 with respective molecular weights of 1900, 4700, and 17,500 g/mole were synthesized (Table 1.1). Each of the M_n s obtained via ^1H NMR differed by no more than $\sim 10\%$ of the target M_n s for each PDMS oligomer.

The number of repeat units and number average molecular weights for all polymers were determined using ^1H NMR by ratioing the area of a proton in a repeat unit to the area of a proton on an endgroup (Figure 4.8). The area of peak **c** at ~ 0.1 ppm was divided by 6 since there are 6 methyl protons in a repeat unit, and the area of peak **a,b** at $\sim 5.7 - 6.2$ ppm was also divided by 6 since there are 6 vinyl protons per PDMS chain. Once the number of repeat units was calculated, this value was then multiplied by the molecular weight of a repeat unit, 74.15 g/mole. The molecular weight of two vinyl endgroups, 54.1 g/mole, and the atomic weight of one oxygen, 16 g/mole, was subtracted to obtain the M_n . An example calculation for a 25 repeat unit, 1900 g/mole, PDMS is illustrated in Figure 4.8.

4.4 Preparation and Characterization of Networks

The PDMS, DV-PCPMS, and HV-PCPMS polymers described above, along with two PMTFPS polymers donated from Dow Corning (Table 1.1), were all crosslinked via two-component addition cures. Each was hydrosilated with hydride functional crosslinking reagents in the presence of platinum (0) complexed with 1,3-divinyltetramethyldisiloxane in xylene (Karstedt's catalyst). Stoichiometric amounts of hydride to vinyl functional groups were used for all cures, and monitored via FTIR for the disappearance of the silane, $\equiv\text{Si-H}$, functional group. All networks were fully cured. The networks were cured at 90°C either in molds or directly on metal adherends depending on the testing to be conducted. Since the networks' crosslink densities also influenced their properties, a complete list of polymers, repeat units, M_n s, and crosslink densities are represented in Table 4.1.

All of the oligomers in this study were crosslinked via a hydrosilation mechanism and catalysed using Karstedt's catalyst. This catalyst is compatible for the following hydrosilation reactions since its active species Pt(0) is complexed with divinyltetramethyldisiloxane which is miscible with each of the vinyl terminated polyorganosiloxanes herein. The amount of Karstedt's catalyst used was based on the concentration of vinyl groups in the resin mixtures and the chemical structure of the repeat units. Sufficient concentrations of catalyst were used to achieve reasonable reaction times ($\sim 2 - 4$ hours for PDMS and $\sim 24 - 48$ hours for PMTFPS and PCPMS) at 90°C. For a given amount of catalyst per mole of vinyl endgroup, reaction rates increased along the series PCPMS < PMTFPS < PDMS. The slower reaction rates of the PCPMS networks are hypothesized to be due to complexation of the platinum species with the electron rich nitrile groups.

4.4.1 Polar, Novel DV-PCPMS and HV-PCPMS Networks

The DV-PCPMS polymers with average numbers of repeat units of 61 and 77 (or M_n s of 7900 and 10,000 g/mole respectively) were thoroughly mixed with 20 g Karstedt's catalyst per mole of vinyl group (first component) using a mechanical stirrer while degassing. The second component, a trifunctional, polar crosslinking reagent, D_4CNH_3 was added stoichiometrically relative to vinyl groups (Figure 3.11) via a syringe

Table 4.1

Series of Polymers with Tailored Repeat Units and
Corresponding Weight % Hard Segments

Network	F	# RU	Mn (g/mol)	XL MW (g/mol)	F	HS %
2K PDMS	2	25	1900	328.73	4	8
5K PDMS	2	62	4700	328.73	4	3.4
17K PDMS	2	235	17,500	328.73	4	0.9
4K PMTFPS	2	26	4200	NA	NA	8
40K PMTFPS	2	261	41,050	NA	NA	0.9
8K DV-PCPMS	2	61	7900	307.6	3	2.5
10K DV-PCPMS	2	77	10,000	307.6	3	2
38K DV-PCPMS	2	298	38,000	307.6	3	0.5
9K HV-PCPMS	6	68	8850	374.69	2	11
25K HV-PCPMS	6	197	25,200	374.69	2	4.3
35K HV-PCPMS	6	275	35,200	374.69	2	3.1

$$1) \left(\frac{MW_{XL}}{functional\ group} \right) = \frac{x\ g\ XL\ needed\ for}{\left(\frac{M_n\ polymer}{functional\ group} \right) 1\ g\ polymer}$$

$$2) \left(\frac{HARD\ segment}{HARD+SOFT\ segments} \right) (100\%) = \% HARD\ segment$$

note:

RU = Average # of Repeat Units

F = functionality

HS = Weight % Hard Segment

while mixing and degassing at room temperature. The nonpolar crosslinking reagent, tetrakis(dimethylsiloxy)silane used for crosslinking PDMS was not miscible with the polar PCPMS oligomers. The cyclics, D_4CNH_3 and $D_4(CN)_2H_2$, synthesized by the modification of D_4H described in section 4.2.3, met the necessary requirements for a hydride functional, polar (and miscible) crosslinking reagent for the hydrosilation of the polar PCPMS polymers. Since network formation requires at least one reagent with a functionality of 3 or greater¹⁵⁸, the trihydride functional cyclic D_4CNH_3 , was used for the DV-PCPMS polymers. The viscous DV-PCPMS resin mixtures were placed in polystyrene molds in a 40°C vacuum oven for ~ 10 – 30 minutes until all visible bubbles in the solution disappeared. The temperature was then increased to 90°C to optimize the rate of the LTV cure, which typically required about 24 – 72 hours. It should be noted that the Karstedt's catalyst may decompose above 100°C, so 90°C was the maximum temperature for all cures in this study. Samples were taken periodically from the molds or adherends from the oven, placed on NaCl plates, as described earlier, and monitored for the disappearance of the silane functional group at ~ 2170 cm^{-1} (FTIR) to confirm network formation.

The networks were formed using stoichiometric amounts of vinyl groups to silane ($\equiv Si-H$). The hard segment for this case is defined as the crosslinking reagent, and the soft segment as the flexible oligomeric chains. The percentages of hard segment in the networks were calculated using equations 1 and 2 (Table 4.1). The resultant networks were slightly yellow, transparent, tacky, and extremely flexible materials.

The HV-PCPMS polymers were cured in the same manner as the DV-PCPMS polymers (Table 4.1), except that the crosslinking reagent was difunctional. As described above, two polar, hydride functional, cyclic crosslinking reagents were derived from the partial hydrosilation (modification) of D_4H , then separated. The higher boiling fraction with two 3-cyanopropyl substituents on the dihydride cyclic, $D_4(CN)_2H_2$, was used for the hydrosilation of the HV-PCPMS. Since the HV-PCPMS polymers have 6 vinyl endgroups, either the difunctional ($D_4(CN)_2H_2$) or trifunctional (D_4CNH_3) crosslinking reagents met the requirements for crosslinking. Due to the lower percent yield of the higher boiling fraction, $D_4(CN)_2H_2$ was used to crosslink HV-PCPMS. The HV-PCPMS resultant networks were slightly yellow, translucent, and flexible materials.

The HV-PCPMS has a functionality of 6 as opposed to 2 for DV-PCPMS. HV-PCPMS provides many more available crosslinking sites, thereby leading to higher hard segment contents. Network properties strongly depend on the hard segment content and will be discussed in Section 4.5 (Network Properties). The networks prepared with the lower M_n HV-PCPMS oligomers had a higher percentage of hard segment than those prepared with the higher M_n chains, and were correspondingly less tacky and less flexible. By contrast, the higher M_n HV-PCPMS networks with hard segment concentrations closer to those of the DV-PCPMS networks had more tack and flexibility.

4.4.2 PMTFPS Networks

PMTFPS (and other fluorine containing polyorganosiloxanes) are of great interest industrially due to their increased polarity relative to PDMS. Thus, the polar PMTFPS networks served as good controls for comparisons with the novel, polar PCPMS networks. Difunctional (vinyl terminated) PMTFPS polymers with average numbers of repeat units of 26 and 261, (respective M_n s of 4200 and 41,050 g/mole) were kindly donated by the Dow Corning Corp. The networks (Table 4.1) were also formed via two-component hydrosilation cures, but with a fluorinated-hydride functional crosslinking reagent (also kindly supplied by the Dow Corning Corp.) (Figure 3.10). All networks were prepared using 1:1 vinyl:silane stoichiometry. The typical time of PMTFPS network formation was between 12 – 24 hours for the lower M_n network, and ~ 72 hours for the higher M_n , depending on the catalyst and vinyl concentrations. Complete hydrosilation was confirmed by the disappearance of the silane functional group absorption at ~ 2170 cm^{-1} via FTIR. The network with the lower M_n PMTFPS (with 8% hard segment) formed a colorless, smooth, tack-free, transparent, and flexible network. By contrast, the network with the higher M_n PMTFPS (with 0.9% hard segment) formed a colorless, transparent, tacky, extremely flexible network. These network properties will be further discussed in section 4.5.

4.4.3 Nonpolar, Control PDMS Networks

The difunctional PDMS polymers were stoichiometrically hydrosilated with the tetrahydride functional crosslinking reagent, tetrakis(dimethylsiloxy)silane, and

Karstedt's catalyst via two-component addition cure. PDMS was freed of its small cyclics (which would not crosslink) before hydrosilation. The primary component was comprised of the vinyl functional PDMS thoroughly mixed with 0.02 grams of Karstedt's catalyst per mole of vinyl groups. The second component was the hydride functional tetrakis-(dimethylsiloxy)silane crosslinking reagent (Figure 3.8). Percentages of hard segment for these networks were calculated as described previously by ratioing the amount of crosslinking reagent relative to the total resin composition (Table 4.1).

The networks were cured at 90°C, which is considered a low temperature vulcanization (LTV), and required ~ 2 – 8 hours under the conditions used. Network formation was also successful at lower temperatures, even room temperature (RTV), although at much slower rates. Networks prepared for tensile tests were approximately 2mm thick, while networks formed directly between adherends were drawn down at a 19 millinch (mil) wet thickness with a drawdown rod. Razor thin samples of the networks were taken at hourly intervals during their cure, and analyzed on NaCl salt plates by FTIR. The disappearance of the silane functional group absorption at ~ 2170 cm⁻¹ was monitored since the hydrosilation cure takes place by the ≡Si-H group of the tetrakis(dimethylsiloxy)silane crosslinking reagent adding across the double bond of the vinyl endgroups of the PDMS polymer chains. The two-component addition cure is an ideal cure for preparing void-free networks, as there are no “byproducts” in the reaction. All resin compositions in this study were prepared from 100% solids yielding networks with low shrinkage. Each PDMS polymer formed a transparent, colorless, tack-free, flexible network.

4.4.4 PDMS with Varied Weight % Hard Segment

A series of networks with varied levels of hard segment were prepared to investigate network property/composition relationships. A 5,000 g/mole PDMS oligomer was crosslinked to yield networks having 3.2, 9.3, 19.6, 34.4, and 57.7% hard segments. The resin compositions for these networks were comprised of a difunctional (vinyl terminated) 5,000 g/mole PDMS oligomer, 1,3-divinyltetramethyldisiloxane dimer, and tetrakis(dimethylsiloxy)silane as the crosslinking reagent. For this series, the hard segments were comprised of tetrakis(dimethylsiloxy)silane and 1,3-divinyltetramethyl-

disiloxane, while the soft segment component was the flexible, divinyl functional PDMS polymer chains (Figure 3.9). All networks were formed by adding stoichiometric amounts of silane, $\equiv\text{Si-H}$, functional group to total vinyl group. As expected, the rates of these hydrosilation curing reactions were similar to those for the previously discussed PDMS networks.

Table 3.1 represents the compositions used to form these networks. The weight percent hard segment was controlled by increasing the amount of disiloxane with vinyl functionality (**hard**) from 0 equivalents up to 1, 1.5, 1.75, and 1.9 equivalents, while decreasing the amount of vinyl from the **soft** PDMS from 2 equivalents down to 1, 0.50, 0.25, and 0.1 equivalents. Thus, the total number of vinyl equivalents was always 2, and equal to the 2 equivalents of **hard** crosslinking reagent, tetrakis(dimethylsiloxy)silane. The weight % hard segments reported in Table 3.1 were calculated from the equations represented in Table 3.2. These resultant networks were colorless, transparent, tack-free, and flexible materials.

4.4.5 Monitoring Hydrosilation Cures via FTIR

All of the hydrosilation reactions described above for PDMS, PMTFPS, DV-PCPMS, and HV-PCPMS were monitored by FTIR. Figure 4.9 presents (as an example) a series of spectra taken during network formation using an 8850 g/mole HV-PCPMS oligomer. The **initial** spectrum represents a sample (between the NaCl plates) before cure, and shows the characteristic silane ($\equiv\text{Si-H}$) absorption band at $\sim 2170\text{ cm}^{-1}$. The same NaCl plate was removed from the oven and scanned after **2h**, **4h**, **6h**, and **20h**. The characteristic silane peak gradually decreased and was absent from the **20h** spectrum (**fully cured**). Although the curing times varied, this was not expected to affect network properties since all materials were fully cured.

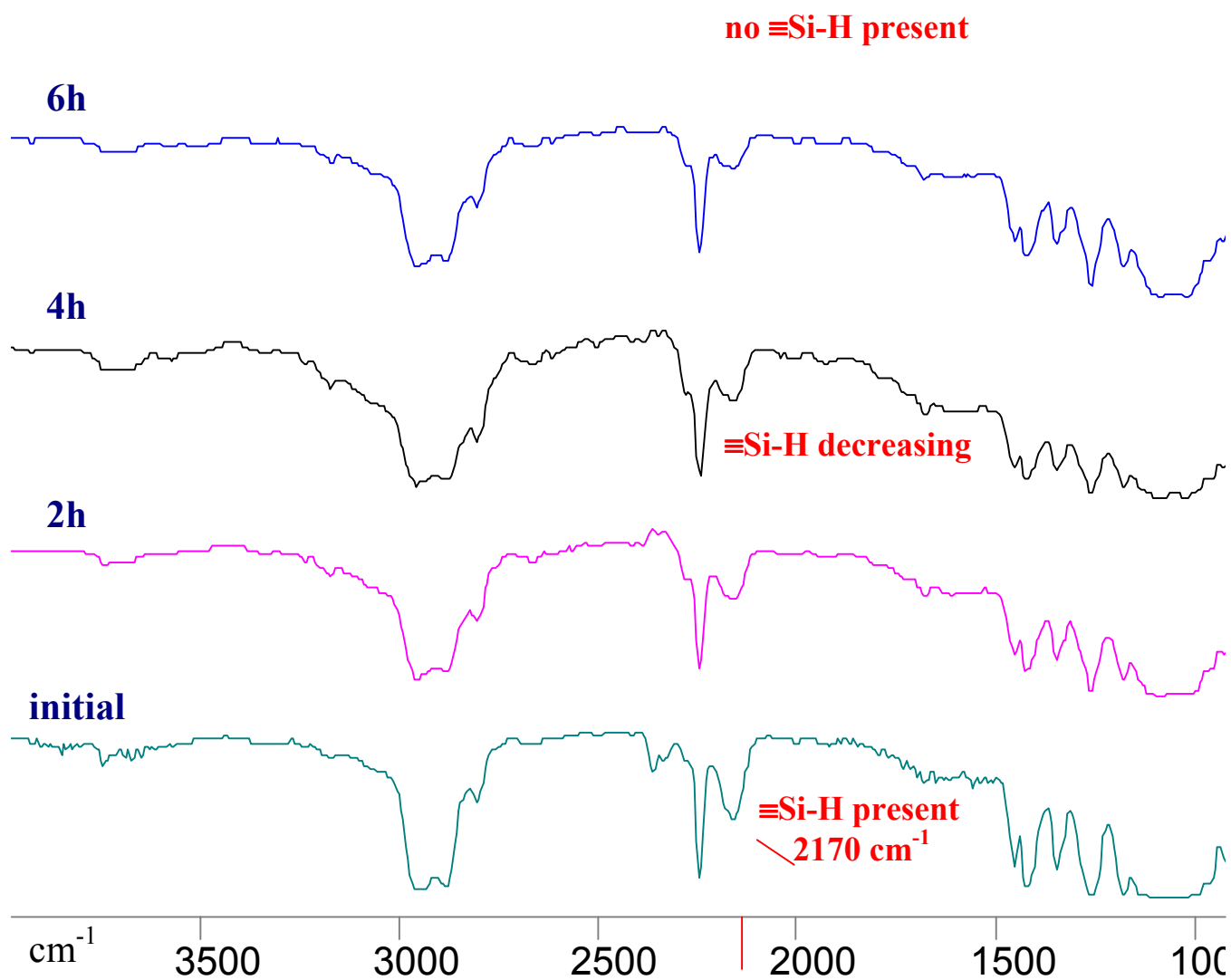
4.5 Network Properties

All of the organosiloxanes described above were chemically crosslinked via two-component hydrosilation cures, where stoichiometric amounts of silane were added across the double bonds of the vinyl endgroups in the presence of platinum(0) complexed with 1,3-divinyltetramethyldisiloxane in xylene. Karstedt's catalyst was not only chosen

Figure 4.9

FTIR Spectral Series Depicting the Progression of a Network Formation Reaction Using an 8850 g/mole HV-PCPMS Crosslinked with $D_4(CN)_2H_2$

20h - fully cured



on the basis of the vinyl groups being miscible with the systems' components, but also to minimize byproducts such as HCl if hexachloroplatinic acid in isopropanol (Speier's catalyst) were used. The linear siloxane chains were terminated with either 2 or 6 vinyl endgroups, which correspond to functionalities of either 2 (PDMS, PMTFPS, DV-PCPMS) or 6 (HV-PCPMS). The hydride functional crosslinking reagents have functionalities of 2 ($D_4(CN)_2H_2$), 3 (D_4CNH_3), or 4 (tetrakis(dimethylsiloxy)silane), depending on which polymer chain was reacted. The thermodynamic equilibrations for each type of polymer resulted in small cyclics and linear chains at equilibrium. As mentioned earlier, all equilibrium solutions were first freed of their cyclics before crosslinking to ensure fully cured networks, without voids or byproducts. Both the polymers' functionalities and M_n s controlled their crosslink densities; the latter sections will describe how each organosiloxanes' side chain chemical structures (polarity) and crosslink densities influenced their network properties. Tensile properties, thermal stabilities, swelling properties, and adhesive properties were measured.

4.5.1 Tensile Properties

The number of functionalities affects the final crosslink density (the number of crosslinks per gram) of the networks, which in turn affects physical behaviors such as strength, extent of elongation at break, elasticity and modulus. Lower molecular weights between crosslink sites, and higher crosslink densities lead to networks with higher tensile strengths and less elongation before breaking.¹⁵⁸

Although silicone networks are known to have lower tensile strengths than most organic elastomers at room temperature, they maintain their properties over a wide temperature range. Since silicones maintain their properties at higher temperatures and remain flexible at lower temperatures, they make excellent potential fuel tank sealants for supersonic aircraft.¹²⁸ The ability of siloxanes to maintain their tensile strength even after aging for weeks at temperatures above 125°C clearly shows an advantage over most organic elastomers which either degrade or show a dramatic drop in mechanical properties. Polydimethylsiloxanes are also known to maintain their mechanical properties after environmental aging in the presence of both ultraviolet radiation and ozone.¹

Tensile properties of siloxanes are influenced by both the size and polarity of their side chain chemical structures, and crosslink densities of the networks. The following three sections will describe how these variables affect the tensile strength, modulus, and percent elongation of the networks. All tensile tests were based on the method described in ASTM D 412 (Standard Test Methods for Vulcanized Rubber and Thermoplastic Rubbers and Thermoplastic Elastomers – Tension).¹⁵⁹ Figure 3.13 depicts a sample being pulled in the Minimat along with an example of the type of data obtained for this test. Each data point discussed in the following sections is the average of 10 samples.

4.5.1.1 Tensile Strength

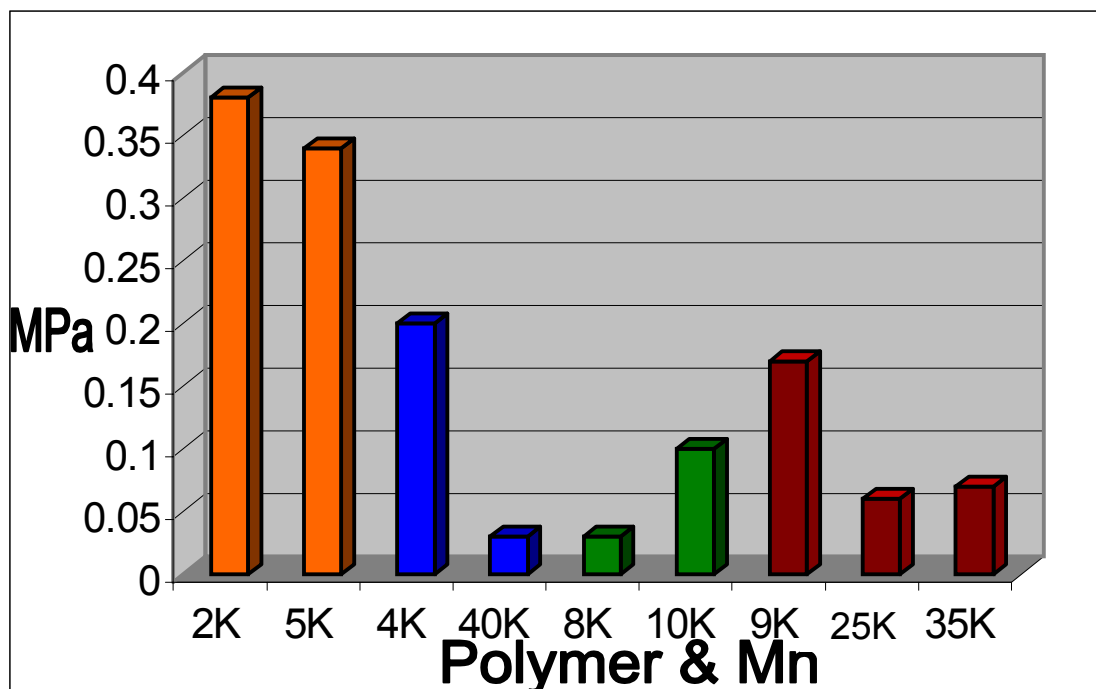
Tensile strength (MPa) is the maximum load or force per unit cross-sectional area within a sample's gauge length, or the pulling stress required to break a given sample. For most sealants, high tensile strength is not necessary (except for high-pressure fluid sealing applications), although sufficient strength is desirable to avoid cohesive failure in adhesive bonds under stress.⁸⁹ The example of a tensile test performed on a 5K PDMS network with a hard segment content of 58% (Figure 3.13), shows a tensile strength at break of 0.4 MPa. This was found by locating the maximum stress obtained from the stress versus strain curve in MPa at break. Although the Minimat automatically computes the data, one can determine the tensile strength (MPa or lbf/in.²) by: tensile strength = F/A ; where F = the force magnitude at rupture, MN (lbf), and A = cross-sectional area of the unstrained sample, m² (in.²).¹⁵⁹

Table 4.2 represents the strength data for all networks with different sidechain chemical structures investigated. It was observed that the strengths followed the expected trend, where the tensile strength increased as the hard segment content (crosslink density) increased within each type of chemical structure. The networks prepared with the 2K and 5K PDMS having respective hard segment contents of 8% and 3.4%, had tensile strengths of 0.38 and 0.34 (MPa). The 4K and 40K PMTFPS networks with respective hard segment contents of 8% and 0.9% had tensile strengths of 0.2 and 0.03 MPa. The 8K and 10K DV-PCPMS networks do not follow the trend, although their M_n s and hard segment contents of 2.5% and 2% are too low and similar to distinguish. The 38K DV-PCPMS had a hard segment content too low to obtain an accurate result. The 9K, 25K,

Table 4.2

Tensile Strength at Break (MPa) Data for Networks

PDMS PMTFPS DV-PCPMS HV-PCPMS



Network	F	# RU	Mn (g/mol)	HS%	Tensile Strength (MPa)
2K PDMS	2	25	1900	8	0.38 +/- 0.06
5K PDMS	2	62	4700	3.4	0.34 +/- 0.06
4K PMTFPS	2	26	4200	8	0.20 +/- 0.05
40K PMTFPS	2	261	41,050	0.9	0.03 +/- 0.01
8K DV-PCPMS	2	61	7900	2.5	0.03 +/- 0.01
10K DV-PCPMS	2	77	10,000	2	0.10 +/- 0.02
38K DV-PCPMS	2	298	38,000	0.5	NA
9K HV-PCPMS	6	68	8850	11	0.17 +/- 0.04
25K HV-PCPMS	6	197	25,200	4.3	0.06 +/- 0.01
35K HV-PCPMS	6	275	35,200	3.1	0.07 +/- 0.01

and 35K HV-PCPMS networks with respective hard segment contents of 11%, 4.3%, and 3.1% had tensile strengths of 0.17, 0.06, and 0.07 MPa. Again, the large difference in crosslink density follows the expected trend, while the 25K and 35K HV-PCPMS networks with similar crosslink densities were indistinguishable within error.

4.5.1.2 Modulus

Tensile modulus (MPa) or Young's modulus is the ratio of normal stress to corresponding strain (initial slope of the stress/strain curve). For most sealants, low to medium moduli (less stiff) networks are sufficient to accommodate greater joint movement without imposing large stresses on the sealant and substrate surfaces.⁸⁹ Most sealants exhibit nonlinear stress-strain curves when they are pulled to rupture. All sealants' moduli change with temperature, but silicone sealants typically exhibit less temperature dependence compared to acrylics and PVA sealants.

The tensile moduli for all networks in the study with different sidechain chemical structures are represented in Table 4.3. The tensile strength and tensile modulus are both expected to increase with crosslink density. When varying only the crosslink density within the same types of networks, it was found that the moduli increased with increasing crosslink density.

4.5.1.3 Percent Elongation

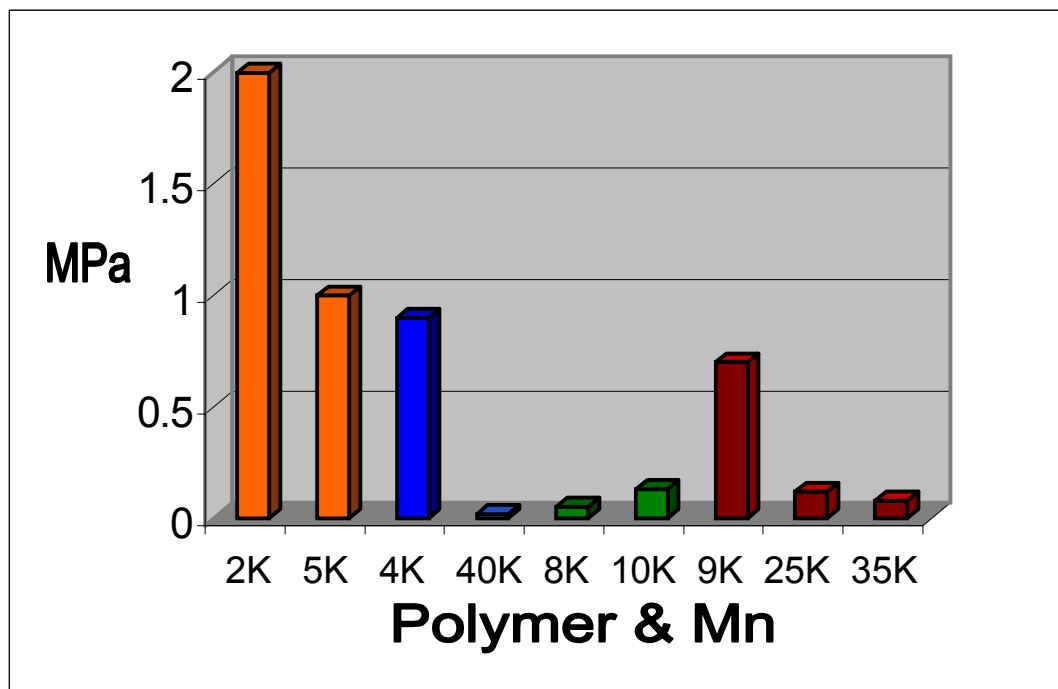
Elongation is the deformation of a sample caused by stretching, or the sample's fractional increase in length when stressed in tension, and may be expressed as a percentage (%) of the sample's original length; elongation at break is the elongation recorded at the moment of the sample's rupture.⁸⁹ The data can easily be calculated from the stress/strain curves using $E = 100[L - L_{(o)}]/L_{(o)}$, where E is the elongation in percent, L is the gauge length at break, and $L_{(o)}$ is the sample's original measured gauge length.¹⁵⁹

The percent elongations for all networks with different sidechain chemical structures in the study are represented in Table 4.4. Percent elongations are expected to increase as the crosslink densities of the networks decrease. Within each type of chemical network structure, this trend was observed. For example, when comparing varying crosslink densities within the PDMS polymer networks, the decreasing hard

Table 4.3

Moduli (MPa) Data for Networks

PDMS PMTFPS DV-PCPMS HV-PCPMS

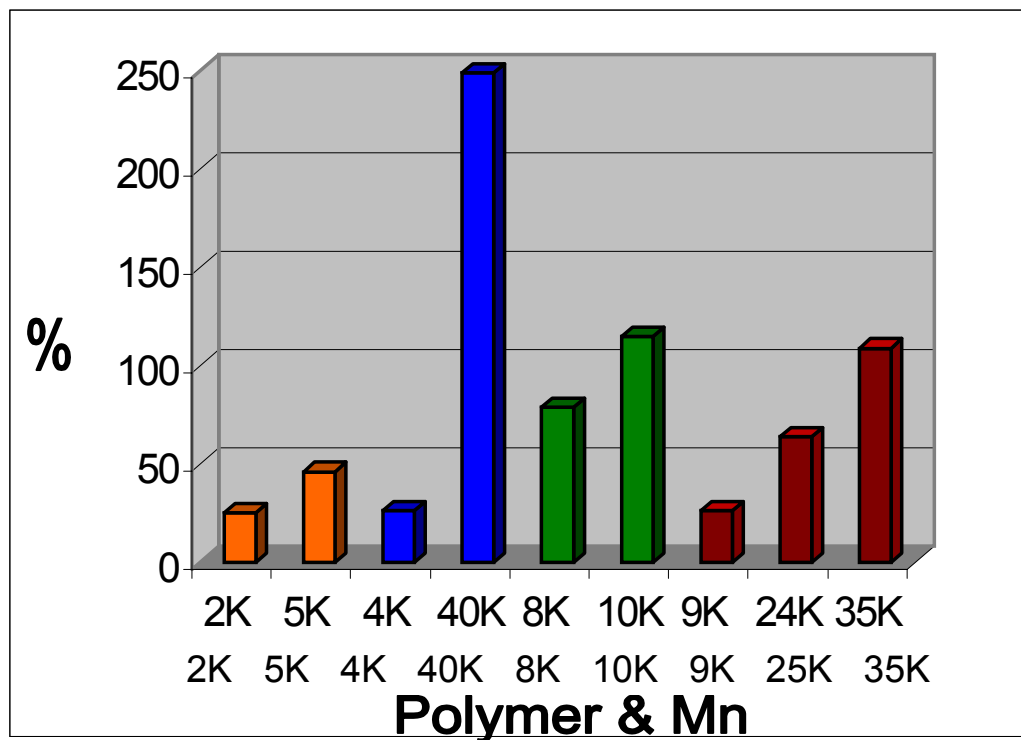


Network	F	# RU	Mn (g/mol)	HS%	Modulus (MPa)
2K PDMS	2	25	1900	8	2.0 +/- 0.2
5K PDMS	2	62	4700	3.4	1.0 +/- 0.2
4K PMTFPS	2	26	4200	8	0.88 +/- 0.08
40K PMTFPS	2	261	41,050	0.9	0.02 +/- 0.01
8K DV-PCPMS	2	61	7900	2.5	0.05 +/- 0.01
10K DV-PCPMS	2	77	10,000	2	0.13 +/- 0.02
38K DV-PCPMS	2	298	38,000	0.5	NA
9K HV-PCPMS	6	68	8850	11	0.69 +/- 0.06
25K HV-PCPMS	6	197	25,200	4.3	0.12 +/- 0.01
35K HV-PCPMS	6	275	35,200	3.1	0.08 +/- 0.01

Table 4.4

Percent Elongation (%) Data for Networks

PDMS **PMTFPS** **DV-PCPMS** **HV-PCPMS**



Network	F	# RU	Mn (g/mol)	HS%	Percent Elongation (%)
2K PDMS	2	25	1900	8	25 +/- 4
5K PDMS	2	62	4700	3.4	46 +/- 7
4K PMTFPS	2	26	4200	8	26 +/- 7
40K PMTFPS	2	261	41,050	0.9	250 +/- 35
8K DV-PCPMS	2	61	7900	2.5	79 +/- 11
10K DV-PCPMS	2	77	10,000	2	115 +/- 22
38K DV-PCPMS	2	298	38,000	0.5	NA
9K HV-PCPMS	6	68	8850	11	26 +/- 6
25K HV-PCPMS	6	197	25,200	4.3	64 +/- 15
35K HV-PCPMS	6	275	35,200	3.1	109 +/- 17

segment contents of 8% and 3.4% had increasing percent elongations at break of 25% and 46%. Similar results are found for the other three systems.

4.5.1.4 Tensile Properties for PDMS with Varied Hard Segment Contents

Table 4.5 represents the tensile properties for a series of networks prepared with a 5K PDMS oligomer with the only variable being their crosslink densities (20%, 34%, and 58% hard segment). The general trend of increasing moduli with increasing crosslink density was observed. As the hard segment content was increased from 20 to 34 to 58 %, the moduli increased from 0.67 to 1.05 to 1.25 MPa. As the hard segment was increased from 20 to 34 to 58%, the expected decrease in percent elongations at break from 65 to 36 down to 32% were observed. This series of networks was prepared with the siloxane dimer added to provide additional crosslink density. The data for the 5K PDMS networks prepared without this dimer do not follow the trend observed with the higher hard segment contents (Table 4.5). The network properties depend on the hard segment structures. The added dimer results in localized “clusters” of network junctions which may be important to tensile properties. The general trend of increasing strength with increasing crosslink density was not observed since this depends on both the modulus and percent elongations. The tensile strengths of the three networks in this series were equal within experimental error.

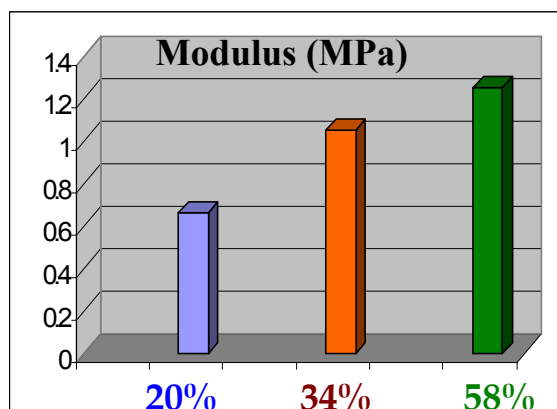
4.5.2 Thermal Properties

Silicones, which are an intermediate chemical class between organic polymers and silicate materials, have better thermal resistance than most organic materials due to their silicate nature and the higher dissociation energy (106 kcal/mol) of the Si-O bond compared to both C-C (88 kcal/mole) and C-O bonds (86 kcal/mol). Thermal stability must be defined in terms of time, temperature, and environment. Although silicone resins are less heat resistant by several hundred degrees in comparison to silicates (glasses and enamels), many silicones may be heated in air between 180°C - 200°C for a year, or up to 350 – 450°C for shorter periods, without any appreciable changes in their properties.¹ The size and type of the organic substituents attached to the siloxane backbone, and the

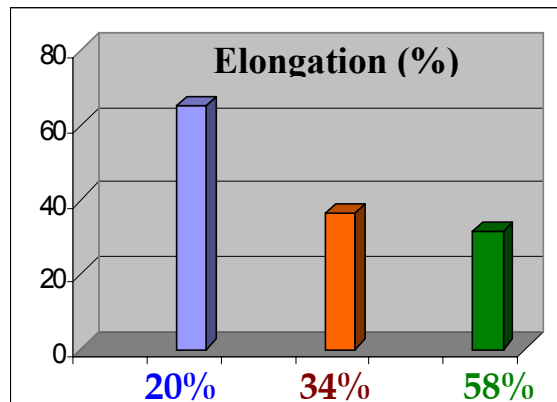
Table 4.5

Tensile Properties for 5K PDMS with Varied Weight % Hard Segments

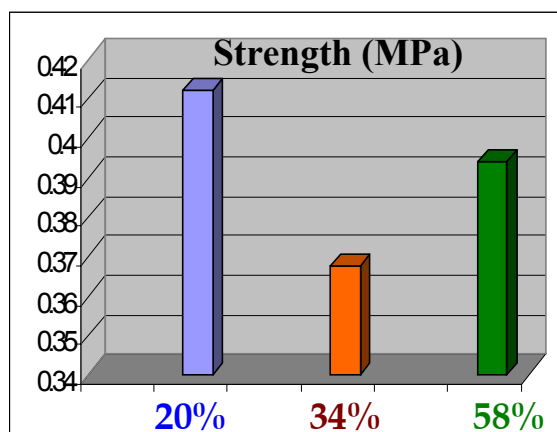
Hard Segment (%)	Modulus (MPa)
20	0.67 +/- 0.1
34	1.05 +/- 0.2
58	1.25 +/- 0.1



Hard Segment (%)	Elongation (%)
20	65 +/- 4
34	36 +/- 8
58	32 +/- 2



Hard Segment (%)	Strength (MPa)
20	0.41 +/- 0.04
34	0.37 +/- 0.01
58	0.40 +/- 0.03



number of crosslink sites along the chain are also important features contributing to the defined heat resistance.¹ The variables in this study were the sidechain chemical structures, average number of repeat units in the oligomers, and crosslink densities of the siloxane networks.

Silicones generally degrade either by oxidative degradation of the organic sidechains, or by thermal depolymerization of organosiloxanes containing D units back to cyclics or smaller molecular weight polymer chains. Organosiloxanes with longer aliphatic sidechains are generally more susceptible to oxidative attack, with the exceptions of aromatic groups. Also, increasing the crosslink densities of networks with organic crosslink sites generally decreases their heat resistance.¹

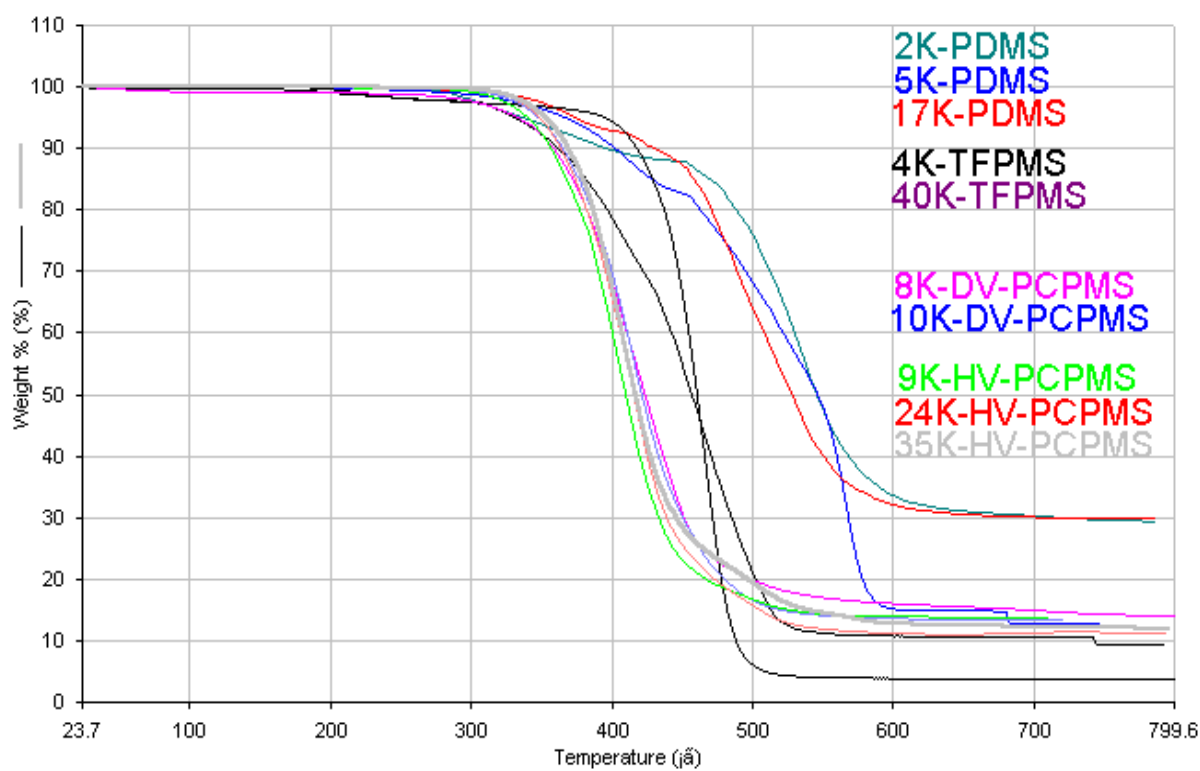
Organosiloxanes are also known for their flexibility at very low temperatures due to the longer Si-O bonds (1.64 Å), and lower energy barriers for rotation (< 0.8 kcal/mol) compared to organic polymers (C-CH₃ ~ 15 kcal/mol)¹¹ The T_g of polydimethylsiloxane is ~ - 123°C. When larger substituents such as phenyl are added to the polymer chains, the T_{gs} increase. Networks prepared from the same type of polyorganosiloxanes with higher crosslink densities are generally less flexible and have higher T_{gs}.¹

4.5.2.1 Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) is the study of the change in mass of a material under various conditions of temperature and atmosphere, and is used to determine the thermal stability of a material.^(89,160) TGA measures the weight loss of a sample as a function of time (isothermal conditions) or temperature.¹⁶⁰ Elastomeric sealants soften when heated, and this is generally followed by degradation and embrittlement.⁸⁹

In this study, samples between 5 – 10 mg were heated at a rate of 10°C/minute in both N₂ and air environments. The temperature of 5% weight loss, and the weight percent of the samples remaining at 800°C (char yield) were evaluated for all of the networks. The TGA curves for all of the networks heated in N₂ are represented in Table 4.6, along with the chart for temperatures at 5% weight loss in N₂. Table 4.7 includes char yield at 800°C and 5% weight loss temperatures for the networks in both air and N₂. All of the networks are thermally stable in both air and N₂ to well above 300°C. Within

Table 4.6

Thermogravimetric Analysis Data for Networks in N₂

PDMS PMTFPS DV-PCPMS HV-PCPMS

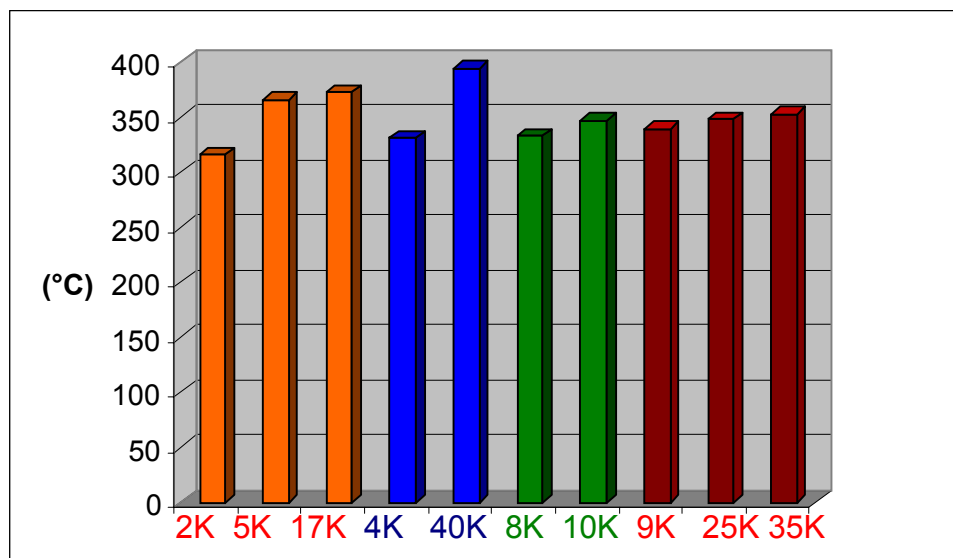
Temperature at 5% Weight Loss in N₂

Table 4.7

Thermogravimetric Analysis Data for Networks in N₂ and Air

Network	# RU	HS %	Temp. at 5% Wt. Loss (°C)	
			N ₂	Air
2K PDMS	25	8	316	304
5K PDMS	62	3.4	366	338
17K PDMS	235	0.9	373	383
4K PMTFPS	26	8	331	310
40K PMTFPS	261	0.9	394	338
8K DV-PCPMS	61	2.5	333	336
10K DV-PCPMS	77	2	347	342
9K HV-PCPMS	68	11	340	330
25K HV-PCPMS	197	4.3	348	368
35K HV-PCPMS	275	3.1	353	336

Network	# RU	HS %	Char Yield Wt. % at 800°C	
			N ₂	Air
2K PDMS	25	8	33	44
5K PDMS	62	3.4	13	41
17K PDMS	235	0.9	30	36
4K PMTFPS	26	8	10	15
40K PMTFPS	261	0.9	9	8
8K DV-PCPMS	61	2.5	14	13
10K DV-PCPMS	77	2	14	28
9K HV-PCPMS	68	11	14	21
25K HV-PCPMS	197	4.3	12	35
35K HV-PCPMS	275	3.1	12	24

each type of polymer network (same substituents), the thermal stability decreases slightly as more organic crosslink sites (for lower M_n oligomers) were introduced. For example, the networks prepared from the 2K, 5K, and 17K PDMS oligomers, have a decreasing average number of organic crosslink sites resulting in lower initial weight loss temperatures. This trend also follows for the networks with larger and more polar sidechain chemical structures.

It has been found that oxidation susceptibility increases with the size of an aliphatic substituent on the siloxane chain and generally decreases the thermal stability. Ethylsiloxanes and butylsiloxanes have lower thermal stabilities than that of methylsiloxanes.¹ It may be observed here that although the 3,3,3-trifluoropropyl and 3-cyanopropyl substituents are larger, their polymers exhibit thermal stabilities which are not dramatically less than the networks prepared from the PDMS networks. This phenomenon is hypothesized to be result of the strong C-F and C≡N bonds, relative to the C-H bonds of methyl- groups. The char yields of each type of network did not vary much with crosslink density; and the PDMS networks had the highest weight percents remaining at 800°C.

4.5.2.2 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) is the measurement of energy absorbed (endotherm) or produced (exotherm), and may be applied to energy changes such as melting, crystallization, resin curing, loss of solvents, and to processes involving a change in heat capacity, such as the glass transition. The glass transition (T_g) is the reversible change in an amorphous polymer or in amorphous regions of a partially crystalline polymer from, or to, a viscous or rubbery condition. T_g can be taken as the temperature of the midpoint of the specific heat change in the glass transition region. Siloxane sealants typically have the highest low-temperature flexibility and lowest T_g s relative to other organic elastomeric sealants.⁸⁹

Sample sizes of about 5 – 10 mg of the polymers and their corresponding networks were heated at a rate of 10°C/minute, and T_g s were recorded from their 2nd heat scans (Table 4.8). Each sample was quenched from room temperature to –150°C, scanned from –150°C to 0°C, quenched again (500°C/minute), then scanned again at

Table 4.8Differential Scanning Calorimetric Data (2nd Heat Scans) for Polymers and Networks

Polymer	# RU	HS %	T_g (°C)
2K PDMS	25	8	-131
5K PDMS	62	3.4	-128
4K PMTFPS	26	8	-77
40K PMTFPS	261	0.9	-67
8K DV-PCPMS	61	2.5	-62
10K DV-PCPMS	77	2	-64
9K HV-PCPMS	68	11	-62
25K HV-PCPMS	197	4.3	-62
35K HV-PCPMS	275	3.1	-62

Network	# RU	HS %	T_g (°C)
2K PDMS	25	8	-121
5K PDMS	62	3.4	-124
4K PMTFPS	26	8	-67
40K PMTFPS	261	0.9	-67
8K DV-PCPMS	61	2.5	-59
10K DV-PCPMS	77	2	-60
9K HV-PCPMS	68	11	-56
25K HV-PCPMS	197	4.3	-60
35K HV-PCPMS	275	3.1	-59

10°C/minute. For PDMS oligomers and networks, this procedure eliminated any crystallinity which might have been present before obtaining the T_g . This allowed a totally amorphous sample to be tested, and for crystallization to be observed during this second heat scan.

The T_g s for all of the polymers and networks are at or below -56°C making them good potential candidates for aircraft sealants which experience service temperatures in this range. The PDMS polymers and networks have T_g s substantially lower ($\sim -130^\circ\text{C}$) than the larger and more polar PMTFPS ($T_g \sim -67^\circ\text{C}$) and PCPMS ($T_g \sim -60^\circ\text{C}$) systems. The T_g s increase (flexibility decreases) with the size of the substituents on the siloxane backbone since they decrease the mobility of the siloxane chains compared to PDMS chains. Comparable M_n s for the more polar oligomers were much more viscous than the PDMS oligomers presumably due to hydrogen bonding. For the PDMS and PMTFPS cases, the T_g s increase with M_n . By contrast, the T_g s for the PCPMS oligomers are relatively independent of temperature. The reason for this is not clear. As expected, the T_g s of the networks with the higher weight % hard segments were increased substantially relative to their corresponding oligomers.

4.5.3 Swelling Properties

The propensity of a network to swell in the presence of certain chemicals or solvents can be measured by immersing a known weight of a sample of the network in a specified solvent for a specified period, temperature and surroundings. After the immersion time, the network sample is removed from the solvent and reweighed. The percent change in mass is recorded. This percent change in mass can be compared to those of other networks in the same solvent, or to other samples of the same network in different solvents. This provides a prediction of how a network will perform in the presence of certain solvents (provided the time and temperature requirements for the application are tested). It is important to investigate whether network integrity will be maintained or whether the solvent will penetrate and swell the network to a distorted unusable mass which no longer retains mechanical properties required by the application.

A sealant for fuel tanks must maintain its adhesive properties to the metal tank, and its tensile properties in the presence of jet fuel and other chemicals (including air)

over long periods and a wide temperature range. PDMS rubbers swell in organic solvents such as aliphatic, aromatic, and chlorinated hydrocarbons. By contrast, considerably less swelling (in organic solvents) has been found with poly- γ -trifluoropropyl, β -cyanoethyl, and γ -cyanopropylmethylsiloxanes.¹ It should be noted that the potential leak path (or area of the actual contact the sealant will experience with the chemicals) is very small in many sealant applications, so that a certain amount of degradation may be tolerable without loss of the seal.⁸⁹ The previous sections have described how organosiloxanes are both stable at high temperatures in air and N₂, and flexible at low temperatures. These characteristics provide the pathway for an excellent potential fuel tank sealant. This section will describe how sidechain chemical structures of each polyorganosiloxane (dimethyl, methyl-3,3,3-trifluoropropyl, and 3-cyanopropylmethyl) influence the corresponding network behavior in the following solvents at room temperature (out of direct sunlight): Jet A jet fuel (Blacksburg Airport), water (deionized), chloroform (Fisher), Reference Fuel B¹⁶¹ (70/30 isooctane/toluene (from Aldrich)), and Reference Fuel C¹⁶¹ (50/50 isooctane/toluene (from Aldrich)).

The swelling properties in solvents and fuels were measured using ASTM D 471 (Standard Test Method for Rubber Property – Effect of Liquids)¹⁶¹ where the average results of three samples of each network were tested, and reported. Table 4.9 represents the network solvent resistance as the percent change in mass after 7 days of immersion in each solvent mentioned above. For the PDMS networks, swelling in the organic solvents increased as the crosslink density decreased. Dramatic differences in swelling were observed in solvents of different polarities among networks having different sidechain chemical structures. For the polar PMTFPS and PCPMS networks, swelling was uniformly low in the organic nonpolar solvents. The Jet A jet fuel (essentially kerosene) and Ref. fuels B and C, all hydrocarbons, swelled the PDMS (least polar) networks to greater extents than the more polar PMTFPS and PCPMS networks. In general, water had little effect on any of the networks, which was expected since siloxanes are generally hydrophobic.¹

The swelling data in chloroform, a relatively acidic polar solvent, provided some interesting points. PMTFPS networks swelled the least, 47% and 39%, PDMS networks swelled by 251% and 441%, and the PCPMS networks swelled to the greatest extents of

Table 4.9

Network Solvent Resistance

ASTM D 471			% Change in Mass after 7 Days of Immersion				
Network	# RU	HS %	Jet A	H ₂ O	CHCl ₃	Ref B	Ref C
2K PDMS	25	8	88	0.7	251	133	141
5K PDMS	62	3.4	155	0.1	441	237	233
4K PMTFPS	26	8	4	0.3	47	13	16
40K PMTFPS	261	0.9	4	7	39	10	13
8K DV-PCPMS	61	2.5	5	34	717	12	13
10K DV-PCPMS	77	2	0	2	724	12	16
9K HV-PCPMS	68	11	7	8	274	12	16
25K HV-PCPMS	197	4.3	5	0.2	591	13	13
35K HV-PCPMS	275	3.1	5	3	769	13	15

Reference Fuel B (Ref B) = 70/30 Isooctane/Toluene

Reference Fuel C (Ref C) = 50/50 Isooctane/Toluene

RU = average number of repeat units in the oligomeric precursor

HS % = weight percent of hard segments

274% - 769%. The fact that the PCPMS networks swelled the most in chloroform can likely be attributed to their basic nature. The lone pairs of electrons on the nitrogens of the 3-cyanopropyl substituent can interact very strongly with the chloroform solvent by hydrogen bonding. It is reasoned that PCPMS networks should also exhibit excellent adhesive properties to metal substrates. Lone pairs of electrons may have strong interactions with hydroxyl groups on oxide layers of the metal (Ti and Al) adherends. The adhesive properties of the networks will be discussed in the next section.

4.5.4 Adhesive Properties

Adhesion is the state in which two surfaces are held together by interfacial forces. Adhesion may be the result of secondary valence forces of the same type as those that give rise to cohesion (specific adhesion), of an interlocking action (mechanical adhesion), or both. Cohesive strength is the intrinsic strength of the adhesive, and cohesive failure is the rupture of an adhesive bond within the adhesive. Adhesive failure is the failure of a bond between the adhesive and adherend. Almost all adhesive and sealant applications with the exception of pressure sensitive adhesives (PSAs) such as Post It Notes[®] require cohesive failure. A sealant is defined as a material applied to a joint in paste or liquid form that hardens or cures in place, thereby forming a seal against gas or liquid passage (or entry).⁸⁹ Once a sealant is applied to a fuel tank, it should maintain its tensile properties over the service temperature range. It also needs to resist swelling in fuel to maintain good adhesion. These requirements formed the basis for selecting the tests conducted on the networks in this study.

While the main function of a sealant is to fill a void, good adhesion to the adherends is critical. Partial adhesive failure will increase the contact area between the sealant and solvent and lead to accelerated failure of the sealant, corrosion of the substrate, or total leakage.⁸⁹ Silicones are excellent surface release agents (or are “abhesive”) since they do not adhere well to many highly adhesive materials such as tars or rubber mixtures, polymer networks, asphalts, and polyethylene without mechanical anchorage to these surfaces. Silicones can have improved adhesion to materials such as metals, glass or ceramics if polar substituents and/or primers and adhesion promoters are used.¹ Adhesion promoters can diffuse to the sealant-surface interface and act as the

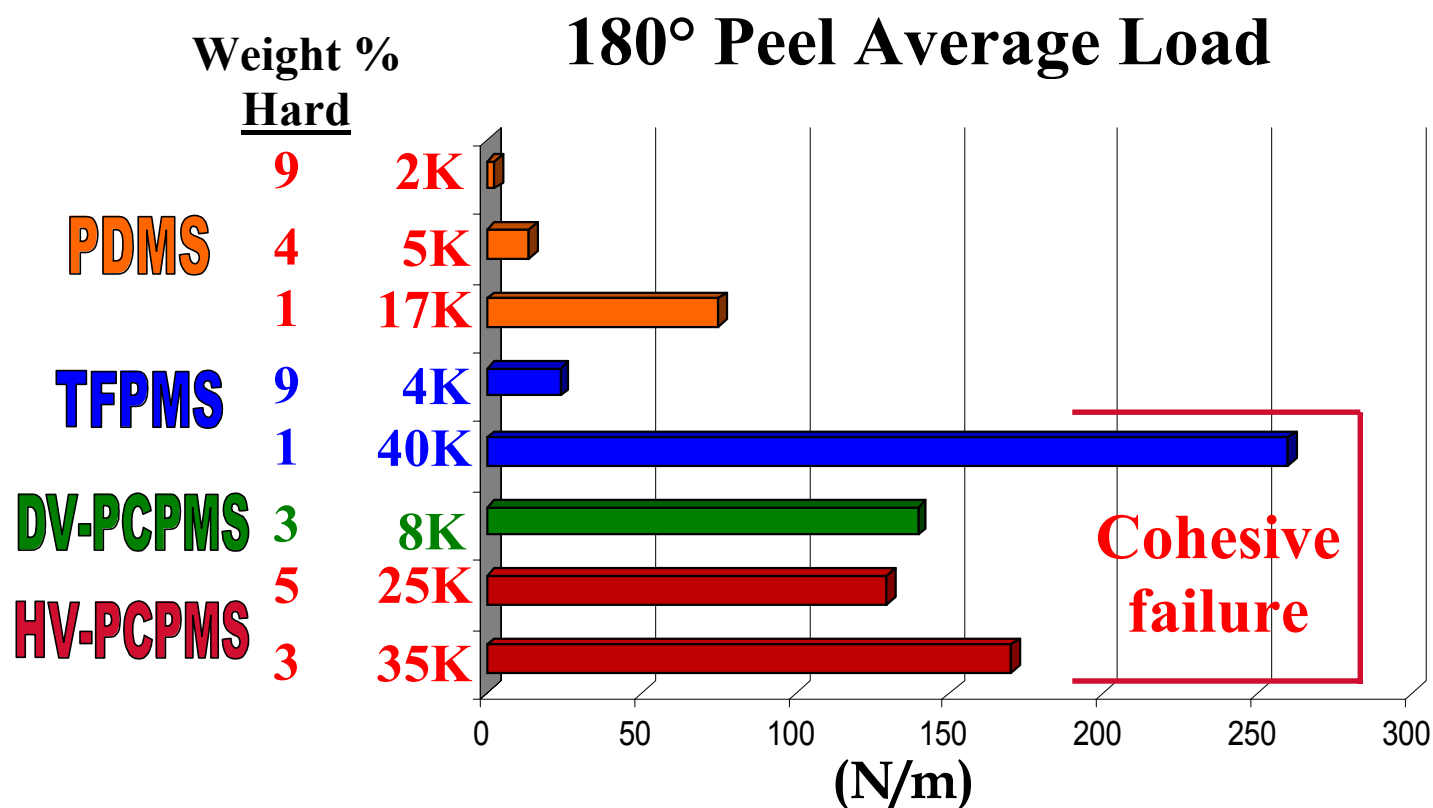
bridge between the sealant and substrate, much like a surfactant bridges hydrophobic and hydrophilic media.

In the following adhesion study, the variables were the chemical structures (in order of increasing substituent polarity) dimethyl < methyl-3,3,3-trifluoropropyl < 3-cyanopropylmethyl, the M_n s of the oligomeric siloxane precursors to the networks, and the crosslink densities. The adhesive properties of the networks were evaluated using 180° peel tests based on ASTM D 903¹⁶² (Standard Test Method for Peel or Stripping Strength of Adhesive Bonds). The metal adherends were a titanium alloy and an aluminum alloy since these are both common materials used for fuel tanks and for testing sealants.⁸⁹ The Ti-6Al-4V and Al 7075-T6 alloy (1" x 8" x 0.125" panels) adherends and the Al foil (1100 grade, 2mil) substrate surfaces were prepared by the following four step method. First, soapy water with a scotchbrite® scrub was employed to remove any oily residues (only on adherends). Secondly, acetone with a scotchbrite® scrub was used to remove any organic chemical impurities. Next, the adherends were mechanically abraded with coarse grain sandpaper to invoke porosity and improve adhesion.⁸⁹ Finally, a solvent rinse with acetone and methyl ethyl ketone^(K1) was used to remove any further foreign chemicals. Once the surfaces were prepared, they were allowed to condition in a 100°C oven to ensure the removal of residual solvent and water, thus reducing the number of variables for comparing adhesion. The resin mixture was drawn down onto the Al foil substrate (placed on a metal sheet to retain the integrity of the foils' flatness) at a 19 mil wet thickness (Figure 3.14). Adherend panels were then placed on top, and finally the entire sheet was placed in a 90°C oven until the network was cured (monitoring small scrapings by FTIR for the disappearance of the silane functionality). Once hydrosilation was complete, the sheet was removed from the oven, and a roller type razor was used to cut along the edges of the adherends to yield 1" wide samples for testing (Figure 3.15).

The 180° peel test (N/m) was used to investigate the average load per unit width of bond line (1" here) required to separate progressively one member from the other over the adhered surfaces. Samples were stripped or pulled at 6" per minute at a 180° separation angle in the Instron (Figure 3.16). An example of the peel adhesion data obtained for a 35K HV-PCPMS network is provided (Figure 3.16). These data show an

Table 4.10

Networks' Adhesion to Metal Adherends (Ti, Al)



Network	# RU	HS %	Average Load (N/m)	Failure
2K PDMS	25	8	2.5 +/- 5	adhesive
5K PDMS	62	3.4	14 +/- 9	adhesive
17K PDMS	235	0.9	75 +/- 20	adhesive
4K PMTFPS	26	8	24 +/- 9	adhesive
40K PMTFPS	261	0.9	260 +/- 50	cohesive
8K DV-PCPMS	61	2.5	140 +/- 20	cohesive
25K HV-PCPMS	197	4.3	130 +/- 20	cohesive
35K HV-PCPMS	275	3.1	170 +/- 20	cohesive

average load of 0.8 lbf/in, and multiplication by a factor of 175 converts the average load to 140N/m. The variance in the curve is due to the common slip-stick nature of adhesives.⁸⁹ All data (Table 4.10) presented are average results of stripping 5 Al and 5 Ti adherends.

Comparative adhesion data for the networks to metal adherends via 180° peel tests on the basis of their crosslink densities and sidechain chemical structures is represented in Table 4.10. Within the same type of polymer, as the crosslink densities were decreased, the adhesion increased. The 2K, 5K, and 17K PDMS networks with hard segment contents of 8%, 3.4%, and 0.9%, had average loads respectively of 2.5, 14, and 75 N/m. The slightly more polar 4K and 40K PMTFPS networks with hard segment contents of 8% and 0.9%, had adhesion values of 24 and 260 N/m. Finally, the most polar 25K and 35K HV-PCPMS networks with decreasing hard segment contents of 4.5% and 3.1% had increasing adhesion values of 130 and 170 N/m. When comparing networks with similar hard segment contents and varying polarities of the sidechain chemical structures, it was found that networks prepared from the longer chain polymers with polar substituents, PMTFPS and PCPMS networks, had higher adhesion. Moreover, the PDMS adhesive sealants failed adhesively whereas the polar networks prepared from the higher M_n oligomers failed cohesively. When comparing the 17K PDMS and 40K PMTFPS networks, both having 0.9% crosslink density, the nonpolar PDMS had a much lower adhesion value of 75 N/m (adhesive failure) compared to the polar network with an adhesion value of 260 N/m (cohesive failure). Networks prepared with the 5K PDMS, 8K DV-PCPMS, and 35K HV-PCPMS oligomers had similar hard segment contents. The network from the 5K PDMS (adhesive failure) had poorer adhesion (14 N/m) than the more polar networks (140 and 170 N/m, respectively) (both cohesive failure). This infers that the lone pairs of electrons on the nitrogens from the 3-cyanopropyl- substituents in the polar PCPMS networks positively influenced the adhesion. Also, the novel, polar PCPMS networks exhibited adhesion comparable to that of the polar PMTFPS networks which are of great interest currently in industry.

Chapter 5

Conclusions

Novel synthetic methods have been established for preparing nitrile containing cyclics, PCPMS oligomers, and their corresponding networks. Complete and partial hydrosilation reactions of D_4H with allyl cyanide were carried out to obtain the cyclics. $LiOH$ was used to equilibrate D_4CN cyclics to yield controlled molecular weight PCPMS oligomers with tailored endgroups. The PCPMS oligomers were subsequently crosslinked with trihydride D_4CNH_3 and dihydride $D_4(CN)_2H_2$ polar cyclics via two-component addition cures. Network studies were performed on polar PCPMS networks and compared to nonpolar PDMS and polar PMTFPS networks prepared with oligomers having similar average numbers of repeat units for use as potential sealant materials. Thermal properties of these novel, polar networks were good and lay within the service temperature range of aircraft applications. Swelling of the PCPMS networks was very low in hydrocarbons and simulated jet fuel solvents. The polar, novel, PCPMS networks proved to adhere better to metal adherends than the nonpolar PDMS networks as expected. These advantageous properties make the PCPMS elastomers good potential candidates for service as integral fuel tank sealants.

5.1 Polymer and Network Synthesis Conclusions

The D_4CN cyclic precursor to PCPMS has been prepared in the past using methods which afford ring rearrangements and higher cyclics (hydrolysis of dichlorosilane). The hydrosilation reaction herein was the addition of an excess of 4 equivalents of allyl cyanide to one equivalent of D_4H using Karstedt's catalyst. The tetracyclic D_4CN monomers which are desirable for equilibration reactions were obtained in an 85 – 90% yield. About 10 – 15% of the hydrosilation reactions are reverse addition, and this portion of 2-cyanoisopropyl substituents was verified via 1H NMR. Partial hydrosilation reactions, using a 1:1 ratio of D_4H :allyl cyanide, yielded cyclic tetramers with one or two 3-cyanopropyl substituents on the hydride functional ring, and were separated via distillation (and characterized via 1H NMR). These are beneficial

crosslinking reagents required for crosslinking the polar DV-PCPMS and HV-PCPMS oligomers which are immiscible with nonpolar crosslinking reagents (such as tetrakisdimethylsiloxysilane used for PDMS).

Earlier methods for the preparation of PCPMS oligomers used siloxanolate catalysts prepared from an anhydrous mixture of D_4CN and tetramethylammonium hydroxide. This method afforded polymers with dark colors and unpredictable molecular weights due to side reactions. Herein, one mole of LiOH initiator was added for every desired mole of PCPMS endgroup (two per chain) to prepare controlled molecular weight oligomers. The lithium siloxanolate endgroups were then quenched with the desired chlorosilane endgroup for polymer chains having tailored functional groups for further reactions. Typical equilibrium mixtures of $\sim 27\%$ cyclics/73% linear chains were confirmed via GPC. This higher percentage of cyclics was expected and is typical for cyclics with substituents larger and more polar than methyls. Extractions with 80% ethanol/20% H_2O were employed to remove the higher boiling D_4CN cyclics. Target molecular weights were in good agreement with the M_n s obtained using 1H NMR. Each of the M_n s obtained for the oligomers were slightly higher than predicted due to the extraction of lower oligomers.

5.2 Comparative Network Overview

Void free PCPMS networks were prepared from the cyclic-free oligomers using hydrosilation cures. These two-component addition cured networks were free of by-products. The cures were monitored via FTIR for the disappearance of silane functional groups. These polar networks were expected to swell less in hydrocarbon solvents and adhere better to metal substrates relative to PDMS elastomers.

Tensile, thermal, swelling, and adhesion studies were performed on nonpolar PDMS, polar PMTFPS, and polar PCPMS networks for comparison as potential sealant materials. PCPMS networks were stable well above $300^\circ C$ (when heated at a rate of $10^\circ C/min.$) in both air and N_2 , exhibited T_g s of $\sim -56^\circ C$, and were very resistant towards hydrocarbon solvents including jet fuel. The lone pair of electrons on the 3-cyanopropyl substituents of PCPMS oligomers have the ability to hydrogen bond. These PCPMS elastomers swelled to great extents in $CHCl_3$ for this reason. It is hypothesized that this

hydrogen bonding phenomenon is what allows the PCPMS networks to adhere better to the hydroxyl groups present in the oxide layer of the metal adherends than do nonpolar PDMS networks.

Adhesion values were obtained using a 180° peel test on Ti alloy and Al alloy. All of the networks prepared from higher M_n oligomers (with lower weight % hard segment contents) exhibited greater adhesion (and lower tensile strengths) to the metal adherends. All of the longer chain, polar networks exhibited cohesive failure. Independent of hard segment content, PCPMS elastomers had adhesion values at least twice those of the PDMS elastomers (adhesive failure), and exhibited cohesive failure.

Chapter 6

Recommendations for Further Work

Although new synthetic routes for the synthesis of PCPMS oligomers and novel PCPMS networks have been developed, the network properties have only been determined to a first approximation. All of these studies were done on resin mixtures containing only monomodal PCPMS oligomers, crosslinking reagent and catalyst. A future goal will be to optimize both the strength and adhesion of these thermally stable, fuel resistant, polar PCPMS networks. Since higher crosslink densities lead to the desired higher strength networks, but lower adhesion to metal adherends, future networks will be prepared using bimodal mixtures of PCPMS (of much longer polymers and some short chain oligomers) and with higher hard segment contents. Other recommended studies include the use of fillers (to improve strength) and adhesion promoters (to improve the adhesion). Surface preparations of the metal adherends such as etching or anodization in acid solutions should also be investigated.

Bimodal networks would be an interesting route to fulfill the requirements of higher strength networks prepared with much longer chains. Generally, networks prepared by endlinking very high M_n polymers have lower strengths than networks prepared using lower M_n s. This study has demonstrated that strength decreases while adhesion increases with increasing chain lengths. Mark found that much higher strength networks were obtained by hydrosilating a bimodal mixture of vinyl terminated PDMS, relative to those formed only with long chains.¹⁰⁰ This discovery could be advantageous for improving these materials.

Highly functional silica fillers are the most common and effective way of increasing the strength of a sealant as well as reducing the overall cost. Fillers typically represent the second highest percentage ingredient by weight in adhesive and sealant formulations next to the base adhesive resin.⁸⁹ As little as a 15% addition of silica can lead to a 30-fold increase in strength.⁴⁶ Large amounts of small particle size fillers may be added to the resin mixture to improve modulus with a decrease in flexibility. Fumed silica not only reinforces a network, but it also imparts thixotropy (flow control) to the

resin mixture which prevents it from flowing out of joints before curing. Most siloxane systems utilize a fumed silica having a surface partially comprised of SiOH. The hydroxyl groups hydrogen bond with one another forming a three-dimensional physical network amongst the resinous network.⁴⁶ The nitrile containing PCPMS networks should work exceptionally well with an acidic silica filler since it should also hydrogen bond to the filler particles. The high swelling properties of nitrile containing siloxanes in CHCl_3 suggests good hydrogen bonding capability.

Reactive silanes are of particular future interest as adhesion promoters to chemically bond the vinyl functional networks to the metal substrates. Although the physical polar and van der Waals forces of the 3-cyanopropyl groups on the PCPMS networks increase adhesion, they are not as strong as chemical bonds. The oxide layers on the metal substrates contain hydroxyl groups which may react with chlorosilane adhesion promoters to yield a surface with $\equiv\text{Si-H}$ functional groups. Hydrosilation of the surface with the vinyl terminated resin solution might invoke additional chemical crosslinks between the sealant and metal adherend and improve adhesion.

Only mechanical abrasion and solvent rinses are employed for applications having less stringent strength and durability requirements. These processes were used here as a first assessment of the relative adhesion properties for the materials. Aerospace applications require more stringent surface applications including etching or anodization in acid solutions (phosphoric acid or chromic acid).⁸⁹ An oxide layer which improves adhesion in most cases can be purposefully grown on the surface of the substrates. The lone pairs of electrons of the nitrile groups in the PCPMS networks could hydrogen bond to the hydroxyl groups present in this oxide layer, thereby improving adhesion. These surface preparation methods should be used to compare the adhesion values of the original monomodal PCPMS networks with the optimized (higher strength and adhesion oriented) PCPMS networks prepared with filled bimodal oligomers, and adhered using silane adhesion promoters.

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VITA

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