

PREPARATION OF NITRILE CONTAINING SILOXANE TRIBLOCK COPOLYMERS AND
THEIR APPLICATION AS STABILIZERS FOR SILOXANE MAGNETIC FLUIDS

[Chenghong Li](#)

Thesis submitted to the Faculty of Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

Master of Science
in
Chemistry

Judy S. Riffle, Chair
James E. McGrath
Harry W. Gibson
James P. Wightman
John G. Dillard

Dec. 11, 1996
Blacksburg, Virginia

Keywords: Polysiloxanes, Block copolymers, Stabilizers
Copyright 1996, Chenghong Li

PREPARATION OF NITRILE CONTAINING SILOXANE TRIBLOCK COPOLYMERS AND THEIR APPLICATION AS STABILIZERS FOR SILOXANE MAGNETIC FLUIDS

Chenghong Li

(Abstract)

Nitrile containing siloxane block copolymers were developed as stabilizers for siloxane magnetic fluids. The siloxane magnetic fluids have been recently proposed as internal tamponades for retinal detachment surgery. PDMS-*b*-PCPMS-*b*-PDMSs (PDMS = polydimethylsiloxane, PCPMS = poly(3-cyanopropylmethylsiloxane)) were successfully prepared through kinetically controlled polymerization of hexamethylcyclotrisiloxane initiated by lithium silanolate endcapped PCPMS macroinitiators. The macroinitiators were prepared by equilibrating mixtures of 3-cyanopropylmethylcyclotrisiloxanes ($D_x\text{CN}$) and dilithium diphenylsilanediolate (DLDPS). $D_x\text{CN}$ s were synthesized by hydrolysis of 3-cyanopropylmethyldichlorosilane, followed by cyclization and equilibration of the resultant hydrolysates. DLDPS was prepared by deprotonation of diphenylsilanediol with diphenylmethyl lithium.

It was found that mixtures of $D_x\text{CN}$ and DLDPS could be equilibrated at 100°C within 5-10 hours. By controlling the $D_x\text{CN}$ -to-DLDPS ratio, macroinitiators of different molecular weights could be obtained. The major cyclics in the macroinitiator equilibrate are tetramer (8.6 ± 0.7 wt%), pentamer (6.3 ± 0.8 wt%) and hexamer (2.1 ± 0.5 wt%). 2.5k-2.5k-2.5k, 4k-4k-4k, and 8k-8k-8k triblock copolymers were prepared and characterized. These triblock copolymers are transparent, microphase separated and highly viscous liquids. It was found that these triblock copolymers can stabilize nanometer $\gamma\text{-Fe}_2\text{O}_3$ and cobalt particles in octamethylcyclotetrasiloxane or hexane. Hence PDMS-*b*-PCPMS-*b*-PDMSs represent a class of promising steric stabilizers for silicone magnetic fluids.

Acknowledgments

I would like to express my sincere gratitude to my advisor and committee chairperson Dr. J. S. Riffle, not only for her financial support and invaluable academic guidance, but for her personal help and encouragement as well. I would also like to thank the other members of my committee which include Dr. J. E. McGrath, Dr. H. W. Gibson, Dr. J. P. Wightman, Dr. J. G. Dillard for their precious time and assistance.

Special thanks are extended to Mr. Tom Glass for NMR training and quantitative ^{13}C NMR and ^{29}Si NMR acquisitions, Ms. Heng (Rose) Shi for supercritical fluid chromatography, Mr. Steve McCartney for transmission electron microscopy, Mr. Jeff Mecham and Dr. Qing Ji for gel permeation chromatography, Dr. Steven Davis for differential scanning calorimetry and to all the people in Dr. Riffle's laboratory including Mr. John Facinelli, Dr. V. Venkatesan, Ms. Hui Li, Dr. Steven Davis, Miss Sheng Lin, Mr. Sam Liao, Mr. John Bronk, Miss Hong Xie, etc. for their friendship, suggestions and help.

Special gratitude to my wife Yan Yang for her sacrifice and all-out support during my three years graduate study. Thanks are also given to mother, father, my mother-in-law and father-in-law, and to my sisters for emotional and financial support. Special thanks should be given to my mother, because without her considerate care of my little baby Roy, it is hard to believe that I could have completed my research.

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 ₅ CN	1,3,5,7,9-pentakis(3-cyanopropyl)-1,3,5,7,9-pentamethylcyclopentasiloxane or 3-cyanopropylmethylcyclopentasiloxane
D _x CN	cyclic poly(3-cyanopropylmethylcyclosiloxane)s
D ₄ H	1,3,5,7-tetrahydrogen-1,3,5,7-tetramethylcyclotetrasiloxane or hydrogenmethylcyclotetrasiloxane
DSC	differential scanning calorimetry
GPC	gel permeation chromatography
IR	infrared spectroscopy
NMR	nuclear magnetic resonance
PDMS	polydimethylsiloxane
PCPMS	poly(3-cyanopropylmethylsiloxane)
SFC	supercritical fluid chromatography
TEGDME	tri(ethylene glycol) dimethyl ether
THF	tetrahydrofuran
TMAH	tetramethylammonium hydroxide
DLDPs	dilithium diphenylsilanediolate

TABLE OF CONTENTS

CHAPTER 0 Preface	1
CHAPTER 1 Introduction to Magnetic Fluids	4
1.1 Magnetic Fluids	4
1.2 Stabilization of Magnetic Fluids	11
1.3 Characterization of Magnetic Fluids	14
1.4 Block Copolymers of PCPMS and PDMS as Stabilizers for Silicone Magnetic Fluids	16
CHAPTER 2 Introduction to Polysiloxane Fluids	20
2.1 Overview of Polysiloxane Syntheses	20
2.2 Preparation of Cyclosiloxanes	22
2.3 Ring-Chain Equilibria: Thermodynamic Considerations	24
2.4 Ring-Opening Polymerization: Kinetic Considerations	28
2.4.1 Cationic Polymerization	28
2.4.2 Anionic Polymerization	31
2.4.2.1 General Principles	31
2.4.2.2 Kinetically Controlled Polymerization	37
2.5 Review of Nitrile Containing Silicones	42
2.6 Preparation of Block Copolymers	44
2.6.1 Introduction	44
2.6.2 Preparation of Triblock Copolymers	46
2.7 Possible Approaches for Preparing PDMS-b-PCPMS-b-PDMSs	56
CHAPTER 3 Synthesis of PDMS-b-PCPMS-b-PDMS Triblock Copolymers	58
3.1 The Synthetic Approach	58
3.2 Skills for Moisture Sensitive Experiments	58
3.3 Chemicals and Purification	59
3.3.1 Tetrahydrofuran	59
3.3.2 Dichloromethane	59
3.3.3 Methyldichlorosilane	61
3.3.4 Tri(ethylene Glycol) Dimethyl Ether	61
3.3.5 1,1,3,3,5,5-Hexamethylcyclotrisiloxane	61
3.3.6 Molecular Sieves	61
3.3.7 Allyl Cyanide	61
3.3.8 Potassium Carbonate	62
3.3.9 Trimethylchlorosilane	62
3.3.10 Vinyl dimethylchlorosilane	62
3.3.11 Diphenylmethane	62
3.3.12 Diphenylsilanedoils	62

3.3.13	2,4,6,8-Tetramethylcyclotetrasiloxane	63
3.3.14	Toluene	63
3.4	Preparation of Monomers and Initiators	63
3.4.1	3-Cyanopropylmethyldichlorosilane	63
3.4.2	3-Cyanopropylmethylcyclosiloxanes	64
3.4.2.1	Hydrolysis of 3-Cyanopropylmethyldichlorosilane	64
3.4.2.2	Hydrosilylation of Hydrogenmethylcyclosiloxanes	66
3.4.3	Random Cyclic PDMS/PCPMS	66
3.4.4	Dilithium Diphenylsilanediolate	67
3.4.4.1	Synthesis	67
3.4.4.2	DLDPS as a Difunctional Initiator	68
3.4.5	Lithium Silanolate Endcapped PCPMS Macroinitiators	69
3.4.6	α,ω-Bis(aminopropyl) PCPMS	72
3.4.7	Random Copolymer of PDMS and PCPMS	73
3.4.8	PDMS-b-PCPMS-b-PDMSs	73
3.4.9	γ-Fe₂O₃ Powder	75
3.4.10	Suspensions of γ-Fe₂O₃ in Octamethylcyclotetrasiloxane	75
3.5	Characterization	76
3.5.1	¹H NMR	76
3.5.2	¹³C NMR	76
3.5.3	²⁹Si NMR	77
3.5.4	Gel Permeation Chromatography	77
3.5.5	Supercritical Fluid Chromatography	78
3.5.6	Differential Scanning Calorimetry	78
3.5.7	Intrinsic Viscosity Measurement	78
3.5.8	Infrared Spectroscopy	78
CHAPTER 4	Results and Discussions	79
4.1	3-Cyanopropylmethyldichlorosilane	79
4.2	3-Cyanopropylmethylcyclosiloxanes	81
4.3	Dilithium Diphenylsilanediolate	99
4.4	PCPMS Macroinitiators	113
4.4.1	Kinetics of Polymerization	113
4.4.2	Molecular Weight Control and Equilibrium Concentrations of Cyclics	115
4.4.3	Molecular Weight Distributions of PCPMS Macroinitiators	121
4.5	PDMS-b-PCPMS-b-PDMSs	122
4.5.1	Synthesis and Kinetics	122
4.5.2	²⁹Si NMR Analyses	126
4.5.3	Thermal Analyses	128
CHAPTER 5	Stability Studies	130
5.1	Stabilization of γ-Fe₂O₃	130
5.2	Stabilization of Cobalt Ultrafine Particles	131

CHAPTER 6 Conclusions	134
CHAPTER 7 Future Work	136
Vita	137

CONTENT OF FIGURES

Figure 0.1	<u>Retinal detachment repair using a scleral buckle</u>	3
Figure 0.2	<u>Retinal detachment repair using an internal tamponade</u>	3
Figure 1.1	<u>Molecular structures of some dispersion media</u>	10
Figure 1.2	<u>Ion concentrations and potential changes near a particle with positive charges</u>	12
Figure 1.3	<u>Electrostatic stabilization of colloidal systems</u>	12
Figure 1.4	<u>Steric stabilization of colloidal systems</u>	14
Figure 1.5	<u>Initial magnetization curve for magnetic materials</u>	15
Figure 1.6	<u>Structures for the proposed stabilizers</u>	18
Figure 1.7	<u>Triblock and diblock copolymers of PDMS and PCPMS as stabilizers for silicone magnetic particles</u>	18
Figure 1.8	<u>Infrared spectra for mixtures of heptamethyl-2-cyanoethylcyclotetrasiloxane and lithium trimethylsilanolate</u>	19
Figure 2.1	<u>Equilibrium concentration of cyclosiloxane $[R(CH_3)_2SiO]_n$ as a function of the volume concentration of the siloxanes in cyclohexanone</u>	26
Figure 2.2	<u>Mechanism for Br⁺ nsted acid initiated polymerization of cyclosiloxanes</u>	30
Figure 2.3	<u>Equilibria among free acid, water, silanol and ester in an acid/siloxane equilibrates</u>	31
Figure 2.4	<u>Mechanism for anionic polymerization of cyclic siloxanes</u>	33
Figure 2.5	<u>Mechanism for specific redistribution</u>	34
Figure 2.6	<u>Kinetics of anionic polymerization of cyclosiloxanes</u>	34
Figure 2.7	<u>Equilibria between cyclic and linear ionic associates</u>	36
Figure 2.8	<u>Polysiloxanes as multidentate ligands</u>	37

Figure 2.9	Structures of some difunctional siloxane initiators	41
Figure 3.1	Flow chart for preparing PDMS-b-PCPMS-b-PDMS triblock copolymers	60
Figure 4.1	¹H NMR for 3-cyanopropylmethyldichlorosilane	81
Figure 4.2	IR spectrum for the hydrolysate of 3-cyanopropylmethyldichlorosiloxane in chlorobenzene	83
Figure 4.3	²⁹Si NMR spectrum of the hydrolysate of 3-cyanopropylmethyldichlorosilane	84
Figure 4.4	¹H NMR spectrum for equilibrated D_xCNs	86
Figure 4.5	²⁹Si NMR spectrum for equilibrated D_xCNs	87
Figure 4.6	Supercritical fluid chromatograms of equilibrated D_xCNs	88
Figure 4.7	Isomers of D_xCNs	89
Figure 4.8	²⁹Si NMR spectrum for distilled D_xCNs	91
Figure 4.9	Supercritical fluid chromatogram for distilled D_xCNs	92
Figure 4.10	¹³C and DEPT NMR spectra of distilled D_xCNs	93
Figure 4.11	¹H NMR spectrum of D₄CN prepared by hydrosilylation of D₄H	95
Figure 4.12	Supercritical fluid chromatography of cyclics prepared by (a) hydrolysis of 3-cyanopropylmethylsilane, (b) hydrosilylation of D₄H	96
Figure 4.13	¹³C NMR spectrum of D₄CN prepared from hydrosilylation of D₄H	97
Figure 4.14	¹³C DEPT spectra of D₄CN prepared by hydrosilylation of D₄H	98
Figure 4.15	²⁹Si NMR spectrum for 1,1,1,3,3,3-hexamethyl-2,2-diphenyltrisiloxane, a derivative of DLDPS	102
Figure 4.16	¹H NMR spectrum of 1,1,1,3,3,3-hexamethyl-2,2-diphenyltrisiloxane	103
Figure 4.17	¹³C NMR spectrum of 1,1,1,3,3,3-hexamethyl-2,2-diphenyltrisiloxane	104
Figure 4.18	Gel permeation chromatograms of a PDMS prepared by D₃ polymerization in CH₂Cl₂ using DLDPS initiator and TEGDME promoter	105

Figure 4.19	Polymerization of D₃ initiated with lithium trimethylsilanolate followed by ¹H NMR	108
Figure 4.20	Polymerization of D₃ at 20 ± 2°C using lithium trimethylsilanolate initiator and TEGDME promoter	110
Figure 4.21	Polymerization of D₃ using DLDPS initiator and TEGDME promoter	112
Figure 4.22	Polymerization of D_xCNs at 100°C (D_xCN/ DLDPS = 5.0 kg/mol)	114
Figure 4.23	The dependence of molecular weight of the macroinitiators on the D_xCN-to-DLDPS ratio (Solvent: chloroform)	116
Figure 4.24	SFC for undistilled cyclics and macroinitiator	117
Figure 4.25	GPC for a) 10k α,ω-bis(3-aminopropyl) PCPMS, b) 10 k α,ω-divinyl PCPMS . 121	121
Figure 4.26	Polymerization of D₃ in CH₂Cl₂ using PCPMS macroinitiator and TEGDME promoter	124
Figure 4.27	GPC for PCPMS macroinitiators and related triblock copolymers	125
Figure 4.28	Sequence possibilities for a random PDMS/PCPMS copolymer at different resolution	127
Figure 4.29	²⁹Si NMR for random and block copolymers of PDMS and PCPMS	128
Figure 4.30	DSC for PCPMS and block copolymers of PDMS and PCPMS	129
Figure 5.1	TEM for suspensions of γ-Fe₂O₃	132
Figure 5.2	γ-Fe₂O₃in D₄ with/without PDMS-b-PCPMS-b-PDMS stabilizers	133

LIST OF TABLES

Table 1.1	<u>Properties of common magnetic materials</u>	6
Table 1.2	<u>Magnetic materials and their Gibbs oxidation energies</u>	7
Table 1.3	<u>Advantages and disadvantages of common dispersion media</u>	9
Table 2.1	<u>Yields of linear polymers in undiluted equilibrates</u>	25
Table 2.2	<u>Weight percentages of dimethylsiloxane cyclics in high pressure equilibrium at 393K</u>	27
Table 2.3	<u>Stabilities of nitrile containing siloxanes</u>	43
Table 2.4	<u>Important organofunctional groups in polysiloxanes</u>	55
Table 3.1	<u>Formulation of PCPMS macroinitiators</u>	71
Table 3.2	<u>Formulation for PDMS-b-PCPMS-b-PDMS triblock copolymers</u>	74
Table 3.3	<u>Formulation for suspensions of γ-Fe₂O₃ in D₄</u>	76
Table 4.1	<u>Yields of D_xCNs by hydrolytic method using different inert solvents</u>	82
Table 4.2	<u>Chemical shifts for ¹H NMR of D_xCNs</u>	90
Table 4.3	<u>Chemical shifts for ¹³C NMR of D_xCNs</u>	90
Table 4.4	<u>Chemical shifts for ²⁹Si NMR of D_xCNs</u>	90
Table 4.5	<u>Kinetic data for polymerization of D₃ in CD₂Cl₂ using lithium trimethylsilanolate initiator and TEGDME promoter</u>	109
Table 4.6	<u>Kinetic data for polymerization of D₃ in dichloromethane using DLDPS initiator and TEGDME promoter</u>	111
Table 4.7	<u>Kinetic data for equilibrium polymerization of D_xCN (x=3-5) at 100°C using DLDPS initiator</u>	114
Table 4.8	<u>Intrinsic viscosities for PCPMSs</u>	115

Table 4.9	<u>Integral results of supercritical fluid chromatograms for dimethylvinylsilyl capped macroinitiators and equilibrium cyclics</u>	118
Table 4.10	<u>Equilibrium concentrations of cyclics and molecular weights of macroinitiators</u>	120
Table 4.11	<u>Kinetic data for polymerization of D₃ in dichloromethane using PCPMS macroinitiators</u>	123
Table 5.1	<u>Formulation for suspensions of γ-Fe₂O₃ in D₄</u>	130
Table 5.2	<u>Magnetic properties for triblock copolymer stabilized suspensions of γ-Fe₂O₃ in D₄</u>	133

TABLE OF SCHEMES

Scheme 2.1	<u>Preparation of polystyrene/butadiene thermoplastic elastomer</u>	47
Scheme 2.2	<u>Preparation of polydiphenylsiloxane-b-PDMS-b-polydiphenylsiloxane</u>	48
Scheme 2.3	<u>Preparation of PDMS-b-poly(methyl methacrylate) by transformation of living polymerization to group transfer polymerization</u>	50
Scheme 2.4	<u>Preparation of PDMS-b-poly(methyl methacrylate) using dilithiobenzophenone dinitiator</u>	51
Scheme 2.5	<u>Preparation of PDMS-b-poly(oxazoline) through transformation of anionic polymerization to cationic polymerization</u>	52
Scheme 2.6	<u>Coupling reactions of (a) telechelic and (b) mono-telechelic oligomers</u>	53
Scheme 3.1	<u>Preparation of 3-cyanopropylmethyldichlorosilane by hydrosilylation</u>	64
Scheme 3.2	<u>Preparation of D_xCN through hydrolysis of 3-cyanopropylmethyldichlorosilane</u> ..	65
Scheme 3.3	<u>Preparation of D₄CN by hydrosilylation of tetramethylcyclotetrasiloxane</u>	66
Scheme 3.4	<u>Preparation of DLDPS</u>	68
Scheme 3.5	<u>Preparation of PDMS by anionic polymerization of D₃ using DLDPS initiator</u>	69
Scheme 3.6	<u>PCPMS macroinitiators by equilibrating mixtures of D_xCNs and DLDPS</u>	70
Scheme 3.7	<u>Preparation of α,ω-difunctional PCPMSs</u>	71
Scheme 3.8	<u>Preparation of α,ω-bis(3-aminopropyl) PCPMSs</u>	72
Scheme 3.9	<u>Preparation of PDMS-b-PCPMS-b-PDMSs</u>	74
Scheme 3.10	<u>Preparation of γ-Fe₂O₃ powders</u>	75

CHAPTER 0

PREFACE

The commonest form of retinal detachment, rhegmatogenous retinal detachment, stems from a hole or a break caused by traumatic or pathological reasons. As vitreous fluid (the gelatinous substance that fills the central cavity of the eye) gradually passes through the hole or the break and stays beneath the retina, the retina gradually becomes separated from its source of metabolic and architectural support, the retinal pigment epithelium. The present techniques to cure retinal detachment^{1,2,3} are to block the hole or break by a): implanting a scleral buckle, an external ocular implant (typically thermoset silicone), to indent the outer wall of the eye and hence to close the retinal break ([Fig. 0.1](#)), or by b): injecting materials like air, sulfur hexafluoride, silicone fluids, or perfluorocarbon fluids into the eye to unfold the retina flap and hence to block the passage of more vitreous fluid into the subretinal space ([Fig. 0.2](#)). As long as no more vitreous fluid can enter the subretina space, the retina will gradually reattach by natural adsorption or manual drainage of subretinal vitreous fluid. However these two methods are unsatisfactory for repairing large retinal tears, especially those extended to 360°. Dr. J. P. Dailey of Erie Biotechnology Corporation, Erie, Pennsylvania, recently suggested that the problem can be solved using a magnetic fluid as an internal tamponade. Under the influence of a magnetic scleral buckle, the magnetic fluid should form an internal band along the scleral buckle, thus providing 360° protection of the retina. Based on this idea, Dr. J. P. Dailey, an ophthalmic surgeon, Dr. S. W. Charles, a physicist in the University College of North Wales, UK, and Dr. J. S. Riffle, a polymer chemist at Virginia Polytechnic Institute and State University, Virginia, have been cooperating to design and evaluate suitable magnetic fluids for this purpose. Since PDMS fluids have already

¹ S. Charles, J. Magn. Mat., **85**, 277-284 (1990)

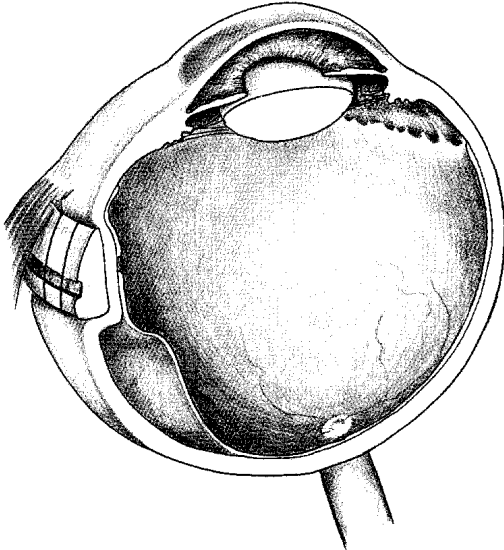
² P. Cibis, B. Becker, E. Okun, Archives of Ophthalmology, **68**, 590-599 (1962)

³ Editorial, Silicone Oil Study Group, Amer. J. Ophthalmology, **99**, 593-595 (1985)

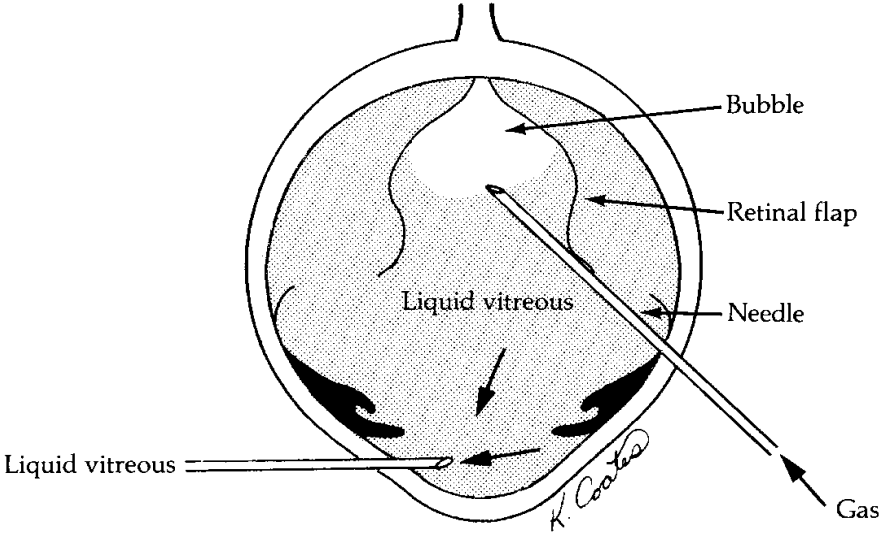
been used as internal tamponades, they have decided to use these liquids as dispersion media for the magnetic particles.

My contribution is the development of potential stabilizers or surfactants which can prevent coagulation of magnetic particles in the silicone fluids. The central point of this thesis is preparation of nitrile containing polysiloxane block copolymers, mainly PDMS-*b*-PCPMS-*b*-PDMSs, and evaluation of these block copolymers as stabilizers for silicone magnetic fluids.

This thesis consists of seven chapters which describe basic concepts of magnetic fluids and their stabilization (Chapter 1), polyorganosiloxane syntheses (Chapter 2), organic synthesis of PDMS-*b*-PCPMS-*b*-PDMSs (Chapter 3), results and discussions (Chapter 4), preliminary evaluations of triblock copolymers (Chapter 5), conclusions (Chapter 6) and recommendations for future work (Chapter 7).



[Figure 0.1](#) Retinal detachment repair using a scleral buckle.



[Figure 0.2](#) Retinal detachment repair using an internal tamponade

CHAPTER 1

INTRODUCTION TO MAGNETIC FLUIDS

1.1 Magnetic Fluids

Magnetic fluids are concentrated, stable suspensions of nanometer particles (~ 10 nm) of ferri- or ferromagnetic materials in carrier liquids like hydrocarbons, esters, etc. Stabilizers are normally required to provide the colloidal stability. No liquids have been found to be intrinsically ferri- or ferromagnetic. All known ferri- and ferromagnetic materials undergo a second order phase transformation to a paramagnetic state at the Curie temperature, which is far below their melting temperatures. For example, the Curie temperature of iron is 770°C which is far below its melting point (1535°C).

The pioneering work of today's magnetic fluids was given by Papell⁴ in 1965 and Rosensweig in 1975.⁵ Since then, numerous patents (~1000) and scientific papers (~2000) have been published related to their preparations, properties and applications. In engineering, magnetic fluids have been applied in frictionless dynamic sealing⁶, damping of undesired vibrations and cooling of loudspeaker coils⁶, etc.. In the medical field, magnetic fluids have been proposed for drug carriers⁷, X-ray contrast intensifiers, for separation of cells or viruses and now for internal tamponades for retinal detachment surgery.

Important properties of magnetic materials include lattice structure and lattice parameters, saturation magnetization (M_s), Curie temperature (T_c) and magnetocrystalline anisotropic constants of magnetism (K_1 and K_2). [Table 1.1](#) lists typical ferro- and ferrimagnetic materials and their properties. As magnetic materials are employed as nanometer particles in magnetic fluids,

⁴ S. S. Papell, U. S. Patent, 3,215,572, assigned to NASA (1965).

⁵ R. E. Rosensweig, U. S. Patent, 3,917,538, assigned to Ferrofluidics Corporation (1975).

⁶ S. Odenbach, *Advances in Colloid and Interface Science*, Elsevier Science Publisher B. V. (1993)

the oxidation stability becomes a critical property. The oxidation stability for common magnetic materials can be roughly reflected by their Gibbs oxidation energy to be oxidized to next higher valency ([Table 1.2](#)). Most commonly used magnetic materials for magnetic fluids are magnetite (Fe_3O_4), berthollide, and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) which only have a moderate saturation magnetization but are stable in the atmosphere. Although magnetite (Fe_3O_4) can be slowly oxidized to $\gamma\text{-Fe}_2\text{O}_3$, there is no significant decrease in saturation magnetization. Transition metals, rare earth metals and their alloys have much higher saturation magnetizations than ferrites can offer, however, their applications in magnetic fluids are limited to inert dispersion media and non-oxidizing atmospheres because particles of these materials suffer quick oxidation in the atmosphere.

Oxidation of nanometer metallic particles has been an obstacle that hinders the applications of these materials in magnetic fluids. Although some metals like cobalt and nickel can form protective film which can hinder further oxidation of inner metals, it is not possible to use oxide films to protect the metal particles without losing the intrinsic magnetization. Since the minimum thickness for an oxide film to effectively prevent the oxidation of inner metals is ~ 1.5 nm, so particles of ~ 10 nm in diameter consist only ~ 34 vol% metal. Therefore, the advantages of metallic magnetic materials is lost. The idea to use surfactants as a barrier for oxygen does not work either since the diffusion of air through a surfactant monolayer proceeds at roughly the same rate as through water and kerosene. Although some cobalt magnetic fluids in hydrocarbons have been made stable for years, the oxidation of metallic magnetic fluids remains an unsolved problem⁸.

⁷ K. J. Wider, A. E. Senyei and D. G. Scarpelli, Proc. Soc. Exp. Biol. **58**, 141 (1978)

⁸ P. C. Scholten, Chem. Eng. Comm. **67**, 331-340 (1988)

Table 1.1 Properties of common magnetic materials⁹

Substances	Lattice Parameter (nm)	M_s (kAm ⁻¹) (298 K)	T_c (K)	Anisotropy Constants (at 298K) ($\times 10^{-3}$ Jm ⁻³)	
				K_1	K_2
MnO \dot{u} Fe ₂ O ₃	0.85 (is)	400	573	- 3	
FeO \dot{u} Fe ₂ O ₃	0.84 (is)	484	858	- 11	
CoO \dot{u} Fe ₂ O ₃	0.84 (is)	425	793	200	
NiO \dot{u} Fe ₂ O ₃	0.83	270	858	- 6.2	
CuO \dot{u} Fe ₂ O ₃	a = 0.82 c = 0.87 (tet)	135	728		
MgO \dot{u} Fe ₂ O ₃	0.84 (is)	120	713	- 2.5	
BaO \dot{u} 6Fe ₂ O ₃	a = 0.59 c = 2.32 (hex)	380	723	330	
Fe ₂ O ₃ -Fe ₃ O ₄	berthollide (is)		863	- 3	
γ - Fe ₂ O ₃	8.33 (defect spinel)		863	- 4.6	
Fe(α)	0.286 (bcc)	1707	1043	48	20
Co(α)	a = 0.25 c = 0.41 (hcp)	1400	1404*	450	150
Ni	0.35 (fcc)	485	631	- 50	- 2
Gd	a = 0.36 c = 0.58 (hcp)	1980	293	20	~0

(is) inverse spinel/cubic, (tet) tetragonal, (fcc) face centered cubic, (bcc) body centered cubic, (hcp) hexagonal close-packed, (hex) hexagonal. M_s is saturation magnetization, T_c is Curie temperature, and K_1 and K_2 are magnetocrystalline anisotropy constants of magnetism.

* hcp Co(α) undergoes transformation to fcc Co(β) at 733 K. However, the structure of small Co particles (< 10 nm) at 290 K is generally fcc

⁹ S. W. Charles, in Studies of Magnetic Properties of Fine Particles and Their Relevance to Materials Science, J. L. Dorman and D. Fiorani (Editors) Elsevier Science Publisher B. V. 270 (1992)

[Table 1.2](#) Magnetic materials and their Gibbs oxidation energies

Materials	M_s (kAm ⁻¹)	ΔG , kJ/mol
γ -Fe ₂ O ₃	410	0
Ferrites	0-420	
Fe ₃ O ₄	477	- 97.2
Ni	490	- 216.3
Co	1400	- 213.4
Fe	1710	- 244.3
FeCo	1910	

M_s is saturation magnetization

ΔG is Gibbs energy of oxidation to the next higher valency

Cited from [reference 6](#), p332

Ideal dispersion liquids should have low evaporation rates, low melting points, low viscosities and chemical inertness. However, these requirements are to a large extent incompatible. [Table 1.3](#) lists the advantages and disadvantages of common dispersion media for magnetic fluids. Hydrocarbons show fairly good chemical inertness, but have either too high vapor pressures or too high melting points. Introduction of branches can lower the melting points, but the viscosities are still too high. Therefore, the serviceable ranges of hydrocarbons are rather narrow. Diesters of dicarboxylic acids have roughly the same vapor pressures as hydrocarbons of the same molecular weights, but have lower viscosities and lower melting points. Therefore, the diesters have much wider serviceable ranges than hydrocarbons with similar molecular weights. Alkyl esters of orthosilicic acid have relatively high vapor pressures, but low melting points and low viscosities, so these compounds are very suitable for low temperature applications. The only limitation of esters of carboxylic acids and orthosilicic acid is that the ester groups are not hydrolytically stable enough. Therefore, these materials may be unsuitable in some situations which involve moisture and acidic or basic gasses. Polyphenylene oxides ([Fig. 1.1a](#)) are very stable and only slowly degraded under ionizing radiation, but these materials have neither

special superiority nor obvious weakness. Polychlorinated biphenyls meet most of the criteria. However, since polychlorinated biphenyls tend to form explosive mixtures with metal ultrafine particles, they cannot be used as dispersion media for metallic magnetic particles. Linear or cyclic PDMSs ([Fig. 1.1b](#)) have excellent high temperature stability and meet most of the criteria, so they make good dispersion media if there are suitable surfactants. Perfluorinated polyethers ([Fig. 1.1e](#)) are superior in most aspects, especially in chemical inertness (they even resist ozone and chlorine). However, the scarcity of surfactants with perfluorinated polyethers are even more acute than with siloxanes.

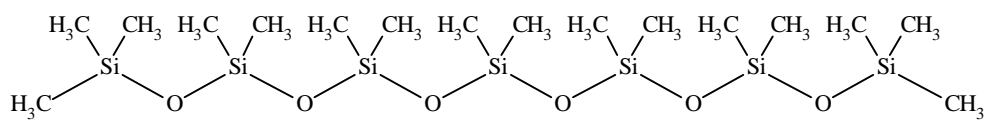
[Table 1.3](#) Advantages and disadvantages of common dispersion media for magnetic fluids

	Viscosity/ melting point	Vapor pressure	Chemical stability	High temp. stability	Radiation resistance	Dispersant availability
Aliphatic hydrocarbons	-	-	+	+/-		++
Diesters	+	+	-	-		++
Orthosilicic acid esters	++	+-	-	-		+
Linear silicones	+	++	+	+		-
Cyclic silicones	+	++	+	+		-
Poly(phenylene oxide)	+	+	+		++	+
Perfluorinated polyethers	++	++	++			-
Polychlorinated biphenyls	+	+	+*	+		+

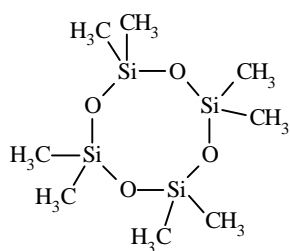
++ Excellent, + Good, - Poor

* Dangerous in combination with metallic particles

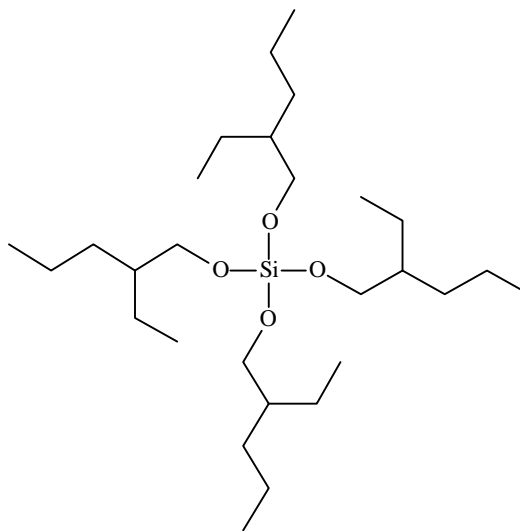
Cited from [reference 6](#) p335



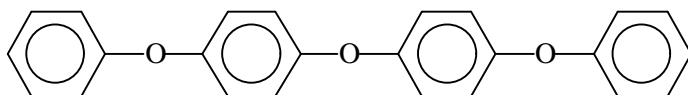
(a) Linear poly(dimethylsiloxane)



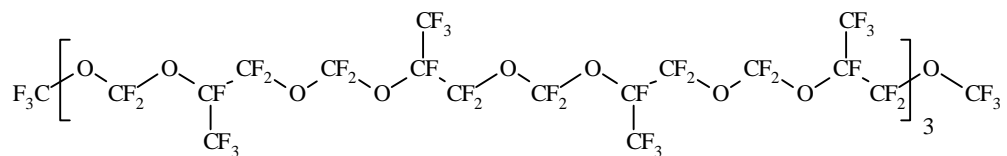
(b) Cyclic poly(dimethylsiloxane)



(d) Tetra(2-ethylhexyl)silicate



(c) Poly(phenylene oxide)



(e) Perfluoro polyether (Fomblin Y25)

Figure 1.1 Molecular structures of some dispersion media

1.2 Stabilization of Magnetic Fluids

Magnetic fluids are thermodynamically unstable. Magnetic particles tend to settle due to aggregation caused by magnetic dipole-dipole interaction and van der Waals' attractions, or due to diffusion growth (Ostwald ripening) of the larger particles at the expense of the small ones. The diffusion growth is negligible if the particles are insoluble in the dispersion media. Assuming magnetic particles are small enough (3-10 nm), the gravity and magnetic dipole-dipole interaction can be balanced by thermal motion. Van der Waals' forces, however, cannot be counteracted by thermal agitation due to a deep potential energy well when particles are in close contact. Therefore, magnetic fluids will coagulate if no measures are taken to stabilize them.

Stabilization of colloidal systems is generally achieved by electrostatic stabilization or steric stabilization. Electrostatic stabilization is widely used for suspensions of particles with surface charge in water or other polar liquids containing electrolytes. Surface charge is usually caused by unbalanced dissolution or adsorption of ionic species. To remain electrically neutral, the particles are surrounded by an ionic atmosphere which has a net charge of opposite sign. Outward from the surface of a charged particle to far from the particles where it is electrically neutral there is a gradient decrease in electrical potential ([Fig. 1.2](#)). The charged layer of particle surface and compact counterion layer make up an electrical double layer, which is usually described by double layer thickness and ζ potential. If the thickness of the double layer is close to or beyond the van der Waals force range, the overlap of two double layers causes electrical repulsion, and thus effectively prevents aggregation of the colloidal particles ([Fig. 1.3](#)). The double layer thickness decreases with increasing concentration of electrolyte and temperature. When the double layer thickness is less than the van der Waals force range, the electrostatic force cannot prevent agglomeration effectively. Therefore, colloidal systems stabilized in this manner can be destroyed by adding an electrolyte or by increasing the temperature. Destabilization of colloids stabilized by electrical repulsion is usually irreversible.

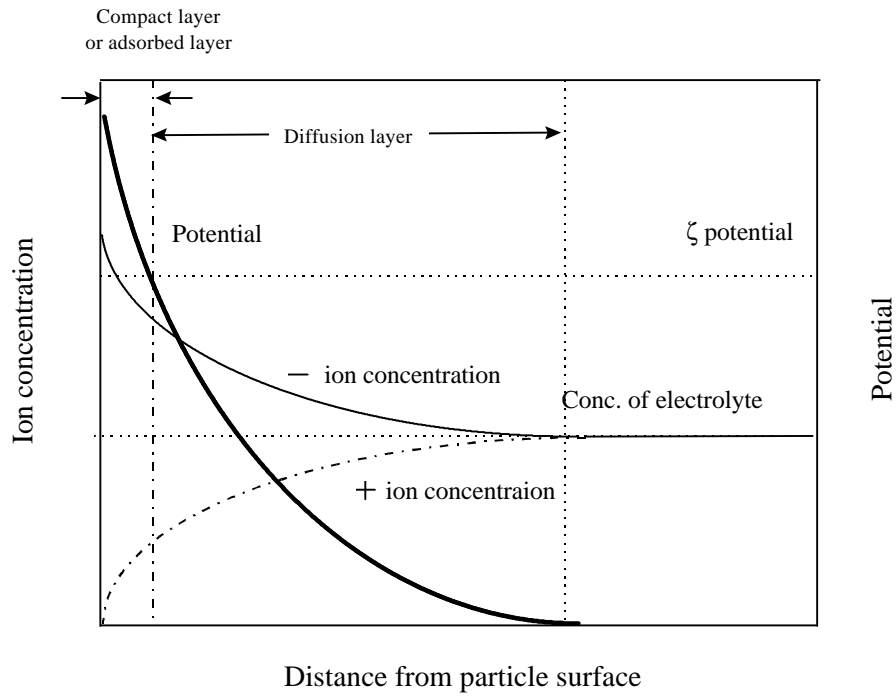


Figure 1.2 Ion concentrations and potential changes near a particle with positive charges

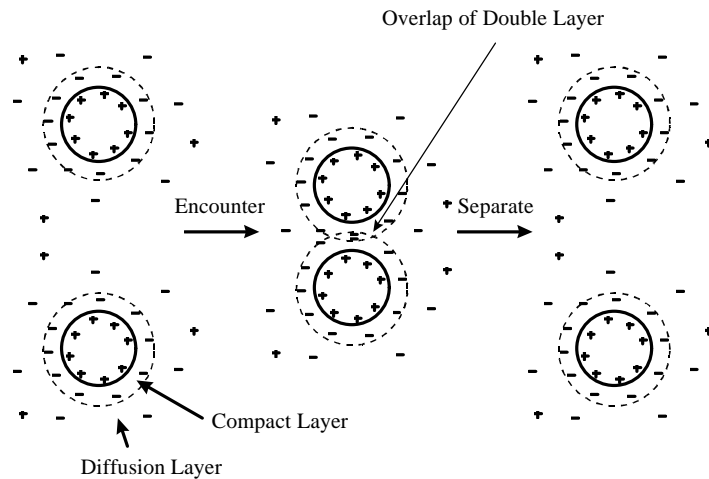


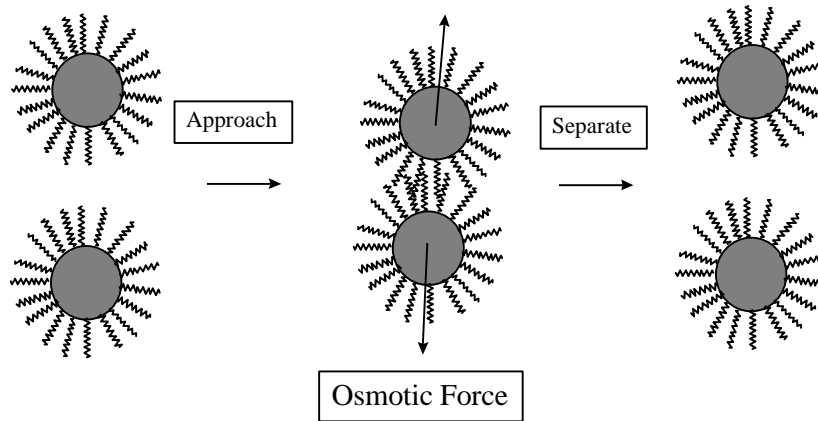
Figure 1.3 Electrostatic stabilization of colloidal systems

Steric stabilization of colloids has been unconsciously used by mankind for almost five millennia. In ancient Egypt and China, people began to use lamp black, obtained by combustion, with a natural polymeric stabilizer (e. g., casein from milk, egg albumin or gum arabic), and animal protein to make ink. However, the scientific study of steric stabilization did not begin until 1857 when Michael Faraday observed that gelatin could stabilize gold particles.

Steric stabilization is achieved through adsorption of polymers, which are soluble in the dispersion medium, onto the surfaces of particles by chemical bonding, ionic interaction or van der Waals's attractions. When two colloidal particles approach each other during a Brownian encounter, adsorbed polymers (tail blocks) on both particles overlap, causing an increase in polymer concentration and a decrease in dispersion medium concentration in the overlapped region. This process is actually a local demixing of polymer and dispersion medium. For a successful steric stabilizer, the demixing process is thermodynamically unfavorable, so the Gibbs free energy of demixing must be greater than zero. Therefore, an osmotic force is created to separate the two particles and hence the suspension remains stable ([Fig. 1.4](#)). Steric stabilization can be further divided into entropy stabilization and enthalpy stabilization according to the major contribution to the Gibbs free energy of demixing. Nonpolar systems which have only weak polymer-solvent interactions are usually entropy stabilized, while polar systems (i. e. aqueous systems) which have strong polymer-solvent interactions may be enthalpy stabilized.

Coagulation of sterically stabilized systems occurs through desorption of stabilizers, lateral movement of stabilizer on particle surfaces, or bridging of stabilizers from one particle to another occur. These mechanisms can be precluded if stabilizers are solidly adsorbed onto the surfaces of colloidal particles, and the colloidal particles are completely covered with stabilizers.

Mathematical treatment of steric stabilization is based on polymer thermodynamics that is still only semi-quantitative, so appropriate chain lengths of polymer stabilizers cannot be predicted.



[Figure 1.4](#) Steric stabilization of colloidal systems

Steric stabilization is insensitive to electrolytes, and equally effective in aqueous and non-aqueous dispersion media, at high and low volume fraction of particles. Sterically stabilized dispersions can often be flocculated reversibly whereas this is less common with electrostatically stabilized dispersions.

Sterically stabilized dispersions may have a critical flocculation temperature (CFT), a critical flocculation pressure (CFP) and a critical flocculation volume (CFV) (flocculation induced by a non-solvent that). These phenomena originate from the transitions of the dispersion medium from a good solvent to a poor solvent for the stabilizer due to changes in temperature, pressure, and composition of dispersion medium.

1.3 Characterization of Magnetic Fluids

Saturation magnetization and initial susceptibility, two of most important properties of magnetic fluids, can be measured by the magnetization behaviors of the magnetic fluids. Fig. 1.5 shows a typical magnetization curve (M-H curve). Saturation magnetization is the maximum magnetization, while initial magnetization is the slope of M-H curve at $H=0$.

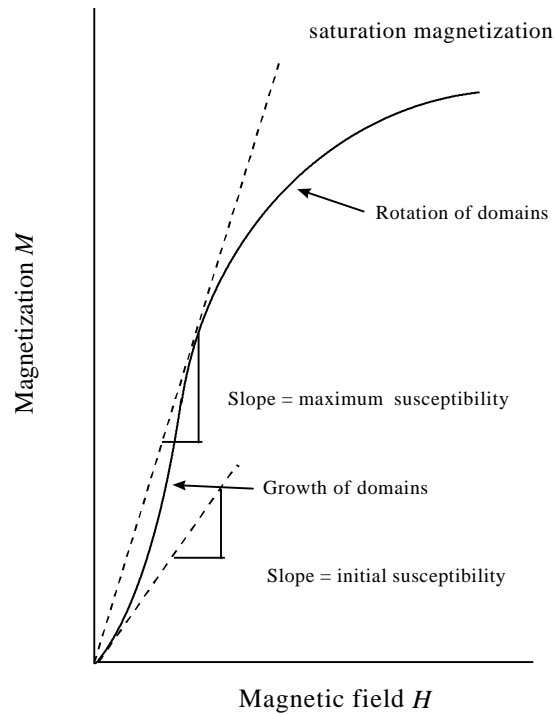


Figure 1.5 Initial magnetization curve for magnetic materials

Bulk ferro- or ferrimagnetic materials have polydomain structures. Their magnetization is mainly through motion of the domain wall. Magnetic particles in magnetic fluids, however, are usually single domains, so their magnetization cannot occur through domain wall motion. In these cases, the magnetization occurs through Brownian rotational diffusion and coherent rotation (Stoner and Wohlfarth mechanism). By the coherent rotation mechanism, the spins of all the atoms in the same particle remain parallel during rotation.

Unlike ferro- or ferrimagnetic materials, magnetic fluids have no hysteresis and the magnetization curves are similar to the Langevin curve for paramagnetic systems (referred to superparamagnetism). However, due to a distribution of particle size, the magnetization curves are not identical to Langevin curves. Assuming that the particle size obeys a log-normal

distribution, average particle diameter and standard deviation can be calculated easily by regression method.¹⁰

Transmission electron microscopy in conjunction with a size analyzer provides another method for measuring the particle size distribution. Generally, this is done by least square refinement assuming the particle size has a log-normal distribution.¹⁰

Average dynamic volume of magnetic particles and its standard deviation can be measured through relaxation of magnetic induced birefringence. Magnetic particles in magnetic fluids under a magnetic field tend to align along the field, hence the medium becomes birefringent. When the magnetic field is removed, the ordered alignment of magnetic particles is relaxed through the Brownian rotation diffusion. Therefore, by measuring the birefringence decay, the average particle size and standard deviation can be calculated by curve fitting assuming the particle size obeys a log-normal distribution. Average dynamic volume of magnetic particles can also be calculated from the relationship between viscosity and concentration of particles as long as no agglomeration occurs. The Einstein law for spherical particles is generally used in the calculation.^{11,12} According to the average particles size and the average dynamic particle size, the thickness of stabilizer layer adsorbed on the particle surfaces can be obtained.

1.4 Block Copolymers of PCPMS and PDMS as Stabilizers for Silicone Magnetic Fluids

The most successful steric stabilizers are amphipathic materials like ordinary ionic or nonionic surfactants. Nonionic amphipathic materials are usually block or graft copolymers with at least two segments. One segment anchors the whole chain to the surface of colloidal particles, while the other extends into the dispersion media to provide steric stabilization.

Today's commercially magnetic fluids are mainly based on water, hydrocarbon or ester dispersion media. Fluorocarbons and silicones are not practically used as dispersion media due to a lack of suitable stabilizers. The direct motivation of this work is to develop stabilizers for

¹⁰ R. W. Chantrell, J. Popplewell and S. W. Charles, *IEEE Trans. Mag.* **14**, 975 (1978)

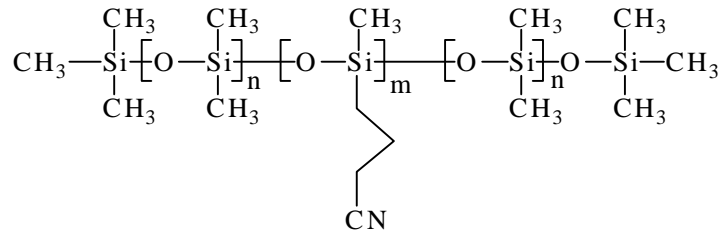
¹¹ J. C. Bacri, R. Perzynski, D. Salin, V. Cabuil and R. Massart, *J. Magn. Magn. Mat.*, **62**, 36-46 (1986)

silicone magnetic fluids for retinal detachment surgery. However, it is obvious that the discovery of suitable stabilizers in silicones will also accelerate the wide acceptance of silicones as dispersion media for magnetic fluids.

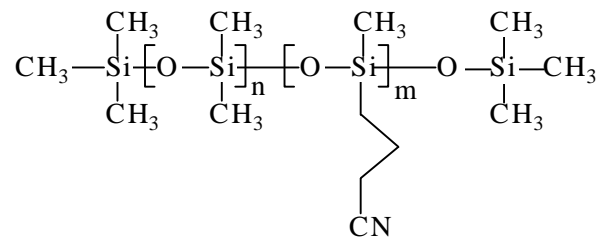
Block copolymers of polydimethylsiloxane (PDMS) and poly(3-cyanopropylmethylsiloxane) (PCPMS) ([Fig 1.6](#)) are developed as stabilizers for PDMS dispersion media ([Fig. 1.7](#)). The PDMS and PCPMS are the expected tail block and anchor block, respectively. The reasons for using PCPMS as the anchor block are that 1) Dr. S. W. Charles in the University College of North Wales, UK, demonstrated that in the presence of pure PCPMS, ultrafine particles of nickel could be obtained by reduction of bis(cyclopentadienyl)nickel ($\text{Ni}(\text{C}_5\text{H}_5)_2$); and 2) literature indicates that the nitrile groups from heptamethyl-2-cyanoethyl-cyclotetrasiloxane can interact with lithium ions¹³ ([Fig. 1.8](#)).

¹² V. Cabuil, N. Hochart, R. Perzynski and P. J. Lutz, *Progr. Colloid Polym. Sci.*, **97**, 71-74 (1994)

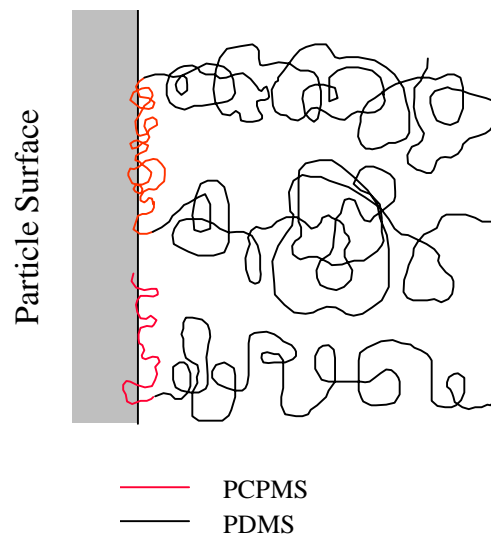
¹³ Yu. A. Yuzhelevskii, E. B. Dmokhovskaya, A. L. Klebanskii, and N. B. Kozlova *Vysokomol. Soedin.*, **11A**, 432 (1969)

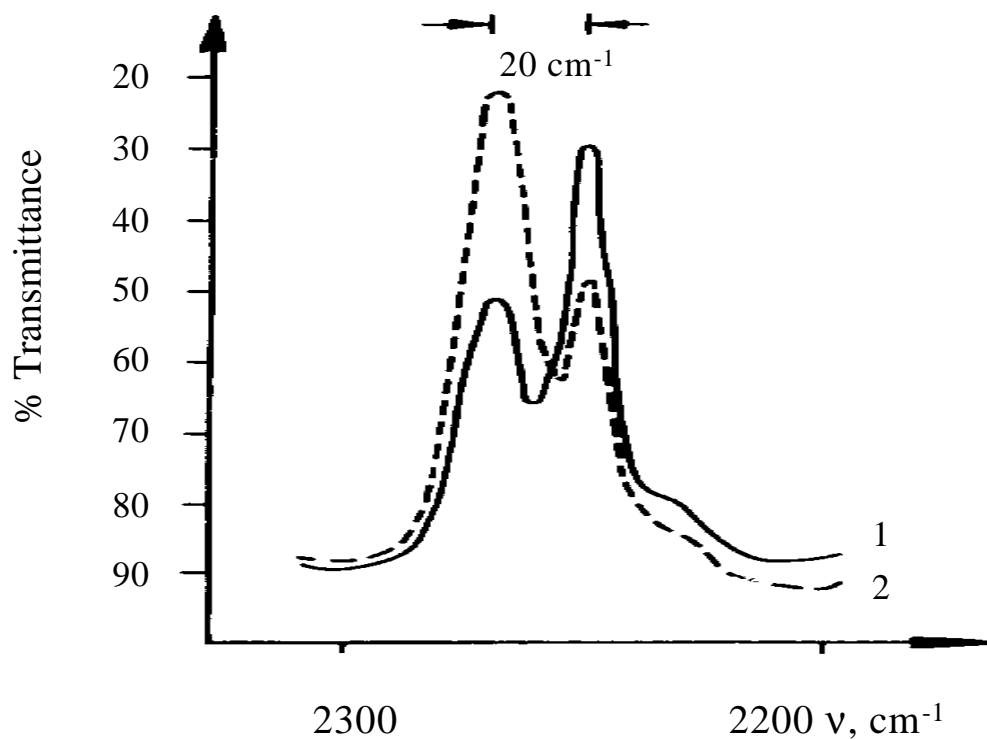


(a) Triblock copolymers



(b) diblock copolymers

Figure 1.6 Structures for the proposed stabilizers**Figure 1.7** Triblock and diblock copolymers of PDMS and PCPMS as stabilizers for silicone magnetic particles



[Figure 1.8](#) Infrared spectra for mixtures of heptamethyl-2-cyanoethylcyclotetrasiloxane (I) and lithium trimethylsilanolate (II): 1) I:II=3:1; 2) I:II=0.8:1. The nitrile absorption peak is divided into two peaks due to complexation of the nitrile group with lithium ions.

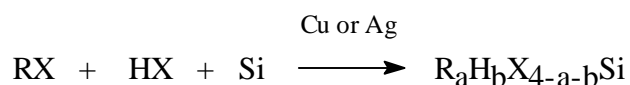
CHAPTER 2

INTRODUCTION TO POLYSILOXANE SYNTHESSES

2.1 Overview of Polysiloxane Syntheses

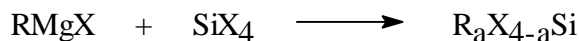
Polysiloxanes or silicones are structurally derived from inorganic silicates by substituting some siloxane components with organic groups. Polysiloxanes offer a wide spectrum of properties that cannot be expected from common organic polymers due to a polar Si-O backbone plus the contribution from the organic substituents. Some of the outstanding properties of polysiloxanes are high temperature stability, low temperature flexibility and excellent dielectric properties. For this reason, the polysiloxane industry has undergone fast development during the past forty years. Today PDMSs have already been used as rubbers, resins, dielectric media, hydraulic or heat transfer fluids, lubricants, medical materials and surfactants, and have become indispensable materials.

The synthesis of polysiloxanes begins with dichlorosilanes. Dichlorosilanes are mainly manufactured by the direct process based on the reactions of alkyl halides with elemental silicon under the catalysis of copper or silver alloys.



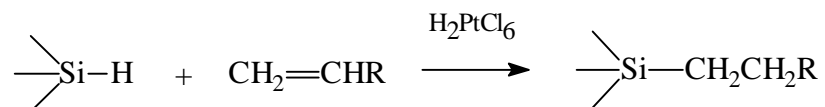
This process provides high yields for methyl, hydrogen or phenyl substituted chlorosilanes. Other silanes are made by modifications of existing chlorosilanes through addition, substitution, oxidation or reduction of one or more silicon containing bonds, most importantly Si-X, Si-H, Si-CH=CH₂ and Si-CH₂Cl.

The Grignard synthesis is a versatile process for preparing many silanes. It is based on reactions of alkyl magnesium halides with chlorosilanes from the direct process or silicon tetrachloride from reaction of silicon with chlorine.



The Grignard synthesis (based on SiCl_4) was a major process for preparation of silanes before the discovery of the direct process. Even today, many special silanes are still prepared by Grignard syntheses.

Hydrosilylation is another important reaction for preparing silanes. This process is based on addition of a silane (Si-H) to an olefin in the presence of catalysts like hexachloroplatinic acid, or complexes of Pt (0) with 1,3-divinyltetramethyldisiloxane.



Hydrolysis and condensation of many functional silanes including dichlorosilanes give linear and cyclic siloxanes. Early polysiloxanes, including silicone oils, elastomers, and resins, were prepared directly from hydrolysis and condensation of chlorosilanes. However, this method usually results in poor molecular weight control. Therefore, it has been gradually replaced by ring opening polymerization of cyclic siloxanes. Condensation polymerization still plays an important role in cold vulcanization of silicone elastomers, and preparation of polysiloxane block and alternating copolymers. The major advantage of equilibrium polymerization is that it can provide various kinds of telechelic polysiloxanes which can be easily incorporated into various kinds of organic polymers to prepare polymers with novel properties. The major limitation of equilibrium polymerization is that it only gives good yields for several simple polysiloxanes like PDMS.

Kinetically controlled polymerization of cyclotrisiloxanes was discovered in the later 1960s and further developed in the early 1970s. This mode of polymerization is based on anionic polymerization of ring strained cyclotrisiloxanes and is quite similar to living polymerization. Therefore, it allows preparation of nearly monodisperse polysiloxanes and novel polysiloxanes with tailored structures. The limitation of kinetically controlled polymerization is that cyclotrisiloxanes are more difficult to synthesize than unstrained cyclics.

Modification of existing polysiloxanes is an indispensable method for preparing novel polysiloxanes which cannot be prepared by equilibrium polymerization. For example, liquid crystalline polysiloxanes, which have various bulky substituents, are difficult to prepare from their

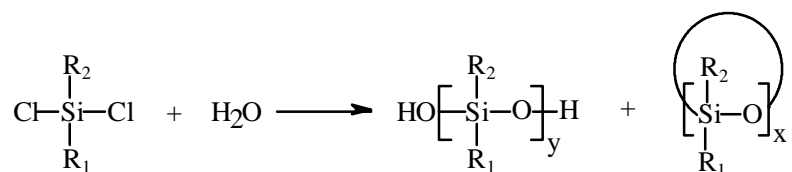
cyclic precursors. However, these polymers can be obtained by hydrosilylation of polyhydrogenmethylsiloxanes with olefin containing mesogenic groups.

This chapter only reviews knowledge relevant to this thesis, which includes preparation of cyclic siloxanes (Section 2.2), ring-chain equilibria (Section 2.3), ring opening polymerization (Section 2.4) and preparation of polysiloxane block copolymers (Section 2.5). For more information on polysiloxanes, references [14-21](#) are recommended.

2.2 Preparation of Cyclosiloxanes

Generally, cyclosiloxanes are prepared by hydrolysis of dichlorosilanes, or by reactions of dichlorosilanes with oxygen containing materials like metal oxides, metal carbonates, metal bicarbonates, sulfates or even dialkyl ethers²².

Hydrolysis of dichlorosilanes gives mixtures of cyclics and linear polymers. The cyclics, predominantly $x=4-6$, may be recovered by fractional distillation assuming that the boiling points are not too high.



¹⁴ M. G. Voronkov, V. P. Mileshevich, Yuzhelevskii Yu. A., *The Siloxane Bond*, Translated by John Livak, Consultant Bureau, New York (1978)

¹⁵ S. J. Clarson, J. A. Semlyen, *Siloxane Polymers*, PTR Prentice Hall, New York (1993)

¹⁶ E. E. Bostick, in K. C. Frisch, and S. L. Reegen, (eds.), *Ring Opening Polymerization*, p327, Dekker, New York (1969)

¹⁷ P. V. Wright in K. J. Ivin, and T. Saegusa (eds.) *Ring Opening Polymerization*, Elsevier, London, New York (1970)

¹⁸ P. V. Wright and M. S. Beevers, in J. A. Semlyen (eds.), p85, *Cyclic Polymers*, Elsevier, London, New York (1986)

¹⁹ A. L. Smith, *The Analytical Chemistry of Silicones*, A Wiley-Interscience Publication, John Wiley & Sons, Inc. New York (1991)

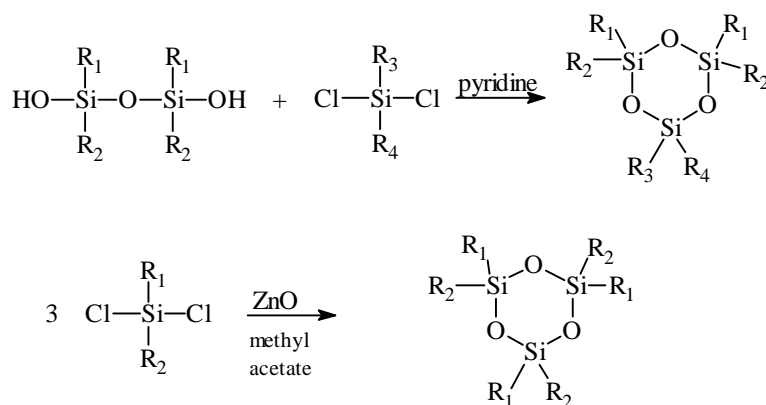
²⁰ W. Noll, p212, *Chemistry and Technology of Silicones*, Academic Press, New York (1968)

²¹ I. Yilgor, J. E. McGrath, *Adv. Polym. Sci.*, **86**, 1 (1988)

²² K. C. Frisch, *Cyclic Monomers*, Wiley-Interscience, John Wiley & Sons, New York (1972)

To increase the yield of the cyclics, small amounts of potassium hydroxide are added to the hydrolysates to transform linear polysiloxanes into cyclics. Cyclics with high boiling points can be prepared by heterogeneous hydrolysis of dichlorosilane in an inert solvent, followed by cyclization and equilibration of the hydrolysates in the presence of small amounts of acid or base.

Strained cyclotrisiloxanes cannot be prepared efficiently using equilibration methods. Industrially, hexamethylcyclotrisiloxane, 1,3,5-tris(3,3,3-trifluoropropyl)-3,3,3-trimethylcyclotrisiloxane, etc. are prepared by pyrolysis of related linear polysiloxanes²³. Organosiloxane trimers can also be prepared by heterocondensation of 1,3-dihydroxydisiloxanes and dichlorosilanes with pyridine as a proton acceptor^{24,25}, or by condensation of dichlorosilanes with 10 mol% excess zinc oxide^{26,27,28}. The yields for these processes, depending on the substituents, was 20-90%.



Cyclosiloxanes can also be prepared by modification of existing cyclics. However, it should be noted that not all cyclosiloxanes are suitable for equilibrium polymerization because ring-chain equilibria of many siloxanes lie to the cyclics sides, especially those with bulky substituents.

²³ B. A. Bluestein, U. S. Patent 4,111,973, assigned to General Electric Company (1978)

²⁴ P. I. Prescott. And T. G. Selin, U. S. Patent 3,317,578 assigned to General Electric Company (1967)

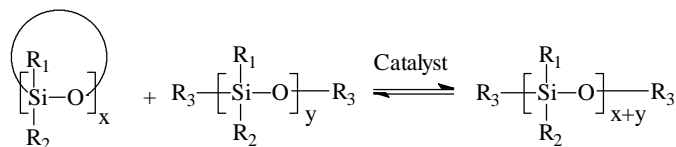
²⁵ N. Grassie, K. F. Francey and I. G. MacFarlane, *Polym. Degrad. and Stab.*, **2**, 67 (1993)

²⁶ T. Takiguchi, M. Sakurai, and T. Kishi, *J. Org. Chem.*, **25**, 310 (1960)

²⁷ B. Momper, Th. Wagner, U. Maschke, M. Ballauff and E. W. Fisher, *Polym. Commun.*, **31**, 186 (1990)

2.3 Ring-Chain Equilibria: Thermodynamic Considerations

Siloxanes are thermally very stable, but in the presence of strong base or strong acid, either cyclics or linear polysiloxanes will become a mixture of cyclic and linear polysiloxanes.



where x , y and $x+y$ indicate the number of siloxane units. The equilibrium concentration of the cyclics depends on polymerization enthalpy change and polymerization entropy change. For most cyclics, the polymerization enthalpy change is close to zero since the reaction involves no net changes of chemical bonding except rearrangements of siloxane bonding. An exception is the cyclotrisiloxane whose polymerization is accompanied by release of ring strain energy (for D_3 , it is 15 kJ/mol). Thus cyclotrisiloxanes have low concentrations in polysiloxane equilibrates. Polymerization of unstrained cyclics is driven by entropy change (+), which includes entropy change due to mixing of cyclics and linear polymer (+), configurational entropy change (+) and translational entropy change (-). Macrocyclics have very low equilibrium concentrations because during polymerization they gain almost the same amount of configurational entropy as small cyclics but lose far less translational entropy.

Since each siloxane unit is equally linked to two other siloxane units, statistically linear polysiloxanes should obey the Flory distribution (geometry distribution), in which case the possibility of finding a chain with n siloxane units is:

$$L_n = p^2(1-p)^{n-1}$$

where $p = \frac{\text{number of end siloxane units}}{\text{total number of siloxane units in chain}}$

The Flory distribution was confirmed in polysiloxane equilibrates with no special endgroup effects²⁹. By using the Flory distribution, the formation constant of cyclics based on the

²⁸ M. K. Lee and D. J. Meier, *Polymer*, **35**, 19, 4197 (1994)

²⁹ D. W. Scott, *J. Am. Chem. Soc.*, **68**, 2294 (1946)

equilibrium between y-unit cyclics (C_y), x-unit and x+y-unit chains (L_x and L_{x+y}), can be simplified as:

$$K_{x,y} = \frac{[L_x][C_y]}{[L_{x+y}]} = \frac{p^2(1-p)^{x-1}[C_y]}{p^2(1-p)^{x+y-1}} = \frac{[C_y]}{(1-p)^y} = K_y \sim \text{independent of } x$$

For polymers with high molecular weight, p is close to 0. Therefore,

$$K_y \sim [C_y]$$

This means the equilibrium concentration of cyclics is not related to the catalyst type and the degree of polymerization. Therefore, if the concentration of total siloxanes (including cyclic and linear polysiloxanes) in a solution is below the critical concentration (= summation of formation constants of all cyclics) no linear polymer should coexist with the cyclics in the equilibrates.

This conclusion has been confirmed experimentally for many polysiloxanes. For example, At 383K the critical concentrations of 3,3,3-trifluoropropyl-methylsiloxane, methylethylsiloxane, and dimethylsiloxane are about 90%, 40%, and 25%, and at 273K the critical concentration of hydrogenmethylsiloxane is 18% ([Fig 2.1](#)).

The equilibrium concentration of cyclosiloxanes depends mainly on the substituents. The general trend is that long or bulky substituents lead to high equilibrium concentrations of cyclics. Equilibrium concentrations for common cyclosiloxanes are listed in [Table 2.1](#)

[Table 2.1](#) Yields of linear polymers in undiluted equilibrates of siloxanes ($-RR'SiO-$)³⁰

R	R'	Approximate yield %
Me	Me	82
Me	Et	74
Me	CF ₃ CH ₂ CH ₂	17
Ph	Me	70
Ph	Ph	0

30 J. Chojnowski in S. J. Clarson, J. A. Semlyen, p21, Siloxane Polymers, PTR Prentice Hall, Englewood Cliffs, New Jersey (1993)

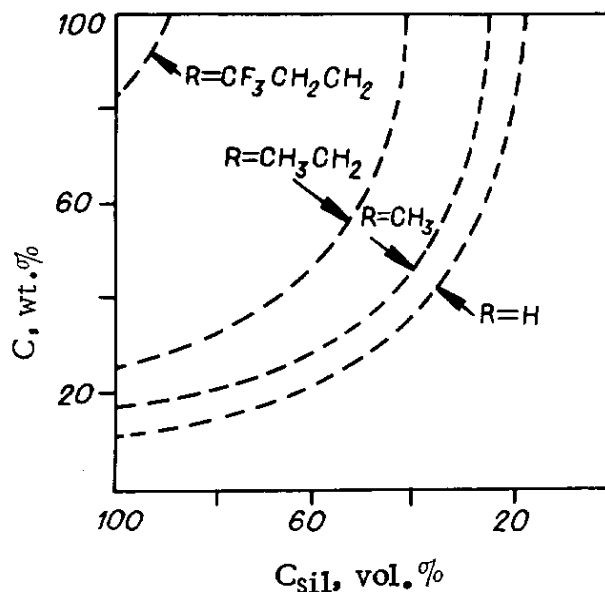


Figure 2.1 Equilibrium concentration (C) of cyclosiloxane $[R(CH_3)SiO]_n$ as a function of the volume concentration of the siloxanes in cyclohexanone ($R=CF_3CH_2CH_2$ at 383K) and in toluene ($R=CH_3, CH_2CH_3$ at 383K and $R=H$ at 273K)³¹

Equilibrium concentrations of unstrained cyclics are nearly independent of temperature since the enthalpy changes of polymerization are negligible. Equilibrium concentrations of cyclotrisiloxanes, however, increase appreciably with temperature because of negative polymerization enthalpy changes. This is the reason why cyclotrisiloxanes can be prepared by pyrolysis of polysiloxanes.

The density of cyclics is usually slightly lower than that of polymer, so increasing pressure results in lower equilibrium concentrations of cyclics (Table 2.2).

³¹ P. V. Wright and J. A. Semlyen, *Polymer*, **10**, 543 (1969)

Table 2.2 Weight percentages of dimethylsiloxane cyclics in high pressure equilibrium at 393K¹⁷

No. of siloxane units	1 atm	3,500 atm
4	6.2	4.4
5	3.8	2.8
6	1.6	1.3
7	0.5	0.5
Total	12.1	9.0

The ring-chain equilibrium of dimethylsiloxane provides a case for testing the validity of polymer conformation theory. Assuming the end-to-end distance of PDMS chains can be described by a Gaussian distribution, Jacobson and Stockmayer³² predicted that the formation constant (K_y) is proportional to y to the 2.5 power. This prediction is only in agreement with experiments for macrocyclics. The ineffectiveness of the Jacobson and Stockmayer³³ theory for small cyclics can be ascribed to the failure of the Gaussian distribution of the end-to-end distance for chains with only a few repeating units. Improved calculations^{34,35} have been implemented using Flory, Crescenzi and Mark's rotational isomeric state model (FCM model), or Monte Carlo methods with consideration of the orientations between terminal bonds. Although these calculations made some improvements for middle size rings, they still give poor results for small rings³⁶.

³² H. Jacobson and W. H. Stockmayer, *J. Chem. Phys.* **18**, 1600 (1950)

³³ H. Jacobson and W. H. Stockmayer, *J. Chem. Phys.* **18**, 1600 (1950)

³⁴ M. S. Beevers and J. A. Semlyen, *Polymer*, **13**, 385 (1972)

³⁵ L. E. Scales and J. A. Semlyen, *Polymer*, **17**, 601 (1976)

³⁶ U. W. Suter, Muter, M. and P. J. Flory, *J. Am. Chem. Soc.*, **14**, 729 (1976)

2.4 Ring-Opening Polymerization: Kinetic Considerations

A wide variety of catalysts have been reported for ring opening polymerization of cyclic siloxanes, including strong organic and inorganic acids or bases³⁷, dispersed metals and metal oxides³⁸, ion-exchange resins³⁹, platinum and palladium compounds⁴⁰, irradiation⁴¹, and lithium-graphite intercalation compounds⁴². According to the type of catalysts, ring opening polymerization can be generally divided into acidic polymerization and basic polymerization. Acidic/basic polymerizations are also called cationic/anionic polymerizations according to the nature of reactive species. This section will briefly describe mechanisms of cationic polymerization, then focus on anionic polymerization.

2.4.1 Cationic Polymerization

Catalysts for cationic polymerization can be strong Brønsted acids like sulfuric acid, or combinations of Lewis acids and Brønsted acids like SnCl₄/H₂O, or irradiation. Cationic polymerization is very complicated in mechanism since the active species depend strongly on the nature of catalysts. For proton initiated acid polymerization, the acid first protonates the cyclosiloxane to form a cyclic silyloxonium salt, which subsequently opens to give short polysiloxane chains ended with a silanol group and a silyl ester group. The silyl ester group may exist as a close-ion pair (silylenium-anion pair) depending on the polarity of the reaction medium. The linear polysiloxane chains can condense bimolecularly to eliminate acid and give longer chains. The regenerated acid then reacts with cyclic siloxane to provide more short siloxane chains. This polymerization path is generally called “acidolysis-condensation mechanism”⁴³. Alternatively, cyclic siloxane can also react with a silyl ester group to form a cyclic silyloxonium

³⁷ J. E. McGrath, J. S. Riffle, I. Yilgor, A. K. Banthia, P. Sormani, *Org. Coat. Appl. Polym. Sci.*, **46**, 693-700, (1981)

³⁸ M. T. Bryk, *Vysokomol. Soedi*, **A20**, 147 (1978)

³⁹ S. Schindler and K. Ruehlmann, *Plaste Kautschuk*, **25**, 384 (1978)

⁴⁰ I. S. Akhrem, N. M. Chistovalova and E. I. Mysor, *Iiv. Akaol. Nank, SSSR ser Khim.* **7**, 1598 (1978)

⁴¹ P. Sigwalt, and D. V. Stannett, *Makromol. Chem. Macromol Symp.* **32**, 217 (1990)

⁴² K. A. Andrianov, M. E. Volpin et al USSR patent 681070, *Chem. Abstr.*, **91**, 194111j (1979)

ion, which immediately opens to regenerate the silyl ester group and form longer polysiloxane chains. This process is called “chain extension mechanism”^{44,45} because by this mechanism chains can continuously react with monomer (Fig. 2.2). In real situations, acidic polymerization usually shows kinetics between these two limiting cases depending on the monomer, initiator and reaction conditions.

In acidic siloxane mixtures, the acid can cleave both cyclic and linear polysiloxanes, and cyclics of various sizes can be formed through intramolecular (unimolecular) acidolysis elimination. Therefore, acid catalyzed polymerization finally yields a dynamic equilibrium mixture of cyclic and linear polysiloxane. It should be noted that in acid-polysiloxane equilibrates, there are not only ring-chain equilibria, but also equilibria among acid, water, silanol and ester (Fig. 2.3). Stable polymers can only be obtained after removing the acid catalyst by washing with water or neutralizing with a base.

Acidic polymerization can be carried out kinetically by using ring strained cyclotrisiloxanes. However, the reaction yields mixtures of macrocyclic and linear polysiloxanes because of the competing unimolecular acidolysis condensation^{46,47}. Thus this method has no important synthetic value.

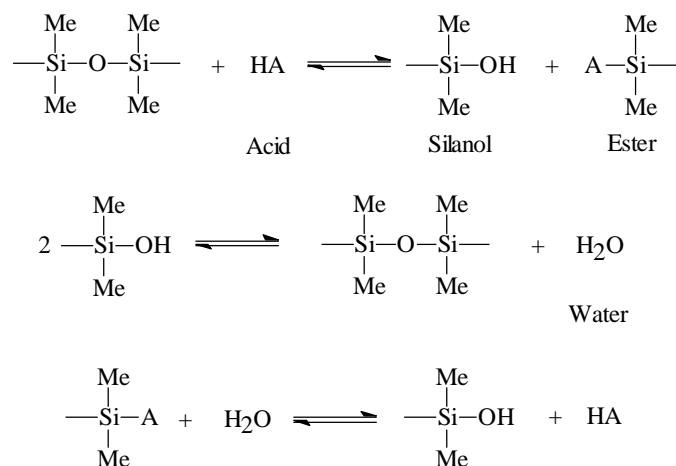
⁴³ W. Patnode, and D. F. Wilcock, *J. Amer. Chem. Soc.* **68**, 358 (1946)

⁴⁴ K. Kojima, N. Tarumi, and S. Wakatuki, *Nippon Kagaku Zasshi*, **76**, 1205 (1975)

⁴⁵ K. A. Andrianov, S. E. Yakushkina, *Vysokomol. Soed.*, **1**, 613, (1959), **2**, 1508 (1960)

⁴⁶ J. Chojnowski and L. Wilczek, *Makromol. Chem.*, **180**, 117 (1979)

⁴⁷ J. Chojnowski, M. Mazurek, M. Scibiorek and L. Wilczek, *Makromol. Chem.* **175**, 3299 (1974)



[Figure 2.3](#) Equilibria among free acid, water, silanol and ester in an acid/siloxane equilibrates

2.4.2 Anionic Polymerization

2.4.2.1 General Principles

Anionic polymerization complements cationic polymerization so that telechelic polysiloxanes with various groups can be prepared. More importantly, it provides an exclusive kinetically controlled reaction mode which can be used for preparing polysiloxanes with narrow molecular distributions⁴⁸. Catalysts for anionic polymerization include alkaline metal hydroxides or silanolate, alkyllithiums, quaternary ammonium hydroxides and quaternary phosphonium hydroxides. The anionic polymerization of cyclosiloxanes is a chain extension reaction. Whatever catalyst is used, it reacts with cyclic monomer to yield short silanolate ended chains (chain initiation). The silanolate ions then attack the cyclic monomer to form cyclic five-coordinated silicon complexes, which subsequently open to form longer silanolate ended chains. By repetitious reaction of silanolate ions (endgroups) with the cyclic monomer and repetitious regeneration of longer silanolate ended chains, high molecular weight polysiloxanes are formed

⁴⁸ A. Norshay, J. E. McGrath, Block Copolymer, Overview and Critical Survey, Acad. Press. (1977)

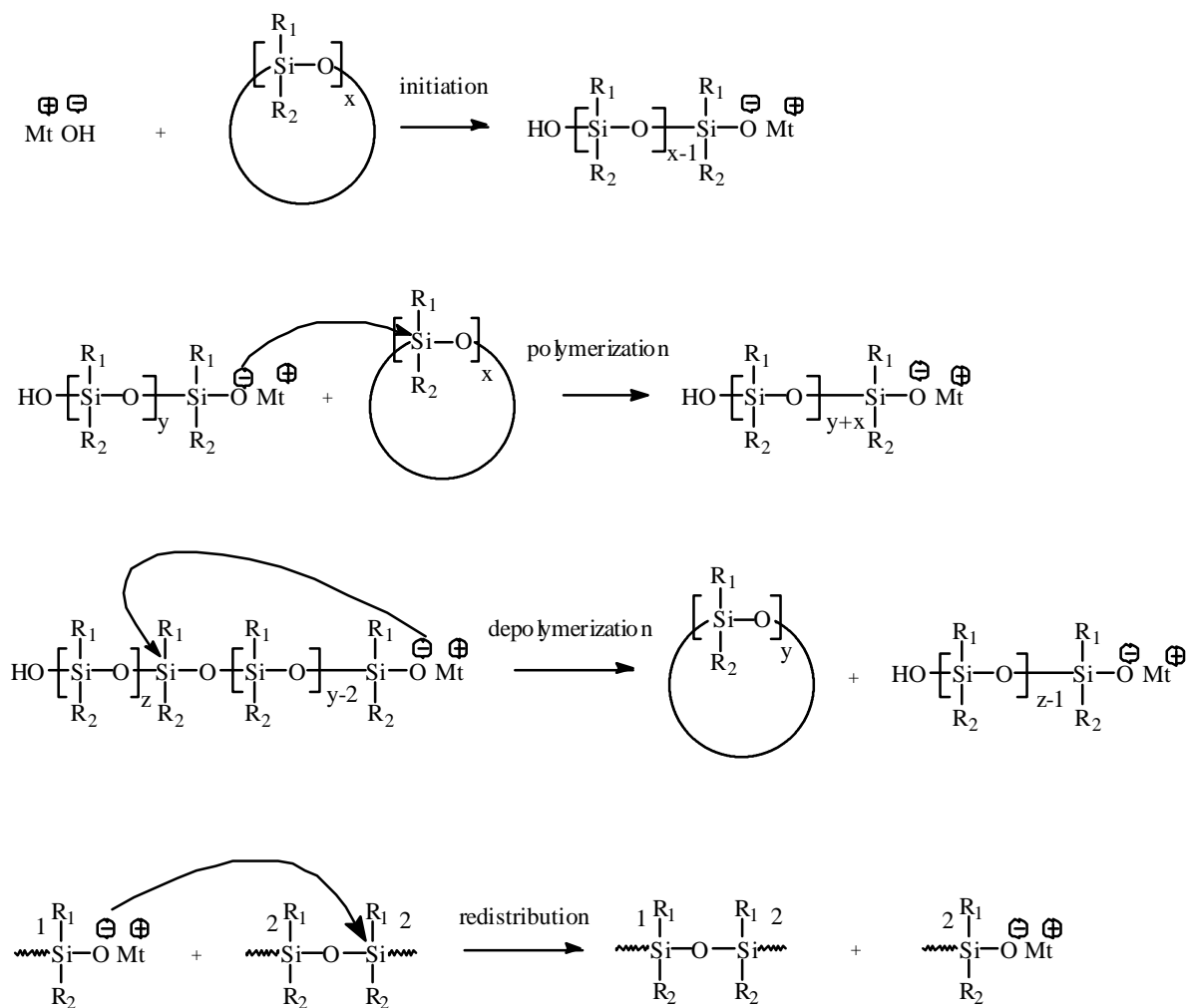
(chain propagation). Silanolate ions are reactive to both cyclic monomers and linear polymers. When reacting with its host chain (backbiting), it causes depolymerization and yields cyclics of various sizes; when reacting with other chains, it leads to redistribution or reshuffling of polymer chains ([Fig. 2.4](#)). The reaction between two silanolate ions (specific redistribution) is much faster than that between a silanolate and a siloxane unit in linear polysiloxanes (normal reshuffling reactions)^{49,50}. The unusual reactivity in a specific redistribution reaction is due to a silicone resonance structure which stabilizes the transition state ([Fig. 2.5](#)). Computer simulation indicated that specific redistribution broadens the molecular weight distribution at least when the degree of polymerization is low.⁵¹

Generally, during the early stages of an anionic polymerization, polymerization is predominant since most siloxane exists as cyclic monomers. As the concentration of linear polysiloxanes increases, depolymerization and redistribution become more and more important; finally ring-chain equilibria are reached. Similar to cationic polymerization, anionic polymerization also gives a dynamic equilibrium mixture of cyclic and linear polysiloxanes. Stable polysiloxanes can be obtained after destroying the silanolate ions by adding acetic acid or chlorosilanes. Tetraalkylammonium hydroxides and tetraalkylphosphonium hydroxides have special advantages because they can be decomposed completely by heating. For this reason, this group of catalysts is called transient catalysts. For example, tetramethylammonium hydroxide (TMAH) can be completely destroyed at 150°C to trimethylamine and methoxy siloxanes. For this reason, those catalysts are industrially important ([reference 19](#), p580-590).

⁴⁹ J. Chojnowski and M. Mazurek, *Makromol. Chem.*, **176**, 2999 (1975)

⁵⁰ C. L. Frye, R. M. Salinger, R. M. Fearon, et al, *J. Org. Chem.*, **35**, 1308 (1970)

⁵¹ T. Suzuki, *Polymer*, **30**, 333 (1989)



[Figure 2.4](#) Mechanism for anionic polymerization of cyclic siloxanes

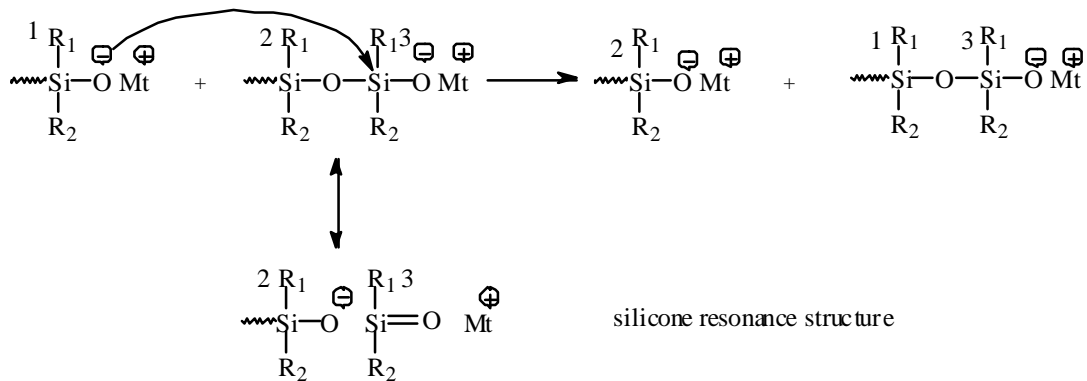


Figure 2.5 Mechanism for specific redistribution

Although it has been established that the silanolate is the active center in anionic polymerization, experiments including conductivity measurements, reaction kinetics of polymerization and model studies of simple silanolates indicate that the silanolate exists more or less as ionic aggregates rather than as free ions ([reference 30](#), p25). Rate law suggests that free silanolates, the most active species, are in equilibrium with silanolate aggregates (dormant active centers) and the equilibrium lies strongly to the side of the aggregates. The polymerization and depolymerization reactions are rate determining steps (Fig 2.6).

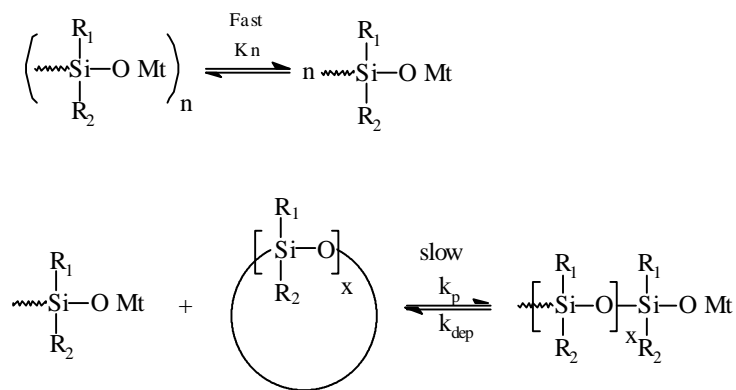
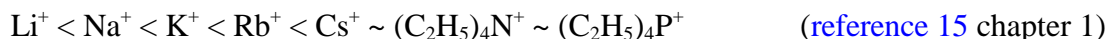


Figure 2.6 Kinetics of anionic polymerization of cyclosiloxanes

The rate law derived from this mechanism is:

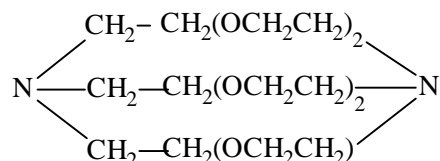
$$-\frac{d[\text{monomer}]}{dt} = \frac{[\text{Silanolate}]_{\text{total}}^{1/n}}{(nK_n)^{1/n}} (k_p [\text{monomer}] - k_{\text{dep}})$$

The rate of anionic polymerization of cyclosiloxanes is strongly dependent on counterions. The catalytic activity for alkali metal or onium hydroxides was reported as



Such a sequence reflects an increasing volume of counterions, therefore a corresponding increase in concentration of free silanolates.

Electron releasing materials, even in trace amounts, can greatly accelerate the rate of polymerization since they can solvate the cations and increase the concentration of free silanolate ions. These electron releasing materials are usually called co-catalysts or promoters. Efficient promoters are compounds which have large dipole moments and include electron-donating elements like nitrogen and oxygen. Multidentate reagents like poly(ethylene glycol), crown ethers, and macrotricyclics⁵² denoted by [2, 2, 1] (see structure below) are extremely effective promoters.



denoted by [2, 2, 1]

It has been reported that ionic aggregation in silanolate endcapped PDMS can result in deviation of molecular weight distribution from the Flory distribution due to a thermodynamic preference for the formation of intramolecular complex A or ring-shape cluster B such as in Fig 2.3⁵³. These phenomena do not affect the number average molecular weight but increase polydispersity.

⁵² S. Boileau, S., in J. E. McGrath, Ring Opening Polymerization, p23, American Chemical Society, Washington DC (1985)

⁵³ M. Mazurek, M. Scibiorek, J. Chojnowski, B. G. Zavin, A. A. Ahdanov, Europ. Polym. J., **16**, 57 (1980)

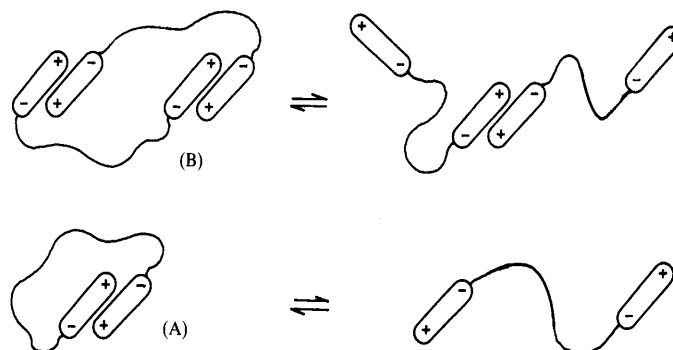


Figure 2.7 Equilibria between cyclic and linear ionic associates

Cited from [reference 30](#), p27

With alternating silicon oxygen backbones, polysiloxanes can also serve as multidentate ligands to complex with counterions although siloxane oxygen is a weaker base than ether oxygen (due to $p\pi(\text{O})-d\pi(\text{Si})$ back donation). Interaction of silanulates with polysiloxanes may play an important role in siloxane bond cleavage since it can reduce the activation energy by providing a multidentate complex (Fig. 2.8). Dimethylcyclsiloxanes with seven or more units, or linear dimethylsiloxanes with more than 10 units showed increased reactivity toward anionic polymerization because siloxane multidentate complexes can be favorably formed in these cases.⁵⁴ When tri(ethylene glycol) dimethyl ether, a promoter which is more electron donating than siloxane oxygen, was added, the reactivity differences among different polysiloxanes were leveled out⁵⁵, thus indirectly confirmed the existence of the multidentate complex between metal ion and polysiloxanes.

⁵⁴ Z. Laita and M. Jelinek, *Vyskomol. Soed.*, **4**, 1739 (1962)

⁵⁵ M. Mazurek and J. Chojnowski, *Makromol. Chem.*, **178**, 1005 (1977)

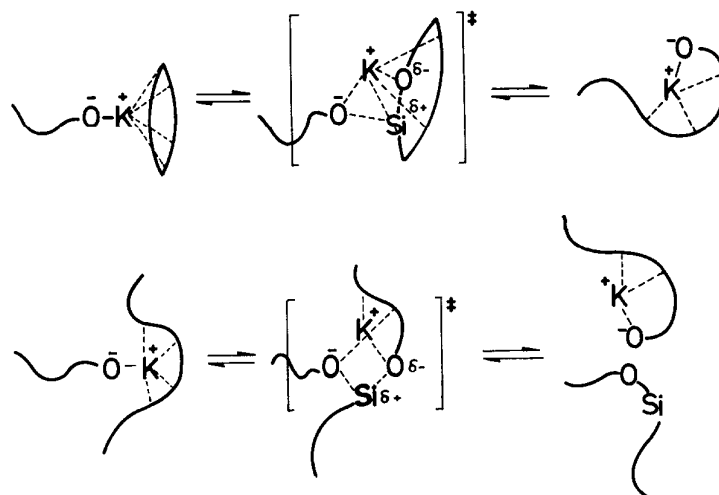


Figure 2.8 Polysiloxanes as multidentate ligands. Cited from reference 30 p31

Siloxane substituents affect the reactivity of the monomer and the silanolate active species in an opposite way, so their influences on the polymerization rate of the cyclosiloxane are unpredictable. For example, phenyl groups decrease the electron density on silicon atoms to which they are attached, thus increasing the electrophilicity of hexaphenylcyclotetrasiloxane while lowering the nucleophilicity of phenyl substituted silanolates. The influences of substituents on monomer and active species are somehow synergistic in copolymerization. For instance, in anionic copolymerization of octaphenylcyclotetrasiloxane (P_4) and octamethylcyclotetrasiloxane (D_4), the phenyl groups increase the reactivity of P_4 , so P_4 prefers to react with silanolate. At the same time, phenyl groups decrease the nucleophilicity of diphenylsilanolate and thus make diphenylsilanolate react more selectively with P_4 . For this reason, it was found that P_4 polymerizes almost exclusively in the early stages of the reaction.¹⁴

2.4.2.2 Kinetically Controlled Polymerization

In anionic polymerization of cyclosiloxanes, depolymerization and redistribution are generally considered bothersome side reactions because they only result in lower conversion of

the monomers and large polydispersity of molecular weight. To minimize or eliminate these two reactions, it is necessary to use cyclic monomers that have much higher reactivities than linear polysiloxanes or to use catalysts that react very selectively with cyclic monomers. Therefore, the polymerization can be terminated before any substantial depolymerization and redistribution occur (kinetically controlled mode). Unfortunately, no selective catalysts have been found for unstrained cyclosiloxanes. All kinetically controlled polymerizations are based on ring strained cyclotrisiloxanes which have higher reactivities than unstrained cyclics and polymers. The preferred catalysts are lithium bases like alkylolithiums or lithium silanolates although tetraalkylammonium bases are also reportedly used in some systems.^{56,57,58} Monodisperse PDMSs have been prepared in nonpolar solvents like hexane or xylene with 1-4% tetrahydrofuran (THF) or dimethylsulfoxide (DMSO) as promoters and butyllithium or lithium trimethylsilanolate as initiators. Without a promoter, lithium bases are ineffective in polymerization of hexamethylcyclotrisiloxane due to ion association.⁵⁹ Promoters are mainly used to increase the reactivity of silanolate, but they also suppress silanolate counterion-siloxane interaction, thus hindering depolymerization and redistribution. Less electrophilic cations such as quaternary ammonium or quaternary phosphonium can also decrease silanolate-siloxane interactions and increase the selectivity of silanolates.^{60,61,62}

With fast initiation, the kinetically controlled polymerizations of cyclotrisiloxanes is quite similar to living polymerization, so the resultant polysiloxanes should have a Poisson distribution. For a k -meric chain (with $3k$ siloxane units), the weight fraction w_k is

$$w_k = \frac{v}{v+1} \cdot \frac{kv^{k-2}e^{-v}}{(k-1)!}$$

where v = average degree of polymerization (averagely $3v$ siloxane units).

⁵⁶ C. L. Lee, C. L. Frye and O. K. Johannson, *J. Polym. Sci., Polym. Chem., Ed.*, **14**, 729 (1976)

⁵⁷ L. M. Tartakovskaya, V. M. Kopylov and A. A. Zhdanov, *Vysokomol. Soed*, **B26**, 234 (1984)

⁵⁸ C. L. Lee, O. W. Marko, and O.K. Johannson, *J. Polym. Sci., Polym. Chem., Ed.*, **14**, 743 (1976)

⁵⁹ C. L. Frye, R. M. Salinger, F. W. G. Fearon, J. M. Klosowski, T. D. Young, *J. Org. Chem.*, **35**, 1308 (1970)

⁶⁰ L. M. Tartakovskaya, V. M. Kopylov and A. A. Zhdanov, *Vysokomol. Soed*, **B26**, 234 (1984)

⁶¹ C. L. Lee, and O. K. Johannson, *J. Polym. Sci. Polym. Chem. Ed.*, **14**, 729 (1976)

⁶² C. L. Lee, O. W. Marko and O. K. Johannson, *J. Polym. Sci. Polym. Chem. Ed.*, **14**, 743 (1976)

The polydispersity is given by:

$$\frac{\overline{\mathbf{n}}_w}{\overline{\mathbf{n}}_n} = 1 + \frac{\overline{\mathbf{v}}}{(\overline{\mathbf{v}} + 1)^2}$$

The molecular weight of polymer depends on the amount of initiator, and the initial and final concentrations of monomer.

$$\overline{\mathbf{M}}_n = ([\mathbf{D}_3]_0 - [\mathbf{D}_3]_t) \mathbf{M}_0 / [\text{initiator}]$$

$[\mathbf{D}_3]_0$, $[\mathbf{D}_3]_t$, and $[\text{initiator}]$ are given in mol/L, where \mathbf{M}_0 is the formula weight of the monomer.

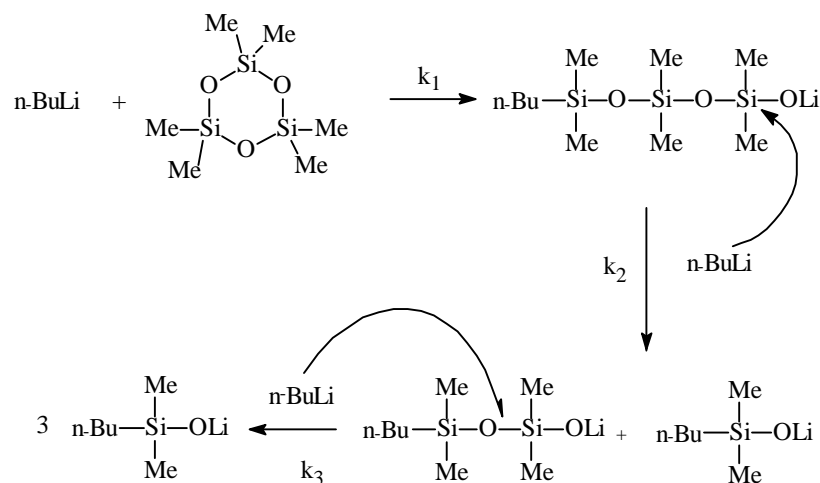
Unlike carbanionic living polymerizations, siloxane polymerizations are not particularly moisture sensitive although moisture does affect the molecular weight of polymers. The reason for this is that the silanol generated by hydrolysis is in rapid equilibrium with silanolate⁶³. In the presence of water, a system initiated with a monofunctional initiator has two groups of chains, one group is initiated directly by the initiator, the other is initiated by hydroxide ions from hydrolysis of silanolate. The former group of chains is monofunctional, while the latter is difunctional. The functional groups can be either silanol or silanolate groups. The molecular weight for difunctional chains should be twice that for monofunctional chains because difunctional chains can grow along two directions. When the concentration of water is much higher than that of initiator or vice versa, contribution from either group of chains can be neglected. Therefore, the polymer shows a narrow molecular weight distribution. However, if the concentrations of initiator and water are close, then the contributions from either group cannot be neglected. In this case, the polymer may exhibit a bimodal molecular weight distribution.

n-Butyllithium and secondary butyllithium are commonly used monobasic initiators for \mathbf{D}_3 polymerizations. It was reported that n-butyllithium reacts with an equivalent amount of hexamethylcyclotrisiloxane in nonpolar solvent like cyclohexane giving exclusively $\text{BuMe}_2\text{SiOLi}$, while 2/3 of \mathbf{D}_3 remains untouched.^{64,65} Therefore, the ring opening must be relatively slow compared to reactions of n-butyllithium with the resultant silanolates (specific redistribution).

⁶³ C. L. Lee, C. L. Frye and O. K. Johannson, *Polym. Prepr.*, **100**, 1361 (1969)

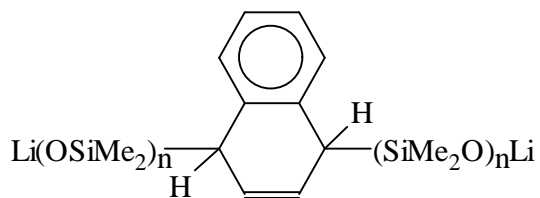
⁶⁴ C. L. Frye, R. M. Salinger, F. W. G. Fearon, J. M. Klosowski, T. D. Young, *J. Org. Chem.*, **35**, 1308 (1970)

⁶⁵ U. Maschke, T. Wagner, *Makromol. Chem.* **193**, 2453-2466 (1992)



However, it was also reported that the reaction between *n*-butyllithium and D_3 in a pure polar solvent like THF gave dibasic silanolates, and monodisperse α,ω -divinyl PDMSs were prepared using these dibasic silanolates as initiators⁶⁶.

Dianionic initiators are of special interest since they can be used to prepare monodisperse telechelic oligomers and A-B-A triblock copolymers. The number of dianionic initiators is much smaller than monoanionic initiators because dianionic species usually have poor solubility and strong ionic association. Successful dianionic initiators for olefins may not be useful for siloxane system. The diadduct of *n*-BuLi (2 parts) and 1,4-diisopropylbenzene (DIB, one part), a successful dianionic initiator for the polymerization of olefins, reacts slowly with D_3 even in moderately polar solvents like THF⁶⁷. Aromatic radical anions such as alkali metal naphthalenides (see below) initiate siloxane polymerization in a complex way⁶⁸ leading to a polymer with a rather broad molecular weight distribution.



⁶⁶ M. A. Villar, M. A. Bibbo and E. M. Valles, *J. M. S.-Pure Appl. Chem.*, **A29**, 4&5, 391-400 (1992)

⁶⁷ Y. Gnanou and P. Rampp, *Makromol. Chem.*, **189**, 1997 (1988)

⁶⁸ M. Morton, and E. E. Bostick, *J. Polym. Sci.*, **A3**, 971 (1965)

Dilithium diphenylsilanediolate (DLDPs) was used as a dianionic initiator by Bostick^{69,70} to make polydiphenylsiloxane-b-PDMS-b-polydiphenylsiloxane. However, Gnanou and Rempp⁶⁷ found that DLDPs was a slow initiator and yielded PDMSs with broad molecular weight distributions. These researchers reported that dilithium dimethylsilanediolate can react quickly with D_3 and give monodisperse PDMSs. Kazama et al,⁷¹ compared the polymerization of D_3 initiated with lithium salts of p-(hydroxydimethylsilyl)phenyl ether (I), p-bis(hydroxydimethylsilyl)benzene (II) and diphenylsilanediol (III). Results showed that the capability for an initiator to give monodisperse PDMSs is (I) > (II) > (III). Dilithium 1,3-tetramethyldisiloxanolate was also reportedly a suitable initiator for preparing monodisperse PDMSs under appropriate conditions^{72,73}.

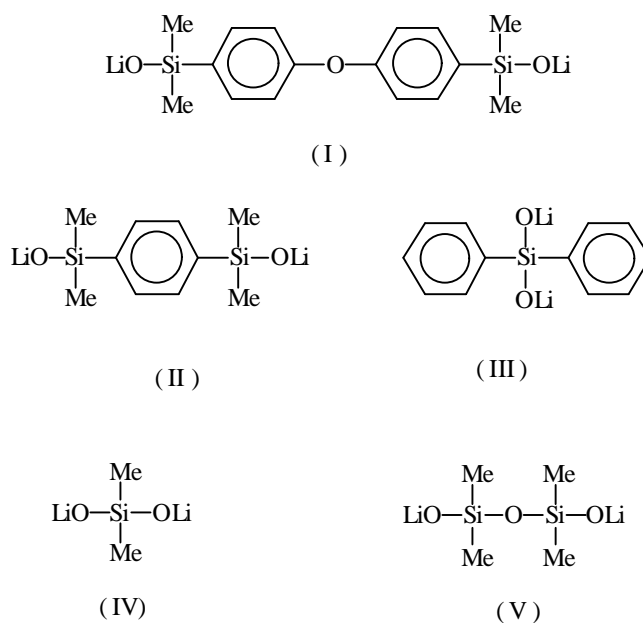


Figure 2.9 Structures of some difunctional siloxane initiators

⁶⁹ E. E. Bostick, Block Copolymer, S. L. Aggarwal, Ed., Plenum, New York (1970)

⁷⁰ E. E. Bostick, US Patent 3,337,497, assigned to General Electric Company (1967)

⁷¹ H. Kazama, Y. Tezuka, and K. Imai, Polymer Bulletin, **21**, 31-37 (1989)

⁷² J. Chojnowski, K. Rozya, W. F. Fortuniak, A. Kowalewska, Makromol Chem., Macromol. Symp. **73**, 183-201 (1993)

⁷³ J. Chojnowski, J. Inorg. Organometal Polym. **1**, 299 (1991)

Dianionic silanolates are usually prepared by reaction of alkyllithiums with silanediols in tetrahydrofuran below -40°C . The reactions are conducted either by addition of silanediols to excess amounts of butyllithium, or by titration of silanediol solutions with butyllithium.⁶⁷⁻⁷⁰ Gnanou and Rempp⁶⁷ indicated that deprotonation of diphenylsilanediol could result in some hexaphenylcyclotrisiloxane. Purification of dianionic initiators was difficult because the initiators are usually insoluble in nonprotonic solvents but solvolyze in protonic solvents. Harmful impurities in dianionic initiators are mainly monofunctional silanolates, which can cause broad molecular weight distributions of the resultant polymers and form diblock copolymer impurities during subsequent preparations of triblock copolymers.

2.5 Review of Nitrile Containing Silicones

Nitrile containing silicones include homopolymers or copolymers of silicones which have nitrile containing substituents like 2-cyanoethyl or 3-cyanopropyl groups. Cyanomethylsiloxane is generally unstable since the cyano group weakens the Si-C bond. Consequently, the cyanomethyl group in $\text{NCCH}_2\text{Si}(\text{CH}_3)_3$ can be easily split off by boiling water⁷⁴, while similar treatment of the corresponding 2- and 3-cyano substituted compounds only causes some saponification of the CN group⁷⁵. 1-Cyanoethylsiloxane is subject to β -decomposition upon heating. Table 2.3 shows thermal stability data for several nitrile containing siloxanes. The right-hand column shows the carbon percentages of the residuals (compared with theoretical carbon contents) after heating in air at 250°C for 100 hours. Obviously, 2-cyanoethyl- and 3-cyanopropyl- siloxanes are most stable in Table 2.3,.

⁷⁴ J. Amer. Chem. Soc. **77**, 3224 (1955)

⁷⁵ S. Nozakura and S. Konotsune, Bull. Chem. Soc. Japan **29**, 322 (1956)

Table 2.3 Stabilities of nitrile containing siloxanes (quoted from [reference 20](#), p181)

Substituents	C(%)
1-Cyanoethyl	<1
2-Cyanoethyl	88.3
2-Cyanopropyl	75.6
3-Cyanopropyl	94.4

Nitrile containing silicones are valuable high dielectric fluids ([reference 20](#), p486). They can be used as dielectric materials, nonaqueous antifoam reagents, solvent resistant greases and antistatic reagents. If incorporated into silicone rubbers, nitrile substituted siloxanes can prevent swelling of silicone rubber in organic solvents such as gasoline and benzene. However, fluorosilicones are used industrially for this purpose. In chromatography, nitrile silicones can be used as stationary phases for the separation of positional or steric isomers.^{76,77} Nitrile containing siloxanes are also precursors for poly(aminoalkylsiloxane)s since the nitrile groups can be transformed into amino group using reducing reagents like lithium hydroborate⁷⁸.

Copolymers of PCPMSs and PDMS can be obtained by cohydrolysis of related dichlorosilanes, followed by equilibration using potassium hydroxide catalyst⁷⁹, or by coequilibrium of cyclics using alkali metal hydroxides or Ba(OH)₂ catalysts.^{54,80} Nitrile containing siloxanes made by hydrolysis of dichlorosilanes may include various amounts of amides due to hydrolysis of cyano groups.⁷⁶ Generally, the hydrolysis of cyano groups can be suppressed by adding sodium bicarbonate. Nitrile siloxanes free of amide can be prepared by hydrolysis of related methoxysilanes or by non-hydrolytic processes like condensation of dichlorosilane using zinc oxide.⁷⁶

⁷⁶ K. Markides, L. Blomberg, s. Hoffmann, J. Buijten and T. Wannman, *J. Chromatography*, **302**, 319-340 (1994)

⁷⁷ B. E. Richter, J. C. Kuei, L. W. Castle, B. A. Jones, J. S. Brashaw and M. L. Lee, *Chromatography*, **17**(10) 570 (1983)

⁷⁸ N. Koyama, Y. Sekiyama, Y. Ueno and Y. Sekine, *Polym. Communication* **36**(5), 128 (1985).

⁷⁹ B. Bluestein, U. S. Patent, 3,448,076, assigned to General Electric Company (1969)

⁸⁰ D. L. Bailey W. T. Black, R. A. Pike, Br. Patent 0,999,984, CA 64: 3812e (1966)

3-Cyanopropylmethylsiloxanes are promising high temperature adhesives. Crosslinked PCPMS resins were prepared by hydrosilylation of polyhydrogenmethylsiloxane and crosslinked by Si-H/Si-OH condensation⁸¹. The transition temperature of these nitrile siloxane resins was below -50°C. Sealants compounded out of these polymers showed excellent fuel resistance and remained flexible down to -50°C. No apparent decomposition of the sealants was noticed after 48 hours at 250°C. PCPMS sealants⁸² were also prepared through curing trimethoxysilane capped polysiloxane oligomers and methyltrimethoxysilane in the presence of titanium alkoxide catalysts.

2-cyanoethyl⁸³ and 3-cyanopropyl^{84,85} containing polysiloxane homopolymers or copolymers were also used as telechelic oligomers for preparing poly(urea-urethane)s. It is speculated that 3-cyanopropyl modified polysiloxanes might increase the interfacial thickness of polysiloxane-urea or polysiloxane-bisphenol A epoxy resin, and hence improve the toughness of epoxy or poly(urea-urethane) materials.⁸³

2.6 Preparation of Block Copolymers

2.6.1 Introduction

Copolymers can show quite different properties with the same composition but different arrangements of monomers. Different structures are illustrated below for copolymer of units A and B.

1) Random: Units A and B are arranged randomly along the polymer chain.

AAABBABAAABBBBABBABBAAABABAAAB

⁸¹ H. Singh, National SAMPE symposium and exhibition, **22**, 227-237 (1977)

⁸² V. Venkatesan, S. Lin, R. B. Jayaraman and J. S. Riffle, Polym. Prepr., **36(1)**, 483 (1995)

⁸³ C. Li, X. Yu, T. A. Speckard, and S. L. Cooper, J. Polym. Sci. Part B: Polym. Phys., **26**, 315-337 (1988)

⁸⁴ L. Chen, X. Yu, Polym. Mater. Sci. and Engin. (in Chinese) **1(1)**, 45 (1992)

⁸⁵ V. Venkatesan, S. Lin, C. Li, S. V. Davis, Q. Ji, H. Parvatareddy, D. A. Dillard, and J. S. Riffle, Polym. Prepr., **37(2)**, 338 (1996)

The major advantage of random copolymers is that the physical properties of polymers such as glass transition temperature etc. can be continuously adjusted by changing the composition of the copolymer.

2) Alternating: Units A and B are arranged alternatively along the polymer chain

ABABABABABABABABABABABABABABABAB

Alternating copolymers may offer properties quite different from homopolymer A or B.

3) Graft: One of the units is attached to the main backbone chain of the other.

AAAAAAAAATAAAAAAAAAATAAAA

B	B
B	B
B	B
B	B

Graft copolymers have microphase separated microstructures if the polarities of units A and B differ significantly. Therefore, these polymers usually have T_g s representing each microphase.

4) Block: Polymer chains include successively linked A units and successively linked B units. Common block copolymers include diblock, triblock and multiblock copolymers.

AAAAAAAAAAAAAAAAABBBBBBBBBBBBBBBBBBBBBBBB

Diblock copolymer

AAAAAAAAAAAAAAAAABBBBBBBBBBBBBBBBBBBBAAAAAAAAAAAAAAAAAAAA

Triblock copolymer

AAAAAABBBBBBBBAAAAAAAAABBBBBBBAAAAA

Multiblock copolymer

Block copolymers tend to have multiphase structures. Similar to graft copolymers, they also show more than one T_g that corresponds to the T_g s of their related homopolymers. Diblock copolymers may be applied as surfactants or stabilizers for suspensions and emulsions, or as compatibilizers for polymer blends. Triblock copolymers can also be used as stabilizers or compatibilizers, but their major applications are as thermoplastic elastomers. Well known examples of multiblock or segmented copolymers include poly(ether-urethane)s or poly(ester-urethane)s which are widely used as seat cushions in automobiles.

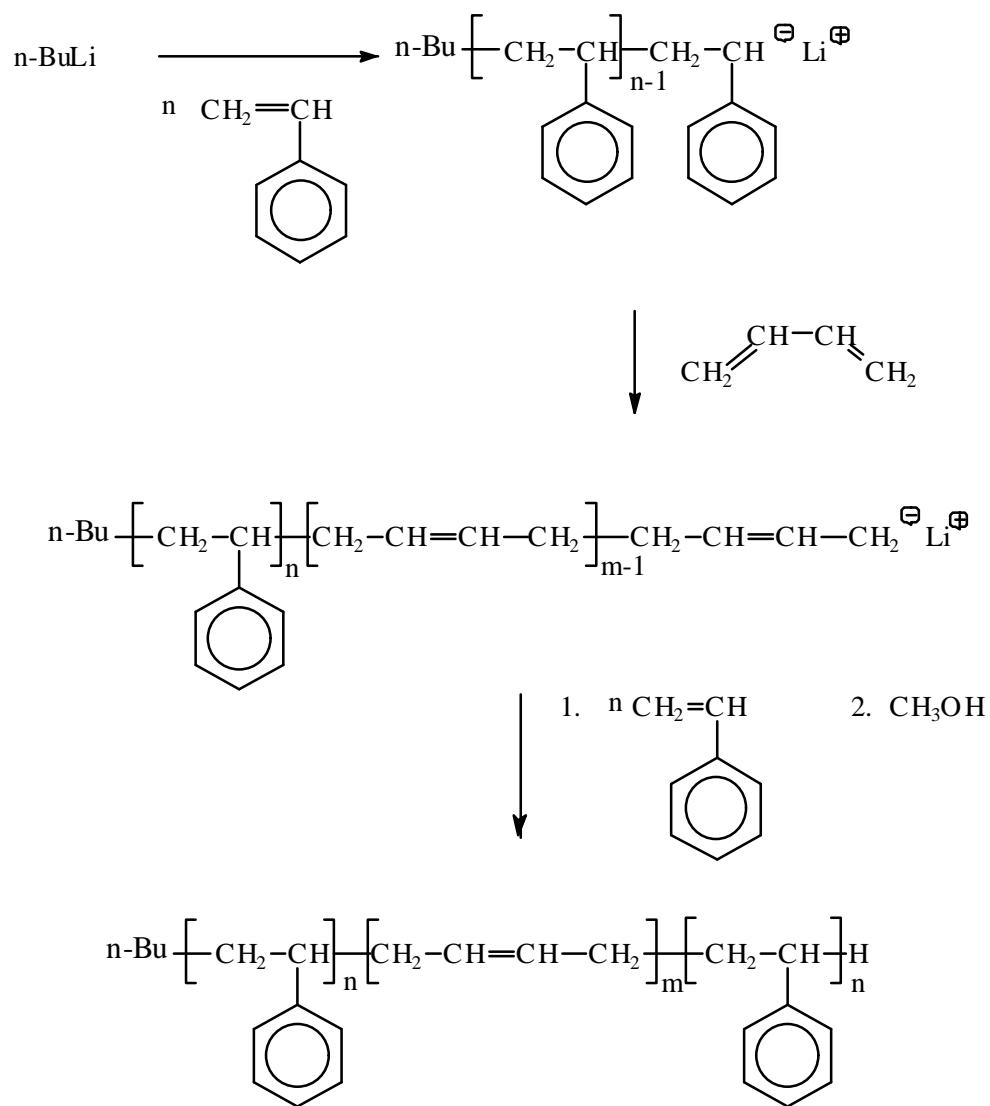
2.6.2 Preparation of Triblock Copolymers

Block copolymers with monodisperse blocks can be prepared by sequential addition of monomers through living polymerization. A classic example of this type is polystyrene-*b*-polybutadiene-*b*-polystyrene, a thermoplastic elastomer, which can be prepared through a three-step sequential addition of styrene, butadiene and styrene using butyllithium or isobutyllithium as an initiator, or through a two-step sequential addition of butadiene and styrene using potassium naphthalenide as a difunctional initiator ([Scheme 2.1](#)). Polydiphenylsiloxane-*b*-PDMS-*b*-polydiphenylsiloxanes were introduced by Bostick^{86,87} using kinetically controlled polymerization of hexamethylcyclotrisiloxane initiated by dilithium diphenylsilanediolate (DLDPs), followed by adding hexaphenylcyclotrisiloxane ([Scheme 2.2](#)). An appropriate solvent for this reaction is diphenylether, which is a good solvent for both hexaphenylcyclotrisiloxane and polydiphenylsiloxane.⁸⁸ Polydiphenylsiloxane has a T_g of 49°C, a crystal mesomorphic transition temperature of 250°C and a mesomorphic isotropic to isotropic transition temperature of 550°C. Like polystyrene in thermoplastic elastomers, polydiphenylsiloxane physically crosslinks the block copolymers so that no viscous flow occurs under deformation. The siloxane triblock copolymers exhibited tensile strengths of 6.5 MPa at 30°C and 5 MPa at 100°C.

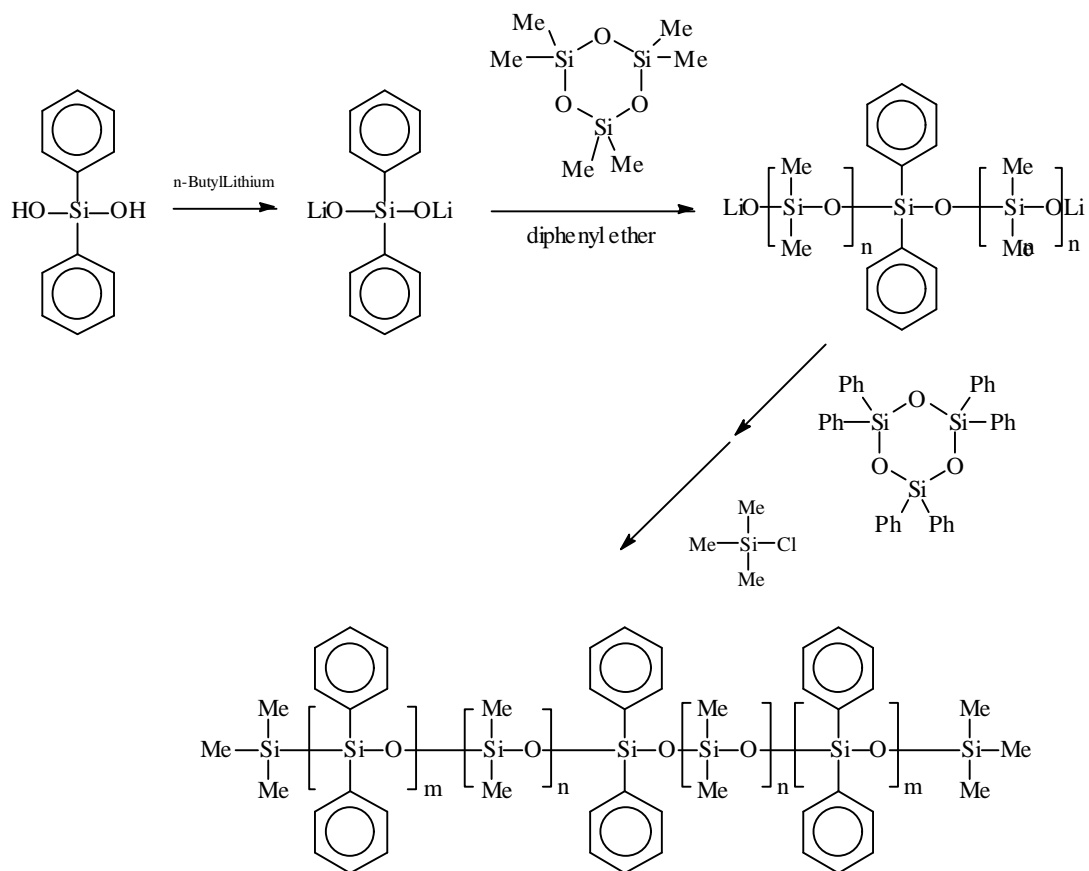
⁸⁶ E. E. Bostick, *Block Copolymers*, S. L. Aggarwal, Ed., Plenum, New York 237 (1970)

⁸⁷ E. E. Bostick, U. S. Patent 3,337,497 granted to General Electric (1967)

⁸⁸ N. V. Gvodzdic, J. Ibemesi, and D. J. Meier, *Proc. IUPAC, Macromol. Symp.*, **69**, 168 (1982)



[Scheme 2.1](#) Preparation of polystyrene/butadiene thermoplastic elastomer.



[Scheme 2.2](#) Preparation of polydiphenylsiloxane-b-PDMS-b-polydiphenylsiloxane

Organic polymer-b-siloxanes and siloxane-b-organic polymer-b-siloxanes may be directly prepared by living polymerization using a monobasic or a dibasic initiator. However, block copolymers which have two or more organic polymer blocks separated by one or more polysiloxane blocks are difficult to prepare using an uninterrupted polymerization process. Kinetically controlled polymerization of cyclotrisiloxanes usually do not transfer to organic monomers like olefins because silanolates, the active species, do not react with common organic monomers. Living polymerization of organic polymers do transfer to cyclosiloxanes, but the carbanions, unless sterically hindered, tend to cleave the siloxane structures already formed in the polymer chains.

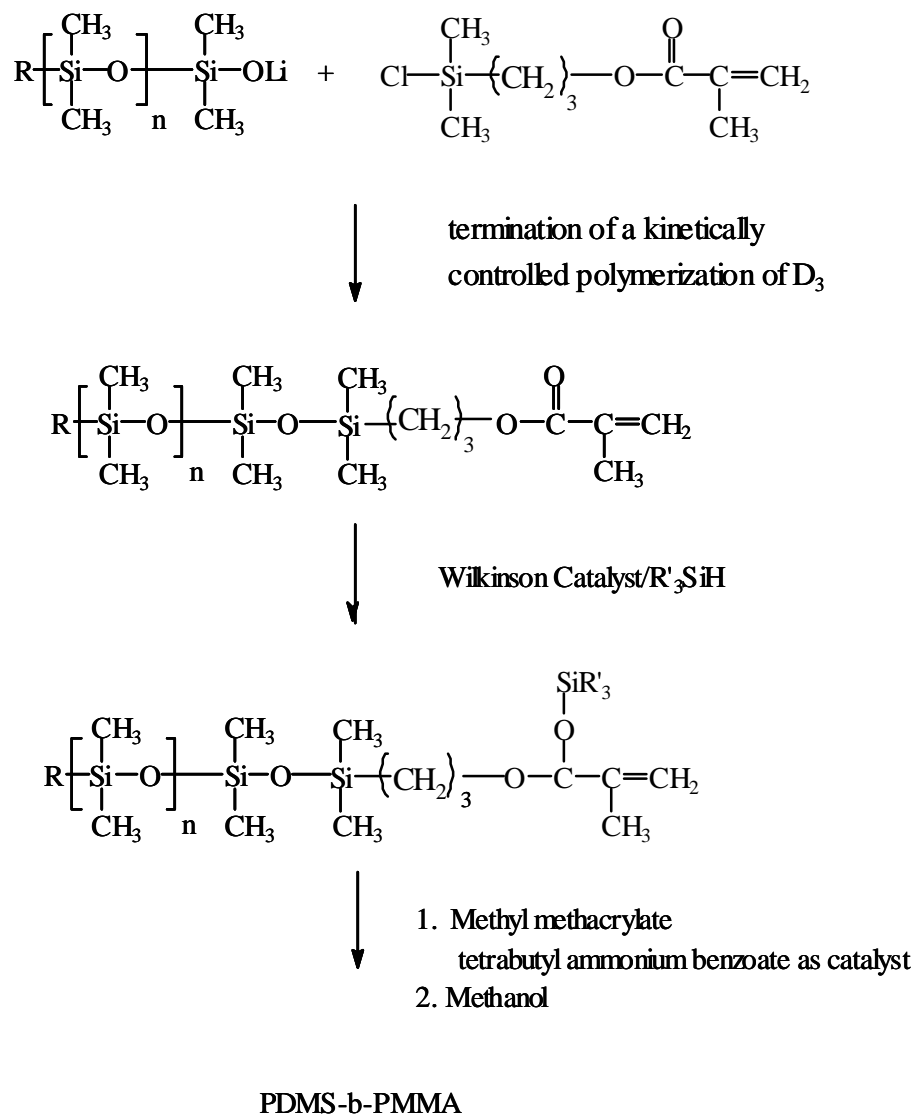
Multiblock copolymers of polystyrene and PDMS were prepared by condensation of PDMS-b-polystyrene-b-PDMS oligomers⁸⁹. The triblock oligomers were prepared by sodium naphthalenide promoted polymerization of styrene, followed by addition of hexamethylcyclotrisiloxane.

Poly(methyl methacrylate)-b-PDMSs are difficult to prepare using an uninterrupted living process because chain reaction can neither be transferred from polymethacrylate to siloxane nor from polysiloxane to methyl methacrylate. Hellstern, Desimone and McGrath prepared these block copolymers by transformation of a kinetically controlled polymerization of D₃ to a group transfer polymerization of MMA ([Scheme 2.3](#))⁹⁰. Mason, Hattori and Thieo also prepared these block polymers by kinetically controlled polymerization of D₃ using an alkoxide containing poly(methyl methacrylate) macroinitiator⁹¹. Unfortunately, this method introduces a hydrolytically unstable C-O-Si bond into the polymer backbone.

⁸⁹ A. Dems, G. Strobin, *Macromol. Chem.* **192**, 2521-2537 (1991)

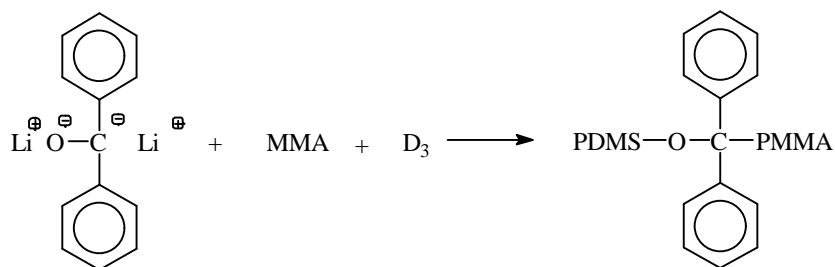
⁹⁰ A. M. Hellstern, J. M. Desimone and J. E. McGrath, *Polym. Prepr.*, **28**(2) 148-149 (1987)

⁹¹ J. P. Mason, T. Hattori and Thieo E. Hogen-Esch, *Polymer Prepr.*, **30**(1) (1989)



[Scheme 2.3](#) Preparation of PDMS-b-poly(methyl methacrylate) by transformation of living polymerization to group transfer polymerization

Poly(methyl methacrylate)-b-polysiloxane)s were also prepared by concurrent anionic polymerization of D_3 and MMA initiated with dilithiobenzophenone diinitiator.⁹² The dilithiobenzophenone initiator has an alkoxide and a sterically hindered carbanion in one molecule. The former initiates D_3 polymerization while the latter initiates polymerization of methyl methacrylate. No randomization occurs since polymerizations of D_3 and MMA do not interfere with each other.



Scheme 2.4 Preparation of PDMS-b-poly(methyl methacrylate) using dilithiobenzophenone diinitiator

Poly(oxazoline)-b-PDMS, a good surfactant or stabilizer, was prepared by transformation of an anionic polymerization to a cationic polymerization.⁸⁴⁻⁸⁸ Oxazoline monomers can be polymerized by cationic living polymerization using an alkyl chlorides catalyst in conjunction with sodium iodide. An alkyl chloride functional macroinitiator was obtained by terminating a polysiloxane living polymerization with 4-chloromethylphenyldimethylchlorosilane. In the presence of sodium iodide, the alkyl chloride endgroup in PDMS became an initiator for polymerization of oxazoline. Therefore, oxazoline polymerized from one side of PDMS macroinitiator to form a poly(oxazoline) block.

⁹² S. K. Varshney, C. L. Beatty, *Org. Coat. Plast. Chem. Proc* **45**, 152 (1981)

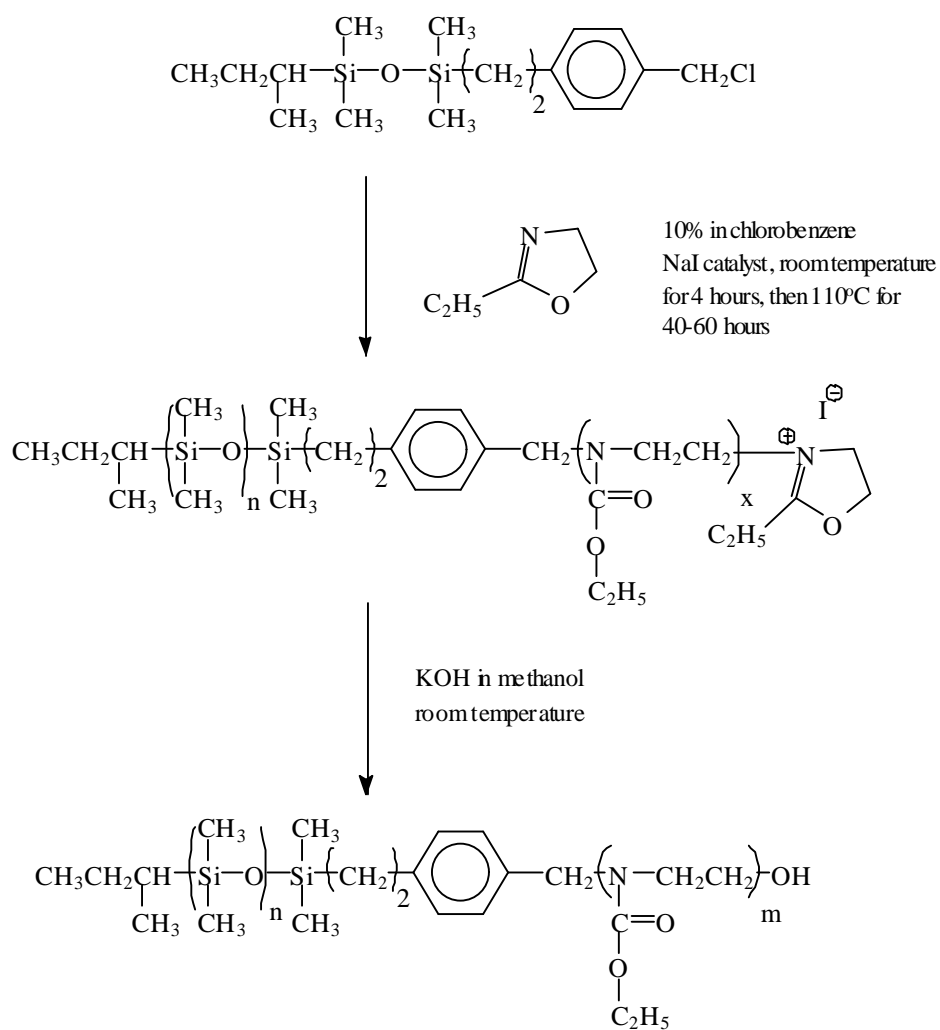
⁹³ J. S. Riffle, I. Yilgor, U. S. Patent, 4,659,777 granted to Thoratec Lab Corp. (1987)

⁹⁴ Q. Liu, Ph. D. Dissertation, Virginia Polytechnic Institute and State University (1992)

⁹⁵ Q. Liu, M. Konas, R. M. Davis and J. S. Riffle, *J. Polym. Sci., Polym. Chem. Ed.*, **31(7)**, 1709-1718 (1993)

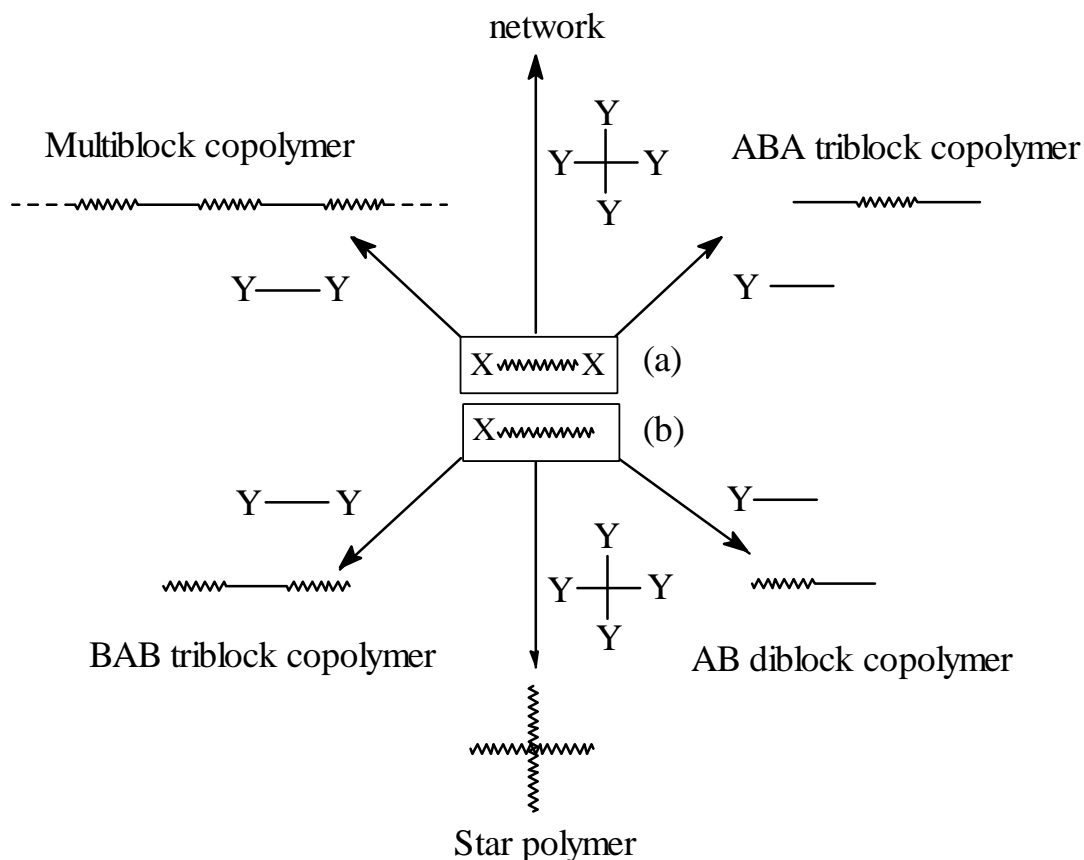
⁹⁶ Q. Liu, G. R. Wilson, R. M. Davis, and J. S. Riffle, *Polymer*, **34(14)**, 3030-3036 (1993)

⁹⁷ I. Yilgor, R. S. Ward, and J. S. Riffle, *Polym. Preprints*, **28(2)**, 369-371 (1987)



Scheme 2.5 Preparation of PDMS-b-poly(oxazoline) through transformation of anionic polymerization to cationic polymerization

Coupling of telechelic α,ω -difunctional oligomers is a versatile method for preparing block copolymers and networks (Scheme 2.6). Telechelic oligomers can be prepared either by addition polymerization or by stepwise polymerization.⁹⁸



Scheme 2.6 Coupling reactions of (a) telechelic and (b) mono-telechelic oligomers.⁹⁹

Reactive functional groups reported for polysiloxane telechelic oligomers can be divided into 1) functional groups directly linked to silicon atoms (Si-X, X = -Cl, -OH, -OR, -H, etc.) and 2) functional groups linked to silicon atoms through an alkyl spacer (Si-R-X). Couplings of Si-X

⁹⁸ E. J. Goethals, *Telechelic Polymers: Synthesis, Properties and Applications*, CRC Press, Boca Raton, Florida (1989)

⁹⁹ P. V. Caeter and E. J. Goethals, *Trend in Polymer Science (TRIP)*, **3**(7), 227 (1995)

groups are very important for curing or crosslinking polysiloxane rubbers and resins since the residual groups are simply siloxane bonds (Si-O-Si). Reactions of Si-X groups with organic functional groups usually lead to strong but hydrolytically unstable linkages like Si-O-C and Si-NH-C. Fortunately, the hydrolysis may be hindered by the hydrophobicity of the polymer matrix. The functional group X in Si-R-X cannot be linked to the α or β carbon outward from the siloxane unit, otherwise, Si-C linkages between polymer backbone and side groups would be weakened, or the reactivity of functional groups would be decreased. Therefore, a spacer of at least three carbons should be used to separate the terminal siloxane unit and functional group. For this reason, couplings of Si-R-X groups usually bring bulky organic segments into the siloxane backbone, and hence deteriorate the high temperature stability of the polysiloxanes. However, couplings of Si-R-X groups do not yield hydrolytically unstable linkages like Si-O-C or Si-NH-C, thus they are very useful for coupling of siloxane oligomers and organic oligomers.

α,ω -Difunctional polysiloxanes can be prepared by equilibrating mixtures of cyclic siloxanes and 1,3-difunctional disiloxanes using a small amount of strong acid or base as a catalyst,^{100,101,102} or by functional initiation or termination of kinetically controlled polymerizations.^{103,104}

¹⁰⁰ J. S. Riffle, I. Yilgor, C. Tran, G. L. Wilkes, J. E. McGrath and A. K. Banththia, Chapter 2, Epoxy Resin Chemistry II, (ed.) Bauer, R. S. : ACS Symp. Ser., **221**, Washington DC (1983)

¹⁰¹ I. Yilgor, J. S. Riffle, J. E. McGrath, Chapter 14, Reactive Oligomers, (eds.), F. W. Harris, H. J. Spinelli: ACS Symp. Ser., **282**, Washington DC (1985)

¹⁰² K. Kojima, C. R. Gore, C. S. Marvel, J. Polym. Sci. A-1, **4**(9), 2325 (1966)

¹⁰³ J. R. Babu, G. Sinai-Zingde and J. S. Riffle, J. Polym. Sci. Part A: Polym. Chem, **31**, 1645-1651 (1993)

¹⁰⁴ M. A. Peter and J. M. DeSimone, Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem. **35**(2), 484 (1994)

Table 2.4 Important organofunctional groups in polysiloxanes

$\text{H}_2\text{N}-(\text{CH}_2)_3$	
$\text{HO}-(\text{CH}_2)_4$	$\text{HOOC}-(\text{CH}_2)_3$
	$\text{Cl}-(\text{CH}_2)_3$

* See reference 105,106. The rest are cited from reference 8

Organofunctionally terminated polysiloxane oligomers are widely used for preparing microphase separated copolymers like poly(siloxane-carbonate)s^{107,108,109,110}, poly(siloxane-

¹⁰⁵ H. S. Ryang, U.S. Patent 4,381,396, assigned to General Electric Co (1986)

¹⁰⁶ J. E. Hallgren and D. Brezniak, U.S. Patent 4,634,755, assigned to General Electric Co (1986)

¹⁰⁷ S. H. Tang, E. Meinecke, J. S. Riffle, and J. E. McGrath, Rubber Chem. And Tech., **53**(5), 1160-1169 (1980)

¹⁰⁸ T. C. Ward, D. P. Sheehy, J. S. Riffle, and J. E. McGrath, Macromolecules, **14**(6), 1791-1797 (1981)

¹⁰⁹ J. S. Riffle, R. G. Freelin, A. K. Banthia, and J. E. McGrath, J. Macromol. Sci., Chem., **A15**(5) 967-998 (1981)

¹¹⁰ S. H. Tang, E. A. Meinecke, J. S. Riffle, and J. E. McGrath, Rubber Chem. And Tech., **57**(1), 184-202 (1984)

urethane)s¹¹¹, poly(aryl ester-siloxane)s¹¹². A detailed review in this area is given by Yilgor and McGrath⁸.

2.7 Possible Approaches for Preparing PDMS-b-PCPMS-b-PDMSs

PDMS-b-PCPMS-PDMSs may be prepared by kinetically controlled polymerization with a monobasic lithium base as an initiator and sequential addition of D_3 , D_3CN and D_3 , or with a divalent lithium base as an initiator and sequential addition of D_3CN and D_3 (similar to scheme 2.2). The key to these methods are the synthesis of monomer grade D_3CN since the other monomer is commercially available. However, D_3CN is difficult to purify due to its noncrystallizability and high boiling point (240-245°C/1 Torr).

An alternative approach is coupling of an α,ω -difunctional PCPMS with an ω -functional PDMS. Here D_3CN is not a necessity because the telechelic PCPMSs can be prepared by equilibrium polymerization of the unstrained cyclics using either an acidic or basic catalyst. The ω -functional PDMSs can be prepared by functional initiation or functional termination of PDMS living polymerization. The major obstacle of this coupling approach is the immiscibility of PCPMS and PDMS oligomers. Without a suitable solvent, the coupling reaction cannot be completed because the reactive groups are distributed in different phases and hence have few opportunities to encounter each other.

In this thesis, the triblock copolymers was prepared by kinetically controlled polymerization of D_3 using lithium silanolate endcapped PCPMS macroinitiators. The

¹¹¹ A. K. Sha'aban, S. McCartney, N. Patel, I. Yilgor, J. S. Riffle, D. W. Dwight, and J. E. McGrath, Polym. Prepr., **24**(2), 130-134 (1983)

¹¹² D. C. Webster, P. J. Andolino, J. S. Riffle, F. L. Keohan, and J. E. McGrath, Polym. Prepr. **24**(1), 161-163 (1983)

macroinitiators were prepared by equilibrating mixtures of D_x CNs and DLDPS. Therefore, obstacles like the immiscibility of PDMS and PCPMS and the purification of D_3 CN can be avoid.

CHAPTER 3

SYNTHESIS OF PDMS-b-PCPMS-b-PDMS TRIBLOCK COPOLYMERS

This chapter first describes the synthetic scheme in this thesis, then focuses on purification of chemicals, preparation and characterization of monomers, initiators and polymers.

3.1 The Synthetic Approach

The synthetic approach for preparing PDMS-b-PCPMS-b-PDMSs is illustrated in [Fig. 3.1](#). The synthesis began with dichloromethylsilane and diphenylsilanediol, which are common chemicals in the silicone industry. 3-Cyanopropylmethyldichlorosilane was prepared through hydrosilylation by reaction of allyl cyanide with dichloromethylsilane. D_xCN ($x = 3-5$) were prepared by hydrolysis of 3-cyanopropylmethyldichlorosilane, followed by cyclization and equilibration of the hydrolysate. Dilithium diphenylsilanediolate (DLDPs) initiator was synthesized by deprotonation of diphenylsilanediol using diphenylmethyl lithium. Lithium silanolate capped PCPMS macroinitiators were prepared by equilibrium polymerization of D_xCN ($x = 3-5$) with DLDPs as both an initiator and a chain stopper. Finally, PDMS-b-PCPMS-b-PDMSs were obtained by kinetically controlled polymerizations of D_3 using the lithium silanolate capped PCPMS macroinitiators.

3.2 Skills for Moisture Sensitive Experiments

The rate of anionic polymerization of cyclic siloxanes is not particularly sensitive to moisture. However, moisture in the system causes deviations of the molecular weight from the target value, and also causes chain transfer reactions if silanol condensations exist. Therefore, all monomers, initiators, solvents and promoters should be dried carefully, and special measures

should be taken to preserve the anhydrous conditions during storage and transfer. Before use, all flasks, reactors and reagent containers were capped with septa, flame-dried and flushed with dry nitrogen to remove any moisture. Liquids were transferred using cannulas or syringes by increasing the pressure in the container with dry nitrogen. Normal pressure distillations were carried out under a dry nitrogen atmosphere. Reagent containers were recharged with dry nitrogen after use. Two-neck flasks were preferred in distillation apparatuses so the whole system could be conveniently flame-dried and flushed with dry nitrogen, and liquids could be added and removed using cannulas or syringes. Transfer of solid materials was done in a drybox or dry bags.

3.3 Chemicals and Purification

3.3.1 Tetrahydrofuran (THF, C₄H₈O, FW 72.11, b. p. 65-67°C, d 0.889)

Major impurities in THF include inhibitors, peroxides and water. To remove these impurities, commercial THF (E. M. Sciences 99.5%) was refluxed over a small amount of sodium (Aldrich, 40 wt% in paraffin) and benzophenone (Aldrich 99%) under an argon or nitrogen atmosphere. The anhydrous state of THF was indicated by a deep purple complex formed from sodium and benzophenone. Pure THF was distilled from this deep purple solution immediately prior to use.

3.3.2 Dichloromethane (CH₂Cl₂, FW 84.93, b.p. 40°C, d 1.325)

Dichloromethane (Baxter, 99.9%) was washed several times with concentrated sulfuric acid until the sulfuric acid phase was no longer yellow (to remove alcohol or olefin impurities), then washed several times with water to remove residual acid and pre-dried with anhydrous magnesium sulfate. Finally pure dichloromethane was distilled over phosphorus pentoxide (Fisher, 99.6%) under a N₂ atmosphere. Purified dichloromethane was stored under nitrogen in a septum capped container.

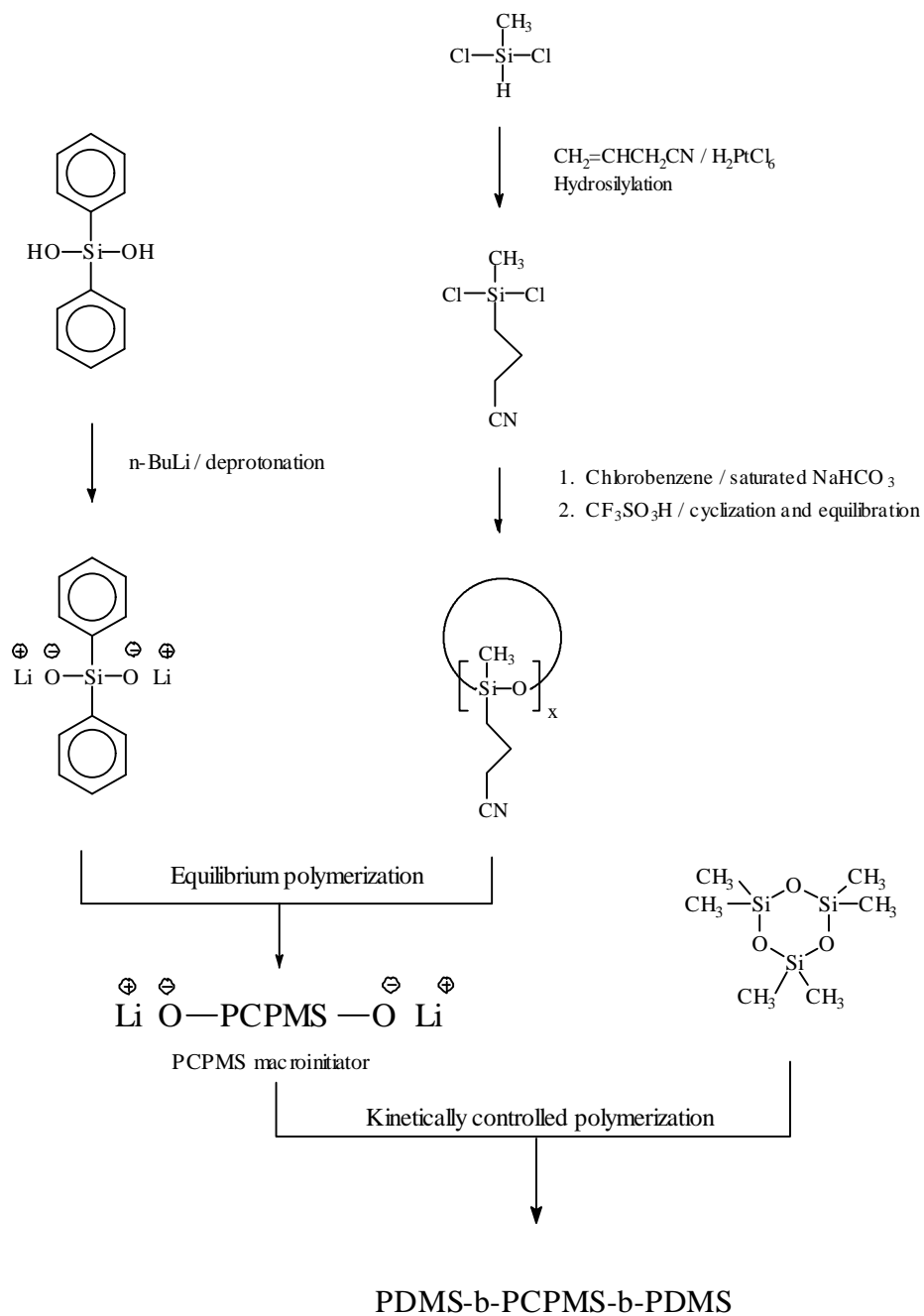


Figure 3.1 Flow chart for preparing PDMS-b-PCPMS-b-PDMS triblock copolymers

3.3.3 Methylchlorosilane ($\text{CH}_3\text{SiHCl}_2$, FW 115.4, b.p. 41°C , d 1.105)

Methylchlorosilane (Aldrich, 97%) was purified by simple distillation to remove impurities which might decrease the activity of hexachloroplatinic acid. The exit of the distillation system was linked to a drying tube filled with anhydrous calcium sulfate (Drierite) to exclude moisture.

3.3.4 Tri(ethylene Glycol) Dimethyl Ether (TEGDME)

$\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$, FW 178.23, b.p. 216°C , d 0.986

Tri(ethylene glycol) dimethyl ether (Aldrich, 99%) was refluxed under nitrogen atmosphere over a small amount of sodium (Aldrich, 40% in paraffin) and benzophenone (Aldrich, 99%) until the liquid was purple, then distilled under reduced pressure and stored in a septum capped container.

3.3.5 1,1,3,3,5,5-Hexamethylcyclotrisiloxane (D_3)

$[(\text{CH}_3)_2\text{SiO}]_3$ FW 222.47, m.p. $64-66^\circ\text{C}$, b.p. 134°C

1,1,3,3,5,5-hexamethylcyclotrisiloxane (GE, Industrial grade) was dried at 80°C under a nitrogen atmosphere over calcium hydride powder for 48 hours, and then fractionally distilled under a nitrogen atmosphere. The fraction distilling at $132-136^\circ\text{C}$ was collected into a pre-weighed dry flask where it was diluted with purified dichloromethane for further application.

3.3.6 Molecular Sieves.

Molecular sieves (Aldrich, 5•) were used as a drying reagent for allyl cyanide. Before use the sieves were activated at 200°C / 0.5-1 torr. for 48 hours.

3.3.7 Allyl Cyanide ($\text{CH}_2=\text{CHCH}_2\text{CN}$, FW 67.09, b.p. $116-121^\circ\text{C}$, d 0.834)

Allyl cyanide (Aldrich, 98%) was dried at room temperature with activated molecular sieves for 48 hours, then distilled at $118-123^\circ\text{C}$ under a nitrogen atmosphere.

3.3.8 Potassium Carbonate (K_2CO_3 , FW 138.21)

Potassium carbonate (Mallinckrodt GR 99+%) was dried at $120^\circ C/1-2$ torr. for 48 hours immediately prior to use.

3.3.9 Trimethylchlorosilane ($(CH_3)_3SiCl$, FW 108.64, b.p. $57^\circ C$, d 0.856)

Impurities in chlorosilanes are mainly hydrochloric acid, silanols or polychlorosiloxanes. Chlorosilanes only react with alkali metal carbonates at above $400^\circ C$, so hydrochloric acid can be removed effectively by treating with anhydrous potassium carbonate. Trimethylchlorosilane (Aldrich 99%) was treated with anhydrous potassium carbonate for 24 hours, then distilled under a N_2 atmosphere. Since chlorosilanes degrade septa, trimethylchlorosilane was only stored in septum capped containers for a maximum of one week.

3.3.10 Vinyltrimethylchlorosilane ($(CH_3)_2CH=CHSiCl$, FW 120.66, b.p. $82-83^\circ C$, d 0.974)

Vinyltrimethylchlorosilane (Aldrich 99%) was treated and distilled similarly to trimethylchlorosilane. As with other chlorosilanes, vinyltrimethylchlorosilane was only stored in septum capped containers for a maximum of one week.

3.3.11 Diphenylmethane ($(C_6H_5)_2CH_2$, FW 169.24, m.p. $22-24^\circ C$, b.p. $264^\circ C$)

Diphenylmethane (Aldrich 99%) was stirred at $80^\circ C$ over calcium hydride (Aldrich) for 24 hours, then distilled under reduced pressure.

3.3.12 Diphenylsilanediol ($(C_6H_5)_2Si(OH)_2$ FW 216.31)

Diphenylsilanediol is one of the few stable silanols under ambient conditions. Commercial products may include various silanol impurities. Diphenylsilanediol tends to polymerize on heating, so all purification procedures were carried out at room temperature.

Diphenylsilanediol (Aldrich 95%) 40 g was dissolved in a minimum amount of 5-methyl-2-pentanone (Aldrich 99%) (about 550 ml). Then about 1000 ml chloroform was added to the diphenylsilanediol solution as slowly as possible to avoid crystallization (diphenylsilanediol forms

supersaturated solution in this mixed solution). This metastable system was left undisturbed to allow crystallization. Needle crystals of diphenylsilanediol were collected by filtration, then dried at room temperature by vacuum desiccation. Dry crystals of diphenylsilanediol were stored in a desiccator for future use.

3.3.13 2,4,6,8-Tetramethylcyclotetrasiloxane (D₄H)

(CH₃SiHO)₄, FW. 240.51, m.p. -69°C, b.p. 134°C, d 0.991)

2,4,6,8-tetramethylcyclotetrasiloxane (H•ls America, 95%) was used without purification.

3.3.14 Toluene (C₆H₅CH₃, FW 92.14, b.p.110.6°C)

Toluene (Fisher) was washed twice with concentrated sulfuric acid at room temperature, then several times with water until neutral, and predried with anhydrous magnesium sulfate and distilled over calcium hydride.

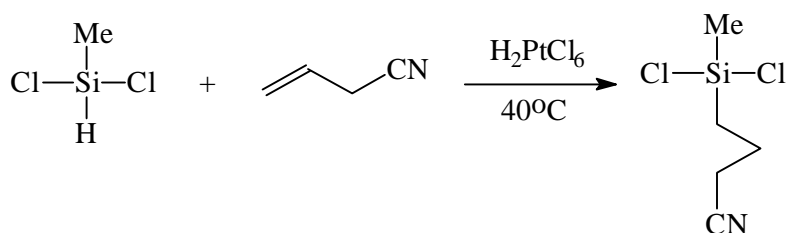
3.4 Preparation of Monomers and Initiators

3.4.1 3-Cyanopropylmethyldichlorosilane

3-Cyanopropylmethyldichlorosilane was prepared by hydrosilylation of methyldichlorosilane with allyl cyanide according to Scheme 3.1. A typical example is provided below.

A 3000 ml two-neck flask was equipped with a condenser, magnetic stirrer, a thermocouple and a septum, and the top of the condenser was linked to a drying tube filled with Drierite. The flask was charged with 200 ml (166 g, 2.47 mol.) dried allyl cyanide, 30 mg hexachloroplatinic acid (Aldrich, ACS grade) (as a catalyst), and 20 ml (16.7 g, 0.24 mol.) distilled methyldichlorosilane (Aldrich, 97%). The flask was gently heated to about 40°C until the hydrosilylation reaction had begun (noted by a slight temperature increase). Then 258 ml (215 g, 3.2 mol.) distilled methyldichlorosilane was added in 20 ml aliquots. Each increment was added following complete reaction of the former (noted by temperature decrease). Complete reaction of

methyldichlorosilane was confirmed by the disappearance of the Si-H IR absorbance at about 2150 cm^{-1} . After all the dichloromethylsilane had been added, the system was refluxed for half an hour. The condenser and the drying tube were replaced by a distillation assembly. The mixture was fractionally distilled and 3-cyanopropylmethyldichlorosilane was collected at $79^\circ\text{C}/1\text{ Torr}$, and stored in a septum capped dry container for future use. A typical reaction yield is 95%. ^1H NMR: δ 0.78 ppm, singlet, 3H; δ 1.2 ppm, multiple peaks, 2H; δ 1.83 ppm, multiple peaks, 2H; δ 2.21 ppm, multiple peaks, 2H.



FW 182°C , b.p. $79^\circ\text{C}/1\text{ torr.}$, d 1.27

Scheme 3.1 Preparation of 3-cyanopropylmethyldichlorosilane by hydrosilylation.

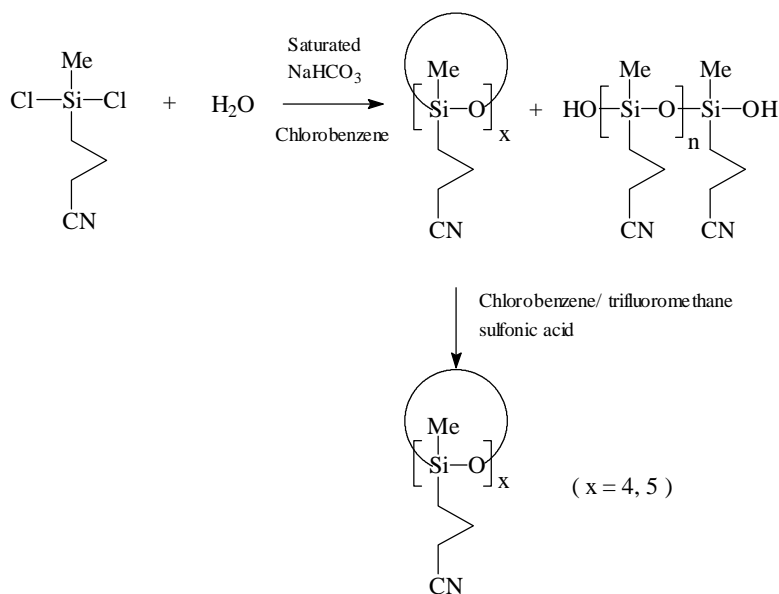
3.4.2 3-Cyanopropylmethylcyclosiloxanes (D_xCN)

3.4.2.1 Hydrolysis of 3-Cyanopropylmethyldichlorosilane

D_xCNs were prepared by heterogeneous hydrolysis of 3-cyanopropylmethyldichlorosilane, followed by cyclization of linear polysiloxanes and equilibration of D_xCNs (Scheme 3.2). A typical procedure is provided below.

A 2000 ml two-neck flask equipped with a mechanical stirrer was charged with 145 ml (177 g, 0.97 mol.) 3-cyanopropylmethyldichlorosilane and 450 ml chlorobenzene (Fisher). 1500 ml sodium bicarbonate slurry (including $\sim 150\text{ g NaHCO}_3$) was added to the rapidly stirring D_xCNs solution within 10-20 minutes. The hydrolytic products, cyclic and linear polysiloxanols, were extracted into the chlorobenzene phase. The chlorobenzene phase was washed several times with deionized water until neutral, then dehydrated by azeotropic distillation at 70°C using an

inverse Dean-Stark trap until the solution was clear. Then 1 ml trifluoromethanesulfonic acid (Aldrich, 99.9%) was added as a catalyst, and the mixture was refluxed for another 6-7 hours. The linear polysiloxanes were cyclized and the cyclics were equilibrated so that the major cyclics in the mixture were D₄CN (~ 60%), D₅CN (30%) and D₆CN (2-5%). After washing several times with deionized water to remove the acid catalyst, chlorobenzene was removed by vacuum distillation (using a Rotavapor). D_xCNs were distilled at 220-280°C/0.1 Torr. Various extents of rearrangement of cyclic siloxanes occurred during distillation. The major components after distillation were D₃CN, D₄CN and D₅CN, but the tetramer still contributed ~60% of the cyclics. ²⁹Si NMR for the distillate: δ -9.7-9.8 ppm, three peaks; δ -20.4 - -20.9 ppm, multiple peaks, tetramer; δ -22.6 - -23.1 ppm, multiple peaks, pentamer. ¹H NMR for the distillate: δ ~0.22 ppm, multiple peaks, 3H; δ ~0.7 ppm, multiple peaks, 2H; δ ~1.69 ppm, multiple peaks, 2H; δ ~2.38 ppm, multiplets, 2H.



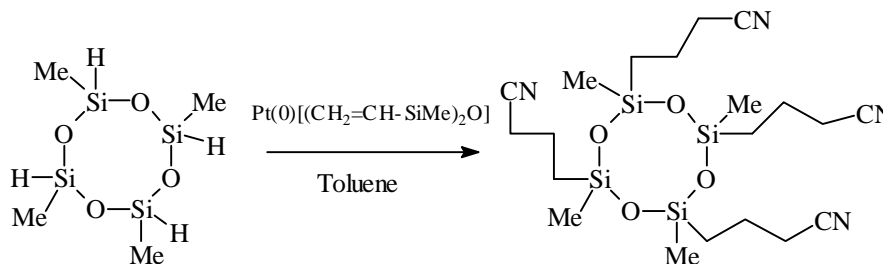
b.p. 220-280°C/ 0.1 torr., d 1.027

Scheme 3.2 Preparation of D_xCN through hydrolysis of 3-cyanopropylmethylchlorosilane

3.4.2.2 Hydrosilylation of Hydrogenmethylcyclsiloxanes (D_xH)

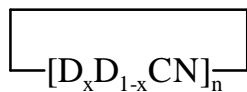
Pure D_xCN s ($x=3, 4, 5\dots$) may be prepared by hydrosilylating related D_xH ($x=3, 4, 5\dots$) with allyl cyanide. Here is an example for preparation of D_4CN .

A dry 500 ml two-neck flask was equipped with a condenser and a magnetic stirring bar. The top of the condenser was linked to a drying tube filled with Drierite and another neck of the flask was capped with a rubber septum. To the flask were charged 50 ml (49 g, 0.20 mol.) D_4H (Gelest, 95%), 100 ml purified toluene, 80 ml (66 g, 1 mol.) purified allyl cyanide and 0.2 ml $Pt(0)$ -1,3-divinyl-1,1,3,3-tetramethyldisiloxane (H•ls America). The mixture was refluxed for 24 hours; then toluene was removed and D_4CN was recovered at 250-280°C/0.5-0.1 torr (yield ~130 g, 90%). No obvious ring rearrangement occurred during distillation. However, about 8.6% Si-H bonds were hydrolylated by the Markownikoff way which gives 1-cyanoisopropyl substituted ($NCCH_2(CH_3)CH-$) products. It was for this reason that D_xCN s prepared by hydrosilylation of D_xH were not used for preparing triblock copolymers.



Scheme 3.3 Preparation of D_4CN by hydrosilylation of tetramethylcyclotetrasiloxane

3.4.3 Random Cyclic PDMS/PCPMS



$$x = 0-1, n \geq 3$$

Random cyclic PDMS/PCPMSs were prepared as starting materials for random copolymer of PDMS and PCPMS. The random copolymer was used as a contrast for the block copolymers in ^{29}Si NMR analyses.

Random cyclics of PDMS/PCPMS ($x = 0.5$, $n \geq 3$) were prepared by hydrolyzing a mixture of 3-cyanopropylmethyldichlorosilane and dimethyldichlorosilane (molar ratio = 1:1) in toluene/saturated sodium bicarbonate (aqueous). The hydrolysates, including cyclics and linear polysiloxanols, were extracted into the toluene phase during the hydrolysis process. Then the hydrolysates were dehydrated, cyclized and equilibrated similarly to 3-cyanopropylmethylsiloxane.

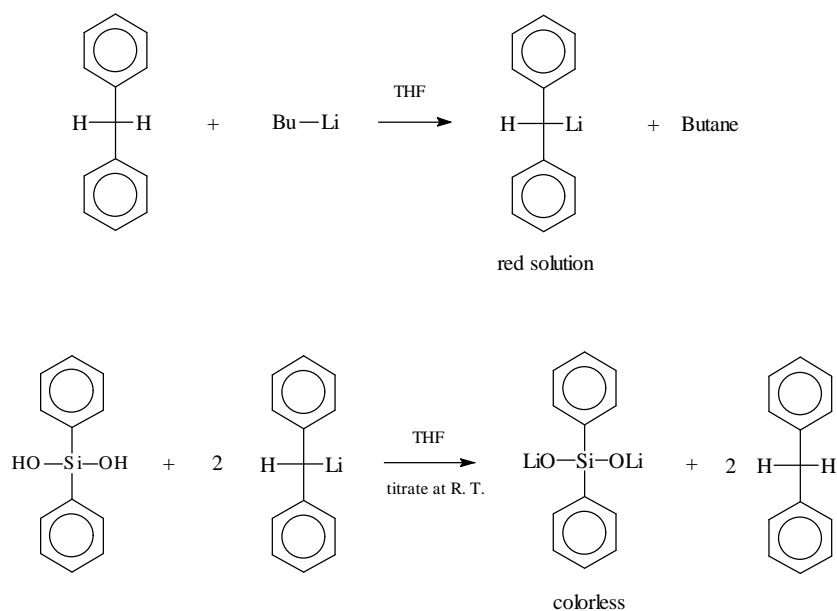
3.4.4 Dilithium diphenylsilanediolate

3.4.4.1 Synthesis

DLDPs were prepared by deprotonating diphenylsilanediol with diphenylmethyl lithium. The diphenylmethyl lithium was prepared by deprotonation of diphenylmethane using butyllithium (Scheme 3.4). Given below is a procedure for preparing DLDPs. Many chemicals in this experiment are highly sensitive to air and moisture, so containers and flasks were capped with septa and flame dried before use, liquids were transferred with double-tip needles or syringes. For safety, the flask reactor was linked to the atmosphere through a bubbler and slowly purged with dry nitrogen so that the inner pressure was close to 1 atmosphere.

A 250 ml one-neck flask with a magnetic stirring bar was charged with 100 ml anhydrous tetrahydrofuran, 14 ml purified diphenylmethane (14 g, 0.083 mol.) and 43 ml (0.069 mol.) 1.6M butyllithium solution (Aldrich, in hexane). After 2 hours, a dark red solution was obtained. A diphenylsilanediol solution was prepared by dissolving 10 g recrystallized diphenylsilanediol in 40 ml anhydrous tetrahydrofuran. Diphenylmethyl lithium solution 10 ml was saved in a small dry container for back-titration. The diphenylmethyl lithium solution was titrated with the diphenylsilanediol solution until the mixture was colorless; then it was back titrated with diphenylmethyl lithium until the solution was pale red so that diphenylmethyl lithium was slightly in excess. The mixture was left undisturbed for 24 hours to allow DLDPs to precipitate (DLDPs

crystallizes very slowly). Then the suspension was transferred to four 100 ml septa capped centrifuge tubes. The dilithium diphenylsilanediolate precipitate was washed in turn by anhydrous tetrahydrofuran, anhydrous dichloromethane and anhydrous tetrahydrofuran again. Separation was carried out in a centrifuge and redispersion was done by ultrasonic agitation. The purified DLDPS was stored as a suspension in dichloromethane, and the concentration of DLDPS was determined by titration in isopropanol with standardized hydrochloric acid before use.



Scheme 3.4 Preparation of DLDPS

3.4.4.2 DLDPS as a Difunctional Initiator

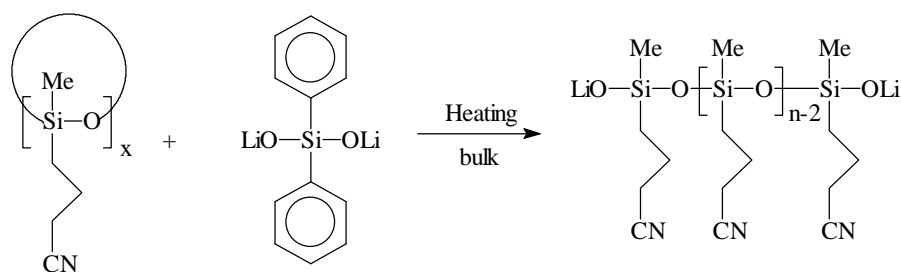
A PDMS was prepared using DLDPS as an initiator to simulate the reaction conditions which would be used in preparing the desired triblock copolymers.

A dry one-neck flask with a stirring bar was capped with a septum, flame dried and purged with dry nitrogen. The flask was charged with 50 ml D_3 solution (16 g D_3 in dichloromethane) and 5 ml tri(ethylene glycol) dimethyl ether as a promoter. Then 4.0 ml DLDPS suspension (0.87 mmol. in dichloromethane) was added to the flask as an initiator. Since DLDPS dissolved

catalyst and a chain stopper. A procedure is provided for preparing 2.5k PCPMS macroinitiator. Since instruments like GPC and endgroup analyses could not provide accurate molecular weights for the macroinitiators, the nomenclature refers to the $D_x\text{CN}$ -to-DLDPS ratio (g/mol.). Other macroinitiators were similarly prepared using different $D_x\text{CN}$ -to-DLDPS ratios. This reaction is sensitive to moisture, so all flasks were capped with septa, flame-dried and purged with dry nitrogen before use, and liquids were transferred with syringes.

A one-neck flask with a magnetic stirrer was charged with 10 ml (10 g) $D_x\text{CN}$ and 0.004 mol DLDPS (monomer/initiator = 2.5 kg/mol). The DLDPS was added as a suspension in dichloromethane. After the reactants had mixed for 2 hours at room temperature, dichloromethane was removed by vacuum distillation. Then the flask was placed in an isothermal oil bath set at 97-103°C for 48 hours to equilibrate the cyclics. The conversion of cyclic monomer in this reaction was 76%.

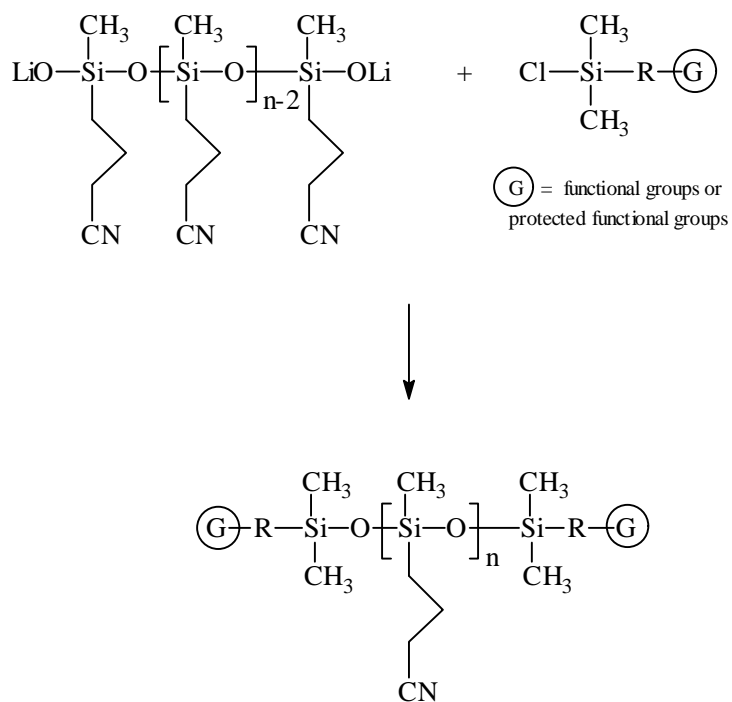
Apart from being used as macroinitiators, PCPMS macroinitiators can be terminated with various functional chlorosilanes to form α,ω -difunctional PCPMS oligomers (Scheme 3.7). α,ω -divinyl PCPMSs were prepared by terminating PCPMS macroinitiators with vinyltrimethylchlorosilane and used for characterizing the precursor macroinitiators (Section 4.4).



Scheme 3.6 Preparation of PCPMS macroinitiators by equilibrating mixtures of $D_x\text{CN}$ s and DLDPS

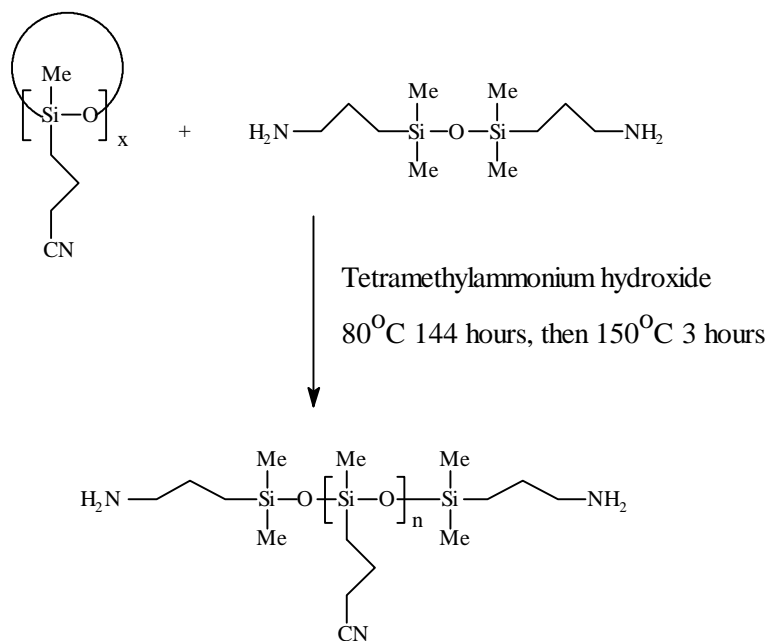
Table 3.1 Formulation of PCPMS macroinitiators

Monomer/initiator (g/mol.)	D _x CN (g)	Li ₂ O ₂ SiPh ₂ (mmol.)
2.5k	10	4.0
4k	10	2.5
5k	10	2.0
7.5k	10	1.33
8k	10	1.25
10k	10	1.0
15k	10	0.67
20k	10	0.50

Scheme 3.7 Preparation of α,ω -difunctional PCPMSs

3.4.6 α,ω -Bis(aminopropyl) PCPMS

A one-neck flask with a magnetic stirring was capped with septa and flamed dried according to the description in Section 3.2. The flask was charged with 10.8 g D_xCN ($x=3-5$), 1.2 g 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane (monomer/chain stopper = 10 kg/mol.) and 4.3 mg (0.024 mmol) TMAH \cdot 5H $_2$ O. The mixture was stirred at room temperature for 2 hours and the flask was evacuated to 1 Torr to remove crystal water brought in along with the catalyst. The crystal water can lower the final molecular weight of the polymer. The flask was placed in an isothermal oil bath ($T = 78-82^\circ\text{C}$). After 48 hours, the equilibrium was heated to 150°C , and purged with dry nitrogen to decompose the catalyst and remove the resultant trimethylamine.



Scheme 3.8 Preparation of α,ω -bis(3-aminopropyl) PCPMSs

3.4.7 Random Copolymer of PDMS and PCPMS

A random copolymer of PDMS and PCPMS was prepared as a reference for ^{29}Si NMR studies of the corresponding block copolymers

A one-neck flask with a magnetic stirring bar was charged with 10 g mixed cyclics ($[\text{D}]/[\text{DCN}] = 0.5$), 0.21 ml (1.0 mmol.) hexamethyldisiloxane (chain stopper), and 18 mg (0.10 mmol.) TMAH \cdot 5H $_2$ O (catalyst). The flask was stirred at room temperature until the TMAH was dissolved. After the mixture had been heated at 80°C for 48 hours, the equilibrium was heated at 150°C for 2 hours to decompose the catalyst, and purged with dry nitrogen and remove the resultant trimethylamine. Finally, the polymer was washed several times with toluene to remove unreacted cyclics, and dried under vacuum.

3.4.8 PDMS-*b*-PCPMS-*b*-PDMSs

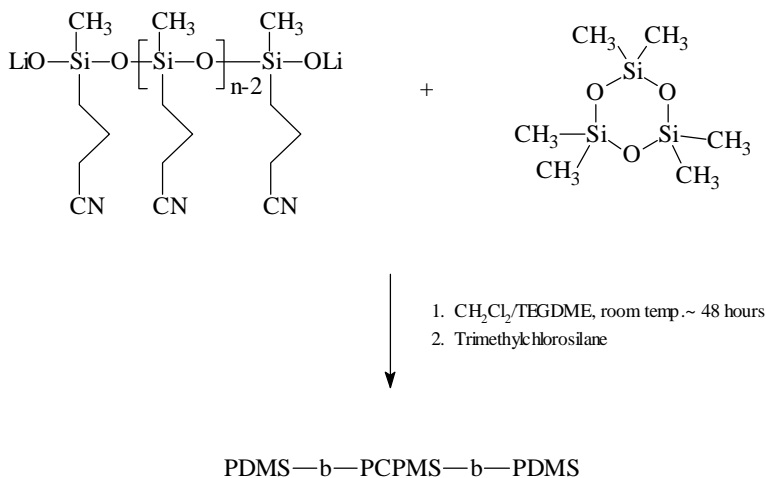
PDMS-*b*-PCPMS-*b*-PDMSs were made according to Scheme 3.8. The procedure provided below is for preparation of a 2.5k-2.5k-2.5k triblock copolymer. Other triblock copolymers were prepared by similar procedures but with different monomer-to-DLDPS ratios (Table 3.2). The nomenclature for block copolymers refers to the monomer-to-DLDPS ratio for each block. The actual molecular weights of these blocks were smaller because the conversions for the central block were about 76% and the conversion for the tail blocks were 80-86% (see chapter 4). These reactions are moisture sensitive, so reactors were capped with septa, flamed-dried and purged with dry nitrogen before use, and liquids were transferred by syringes.

2.5k PCPMS macroinitiator 10 g (containing 8.0 mmol lithium silanolate) was dissolved in 60 ml dry dichloromethane; then the solution was transferred to a dry 250 ml one-neck flask which contained 140 ml D $_3$ /dichloromethane solution (containing 20 g D $_3$), 20 ml dry tri(ethylene glycol) dimethyl ether (TEGDME) and a magnetic stirring bar. The mixture was stirred at room temperature for about 48 hours, then it was terminated with 1.5 ml (12 mmol.) purified trimethylchlorosilane. ^1H NMR indicated that the conversion of D $_3$ at this time was ~ 85%. After the solvent and residual trimethylchlorosilane were removed by vacuum distillation, the polymer was dissolved in a small amount of chloroform and re-precipitated into 200 ml methanol to

remove the promoter and nitrile containing cyclics; then it was dried at 80°C in a vacuum oven for 24 hours to remove residual solvents.

Table 3.2 Formulations of PDMS-b-PCPMS-b- PDMS triblock copolymers

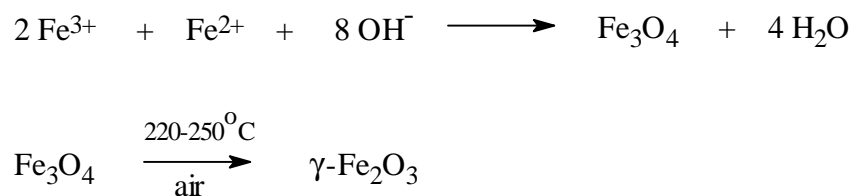
Triblock Copolymers	2.5k-2.5k-2.5k	4k-4k-4k	8k-8k-8k
Macroinitiators	10 g / 2.5 k	10 g / 5k	10 g /10k
D ₃	20 g	20 g	20 g
TEGDME	20 ml	20 ml	20 ml
Total Volume	180 ml	180 ml	180 ml
Me ₃ SiCl	1.5 ml	0.95 ml	0.47 ml



Scheme 3.9 Preparation of PDMS-b-PCPMS-b-PDMSs

3.4.9 γ -Fe₂O₃ Powder

γ -Fe₂O₃ nanometer powder was prepared by oxidizing Fe₃O₄ powder in air at 220-250° (Scheme 3.10), and the Fe₃O₄ powder was precipitated from a mixed solution of FeCl₃ and FeCl₂ (Fe³⁺:Fe²⁺ = 2 : 1) using ammonium hydroxide.



Scheme 3.10 Preparation of γ -Fe₂O₃ powders

A mixed solution of iron salts was prepared by dissolving 34 g FeCl₂·4H₂O (Aldrich 99%) and 90 g FeCl₃·6H₂O (Aldrich 97%) in 500 ml deionized water. An ammonium hydroxide solution was prepared by dissolving 126 ml 30 % ammonium hydroxide (Aldrich ACS reagent) in 1000 ml deionized water. The solution of iron salts was slowly added to strongly stirring ammonium hydroxide solution, and Fe₃O₄ black precipitate formed immediately. After adding all iron chloride solution, the reaction container was left undisturbed for several hours to allow Fe₃O₄ to settle. The Fe₃O₄ precipitate was washed three times with deionized water to remove ammonium chloride, and placed in a mortar and dried at 120-150°C. The dried Fe₃O₄ was ground to a powder first, then oxidized to γ -Fe₂O₃ at 220-250°C. Transformation of Fe₃O₄ to γ -Fe₂O₃ was readily indicated by a change of color from black to red. Fig. 5.1 shows a TEM picture for γ -Fe₂O₃ powder. The average particle size of γ -Fe₂O₃ is about 100•.

3.4.10 Suspensions of γ -Fe₂O₃ in Octamethylcyclotetrasiloxane

Suspensions of γ -Fe₂O₃ in D₄ were prepared according to the formulations in Table 3.3. A suspension without triblock copolymer stabilizer was also prepared as a reference. Ultrasonic

agitation was used to disperse $\gamma\text{-Fe}_2\text{O}_3$ particles in the D_4 dispersion medium. Note the names of the stabilizers were also used as the names for the suspensions.

Table 3.3 Formulation for suspensions of $\gamma\text{-Fe}_2\text{O}_3$ in D_4

Sample name	2.5k-2.5k-2.5k	4k-4k-4k	8k-8k-8k	Reference
D_4 (ml)	10	10	10	10
$\gamma\text{-Fe}_2\text{O}_3$	2	2	2	2
Stabilizers (g)	2	2	2	0

3.5 Characterization

3.5.1 ^1H NMR

All ^1H NMR spectra were obtained on a Varian Unity 400 NMR spectrometer, and the NMR instrument was operated (with 5 mm multinuclear probe) at 399.9 MHz with a sweep width of 5000 Hz and a 22° pulse with a width of 4.1 μs . For simple compounds, CDCl_3 was used as a solvent and sample concentrations were in the range of 1 - 10%. For diphenylsilanediol, CD_3COCD_3 was used since the silanediol is insoluble in CDCl_3 . For endgroup analyses of PCPMSs, CDCl_3 was used as a solvent, but the sample concentrations were increased to 20-30% to improve the signal-to-noise ratio of the endgroups. Some kinetic studies of polymerizations of D_3 were carried out in CD_2Cl_2 to simulate the reaction conditions used for preparing the triblock copolymers.

3.5.2 ^{13}C NMR

All qualitative and quantitative ^{13}C NMR and DEPT (Distortionless Enhancement by Polarization Transfer) experiments were performed on a Varian 400 NMR spectrometer and the NMR instrument was operated at 100.6 MHz with a sweep width of 25000.0 and a 90° pulse with a width of 12.3 μs . Samples were dissolved in CDCl_3 with sample concentrations in the range of

10-15%. For quantitative ^{13}C NMR, the nuclear Overhauser effect (NOE) was minimized by gated decoupling. Tris(acetylacetonato)chromium (III) ($\text{Cr}(\text{acac})_3$, 1×10^{-2} - 3×10^{-2} M) was added in some cases to decrease spin-lattice relaxation times (T_1). The relaxation delay time in quantitative ^{13}C NMR was set to five times T_1 for each sample. Quantitative ^{13}C NMR and DEPT spectra were kindly acquired by Mr. Tom Glass.

3.5.3 ^{29}Si NMR

All ^{29}Si NMR were collected on a Varian 400 NMR spectrometer operated at 79.46 MHz with a spectral width of 25000.0 Hz, 90° pulse with a width of 25 μs . Samples were dissolved in CDCl_3 and the sample concentrations were in the range of 10-20 wt%. For R_3SiH , the spin-lattice relaxation time (T_1) is in the range of 10-45 seconds and negative nuclear Overhauser effect (NOE) is in the range of $-0.3 \sim -2.24 \eta$. For silanes without hydrogen substituent, T_1 s are in the range of 35-100 seconds while NOE is in the range of $-0.21 \sim -2.42 \eta^{113}$. Thus $\text{Cr}(\text{acac})_3$ was added to decrease T_1 and minimize NOE. With $1 \sim 3 \times 10^{-2}$ M $\text{Cr}(\text{acac})_3$, the T_1 was generally less than a few seconds. During experiments, the relaxation delay was set to five times as large as T_1 . General conditions were:

$[\text{Cr}(\text{acac})_3] = 1 \times 10^{-2}$ M, Relaxation time was 11 seconds

Acquisition time 1.19 seconds, No of repetitions 200

Quantitative ^{29}Si NMR results were kindly collected by Mr. Tom Glass.

3.5.4 Gel Permeation Chromatography (GPC)

All gel permeation chromatograms were acquired with a Waters 490 Instrument with a set of $500 \cdot$, $10^3 \cdot$, $10^4 \cdot$ and $10^5 \cdot$ ultrastryragel columns at 30°C with flow rate at 1 cm/min. A reflective index detector (Viscotek Laser Refractometer) and a viscosity detector (Viscotek Model 100) were linked in parallel for sample detection. Polystyrene standard samples were used to establish a universal calibration curve. Samples were prepared by dissolving 20-40 mg samples in 10 ml HPLC grade chloroform. The sample solutions were filtered through a 0.45μ filter

¹¹³ E. A. Williams, Annual Reports on NMR Spectroscopy, **15**, 281, Academic Press, London (1983)

before loading into the GPC autosampler. GPC results were kindly acquired by Mr. J. Mecham and Dr. Qing Ji.

3.5.5 Supercritical Fluid Chromatography (SFC)

All supercritical fluid chromatograms were acquired on an HP G1205A SFC system with a nitrogen chemiluminescent detector Model 705D CLND from ANTEK Instruments Inc.. Given below are the experimental conditions:

Column: Delta-bond phenyl (Particle Size 5 μm , 250 \times 4.6 mm);

Methanol modifier concentration: from 5 vol% to 14 vol% at 1 vol%/min;

Pressure: 150 atm for 2 min, then ramp to 250 atm/min at 15 atm/min, then hold constant;

Liquid CO₂ flow: 2.0 ml/min;

Sample solvent: chloroform;

Total sample concentration: 5-10 mg/ml

All SFC results were acquired by Ms. Heng (Rose) Shi.

3.5.6 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry was conducted using a DuPont 2400 Instrument and aluminum crucibles. Samples (8-20 mg) were quickly quenched to liquid nitrogen temperature then scanned from -130°C to 0°C. All scanning rates were 10°C/min. Each sample was scanned twice and no obvious differences were found between the first and the second scan. DSC measurements were acquired by Dr. Stephen Davis.

3.5.7 Intrinsic Viscosity Measurement

Intrinsic viscosity measurements were conducted with 50 ml Ubbelohde viscometers at 26°C in NMP.

3.5.8 Infrared Spectroscopy (IR)

IR spectra were acquired on a Nicolet Impact 400 Fourier transform infrared spectrometer. Potassium bromide plates were used as sample holders.

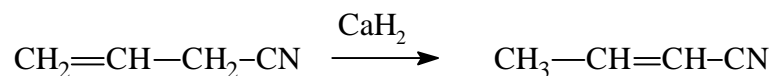
CHAPTER 4

RESULTS AND DISCUSSION

4.1 3-Cyanopropylmethyldichlorosilane

3-Cyanopropylmethyldichlorosilane was prepared by hydrosilylation via reaction of methyldichlorosilane with allyl cyanide in the presence of hexachloroplatinic acid catalyst. The hydrosilylation reaction is a well-known and versatile reaction used in organosilicon chemistry which involves addition of a silicon hydrogen bond to an unsaturated carbon carbon bond. Here are some main points for a successful synthesis of 3-cyanopropylmethyldichlorosilane.

Dimethylchlorosilane and allyl cyanide should be purified before use because these materials may contain sulfur or phosphorus containing impurities which may poison the hexachloroplatinic acid catalyst. Activated molecular sieves (Aldrich 5•) were found to be efficient drying reagents for allyl cyanide. Calcium hydride cannot be used because strong bases result in rearrangement of allyl cyanide to 1-cyanopropylene.



Freshly prepared hexachloroplatinic acid usually have poor activity due to the presence of an induction period. The catalyst can be activated at 40°C in the presence of a small amount of methyldichlorosilane. For this reason, hexachloroplatinic acid catalyst was often prepared several hours before use.¹¹⁴ Currently two mechanisms of hydrosilylation have been proposed for platinum catalysts. With the Speier catalyst (hexachloroplatinic acid in isopropanol) the catalyst is homogeneous, and the active species is a Pt(II) complex.¹¹⁵ However, with

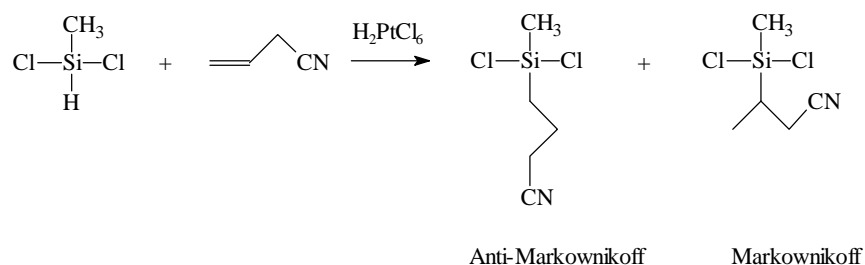
¹¹⁴ S. A. Smith, Master's Thesis, Blacksburg, VPI&SU (1991)

¹¹⁵ A. J. Chalk and J. F. Harrod, J. Amer. Chem. Soc., **87**, 16 (1965)

Pt(0)[((CH₂=CH)Si(CH₃)₂)₂O], the active species is colloidal platinum^{116,117} and the catalysis is heterogeneous.¹¹⁸ In general, the mechanism of hydrosilylation depends on reactants, catalyst, and the reaction conditions employed.

The hydrosilylation reaction is an exothermic and self-accelerating reaction. Thus, adding methylchlorosilane all at once can be disastrous, considering that the boiling point of methylchlorosilane is only 41°C. A safe way to conduct this experiment is to add methylchlorosilane in aliquots (each aliquot is about 10% of the volume of allyl cyanide). Before adding each aliquot, one should make sure previous dichloromethylsilane has been consumed. Complete reaction of dichloromethylsilane is confirmed easily by the disappearance of Si-H IR absorbance at about 2150 cm⁻¹.

The reaction yields almost exclusively the anti-Markownikoff product with typical yields of 90-95 %. The ¹H NMR for 3-cyanopropylmethylchlorosilane is given in Fig. 4.1.



¹¹⁶ L. N. Lewis and N. Lewis, *J. Amer. Chem. Soc.*, **87**, 16 (1965)

¹¹⁷ L. N. Lewis, *J. Amer. Chem. Soc.* **112**, 5998 (1990)

¹¹⁸ I. Ojima, *The Chemistry of Organic Silicon Compounds*, Wiley, New York, 1479 (1989)

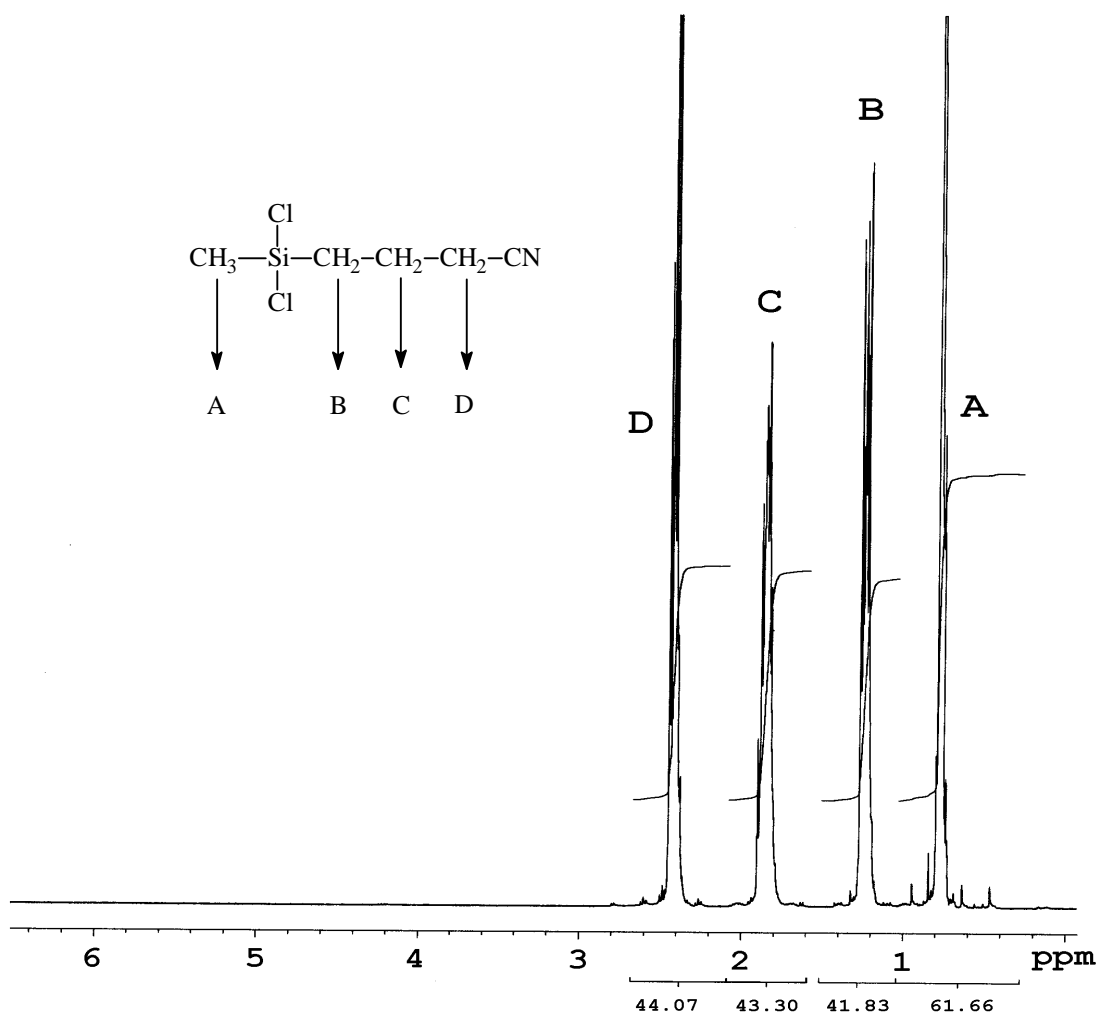


Figure 4.1 ¹H NMR for 3-cyanopropylmethyldichlorosilane

4.2 3-Cyanopropylmethylocyclosiloxanes (D_xCN, x = 3-6)

D_xCN (x = 3-6) can be prepared by hydrolysis of the dichlorosilane, or reactions of the dichlorosilane with zinc oxide or sodium bicarbonate, or hydrosilylation of hydrogenmethylocyclosiloxanes (D_xH) with allyl cyanide. The hydrolytic method is the commonest method in preparing cyclic polysiloxanes.

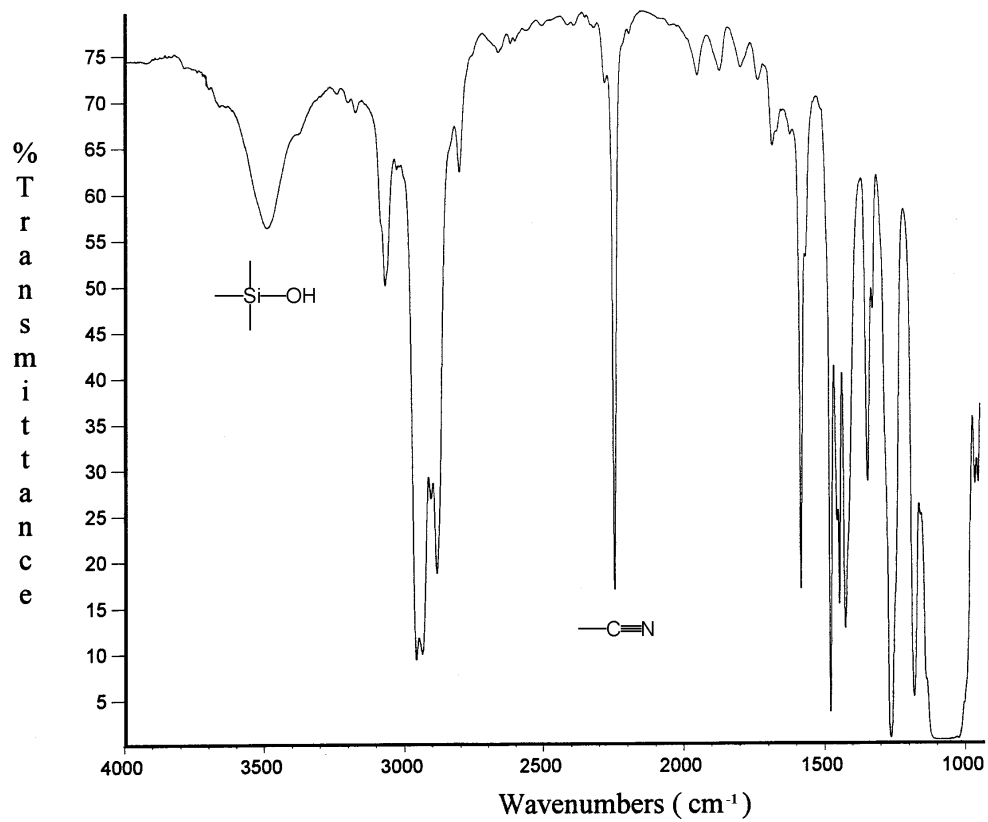
The hydrolysis was conducted heterogeneously in an inert solvent and saturated sodium bicarbonate. The hydrolysates, including cyclics and linear polysiloxanols, were extracted into the inert solvent. When trifluoromethanesulfonic acid, an equilibration catalyst, was added, the linear polysilanol were cyclized through intrachain condensations, and the cyclics were rearranged until an equilibrium distribution was reached. The principle for this redistribution is based on the fact that if the concentration of total siloxanes in a system is below the critical concentration, no linear siloxanes should coexist with the desired cyclic siloxanes.

The yield of the reaction depends highly on the solubility of polysiloxanols in the inert solvent. Toluene, 1,1,2,2-tetrachloroethane and chlorobenzene were used as the inert solvent in this reaction. The yields using these solvents are listed in Table 4.1.

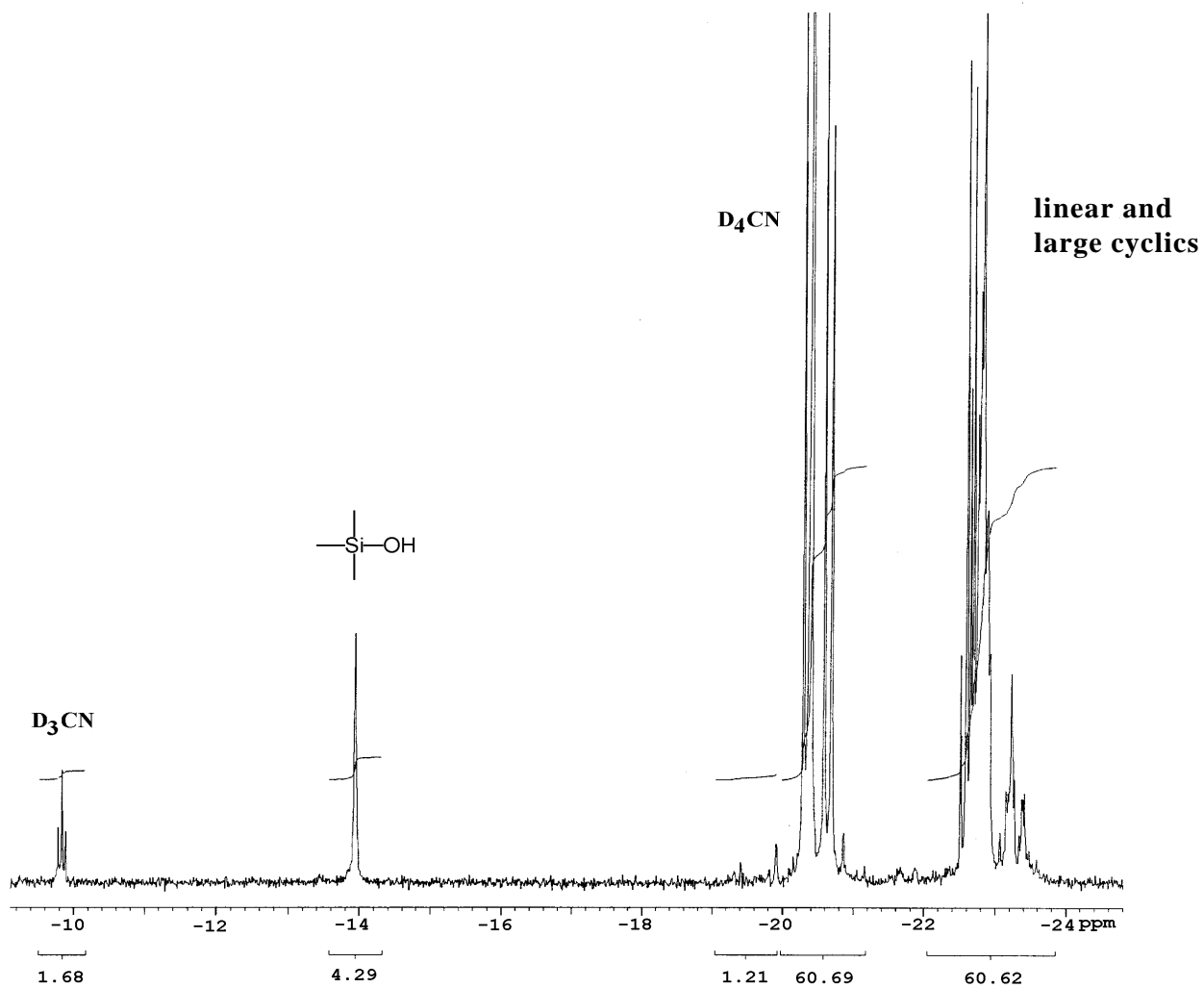
Table 4.1 Yields of D_x CNs by hydrolytic method using different inert solvents

Inert Solvent	Ratio of the solvent to the dichlorosilane	yield (%)
Toluene	3:1	45-55
1,1,2,2-Tetrachloroethane	3:1	85-95
Chlorobenzene	3:1	75-85

As expected, the hydrolysate in chlorobenzene included D_x CN ($x = 3-6$) and linear poly(3-cyanopropylmethylsiloxanol)s. The IR spectrum in [Fig 4.2](#) reveals the existence of silanols (broad adsorption at 3550 cm^{-1}) in the dehydrated hydrolysate in chlorobenzene. The ^{29}Si NMR spectrum in [Fig 4.3](#) also indicates that among the hydrolysate are small amounts of D_3 CN (δ -9 ppm), silanols (δ -14 ppm), and D_4 CN (δ -22 ppm). Cyclics with more than 4 siloxane units cannot be differentiated by ^{29}Si NMR due to the interferences from the linear siloxanes (δ -22.5~-23 ppm) and due to a lack of resolution.



[Figure 4.2](#) IR spectrum for the hydrolysate of 3-cyanopropylmethyldichlorosiloxane in chlorobenzene.



[Figure 4.3](#) ^{29}Si NMR spectrum of the hydrolysate of 3-cyanopropylmethylchlorosilane

The ^1H NMR spectrum for the equilibrated cyclics (Fig. 4.4) shows four signals for the four kinds of protons in D_xCNs , respectively. The ^{29}Si NMR (Fig. 4.5) further indicates that there are trace amounts of D_3CN , significant amounts of D_4CN (63.6 wt%) and D_5CN (29.1 wt%). The low equilibrium concentrations for D_3CN and macrocyclics are attributed their higher Gibbs free energies than small unstrained cyclics like D_4CN and D_5CN (see Section 2.3). The ^{29}Si NMR results are supported by supercritical fluid chromatograms (Fig. 4.6) which show D_3CN (two peaks at 3.9, 4.1 min, trace), D_4CN (two peaks at 5.1 and 5.6 min, 62 wt%), D_5CN (two peaks at 6.8 and 7.0 min, 30 wt%) and D_6CN (two peaks at 8.0 and 8.3 min, 3 wt%). The peak at 6.4 min is possibly due to an impurity because it disappears after distillation. The correspondence between ^{29}Si NMR and supercritical fluid chromatography (nitrogen chemiluminescence detector signal) also confirms that the nitrogen chemiluminescence signal is proportional to the weight concentration of the cyclics.

Multiple peaks for each cyclic species in the ^{29}Si NMR and SFC are due to isomers (Fig. 4.7). As reflected by the ^{29}Si NMR and SFC, D_3CN has two isomers, three nonequivalent Si atoms. While D_4CN has four isomers and six nonequivalent Si atoms, only 2 peaks appear in SFC and 4 peaks in ^{29}Si NMR. Fewer than expected isomers are observed for cyclics larger than D_4CN because of the limited resolutions of the instruments, similarities in some isomers and low concentrations of some sterically hindered isomers. Generally, as the cyclics become larger, the isomers become more similar, so only a few peaks may be separated by chromatography. Similarly, chemical shift differences of ^{29}Si due to cyclic isomerism become less indistinguishable as the size of cyclics increases.

The distribution of D_xCNs can change significantly during high temperature distillation. This is indicated by the ^{29}Si NMR spectra before (Fig. 4.5) and after distillation (Fig. 4.8) which show the concentration of D_3CN was increased from a trace to ~38.6 wt% while that of D_5CN dropped from 30 wt% to 1.5 wt%. Similar conclusions can be made by comparing SFC graphs before (Fig. 4.6) and after distillation (Fig. 4.9). The mechanism for the rearrangements of the cyclics is unclear. However, the high concentration of D_3CN after distillation can be accredited to its low boiling point relative to higher cyclics. As D_3CN was preferentially distilled from the

equilibrium cyclic mixture, more D_3CN formed through rearrangement of larger cyclics. Up to 38 wt% D_3CN had been distilled this way. This may provide a reasonable approach for D_3CN synthesis in the future.

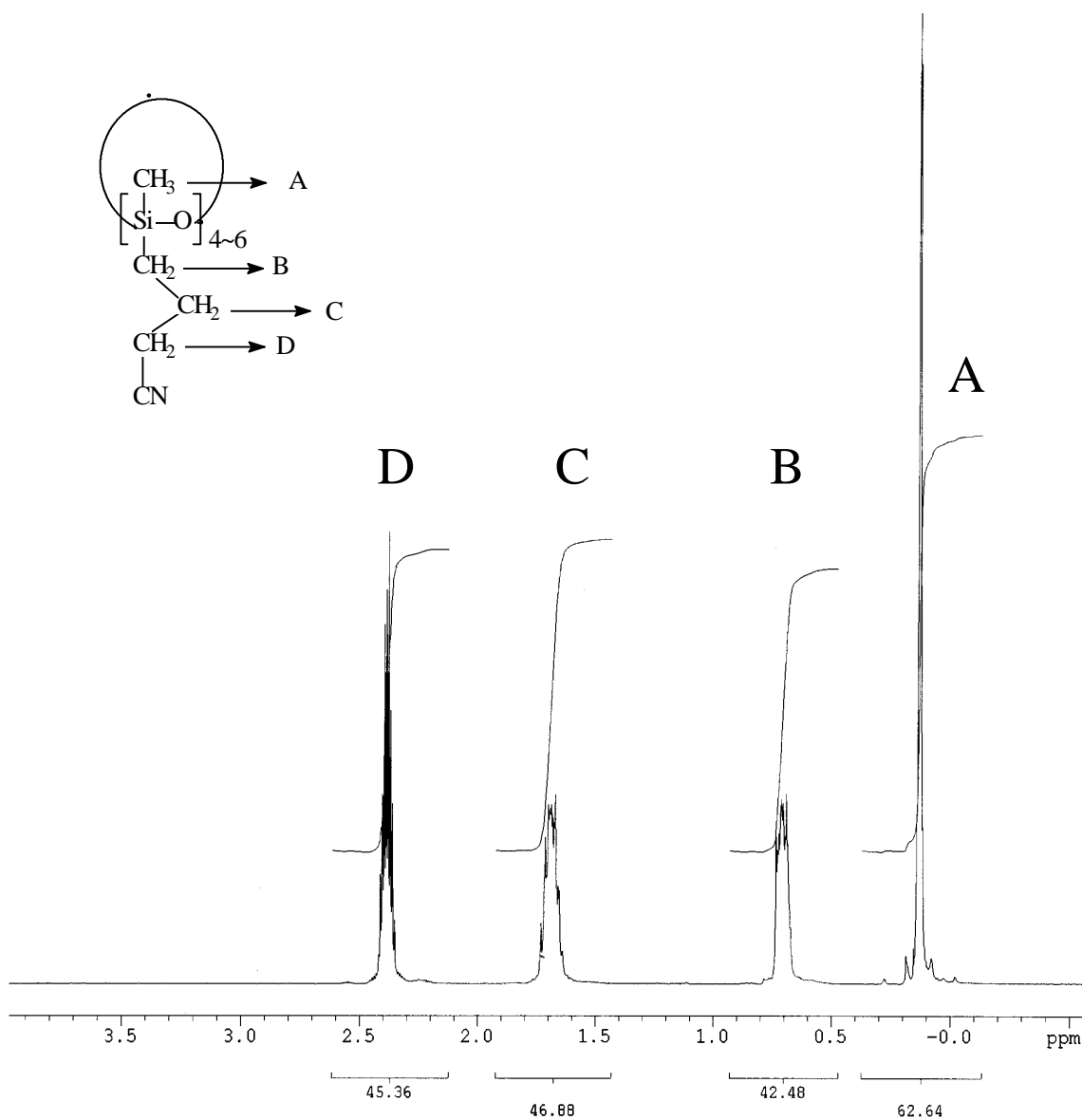
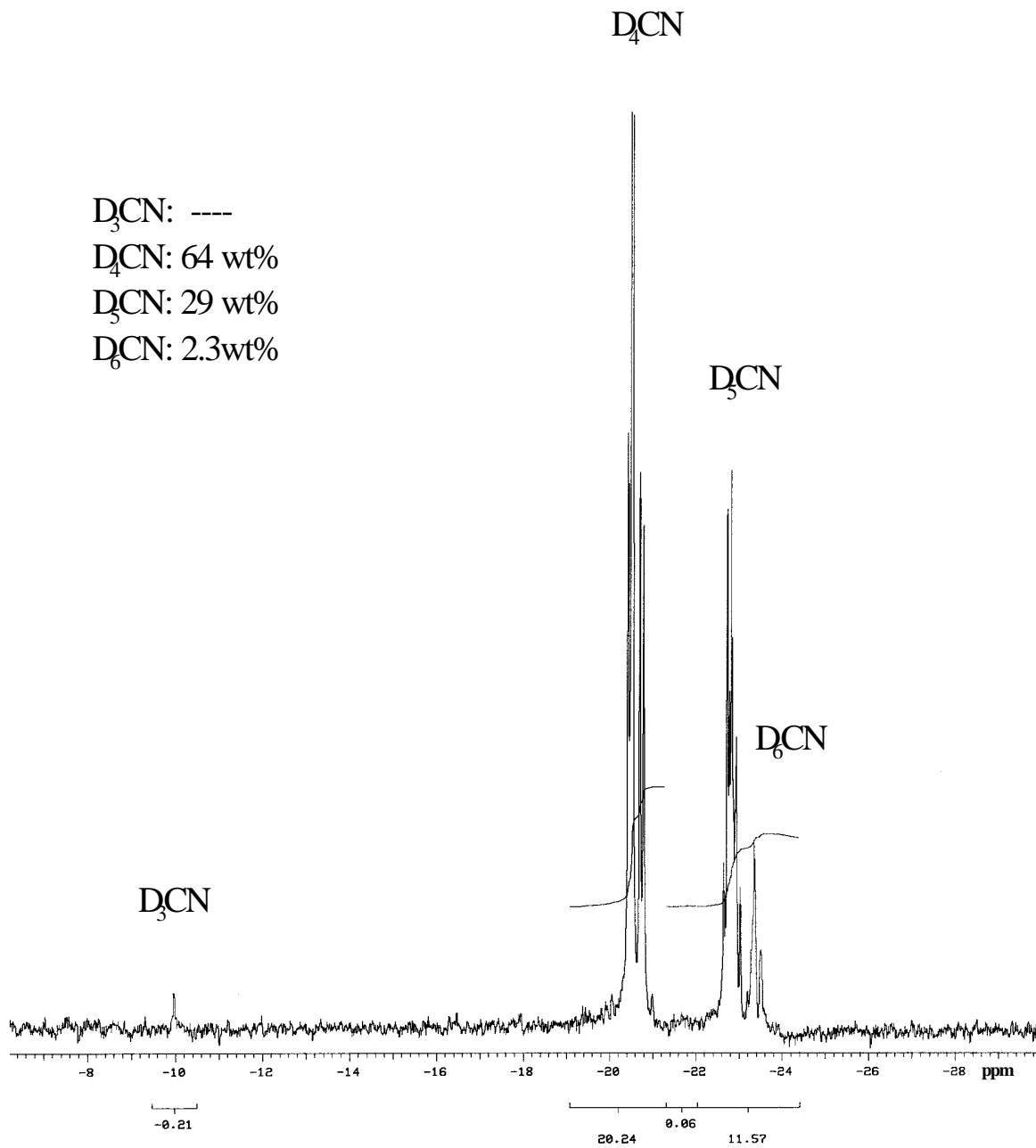
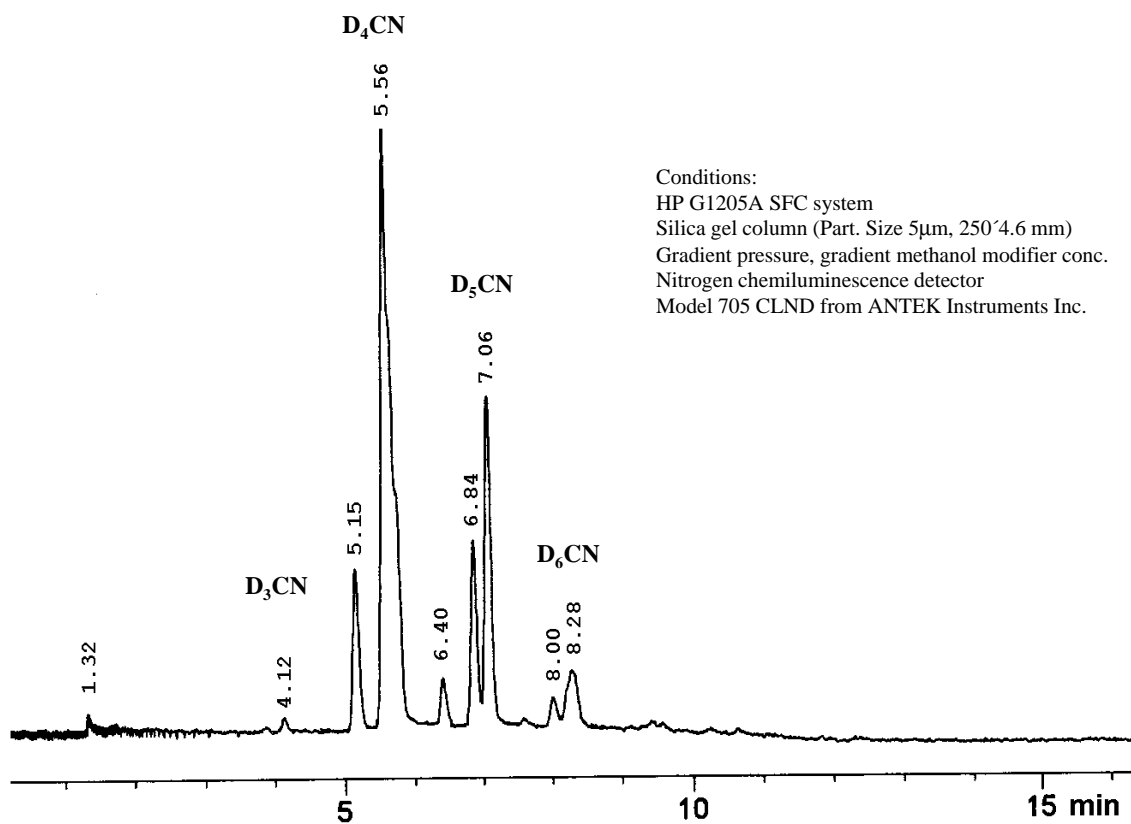


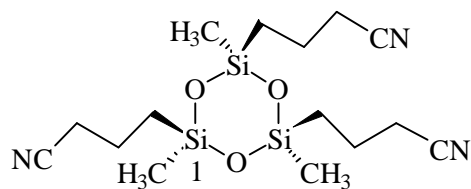
Figure 4.4 1H NMR spectrum for equilibrated D_xCN s



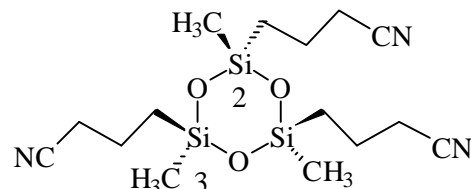
[Figure 4.5](#) ^{29}Si NMR spectrum for equilibrated D_xCNs



[Figure 4.6](#) Supercritical fluid chromatograms of equilibrated D_xCN s

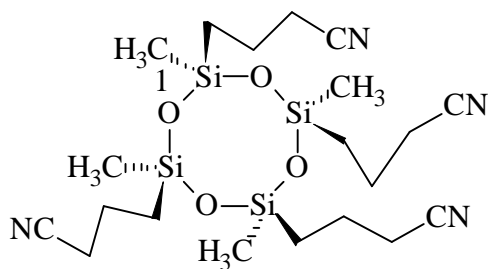


(I)

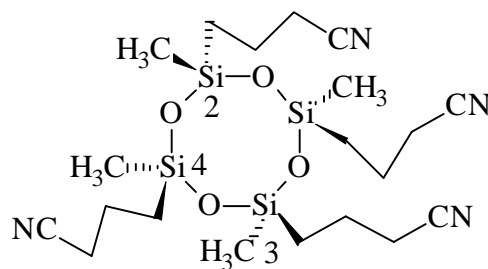


(II)

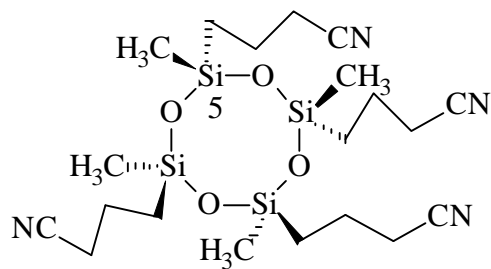
D₃CN has two isomers and three nonequivalent Si atoms



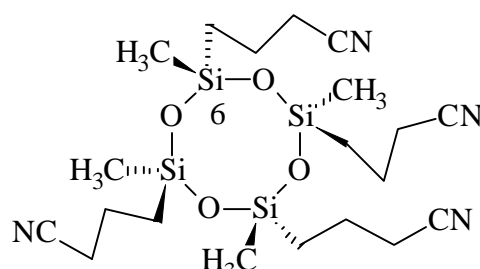
(1)



(2)



(3)



(4)

D₄CN has four isomers and six nonequivalent Si atoms

[Figure 4.7](#) Isomers of 3-cyanopropylmethylcyclosiloxanes

In addition to SFC and ^{29}Si NMR, ^1H NMR and ^{13}C NMR can also be used to differentiate D_3CN from larger cyclics. Listed in Table 4.2, 4.3 and 4.4 are chemical shifts for ^1H NMR, ^{13}C NMR and ^{29}Si NMR, respectively.



Table 4.2 Chemical shifts (δ ppm) for ^1H NMR of D_xCNs

Type of Protons	Si- <u>CH</u> ₃	Si- <u>CH</u> ₂ -	Si-CH ₂ - <u>CH</u> ₂ -	- <u>CH</u> ₂ -CN
D_3CN	0.14-0.17	0.72-0.76	1.62-1.74	2.32-2.40
$\text{D}_{x \geq 4}\text{CN}$	0.08-0.12	0.64-0.72	1.62-1.74	2.32-2.40

Table 4.3 Chemical shifts (δ ppm) for ^{13}C NMR of D_xCNs

Type of Carbons	Si- <u>CH</u> ₃	Si- <u>CH</u> ₂ -	Si-CH ₂ - <u>CH</u> ₂ -	- <u>CH</u> ₂ -CN
D_3CN	-1	19.1	17	20.5
$\text{D}_{x \geq 4}\text{CN}$	-1	19.5	17	20.5

Table 4.4 Chemical shifts (δ ppm) for ^{29}Si NMR of D_xCNs

D_3CN	-9.5	usually three peaks
D_4CN	-21-21.8	usually four peaks
$\text{D}_{x \geq 5}\text{CN}$	-22.7-23.0	multipeaks

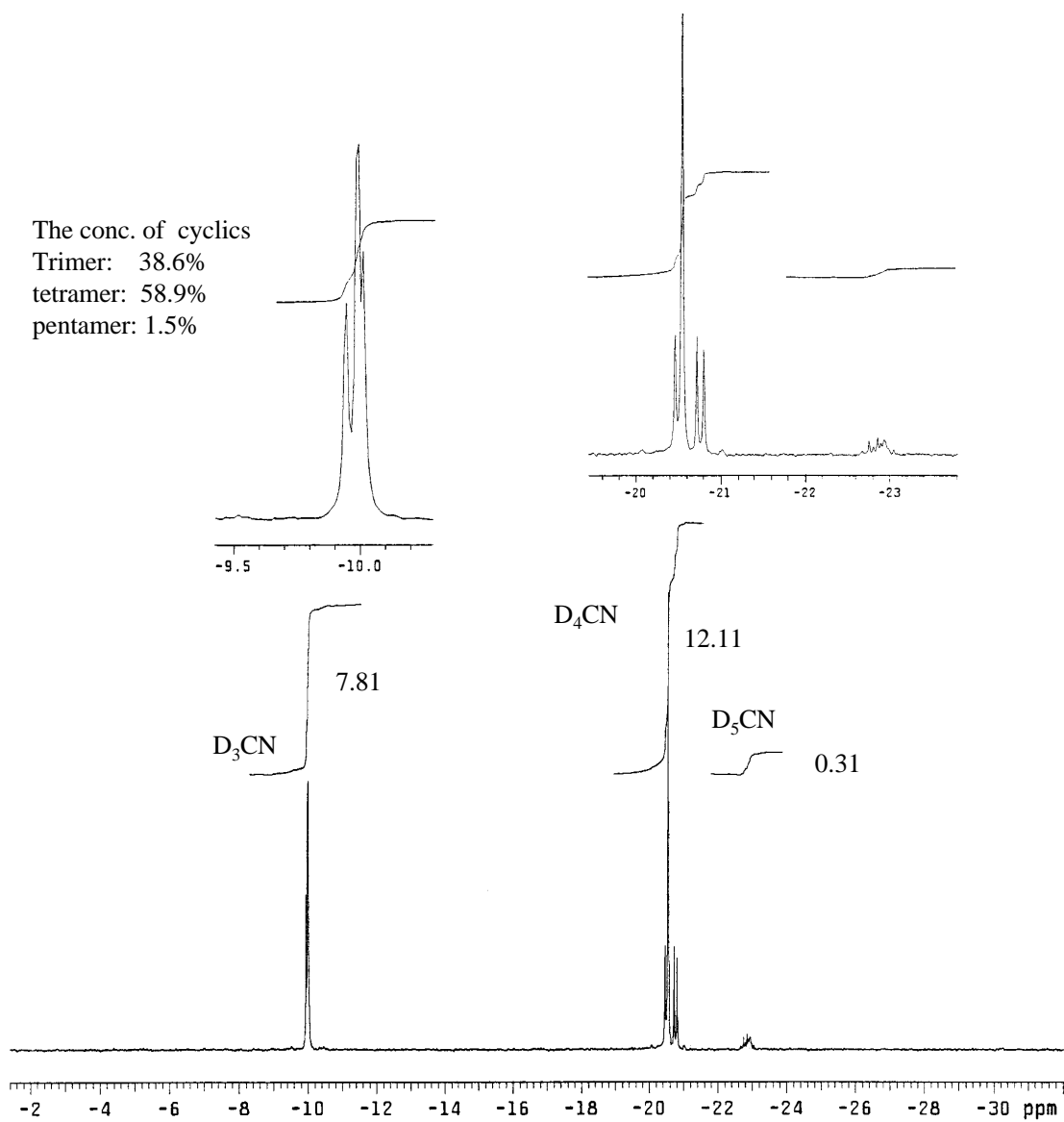
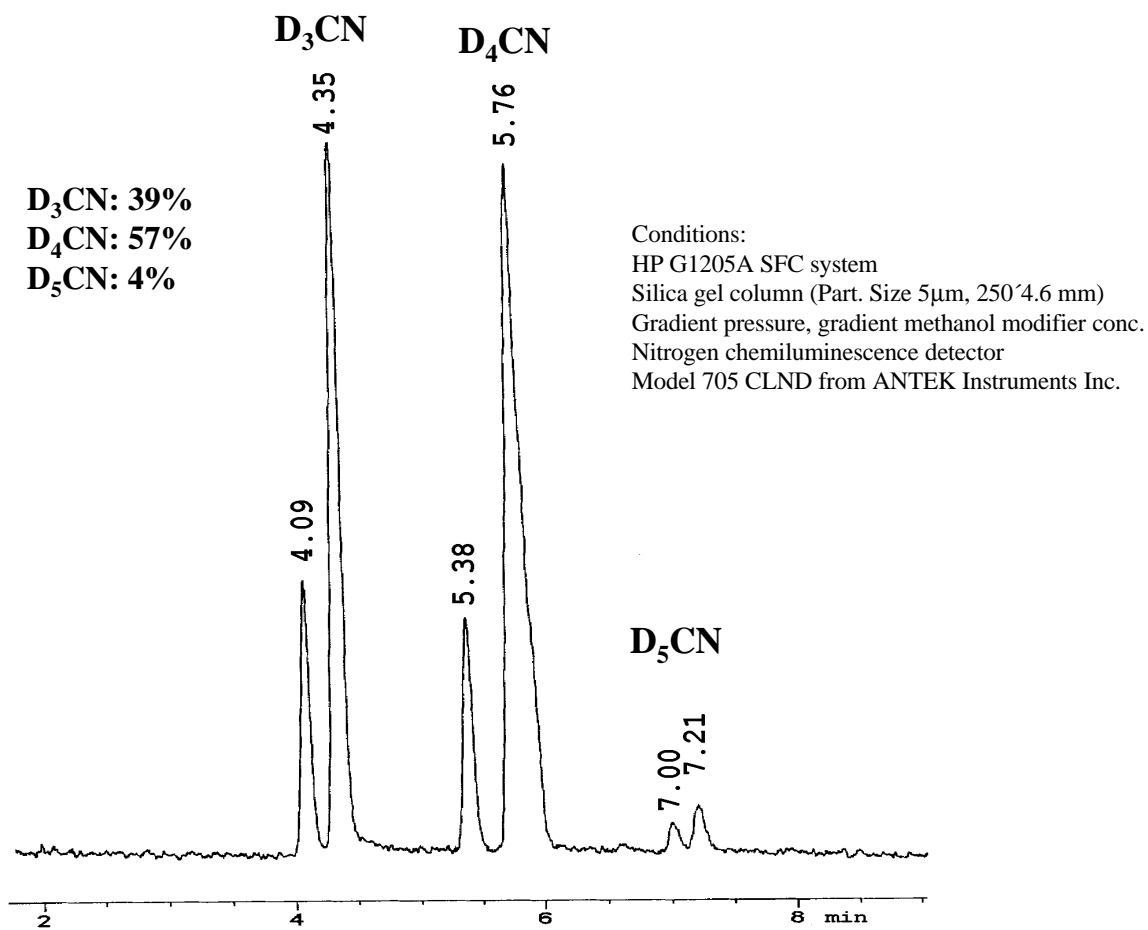
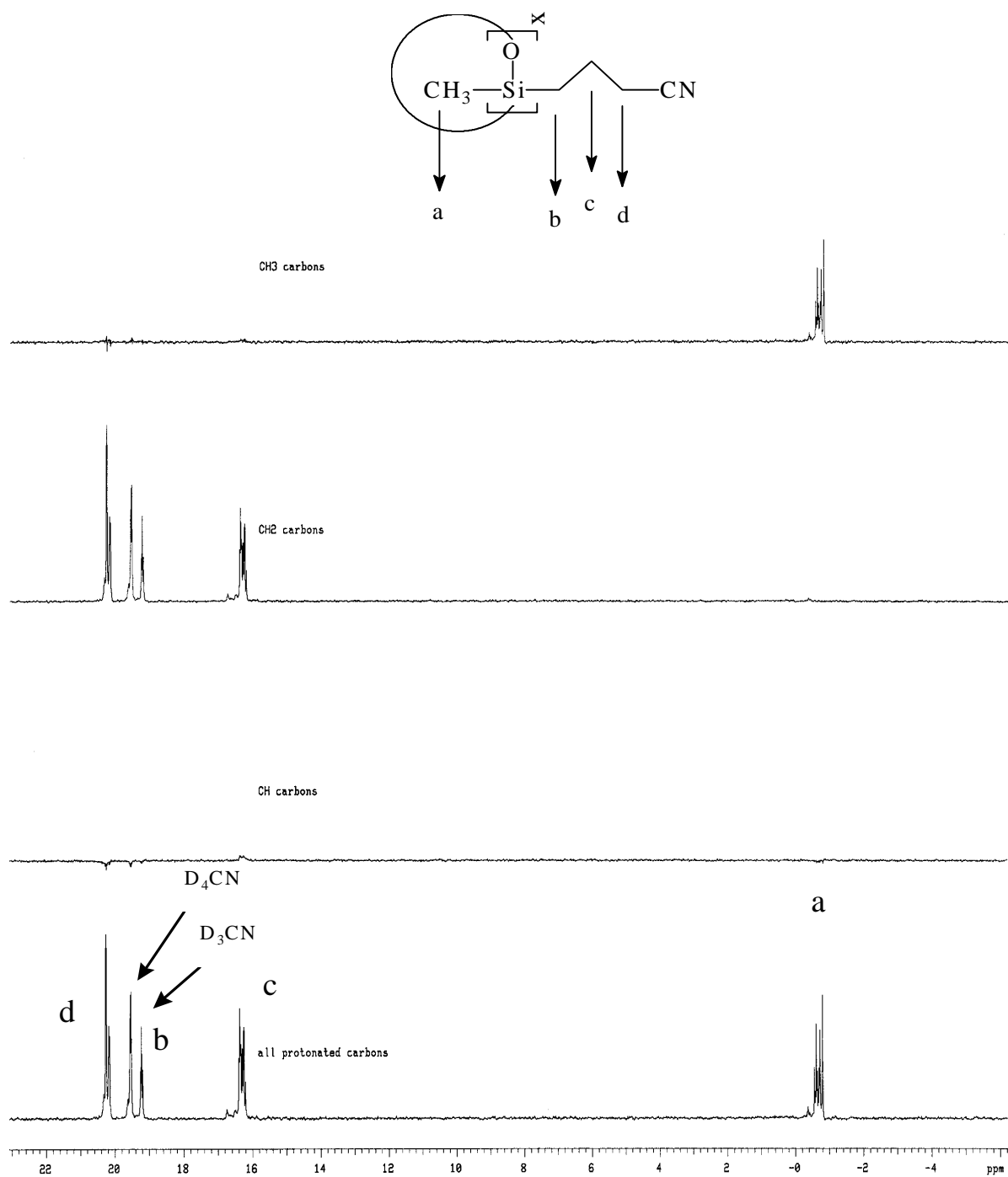


Figure 4.8 ^{29}Si NMR spectrum for distilled D_xCNs



[Figure 4.9](#) Supercritical fluid chromatogram for distilled D_xCNs

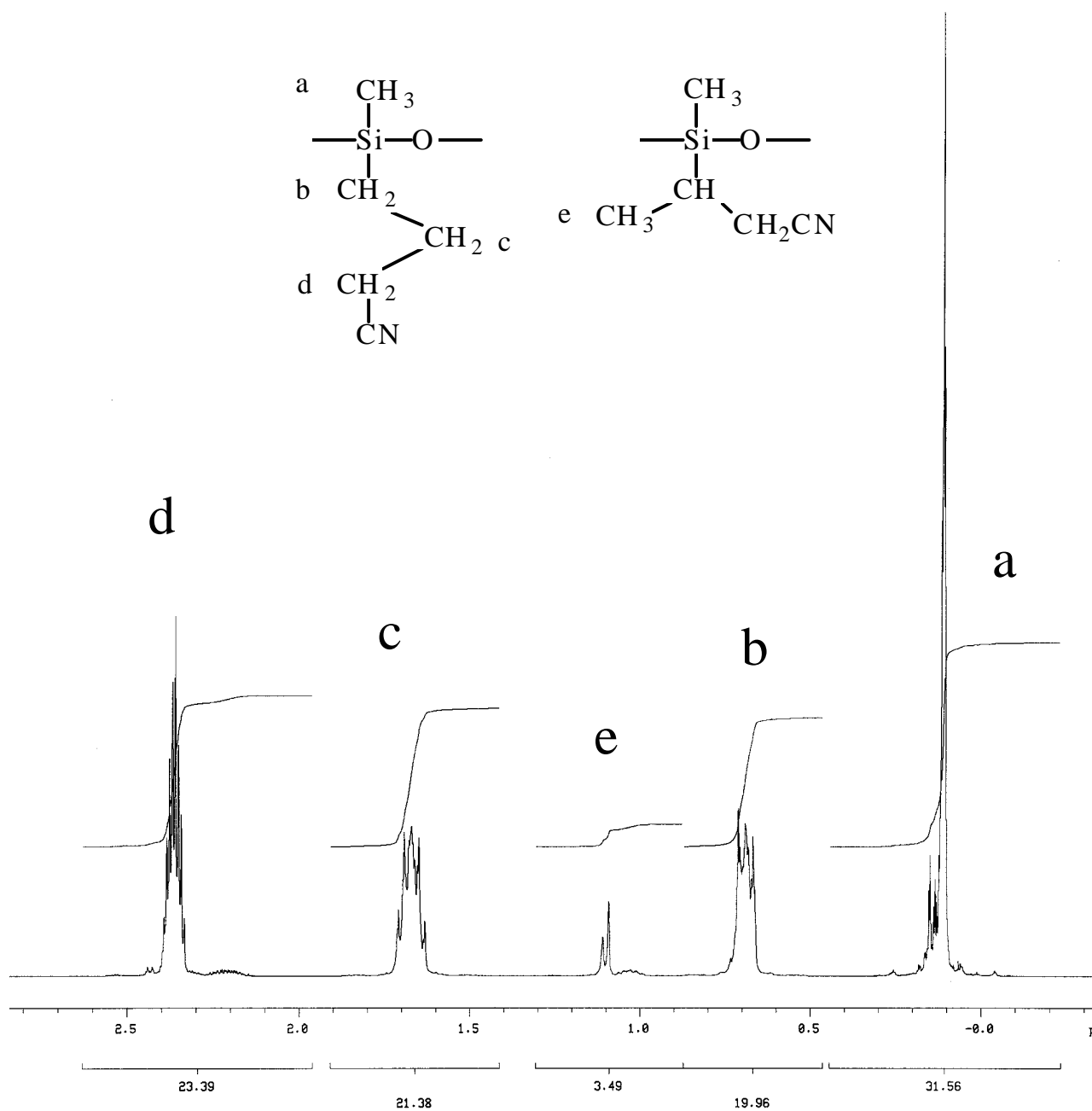


[Figure 4.10](#) ^{13}C and DEPT NMR spectra of distilled D_xCN s.

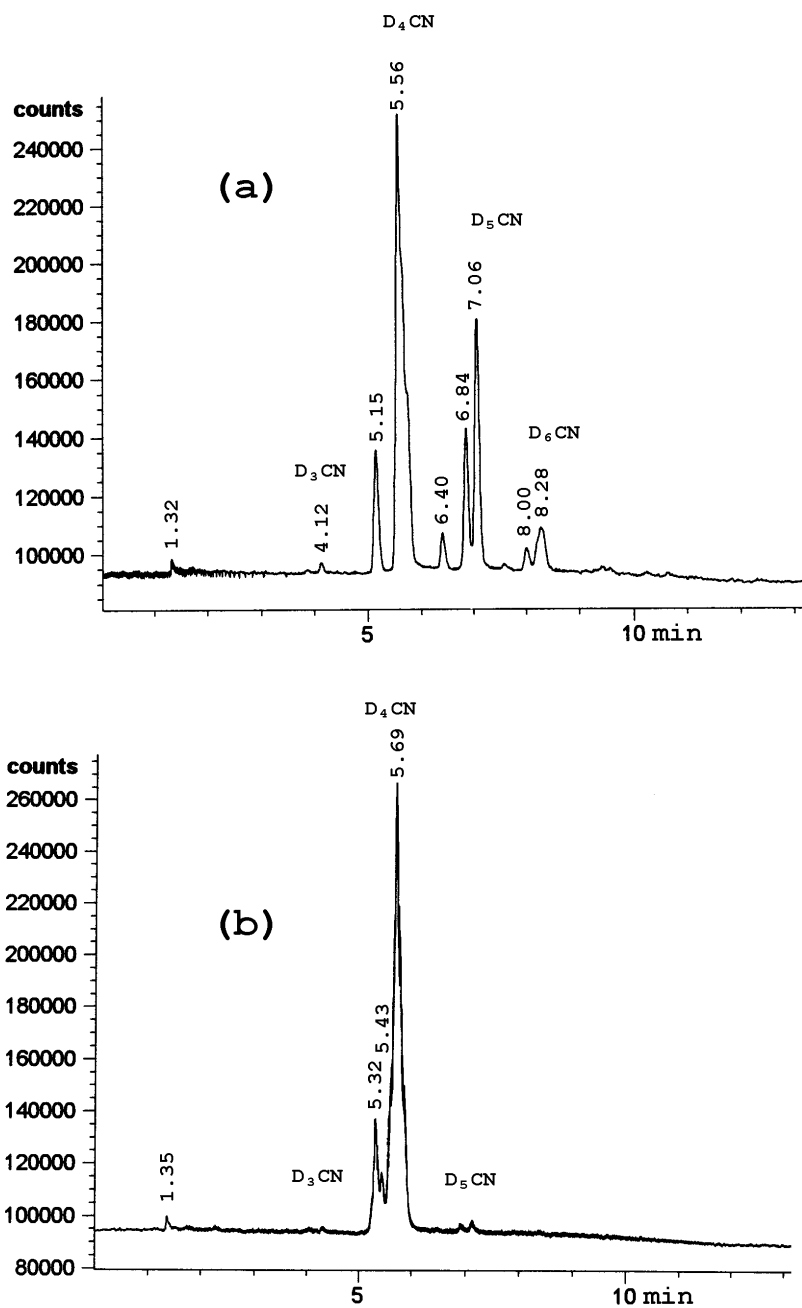
D_x CN prepared by direct hydrolysis contain cyclics of various ring sizes. With boiling points as high as 220-280°C/0.1 Torr, it is not practical to separate those cyclics by fractional distillation because long term exposure of the cyclics to high temperature may cause decomposition.

Pure D_x CN may be prepared by hydrosilylation of pure hydrogenmethylcyclosiloxanes (D_x H, $x = 3$ or 4 or 5), which can be separated easily by normal pressure fractional distillation. Actually, D_4 H and D_5 H are commercially available. This approach was tried with D_4 H in an attempt to prepare pure D_4 CN. The complex of platinum (0) with 1,3-divinyltetramethyldisiloxane in xylene was used as a catalyst since hexachloroplatinic acid might cause ring rearrangement. As expected, supercritical fluid chromatograms (Fig. 4.12) indicate that the product was mostly D_4 CN.

Fig. 4.11 shows ^1H NMR spectrum of D_4 CN prepared by hydrosilylation of D_4 H. The peaks (e) at 1.2 ppm was due to Markownikoff addition, and the ratio of Markownikoff to anti-Markownikoff products was ~11 % (determined by the integral ratio of e/a). The ^{13}C NMR (Fig. 4.13) shows peaks a', f, e respectively for methyl group a', methyl group f and methine group e in the Markownikoff addition products. Assignment of these peaks was based on the DEPT experiments (Fig. 4.14). The calculated yield of Markownikoff products from ^{13}C NMR was 8.5%. This result may be more accurate than the ^1H NMR results because no interfering peaks exist. The cyclics free of Markownikoff addition is actually much lower than the level of Markownikoff addition. If the Markownikoff level is 10%, and the hydrosilylation addition does not depend on the environment of the Si-H bond (i. e. whether its neighboring substituents are anti-Markownikoff or Markownikoff products), the yield of cyclic tetramer which are completely anti-Markownikoff is only 66% ($= 0.9^4$). IR spectroscopy indicated that there were no amide impurities in the cyclics prepared by this method.



[Figure 4.11](#) ^1H NMR spectrum of D_4CN prepared by hydrosilylation of D_4H



[Figure 4.12](#) Supercritical fluid chromatography of cyclics prepared by (a) hydrolysis of 3-cyanopropylmethylsilane, (b) hydrosilylation of D₄H see Section 3.55 for experimental conditions.

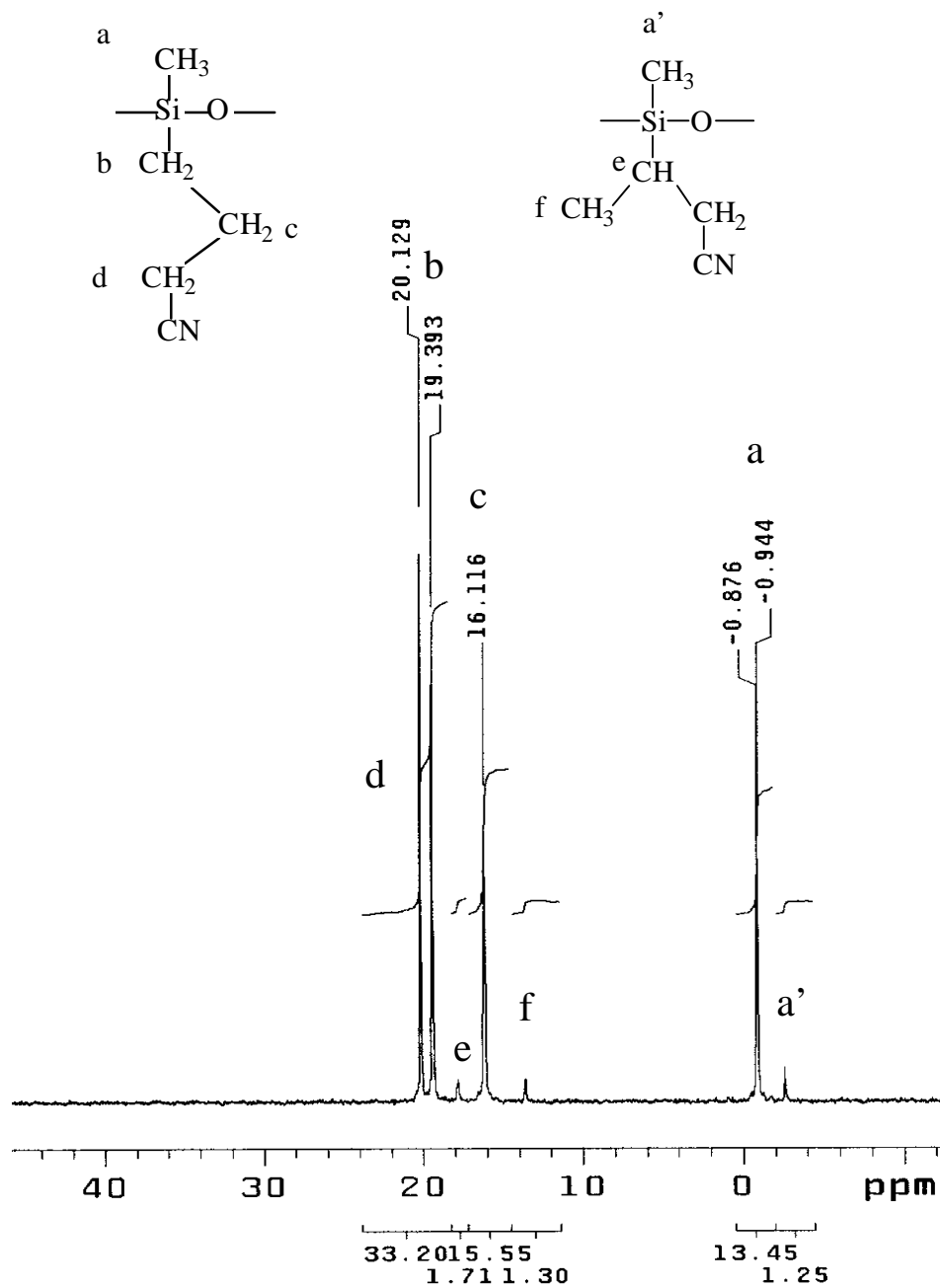
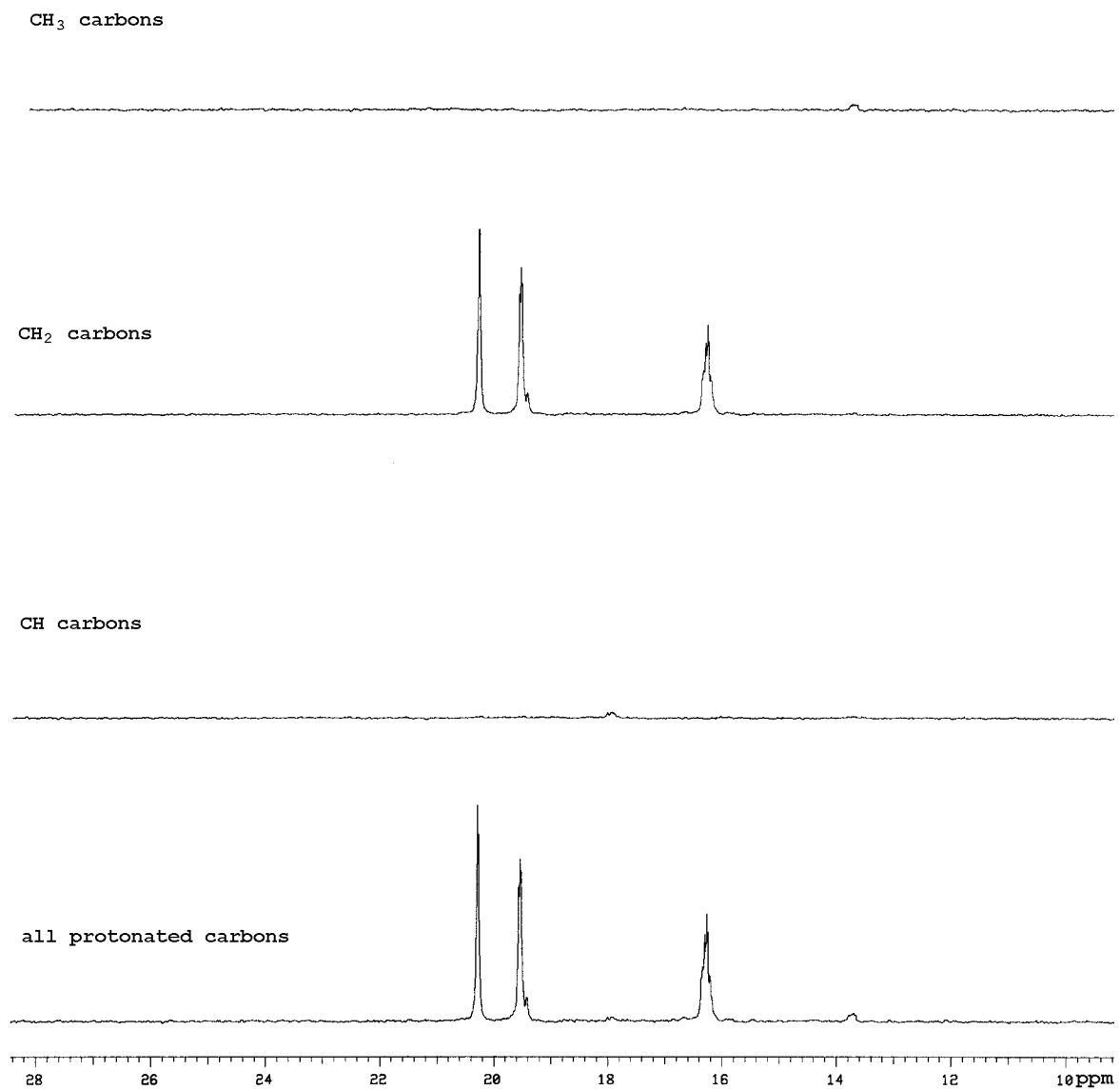


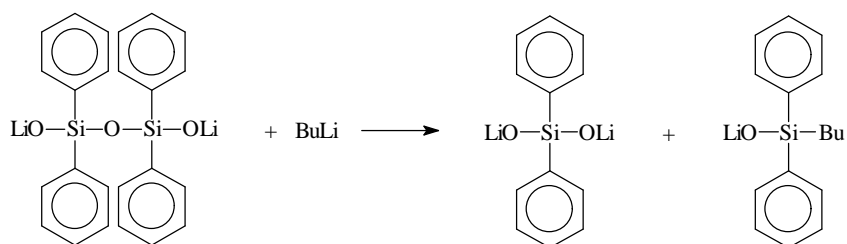
Figure 4.13 ^{13}C NMR spectrum of D_4CN prepared from hydrosilylation of D_4H



[Figure 4.14](#) ^{13}C DEPT spectra of D_4CN prepared by hydrosilylation of D_4H

4.3 Dilithium diphenylsilanediolate

DLDPDS was used as a dianionic initiator for preparing triblock polysiloxane copolymers (Section 2.4.2.2). Diphenylsilanediol exists as white needle crystals, but it has no definite melting point. Diphenylsilanediol gradually condenses to linear or cyclic polydiphenylsiloxanes when heated to above 100°C, so commercial products contain minor amounts of polydiphenylsiloxanol impurities. The preparation of DLDPDS was explored by reaction of butyllithium with diphenylsilanediolate in tetrahydrofuran at -40°C. However, products prepared in this manner contained impurities like lithium diphenylbutylsilanolate caused by specific redistribution (shown below). This monobasic compound was detected by ^1H NMR.



Monofunctional initiator impurities like lithium diphenylbutylsilanolate cause diblock copolymer impurities during triblock copolymer syntheses. To avoid this side reaction, the diphenylsilanediol was recrystallized twice in methyl isopentyl ketone and chloroform to remove polydiphenylsiloxanols. ^{29}Si NMR spectrum (in deuterated acetone) of purified diphenylsilanediol showed only one peak at -35 ppm, while the reported chemical shift for this compound is from -32 to -37 ppm depending on the solvent.¹¹⁹

Diphenylmethyl lithium was used as a deprotonation reagent instead of butyllithium to minimize possible specific redistribution. Diphenylmethyl lithium reportedly does not react with PDMSs including D_3 ^{120,121} if the temperature is below 50°C. Diphenylmethyl lithium was prepared

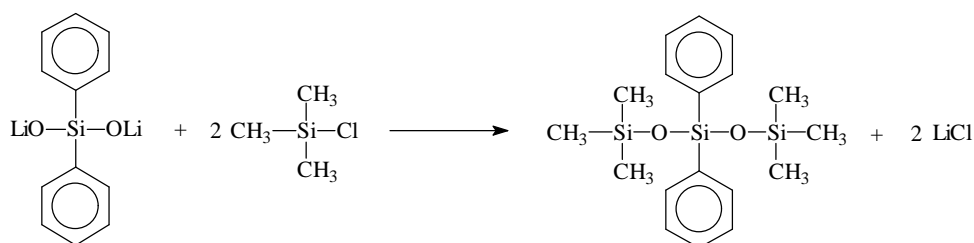
¹¹⁹ E. A. Williams, Annual reports on NMR technology, **15**, 262, Academic Press, London, (1983)

¹²⁰ J. W. Dean, J. Polym. Sci., Part B, **8**(10), 677 (1970)

by deprotonation of diphenylmethane ($pK_a \sim 33$ in THF¹²²) with butyllithium (the pK_a for methane is around 55¹²³). Diphenylmethyl lithium have a dark red color which can serve as an indicator for titration. The titration (deprotonation) was conducted in THF at room temperature. Generally, DLDPS forms a supersaturated solution in THF, and it can precipitate as white ultrafine crystals within 24 hours.

DLDPS samples were titrated with a standardized acid. The equivalent weight for samples of two batches were 121 g/mol and 114 g/mol. These results are close to the theoretical equivalent weight of $Li_2O_2Si(C_6H_5)_2$ (114 g/mol.).

DLDPS is insoluble in common nonprotic solvents, and tends to hydrolyze in protic solvents. Therefore, analyses were based on its derivative 1,1,1,3,3,3-hexamethyl-2,2-diphenyldisiloxane which was formed by the reaction shown below.



1,1,1,3,3,3-hexamethyl-2,2-diphenyltrisiloxane

Excess trimethylchlorosilane was removed by evaporation and lithium chloride was separated by centrifugation. The residual liquid was analyzed by 1H , ^{29}Si and ^{13}C NMR spectroscopy. The ^{29}Si NMR spectrum of the liquid (Fig. 4.15) revealed a singlet (A) at δ 10 ppm and a singlet (B) at δ -47.7 ppm with the ratio of A to B exactly 2 : 1. According to chemical shifts reported for trimethylsilyl groups and the diphenylsiloxane group¹⁰⁴, peaks A and B were assigned respectively to the trimethylsilyl groups and the diphenylsiloxane group in 1,1,1,3,3,3-hexamethyl-2,2-diphenyltrisiloxane. Small peaks near A were due to impurities in the trimethylchlorosilane reagent such as hexamethyldisiloxane, trimethylsilanol, etc. The 1H NMR

¹²¹ P. C. Juliano, D. E. Floryan, R. W. Hand and D. D. Karttunen, Block and graft copolymers proceedings, 1st ed. Sagamore Army Material Research Conference 62-83 (1973)

¹²² F. A. Carey and R. J. Sundberg. Advanced Organic Chemistry, **A**, 401, Plenum Press, New York (1990)

¹²³ F. A. Carey and R. J. Sundberg. Advanced Organic Chemistry, **B**, **3**, Plenum Press, New York (1990)

spectrum (Fig. 4.16) indicates that the integral ratio of phenyl protons (at δ 7.2-7.5 ppm) to trimethylsilyl protons (at δ 0 ppm) is 1.7, rather close to the theoretical value of 1.8. The ^{13}C NMR spectrum (Fig. 4.17) also revealed carbons of trimethylsilyl groups at δ 2 ppm (a), and carbons of the phenyl groups at δ 136.8 ppm (b), δ 134 ppm (c/d), δ 127.6 ppm (d/c) and δ 129.5 ppm (e). The assignments of b and e were confirmed by DEPT experiments.

DLDPDS was reportedly a poor initiator for kinetically controlled polymerization of D_3 even in moderately polar solvents like THF⁶⁷. Generally, the polydispersity of PDMSs depends on the initiation rate and the purity of the dianionic initiator. If the DLDPDS was contaminated with monofunctional species, it would not be possible to obtain monodisperse PDMS.

A PDMS polymer was prepared by D_3 anionic polymerization in dichloromethane with DLDPDS as an initiator and TEGDME as a promoter. After accounting for unreacted D_3 , the target number average molecular weight was 14 kg/mol. The molecular weight of this polymer by GPC (Fig. 4.18) was

$$M_n = 13.7 \times 10^3 \text{ g/mol}$$

$$M_w = 15.8 \times 10^3 \text{ g/mol}$$

$$\text{Polydispersity} = 1.15$$

Compared to polymers prepared by equilibrium polymerization, this PDMS had a rather narrow molecular weight distribution. Therefore, in dichloromethane with TEGDME as a promoter, the initiation of D_3 by DLDPDS is fast enough to prepare useful PDMSs.

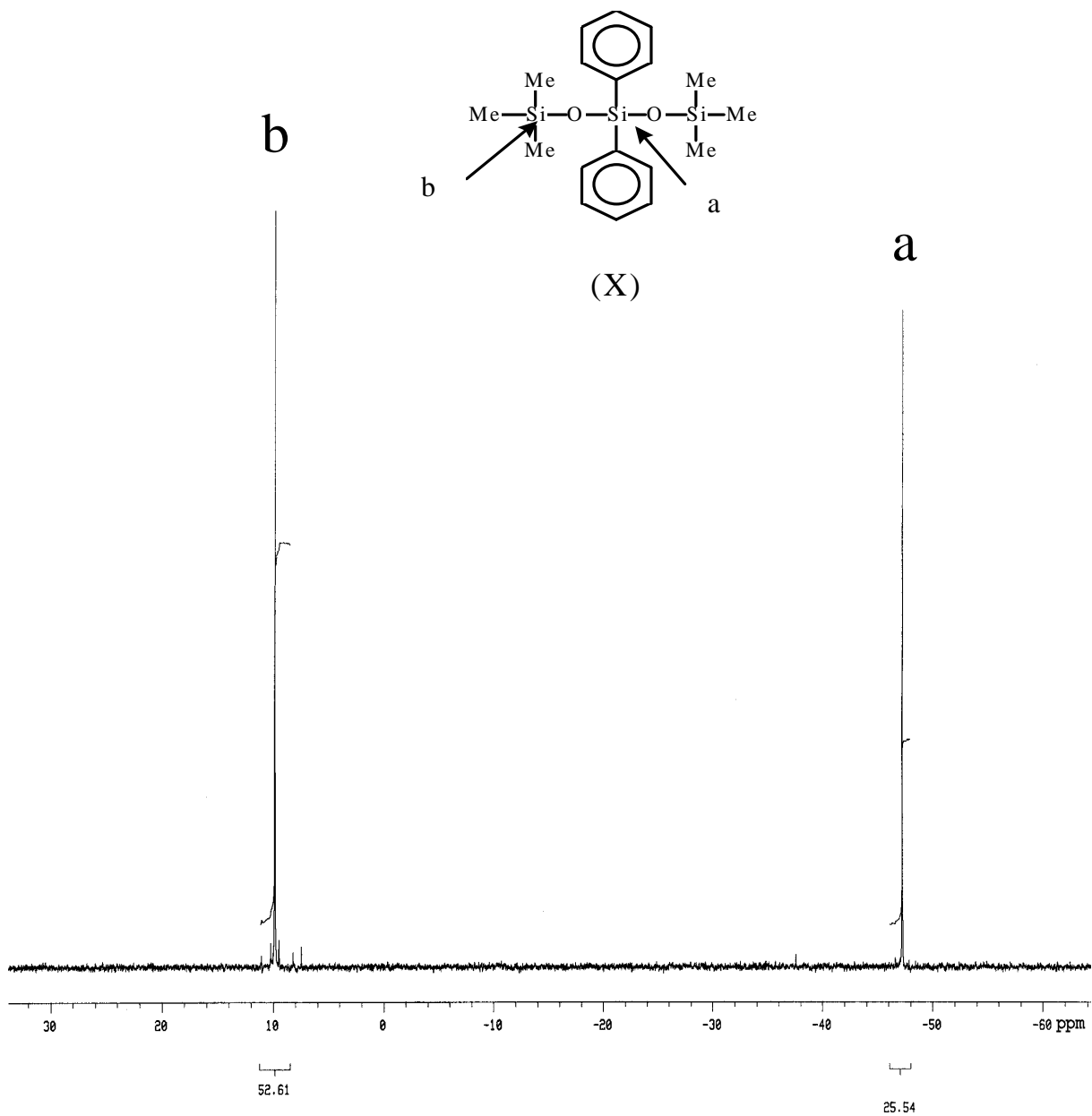
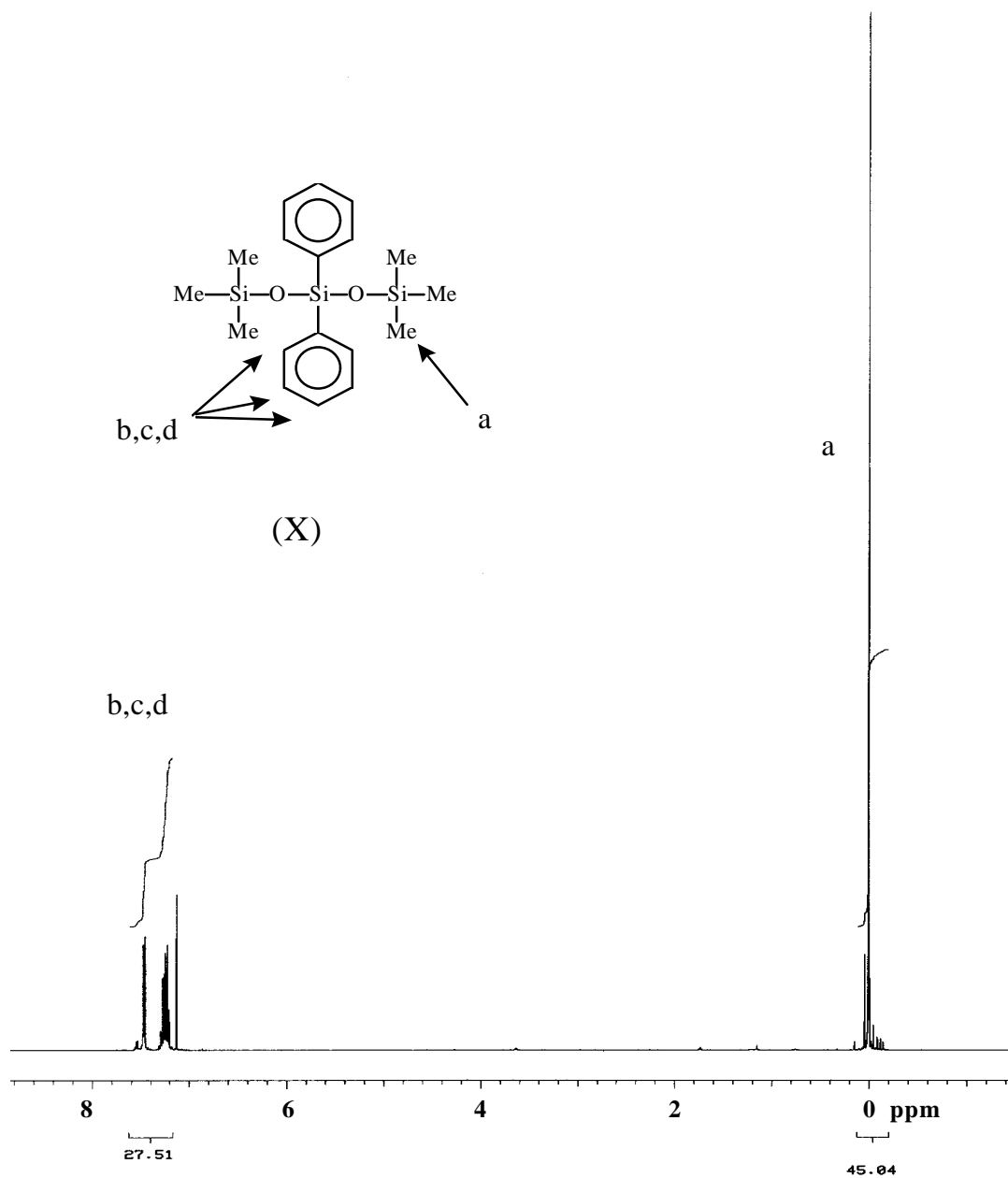
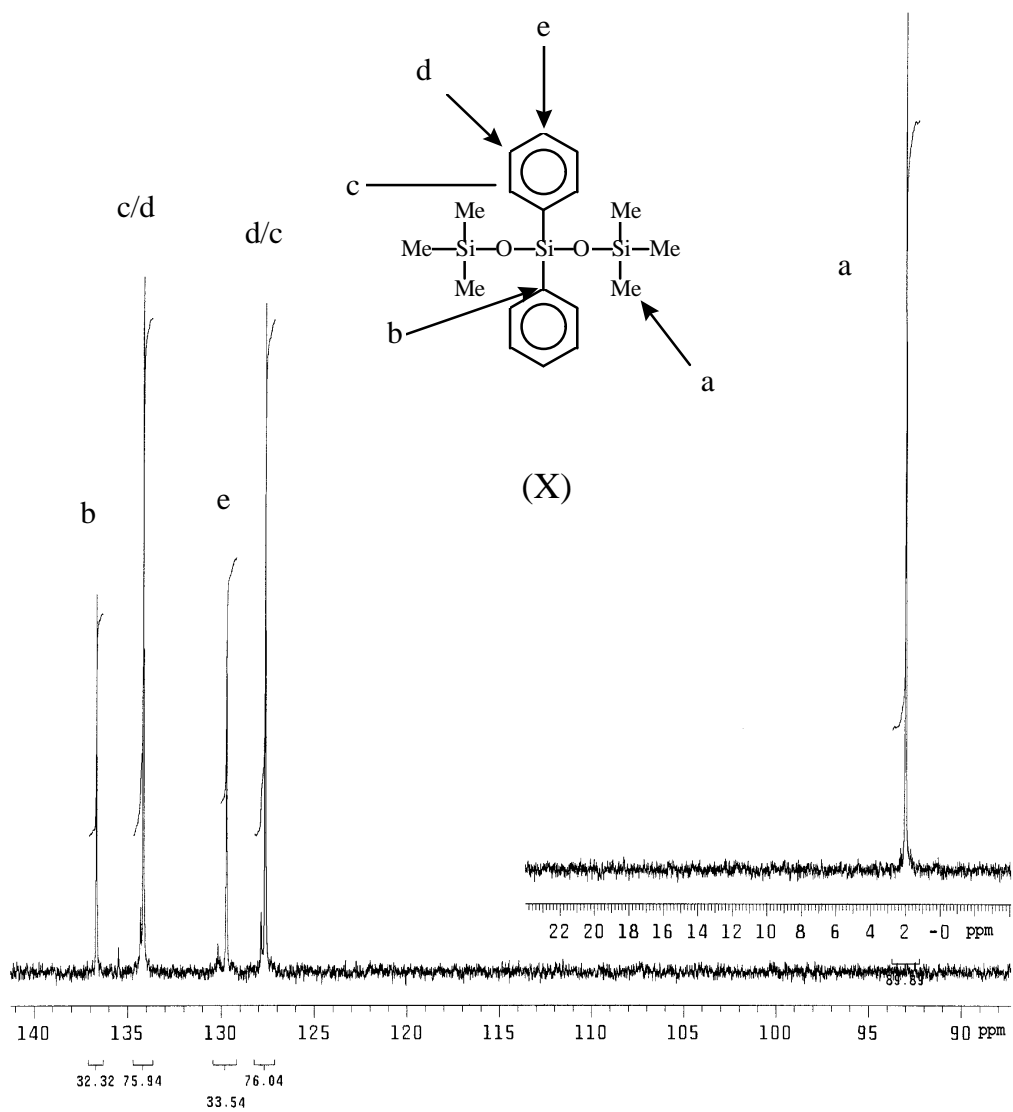


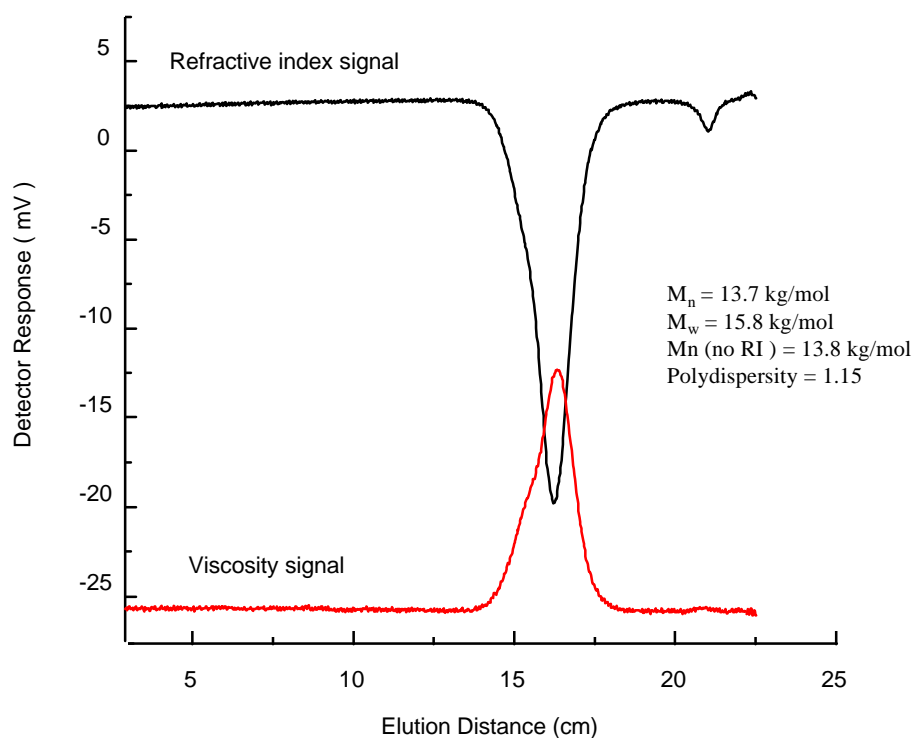
Figure 4.15 ^{29}Si NMR spectrum for 1,1,1,3,3,3-hexamethyl-2,2-diphenyltrisiloxane, a derivative of DLDPS



[Figure 4.16](#) ^1H NMR spectrum of 1,1,1,3,3,3-hexamethyl-2,2-diphenyltrisiloxane

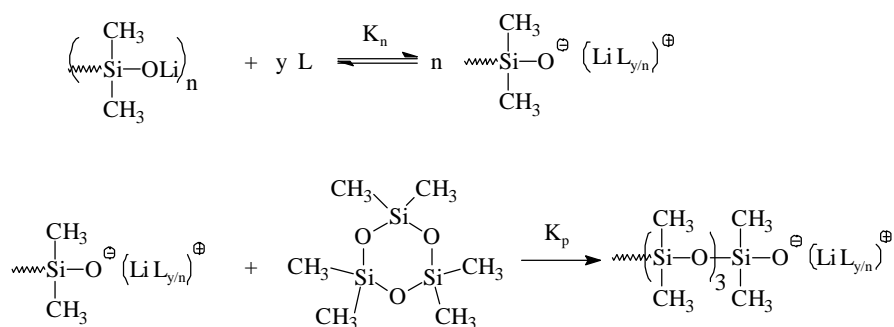


[Figure 4.17](#) ^{13}C NMR spectrum of 1,1,1,3,3,3-hexamethyl-2,2-diphenyltrisiloxane



[Figure 4.18](#) Gel permeation chromatograms (in CHCl_3) of a PDMS sample prepared by D_3 polymerization in CH_2Cl_2 using DLDPS initiator and TEGDME promoter.

The rate law for anionic polymerization of cyclosiloxanes is first order in monomer, and a fractional order in the silanolate concentration (Chapter 2). In kinetically controlled polymerization, the rate of depolymerization should be close to zero. If the interaction of promoter with the counterion is treated as a complexation reaction, then the kinetics can be expressed as:



so the rate law can be rewritten as:

$$-\frac{d[D_3]}{dt} = k'_{\text{obs}} [\text{silanolate}]^{1/n} [\text{promoter}]^{y/n} [D_3]$$

$$\ln([D_3]/[D_3]_0) = -k'_{\text{obs}} [\text{silanolate}]^{1/n} [\text{promoter}]^{y/n} t$$

These kinetic equations show that the polymerization is first order in $[D_3]$, $1/n$ order in the silanolate, and y/n order in the promoter.

$1/n = 1,$	$y/n = 0,$	free silanolate
$1/n = 1,$	$y/n > 0$	ion pairs
$1/n < 1,$	$y/n \gg 0$	ion association

The kinetics of D_3 polymerization with lithium trimethylsilanolate and DLDPS as initiators and dichloromethane as a solvent was explored to simulate reaction conditions which would be used in the synthesis of the desired triblock copolymers.

Polymerization reactions of D_3 initiated with lithium trimethylsilanolate and DLDPS were followed by ^1H NMR (operated at 400 MHz). The reactions were carried out in 5 mm NMR tubes at 20°C and deuterated dichloromethane was used as the reaction solvent. The chemical shifts for protons in D_3 are at δ 0.16 ppm, while protons from PDMS have chemical shifts at about δ 0.10 ppm. [Fig. 4.19](#) shows a series of spectra collected at different reaction times during a D_3 polymerization reaction using lithium trimethylsilanolate catalyst. The conversion of D_3 was calculated from the integrals of D_3 and PDMS. Several reactions were followed by ^1H NMR. Conversions at different reaction times were calculated and listed in [Table 4.5](#). Plots of $\ln([D_3]/[D_3]_0)$ vs reaction time ([Fig. 4.20](#)) were constructed according to data in Table 4.5. [Fig. 4.20](#) shows that the D_3 polymerization is, just as expected, first order in $[D_3]$, a fractional order in the silanolate and greater than 1 in the promoter. Therefore, association of silanolates exists under these reaction conditions.

D_3 polymerization in CD_2Cl_2 initiated with DLDPS was also followed by ^1H NMR. Kinetic data for two reactions with different initiator concentrations are listed in [Table 4.6](#). Graphs of $\ln([D_3]/[D_3]_0)$ vs reaction time are similarly constructed and given in [Fig 4.21](#). [Fig. 4.21](#) indicates that the reactions are first order in D_3 after conversion is beyond $\sim 40\%$ (reaction

time > 1200 minutes), but deviate from that at low conversions. The deviation may be due to strong ionic associations between the dianionic species. During the early stages of reaction, two silanolate ions were closely linked together by a polysiloxane chain, and hence the ionic interactions herein were much stronger than those in monobasic initiator systems. As the reaction proceeds, the average length of polysiloxane chains increases. Therefore, two silanolate ions can stay further away from each other (the end-to-end distance of polymer chain increases), thus resulting in a decrease in ionic interactions and an increase in free silanolate concentration. When polymer chains grow long enough that two silanolate ions do not influence each other, then the reaction might begin to exhibit first order kinetics. The deviation may also be accredited to the reactivity difference between lithium diphenylsilanediolate and lithium dimethylsilanolate. When dilithium reacts with D_3 , it gives short polysiloxane chains ended with a lithium dimethylsilanolate and a lithium diphenylsilanolate. Since dimethylsilanolate ions are more reactive than diphenylsilanolate ions, hence the polymerization is slow during the early stages of reaction. As diphenylsilanolate ions gradually transform to dimethylsilanolate ions by reacting with D_3 , the whole reaction should begin to exhibit normal first order kinetics. To find out whether the first or the second explanation is correct, it is recommended that the kinetics for D_3 polymerization initiated with dilithium dimethylsilanediolate be investigated.

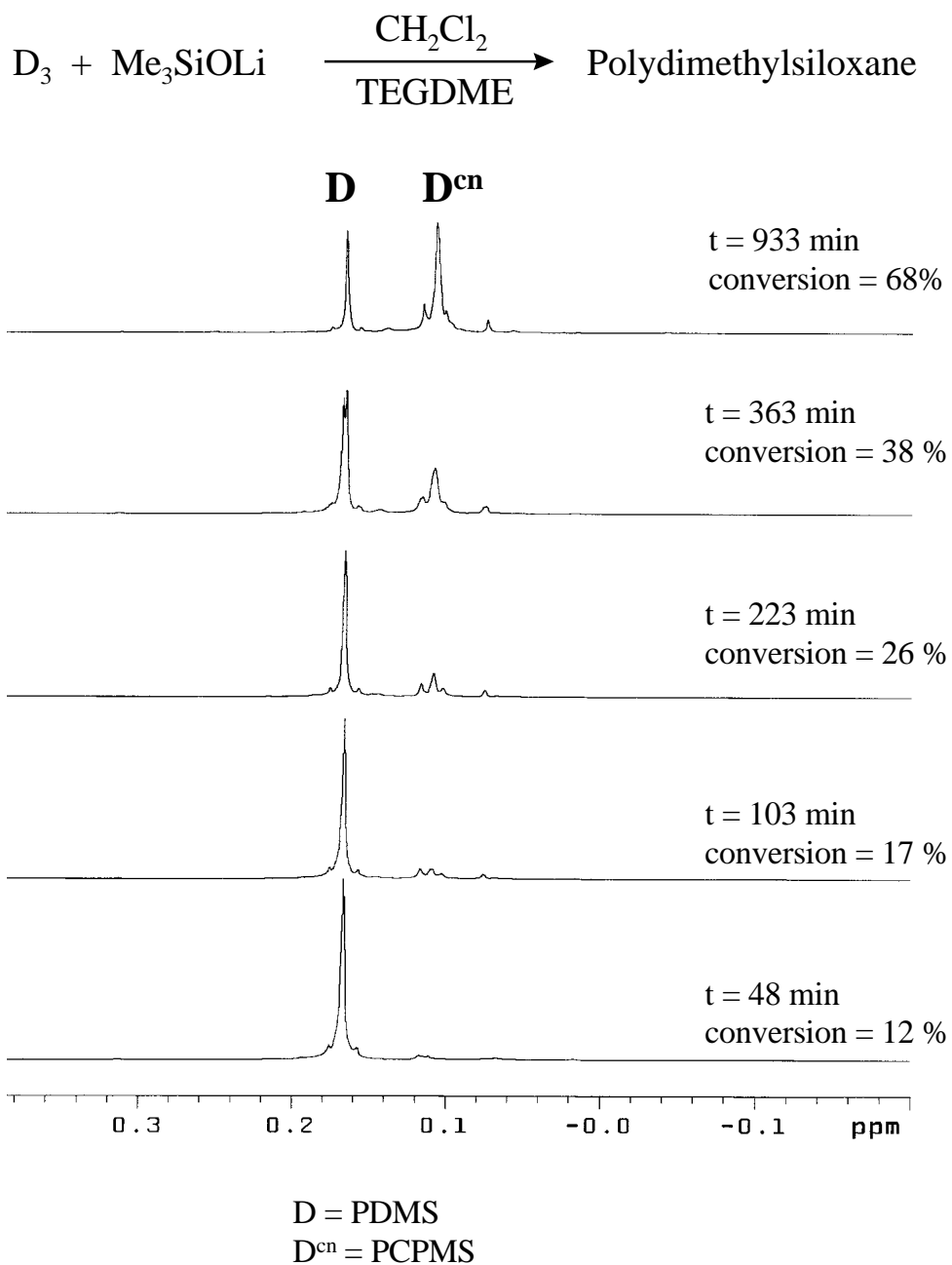
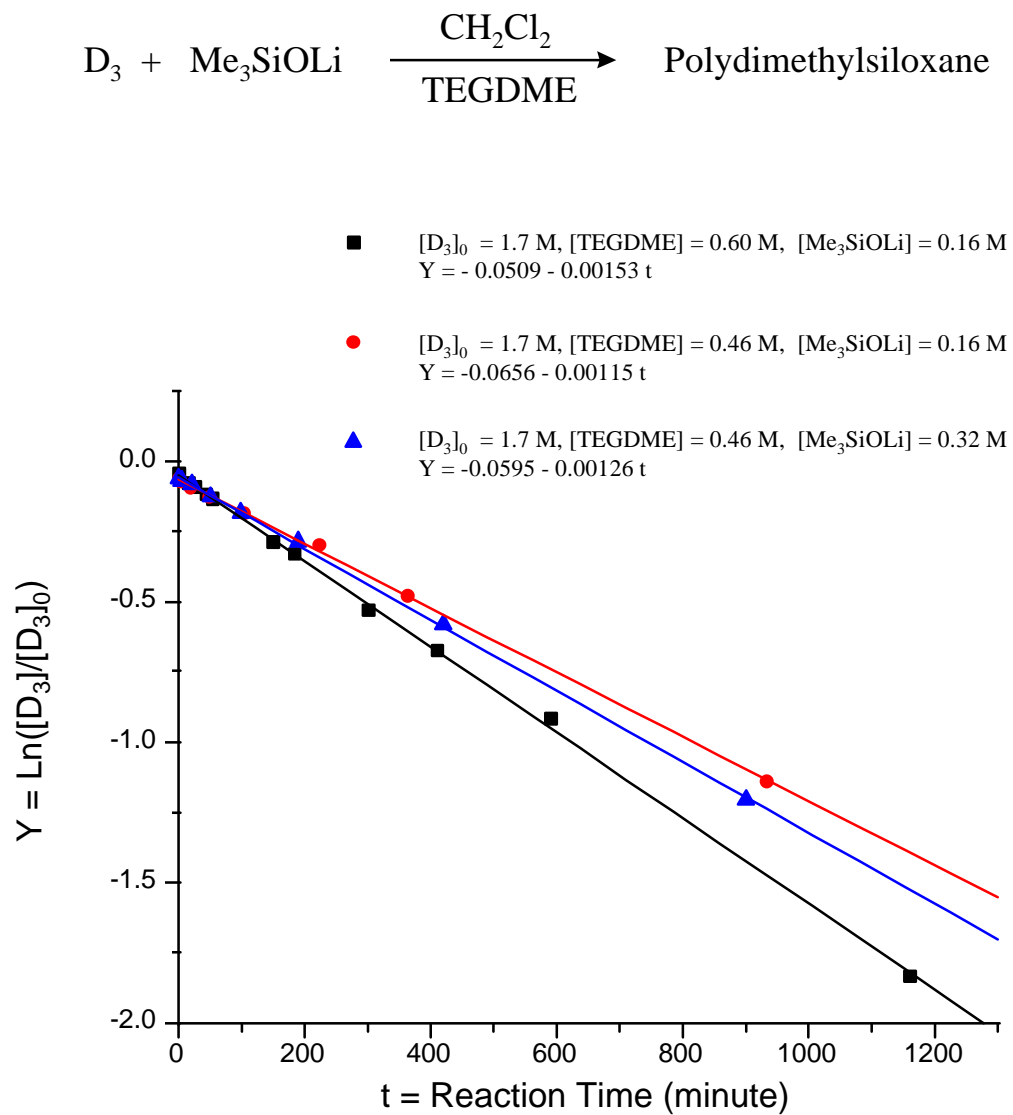


Figure 4.19 Polymerization of D_3 initiated with lithium trimethylsilanolate followed by 1H NMR

Table 4.5 Kinetic data for polymerization of D_3 in CD_2Cl_2 using lithium trimethylsilanolate initiator and TEGDME promoter

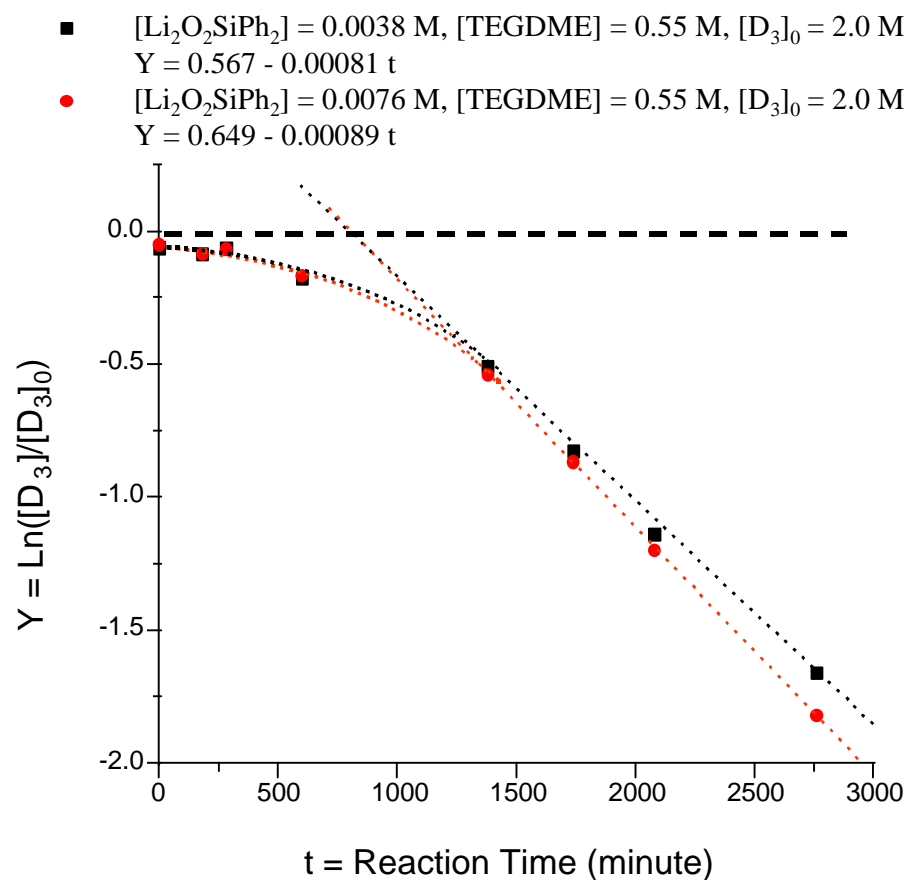
	[TEGDME]= 0.60 M [Me ₃ SiOLi] = 0.16 M [D ₃] ₀ = 1.7 M	[TEGDME]= 0.46 M [Me ₃ SiOLi] = 0.16 M [D ₃] ₀ = 1.7 M	[TEGDME]= 0.46 M [Me ₃ SiOLi] = 0.32 M [D ₃] ₀ = 1.7 M
Time (min)	[D ₃]/[D ₃] ₀	[D ₃]/[D ₃] ₀	[D ₃]/[D ₃] ₀
0	0.96	0.94	0.94
3	--	0.93	--
5	--	--	0.93
15	0.926	--	--
18	--	0.91	--
20	--	--	0.92
25	0.912	--	--
43	0.89	--	--
48	--	0.88	--
50	--	--	0.88
53	0.874	--	--
98	--	--	0.83
103	--	0.83	--
150	0.75	--	--
183	0.72	--	--
190	--	--	0.75
223	--	0.74	--
300	0.59	--	--
363	--	0.62	--
410	0.51	--	--
420	--	--	0.56
590	0.4	--	--
900	--	--	0.3
933	--	0.32	--
1160	0.16	--	--



[Figure 4.20](#) Polymerization of D_3 at $20 \pm 2^\circ\text{C}$ using lithium trimethylsilanolate initiator and TEGDME promoter

Table 4.6 Kinetic data for polymerization of D_3 in dichloromethane using DLDPs initiator and TEGDME promoter

	[Li ₂ O ₂ SiPh ₂] = 0.0038 M [TEGDME] = 0.55 M [D ₃] ₀ = 2.0 M		[Li ₂ O ₂ SiPh ₂] = 0.0076 M [TEGDME] = 0.55 M [D ₃] ₀ = 2.0 M	
Time (min)	[D ₃]/[D ₃] ₀	Ln ([D ₃]/[D ₃] ₀)	[D ₃]/[D ₃] ₀	Ln ([D ₃]/[D ₃] ₀)
0	0.94	-0.06188	0.95	-0.05129
180	0.92	-0.08338	0.919	-0.08447
280	0.938	-0.06401	0.936	-0.06614
600	0.837	-0.17793	0.845	-0.16842
1380	0.601	-0.50916	0.582	-0.54128
1740	0.438	-0.82554	0.42	-0.8675
2080	0.32	-1.13943	0.302	-1.19733
2760	0.19	-1.66073	0.162	-1.82016



[Figure 4.21](#) Polymerization of D_3 at $20 \pm 2^\circ\text{C}$ using DLDPs initiator and TEGDME promoter

4.4 PCPMS Macroinitiators

Mixtures of cyclosiloxanes can be polymerized by lithium bases although lithium bases are less reactive than other alkali metal or onium bases. The purpose here is to establish how fast DLDPS reacts with D_x CNs, what is the concentration of cyclics in the final equilibrate, and if the molecular weight of the equilibrate is controllable by the D_x CN-to-DLDPS ratio.

4.4.1 Kinetics of Polymerization

Polymerization of D_x CN catalyzed with DLDPS was followed by ^{29}Si NMR and GPC. The initial concentrations of the monomer were D_3 CN 41%, D_4 CN 56% and D_5 CN 3%. The D_x CN-to-DLDPS ratio in the reaction was 5 kg/mol. The mixture was mixed at room temperature for two hours before heating to 100°C. Due to its high reactivity, the concentration of D_3 decreased from 41% to 16% during the mixing process. Table 4.7 lists concentrations of D_3 CN, D_4 CN (by ^{29}Si NMR) and the concentration of total cyclics (by GPC) at different reaction times (at 100°C). Samples for ^{29}Si NMR and GPC were terminated with small amounts of acetic acid immediately after they were taken out of the reactors. The total concentration of cyclics was calculated using the areas due to cyclic and linear polysiloxanes in the GPC RI curves assuming that the monomer had the same refractive index as the polymer. This assumption is generally used in GPC calculations although monomers usually have a slightly lower refractive index than the related polymers. The equilibrium state was indicated by no more changes in concentrations of cyclics and GPC diagrams. Fig. 4.22 reflects concentration changes for trimer, tetramer and total amounts of cyclics with reaction time. The results clearly exhibit that D_x CNs can be equilibrated by DLDPS within 5-10 hours at 100°C. Similar experiments indicated that 25-30 hours was required for the mixture of D_x CNs and DLDPS to reach equilibrium at 80°C.

Table 4.7 Kinetic data for equilibrium polymerization of D_xCN ($x=3-5$) at $100^\circ C$ using DLDPS initiator.

Time (hour)	$[D_3CN]$ by ^{29}Si NMR	$[D_4CN]$ ^{29}Si NMR	[cyclics] by GPC
0	16	62	74
2.5	0	17	25
5	0	7.9	20
8	0	10	16
19	0	9	21

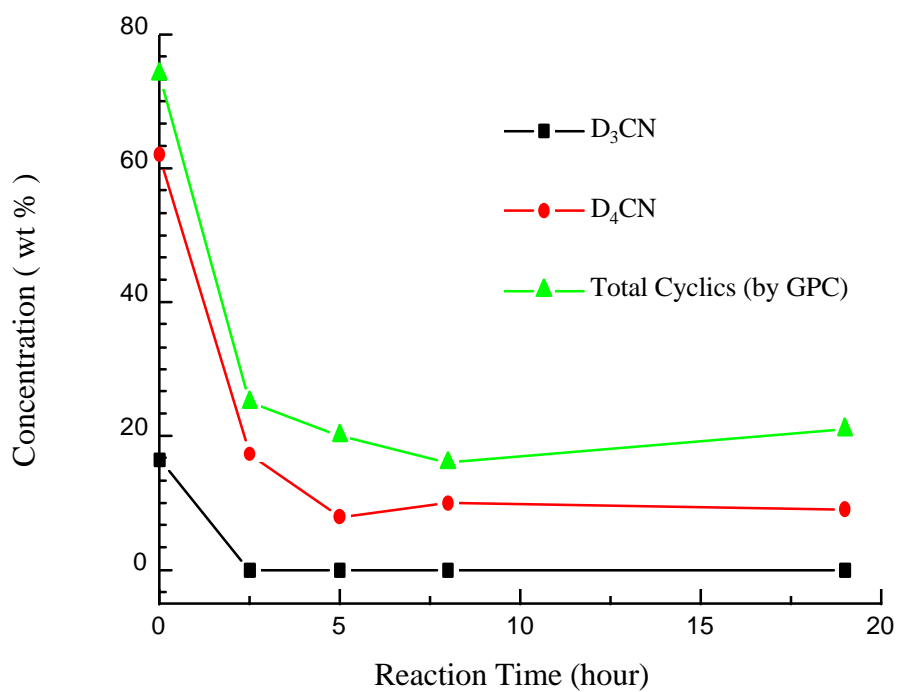


Figure 4.22 Polymerization of D_xCN s at $100^\circ C$. $D_xCN/ DLDPS = 5.0$ kg/mol.

4.4.2 Molecular Weight Control and Equilibrium Concentrations of Cyclics

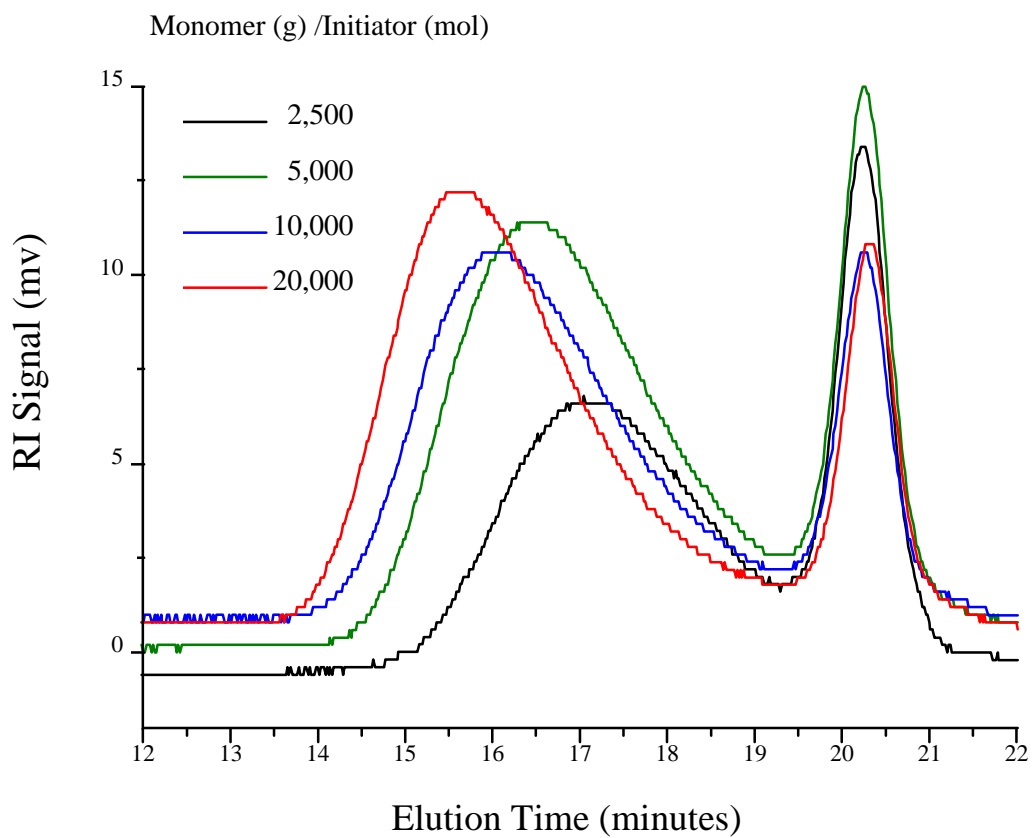
It was established the molecular weight of the macroinitiator could be controlled by the $D_x\text{CN}$ -to-DLDPS ratio. Several macroinitiators were terminated with vinyltrimethylchlorosilane for GPC and NMR endgroup analyses. Fig. 4.23 contains the GPC traces (RI signals) for the terminated macroinitiators with $D_x\text{CN}$ -to-DLDPS ratios as 2.5k, 5k, 10k, and 20k. The sharp peaks (at 20.3 min) are for cyclics, while the broad peaks are due to linear polysiloxanes. Since high molecular species elute first in GPC, it is clear that the molecular weight of the macroinitiator increases with the $D_x\text{CN}$ -to-DLDPS ratio. Absolute molecular weights could not be calculated for these polymers because PCPMS standards were not available and universal calibration failed to provide reasonable results due to the interference from the cyclics.

The controllability of the molecular weight of the macroinitiators by the $D_x\text{CN}$ -to-DLDPS ratio were also confirmed by the intrinsic viscosity of the macroinitiators. Table 4.8 shows an increasing tendency of intrinsic viscosity with the $D_x\text{CN}$ -to-DLDPS ratio for the polymer series. The polymer samples were repeatedly washed with ethanol to remove the cyclics before viscosity measurements.

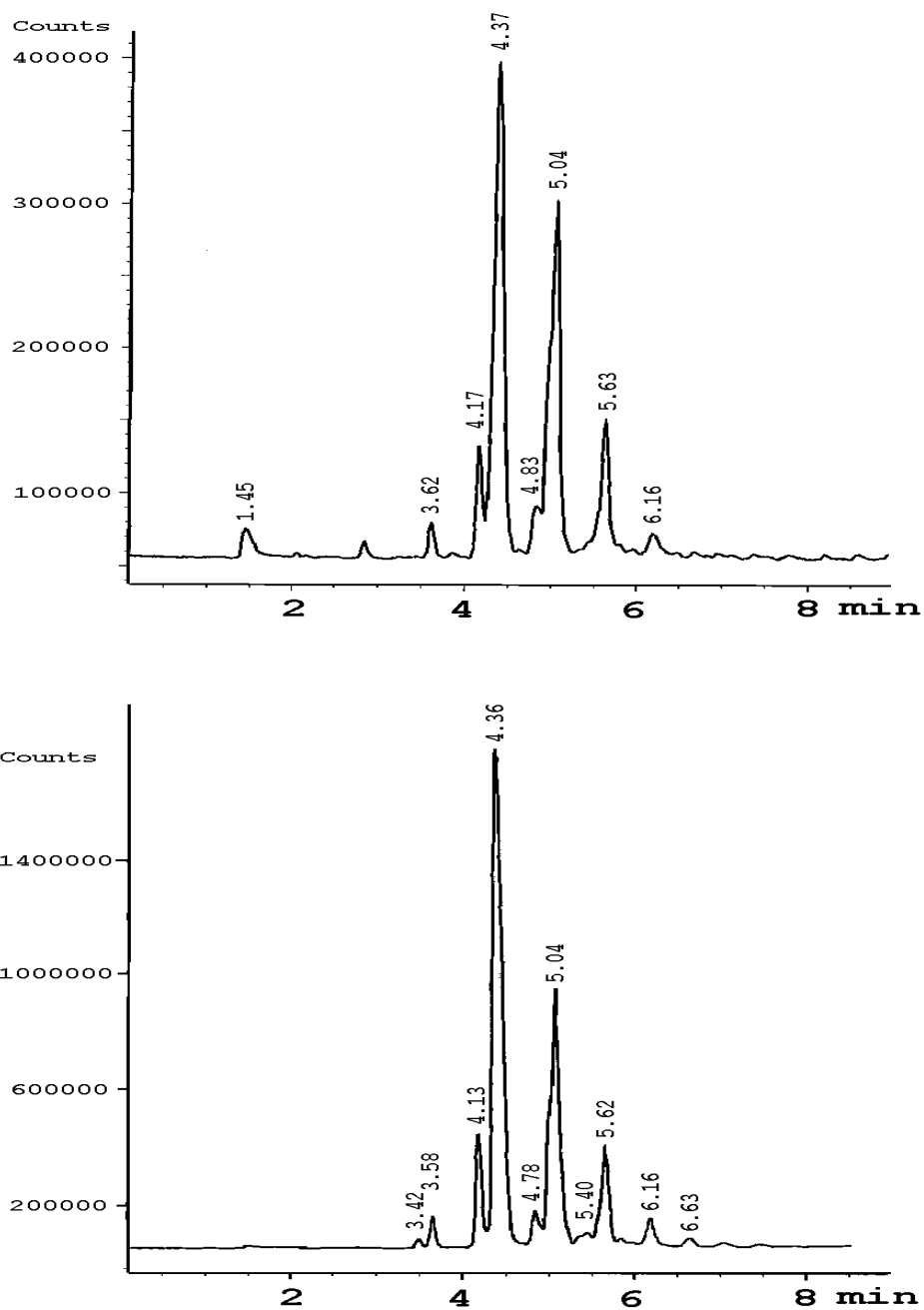
Table 4.8 Intrinsic viscosities for PCPMSs (26°C in NMP)

	2.5k	5k	10k	20k
$[\eta]$ (dl/g)	0.09	0.12	0.18	0.20

The major cyclics in the macroinitiator equilibrates were tetramer ($D_4\text{CN}$), pentamer ($D_5\text{CN}$) and hexamer ($D_6\text{CN}$) by supercritical fluid chromatography of vinyltrimethylchlorosilane terminated macroinitiators (Fig. 4.24). Peaks in the SFC of polymers were identified by comparison to the SFC of equilibrated cyclics. Experimental conditions for SFC are give in Section 3.5.5. Since the nitrogen chemiluminescence response used in SFC is proportional to the mass concentration of the nitrogen containing sample, the relative concentrations of these cyclics could be derived from the related peak integrals.



[Figure 4.23](#) The dependence of molecular weight of the macroinitiators on D_xCN -to- $DLDP$ S ratio (Solvent: chloroform)



[Figure 4.24](#) SFC for undistilled cyclics and macroinitiator

(see Section 3.5.5 for experimental conditions)

Table 4.9 Integral results of supercritical fluid chromatograms for dimethylvinylsilyl endcapped macroinitiators and equilibrium cyclics

Sample Identity	Peak #	Retention Time (min)	Area (Counts × Sec)	Identity
Undistilled Cyclics	1	3.42	1.54×10^5	D ₃ CN
	2	3.58	5.30×10^5	D ₃ CN
	3	4.13	2.06×10^6	D ₄ CN
	4	4.36	1.35×10^7	D ₄ CN
	5	4.78	7.75×10^5	D ₅ CN
	6	5.04	7.31×10^6	D ₅ CN
	7	5.40	5.09×10^5	D ₆ CN
	8	5.62	2.45×10^6	D ₆ CN
	9	6.16	7.68×10^5	D ₇ CN
	10	6.63	2.05×10^5	D ₈ CN
2.5k Macroinitiator	1	1.44	1.51×10^5	?
	2	2.75	1.66×10^5	?
	3	3.54	4.29×10^5	?
	4	4.17	6.64×10^5	D ₄ CN
	5	4.37	4.86×10^5	D ₄ CN
	6	4.83	7.91×10^5	D ₅ CN
	7	4.98	2.83×10^5	D ₅ CN
	8	5.57	1.33×10^5	D ₆ CN
	9	6.15	2.14×10^5	D ₇ CN
5k Macroinitiator	1	1.44	1.48×10^5	?
	2	2.90	8.17×10^4	?
	3	3.66	1.56×10^5	?
	4	4.19	3.43×10^5	D ₄ CN
	5	4.39	2.77×10^6	D ₄ CN
	6	5.03	2.22×10^6	D ₅ CN
	7	5.61	7.30×10^5	D ₆ CN

Cont.

Sample Identity	Peak #	Retention Time (min)	Area (Counts × Sec)	Identity
7.5k Macroinitiator	1	1.45	1.79×10^5	?
	2	3.62	1.47×10^5	?
	3	4.17	3.76×10^5	D ₄ CN
	4	4.37	2.80×10^6	D ₄ CN
	5	4.83	2.23×10^5	D ₅ CN
	6	5.04	2.00×10^6	D ₅ CN
	7	5.63	7.53×10^5	D ₆ CN
10 k Macroinitiator	1	1.46	1.73×10^5	?
	2	4.16	3.00×10^5	D ₄ CN
	3	4.37	2.34×10^6	D ₄ CN
	4	4.83	1.63×10^5	D ₅ CN
	5	5.07	1.82×10^6	D ₅ CN
	6	5.64	5.36×10^5	D ₆ CN
15 k Macroinitiator	1	1.44	1.96×10^5	?
	3	4.04	3.03×10^5	D ₄ CN
	4	4.25	2.32×10^6	D ₄ CN
	5	4.71	1.66×10^5	D ₅ CN
	6	4.97	1.93×10^6	D ₅ CN
	7	5.55	6.12×10^5	D ₆ CN
20 k Macroinitiator	1	1.45	1.50×10^5	?
	2	4.12	2.63×10^5	D ₄ CN
	3	4.34	2.06×10^6	D ₄ CN
	4	4.80	1.42×10^5	D ₅ CN
	5	5.07	1.74×10^6	D ₅ CN
	6	5.68	4.85×10^5	D ₆ CN

The absolute concentration for D₄CN was directly measured by ²⁹Si NMR. The concentrations of D₅CN and D₆CN were calculated based on the relative concentrations of the cyclics using the SFC chromatograms. The concentrations of D₄CN, D₅CN and D₆CN are listed in Table 4.10. The average concentrations of D₄CN, D₅CN and D₆CN in all macroinitiators were $8.6 \pm 0.6\%$, $6.4 \pm 0.8\%$ and $2.1 \pm 0.4\%$, respectively. The average total concentration of macroinitiators was $17.3 \pm 1.5\text{ wt}\%$, which is close to the value derived by GPC ($\sim 24\text{ wt}\%$). By subtracting all cyclics from the formulation, the number average molecular weights were

calculated (5th row of Table 4.10). The number average molecular weights of the macroinitiators were also measured by ¹H NMR endgroup analysis (6th row of Table 4.10). ¹H NMR endgroup analysis was based on integrals of vinyl protons and methylene protons in the polysiloxanes. Samples for endgroup analysis were repeatedly washed with ethanol so cyclic species were mostly removed. By comparing the last two rows in Table 4.10, it is clear that the molecular weight derived from ¹H NMR endgroup analysis is quite close to the predicted molecular weight for the nominally 20k macroinitiator, but much higher than the predicted for the low molecular weight materials. This is expected because when the polymers were washed with ethanol, more short chains were removed from systems of low molecular weight, so endgroup analyses gave much higher molecular weights for those systems.

Table 4.10 Equilibrium concentrations of cyclics and molecular weights of the macroinitiators

Cyclics/Initiator (g/mol)	2.5K	5K	7.5K	10K	15K	20K
Conc. of D ₄ ^{cn} (wt %) ^a	8.3	9.8	8.5	7.7	8.5	9.0
Conc. of D ₅ ^{cn} (wt %) ^b	5.5	7.2	5.6	5.8	6.8	7.3
Conc. of D ₆ ^{cn} (wt %) ^b	2.0	2.3	2.0	1.5	2.0	3.0
Estimated M _n ^c	2,100	4,000	7,100	8,500	12,400	16,100
M _n after extraction of cyclics ^d	6,100	8,100	11,100	12,400	14,600	16,400

All measurements are based on macroinitiators terminated with vinyl dimethylchlorosilane

a Determined by ²⁹Si NMR

b Calculated based on results of ²⁹Si NMR and SFC

c Estimated according to the monomer-to-initiator ratio. The cyclics at equilibrium were subtracted.

d Calculated by ¹H NMR endgroup analysis according to the integrals of vinyl endgroup and siloxane methyl groups. The cyclics were removed by repeatedly washing the polymers with ethanol.

4.4.3 Molecular Weight Distributions of PCPMS Macroinitiators

A 10k PCPMS was prepared by terminating a PCPMS macroinitiator with vinyltrimethylchlorosilane. The GPC graph of this polymer was compared to that of a 10k α,ω -bis(aminopropyl) PCPMS to evaluate the molecular weight distribution for the macroinitiators.

GPC graphs for these polymers are shown in Fig. 25 (a) and (b). From the GPC results, it can be concluded that the molecular weight distribution of the PCPMS macroinitiator is comparable to other PCPMS polymers whose molecular weight are controlled by the same monomer-to-chain stopper ratio.

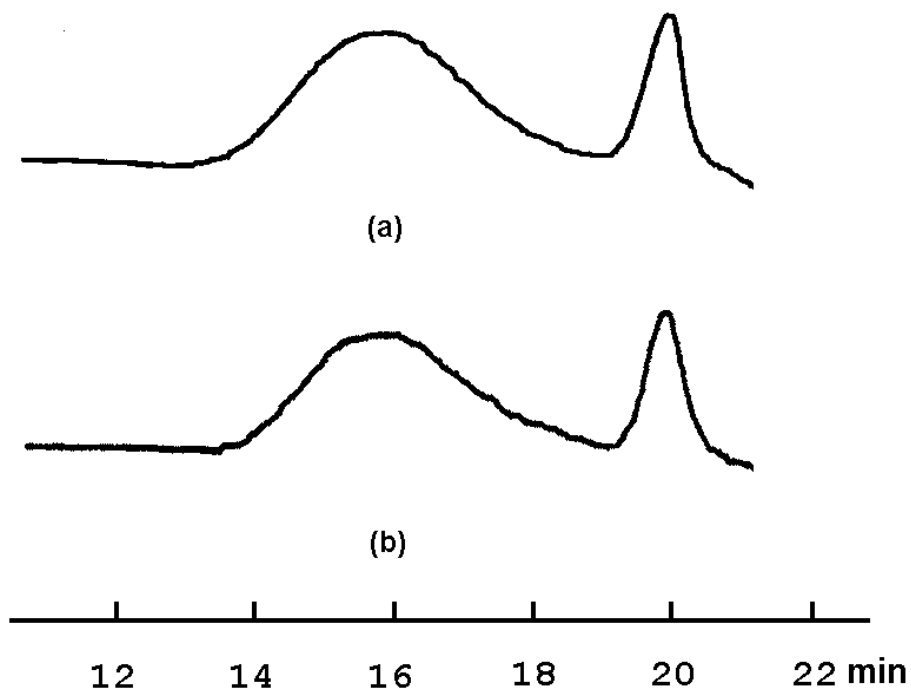


Figure 4.25 GPC for a) 10k α,ω -bis(3-aminopropyl) PCPMS, b) 10 k α,ω -divinyl PCPMS.

Solvent: CHCl_3 , Detector Type: Refractive Index

4.5 PDMS-b-PCPMS-b-PDMSs

4.5.1 Synthesis and Kinetics

The stability of PCPMS macroinitiators in common solvents like dichloromethane, tetrahydrofuran, acetonitrile/tetrahydrofuran (90/10) was studied by GPC and ^{29}Si NMR. No obvious decomposition was revealed by comparing GPC and ^{29}Si NMR for samples collected at the beginning and 48 hours after a macroinitiator solution was prepared. Therefore, PDMS-b-PCPMS-b-PDMS triblock copolymers could be prepared by D_3 anionic polymerization without causing significant cleavage of the central blocks.

Polymerization reactions were explored in acetonitrile/THF and dichloromethane with THF or TEGDME promoter. Dichloromethane was found to be a better solvent than acetonitrile/THF. 100 ml dichloromethane can dissolve ~ 13 g D_3 and ~ 6 g PCPMS, while acetonitrile and THF cannot dissolve significant amounts of macroinitiator or D_3 without separation of the other. To dissolve both materials, a mixture of acetonitrile and THF was required and the required composition was dependent on macroinitiator molecular weight.

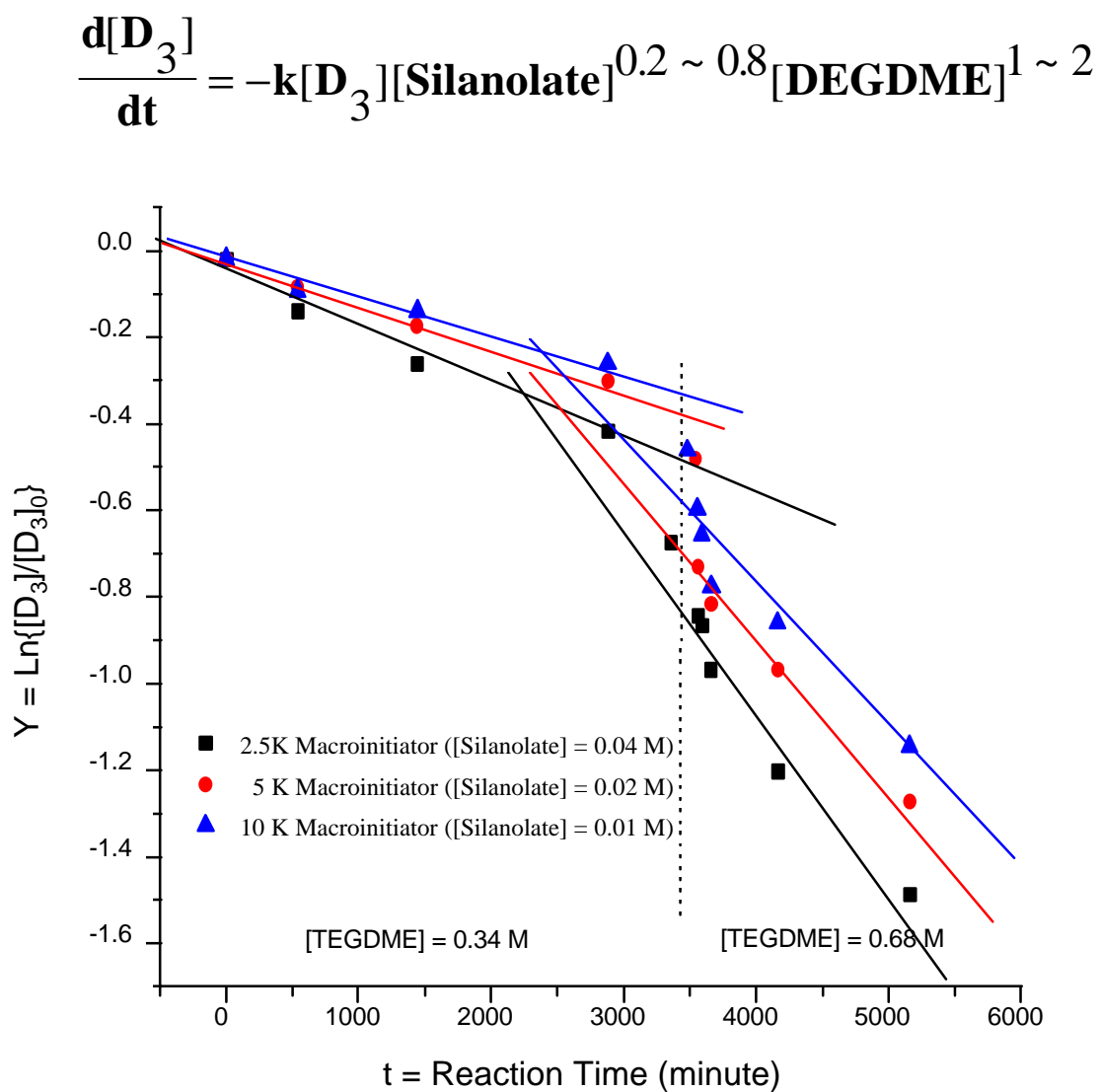
Several batches of 2.5k-2.5k-2.5k, 5k-5k-5k and 8k-8k-8k block copolymers were prepared using either THF or TEGDME as a promoter. The kinetics for D_3 polymerization with macroinitiator were also studied using ^1H NMR. Protons in D_3 resonate at δ 0.16 ppm (A), while protons from the methyl groups in PDMS and PCPMS are at $\delta \sim 0.10$ ppm (B). The contribution of methyl groups in PCPMS to the 0.10 ppm signal (C) was calculated from cyanopropyl signals at δ 0.7 ppm, δ 1.7 ppm and δ 2.4 ppm. Conversions of D_3 were calculated by (integral B - integral C) / (integral A + integral B - integral C). [Table 4.11](#) lists conversions of D_3 at different reaction times for three reactions. The concentrations of TEGDME were set to 0.34 M when the reaction time was less than 3480 minutes, then increased to 0.68 M after the reaction time was greater than 3480 minutes to study the influences of the promoter to the reaction rates. [Fig. 4.26](#) presents plots of $\ln([\text{D}_3]/[\text{D}_3]_0)$ vs reaction time for the D_3 polymerization reactions. With macroinitiators and TEGDME promoter, polymerization reactions of D_3 in dichloromethane were found to be first order in D_3 (unlike to DLDPS system which show deviations at early stages of

polymerization). Similar to lithium trimethylsilanolate and DLDPS initiators, the influence of the silanolate concentration (0.2-0.8 order) was much lower than that of the promoter concentration (1-2).

[Fig. 4.27](#) shows GPC traces (viscosity signals) for the 2.5k-2.5k-2.5k and 5k-5k-5k triblock copolymers and their related macroinitiators. GPC was conducted in chloroform. PDMS gives negative RI signal in this solvent while PCPMS gives positive signals, so block copolymers of PDMS and PCPMS do not yield useful RI peaks. GPC indicates that molecular weights had increased after polymerization of D_3 , so it is concluded that D_3 was polymerized and the resultant PDMSs were linked to the macroinitiators.

[Table 4.11](#) Kinetic data for polymerization of D_3 in dichloromethane using PCPMS macroinitiators and TEGDME promoter

[TEGDME]	Time (min)	2.5 k Macroinitiator [silanolate] = 0.04 M	5 k Macroinitiator [silanolate] = 0.02M	10 k Macroinitiator [silanolate] = 0.01 M
0.34 M	0	0.98	0.98	[0.98
	540	0.87	0.92	0.91
	1440	0.77	0.84	0.87
	2880	0.66	0.74	0.77
	3360	0.51	--	--
	3480	--	--	0.63
0.68 M	3540	--	0.618	--
	3560	0.43	0.482	0.55
	3590	0.421	--	0.519
	3660	0.38	0.442	0.46
	4165	0.3	0.38	0.423
	5160	0.226	0.28	0.318



[Figure 4.26](#) Polymerization of D_3 in CH_2Cl_2 using PCPMS macroinitiator and TEGDME promoter.

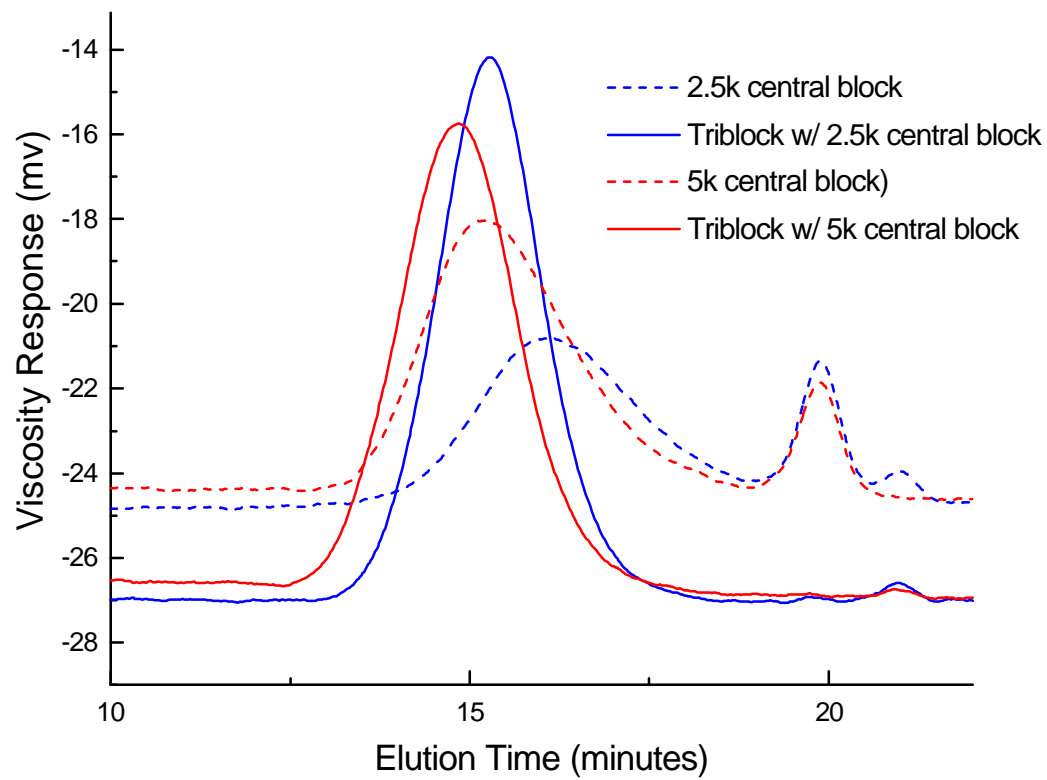


Figure 4.27 GPC (in CHCl_3) for PCPMS macroinitiators and related triblock copolymers. Cyclics in the triblock copolymers were removed.

4.5.2 ^{29}Si NMR Analyses

2.5k-2.5k-2.5k, 4k-4k-4k and 8k-8k-8k block copolymers were prepared. These copolymers are colorless, transparent and highly viscous liquids. While corresponding homo-PDMS and homo-PCPMSs with similar molecular weights have much lower viscosities. This is characteristic of microphase separated block copolymers^{124,125}.

[Fig. 4.28](#) shows possible sequences ^{29}Si NMR might reveal (only D is shown) at different levels of resolution for copolymers of dimethylsiloxane (D) or 3-cyanopropylmethylsiloxane (D^{cn}). At low resolution, D units are resolved to the monad level. Therefore, one peak can be observed in ^{29}Si NMR corresponding to D unit (left part). As resolution increases, subtle difference caused by the presence of closest neighbors are revealed and peaks are resolved to the triad level (central part). At this resolution, three peaks are observed in ^{29}Si NMR for D units arising from the possibilities of three triads, $\underline{\text{DDD}}$, $\underline{\text{DDD}}^{\text{cn}}$ ($\text{D}^{\text{cn}}\underline{\text{DD}}$ is equivalent to $\underline{\text{DDD}}^{\text{cn}}$) and $\text{D}^{\text{cn}}\underline{\text{DD}}^{\text{cn}}$, (observed units are underlined). The strength of ^{29}Si NMR signals corresponding to these sequences depends on their abundance in the polymer. As the resolution is further increased, influences from second closest neighbors are also revealed so the peaks are resolved to pentads level. Statistical parameters like sequence length, run number, etc. can be calculated based on the counts of those peaks in NMR spectra¹²⁶. Until now ^{29}Si NMR sequence studies have been carried out for copolymers of PDMS with methylvinylsiloxane, methylphenylsiloxane, diphenylsiloxane, methylhydrogensiloxanes and 3,3,3-trifluoropropyl-methylsiloxane.^{127,128,129,130}

^{29}Si NMR spectra for three triblock copolymers and one random copolymer of dimethylsiloxane and 3-cyanopropylmethylsiloxane are shown in [Fig. 4.29](#). For the block copolymers, two sharp peaks are present with chemical shift corresponding to the homo PDMS (δ -22 ppm) and homo PCPMS (δ -22.8 ppm), respectively. In order to have sharp ^{29}Si NMR peaks

¹²⁴ G. E. Molau, in *Block Copolymers*, Aggarwal, S. L., Ed., Plenum Press., New York (1970)

¹²⁵ J. J. Burke and V. Weiss, *Block and Graft Copolymers*, Syracuse University Press, New York (1973)

¹²⁶ J. L. Koenig, *Chemical Microstructure of Polymer Chains*, Wiley, New York (1980)

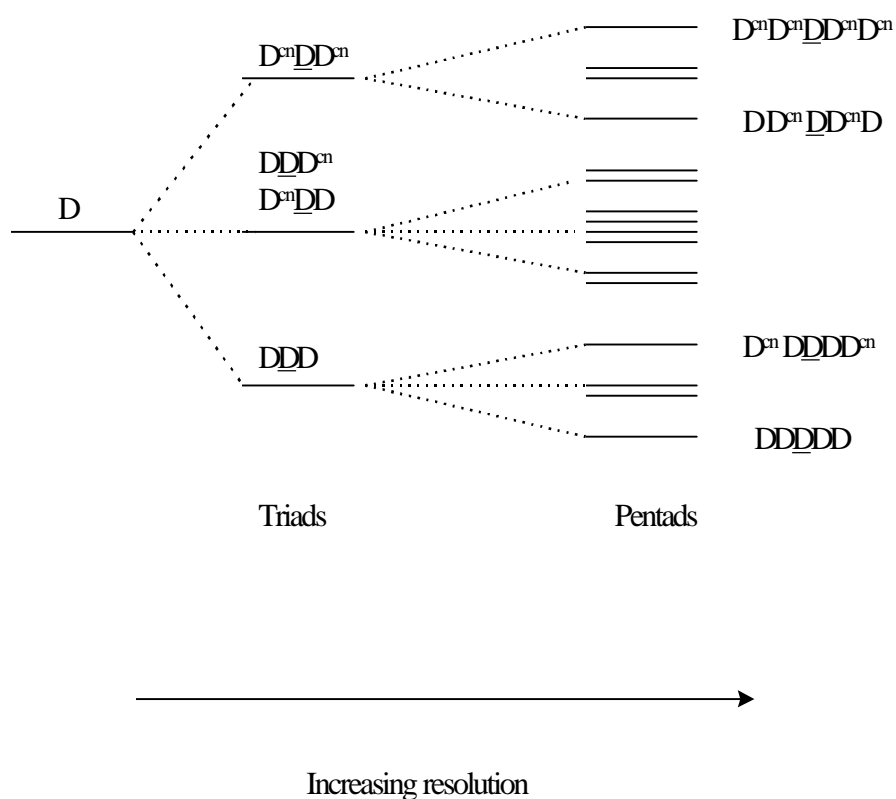
¹²⁷ H. Jancke, and W. M. Richey, *Polym. Let.*, **2**, 601 (1964)

¹²⁸ M. J. Zioemelis and J. C. Saam, *Macromolecules*, **22** 2111 (1989)

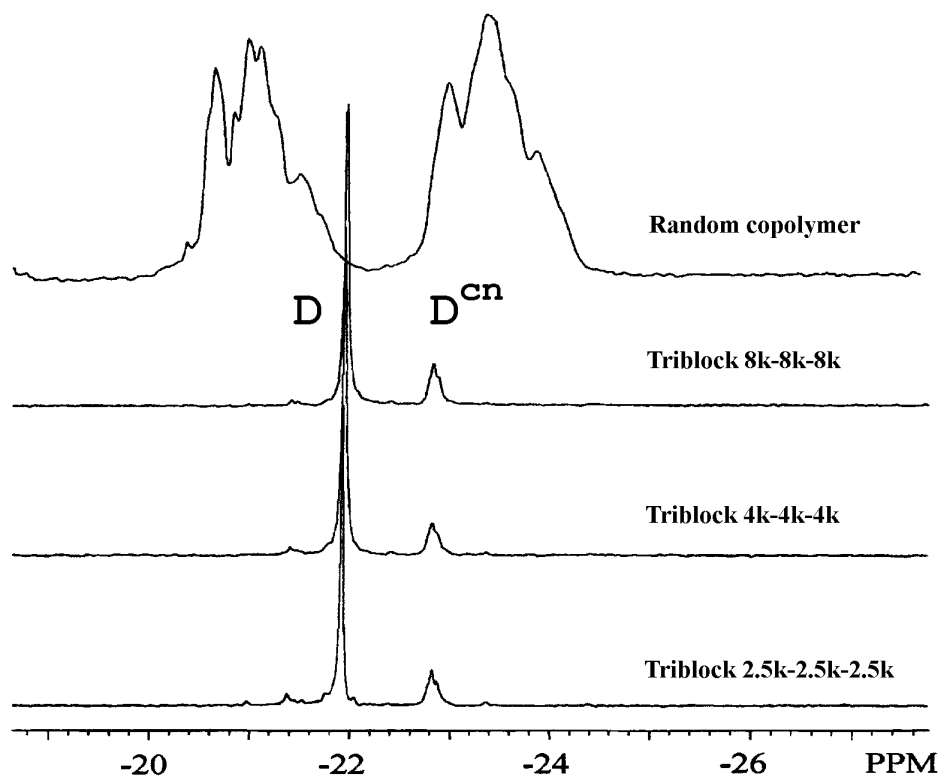
¹²⁹ G. N. Babu, S. S. Christopher and R. A. Newmark, *Macromolecules*, **20**, 2654 (1987)

¹³⁰ E. R. Evans U. S. Patent, 4,157,337, assigned to General Electric Company (1979)

at the exact positions of PDMS and PCPMS, major pentads in the polysiloxanes should be DDDD and $\text{D}^{\text{cn}}\text{D}^{\text{cn}}\text{D}^{\text{cn}}\text{D}^{\text{cn}}\text{D}^{\text{cn}}$. The only two systems which meet these requirements are block copolymers of PDMS and PCPMS and blends of PDMS and PCPMS. As expected, the random copolymer gives three groups of peaks at δ -20.4~ -22.8 ppm and δ -22.8~ -24 ppm for PDMS and PCPMS, respectively. Since PDMS and PCPMS differ so much in polarity, it is inevitable that their blends have strong macroscale phase separation. Therefore, blends of PDMS and PCPMS should show strong light scattering. Triblock copolymers have microscale phase separation (domain diameter \ll light wavelength), which cannot develop to macroscale phase separation due to the hindrance of chemical bonding. Since the triblock copolymers are transparent, so the possibility of having a polymer blend is unlikely.



[Figure 4.28](#) Sequence possibilities for a random PDMS/PCPMS copolymer at different resolution. (cited from reference 12 p90)



[Figure 4.29](#) ^{29}Si NMR for random and block copolymers of PDMS and PCPMS

4.5.3 Thermal Analyses

DSC confirmed that the PDPMS-*b*-PCPMS-*b*-PDMS triblock copolymers have microphase separated morphologies. Pure PDMSs have T_g at around -123°C , and tend to crystallize at $-90\sim -70^\circ\text{C}$ and melt at $-60\sim -40^\circ\text{C}$. Cyclic PDMS $[(\text{CH}_3)_2\text{SiO}]_x$ melts at $64\text{--}66^\circ\text{C}$ ($x=3$), $17\text{--}18^\circ\text{C}$ ($x=4$), -40°C ($x=5$) (Chapter 5, [reference 15](#)). PCPMS has a T_g -65°C , and does not show crystallization ([Fig. 4.30](#)). DSC curves for two copolymers with PDMS/PCPMS = 2 : 1 and 1 : 1 are given at the top and the center of [Fig. 4.30](#). These two polymers have T_g s at -119°C and -63°C , a crystallization peak at -90°C and a melting peak at $\sim -48^\circ\text{C}$. This is expected for microphase separated block copolymers of PDMS and PCPMS. The heat capacity

changes of the T_g 's also closely match the relative compositions of PDMS and PCPMS in the block copolymers. Two melting peaks are exhibited for PDMS in the central DSC diagram. Multiple melting points are often observed for polymeric materials due to 1) different crystalline size distributions, 2) melting-recrystallization of the original crystallites and their subsequent melting and 3) different crystalline forms of polymers. It has been suggested that double melting peaks in the PDMS system are caused by melting-recrystallization-melting¹³¹. Although blends of PDMS and PCPMS have similar thermal behavior, this possibility had been excluded here since the copolymers are transparent.

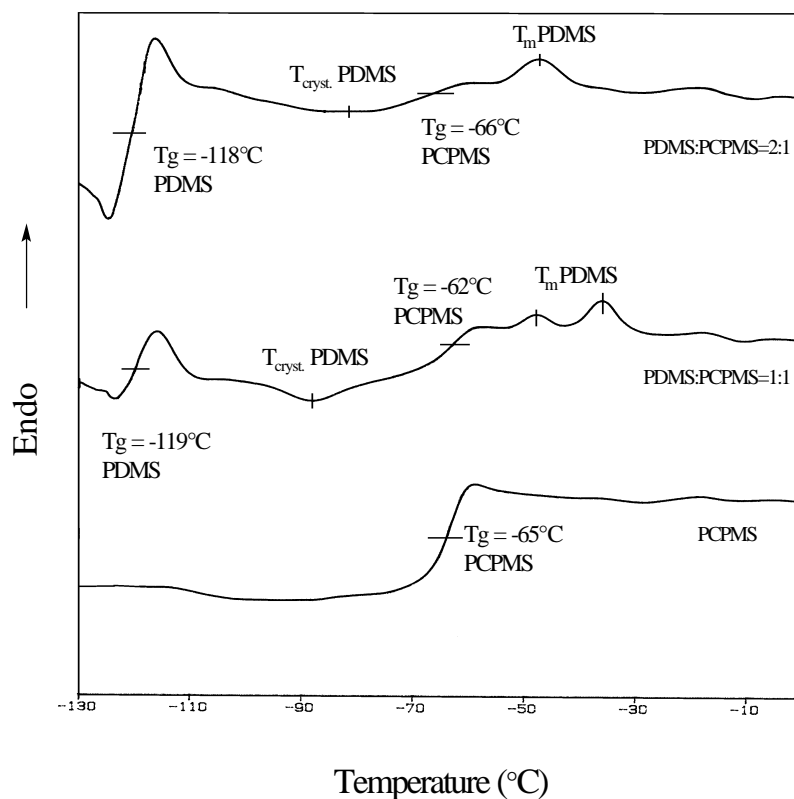


Figure 4.30 DSC for PCPMS and block copolymers of PDMS and PCPMS

¹³¹ S. J. Clarson K. Dodgeson and J. A. Semlyen, *Polymer*, **26**, 930 (1985)

CHAPTER 5

STABILIZATION STUDIES

Preliminary results for stabilization of magnetic particles with PDMS-b-PCPMS-b-PDMS triblock copolymers are presented in this chapter. These studies were intended to establish the feasibility of using the triblock copolymers prepared in this research as stabilizers for metal and metal oxide particles.

5.1 Stabilization of $\gamma\text{-Fe}_2\text{O}_3$

$\gamma\text{-Fe}_2\text{O}_3$ is the most commonly used magnetic material for commercial magnetic fluids. In order to have sufficient magnetism, commercial magnetic fluids usually include 20-40 % $\gamma\text{-Fe}_2\text{O}_3$. Those magnetic fluids are prepared either by grinding bulk $\gamma\text{-Fe}_2\text{O}_3$ to ultrafine powder in the presence of stabilizers, or by precipitating ultrafine particles from solutions of iron salts. The purpose here is not to make “practical” magnetic fluids but to demonstrate the potential for PDMS-b-PCPMS-b-PDMS triblock copolymers as colloidal stabilizers. Suspensions of $\gamma\text{-Fe}_2\text{O}_3$ powder in D_4 were prepared with or without adding the triblock copolymer stabilizers.

Three suspensions of $\gamma\text{-Fe}_2\text{O}_3$ in D_4 were prepared according to formulation in Table 5.1. A suspension without triblock copolymer stabilizer was also prepared as a reference. Note the names of stabilizers were also used as the names for suspensions.

Table 5.1 Formulation for suspensions of $\gamma\text{-Fe}_2\text{O}_3$ in D_4

Sample name	2.5k-2.5k-2.5k	4k-4k-4k	8k-8k-8k	reference
D_4 (ml)	10	10	10	10
$\gamma\text{-Fe}_2\text{O}_3$ (g)	2	2	2	2
Stabilizers (g)	2	2	2	0
Stability	good	good	good	very poor

The mixtures in Table 5.1 were agitated ultrasonically for 20 minutes to suspend the γ -Fe₂O₃ particles (Fig. 5.1). Without any stabilizer, γ -Fe₂O₃ particles quickly coagulated and settled, and the liquid became transparent within 10 minutes. In the presence of the triblock copolymers, γ -Fe₂O₃ suspensions were quite stable although some big particles settled gradually. The suspensions were left undisturbed after removing large particles which settled during 5-minutes centrifugation. No obvious precipitation of γ -Fe₂O₃ was observed after 4 months (Fig. 5.2). Therefore, PDMS-b-PCPMS-b-PDMS triblock copolymers have the potential to be used as stabilizers for silicone magnetic fluids.

Samples of these magnetic fluids were sent to Dr. S. W. Charles in University College of North Wales. Table 5.2 gives saturation magnetizations and susceptibilities for the three γ -Fe₂O₃ suspensions. Measurements were based on magnetization curves (M-H curves). Mean particle sizes and the standard deviations were measured by TEM in conjunction with size analyzer. Saturation magnetization and susceptibility of these magnetic fluids are in the range of 0.6-2.2 kAm⁻¹ and 0.03-0.1, respectively. Therefore, the magnetism of these magnetic fluids was very weak compared to commercial magnetic fluids, whose saturation magnetizations and initial susceptibilities are in the range of several 20-40 kAm⁻¹ and 0.4-2.5¹³². The weak magnetism of the suspensions is due to low concentrations of the magnetic materials because many big particles were removed during centrifugation.

5.2 Stabilization of Cobalt Ultrafine Particles

Nanometer particles of cobalt in silicone are expected to be prepared by thermal decomposition of dicobalt octacarbonyl in hexane in the presence of a stabilizer. Then the suspensions of cobalt particles are recovered and transferred into silicones. Ultrafine particles of cobalt were prepared in hexane by Dr. S. W. Charles using our 2.5k-2.5k-2.5k PDMS-PCPMS-PDMS triblock copolymer as a stabilizer. 4k-4k-4k, 10k-10k-10k block copolymers were found

¹³² N. Buske, H. Sonntage and T. Gotze, *Colloids and Surfaces*, **12**, 195-202 (1984)

to be less efficient than 2.5k-2.5k-2.5k block copolymers in stabilizing the $\gamma\text{-Fe}_2\text{O}_3$ suspensions. Without adding stabilizers, decomposition of carbonyl cobalt gave only large cobalt particles. Similar systems with nickel particles are being explored by reducing bis(cyclopentadienyl)nickel ($\text{Ni}(\text{C}_5\text{H}_5)_2$) in the presence of the triblock copolymers.

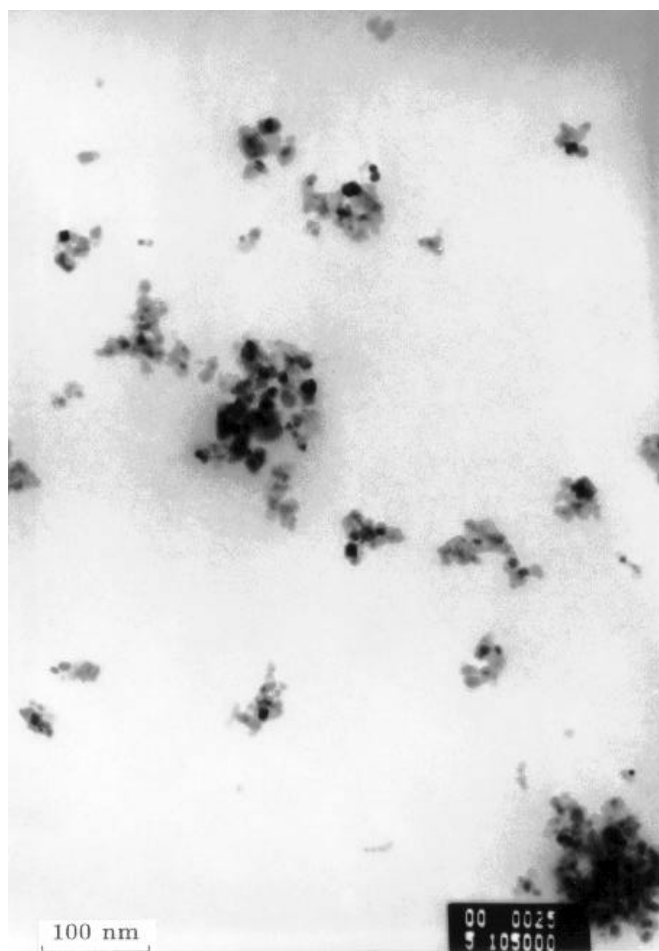
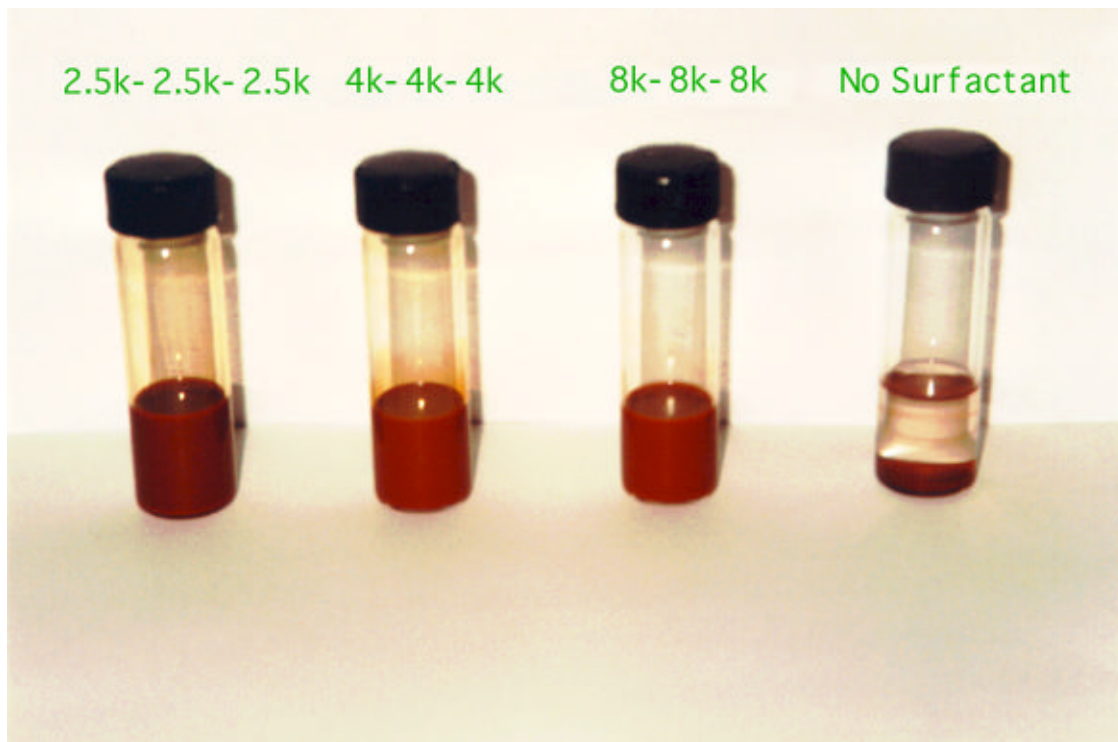


Figure 5.1 TEM for suspensions of $\gamma\text{-Fe}_2\text{O}_3$

Table 5.2 Magnetic properties for triblock copolymer stabilized suspensions of $\gamma\text{-Fe}_2\text{O}_3$ in D_4

	2.5k-2.5k-2.5k	4k-4k-4k	8k-8k-8k
Number of data sets	11	12	11
Saturation Magnetization (kAm^{-1})	1.28	2.27	0.61
H_0 (kAm^{-1})	15.0	32.1	24.0
Number of data sets for χ_i	31	31	31
Initial Permeability	0.0736	0.102	0.0291
Mean magnetic particle size (\bullet)	125	106	112
Standard deviation of particle size (\bullet)	0.32	0.40	0.37

Figure 5.2 $\gamma\text{-Fe}_2\text{O}_3$ in D_4 with/without PDMS-b-PCPMS-b-PDMS stabilizers

CHAPTER 6

Conclusions

Nitrile containing block copolymers, particularly PDMS-b-PCPMS-b-PDMSs have been synthesized and demonstrated as stabilizers for silicone magnetic fluids.

The mixed D_x CNs ($x = 3-5$) were prepared by heterogeneous hydrolysis of 3-cyanopropylmethyldichlorosilane in chlorobenzene/saturated NaHCO_3 , followed by cyclization and equilibration of the hydrolysis products using trifluoromethanesulfonic acid catalyst. The cyclic monomer prepared in this manner contains trimer (5-37%), tetramer (~60%) and pentamer (5-15%). 3-Cyanopropylmethyldichlorosilane was prepared by hydrosilylation of methyldichlorosilane with allyl cyanide using hexachloroplatinic acid catalyst. The reaction proceeded almost exclusively in an anti-Markownikoff way under these conditions.

D_4 CN was prepared by hydrosilylation of D_4 H with allyl cyanide using $\text{Pt}(0)[((\text{CH}_2=\text{CH})\text{Si}(\text{CH}_3)_2)_2\text{O}]$ catalyst. D_4 CN made in this manner includes ~8% Markownikoff addition products.

DLDPs were prepared by deprotonation of diphenylsilanediol with diphenylmethyl lithium. It was found that α,ω -Difunctional PDMSs can be prepared with DLDPs initiator with reasonably narrow molecular weight distributions.

D_x CN ($x = 3-5$) can be equilibrated at 100°C within 5-10 hours with DLDPs. The molecular weight of the macroinitiators was controlled by the D_x CN-DLDPs ratio. The major cyclics in the equilibrated macroinitiators are D_4 CN ($8.6 \pm 0.6 \%$), D_5 CN ($6.4 \pm 0.8 \%$) and D_6 CN ($2.1 \pm 0.4 \%$). The macroinitiator showed a similar molecular weight distribution to the polymer whose molecular weight is controlled by disiloxane chain stopper.

The PDMS-b-PCPMS-b-PDMSs were prepared through kinetically polymerization of D_3 (in dichloromethane) using lithium silanolate endcapped PCPMS macroinitiators. The polymerization proceeds well in both THF and DEGDM promoters. With the macroinitiator and DEGDM promoter, the polymerization of D_3 initiated shows first order kinetics with respect

to D₃. However, under similar conditions but with DLDPS initiator, the reaction shows deviations from first order kinetics during early stages of the reaction.

The PDMS-*b*-PCPMS-*b*-PDMSs are transparent, highly viscous liquids. The block structure of these polymers was confirmed by ²⁹Si NMR spectroscopy. DSC indicated that the triblock copolymers have microphase separated morphologies.

PDMS-*b*-PCPMS-*b*-PDMS triblock copolymers can stabilize suspensions of γ -Fe₂O₃ particles in D₄ and particles of cobalt in hexane, so these triblock copolymers are promising stabilizers for magnetic fluids.

CHAPTER 7

FUTURE WORK

As a new block copolymers, very few properties of PDMS-b-PCPMS-b-PDMS have been determined. The interactions of the new PCPMS stabilizers with the surface of colloidal particles and the stabilities of suspensions using these block copolymers stabilizers need more studies. Therefore, the following researches are recommended.

- 1) Prepare a series of block copolymers with different lengths of the central block and tail blocks and establish the relationships between microstructure and physical properties.
- 2) Using those block copolymers as stabilizers to prepare suspensions of various magnetic materials in silicones, and find out A) what is the suitable block length for optimum stabilization, B) how temperature, pressure, concentration and solvents influence their stability, C) whether their flocculation is reversible or not.
- 3) Investigate alternative applications for the -CN substituted siloxane polymers.
- 4) Develop stabilizers with adhesive groups other than -CN groups.

Vita

Chenghong Li

The author was born in Ningxiang, Hunan, P. R. C. on September 18, 1964. He graduated in the First High School in Ningxiang in July 1980. Then he enrolled in East China Normal University, Shanghai and received his B. S. in chemistry in July 1985. In August 1985, he enrolled in Shanghai Institute of Ceramics, Chinese Academy of Science and received his M. Eng. in inorganic materials in August 1988. Soon he joined in Advanced Research Institute, Wuhan University of Technology as a research engineer to develop high performance metal-ceramic composites. In May 1991, He joined Donghu Corp. Wuhan as a senior engineer and there he became interested in polymer science. In August 1993, he enrolled in Dept. of Chemistry, Virginia Polytechnic Institute and State University and joined Dr. J. S. Riffle's research group in May, 1994.