

Synthesis of Functionalized Poly(dimethylsiloxane)s and the Preparation of Magnetite Nanoparticle Complexes and Dispersions

Kristen Wilson O'Brien

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

Doctor of Philosophy

In

Chemistry

Approved by:

Judy S. Riffle, Chair

Alan Esker

Jack Lesko

Timothy E. Long

James E. McGrath

August 21, 2003
Blacksburg, Virginia

Keywords: Polymers, iron oxides; steric stabilization; magnetic fluids

Copyright 2003, Kristen Wilson O'Brien

Synthesis of Functionalized Poly(dimethylsiloxane)s and the Preparation of Magnetite Nanoparticle Complexes and Dispersions

Kristen Wilson O'Brien

(ABSTRACT)

Poly(dimethylsiloxane) (PDMS) fluids containing magnetite nanoparticles stabilized with carboxylic acid-functionalized PDMS were prepared. PDMS-magnetite complexes were characterized using transmission electron microscopy, elemental analysis, and vibrating sample magnetometry. PDMS-magnetite complexes containing up to 67 wt% magnetite with magnetizations of ~ 52 emu gram⁻¹ were prepared. The magnetite particles were 7.4 ± 1.7 nm in diameter. Calculations suggested that the complexes prepared using mercaptosuccinic acid-functionalized PDMS (PDMS-6COOH) complexes contained unbound acid groups whereas the mercaptoacetic acid-functionalized PDMS (PDMS-3COOH) complexes did not. Calculations showed that the PDMS-3COOH and PDMS-6COOH covered the same surface area on magnetite. Calculations were supported by molecular models and FTIR analyses. The complexes were dispersed into PDMS carrier fluids by ultrasonication, resulting in magnetic PDMS fluids with potential biomedical applications.

Magnetite particles (100 nm to 1 μ m in diameter) were prepared by crystallization from goethite/glycol/water solutions under pressure. Two methods for particle growth were investigated in which the crystallization medium was varied by adjusting the amount of water or by adding itaconic acid. Particle surfaces were analyzed by x-ray photoelectron spectroscopy (XPS). Particles with clean surfaces were coated with carboxylic acid-functionalized poly(ϵ -caprolactone) stabilizers. Adding itaconic acid to the reactions afforded particles ~ 100 nm in diameter. The magnetite particles displayed magnetic hysteresis. The particles were dispersed into vinyl ester resins by ultrasonication and it was demonstrated that the ~ 100 nm particles remained dispersed for

three days without agitation. These dispersions have applications in magnetic induction heating for composite repair.

Living polymerizations of hexamethylcyclotrisiloxane were terminated with dimethylchlorosilane, phenylmethylchlorosilane, or diisopropylchlorosilane (DIPCS). Platinum-catalyzed hydrosilation of the hydrosilane-terminated PDMS with allyloxyethanol afforded a systematic series of hydroxyalkyl-terminated PDMS. The reactions were successful except for the hydrosilation of the sterically-hindered DIPCS-functionalized PDMS where no reaction was observed. Hydroxyalkyl-terminated PDMS oligomers were successful in initiating the stannous octoate-catalyzed copolymerization of ϵ -caprolactone, which afforded PDMS-*b*-PCL diblock copolymers of controlled composition.

ACKNOWLEDGEMENTS

I would like to thank my advisor, Dr. Judy Riffle, for guiding me in my research over the past four years. She has provided me with the knowledge, the tools, and the motivation that I will need to succeed in the future. I would also like to thank her for the many smiles, handshakes, and hugs she has given me as I have progressed through my graduate career. I also thank the members of my committee, Dr. Alan Esker, Dr. Jack Lesko, Dr. Timothy E. Long, and Dr. James E. McGrath for their valuable insight and suggestions.

Many people at Virginia Tech have provided me with chemistry knowledge, constructive criticisms, and technical support including Tom Glass, Steve McCartney, Metha Rutnakornpituk, Linda Harris, Jennifer Lalli, Mike Sumner, Ragy Ragheb, Dave Williamson, Jeremy Lizotte, Dr. Lin, Mark Flynn, and Angie Flynn. My professors at Virginia Tech (Dr. Riffle, Dr. McGrath, Dr. Long, Dr. Gibson, Dr. Tanko, Dr. Kingston, Dr. Ducker, Dr. McNair, Dr. Wilkes, and Dr. Deck), although they have put me through some of the most tormenting homework and exams, have all been instrumental in shaping me into the chemist that I am now.

I must acknowledge my very helpful undergraduate student for two years and good friend, Jonathan Goff, whose unending inquisitiveness and intellectual ramblings both entertained and inspired me. Thanks to Linda Harris for her brainchild, the band “One Night Stand”, which allowed me to realize my dream of being a rock-and-roll star, at least for that one night. Thanks go to all my other close friends (Meghan, Sonya, Amy, Jill, Lacey, Mike Z.) for the good times, good advice, and good friendships that kept me happy along the way.

I am grateful for the immeasurable love and support I have received from my parents who have taught me many of life’s important lessons. Thank you to my brothers Jon, Tom, and Joe, whom I have always looked up to and admired as role models. Also thanks to my sisters-in-law, Victoria and Lisa, who are both very special to me. Finally, a big thanks to my new, loving, understanding husband and best friend, Emmett, with whom I’m looking forward to spending the rest of my life.

TABLE OF CONTENTS

Introduction	1
1 Chapter 1. Literature Review	5
1.1 Overview of Polysiloxane Chemistry	5
1.1.1 Background	5
1.1.2 Synthesis of α,ω -Difunctional Polysiloxanes by Equilibration Polymerization	8
1.1.3 Recent Examples of α,ω -Difunctional Polysiloxanes.....	10
1.1.4 Synthesis and Functionalization of Polysiloxanes with Pendant Hydrosilyl Groups	18
1.1.5 Synthesis and Recent Examples of Monofunctional Polysiloxanes	25
1.1.6 Carboxylic Acid-Functionalized Polysiloxanes.....	30
1.2 Overview of Poly(ϵ -caprolactone) Chemistry.....	34
1.2.1 Background	34
1.2.2 Coordination-Insertion and Anionic Polymerizations of ϵ -Caprolactone.	36
1.2.3 Biodegradability of Poly(ϵ -caprolactone)	41
1.2.4 Miscibility of Poly(ϵ -caprolactone) With Other Polymers	42
1.3 Nanoparticle Synthesis Within Block Copolymer Micelles	43
1.3.1 Introduction to Nanotechnology and Block Copolymer Micelles	43
1.3.2 Reactions in Block Copolymer Micelles.....	45
1.3.3 Synthesis of Metal Nanoparticles via Reduction of Metal Salts.....	46
1.4 Magnetic Nanoparticles.....	49
1.4.1 Background on Magnetic Nanoparticles	49
1.4.2 Synthesis of Magnetic Iron, Cobalt, and Nickel Nanoparticles	51
1.4.3 Synthesis of Magnetite Nanoparticles.....	55
1.4.4 Surface Properties of Magnetite Nanoparticles.....	56
1.4.5 Magnetite-Polymer Complexes and Dispersions	58
2 Chapter 2. Poly(dimethylsiloxane)-Magnetite Nanoparticle Complexes and Dispersions.....	62
2.1 Introduction	62
2.2 Experimental	63
2.2.1 Materials.....	63
2.2.2 Synthesis of Trivinylsilyl-Terminated PDMS	64
2.2.3 Thiol-ene Addition of Mercaptoacetic Acid to the Trivinylsilyl End group 65	65
2.2.4 Thiol-ene Addition of Mercaptosuccinic Acid to the Trivinylsilyl End Group	66
2.2.5 Studies to Determine the Effect of Acidic Conditions on PDMS Molecular Weight Distribution.....	66
2.2.6 Preparation of PDMS-Magnetite Nanoparticle Complexes.....	67
2.2.7 Preparation of Magnetic Poly(dimethylsiloxane) Fluids	67
2.2.8 Rheometric Studies of Magnetic Fluids	68
2.2.9 Instrumentation.....	68
2.3 Results and Discussion.....	69
2.3.1 PDMS Stabilizer Synthesis	69

2.3.2	PDMS-Magnetite Nanoparticle Complex Preparation.....	80
2.3.3	Magnetic Silicone Fluid Preparation.....	93
2.4	Conclusions.....	96
3	Chapter 3. Preparation of Controlled-Size Magnetite Nanoparticles and Their Dispersibility in Vinyl Ester Resins.....	98
3.1	Introduction.....	98
3.2	Experimental.....	100
3.2.1	Materials.....	100
3.2.2	Preparation of Controlled-Size Magnetite by Reduction of Goethite and Crystallization from Propylene Glycol-Water Solutions (designated Method 1)...	100
3.2.3	Preparation of Controlled-Size Magnetite by Reduction of Goethite and Crystallization from Ethylene Glycol-Water Solutions in the Presence of Carboxylic Acids (designated Method 2).....	101
3.2.4	Synthesis of Carboxylic Acid-Functionalized Triblock Copolymers for the Steric Stabilization of Magnetite Nanoparticles.....	101
3.2.5	Adsorption of PCL- <i>b</i> -PMVSCOOH- <i>b</i> -PCL onto Magnetite Nanoparticles 103	103
3.2.6	Preparation of Dispersions of Magnetite Nanoparticles in Vinyl Ester Resins	103
3.2.7	Instrumentation.....	103
3.3	Results and Discussion.....	104
3.3.1	Preparation of Controlled-Size Magnetite.....	104
3.3.2	Synthesis of Carboxylic Acid-Functionalized Triblock Copolymers for the Steric Stabilization of Magnetite Nanoparticles.....	109
3.3.3	Adsorption of PCL- <i>b</i> -PMVSCOOH- <i>b</i> -PCL onto Magnetite Nanoparticles 114	114
3.3.4	Characterization of Magnetite Nanoparticles by X-Ray Photoelectron Spectroscopy.....	114
3.3.5	Preparation of Dispersions of Magnetite Nanoparticles in Vinyl Ester Resins	118
3.4	Conclusions.....	120
4	Chapter 4. Synthesis and Characterization of Monohydroxyalkyl-Functional Poly(dimethylsiloxane).....	121
4.1	Introduction.....	121
4.2	Experimental.....	122
4.2.1	Materials.....	122
4.2.2	Synthesis of Dimethylhydrosilane-Terminated Poly(dimethylsiloxane)	123
4.2.3	Synthesis of Diisopropylhydrosilane-Terminated PDMS.....	123
4.2.4	Synthesis of Phenylmethylhydrosilane-Terminated PDMS.....	124
4.2.5	Synthesis of a Hydroxyalkyl-Terminated Poly(dimethylsiloxane) Oligomer	124
4.2.6	Synthesis of a Poly(dimethylsiloxane- <i>b</i> - ϵ -caprolactone) Diblock Copolymer Utilizing a Hydroxyalkyl-Functionalized Poly(dimethylsiloxane) Oligomer as a Macroinitiator.....	124
4.2.7	Instrumentation.....	125
4.3	Results and Discussion.....	125

4.3.1	Synthesis of Dialkylhydrosilane-Terminated PDMS.....	125
4.3.2	Synthesis of Hydroxyalkyl-Terminated Poly(dimethylsiloxane).....	134
4.3.3	Copolymerization of ϵ -Caprolactone from a Hydroxyalkyl-Terminated Poly(dimethylsiloxane) Macroinitiator	139
4.4	Conclusions	144
5	Concluding Remarks and Recommendations for Future Work	145
6	Vita.....	149

LIST OF FIGURES

FIGURE 0-1. STERIC STABILIZATION OF MAGNETITE NANOPARTICLES USING CARBOXYLIC ACID-FUNCTIONALIZED PDMS.....	1
FIGURE 0-2. INSERTION OF THE PERMANENT MAGNETIC PASTE IN THE EYE BETWEEN THE SCLERA AND THE TENON’S CAPSULE USING THE SPECIALLY DESIGNED APPLICATOR....	2
FIGURE 0-3. PROPOSED METHOD FOR THE REPAIR OF RETINAL DETACHMENT.....	3
FIGURE 1-1. GENERAL POLYSILOXANE BACKBONE STRUCTURE.....	5
FIGURE 1-2. ONE EXAMPLE OF A ω -ALKENYL BENZO-15-CROWN-5 DERIVATIVE THAT WAS INCORPORATED INTO THE POLYSILOXANE VIA HYDROSILATION.....	19
FIGURE 1-3. MOLECULAR WEIGHT AS A FUNCTION OF CONVERSION FOR STEP-GROWTH, FREE RADICAL, AND LIVING POLYMERIZATIONS.....	26
FIGURE 1-4. CORE AND CORONA OF A BLOCK COPOLYMER MICELLE.....	45
FIGURE 1-5. POLY(MTD)- <i>B</i> -POLY(NORCOOH).....	48
FIGURE 1-6. BEHAVIOR OF SUPERPARAMAGNETIC PARTICLES WITH AND WITHOUT THE PRESENCE OF AN APPLIED EXTERNAL MAGNETIC FIELD.....	50
FIGURE 1-7. SURFACE CHEMISTRY OF MAGNETITE AS A FUNCTION OF pH.....	56
FIGURE 1-8. ELECTROSTATIC DOUBLE LAYER CAUSING REPULSIVE FORCES BETWEEN PARTICLES.....	57
FIGURE 1-9. BIDENTATE CHELATION OF CARBOXYLIC ACID ON MAGNETITE SURFACE.....	57
FIGURE 2-1. ^1H NMR SPECTRA SHOWING MONOMER DEPLETION DURING THE LIVING RING OPENING POLYMERIZATION OF HEXAMETHYLCYCLOTRISILOXANE AT 25 °C.....	71
FIGURE 2-2. ^1H NMR SPECTRA OF A 1230 G MOL ⁻¹ TRIVINYLSILYL-TERMINATED POLY(DIMETHYLSILOXANE) OLIGOMER.....	72
FIGURE 2-3. ^{29}Si NMR SPECTRA SHOWING A) 2200 G MOL ⁻¹ TRIVINYLSILYL-TERMINATED PDMS AND B) 2600 G MOL ⁻¹ TRIMERCAPTOACETIC ACID-TERMINATED PDMS.....	73
FIGURE 2-4. ^1H NMR SPECTRA MONITORING THE THIOL-ENE ADDITION OF MERCAPTOACETIC ACID TO A 2000 G MOL ⁻¹ TRIVINYLSILYL-TERMINATED PDMS AT i) 0 MINUTES ii) 15 MINUTES AND iii) 45 MINUTES.....	76
FIGURE 2-5. GPC CHROMATOGRAMS OF 4270 G MOL ⁻¹ PDMS A) TRIVINYLSILYL-TERMINATED B) AFTER THE THIOL-ENE ADDITION OF MERCAPTOACETIC ACID AND C) AFTER THE THIOL-ENE ADDITION OF MERCAPTOSUCCINIC ACID SUGGEST THAT SOME CHAIN COUPLING OCCURS UNDER THESE CONDITIONS.....	78
FIGURE 2-6. GPC CHROMATOGRAMS SHOWING A) 1270 G MOL ⁻¹ TRIVINYLSILYL-TERMINATED PDMS AND B) 1270 G MOL ⁻¹ TRIVINYLSILYL-TERMINATED PDMS AFTER EXPOSURE TO ACIDIC CONDITIONS AT 80 °C FOR 45 MINUTES.....	80
FIGURE 2-7. TEM IMAGES A) PDMS-MAGNETITE COMPLEX CONTAINING 50 WT% MAGNETITE AND A 3500 G MOL ⁻¹ PDMS(COOH) ₃ STABILIZER AND B) THE SAME COMPLEX DISPERSED IN A 2000 G MOL ⁻¹ PDMS CARRIER FLUID.....	83
FIGURE 2-8. HISTOGRAM DEPICTING THE DISTRIBUTION OF MAGNETITE PARTICLE DIAMETERS.....	83
FIGURE 2-9. SCHEMATIC REPRESENTATION OF THE MAGNETITE SURFACE AREA COVERED BY A PDMS CHAIN FUNCTIONALIZED WITH EITHER MERCAPTOACETIC ACID OR MERCAPTOSUCCINIC ACID.....	85
FIGURE 2-10. A COMPARISON OF THE NUMBER OF COOH GROUPS AND MAGNETITE BINDING SITES IN PDMS-MAGNETITE COMPLEXES PREPARED USING A) 2620 G MOL ⁻¹	

PDMS-(COOH) ₃ AND 2800 G MOL ⁻¹ PDMS-(COOH) ₆ . B) 4540 G MOL ⁻¹ PDMS-(COOH) ₃ AND 4720 G MOL ⁻¹ PDMS-(COOH) ₆ . C) 7560 G MOL ⁻¹ PDMS-(COOH) ₃ AND 7740 G MOL ⁻¹ PDMS-(COOH) ₆	88
FIGURE 2-11. MOLECULAR MODELS GENERATED USING MM2 ENERGY MODELS AND CHEM3D PRO SOFTWARE A) MAGNETITE SURFACE (TOP AND SIDE VIEWS) B) PDMS MERCAPTOACETATE END GROUPS AND C) PDMS MERCAPTOSUCCINATE END GROUPS AFTER ENERGY MINIMIZATION NEAR MAGNETITE SURFACE. CATIONIC SURFACE SITES ARE DENOTED WITH BLACK ARROWS. HYDROGEN = BLUE; CARBON = GRAY; OXYGEN = RED; SILICON = PURPLE; SULFUR = YELLOW; IRON = BROWN.	90
FIGURE 2-12. FTIR SPECTRA SHOWING PDMS-(COOH) ₃ , THE SAME POLYMER IN ITS SALT-FORM, PDMS-(COO ⁻ K), AND PDMS-MAGNETITE COMPLEXES PREPARED USING PDMS-(COOH) ₃ AND PDMS-(COOH) ₆	93
FIGURE 2-13. ARRHENIUS PLOT OF LNη VS. 1/T FOR THE MAGNETITE DISPERSIONS IN 20,200 G MOL ⁻¹ PDMS CARRIER FLUID.	96
FIGURE 3-1. AN EXEMPLARY MAGNETIC HYSTERESIS LOOP SHOWING SATURATION MAGNETIZATION (M _{SAT}), REMANENCE MAGNETIZATION (M _R), AND COERCIVITY (H _C).	99
FIGURE 3-2. SEM IMAGES OF MAGNETITE NANOPARTICLES PREPARED ACCORDING TO THE REPORTED PROCEDURE WITH 1 mL WATER (TOP), 3 mL WATER (MIDDLE), OR 5 mL WATER (BOTTOM). THE WHITE LINES INDICATE 1 μM MARKERS.	106
FIGURE 3-3. SEM IMAGES OF MAGNETITE NANOPARTICLES PREPARED USING METHOD 2 ACCORDING TO THE REPORTED PROCEDURE WITH A) NO ITACONIC ACID B) 0.6 G ITACONIC ACID C) 1.0 G ITACONIC ACID AND D) 1.4 G ITACONIC ACID.	108
FIGURE 3-4. MAGNETIC HYSTERESIS LOOP OBTAINED BY VIBRATING SAMPLE MAGNETOMETRY FOR MAGNETITE NANOPARTICLES PREPARED USING METHOD 1 (~400 NM DIAMETER).	109
FIGURE 3-5. ¹ H NMR SPECTRUM OF THE 1150 G MOL ⁻¹ α,ω-DIHYDROXYBUTYL-TERMINATED PMVS.	110
FIGURE 3-6. DSC THERMOGRAMS FOR THE PCL AND PMVS COPOLYMERS AND HOMOPOLYMERS.	112
FIGURE 3-7. XPS BINDING ENERGIES FOR CARBON ON THE SURFACE OF ORIGINAL MAGNETITE PREPARED USING METHOD 1 (LEFT) AND MAGNETITE AFTER THE ADSORPTION OF PCL- <i>B</i> -PVMS-COOH- <i>B</i> -PCL (RIGHT).	116
FIGURE 3-8. XPS BINDING ENERGIES OF CARBON ON THE SURFACE OF MAGNETITE PREPARED USING METHOD 2 IN WHICH ITACONIC ACID WAS ADDED TO THE CRYSTALLIZATION MEDIUM.	117
FIGURE 3-9. VARIATION IN DISPERSION QUALITY WITH TIME FOR 10 WT% DISPERSIONS OF MAGNETITE NANOPARTICLES IN VINYL ESTER RESIN.	118
FIGURE 3-10. TIME FOR THE ONSET OF MAGNETITE NANOPARTICLE SEDIMENTATION FROM 10 WT% DISPERSIONS IN VINYL ESTER RESINS.	119
FIGURE 4-1. TERMINATING REACTIONS WITH DIISOPROPYLCHLOROSILANE, DIMETHYLCHLOROSILANE, AND PHENYLMETHYLCHLOROSILANE THAT WERE USED TO INCORPORATE ONE HYDROSILANE FUNCTIONALITY AT THE END OF PDMS CHAINS.	128
FIGURE 4-2. ¹ H NMR SPECTRA OF DIMETHYLSILANE-TERMINATED 6150 G MOL ⁻¹ PDMS (TOP), DIISOPROPYLSILANE-TERMINATED 13,700 G MOL ⁻¹ PDMS (MIDDLE), AND PHENYLMETHYLSILANE-TERMINATED 16,600 G MOL ⁻¹ PDMS (BOTTOM).	129

FIGURE 4-3. ^{29}Si NMR SPECTRA OF DIMETHYLSILANE-, DIISOPROPYLSILANE-, AND PHENYLMETHYLSILANE-TERMINATED PDMS.	131
FIGURE 4-4. GPC CHROMATOGRAM OF 6150 G MOL^{-1} DIMETHYLHYDROSILANE-TERMINATED PDMS.	132
FIGURE 4-5. PROPOSED RESONANCE STRUCTURES FOR PHENYLMETHYLHYDROSILANE-TERMINATED PDMS THAT ILLUSTRATE THE REDUCED SENSITIVITY OF THE TERMINAL SILICON ATOM TOWARDS NUCLEOPHILIC ATTACK.	134
FIGURE 4-6. REACTION SCHEME FOR THE SYNTHESIS OF HYDROXYALKYL-TERMINATED PDMS BY HYDROSILATION OF HYDROSILANE-TERMINATED PDMS WITH ALLYLOXYETHANOL.	135
FIGURE 4-7. ^1H NMR SPECTRA OF 6150 G MOL^{-1} DIMETHYLHYDROSILANE-TERMINATED PDMS BEFORE (TOP) AND AFTER (BOTTOM) HYDROSILATION WITH ALLYLOXYETHANOL.	136
FIGURE 4-8. ^{29}Si NMR SPECTRA OF 6200 G MOL^{-1} DIMETHYLSILANE-TERMINATED PDMS BEFORE AND AFTER HYDROSILATION WITH ALLYLOXYETHANOL SHOWING INTEGRAL VALUES.	137
FIGURE 4-9. FTIR SPECTRA OF PHENYLMETHYLHYDROSILANE-TERMINATED PDMS (TOP) AND THE SAME POLYMER FOLLOWING THE HYDROSILATION REACTION WITH ALLYLOXYETHANOL (BOTTOM).	138
FIGURE 4-10. ^1H NMR SPECTRUM OF ϵ -CAPROLACTONE COPOLYMERIZATION REACTION AT ~64% MONOMER CONVERSION.	141
FIGURE 4-11. ^1H NMR SPECTRUM OF POLY(DIMETHYLSILOXANE- <i>B</i> - ϵ -CAPROLACTONE).	142
FIGURE 4-12. GPC CHROMATOGRAMS OF HYDROXYL-TERMINATED PDMS (GRAY CHROMATOGRAM) AND PDMS- <i>B</i> -PCL (BLACK CHROMATOGRAM).	143

LIST OF SCHEMES

SCHEME 1-1. GENERAL HYDROSILATION REACTION OF $\equiv\text{Si-H}$ WITH AN ALKENE.	6
SCHEME 1-2. TWO TYPICAL CONDENSATION REACTIONS IN SILOXANE CHEMISTRY.....	7
SCHEME 1-3. THIOL-ENE FREE RADICAL ADDITION TO VINYLSILANES.....	8
SCHEME 1-4. GENERAL REACTION MECHANISM FOR EQUILIBRATION POLYMERIZATION TO ACHIEVE α,ω -DIFUNCTIONAL POLYSILOXANES.	9
SCHEME 1-5. SYNTHESIS AND HYDROLYSIS OF PERFECTLY ALTERNATING BLOCK COPOLYMERS OF PSX AND PEEKT.	12
SCHEME 1-6. SYNTHESIS OF QUADRUPLE HYDROGEN BONDING DIFUNCTIONAL POLYSILOXANE OLIGOMERS.	14
SCHEME 1-7. SYNTHESIS OF POLAR POLYSILOXANE MACROTERMINATORS.	15
SCHEME 1-8. SYNTHESIS OF α,ω -DIFUNCTIONAL POLYSILOXANES USING A DIFUNCTIONAL INITIATOR AND HEXAMETHYLCYCLOTRISILOXANE MONOMER.	16
SCHEME 1-9. SYNTHESIS OF THE ARYLAMINE-FUNCTIONAL INITIATOR AND TERMINATING REAGENT FOR THE LIVING POLYMERIZATION OF HEXAMETHYLCYCLOTRISILOXANE AND DEPROTECTION OF THE AMINO GROUPS ON THE POLYMER.	18
SCHEME 1-10. SYNTHESIS OF PYRROLE-FUNCTIONALIZED POLYSILOXANE AND GRAFT COPOLYMERIZATION WITH PYRROLE.	21
SCHEME 1-11. SYNTHESIS OF POLYSILOXANES FUNCTIONALIZED VIA Si-O-C BONDS.....	22
SCHEME 1-12. SYNTHESIS OF CYANOPROPYL-FUNCTIONALIZED TRIBLOCK COPOLYMERS FROM PCPMS MACROINITIATORS.....	24
SCHEME 1-13. MECHANISM FOR THE LIVING ANIONIC POLYMERIZATION OF HEXAMETHYLCYCLOTRISILOXANE.	27
SCHEME 1-14. SYNTHESIS OF <i>t</i> -BUTYLDIMETHYLSILYL-3-(CHLORODIMETHYLSILYL)PROPYL ETHER.....	28
SCHEME 1-15. SYNTHESIS OF POLY(DIMETHYLSILOXANE- <i>B</i> -2-ETHYL-2-OXAZOLINE) USING A PDMS MACROINITIATOR.	29
SCHEME 1-16. SYNTHESIS OF ALLYL-FUNCTIONALIZED DICARBOXYLIC REAGENTS FOR HYDROSILATION.	31
SCHEME 1-17. POLYCONDENSATION OF DIHYDROXYL-TERMINATED PDMS WITH 4- (DICHLOROMETHYLSILYL)- <i>t</i> -BUTYLBUTANOATE.	32
SCHEME 1-18. GTP OF SILYL KETENE ACETAL TERMINATED PDMS WITH (METH)ACRYLATES.....	33
SCHEME 1-19. THIOL-ENE ADDITION OF MERCAPTOACETIC ACID TO PDMS- <i>B</i> - POLY(METHYLVINYLSILOXANE).	34
SCHEME 1-20. SYNTHESIS OF ϵ -CAPROLACTONE BY THE DEHYDRATION AND SELF- ESTERIFICATION OF ϵ -HYDROXYCAPROIC ACID.....	35
SCHEME 1-21. BAEYER-VILLIGER OXIDATION OF CYCLOHEXANONE TO YIELD ϵ - CAPROLACTONE.....	35
SCHEME 1-22. RING-CHAIN EQUILIBRIUM IN THE TRANSESTERIFICATION BACKBITING REACTIONS FOR ALKOXIDE-INITIATED POLYMERIZATION OF ϵ -CAPROLACTONE.	37
SCHEME 1-23. SYNTHESIS OF α,ω -HETEROTELECHELIC PCL USING POTASSIUM TERT- BUTOXIDE INITIATOR AND A FUNCTIONALIZED ACYCLIC ESTER CHAIN-TRANSFER AGENT.	38

SCHEME 1-24. MECHANISM FOR THE COORDINATION-INSERTION POLYMERIZATION OF ϵ -CAPROLACTONE INITIATED AND CATALYZED BY TRIBUTYL TIN METHOXIDE	39
SCHEME 2-1. THIOL-ENE ADDITION OF MERCAPTOCARBOXYLIC ACIDS TO TRIVINYLSILYL-TERMINATED PDMS.....	75
SCHEME 2-2. PROPOSED FREE RADICAL MECHANISM INVOLVING PDMS-VINYLSILYL CHAIN COUPLING.....	79
SCHEME 3-1. COPOLYMERIZATION OF ϵ -CAPROLACTONE USING A α,ω -DIHYDROXYBUTYL-FUNCTIONALIZED PMVS OLIGOMER AS A MACROINITIATOR.....	111
SCHEME 3-2. ENE-THIOL ADDITION OF MERCAPTOACETIC ACID TO PCL- <i>B</i> -PMVS- <i>B</i> -PCL.....	113

LIST OF TABLES

TABLE 1-1. THERMODYNAMIC AND PHYSICAL PROPERTIES OF ϵ -CAPROLACTONE AND POLY(ϵ -CAPROLACTONE).	36
TABLE 1-2. CRITICAL PARTICLE DIAMETERS FOR SINGLE MAGNETIC DOMAINS IN MAGNETIC METALS.	50
TABLE 2-1. NUMBER AVERAGE MOLECULAR WEIGHTS AND POLYDISPERSITIES OBTAINED FROM ^1H NMR, ^{29}Si NMR, AND GPC FOR THE TRIVINYLSILYL-TERMINATED PDMS SERIES.	74
TABLE 2-2. CHARACTERIZATION OF THE CARBOXYLIC ACID-CONTAINING PDMS SURFACTANT SERIES.	77
TABLE 2-3. CHARACTERIZATION OF PDMS-MAGNETITE COMPLEXES.	82
TABLE 2-4. RESULTS OF CALCULATIONS TO DETERMINE THE RELATIONSHIP BETWEEN THE NUMBER OF COOH GROUPS IN THE POLYMER AND THE NUMBER OF ACTIVE MAGNETITE BINDING SITES IN THE COMPLEXES. THE CALCULATIONS ASSUME 100 GRAMS OF COMPLEX AND THE AMOUNT OF MAGNETITE AND PDMS ARE TAKEN FROM ELEMENTAL ANALYSIS DATA.	86
TABLE 2-5. CHARACTERIZATION OF PDMS CARRIER FLUIDS USED FOR RHEOMETRIC STUDIES.	95
TABLE 2-6. MAGNETIC FLUID COMPOSITIONS AND VISCOSITIES AT 37 °C.	95
TABLE 3-1. CHARACTERIZATION OF THE PCL- <i>B</i> -PMVSCOOH- <i>B</i> -PCL COPOLYMER SERIES.	114
TABLE 3-2. ELEMENTAL COMPOSITIONS ON THE SURFACES OF MAGNETITE NANOPARTICLES BY XPS ANALYSIS.	115
TABLE 4-1. DEGREE OF HYDROSILANE FUNCTIONALITY DETERMINED BY ^1H NMR AND ^{29}Si NMR.	127
TABLE 4-2. CHARACTERIZATION OF THE HYDROSILANE-TERMINATED PDMS SERIES. ...	127
TABLE 4-3. CHARACTERIZATION OF HYDROXYALKYL-TERMINATED PDMS SERIES.	135

Introduction

The content of this dissertation spans two major themes: the synthesis of functionalized PDMS and the synthesis of magnetite nanoparticle-complexes and dispersions. Chapter two spans both of these themes because it covers the synthesis of carboxylic acid-functionalized PDMS surfactants as well as the preparation of magnetic PDMS fluids using these surfactants as steric stabilizers for magnetite nanoparticles (Figure 0-1). These magnetic PDMS fluids have the potential to be used for biomedical applications such as retinal detachment treatment.

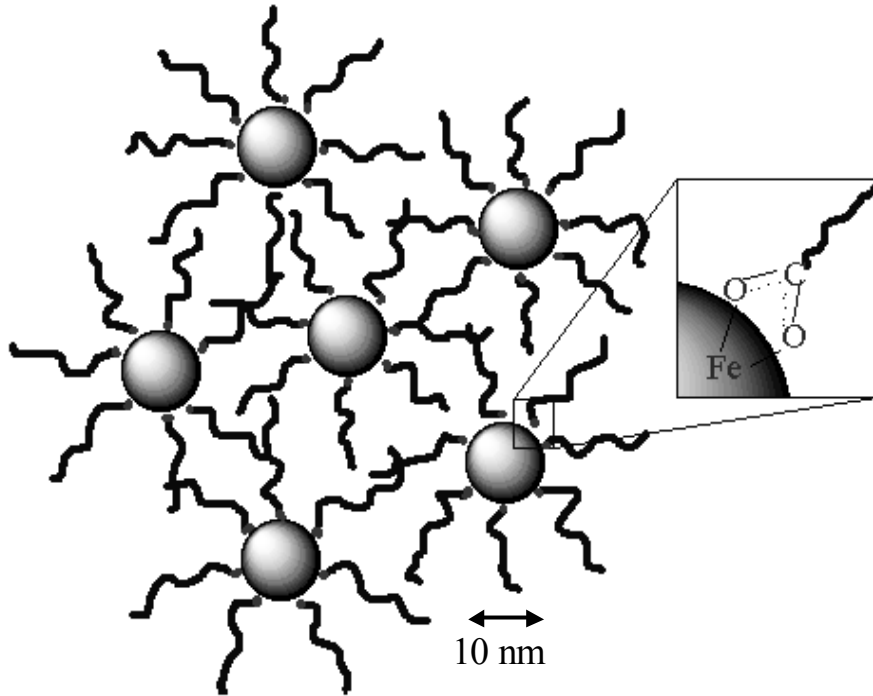


Figure 0-1. Steric stabilization of magnetite nanoparticles using carboxylic acid-functionalized PDMS.

Retinal detachment is a leading cause of blindness in adults and affects approximately one million people per year worldwide. A retina may detach as a result of trauma to the eye, as a result of a disease known as diabetes mellitus, or naturally through aging in a process called rhegmatogenous retinal detachment.¹ In this study, the

¹ Riffle, J. S.; Dailey, J. P. In *Polymers in Medicine and Biology*; Rohnert Park, CA, 2002.

proposed method for repairing the retinal detachment is to insert a permanent magnetic paste between the sclera and the Tenon's capsule using a specially designed applicator following by crosslinking the paste *in-situ* (Figure 0-2). A magnetic PDMS fluid will then be inserted into the eye. This magnetic fluid will be attracted to the permanent magnet surrounding the eye, thereby providing 360 degrees of pressure to help reattach the retina (Figure 0-3). The focus of the research in this study is on the preparation of a suitable magnetic PDMS fluid that is biocompatible, has a strong magnetic susceptibility, and will retain its magnetization over time.

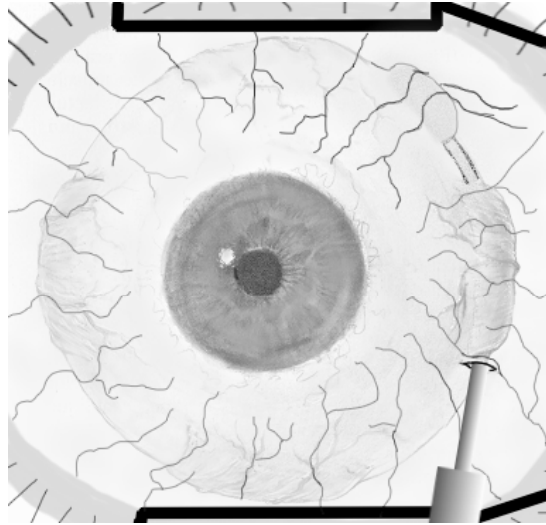


Figure 0-2. Insertion of the permanent magnetic paste in the eye between the sclera and the Tenon's capsule using the specially designed applicator.

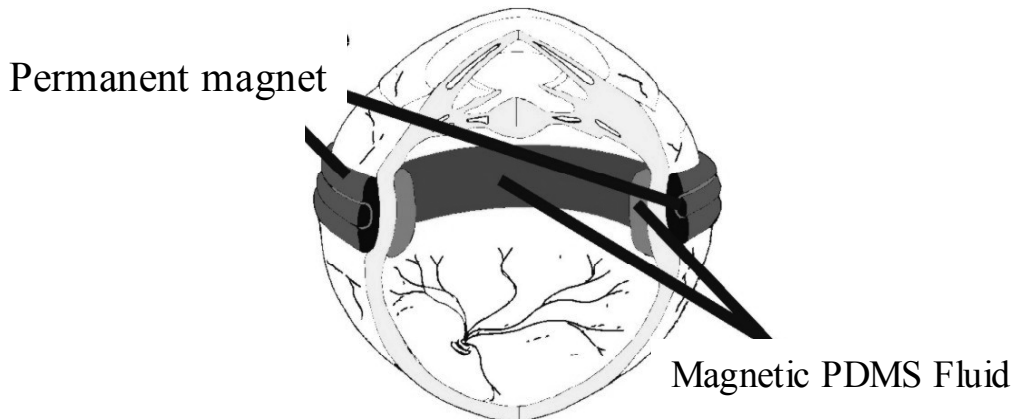


Figure 0-3. Proposed method for the repair of retinal detachment.

Chapter three focuses on the preparation of controlled size magnetite particles in the size range of ~100-500 nm in diameter. Magnetite particles in this size range will generate heat in the presence of an AC magnetic field due to hysteresis loss. This is a process known as magnetic induction heating.^{2,3} Magnetic induction heating has been investigated as a method for hyperthermia cancer treatment.^{4,5,6,7} In this study, the objective is to use magnetic induction heating to cure vinyl ester resins. PDMS chemistry is touched upon in this chapter since α,ω -dihydroxybutyl-terminated poly(methylvinylsiloxane) is used as a precursor to carboxylic acid-functionalized poly(ϵ -caprolactone-*b*-methylvinylsiloxane-*b*- ϵ -caprolactone) copolymer stabilizers. This triblock copolymer is subsequently adsorbed onto the magnetite particles to promote stabilization of the particles in vinyl ester resins. Magnetite particles are dispersed into vinyl ester resins by ultrasonication. It is proposed that the magnetite particles will generate enough heat in the presence of an AC magnetic field to cure the resins.

² McGaffigan, T. H. In *US 5,208,443*; Metcal, Inc.: United States, 1993.

³ Monovoukas, Y. A. In *US 5,378,879*; Raychem Corporation: United States, 1995.

⁴ Kawashita, M.; Tanaka, M.; Kokubo, T.; Yao, T.; Hamada, S.; Shinjo, T. *Key Eng. Mater.* **2002**, 218-220, 645-648.

⁵ Jordan, A.; Scholz, R.; Wust, P.; Fahling, H.; Felix, R. *J. Magn. Magn. Mater.* **1999**, 201, 413-419.

⁶ Jordan, A.; Wust, P.; Fahling, H.; John, W.; Hinz, A.; Felix, R. *Int. J. Hyperthermia* **1993**, 9, 51-68.

⁷ Brusentsov, N. A.; Brusentsova, T. N.; Sergeev, A. V.; Shumakov, L. I. *Pharmaceutical Chemistry Journal* **2000**, 34, 201-207.

Finally, chapter four is focused only on the synthesis of functionalized PDMS. A method for the preparation of hydroxyalkyl-terminated PDMS is described in which the PDMS contains one terminal hydroxyalkyl group. The method involves the preparation of hydrosilyl-terminated PDMS followed by platinum-catalyzed hydrosilation with allyloxyethanol. The monofunctional PDMS oligomers may be used for the preparation of block copolymers or graft copolymers or as endcapping reagents in step-growth polymerizations.

1 Chapter 1. Literature Review

1.1 Overview of Polysiloxane Chemistry

1.1.1 Background

Polysiloxanes are an important class of polymers that have been commercially available since the 1940's. The repeat unit of a polysiloxane contains alternating silicon and oxygen atoms with two organic groups bound to each silicon atom as shown in Figure 1-1.

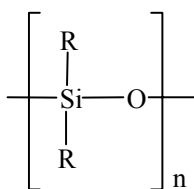


Figure 1-1. General polysiloxane backbone structure.

The R groups are organic substituents that may include methyl (CH₃), vinyl (CH=CH₂), phenyl (C₆H₅), hydrogen (H), and trifluoropropyl (CF₃CH₂CH₂) groups, but the most important species is the methyl group.

The siloxane (Si-O) bond is partially ionic in nature (40-50%)⁸ and can be cleaved by strong acids or bases.^{9,10} The ionic character of the siloxane bond may be partially responsible for the thermal stability of these inorganic-organic polymers. Polysiloxanes have many interesting properties including good thermo-oxidative stability, ozone and UV resistance, low glass transition temperatures (PDMS T_g = -123 °C), low surface energy, low solubility parameter, hydrophobicity, transparency to visible light, high gas permeability, and biological inertness. Polysiloxanes do not have good mechanical strength so they must be chemically crosslinked to form elastomers or incorporated as

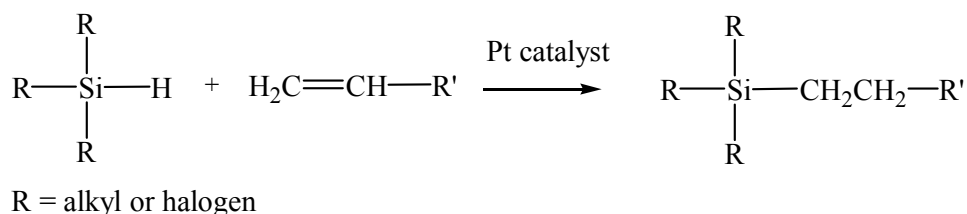
⁸ Yilgor, I.; McGrath, J. E. In *Polysiloxane Copolymers/Anionic Polymerization*; Springer-Verlag: New York, 1988; pp 1-86.

⁹ Voronkov, M. G.; Mileshekevich, V. P.; Yuzhelevskii, Y. A. *The Siloxane Bond*; Consultants Bureau: New York, 1978.

¹⁰ Noll, W. *Chemistry and Technology of Silicones*; Academic Press: New York, 1968.

components of larger systems, and they are often reinforced with fillers (particularly silica). Polysiloxanes are often incorporated into high T_g materials as block or segmented copolymers to impart their unique characteristics to the materials while maintaining good mechanical properties.

One of the most important reactions utilized in polysiloxane chemistry is hydrosilation. In a hydrosilation reaction, a new Si-C bond is formed by adding a hydrosilyl group ($\equiv\text{Si-H}$) across an alkene ($-\text{C}=\text{C}-$) or alkyne ($-\text{C}\equiv\text{C}-$) bond usually with the help of a platinum catalyst (Scheme 1-1), although palladium, peroxides, UV light, and azodinitriles are also known to be effective catalysts.¹¹ These reactions are useful for functionalizing siloxane monomers and polymers and can also be used for crosslinking polysiloxanes. One benefit of using hydrosilation as a crosslinking reaction is that there are no low molecular weight by-products formed in the reaction, and it is therefore possible to obtain void-free networks. Another significant characteristic of this reaction is that the Si-C bonds formed are hydrolytically stable, compared to Si-O-C bonds, for example. One complication with hydrosilation reactions is that certain functional groups including hydroxyl and amino groups will react with the hydrosilyl moiety under hydrosilation conditions, and must therefore be protected to allow the hydrosilyl to add across the alkene.^{12,13} Amino groups also complex strongly to the hydrosilation catalysts and can inhibit the reactions severely.



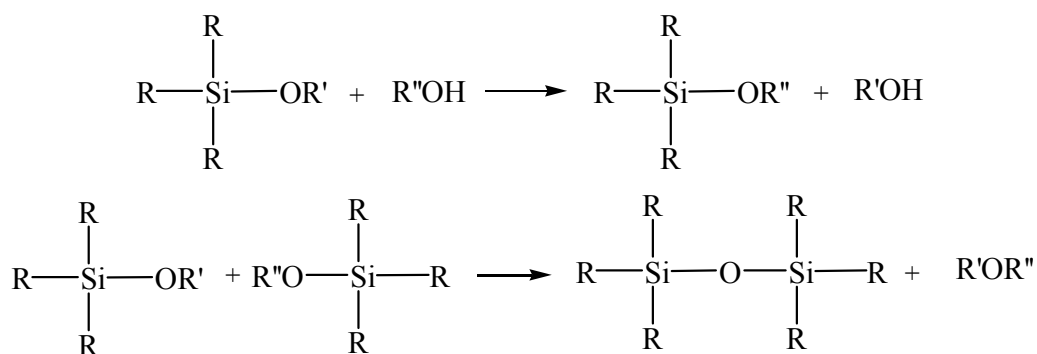
Scheme 1-1. General hydrosilation reaction of $\equiv\text{Si-H}$ with an alkene.

¹¹ Noll, W. *Chemistry and Technology of Silicones*; Academic Press: New York, 1968.

¹² Yilgor, I.; McGrath, J. E. In *Polysiloxane Copolymers/Anionic Polymerization*; Springer-Verlag: New York, 1988; pp 1-86.

¹³ Zhang, C.; Laine, R. M. *J. Am. Chem. Soc.* **2000**, *122*, 6979-6988.

Another useful reaction in siloxane chemistry is the condensation reaction to form new Si-O-Si bonds or Si-O-C bonds (Scheme 1-2).^{14,15} These reactions are usually acid or base catalyzed. If the siloxane precursors contain multiple alkoxy silane groups, then condensation reactions will lead to a sol-gel process resulting in the formation of a glassy silica network.



R', R'' = alkyl or hydrogen

Scheme 1-2. Two typical condensation reactions in siloxane chemistry.

One last type of reaction that is particularly important in the context of this manuscript is the thiol-ene free radical addition reaction. Thiols, or “mercaptans”, are molecules containing S-H bonds, and will add free radically to alkenes or alkynes (Scheme 1-3).¹⁶ This type of reaction is not exclusive to siloxane chemistry and has been used, for example, as a curing mechanism for organic polymers¹⁷ and as a means of synthesizing surfactant molecules.¹⁸ Studies that used the thiol-ene addition in silicon chemistry go back as far as the 1960's.¹⁹ More recently, Chojnowski and coworkers have

¹⁴ Noll, W. *Chemistry and Technology of Silicones*; Academic Press: New York, 1968.

¹⁵ Koerner, G. In *Silicones Chemistry and Technology*; Koerner, G., Schulze, M., Weis, J., Eds.; Vulkan-Verlag: Essen, 1991; pp 1-6.

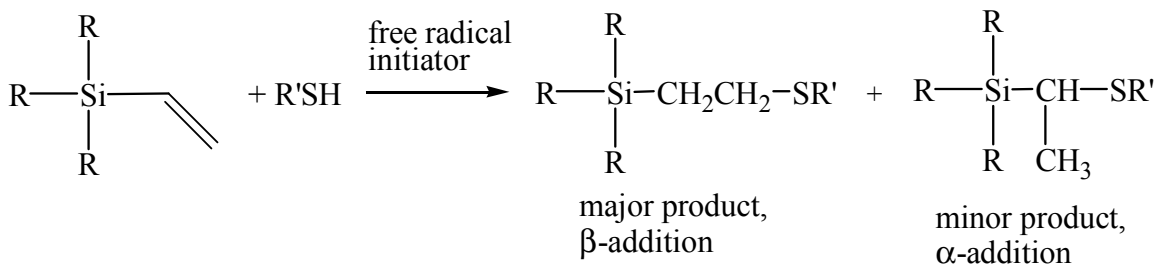
¹⁶ Janssen, M. J. In *Sulfur in Organic and Inorganic Chemistry*; Senning, A., Ed.; Marcel Dekker, Inc.: New York, 1972; Vol. 3, pp 355-375.

¹⁷ Chiang, W. Y.; Ding, F. C. *J. Appl. Polym. Sci.* **2002**, *86*, 1878-1885.

¹⁸ Anton, P.; Laschewsky, A. *European Polymer Journal* **1995**, *31*, 387-394.

¹⁹ Gornowicz, G. A.; Ryan, J. W.; Speier, J. L. *J. Org. Chem.* **1968**, 2918-2923.

used the thiol-ene addition reaction to add several functional groups to polysiloxanes including *t*-butyl,²⁰ pyridyl,²¹ and carboxyl groups.²²



Scheme 1-3. Thiol-ene free radical addition to vinylsilanes.

1.1.2 Synthesis of α,ω-Difunctional Polysiloxanes by Equilibration Polymerization

Equilibration polymerization, or “redistribution” polymerization, involves the acid or base-catalyzed ring opening polymerization of cyclic siloxane monomers. In this reaction, a mixture of cyclic and linear siloxanes is produced by the continuous breaking and reforming of siloxane bonds until a thermodynamic equilibrium is reached. For the polymerization of octamethylcyclotetrasiloxane, there are typically 10-15% cyclics by weight present in the reaction mixture at equilibrium.²³ However, the amount of cyclics in the reaction increases with increasing bulkiness and polarity of the R groups on the monomer from 6% cyclics for R=H up to 78% cyclics for R= CF₃CH₂CH₂.²⁴ To achieve α,ω-difunctional polysiloxanes, a functional disiloxane endcapper, or chain transfer agent, can be added to the initial reaction mixture. A general reaction scheme is shown in

²⁰ Rozga-Wijas, K.; Chojnowski, J.; Zundel, T.; Boileau, S. *Macromolecules* **1996**, *29*, 2711-2720.

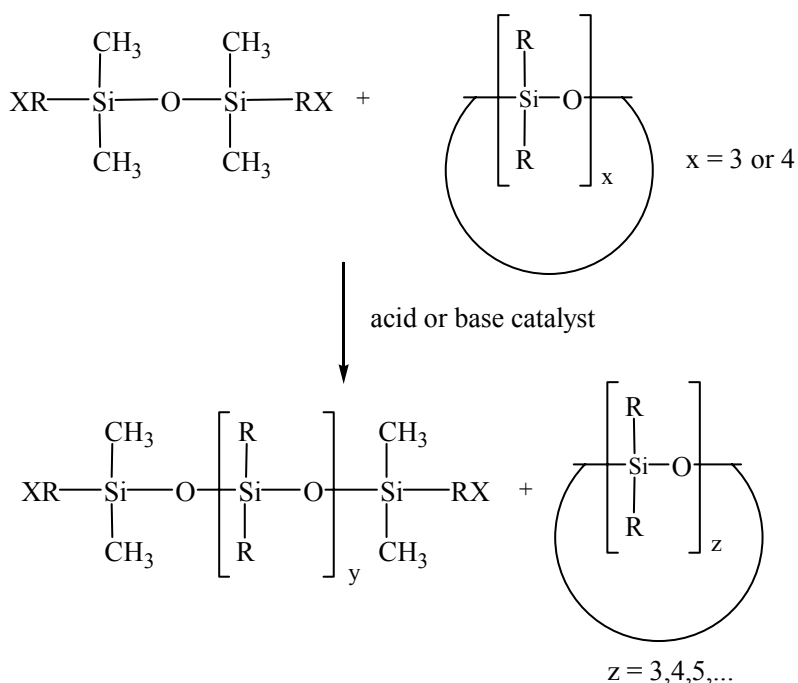
²¹ Herczynska, L.; Lestel, L.; Boileau, S.; Chojnowski, J.; Polowinski, S. *European Polymer Journal* **1999**, *35*, 1115-1122.

²² Scibiorek, M.; Gladkova, N. K.; Chojnowski, J. *Polymer Bulletin* **2000**, *44*, 377-384.

²³ Yilgor, I.; McGrath, J. E. In *Polysiloxane Copolymers/Anionic Polymerization*; Springer-Verlag: New York, 1988; pp 1-86.

²⁴ Wright, P. V.; Semlyen, J. A. *Polymer* **1970**, *11*, 462-471.

Scheme 1-4. Alternatively, the reaction can be conducted in the presence of a base such as KOH and then functional chlorosilanes can be utilized as terminating reagents to afford difunctional oligomers. Many different types of functional groups have been incorporated into α,ω -difunctional polysiloxanes, including amine, piperazine, carboxylic acid, epoxy, hydroxyl, vinyl, and hydrogen groups.^{25,26,27,28}



Scheme 1-4. General reaction mechanism for equilibration polymerization to achieve α,ω -difunctional polysiloxanes.

α,ω -Difunctional polysiloxanes are readily used as precursors for block copolymers. The copolymers can be achieved by step growth polymerization from the terminal functional groups or by ring opening polymerization using the end groups as the initiating sites. A survey of many copolymers prepared from polysiloxane oligomers

²⁵ Yilgor, I.; McGrath, J. E. In *Polysiloxane Copolymers/Anionic Polymerization*; Springer-Verlag: New York, 1988; pp 1-86.

²⁶ Yilgor, I.; Riffle, J. S.; McGrath, J. E. In *Reactive Oligomers*; Harris, F. W., Spinelli, H. J., Eds.; American Chemical Society: Washington, D.C., 1985; pp 161-174.

²⁷ Quirk, R. P.; Kim, J. In *Ring-Opening Polymerization: Mechanisms, Catalysis, Utility*; Brunelle, D. J., Ed.; Hanser: New York, 1993; pp 263-293.

²⁸ Riffle, J. S.; Yilgor, I.; Tran, C.; Wilkes, G. L.; McGrath, J. E.; Banthia, A. K. In *Epoxy Resin Chemistry II*; Bauer, R. S., Ed.; American Chemical Society: Washington, D.C., 1983; Vol. 221, pp 21-54.

prior to 1988 can be found in the first chapter of *Polysiloxane Copolymers/Anionic Polymerization* by Yilgor and McGrath entitled “Polysiloxane Containing Copolymers: A Survey of Recent Developments.”²⁹ Polysiloxanes have been copolymerized with urea, amide, imide, urethane, ester, carbonate, sulfone, and hydroxyether.

1.1.3 Recent Examples of α,ω -Difunctional Polysiloxanes

The use of α,ω -difunctional polysiloxanes as precursors to block or segmented copolymers has continued over the past decade, and much of the work has been done by McGrath and coworkers at Virginia Tech. For example, perfectly alternating segmented polyimide-polydimethylsiloxane copolymers were synthesized by McGrath and coworkers using a low temperature transimidization polymerization process.³⁰ α,ω -Aminopropyl terminated poly(dimethylsiloxanes) in the range of 1.09 – 9.30 kg mol⁻¹ were reacted with N-(2-pyrimidyl)phthalimide terminated imide oligomers (4.6 kg mol⁻¹) in chlorobenzene at ~110 °C for 4-5 hours. The viscous solutions were then cast on glass plates and heated in a vacuum oven at 100 °C for 1 hour, 250-280 °C for 3 hours, and 30 minutes at 315 °C in a convection oven. These copolymers were exhibited two T_gs by dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC), indicating microphase separation. ¹H NMR analysis confirmed that incorporation of the PDMS oligomers was nearly quantitative.

The fire resistance of thermoplastic polyurethanes has been improved by incorporating difunctional polysiloxane oligomers.³¹ α,ω -Diaminoalkyl-terminated polysiloxane (M_n = 1235 g mol⁻¹) was reacted in a solution of dimethylacetamide (DMAc) and tetrahydrofuran (THF) with hydroxyl-terminated poly(tetramethylene oxide), 1,4-butanediol, and methylene diisocyanate. These reactions afforded polysiloxane-modified segmented polyether polyurethanes. Microphase separation was verified by DSC, DMA, and TEM. Elastomers containing 15% PDMS showed a heat

²⁹ Yilgor, I.; McGrath, J. E. In *Polysiloxane Copolymers/Anionic Polymerization*; Springer-Verlag: New York, 1988; pp 1-86.

³⁰ Rogers, M. E.; Glass, T. E.; Mechem, S. J.; Rodrigues, D.; Wilkes, G. L.; McGrath, J. E. *J. Polym. Sci. A: Polymer Chemistry* **1994**, *32*, 2663-2675.

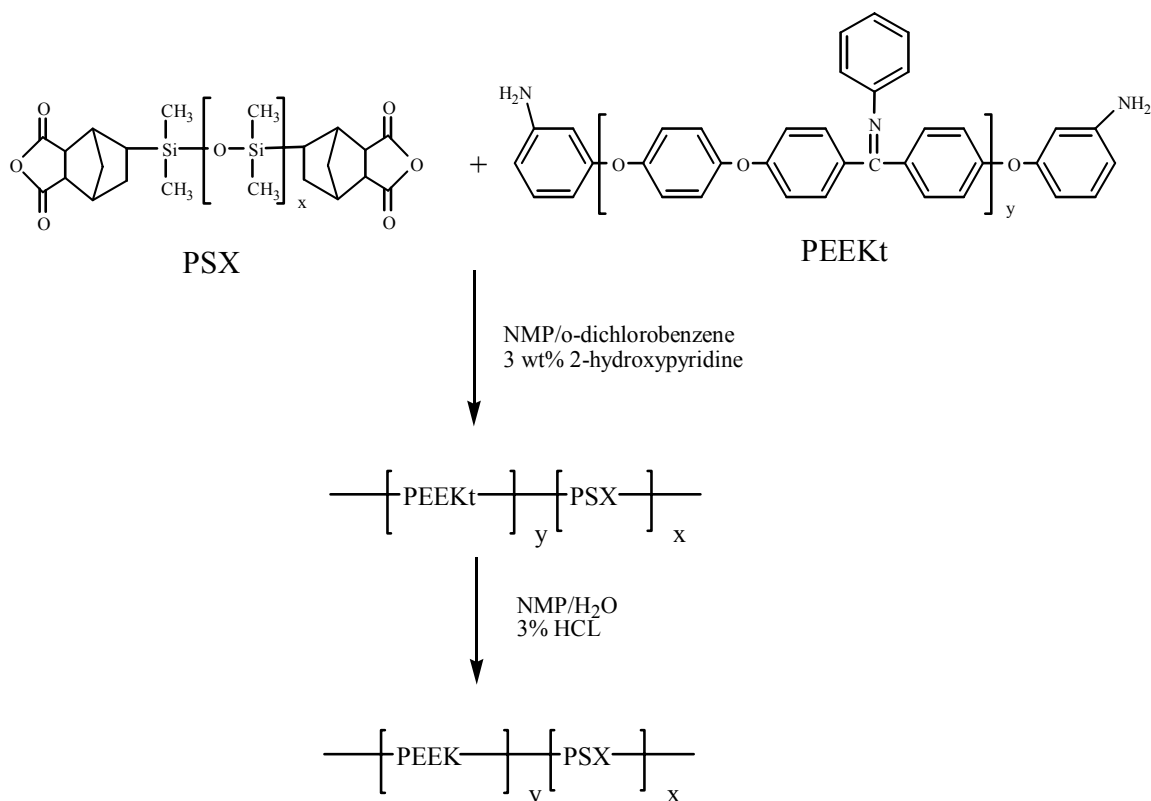
³¹ Wang, L. F.; Ji, Q.; Glass, T. E.; Ward, T. C.; McGrath, J. E.; Muggli, M.; Burns, G.; Sorathia, U. *Polymer* **2000**, *41*, 5083-5093.

release rate (measured by cone calorimetry) one third that of the polyurethane control while still maintaining mechanical properties similar to the control. The authors suggested that the polysiloxane migrated to the surface of the material and formed a silicate-like protective barrier upon heating.³²

In a study by McGrath and coworkers, α,ω -norbornene anhydride-terminated difunctional polysiloxanes were prepared and reacted with aryl amine terminated poly(ether ether ketimine) (PEEKt) in a condensation reaction to prepare perfectly alternating copolymers.³³ Hydrolysis of the ketimine resulted in perfectly alternating copolymers of polysiloxane and poly(ether ether ketone) (PEEK). The reaction scheme is shown below (Scheme 1-5). Phase separation was verified by DMA, transmission electron microscopy (TEM), and small angle x-ray scattering (SAXS). The mechanical and structural properties of the precursor and hydrolyzed block copolymers were studied as a function of copolymer composition.

³² Wang, L. F.; Ji, Q.; Glass, T. E.; Ward, T. C.; McGrath, J. E.; Muggli, M.; Burns, G.; Sorathia, U. *Polymer* **2000**, *41*, 5083-5093.

³³ Risch, B. G.; Rodrigues, D. E.; Lyon, K.; McGrath, J. E.; Wilkes, G. L. *Polymer* **1996**, *37*, 1229-1242.



Scheme 1-5. Synthesis and hydrolysis of perfectly alternating block copolymers of PSX and PEEKt.

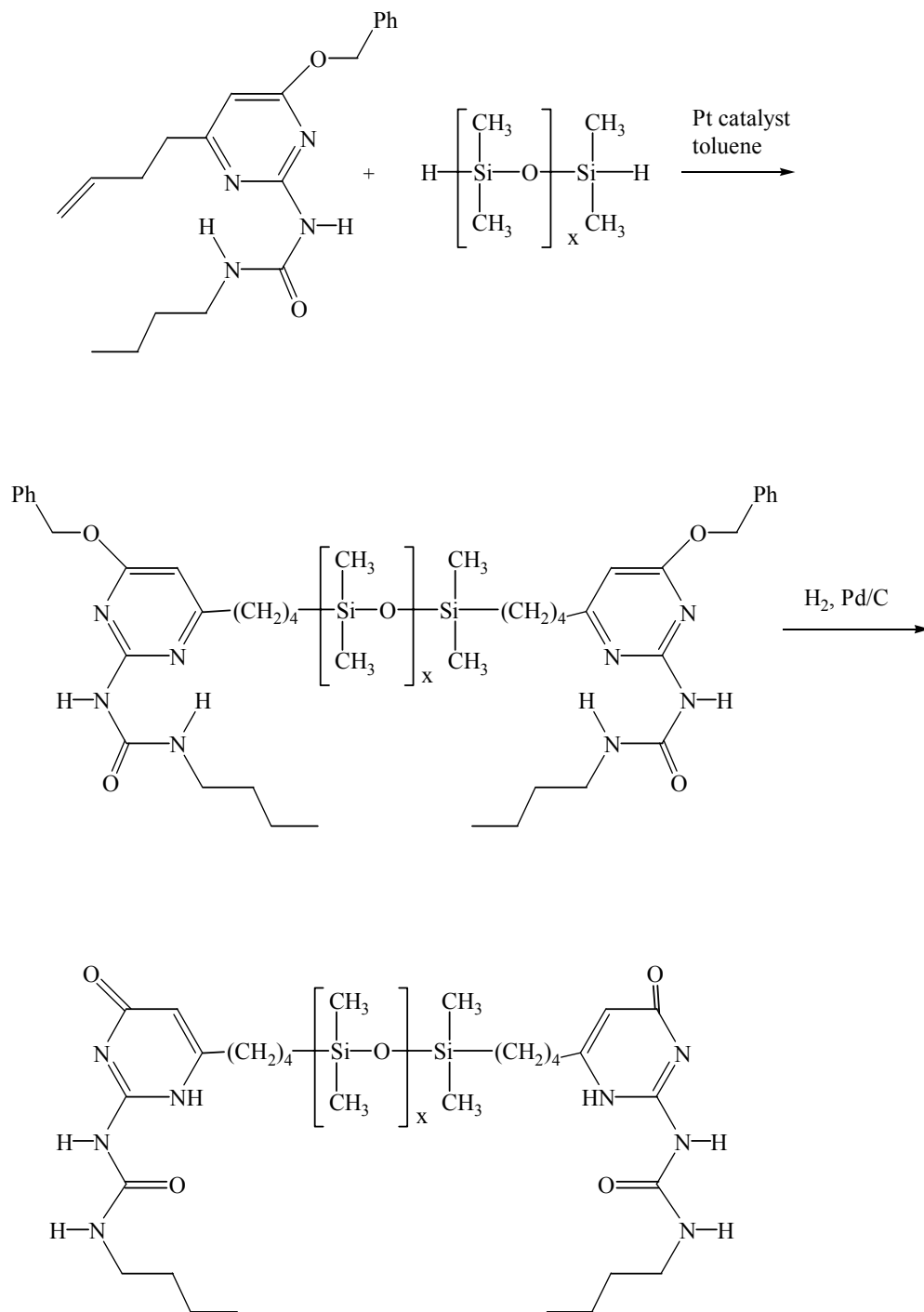
Matyjaszewski and coworkers used α,ω -dihydrosilyl-terminated PDMS as a precursor to macroinitiators for atom transfer radical polymerization (ATRP) of (meth)acrylates.³⁴ The end groups were hydrosilated with allyl 2-bromoisobutyrate in the presence of Karstedt's catalyst in THF at reflux. The difunctional bromoisobutyrate-terminated polysiloxane was subsequently used to initiate the ATRP of methyl methacrylate using a $\text{CuBr}(\text{dnNbpy})_2$ catalyst at 90 °C in xylene, thereby producing triblock copolymers with central polysiloxane blocks.

α,ω -Difunctional hydrosilyl-terminated polysiloxanes were also functionalized via hydrosilation by Meijer and coworkers.³⁵ In this case, quadruple hydrogen bonding units were incorporated into PDMS by hydrosilation with benzyl-protected

³⁴ Miller, P. J.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 8760-8767.

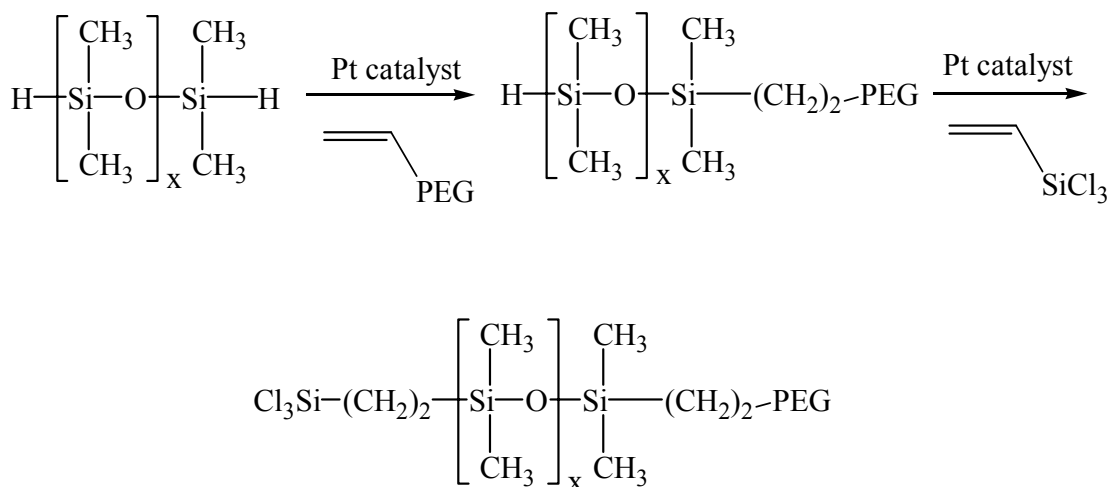
³⁵ Ky Hirschberg, J. H. K.; Beijer, F. H.; van Aert, H. A.; Magusin, P. C. M. M.; Sijbesma, R. P.; Meijer, E. W. *Macromolecules* **1999**, *32*, 2696-2705.

ureidopyrimidone (UPy) followed by hydrogenolysis. The scheme for this reaction is shown below (Scheme 1-6). These telechelic polysiloxane oligomers with either 2 or 100 repeat units behaved like entangled polymer chains. The pairwise association of the hydrogen bonding UPy end groups allowed for degrees of polymerization above the entanglement molecular weight for polysiloxanes.



Scheme 1-6. Synthesis of quadruple hydrogen bonding difunctional polysiloxane oligomers.

α,ω -Difunctional hydrosilyl-terminated polysiloxanes were used to prepare macroterminators.³⁶ Half of the hydrosilyl groups were first hydrosilated with vinyl-terminated poly(ethylene glycol) and the other half were hydrosilated with vinyltrichlorosilane according to the following reaction (Scheme 1-7). These reactions most likely resulted in a mixture of PEG-*b*-PDMS-SiCl₃, PEG-*b*-PDMS-*b*-PEG, and Cl₃Si-PDMS-SiCl₃. GPC data was not reported so the percentage of each product in the mixture is unknown. The functionalized PDMS was used to terminate the living polymerization of poly(styrene-butadiene).



Scheme 1-7. Synthesis of polar polysiloxane macroterminators.

As an example of difunctional polysiloxanes being used to initiate ring opening polymerizations, poly(2-methyloxazoline)-*b*-PDMS-*b*-poly(2-methyloxazoline) was synthesized from α,ω -hydroxypropyl-terminated PDMS precursors.³⁷ The hydroxyl end groups were reacted with triflic anhydride and subsequently used to initiate the ring opening polymerization of 2-methyl-2-oxazoline. The triblock copolymers were used to study to formation of self-assembling structures and the thermal and chemical properties were not discussed. α,ω -Dihydroxybutyl-terminated PDMS has been used to initiate the ring opening polymerization of ϵ -caprolactone.³⁸ These reactions were performed in the

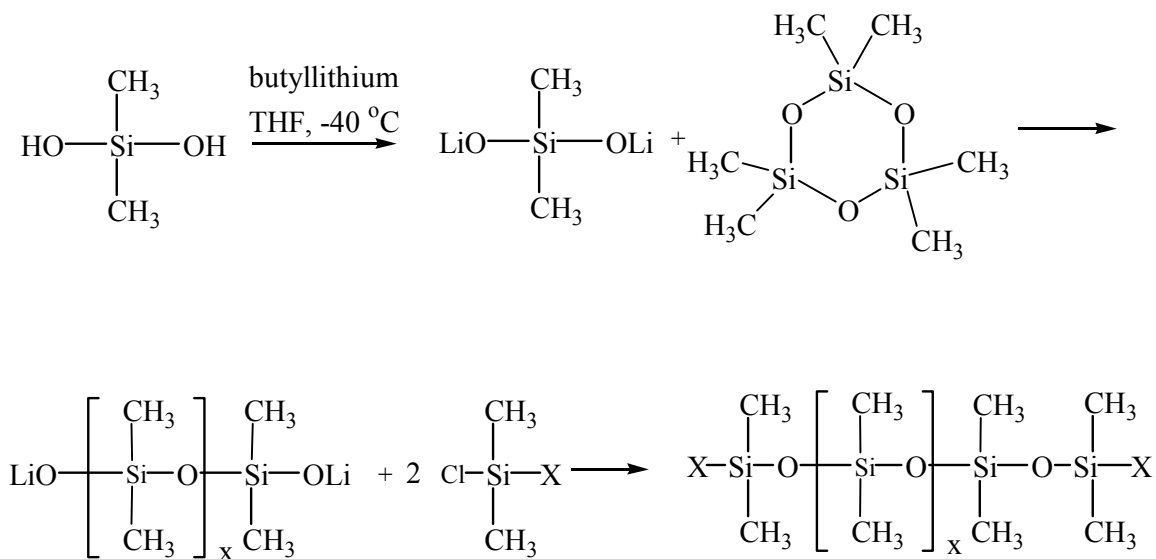
³⁶ Kim, E.; Lee, E.; Park, I.; Chang, T. *Polymer Journal* **2002**, *34*, 674-681.

³⁷ Nardin, C.; Hirt, T.; Leukel, J.; Meier, W. *Langmuir* **2000**, *16*, 1035-1041.

³⁸ Ward, R. S.; Riffle, J. S. In *US Pat. 4,963,595*; Thoratec Laboratories Corp.: United States, 1990.

melt at 75 °C for three hours followed by 140 °C for three hours using stannous octoate as a catalyst.

One of the key characteristics of the equilibration polymerizations is that the resultant polymers have relatively broad molecular weight distributions in comparison to polysiloxanes prepared by living polymerization technologies which have $M_w/M_n \sim 1$.³⁹ There have been some methods in the literature that utilize living polymerization to synthesize α,ω -difunctional polysiloxanes with relatively narrow molecular weight distributions. One of these methods, reported in 1988 by Rempp and Gnanou,⁴⁰ utilized a difunctional initiator for the polymerization of hexamethylcyclotrisiloxane (D₃). In this method (Scheme 1-8), dimethylsilanediol was metalated with a stoichiometric quantity of butyllithium in anhydrous THF, using a few drops of styrene as an indicator. The authors did not differentiate the type of butyllithium used. A solution of D₃ in benzene was added to the metalated initiator. The polymerizations were conducted at room temperature and were terminated with functional chlorosilane terminating reagents prior to complete conversion of the monomer (Scheme 1-8). GPC chromatograms were unimodal and molecular weight distributions ranged from 1.07-1.9.



Scheme 1-8. Synthesis of α,ω -difunctional polysiloxanes using a difunctional initiator and hexamethylcyclotrisiloxane monomer.

³⁹ Szwarc, M.; Levy, M.; Milkovich, R. *J. Am. Chem. Soc.* **1956**, 78, 2656.

⁴⁰ Gnanou, Y.; Rempp, P. *Makromol. Chem.* **1988**, 189, 1997-2005.

Living polymerization techniques have been used to prepare α,ω -arylamine functionalized poly(dimethylsiloxane)s by Riffle et al.⁴¹ This research utilized both a functionalized initiator as well as a functionalized terminating reagent to achieve difunctionality and narrow molecular weight distributions. The arylamine initiator was synthesized by reacting 4-bromo-N,N-bis(trimethylsilyl)aniline with 1 equiv. of *n*-BuLi in a solution of dry ether at 0 °C, then stirring at room temperature for four hours. The terminating reagent was prepared by again reacting 4-bromo-N,N-bis(trimethylsilyl)aniline with *n*-BuLi in dry ether at 0 °C. The 4-lithio-N,N-bis(trimethylsilyl)aniline was subsequently transferred via cannula to a 0 °C solution of dichlorodimethylsilane in ether. The α,ω -arylamine functionalized PDMS was prepared by living polymerization of D₃ in cyclohexane using a calculated quantity of initiator and THF as a promoter. The living polymer chains were terminated with 10-15% excess of the terminating reagent. The amino end groups were finally deprotected by stirring the polymer in methanol overnight (Scheme 1-9).

⁴¹ Babu, J. R.; Sinai-Zingde, G.; Riffle, J. S. *J. Polym. Sci. A: Polymer Chemistry* **1993**, *31*, 1645-1651.

resulting polymer can be functionalized via hydrosilation using appropriate vinyl-containing reagents and a platinum catalyst. In addition, D₄H may be copolymerized with the nonfunctional D₄ monomer to achieve a random distribution of functional groups. Alternatively, the monomer can be functionalized first via hydrosilation and subsequently polymerized.

There have been several examples of this type of macromolecular chemistry reported recently in the literature. In one example, polysiloxane-based ion selective membranes were synthesized by integrating receptor molecules along the backbone of polysiloxane chains.⁴² Poly(dimethylsiloxane-*co*-methylhydrosiloxane) copolymers in a range of compositions were first prepared by triflic acid catalyzed equilibration polymerization. The randomly distributed hydrosilyl groups were reacted with alkenyl-functional benzo-15-crown-5 (Figure 1-2) and calix[4]arene derivatives. The series of polymers was characterized by DSC and a significant increase in T_g was found for polysiloxanes containing greater than 7.5 mol% receptor molecules. It was suggested that the increase in T_g corresponds to the association of the receptor molecules, resulting in hindered chain mobility.

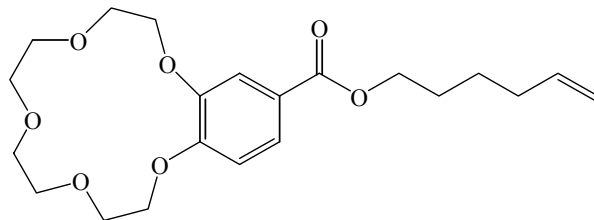


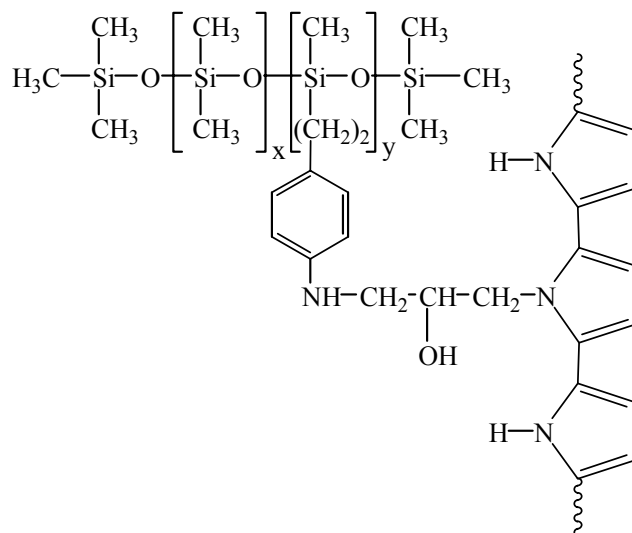
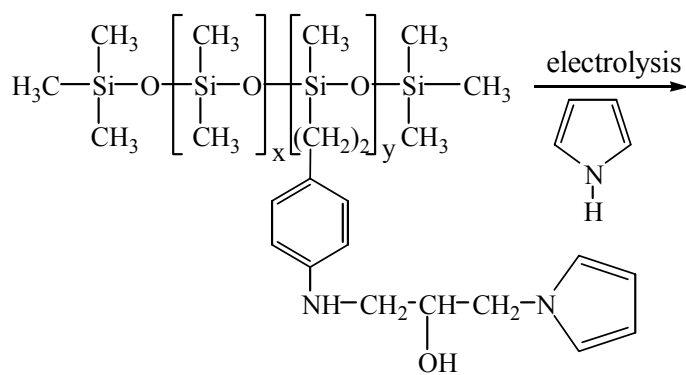
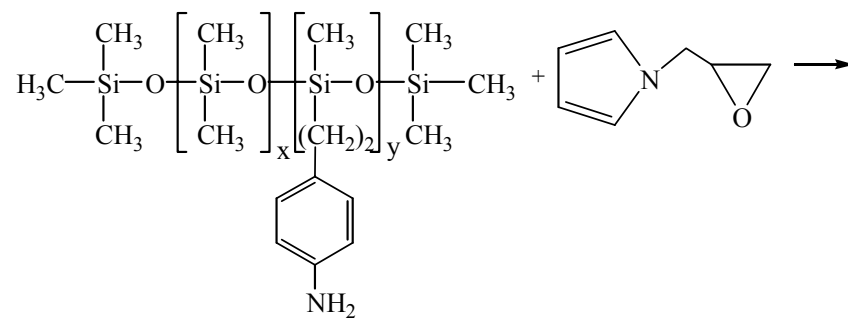
Figure 1-2. One example of a ω -alkenyl benzo-15-crown-5 derivative that was incorporated into the polysiloxane via hydrosilation.

Poly(dimethylsiloxane-*co*-methylhydrosiloxane) copolymers have also been functionalized with 4-aminophenyl groups.⁴³ A polysiloxane with 8000 g mol⁻¹ number average molecular weight and a Si(CH₃)₂/SiHCH₃ molar ratio 6.5/1 was reacted with 4-vinylaniline in toluene at 100-110 °C with H₂PtCl₆ catalyst. The functionalized

⁴² Klok, H. A.; Eibeck, P.; Moller, M.; Reinhoudt, D. N. *Macromolecules* **1997**, *30*, 795-802.

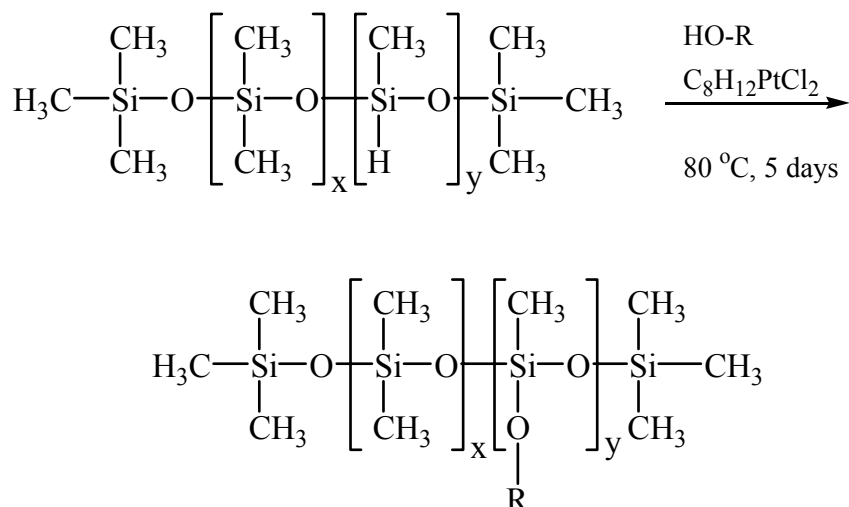
⁴³ Gunaydin, O.; Toppare, L.; Yagci, Y.; Harabagiu, V.; Pintela, M.; Simionescu, B. C. *Polymer Bulletin* **2002**, *47*, 501-508.

polysiloxane was used as a precursor to polysiloxane-polypyrrole graft copolymers. The pendant amino groups were reacted with N-glycidylpyrrole in isopropanol at 80 °C for 24 hours to achieve pyrrole-functionalized polysiloxane. These polymers were subsequently grafted electrochemically with pyrrole to prepare graft copolymer films (Scheme 1-10).



Scheme 1-10. Synthesis of pyrrole-functionalized polysiloxane and graft copolymerization with pyrrole.

Poly(dimethylsiloxane-*co*-methylhydrosiloxane) copolymers with ~4%, ~15%, and ~30% methylhydrosiloxane were functionalized with a series of primary alcohols to achieve polysiloxanes containing amine, ether, ester, or alkyl side-chains linked via Si-O-C bonds according to the reaction shown below (Scheme 1-11).⁴⁴ The authors found that the density and viscosity of the polysiloxane fluids increased as the concentration of functional groups was increased. It is well known that Si-O-C bonds are hydrolytically unstable. The authors, however, did not explain how this behavior was expected to affect the long-term stability or viscosity of their materials.



Scheme 1-11. Synthesis of polysiloxanes functionalized via Si-O-C bonds.

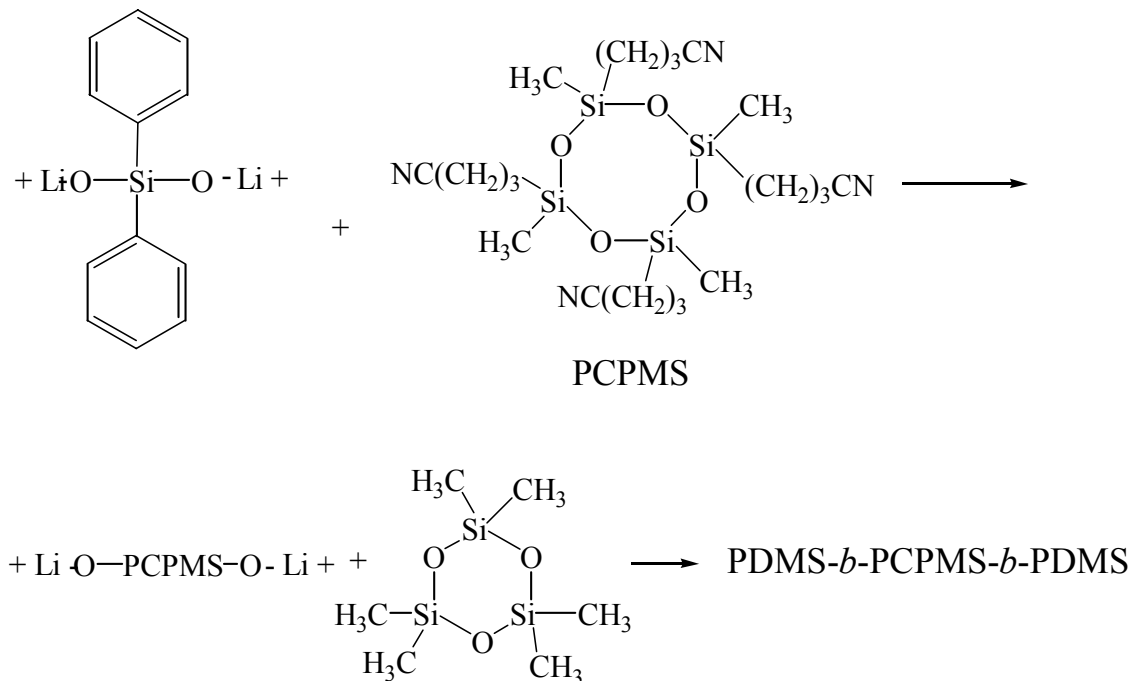
Examples of the preparation of functionalized polysiloxanes using functionalized monomers can also be found in the literature. For instance, cyanopropyl-functionalized D₄H monomers (D₄CN) have been utilized to prepare tailored cyanopropyl-functionalized (PCPMS) polysiloxane block copolymers.⁴⁵ The D₄CN was synthesized by the hydrosilation of D₄H with allyl cyanide in toluene at reflux temperature using Karstedt's catalyst. The equilibration polymerization of D₄CN was initiated using dilithium diphenylsilylanediolate and the polymer molecular weight was controlled by the ratio of monomer to initiator. PDMS-*b*-PCPMS-*b*-PDMS was synthesized by using

⁴⁴ Yahaya, G. O.; Brisdon, B. J.; Maxwell, M.; England, R. *J. Appl. Polym. Sci.* **2001**, *82*, 808-817.

⁴⁵ Dailey, J. P.; Phillips, J. P.; Riffle, J. S. *Journal of Magnetism and Magnetic Materials* **1999**, *194*, 140-148.

lithium silanolate endcapped PCPMS as a macroinitiator for the living polymerization of D₃ in dichloromethane using tetra(ethyleneglycol)dimethylether as a promoter (Scheme 1-12). Finally, the triblock copolymers were terminated with trimethylchlorosilane. Microphase separated morphology was verified by DSC analysis, which showed two T_gs at -118 °C and -63 °C. Similar triblock copolymers were prepared by the equilibration of D₄CN with lithium hydroxide at 140 °C for 48 hours.⁴⁶ There were ~27 wt% cyclics at equilibrium. The PDMS tail blocks were subsequently initiated from the lithium silanolate species by the addition of dichloromethane, D₃, and THF at room temperature followed by termination with trimethylchlorosilane.

⁴⁶ Rutnakornpituk, M.; Thompson, M. S.; Harris, L. A.; Farmer, K. E.; Esker, A. R.; Riffle, J. S.; Connolly, J.; St. Pierre, T. G. *Polymer* **2002**, *43*, 2337-2348.



Scheme 1-12. Synthesis of cyanopropyl-functionalized triblock copolymers from PCPMS macroinitiators.

In addition to hydrosilyl-containing polysiloxanes, vinylsilyl-containing polysiloxanes are also important precursors to functionalized polymers. Polysiloxanes containing pendant vinyl groups can be reacted via hydrosilation with hydrosilyl-functional reagents⁴⁷ or via thiol-ene addition with various mercaptans.^{48,49,50}

It is clear from the preceding examples that multifunctional PDMS has been prepared with a host of different moieties. These groups have been integrated into PDMS as α,ω -difunctionalities or as pendant groups to the polysiloxane backbone. PDMS has even be functionalized with groups as esoteric as fullerenes⁵¹ and ferrocenes.⁵²

⁴⁷ Cai, G.; Weber, W. P. *Polymer* **2002**, *43*, 1753-1759.

⁴⁸ Rozga-Wijas, K.; Chojnowski, J.; Zundel, T.; Boileau, S. *Macromolecules* **1996**, *29*, 2711-2720.

⁴⁹ Herczynska, L.; Lestel, L.; Boileau, S.; Chojnowski, J.; Polowinski, S. *European Polymer Journal* **1999**, *35*, 1115-1122.

⁵⁰ Scibiorek, M.; Gladkova, N. K.; Chojnowski, J. *Polymer Bulletin* **2000**, *44*, 377-384.

⁵¹ Zeng, Z. R.; Ye, H. Y.; Liu, Y.; Chen, Y. Y. *Chromatographia* **1999**, *49*, 293-295.

⁵² Deschenaux, R.; Jauslin, I.; Scholten, U.; Turpin, F.; Guillon, D.; Heinrich, B. *Macromolecules* **1998**, *31*, 5647-5654.

1.1.5 Synthesis and Recent Examples of Monofunctional Polysiloxanes

The best method for preparing monofunctional polysiloxanes with narrow polydispersities and accurately controllable molecular weights is by living anionic ring-opening polymerization. The term “living polymerization” was first used by Szwarc, et al. in 1956⁵³ and is presently used to describe polymerizations that proceed without termination.^{54,55} Another fundamental characteristic of living polymerizations is that polymer molecular weight increases linearly with respect to conversion of monomer species. This is in contrast to step-growth and free radical polymerizations as shown in Figure 1-3. Besides anionic polymerizations, other living polymerization techniques include living cationic,^{56,57,58} free radical,^{59,60,61,62,63,64,65} atom transfer radical (ATRP),^{66,67} group transfer (GTP),^{68,69,70,71,72} and metathesis polymerizations.^{73,74,75,76,77}

⁵³ Szwarc, M.; Levy, M.; Milkovich, R. *J. Am. Chem. Soc.* **1956**, *78*, 2656.

⁵⁴ Noshay, A.; McGrath, J. E. *Block Copolymers. Overview and Critical Survey*; Academic Press: New York, 1977.

⁵⁵ McGrath, J. E. In *Block Copolymers*; Meier, D. J., Ed.; MMI Press: New York, 1983; Vol. 3, pp 1-16.

⁵⁶ Sawamoto, M.; Enoki, T.; Higashimura, T. *Macromolecules* **1987**, *20*, 1-6.

⁵⁷ Storey, R. F.; Baugh, D. W.; Choate, K. R. *Polymer* **1999**, *40*, 3083-3090.

⁵⁸ Sawamoto, M.; Fugimori, J.; Higashimura, T. *Macromolecules* **1987**, *20*, 916-920.

⁵⁹ Veregin, R. P. N.; Odell, P. G.; Michalak, L. M.; Georges, M. K. *Macromolecules* **1996**, *29*, 3346-3352.

⁶⁰ Connolly, T. J.; Baldovi, M. V.; Mohtat, N.; Scaiano, J. C. *Tetrahedron Letters* **1996**, *37*, 4919-4922.

⁶¹ Hawker, C. J.; Elce, E.; Dao, J.; Volksen, W.; Russell, T. P.; Barclay, G. G. *Macromolecules* **1996**, *29*, 2686-2688.

⁶² Kazmaier, P. M.; Daimon, K.; Georges, M. K.; Hamer, G. K.; Veregin, R. P. N. *Macromolecules* **1997**, *30*, 2228-2231.

⁶³ Li, I. Q.; Howell, B. A.; Dineen, M. T.; Kastl, P. E.; Lyons, J. W.; Meunier, D. M.; Smith, P. B.; Priddy, D. B. *Macromolecules* **1997**, *30*, 5195-5199.

⁶⁴ Hawker, C. J. *Acc. Chem. Res.* **1997**, *30*, 373-382.

⁶⁵ Skene, W. G.; Connolly, T. J.; Scaiano, J. C. *Int. J. Chem. Kinet.* **2000**, *32*, 238-244.

⁶⁶ Grimaud, T.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 2216-2218.

⁶⁷ Matyjaszewski, K.; Patten, T. E.; Xia, J. *J. Am. Chem. Soc.* **1997**, *119*, 674-680.

⁶⁸ Simmons, M. R.; Yamasaki, E. N.; Patrickios, C. S. *Macromolecules* **2000**, *33*, 3176-3179.

⁶⁹ Patrickios, C. S.; Simmons, M. R. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2000**, *167*, 61-72.

⁷⁰ Webster, O. W. *J. Polym. Sci. A: Polymer Chemistry* **2000**, *38*, 2855-2860.

⁷¹ Shimano, Y.; Sato, K.; Kobayashi, S. *Polymer Journal* **1999**, *31*, 458-463.

⁷² Yousi, Z.; Donghai, L.; Lizong, D.; Jinghui, Z. *Polymer* **1998**, *39*, 2665-2668.

⁷³ Masuda, T.; Mishima, K.; Fujimori, J.; Nishida, M.; Muramatsu, H.; Higashimura, T. *Macromolecules* **1992**, *25*, 1401-1404.

⁷⁴ Masuda, T.; Hayano, S.; Iwawaki, E.; Nomura, R. *Journal of Molecular Catalysis A: Chemical* **1998**, *133*, 213-220.

⁷⁵ Masuda, T.; Mishima, K.; Seki, H.; Nishida, M.; Higashimura, T. *Polymer Bulletin* **1994**, *32*, 19-25.

⁷⁶ Kaneshiro, H.; Hayano, S.; Masuda, T. *Polymer Journal* **1999**, *31*, 348-352.

⁷⁷ Buchmeiser, M. R.; Schuler, N.; Kaltenhauser, G.; Ongania, K. H.; Lagoja, I.; Wurst, K.; Schottenberger, H. *Macromolecules* **1998**, *31*, 3175-3183.

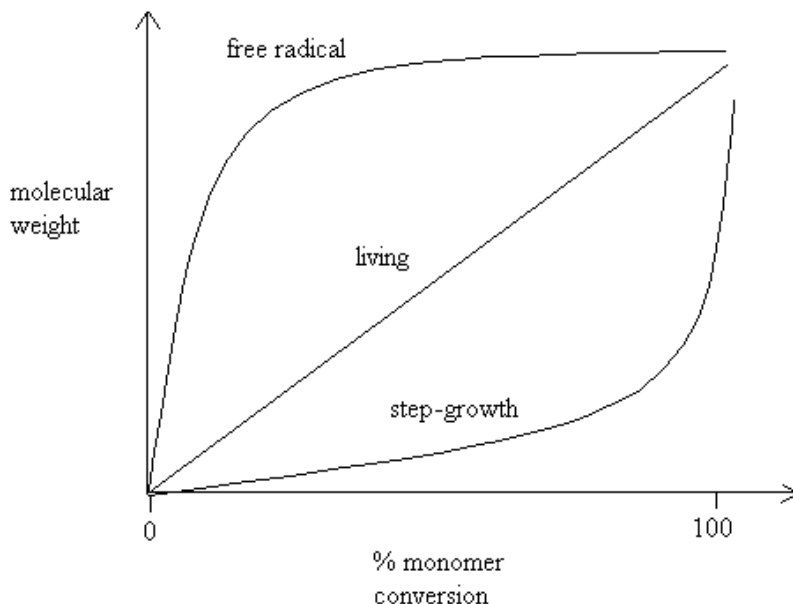


Figure 1-3. Molecular weight as a function of conversion for step-growth, free radical, and living polymerizations.

The living anionic synthesis of poly(dimethylsiloxane) is well documented.^{78,79,80,81,82,83,84} The reaction is usually initiated at room temperature with an organolithium reagent (*n*-butyllithium or *sec*-butyllithium) or lithium siloxanates and cyclic trimers (hexamethylcyclotrisiloxane) as monomers (Scheme 1-13). If these reactions are conducted in nonpolar solvents such as cyclohexane, then it is necessary to add electron-donating reagents as promoters. The most common promoter utilized is THF, but glycol ethers, anisole, triethylamine, and dioxane are also effective.⁷² As the monomer concentration is depleted, backbiting and redistribution reactions become more

⁷⁸ Yilgor, I.; McGrath, J. E. In *Polysiloxane Copolymers/Anionic Polymerization*; Springer-Verlag: New York, 1988; pp 1-86.

⁷⁹ McGrath, J. E. In *Ring-Opening Polymerization: Kinetics, Mechanisms, and Synthesis*; McGrath, J. E., Ed.; American Chemical Society: Washington, D.C., 1985; Vol. 286, pp 1-22.

⁸⁰ Kawakami, Y.; Yamashita, Y. In *Ring-Opening Polymerization: Kinetics, Mechanisms, and Synthesis*; McGrath, J. E., Ed.; American Chemical Society: Washington, D.C., 1985; Vol. 286, pp 245-261.

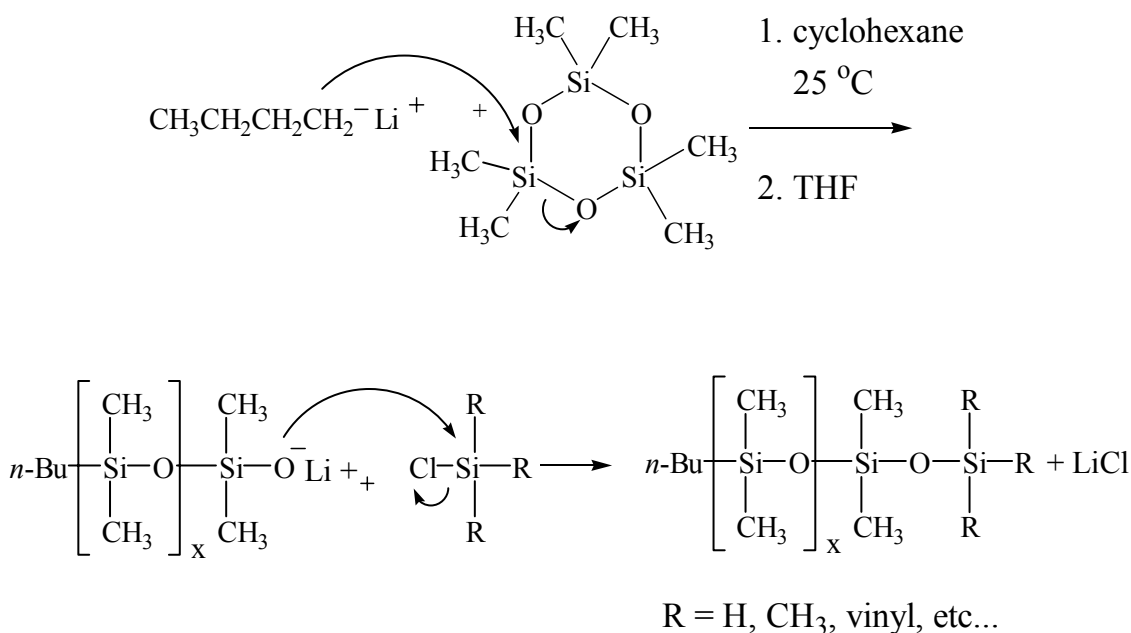
⁸¹ McGrath, J. E. In *Block Copolymers*; Meier, D. J., Ed.; MMI Press: New York, 1983; Vol. 3, pp 1-16.

⁸² McGrath, J. E. *Makromol. Chem., Macromol. Symp.* **1991**, 42/43, 69-91.

⁸³ Liu, Q.; Wilson, G. R.; Davis, R. M.; Riffle, J. S. *Polymer* **1993**, 34, 3030-3036.

⁸⁴ Peters, M. A.; Belu, A. M.; Linton, R. W.; Dupray, L.; Meyer, T. J.; DeSimone, J. M. *J. Am. Chem. Soc.* **1995**, 117, 3380-3388.

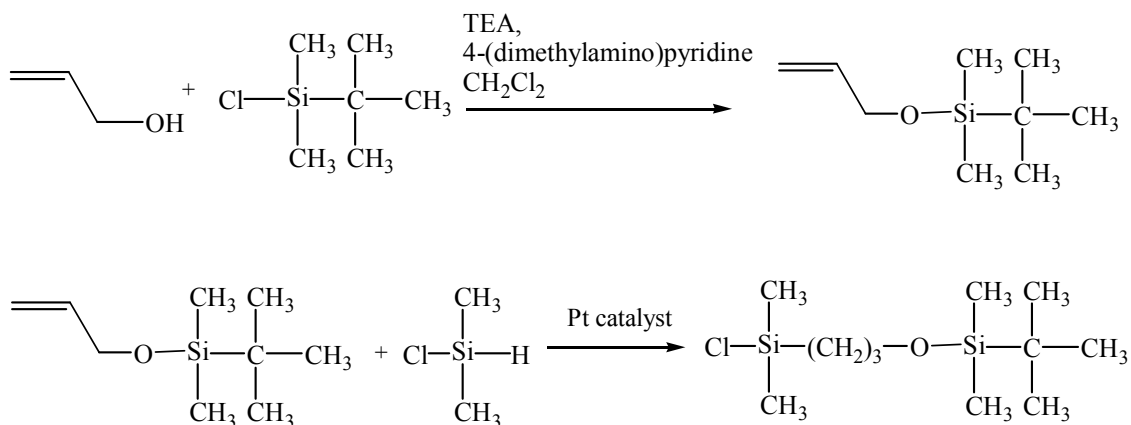
likely. To avoid these side reactions, the polymerizations may be terminated prior to full monomer conversion (usually 85-95% conversion).



Scheme 1-13. Mechanism for the living anionic polymerization of hexamethylcyclotrisiloxane.

Since there are no terminating reactions in living polymerizations, terminating reagents must be added deliberately. These terminating reagents are typically electrophilic chlorosilanes that cause the formation of lithium chloride as a by-product. The type and number of terminal functional groups can therefore be strictly controlled by the type of terminating reagent used. In 1995, a general methodology was reported for terminating living anionic polymerizations with a wide variety of functional groups including amine and hydroxyl groups using protected chlorosilane derivatives.⁸⁵ The synthesis of the protected chlorosilane derivative used to prepare primary aliphatic hydroxyl-terminated PDMS is shown below (Scheme 1-14).

⁸⁵ Peters, M. A.; Belu, A. M.; Linton, R. W.; Dupray, L.; Meyer, T. J.; DeSimone, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 3380-3388.

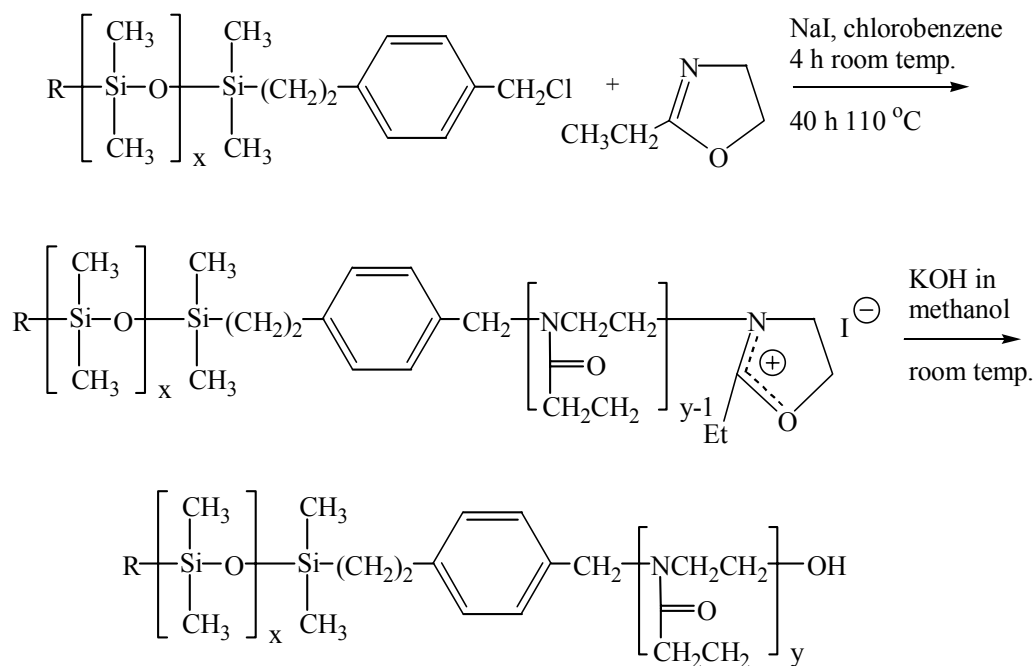


Scheme 1-14. Synthesis of *t*-butyldimethylsilyl-3-(chlorodimethylsilyl)propyl ether.

Monofunctional polysiloxanes may be used as macroinitiators or macromonomers for subsequent polymerizations. For example, Riffle and coworkers synthesized monofunctional benzylchloride terminated PDMS that was subsequently used as a macroinitiator for the living cationic polymerization of 2-ethyl-2-oxazoline (Scheme 1-15).^{86,87} The terminating agent was synthesized by hydrosilation of vinylbenzylchloride with dimethylchlorosilane. The living PDMS chains were terminated with a slight excess of the purified terminating reagent. The functionalized PDMS chains were reacted with sodium iodide for four hours in the presence of chlorobenzene and 2-ethyl-2-oxazoline to prepare the more reactive benzyliodide functionality *in-situ*. The living cationic polymerizations were subsequently initiated by increasing the reaction temperature to 110 °C and terminated with potassium hydroxide in methanol.

⁸⁶ Liu, Q.; Wilson, G. R.; Davis, R. M.; Riffle, J. S. *Polymer* **1993**, *34*, 3030-3036.

⁸⁷ Riffle, J. S.; Sinai-Zingde, G.; DeSimone, J. M.; Hellstern, A. M.; Chen, D. H.; Yilgor, I. *Polym. Prepr.* **1988**, *29*, 93-96.



Scheme 1-15. Synthesis of poly(dimethylsiloxane-*b*-2-ethyl-2-oxazoline) using a PDMS macroinitiator.

One common way that polysiloxanes can be used as macromonomers is in free radical graft copolymerizations. The macromonomers are prepared by terminating living siloxanolate end groups with 3-methacryloxypropyldimethylchlorosilane (MA-SiCl) to achieve a polymerizable monomethacrylate functionality.^{88,89,90,91} These macromonomers have been used to prepare poly(methylmethacrylate)-*g*-PDMS⁸³ and poly(methyl methacrylate)-*g*-trifluoropropylmethylsiloxane⁸⁵ by free radical polymerization in toluene using AIBN as an initiator.

⁸⁸ Smith, S. D.; DeSimone, J. M.; Huang, H.; York, G.; Dwight, D. W.; Wilkes, G. L.; McGrath, J. E. *Macromolecules* **1992**, *25*, 2575.

⁸⁹ Smith, S. D.; Long, T. E.; McGrath, J. E. *J. Polym. Sci. A: Polymer Chemistry* **1994**, *32*, 1747-1753.

⁹⁰ Suzuki, T.; Lo, P. Y. *Macromolecules* **1991**, *24*, 460-463.

⁹¹ Mera, A. E.; Goodwin, M.; Pike, J. K.; Wynne, K. J. *Polymer* **1999**, *40*, 419-427.

1.1.6 Carboxylic Acid-Functionalized Polysiloxanes

There has been some interest in the synthesis of carboxylic acid-functionalized polysiloxanes because of the hydrogen bonding capabilities of carboxylic acid groups that affect the viscosity and surface-active properties of polysiloxanes. In addition, α,ω -dicarboxylic acid functionalized polysiloxanes are potential building blocks to block copolymers prepared by polycondensation reactions. The synthesis of these functionalized polysiloxanes is not straightforward. Direct anionic polymerization of carboxylic acid functionalized cyclic siloxane monomers is not possible because the anionic propagating sites are deactivated by the acidic protons. Several different methods have been developed for the synthesis of polysiloxanes containing carboxylic acid groups at one end,^{92,93} both ends,⁹⁴ distributed along the polysiloxane backbone,^{95,96} and incorporated in block copolymers.^{97,98}

Some of these synthetic methods involve hydrosilation reactions using protected carboxyl-containing reagents. In the simplest of these methods, vinylacetic acid protected with a trimethylsilyl group was reacted with PDMS terminated with a hydrosilyl group at one or both ends.⁹⁹ To incorporate two terminal carboxylic acid groups, Kawakami et al. used trimethylsilyl-protected, aromatic, allyl-functionalized, dicarboxylic acid reagents (Scheme 1-16).¹⁰⁰ These reagents were reacted via hydrosilation with hydrosilyl-terminated PDMS and deprotected by washing with dilute hydrochloric acid. Finally, carboxylic acid groups were incorporated along the backbone of polysiloxanes by the hydrosilation reaction between poly(methylhydrosiloxane) or poly(methylhydro-*co*-dimethylsiloxane) and a protected, aromatic, monocarboxylic acid reagent.¹⁰¹ The details of the chemistry were not described.

⁹² Kawakami, Y.; Saibara, S.; Suzuki, F.; Abe, T.; Yamashita, Y. *Polymer Bulletin* **1991**, *25*, 521-527.

⁹³ Kazama, H.; Tezuka, Y.; Imai, K. *Macromolecules* **1991**, *24*, 122-125.

⁹⁴ Kazama, H.; Tezuka, Y.; Imai, K. *Macromolecules* **1991**, *24*, 122-125.

⁹⁵ Kumar, U.; Kato, T.; Frechet, J. M. J. *Polymer Materials Science and Engineering* **1991**, *64*, 231-232.

⁹⁶ Klok, H. A.; Rebrov, E. A.; Aziz, M. M.; Michelberger, W.; Moller, M. J. *Polym.Sci.: Part B: Polymer Physics* **1999**, *37*, 485-495.

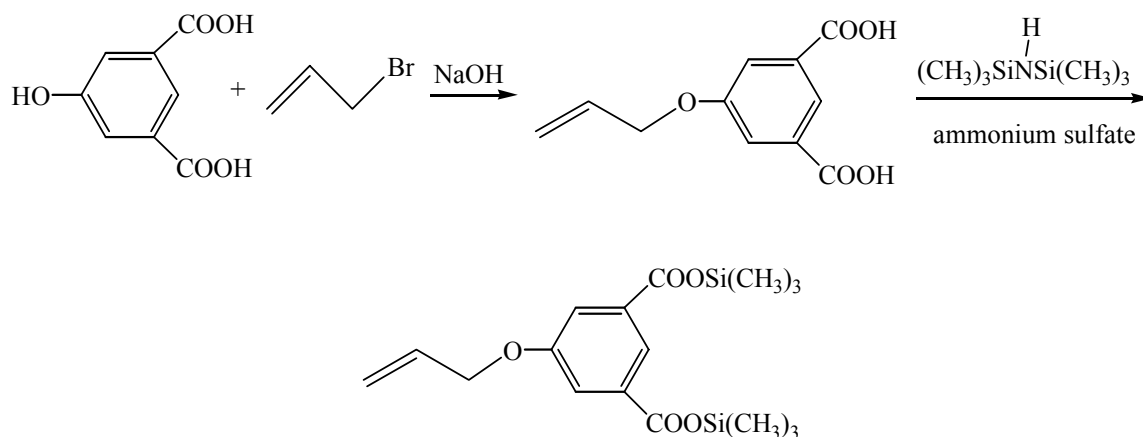
⁹⁷ Lim, K. T.; Webber, S. E.; Johnston, K. P. *Macromolecules* **1999**, *32*, 2811-2815.

⁹⁸ Scibiorek, M.; Gladkova, N. K.; Chojnowski, J. *Polymer Bulletin* **2000**, *44*, 377-384.

⁹⁹ Kazama, H.; Tezuka, Y.; Imai, K. *Macromolecules* **1991**, *24*, 122-125.

¹⁰⁰ Kawakami, Y.; Saibara, S.; Suzuki, F.; Abe, T.; Yamashita, Y. *Polymer Bulletin* **1991**, *25*, 521-527.

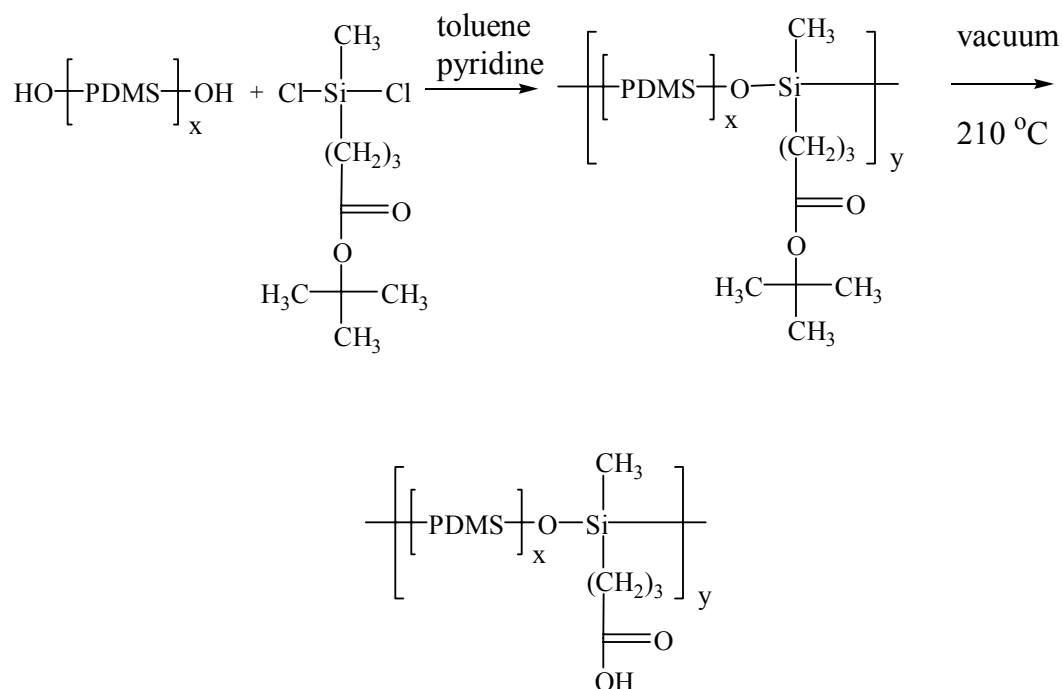
¹⁰¹ Kumar, U.; Kato, T.; Frechet, J. M. J. *Polymer Materials Science and Engineering* **1991**, *64*, 231-232.



Scheme 1-16. Synthesis of allyl-functionalized dicarboxylic reagents for hydrosilation.

Carboxylic acid groups were distributed evenly throughout a PDMS chain by a polycondensation reaction.¹⁰² In this reaction, α,ω -dihydroxyfunctional PDMS was condensed with 4-(dichloromethylsilyl)-*t*-butylbutanoate in a solution of toluene and pyridine (Scheme 1-17). The polymers were deprotected by heating at 210 °C under vacuum for 3 hours, thereby eliminating isobutene. Interestingly, the researchers reported a significant change in material properties with increasing temperature. As the temperature increased above 70 °C, there was a dramatic rise in viscosity. This was explained as a transition from a single phase to a two-phase morphology as carboxylic acid groups were mobilized, aggregated into hydrogen bonding clusters, and formed physical crosslinks.

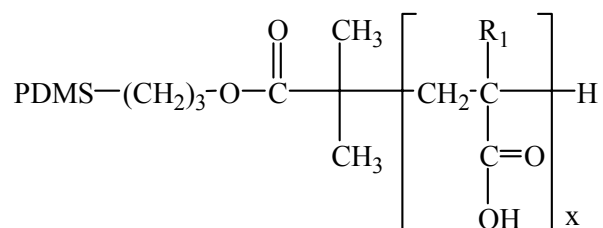
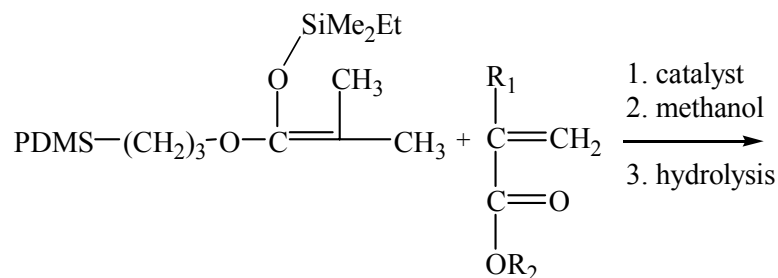
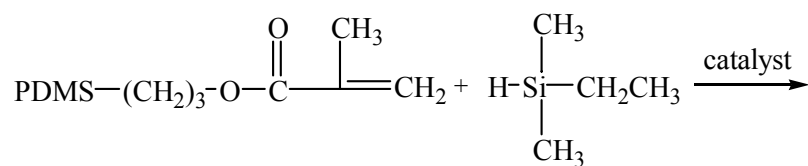
¹⁰² Klok, H. A.; Rebrov, E. A.; Aziz, M. M.; Michelberger, W.; Moller, M. *J. Polym.Sci.: Part B: Polymer Physics* **1999**, *37*, 485-495.



Scheme 1-17. Polycondensation of dihydroxyl-terminated PDMS with 4-(dichloromethylsilyl)-*t*-butylbutanoate.

The macroinitiator technique has been used to prepare PDMS-*b*-poly[alkyl(meth)acrylic acid] block copolymers by GTP using silyl ketene acetal terminated PDMS (Scheme 1-18).¹⁰³ The PDMS macroinitiator was synthesized by reacting methacryloxypropyl-terminated PDMS with ethyldimethylsilane in the presence of Wilkinson's catalyst for two hours at 55 °C. This macroinitiator was reacted with several different acrylates and methacrylates in the presence of the GTP catalyst, tetrabutylammoniumbibenzoate. These polymerizations were quenched with methanol. The (meth)acrylate groups were hydrolyzed to (meth)acrylic acid groups by three different methods depending on the chemistry of the monomer used, and between 85 and 100% hydrolysis was obtained. The block copolymers were prepared with controlled molecular weights and narrow polydispersities. Microphase separation was verified by DSC. TGA analysis indicated 6% weight loss at 250 °C corresponding to dehydration of the acid block to form a polyanhydride and backbone degradation starting at 360 °C.

¹⁰³ Lim, K. T.; Webber, S. E.; Johnston, K. P. *Macromolecules* **1999**, *32*, 2811-2815.

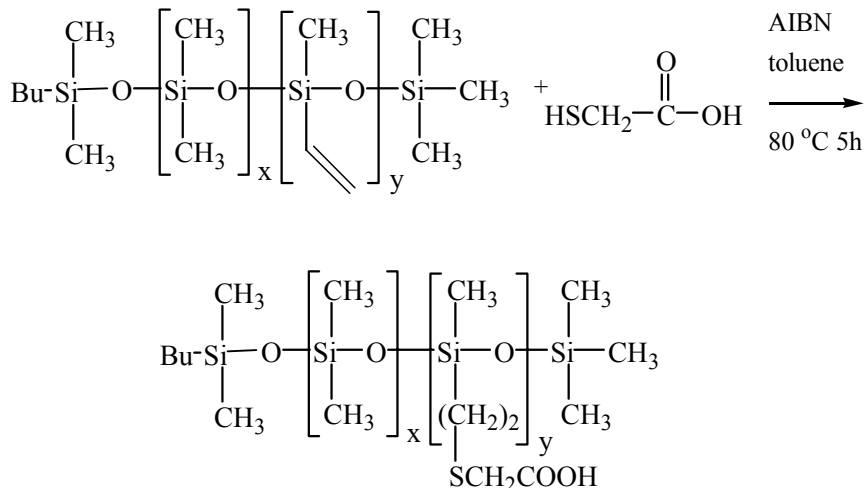


Scheme 1-18. GTP of silyl ketene acetal terminated PDMS with (meth)acrylates.

Chojnowski and coworkers utilized thiol-ene free radical additions to react pendant trivinylsilyl groups on the PDMS backbone with mercaptoacetic acid in toluene using AIBN as an initiator (Scheme 1-19).¹⁰⁴ The two polysiloxanes used in these reactions were poly(methylvinylsiloxane)-*b*-PDMS and poly(dimethyl-*co*-methylvinylsiloxane)-*b*-PDMS. By ¹H NMR analysis, it was determined that the reactions converted over 98% of the vinyl groups. GPC analysis of the carboxylic acid-containing polymers resulted in unimodal chromatograms, indicating no chain cleavage during the reactions. The authors noted that after storing the polymers for 100 days at room temperature, there was evidence that the carboxylic acid functionality caused

¹⁰⁴ Scibiorek, M.; Gladkova, N. K.; Chojnowski, J. *Polymer Bulletin* **2000**, *44*, 377-384.

cleavage of the polysiloxane backbone. This degradation was reasonable since polysiloxanes typically undergo chain cleavage in the presence of acids or bases.^{105,106}



Scheme 1-19. Thiol-ene addition of mercaptoacetic acid to PDMS-*b*-poly(methylvinylsiloxane).

1.2 Overview of Poly(ϵ -caprolactone) Chemistry

1.2.1 Background

The term “lactone” refers to internal cyclic esters formed from hydroxycarboxylic acids. Lactones are different from “lactides” or “glycolides” which are internal cyclic diesters.¹⁰⁷ The first reported synthesis of ϵ -caprolactone and subsequent polymerization was in 1934 by Carothers and coworkers.¹⁰⁸ The synthesis involved the self-esterification of ϵ -hydroxycaproic acid at 150-210 °C (Scheme 1-20). The monomer was then polymerized by adding potassium carbonate and heating to 150 °C for five hours. In

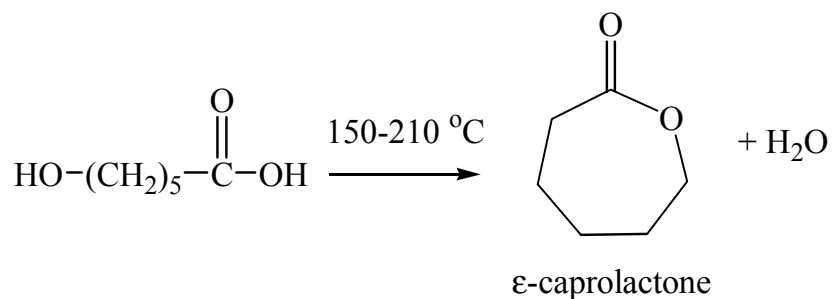
¹⁰⁵ Voronkov, M. G.; Mileshekevich, V. P.; Yuzhelevskii, Y. A. *The Siloxane Bond*; Consultants Bureau: New York, 1978.

¹⁰⁶ Noll, W. *Chemistry and Technology of Silicones*; Academic Press: New York, 1968.

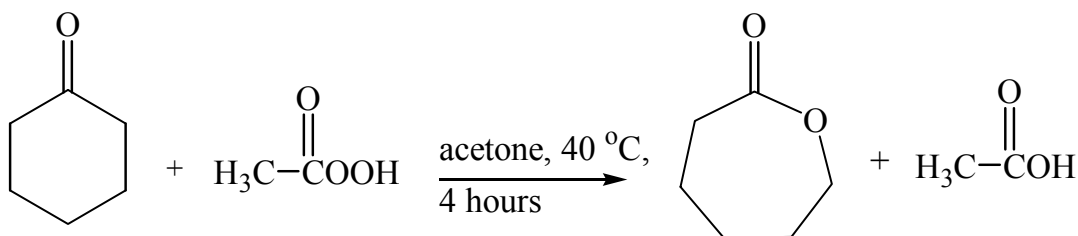
¹⁰⁷ Goodman, I. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; Wiley-Interscience: New York, 1999; Vol. 12, pp 1-75.

¹⁰⁸ van Natta, F. J.; Hill, J. W.; Carothers, W. H. *J. Am. Chem. Soc.* **1934**, *56*, 455.

1958, a procedure was developed by researchers at Union Carbide, Corp. for the preparation of ϵ -caprolactone by the Baeyer-Villiger oxidation of cyclohexanone with peracetic acid (Scheme 1-21). These reactions were performed in acetone at 40 °C and resulted in the synthesis of ϵ -caprolactone in high yields.¹⁰⁹ Some of the thermodynamic and physical properties of ϵ -caprolactone and of semicrystalline poly(ϵ -caprolactone) are listed in Table 1-1.



Scheme 1-20. Synthesis of ϵ -caprolactone by the dehydration and self-esterification of ϵ -hydroxycaproic acid.



Scheme 1-21. Baeyer-Villiger oxidation of cyclohexanone to yield ϵ -caprolactone.

¹⁰⁹ Starcher, P. S.; Phillips, B. *J. Am. Chem. Soc.* **1958**, *80*, 4079-4082.

Table 1-1. Thermodynamic and physical properties of ϵ -caprolactone and poly(ϵ -caprolactone).

	Property	Value
ϵ -caprolactone	ΔH_p°	-28.8 kJ mol ⁻¹ ¹¹⁰
	ΔS_p°	-53.9 J mol ⁻¹ K ⁻¹ ¹¹¹
	T_m	-5 °C ¹¹²
	appearance	clear, colorless liquid
poly(ϵ -caprolactone)	T_g	-60 °C ¹¹³
	T_m	63 °C ¹¹⁴

1.2.2 Coordination-Insertion and Anionic Polymerizations of ϵ -Caprolactone

The ring-opening polymerization of ϵ -caprolactone has been well documented and several reviews have been written on the subject.^{115,116,117,118,119} ϵ -Caprolactone can be polymerized by anionic, cationic, or coordination-type initiators. This section will provide an overview of the ring-opening polymerization of ϵ -caprolactone by anionic and coordination-insertion initiators and catalysts.

The anionic polymerization of ϵ -caprolactone can be initiated with alcohols or alkoxides. When alkoxides are used as initiators, the polymerizations are typically plagued by intramolecular transesterification backbiting reactions that result in the formation of macrocyclic byproducts. For example, ϵ -caprolactone polymerization was

¹¹⁰ Goodman, I. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; Wiley-Interscience: New York, 1999; Vol. 12, pp 1-75.

¹¹¹ Goodman, I. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; Wiley-Interscience: New York, 1999; Vol. 12, pp 1-75.

¹¹² van Natta, F. J.; Hill, J. W.; Carothers, W. H. *J. Am. Chem. Soc.* **1934**, *56*, 455.

¹¹³ Brode, G. L.; Koleske, J. V. *J. Macromol. Sci., Chem.* **1972**, *A6*, 1109-1144.

¹¹⁴ Brode, G. L.; Koleske, J. V. *J. Macromol. Sci., Chem.* **1972**, *A6*, 1109-1144.

¹¹⁵ Lundberg, R. D.; Cox, E. F. In *Ring-Opening Polymerization*; Frisch, K. C., Reegen, S. L., Eds.; Marcel Dekker: New York, 1969; Vol. 2, pp 247-302.

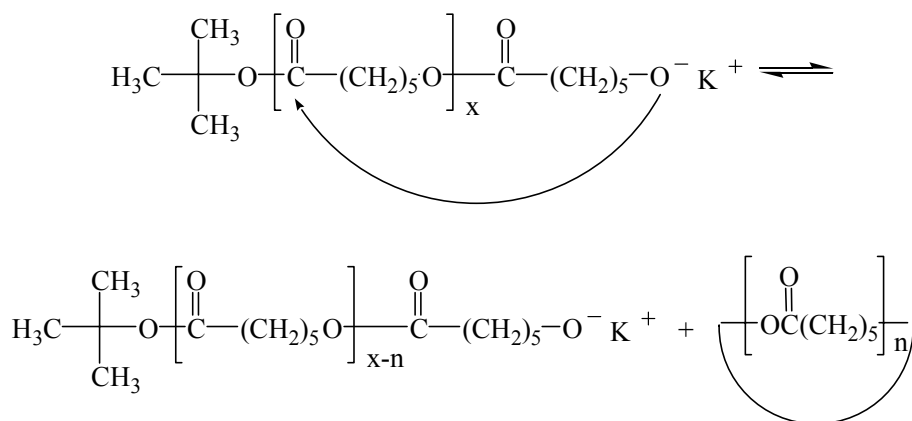
¹¹⁶ Young, R. H.; Matzner, M.; Pilato, L. A. In *Ring-Opening Polymerization*; Gould, R. F., Ed.; American Chemical Society: Washington, D.C., 1977; Vol. 59, pp 152-164.

¹¹⁷ Quirk, R. P.; Kim, J. In *Ring-Opening Polymerization: Mechanisms, Catalysis, Utility*; Brunelle, D. J., Ed.; Hanser: New York, 1993; pp 263-293.

¹¹⁸ Brode, G. L.; Koleske, J. V. *J. Macromol. Sci., Chem.* **1972**, *A6*, 1109-1144.

¹¹⁹ McGrath, J. E. In *Ring-Opening Polymerization: Kinetics, Mechanisms, and Synthesis*; McGrath, J. E., Ed.; American Chemical Society: Washington, D.C., 1985; Vol. 286, pp 1-22.

initiated with potassium *tert*-butoxide in THF and resulted in the formation of polymer and cyclic oligomers within seconds.¹²⁰ This was a ring-chain equilibrium system in which the cyclic oligomers were favored at higher dilution due to entropic factors (Scheme 1-22). In this reaction, the anionic growing chain end was a potassium alkoxide species and was terminated with HCl to yield an alcohol on the polymer chain end. Other initiators such as sodium trimethylsilanolate¹²¹ and potassium trimethylsilanolate¹²² have been used for anionic ϵ -caprolactone polymerization and these also resulted in intramolecular transesterification side reactions.



Scheme 1-22. Ring-chain equilibrium in the transesterification backbiting reactions for alkoxide-initiated polymerization of ϵ -caprolactone.

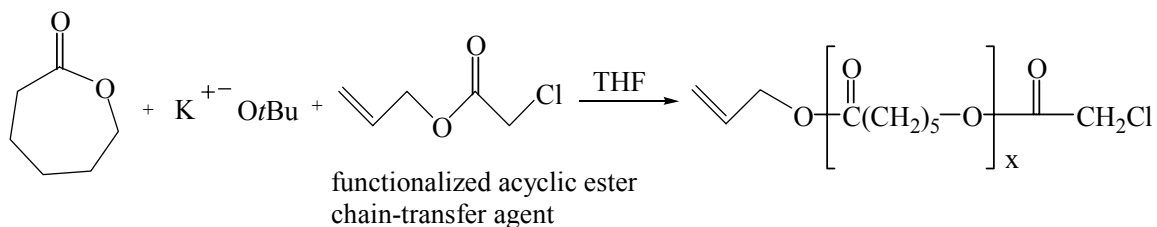
Recently, the potassium *tert*-butoxide initiating system has been modified by Gagne, et al. to yield α,ω -heterotelechelic PCL.¹²³ This was accomplished by using potassium *tert*-butoxide in tandem with functionalized acyclic esters that acted as chain transfer agents (Scheme 1-23). These polymerizations were completed within minutes and resulted in polymers with molecular weight distributions of 1.16-2.1 in yields of 46-83%.

¹²⁰ Ito, K.; Hashizuka, Y.; Yamashita, Y. *Macromolecules* **1977**, *10*, 821-824.

¹²¹ Sosnowski, S.; Slomkowski, S.; Penczek, S.; Reibel, L. *Makromol. Chem.* **1983**, *184*, 2159-2171.

¹²² Sosnowski, S.; Slomkowski, S.; Penczek, S. *J. Macromol. Sci., Chem.* **1983**, *A20*, 979-988.

¹²³ Korn, M. R.; Lennon, J. D.; Glish, G. L.; Gagne, M. R. *Macromolecules* **1999**, *32*, 5149-5153.

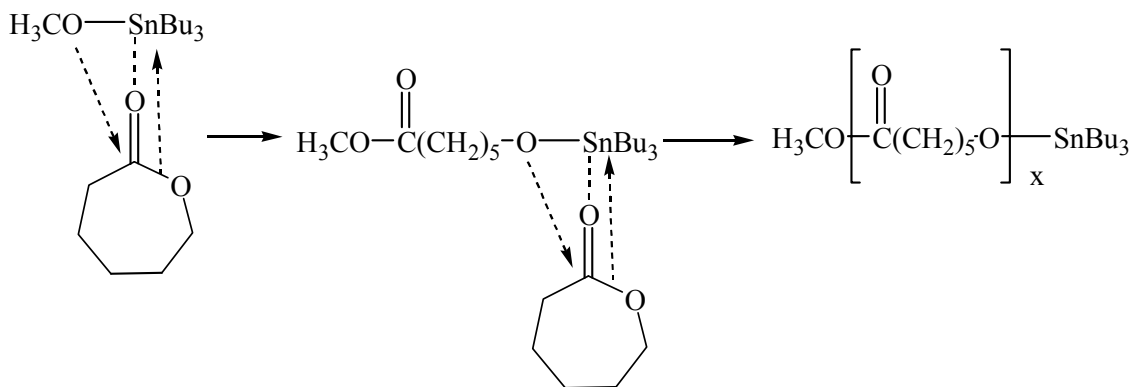


Scheme 1-23. Synthesis of α,ω -heterotelechelic PCL using potassium tert-butoxide initiator and a functionalized acyclic ester chain-transfer agent.

Metal alkoxides are often used in ϵ -caprolactone polymerizations. The metal alkoxides serve a dual function as both initiator and catalyst. For example, tributyltin methoxide was found to initiate and catalyze the polymerization of ϵ -caprolactone via a coordination-insertion mechanism (Scheme 1-24).¹²⁴ Other metal alkoxides were found to both initiate and catalyze ϵ -caprolactone coordination-insertion polymerization, including magnesium ethoxide, aluminum isopropoxide, zinc *n*-butoxide, titanium *n*-butoxide, zirconium *n*-propoxide, and dibutyltin methoxide.¹²⁵ These polymerizations did not need to be terminated, and were purified by precipitation into methanol. Polymerizations using these metal alkoxide catalysts resulted in broad molecular weight distributions because propagation was faster than initiation and also because of intramolecular transesterification reactions. The mechanism for metal alkoxide-initiated polymerizations begins with coordination of the carbonyl oxygen of ϵ -caprolactone with the empty orbitals of the metal atom. Coordination is followed by cleavage of the acyl-oxygen bond, or insertion of ϵ -caprolactone into the metal-oxygen bond.

¹²⁴ Kricheldorf, H. R.; Sumbel, M. V.; Kreiser-Saunders *Macromolecules* **1991**, *24*, 1944-1949.

¹²⁵ Kricheldorf, H. R.; Berl, M.; Scharnagl, N. *Macromolecules* **1988**, *21*, 286-293.



Scheme 1-24. Mechanism for the coordination-insertion polymerization of ϵ -caprolactone initiated and catalyzed by tributyltin methoxide.

The living polymerization of ϵ -caprolactone has been initiated with dialkyl aluminum alkoxides and proceeded by a coordination-insertion mechanism.¹²⁶ ϵ -Caprolactone was polymerized up to 99% conversion in THF at 20 or 25 °C, was terminated with acetic acid, and resulted in polymers with polydispersities from 1.03-1.13. No macrocycles were formed during these reactions, indicating that there were no chain transfer reactions (intramolecular transesterification). The polymerizations resulted in poly(ϵ -caprolactone)s with an ester functionality at the initiated end and an alcohol group at the terminated end. The authors suggested a mechanism that involved coordination of the ether oxygen in the ϵ -caprolactone ester, rather than coordination of the carbonyl oxygen. This mechanism seems unlikely since there is FT IR spectroscopic evidence that the reaction proceeds by coordination of the carbonyl oxygen.¹²⁷

Other polymerizations that displayed living character were obtained by using bimetallic μ -oxoalkoxides as initiators and catalysts.¹²⁸ For example, Al_2Zn and $\text{Al}_2\text{Co(II)}$ μ -oxoalkoxides were used to initiate ϵ -caprolactone polymerization in toluene at room temperature. Evidence for living character included a lack of chain transfer or termination reactions, narrow polydispersities in the resultant polymers, and that the polymerization could be continued when additional monomer was added. This

¹²⁶ Duda, A.; Florjanczyk, Z.; Hofman, A.; Slomkowski, S.; Penczek, S. *Macromolecules* **1990**, *23*, 1640-1646.

¹²⁷ Kohn, F. E.; Von Ommen, J. G.; Feijen, J. *Eur. Polym. J.* **1983**, *19*, 1081-1088.

¹²⁸ Hamitou, A.; Ouhadi, T.; Jerome, R.; Teyssie, P. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 865-873.

polymerization was also predicted to proceed via a coordination-insertion mechanism resulting in acyl-oxygen cleavage.

Carboxylates should not be utilized to initiate the polymerization of ϵ -caprolactone because this would result in formation of unfavorable anhydride linkages. When metal carboxylates are used for the polymerization of ϵ -caprolactone, these serve only as catalysts and not initiators. These polymerizations must be initiated with sources such as water, alcohols, or alkoxides. For example, ϵ -caprolactone polymerization was initiated with water and catalyzed with triphenyltin acetate.¹²⁹ This polymerization afforded PCL with broad molecular weight distributions. There was no tin detected in the polymer after purification, suggesting that the triphenyltin acetate acted as a catalyst, not an initiator.

Tin (II) octoate, or stannous octoate, is a commonly used catalyst for ϵ -caprolactone polymerization and is typically used in conjunction with hydroxyalkyl initiators.^{130,131,132} Storey and Taylor have studied the effect of stannous octoate concentration on ethylene glycol-initiated polymerizations of ϵ -caprolactone.¹³³ Reactions were conducted at 120 °C in the bulk and resulted in relatively broad molecular weight distributions ranging from 1.34-1.79. They found little effect of stannous octoate concentration on molecular weight and molecular weight distribution when ethylene glycol was used as an initiator. However, when no ethylene glycol was added, the reactions were presumably initiated with residual water incorporated along with the stannous octoate. The molecular weight distributions for ethylene glycol-free polymerizations were broader and ranged from 1.94-3.95. The broader molecular weight distributions were attributed to a coordination-insertion/condensation polymerization mixed mechanism. Polymerizations initiated with water contain one carboxylic acid end group and one alcohol end group. These end groups allowed the PCL oligomers to undergo condensation polymerizations that resulted in higher polydispersity indices.

¹²⁹ Bassi, M. B.; Padias, A. B.; Hall, H. K. *Polymer Bulletin* **1990**, *24*, 227-232.

¹³⁰ Ward, R. S.; Riffle, J. S. In *US Pat. 4,963,595*; Thoratec Laboratories Corp.: United States, 1990.

¹³¹ Storey, R. F.; Taylor, A. E. *J.M.S. - Pure Appl. Chem.* **1998**, *35*, 723-750.

¹³² Storey, R. F.; Sherman, J. W. *Macromolecules* **2002**, *35*, 1504-1512.

¹³³ Storey, R. F.; Taylor, A. E. *J.M.S. - Pure Appl. Chem.* **1998**, *35*, 723-750.

1.2.3 Biodegradability of Poly(ϵ -caprolactone)

Poly(ϵ -caprolactone) is well known to be a biodegradable polymer.^{134,135,136,137} The biodegradability is due to the hydrolytic instability of its ester linkages. However, PCL is a semicrystalline polymer, its high degree of crystallinity causes it to degrade more slowly than poly(lactide), for example.¹³⁸ This difference in the rate of degradation is fortuitous, because by blending two polymers with different rates of degradation, one can obtain materials with tailored degradation rates intermediate between the two polymer components.¹³⁹ Alternatively, block copolymers containing PCL with different block lengths can be prepared with varying degradation rates.^{140,141,142}

The degradation of PCL within the body has been determined to occur in three stages.^{143, 144} In the first stage, PCL undergoes nonenzymatic bulk hydrolysis that results in a decrease in molecular weight but does not result in weight loss. In the second stage, short chain oligomers are formed, resulting in weight loss. Finally, in the third stage, the low molecular weight PCL is rapidly degraded inside macrophage and giant cells into ϵ -hydroxycaproic acid.

¹³⁴ Perrin, D. E.; English, J. P. In *Handbook of Biodegradable Polymers*; Domb, A. J., Kost, J., Wiseman, D. M., Eds.; Harwood: Amsterdam, 1997; pp 63-76.

¹³⁵ Siparsky, G. L. In *Polymers from Renewable Resources: Biopolyesters and Biocatalysis*; Scholz, C., Gross, R. A., Eds.; American Chemical Society: Washington, D.C., 2000; Vol. 764, pp 230-251.

¹³⁶ McGrath, J. E. In *Ring-Opening Polymerization: Kinetics, Mechanisms, and Synthesis*; McGrath, J. E., Ed.; American Chemical Society: Washington, D.C., 1985; Vol. 286, pp 1-22.

¹³⁷ Gilbert, R. D.; Stannett, V.; Pitt, C. G.; Schindler, A. In *Developments in Polymer Degradation*; Grassie, N., Ed.; Applied Science Publishers: London, 1982; Vol. 4, p 259.

¹³⁸ Siparsky, G. L. In *Polymers from Renewable Resources: Biopolyesters and Biocatalysis*; Scholz, C., Gross, R. A., Eds.; American Chemical Society: Washington, D.C., 2000; Vol. 764, pp 230-251.

¹³⁹ Perrin, D. E.; English, J. P. In *Handbook of Biodegradable Polymers*; Domb, A. J., Kost, J., Wiseman, D. M., Eds.; Harwood: Amsterdam, 1997; pp 63-76.

¹⁴⁰ Cai, Q.; Bei, J.; Wang, S. *Polym. Adv. Technol.* **2000**, *11*, 159-166.

¹⁴¹ Lang, M.; Bei, J.; Wang, S. *J. Biomater. Sci. Polymer Edn.* **1999**, *10*, 501-512.

¹⁴² Chen, H.; Bei, J.; Wang, S. *Polym. Adv. Technol.* **2000**, *11*, 180-184.

¹⁴³ Woodward, S. C.; Brewer, P. S.; Moatmed, F.; Schindler, A.; Pitt, C. G. *J. Biomedical Mat. Res.* **1985**, *19*, 437-444.

¹⁴⁴ Perrin, D. E.; English, J. P. In *Handbook of Biodegradable Polymers*; Domb, A. J., Kost, J., Wiseman, D. M., Eds.; Harwood: Amsterdam, 1997; pp 63-76.

1.2.4 Miscibility of Poly(ϵ -caprolactone) With Other Polymers

An important characteristic of PCL is its miscibility with a variety of other polymers, making it useful in many polymer blends. A material that forms a soluble blend of two polymers displays one glass transition temperature (T_g) intermediate between the T_g s of the two homopolymers. Some of the polymers that are known to blend well with PCL include poly(carbonate), poly(vinyl chloride), poly(hydroxy ether), cellulosic polymers, and poly(epichlorohydrin).¹⁴⁵ However, at high PCL contents, the physical properties of such blends tend to change with time (increased modulus) as PCL slowly crystallizes with aging. Optical microscopy, dynamic mechanical analysis, and differential scanning calorimetry were used to analyze blends of PCL in low-density polyethylene.¹⁴⁶ It was determined that the two polymers were miscible at high and low PCL contents and phase separation became apparent at an intermediate PCL content. Random copolymers of PCL-*co*-poly(ϵ -methyl- ϵ -caprolactone) and PCL-*co*-poly(β , δ -methyl- ϵ -caprolactone) are completely miscible with poly(vinylchloride) at all composition ratios.¹⁴⁷ These polymers are miscible most likely because the additional methyl groups on the caprolactone repeat units serve to disrupt its ability to crystallize.

Because of the unique blending capabilities of PCL, PCL-containing block copolymers have the ability to permanently adhere or “anchor” other polymer block segments onto the surface of a third polymer. For example, PCL-PDMS-PCL triblock copolymers were used to biocompatibilize the surface of poly(vinyl chloride) films.¹⁴⁸ When the block copolymer was blended with PVC, the PDMS blocks migrated to the PVC surface because of their very low surface energies while the PCL blocks remained anchored in the PVC. This allowed for permanent PVC surface modification.

¹⁴⁵ Koleske, J. V. In *Polymer Blends*; Paul, D. R., Newman, S., Eds.; Academic Press: New York, 1978; Vol. 2, pp 369-389.

¹⁴⁶ Kalfoglou, N. K. *J. Appl. Polym. Sci.* **1983**, *28*, 2541-2551.

¹⁴⁷ Vion, J. M.; Jerome, R.; Teyssie, P.; Aubin, M.; Prudhomme, R. E. *Macromolecules* **1986**, *19*, 1828-1838.

¹⁴⁸ Tang, L.; Sheu, M. S.; Chu, T.; Huang, Y. H. *Biomaterials* **1999**, *20*, 1365-1370.

1.3 Nanoparticle Synthesis Within Block Copolymer Micelles

1.3.1 Introduction to Nanotechnology and Block Copolymer Micelles

In recent years, concepts relating to nanotechnology have been explored and utilized at great length. Because the components of everyday instruments and computerized systems continue to decrease in size, the ability to synthesize materials as small as possible becomes a limiting factor. Synthetic routes to nanoparticles are in high demand since these are used in high-density information storage, magnetic fluids, catalysis,¹⁴⁹ ceramics, paint and cosmetic pigments,¹⁵⁰ and light-emitting diodes.¹⁵¹ The properties of metal nanoparticles are important in technology for many reasons. Their small size causes them to have a large surface area/volume ratio, which is especially important in catalysis. Also, metal nanoparticles display unique magnetic, optical, reactive, and spectroscopic properties.¹⁵² Certain block copolymers have been proven to work exceptionally well in the synthesis of controlled-size nanoparticles.

Using amphiphilic block copolymers in the synthesis of nanoparticles takes advantage of their self-assembling properties. Amphiphilic block copolymers are an important subset of block copolymers. The word “amphiphilic” is derived from *amphi*, which means “of both kinds” and *philic*, which means “having an affinity for”.¹⁵³ As the name suggests, amphiphilic block copolymers contain both hydrophobic and hydrophilic segments. This dualistic character has some interesting practical implications. For example, polymeric self-assembly is widely demonstrated in biological systems, such as in protein folding into helices or sheets and aggregation into larger structures such as ribosomes.¹⁵⁴ Biological systems may also use polymer self-assembly in the synthesis of biologically relevant metal or mineral nanoparticles.^{155,156}

¹⁴⁹ Bonnemann, H.; Brijoux, W.; Brinkmann, R.; Fretzen, R.; Jousen, T.; Koppler, R.; Korall, B.; Neiteler, P.; Richter, J. *J. Mol. Catal.* **1994**, *86*, 129-177.

¹⁵⁰ Forster, S.; Antonietti, M. *Adv. Mater.* **1998**, *10*, 195-217.

¹⁵¹ Alivisatos, A. P. *Science* **1996**, *271*, 933-937.

¹⁵² Antonietti, M.; Wenz, E.; Bronstein, L.; Seregina, M. *Adv. Mater.* **1995**, *7*, 1000-1005.

¹⁵³ Forster, S.; Antonietti, M. *Adv. Mater.* **1998**, *10*, 195-217.

¹⁵⁴ Whitesides, G. M.; Mathias, J. P.; Seto, C. T. *Science* **1991**, *254*, 1312.

¹⁵⁵ Blakemore, R. *Science* **1975**, *190*, 377-379.

¹⁵⁶ Mann, S. *Nature* **1988**, *332*, 119-124.

When amphiphilic block copolymers are added to a solvent that preferentially dissolves only one block, called a *selective solvent*, the block copolymers will tend to organize in a way that places the non-solvated block out of the environment of the solvent. For example, in an organic solvent, the hydrophobic segment may be highly solvated and hydrophilic segments may aggregate at the surface of the liquid or aggregate with other hydrophilic segments creating their own hydrophilic environment, and vice versa. The self-organization of amphiphilic block copolymers results in several possible morphologies including micelles, rods, lamellae, and vesicles.¹⁵⁷ Micelle formation is the most common type of self-organization. The micelles formed by amphiphilic block copolymers are nanoscopic and can be considered nanoscopic reaction vessels¹⁵⁸ containing specific chemical environments.

Small molecule surfactants also form nanoscopic micelles, but there are a number of important advantages to using amphiphilic block copolymers instead of small molecules for particle synthesis. First, the architectures of block copolymers can be precisely controlled since living polymerizations are typically used for their synthesis. Through control of the polymer architecture, one may be able to control the size of the micelle core and corona (Figure 1-4). Also, one can readily tailor the chemical structure of either block of the polymer to impart a desired behavior in a particular chemical environment. The requirements are that one block is soluble in the environment chosen and the other block is able to bind to the particle by dipolar interactions, hydrogen bonding, complexation, or covalent bonding.¹⁵⁹ Another advantage is that low critical micelle concentrations are usually achieved, so that the micelle structure and particle stability are not compromised upon dilution. This attribute becomes important in the case of drug delivery when the nanoparticles are diluted with body fluids.¹⁶⁰

¹⁵⁷ Zhang, L.; Eisenberg, A. *Science* **1995**, *268*, 1728-1731.

¹⁵⁸ Antonietti, M.; Wenz, E.; Bronstein, L.; Seregina, M. *Adv. Mater.* **1995**, *7*, 1000-1005.

¹⁵⁹ Forster, S.; Antonietti, M. *Adv. Mater.* **1998**, *10*, 195-217.

¹⁶⁰ Forster, S.; Antonietti, M. *Adv. Mater.* **1998**, *10*, 195-217.

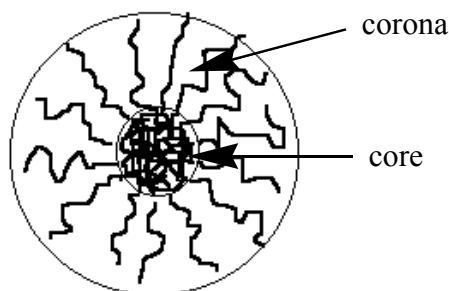


Figure 1-4. Core and corona of a block copolymer micelle.

1.3.2 Reactions in Block Copolymer Micelles

The types of reactions that can take place in the nanoscopic environment of a block copolymer micelle are seemingly unlimited. The present scope of nanoreactions includes redox, decomposition, and even polymerization reactions. For example, free radically initiated cure reactions have been performed within poly(ethylene glycol-*b*-lactic acid) micelles.¹⁶¹ In order to achieve these cure reactions, a polymerizable methacryloyl functionality was attached to the end of the PLA block. Curing was initiated chemically using azobis-2,4-dimethylvaleronitrile at an elevated temperature and photochemically using 2,2-dimethoxy-1,2-diphenylethane-1-one. In each case, micelles with polymerized cores were obtained with an average diameter of 20 nm.

One example of a nanoscopic decomposition reaction has been achieved within micelles of poly(ethylene oxide-*b*-butylene oxide-*b*-ethylene oxide) triblock copolymers. This system has been used in the synthesis of MoO₃ nanoparticles.¹⁶² The reaction took place by adding water-soluble MoO₂(OH)(OOH) to an aqueous solution containing the polymeric micelles. The system was refluxed at 100 °C and the molybdenum reagent decomposed in the hydrophilic matrix. Nanoparticles formed as the water-insoluble decomposition byproduct, MoO₃, was deposited in the hydrophobic micelle cores. This reaction is unique because the core of the micelle does not function as a true nanoreactor. It acts simply as a receptacle for the product of a reaction that occurs in the environment surrounding the micelle core.

¹⁶¹ Kim, J. H.; Iijima, M.; Nagasaki, Y.; Kataoka, K. *Polym. Prepr.* **1998**, *39*, 130-131.

¹⁶² Xie, Y.; Liu, T.; Liu, L.; Chu, B. *Polym. Mater. Sci. Eng.* **1998**, *79*, 334-335.

The micelle cores act as true nanoreactors in the following reactions that produce metal ion nanoparticles. Poly(styrene-*b*-2-vinylpyridine) micelles are able to entrap the gold salt, H₂AuCl₄, via neutralization of the vinyl-pyridine blocks in the core.¹⁶³ Eisenberg, et al. has extensively investigated ionic stabilization of metal salts using poly(styrene-*b*-acrylic acid) stabilizers.¹⁶⁴ Neutralization of the PAA blocks with various metal salts induced micellization because the blocks became ionic while the polystyrene was nonionic. Control over the incorporated amount of metal is possible because the neutralization of PAA with metal salts is essentially an acid-base titration. Each metal salt acted as a counter-ion to the polymer block. Salts of cesium, barium, cadmium, lead, nickel, and cobalt have all been used as counter-ions. In two of these studies, the salt-containing micelles could potentially have been utilized as precursors to zero-valent metal particles.

1.3.3 Synthesis of Metal Nanoparticles via Reduction of Metal Salts

The process of reducing metal salts in block copolymer micelles typically requires three steps: 1) dissolution of the block copolymer in the solvent to achieve micelles 2) addition of the metal salt that diffuses into the micelle core and 3) addition of the reducing agent accompanied by a nearly immediate color change. Variations on this method also exist.

Poly(4-vinylpyridine) (P4VP) is an excellent metal-complexing moiety. Antonietti and coworkers have taken advantage of this feature by using it as a nanoreactor core for gold colloid synthesis.^{165,166} Block copolymers consisting of polystyrene and P4VP were dissolved in toluene and a gold acid, H₂AuCl₄, was dissolved into the micelle cores. The gold salts were reduced either with sodium borohydride (NaBH₄), superhydride, or hydrazine hydrate (N₂H₄·H₂O). A violet color was immediately observed upon addition of hydrazine whereas orange solutions were observed for NaBH₄ and superhydride. The reactivity of the reducing agent used was

¹⁶³ Spatz, J. P.; Sheiko, S.; Moller, M. *Macromolecules* **1996**, *29*, 3220-3226.

¹⁶⁴ Moffitt, M.; Eisenberg, A. *Macromolecules* **1997**, *30*, 4363-4373.

¹⁶⁵ Antonietti, M.; Wenz, E.; Bronstein, L.; Seregina, M. *Adv. Mater.* **1995**, *7*, 1000-1005.

¹⁶⁶ Antonietti, M.; Thunemann, A.; Wenz, E. *Colloid Polym. Sci.* **1996**, *274*, 795-800.

found to be an important factor in determining the type and size of metal colloid produced. Antonietti, et al., found that one single colloidal particle was formed in each micelle when a slow-reacting, soluble reducing agent was used. Small clusters of particles were formed in each micelle when a fast, soluble reducing agent, such as sodium borohydride (NaBH_4) or a superhydride, was used. However, if a heterogeneous (insoluble) reducing agent such as hydrazine was used, colloid size depended on the reaction time.^{167,168}

Other researchers have synthesized similar gold colloids by different means, using anionic or cationic surfactants. Bis(2-ethylhexyl) sulfosuccinate sodium salt (AOT) and didodecyldimethylammonium bromide (DDAB) are surfactants that form micelles in organic solvents. Reduction of gold salts using a variety of reducing agents results in stable gold colloids.¹⁶⁹

Many other metal colloids have been synthesized in amphiphilic block copolymer micelles including silver, palladium, rhodium, zinc, copper, nickel, lead, platinum, iron and cobalt. Antonietti and coworkers have synthesized a broad range of block copolymers useful for this purpose by the chemical modification of polystyrene-*b*-butadiene.¹⁷⁰ First, the double bonds of polybutadiene were epoxidized using 3-chloroperbenzoic acid. Ring opening of the epoxy functionality using a variety of reactions created a wide variety of hydrophilic blocks. For example, small molecules such as diethylamine, benzoic acid, and 2-mercaptopyridine were used to open the epoxy rings. The resultant polymers consisted of polystyrene blocks along with metal complexing blocks containing various ligands. Upon addition of acetates, chlorides, or nitrates of Au, Ag, Pd, Rh, Zn, and Cu and reduction with hydrazine or superhydride (LiBEt_3H), metal colloids ranging from 56 to 309 nm in diameter were produced.¹⁷¹ This study delineates a creative method for the development of a wide variety of schemes for syntheses of metal colloids.

Some studies have reported the synthesis of metal colloids from metal salts without the need for the addition of a reducing agent. In these cases, the solvent acts as a

¹⁶⁷ Antonietti, M.; Wenz, E.; Bronstein, L.; Seregina, M. *Adv. Mater.* **1995**, *7*, 1000-1005.

¹⁶⁸ Antonietti, M.; Thunemann, A.; Wenz, E. *Colloid Polym. Sci.* **1996**, *274*, 795-800.

¹⁶⁹ Wilcoxon, J. P.; Williamson, R. L.; Baughman, R. *J. Chem. Phys.* **1993**, *98*, 9933-9950.

¹⁷⁰ Antonietti, M.; Forster, S.; Hartmann, J.; Oestreich, S. *Macromolecules* **1996**, *29*, 3800-3806.

¹⁷¹ Antonietti, M.; Forster, S.; Hartmann, J.; Oestreich, S. *Macromolecules* **1996**, *29*, 3800-3806.

reducing agent. One of these studies describes a synthesis for gold colloids in a polypyrrole matrix using polystyrene-*b*-2-vinyl pyridine.¹⁷² The block copolymer and gold salt were dissolved in pyrrole and cast into films. Reduction of the salts occurred during the process of vapor-phase polymerization of the pyrrole. Another example involves the same type of PS-*b*-P2VP polymer for the reduction of palladium salts in benzyl alcohol.¹⁷³ The solution of polymer, metal salt, and benzyl alcohol was cast into a film and heated to 140 °C for 8 hours. Benzyl alcohol functioned as a reducing agent for the Pd(II). Nanoparticles approximately 4 nm in diameter formed.

Both of the previous approaches involved casting of metal salt-containing films followed by reduction. In a variation on this approach, one group developed a general method for the *in situ* synthesis of metal colloids within polymer films by immersing the diblock copolymer film in a solution containing the desired metal salt, followed by reduction at high temperatures using hydrogen gas.^{174,175} The diblock copolymer was poly(methyltetracyclododecane-*b*-2-norbornene-5-6-dicarboxylic acid) (poly-MTD-*b*-polyNORCOOH) where the polyNORCOOH was the hydrophilic unit that solubilized the metal salts (Figure 1-5). Metal nanoclusters produced by this method included Ag, Au, Cu, Ni, Pb, and Pd.

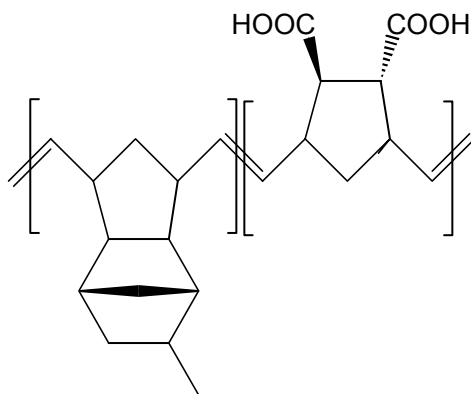


Figure 1-5. Poly(MTD)-*b*-poly(NORCOOH).

¹⁷² Selvan, S. T.; Hayakawa, T.; Nogami, M.; Moller, M. *J. Phys. Chem. B* **1999**, *103*, 7441-7448.

¹⁷³ Hashimoto, T.; Harada, M.; Sakamoto, N. *Macromolecules* **1999**, *32*, 6867-6870.

¹⁷⁴ Clay, R. T.; Cohen, R. E. *Supramol. Sci.* **1995**, *2*, 183-191.

¹⁷⁵ Clay, R. T.; Cohen, R. E. *Supramol. Sci.* **1997**, *4*, 113.

Metal nanoclusters doped with a second metal can also be synthesized by this method via sequential metal ion loading.^{176,177,178} For example, manganese-doped ZnS nanoparticles were formed by treatment of the films with diethyl-zinc or zinc acetate followed by treatment with manganese acetate. The entire film was then reacted with H₂S to obtain the final doped product. These 1-10 nm diameter nanoparticles were photoluminescent, with emission wavelengths corresponding to those of the doped metal (Mn).

Alternately, the chemistry of the nanoparticles was interconverted in one particular case that utilized poly-MTD-*b*-2,3-trans-bis[tert-butylamidomethyl] norborn-5-ene films.¹⁷⁹ Conversion between ZnF₂ and ZnS nanoclusters was accomplished by sequential treatments with hydrogen fluoride-pyridine at room temperature and H₂S at 140 °C for 12 hours. Similar composite nanoparticles of ZnS/CdS have been synthesized in poly(styrene-*b*-butadiene (hydroxylated)-*b*-styrene) triblock copolymer solutions.¹⁸⁰ Alternately, this process has been used as a means of controlling CdS nanoparticle size by repeating the same synthetic sequence for a particular number of cycles.¹⁸¹ After three repetitions of the synthesis, CdS particle size was increased from 2.8 to 9.7 nm.

1.4 Magnetic Nanoparticles

1.4.1 Background on Magnetic Nanoparticles

Some basic material properties change significantly as overall size decreases from bulk to nanoscopic. Magnetism is one such property. Typically, macroscopic magnetic materials are separated into domains, or sections where magnetic spins are cooperatively oriented in the same direction. In the presence of an external magnetic field, these

¹⁷⁶ Kane, R. S.; Cohen, R. E.; Silbey, R. J. *Chem. Mater.* **1996**, *8*, 1919-1924.

¹⁷⁷ Kane, R. S.; Cohen, R. E.; Silbey, R. J.; Kuno, M.; Bawendi, M. G. *Mat. Res. Soc. Symp. Proc.* **1997**, *471*, 313-317.

¹⁷⁸ Kane, R. S.; Cohen, R. E.; Silbey, R. J. *Chem. Mater.* **1999**, *11*, 90-93.

¹⁷⁹ Yue, J.; Sankaran, R. E.; Cohen, R. E.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 4409-4410.

¹⁸⁰ Wang, D.; Cao, Y.; Zhang, X.; Qian, X.; Ai, X.; Liu, Z.; Liu, F.; Wang, D.; Bai, Y.; Li, T.; Tang, X. *J. Mater. Res.* **1999**, *14*, 2381-2384.

¹⁸¹ Wang, D.; Cao, Y.; Zhang, X.; Liu, Z.; Qian, X.; Ai, X.; Liu, F.; Wang, D.; Bai, Y.; Li, T.; Tang, X. *Chem. Mater.* **1999**, *11*, 392-398.

domain spins will tend to align with that field, creating an overall magnetic moment. Ferromagnets are materials that retain a residual magnetic moment in the absence of an external magnetic field. A critical particle diameter exists for each type of material below which domain walls cease to exist. Particles smaller than this critical particle diameter will be comprised of one single domain. Estimates for the critical particle diameters for single magnetic domains are illustrated in Table 1-2:

Table 1-2. Critical particle diameters for single magnetic domains in magnetic metals.¹⁸²

Metal	Critical particle diameter (nm)
Cobalt	70
Iron	14
Nickel	55
Iron oxide (Fe ₃ O ₄)	128

When single domain particles are subjected to an external magnetic field, the particle magnetic moments align with the field. If there is complete randomization of the orientations of the particle magnetic moments when the applied magnetic field is removed, the material is considered to be superparamagnetic (Figure 1-6).

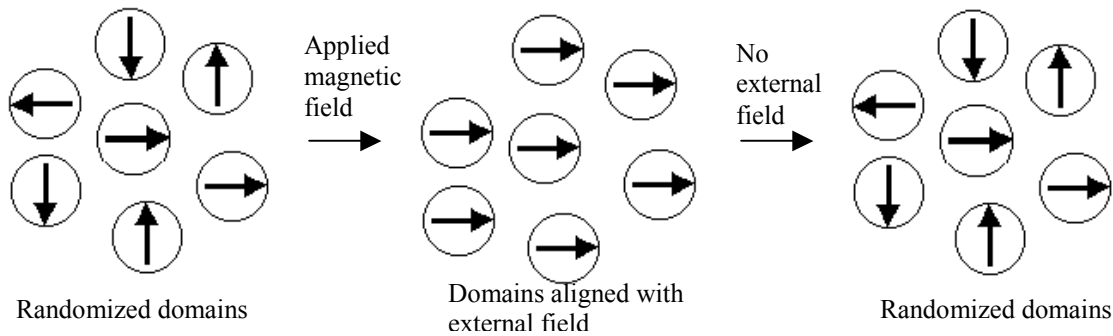


Figure 1-6. Behavior of superparamagnetic particles with and without the presence of an applied external magnetic field.

¹⁸² Kittel, C. *Phys. Rev.* **1946**, 70, 965.

Magnetic nanoparticles are especially important for applications such as information storage,¹⁸³ contrast agents for magnetic resonance imaging,¹⁸⁴ magnetic fluids^{185,186,187,188,189,190,191} (ferrofluids). In the case of magnetic fluids, single domain particles with high saturation magnetization, high magnetic susceptibility, and low or zero coercivities are ideal. To synthesize single domain particles, control over particle size and the absence of particle aggregation is desirable. The magnetic behavior of aggregated particles deviates significantly from that of isolated single particles, resulting in inconsistent and uncontrollable behavior. Amphiphilic block copolymer micelles may be used as nanoreactors, since fair control over particle size can be achieved and the solvated polymer serves to sterically stabilize the particles.

Interestingly, magnetic nanoparticles are not only found in modern technology, but also in biology. One particular species of bacteria, known as magnetotactic bacteria, contain iron-rich nanoparticles that presumably allow for geomagnetic orientation as a guiding system.¹⁹² It can be inferred that some sort of biomolecular self-assembly process promotes the synthesis of these inorganic particles within the living organism.

1.4.2 Synthesis of Magnetic Iron, Cobalt, and Nickel Nanoparticles

Iron nanoparticles have been prepared by several methods. One of these methods involves the reduction of iron salts in ionic surfactant-stabilized microemulsions. Nanoparticles between 1.4 and 15 nm in diameter were prepared by reducing FeCl₃ using a dodecyltrimethyl ammonium chloride surfactant.¹⁹³ A similar method was used to prepare iron nanoparticles less than 100 nm in diameter by reducing FeCl₂ using bis-2-

¹⁸³ Simonds, J. L. *Physics Today* **1995**, *48*, 26.

¹⁸⁴ Chouly, C.; Pouliquen, D.; Lucet, I.; Jeune, J. J.; Jallet, P. *J. Microencapsulation* **1996**, *13*, 245-255.

¹⁸⁵ Raj, K.; Rosenzweig, R. E.; Aziz, L. M. In *Eur. Patent No. 0,859,379*, 1998.

¹⁸⁶ Rocchiccioli-Deltcheff, C.; Franck, R.; Cabuil, V.; Massart, R. *Journal of Chemical Research, Synopses* **1987**, *5*, 126-127.

¹⁸⁷ Morais, P. C.; DaSilva, S. W.; Soler, M. A. G.; Buske, N. *IEEE Trans. Magn.* **2000**, *36*, 3712-3714.

¹⁸⁸ Lesnikovich, A. I.; Shunkevich, T. M.; Naumenko, V. N.; Vorobyova, S. A.; Baykov, M. V. *J. Magn. Mater.* **1990**, *85*, 14-16.

¹⁸⁹ Moeser, G. D.; Roach, K. A.; Green, W. H.; Laibinis, P. E.; Hatton, T. A. *Ind. Eng. Chem. Res.* **2002**, *41*, 4739-4749.

¹⁹⁰ Mendenhall, G. D.; Geng, Y.; Hwang, J. *Journal of Colloid and Interface Science* **1996**, *184*, 519-526.

¹⁹¹ Massart, R. *IEEE Trans. Magn.* **1981**, *17*, 1247.

¹⁹² Blakemore, R. *Science* **1975**, *190*, 377-379.

¹⁹³ Venturini, E. L.; Wilcoxon, J. P.; Newcomer, P. P. *Mat. Res. Soc. Symp. Proc.* **1994**, *351*, 311-316.

ethylhexyl sodium sulphosuccinate (AOT) as a surfactant.¹⁹⁴ Vapor deposition techniques are also applicable to iron nanoparticle synthesis.¹⁹⁵

Magnetic cobalt nanoparticles have also been prepared by a variety of methods. They have been prepared by the reduction of CoCl_2 in microemulsions stabilized by ionic surfactants,^{196,197} reducing CoCl_2 in amphiphilic block copolymer micelles,¹⁹⁸ and by reducing cobalt halides in a matrix of polystyrene with metal-complexing triphenylphosphine side chains.¹⁹⁹ Additionally, a novel cobalt precursor, $\text{Co}(\eta^3\text{-C}_8\text{H}_{13})(\eta^4\text{-C}_8\text{H}_{12})$, was reduced with hydrogen to form cobalt nanoparticles in a poly(vinylpyrrolidone) homopolymer solution.²⁰⁰ Superparamagnetic cobalt ferrite (CoFe_2O_4) nanoparticles have been synthesized by reacting FeCl_2 and cobalt acetate with sodium dodecyl sulfate surfactant to produce cobalt(II) and iron(II) dodecyl sulfate.²⁰¹ These micelles were subsequently mixed with aqueous methylamine to obtain the product.

Decompositions of organometallic reagents have been used for preparing magnetic nanoparticles. The first thermal decomposition method used for the synthesis of cobalt nanoparticles was reported in 1966 by Thomas.²⁰² The organometallic reagent was dicobalt octacarbonyl ($\text{Co}_2[\text{CO}]_8$) which thermally degrades and eliminates carbon monoxide gas to form metallic cobalt. Thomas prepared the cobalt nanoparticles in a poly(methylmethacrylate)-poly(ethylacrylate)-poly(vinylpyrrolidone) terpolymer solution to form a stable colloidal solution.²⁰³ The cobalt particle size distributions were narrow and sizes were varied from 2 to 30 nm in diameter by varying concentration, temperature, or polymer composition. Other polymer systems were also successfully employed as

¹⁹⁴ Rivas, J.; Lopez-Quintela, M. A.; Lopez-Perez, J. A.; Liz, L.; Duro, R. J. *IEEE Transactions on Magnetics* **1993**, *29*, 2655-2657.

¹⁹⁵ Gangopadhyay, S.; Hadjipanayis, G. C.; Dale, B.; Sorensen, C. M.; Klabunde, K. J.; Papaefthymiou, V.; Kostikas, A. *Phys. Rev. B: Condens. Matter* **1992**, *45*, 9778-9787.

¹⁹⁶ Chen, J. P.; Lee, K. M.; Sorensen, C. M.; Klabunde, K. J.; Hadjipanayis, G. C. *J. Appl. Phys.* **1994**, *75*, 5876-5878.

¹⁹⁷ Chen, J. P.; Sorensen, C. M.; Klabunde, K. J.; Hadjipanayis, G. C. *J. Appl. Phys.* **1994**, *76*, 6316-6318.

¹⁹⁸ Platonova, O. A.; Bronstein, L. M.; Solodovnikov, S. P.; Yanovskaya, I. M.; Obolonkova, E. S.; Valetsky, P. M.; Wenz, E.; Antonietti, M. *Colloid Polym. Sci.* **1997**, *275*, 426-431.

¹⁹⁹ Leslie-Pelecky, D. L.; Zhang, X. Q.; Rieke, R. D. *J. Appl. Phys.* **1996**, *79*, 5312-5314.

²⁰⁰ Osuna, J.; de Caro, D.; Amiens, C.; Chaudret, B.; Snoeck, E.; Respaud, M.; Broto, J. M.; Fert, A. *J. Phys. Chem.* **1996**, *100*, 14571-14574.

²⁰¹ Moumen, N.; Pileni, M. P. *Chem. Mater.* **1996**, *8*, 1128-1134.

²⁰² Thomas, J. R. *J. Appl. Phys.* **1966**, *37*, 2914-2915.

²⁰³ Thomas, J. R. *J. Appl. Phys.* **1966**, *37*, 2914-2915.

surfactants in 1966 for the thermal degradation process.²⁰⁴ More recent studies have investigated the mechanism by which the decomposition occurs.^{205,206}

Recent developments using well-defined amphiphilic block copolymer stabilizers have resulted in more sophisticated control over cobalt particle size. In the work of Antonietti and coworkers, polystyrene-*b*-4-vinyl pyridine) micelles were used as nanoreactors for thermally decomposing Co₂(CO)₈.²⁰⁷ Thermolyses were performed at 110 °C for one hour in toluene under an inert argon atmosphere. FTIR data indicated that the Co₂(CO)₈ formed ionic complexes with pyridine units prior to heating. This complexation promoted the localization of the cobalt within the core of the micelles. TEM images obtained indicated a mean particle diameter of 10 nm and a primarily spherical shape. A similar process was used by Riffle and coworkers for preparing polysiloxane magnetic fluids.²⁰⁸ Dicobalt octacarbonyl was thermally decomposed in the presence of a PDMS-*b*-poly(cyanopropylmethylsiloxane)-*b*-PDMS stabilizer in toluene. The cobalt particles were approximately 7 nm in diameter.

Smith and coworkers prepared iron nanoparticle dispersions by thermolysis of Fe(CO)₅ at 150 °C in the presence of functional block copolymers under an argon atmosphere.²⁰⁹ Several different block copolymers were used including poly(butadiene-*b*-styrene) (PBD-*b*-PS), poly(4-vinylpyridine-*b*-styrene), poly(phenylvinylketoxime-*b*-styrene), and poly(N-vinylpyrrolidinone-*b*-styrene). Depending on the polymer/solvent system used and the iron/polymer ratio, different particle sizes were prepared in the range of 1.5-20 nm in diameter.

Nickel nanoparticles were successfully synthesized by hydrogenating Ni(COD)₂ in a solution of dichloromethane and poly(vinylpyrrolidone) homopolymer.²¹⁰ This resulted in magnetic nickel particles in the size range of 20-30 nm in diameter.

²⁰⁴ Hess, P. H.; Parker, P. H. *J. Appl. Polym. Sci.* **1966**, *10*, 1915-1927.

²⁰⁵ Tannenbaum, R.; Flenniken, C. L.; Goldberg, E. P. *J. Polym. Sci., Part B: Polym. Phys.* **1990**, *28*, 2421-2433.

²⁰⁶ Tannenbaum, R. *Inorganica Chimica Acta* **1994**, *227*, 233-240.

²⁰⁷ Platonova, O. A.; Bronstein, L. M.; Solodovnikov, S. P.; Yanovskaya, I. M.; Obolonkova, E. S.; Valetsky, P. M.; Wenz, E.; Antonietti, M. *Colloid Polym. Sci.* **1997**, *275*, 426-431.

²⁰⁸ Stevenson, J. P.; Rutnakornpituk, M.; Vadala, M.; Esker, A. R.; Charles, S. W.; Wells, S.; Dailey, J. P.; Riffle, J. S. *Journal of Magnetism and Magnetic Materials* **2001**, *225*, 47-58.

²⁰⁹ Griffiths, C. H.; O'Horo, M. P.; Smith, T. W. *J. Apply* **1979**, *50*, 7108-7115.

²¹⁰ Ely, T. O.; Amiens, C.; Chaudret, B. *Chem. Mater.* **1999**, *11*, 526-529.

The use of energy generated via ultrasonication as a means of decomposing organometallic precursors to form metallic nanoparticles has been an interesting area of research. Sonochemical decomposition is caused by extremely high localized temperatures and pressures that are formed during a so-called “acoustic cavitation” process.²¹¹ The process of sonochemistry, or sonolysis, was pioneered by Suslick^{212,213} and has been used to decompose Fe(CO)₅ to iron nanoparticles.^{214,215,216,217,218} Ultrasonic energy has also been used successfully in the synthesis of cobalt nanoparticles from Co(NO)(CO)₃,²¹⁹ nickel nanoparticles from Ni(CO)₄,²²⁰ iron-nickel alloy nanoparticles from mixtures of Fe(CO)₅ and Ni(CO)₄,²²¹ and CoFe₂O₄ nanoparticles from solutions of Fe(CO)₅ and Co(NO)(CO)₃.²²²

The magnetic transition metals (iron, cobalt, and nickel) have higher magnetizations compared to the magnetic iron oxides. However, the metals are highly susceptible to oxidation, especially in the nano- size range because of the large exposed surface areas. One disadvantage to using iron, cobalt, or nickel nanoparticles for magnetic applications is that the magnetization of these metals decreases as the surfaces oxidize upon exposure to atmospheric oxygen. Iron nanoparticles, for example, undergo surface oxidation and concurrent loss of magnetization upon exposure to atmospheric oxygen.²²³ Loss of magnetization was found to be dependent upon particle size, with the smaller particles (6 nm diameter) being more susceptible and oxidizing faster than larger

²¹¹ Suslick, K. S. In *Ultrasound: Its Chemical, Physical, and Biological Effects*; Suslick, K. S., Ed.; VCH Publishers: New York, 1988; pp 123-163.

²¹² Suslick, K. S. In *Ultrasound: Its Chemical, Physical, and Biological Effects*; Suslick, K. S., Ed.; VCH Publishers: New York, 1988; pp 123-163.

²¹³ McNamara, W. B.; Didenko, Y. T.; Suslick, K. S. *Nature* **1999**, *401*, 772-775.

²¹⁴ Suslick, K. S.; Fang, M.; Hyeon, T. *J. Am. Chem. Soc.* **1996**, *118*, 11960-11961.

²¹⁵ Suslick, K. S.; Choe, S. B.; Cichowlas, A. A.; Grinstaff, M. W. *Nature* **1991**, *353*, 414-416.

²¹⁶ Suslick, K. S.; Goodale, J. W.; Schubert, P. F.; Wang, H. H. *J. Am. Chem. Soc.* **1983**, *105*, 5781-5785.

²¹⁷ Cao, X.; Koltypin, Y.; Kataby, G.; Prozorov, R.; Gedanken, A. *J. Mater. Res.* **1995**, *10*, 2952-2957.

²¹⁸ Wizel, S.; Prozorov, R.; Cohen, Y.; Aurbach, D.; Margel, S.; Gedanken, A. *J. Mater. Res.* **1998**, *13*, 211-216.

²¹⁹ Shafi, K. V. P. M.; Gedanken, A.; Prozorov, R. *Adv. Mater.* **1998**, *10*, 590-593.

²²⁰ Ramesh, S.; Koltypin, Y.; Prozorov, R.; Gedanken, A. *Chem. Mater.* **1997**, *9*, 546-551.

²²¹ Shafi, K. V. P. M.; Gedanken, A.; Goldfarb, R. B.; Felner, I. *J. Appl. Phys.* **1997**, *81*, 6901-6905.

²²² Shafi, K. V. P. M.; Gedanken, A.; Prozorov, R.; Balogh, J. *Chem. Mater.* **1998**, *10*, 3445-3450.

²²³ Griffiths, C. H.; O'Horo, M. P.; Smith, T. W. *J. Apply* **1979**, *50*, 7108-7115.

particles (16 nm).²²⁴ A core-shell structure has been proposed in which an iron oxide shell approximately 1-2 nm in diameter forms around the iron core.²²⁵

1.4.3 Synthesis of Magnetite Nanoparticles

Magnetite is a ferrimagnetic iron oxide, Fe₃O₄, with an inverse spinel crystalline structure in which part of the iron atoms are octahedrally coordinated to oxygen and the rest are tetrahedrally coordinated to oxygen.²²⁶ The major advantage to using magnetite for magnetic applications is that it is much less susceptible to oxidation and loss of magnetization. One potential disadvantage to magnetite is that it has a lower specific saturation magnetization compared to the magnetic transition metals.

There are numerous methods for the synthesis of magnetite particles. One of the first methods dates back to 1852.²²⁷ The synthesis involves the treatment of an aqueous solution of Fe(III) and Fe(II) in a 2:1 ratio with a hydroxide base.^{228,229} This reaction is known as the chemical co-precipitation method. Elmore reported a method for preparing stabilized magnetite colloids in 1938.²³⁰ In this method, FeCl₂·4H₂O and FeCl₃·6H₂O were dissolved in water and an aqueous NaOH solution was added with stirring. The precipitate was rinsed with water and 0.01 N HCl and then boiled in a soap solution to stabilize the colloidal particles. Few details were given regarding reaction time, temperature, or particle size and shape. Nine different synthetic methods for the preparation of magnetite are outlined in the comprehensive book on iron oxides by Cornell and Schwertmann.²³¹ Other more recent methods include ultrasonication of iron(II) acetate in water²³² and reduction of goethite (α-FeOOH) from glycol/water

²²⁴ Griffiths, C. H.; O'Horo, M. P.; Smith, T. W. *J. Apply* **1979**, *50*, 7108-7115.

²²⁵ Gangopadhyay, S.; Hadjipanayis, G. C.; Dale, B.; Sorensen, C. M.; Klabunde, K. J.; Papaefthymiou, V.; Kostikas, A. *Phys. Rev. B: Condens. Matter* **1992**, *45*, 9778-9787.

²²⁶ Cornell, R. M.; Schwertmann, U. *The Iron Oxides*; VCH: New York, 1996.

²²⁷ LeFort, J. C. *R. Acad. Sci. Paris* **1852**, *34*, 480.

²²⁸ Welo, L. A.; Baudish, O. *Phil. Mag.* **1925**, *50*, 399-408.

²²⁹ Schwertmann, U.; Cornell, R. M. *Iron Oxides in the Laboratory*; VCH: New York, 1991.

²³⁰ Elmore, W. C. *Phys. Rev.* **1938**, *54*, 309-310.

²³¹ Cornell, R. M.; Schwertmann, U. *The Iron Oxides*; VCH: New York, 1996.

²³² Vijayakumar, R.; Kolytyn, Y.; Felner, I.; Gedanken, A. *Materials Science and Engineering* **2000**, *A286*, 101-105.

solutions at elevated temperatures and pressures, with subsequent controlled crystallization processes.²³³

1.4.4 Surface Properties of Magnetite Nanoparticles

At a neutral pH, the surface of magnetite primarily consists of hydroxyl groups.²³⁴ The surface chemistry of magnetite can be altered by adjusting the pH of the medium.^{235,236} At low pH, surface hydroxyl groups become protonated and at high pH the hydroxyl groups are deprotonated (Figure 1-7). The positive or negative surface charges at any particular pH are balanced by counterions to maintain electro-neutrality, resulting in an electrostatic double layer.²³⁷ The double layer of surface charge promotes the repulsion of colloidal magnetite particles (Figure 1-8). The electrostatic double layer repulsive force results from decreased entropy of the counterion distribution as two surfaces approach each other.^{238,239} The isoelectric point of magnetite is pH 6.8.²⁴⁰ This is the pH at which an equal number of positive and negative surface charges co-exist. At the isoelectric point, there is no electrostatic double layer, no double layer repulsive forces, and so particles begin to aggregate. It is for this reason that surfactants that stabilize via a steric mechanism are valuable for preparing stable nanomagnetite fluids at neutral pH.

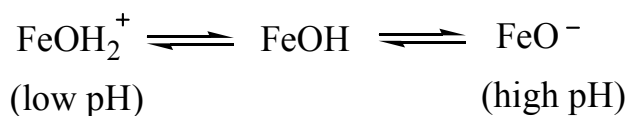


Figure 1-7. Surface chemistry of magnetite as a function of pH.

²³³ Han, K. S.; Bae, D. S.; Noh, J. S.; Choi, S. H.; Cho, S. B. In *US Pat. 6,203,774 B1*; Korea Institute of Science and Technology: United States, 2001.

²³⁴ Cornell, R. M.; Schwertmann, U. *The Iron Oxides*; VCH: New York, 1996.

²³⁵ Massart, R. *IEEE Trans. Magn.* **1981**, *17*, 1247.

²³⁶ Cornell, R. M.; Schwertmann, U. *The Iron Oxides*; VCH: New York, 1996.

²³⁷ Cornell, R. M.; Schwertmann, U. *The Iron Oxides*; VCH: New York, 1996.

²³⁸ Evans, D. F.; Wennerstrom, H. *The Colloidal Domain*; 2nd ed.; Wiley-VCH: New York, 1999.

²³⁹ Israelachvili, J. *Intermolecular and Surface Forces*; 2nd ed.; Academic Press: New York, 1992.

²⁴⁰ Tewari, P. H.; McLean, A. W. *J. Colloid Interface Sci.* **1972**, *40*, 267.

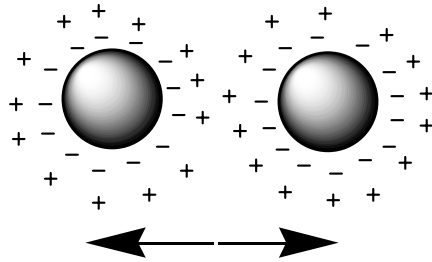


Figure 1-8. Electrostatic double layer causing repulsive forces between particles.

It is known that organic ligands (carboxylic acids) and inorganic ligands (phosphates) bind to the surface of iron oxides.²⁴¹ This has been exploited for preparing stable dispersions of magnetite nanoparticles. Oleic acid is a common stabilizer used to prepare magnetite dispersions in hydrocarbon fluids.²⁴² The chemical structure of the magnetite-carboxylate bond has been investigated by Massart and coworkers using magnetite coated with oleic acid. Based on FTIR spectrometry results, the researchers concluded that carboxylic acids bind to magnetite in a chelating bidentate configuration (Figure 1-9).²⁴³

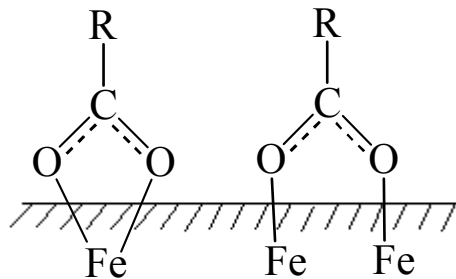


Figure 1-9. Bidentate chelation of carboxylic acid on magnetite surface.

²⁴¹ Cornell, R. M.; Schwertmann, U. *The Iron Oxides*; VCH: New York, 1996.

²⁴² Lesnikovich, A. I.; Shunkevich, T. M.; Naumenko, V. N.; Vorobyova, S. A.; Baykov, M. V. *J. Magn. Mater.* **1990**, *85*, 14-16.

²⁴³ Rocchiccioli-Deltcheff, C.; Franck, R.; Cabuil, V.; Massart, R. *Journal of Chemical Research, Synopses* **1987**, *5*, 126-127.

1.4.5 Magnetite-Polymer Complexes and Dispersions

To successfully prepare stable magnetite dispersions, any attractive forces between the nanoparticles must be overcome. This can be achieved with polymeric surfactants in which a functionalized portion of the polymer binds to the particle surface and the remaining part of the polymer is solvated by the dispersion medium, or carrier fluid. Particle aggregation is prevented by a repulsive entropic force that results when particles approach each other and the polymer chains on the surface begin to lose their conformational entropy. This process is known as entropic, or steric, stabilization. Homopolymers, block copolymers, or terminally functionalized polymers are useful for this application.

Appropriately functionalized water-soluble stabilizers must be used to prepare aqueous magnetite fluids. The most commonly utilized functional group for binding to magnetite is the carboxylic acid. For example, poly(meth)acrylic acids have been used recently for binding to magnetite surface.^{244,245,246,247} A convenient method was developed wherein magnetite, which had been freshly prepared by chemical coprecipitation, was sonicated in a solution of poly(methacrylic acid). Stable fluids were achieved.²⁴⁸

In another study, magnetite particles are used as “seeds” for the free radical polymerization of methacrylic acid (MAA) and hydroxyethyl methacrylate (HEMA).²⁴⁹ A 1 wt% solution of magnetite particles in ethyl acetate was mixed with monomers, crosslinker, and AIBN initiator and reacted at 65 °C for eight hours. Magnetic polymer particles were formed with hydrodynamic radii ranging from 150-200 nm, and these formed stable colloids in neutral aqueous solutions.

²⁴⁴ Mendenhall, G. D.; Geng, Y.; Hwang, J. *Journal of Colloid and Interface Science* **1996**, *184*, 519-526.

²⁴⁵ Zaitsev, V. S.; Filimonov, D. S.; Presnyakov, I. A.; Gambino, R. J.; Chu, B. *J. Colloid Interface Sci.* **1999**, *212*, 49-57.

²⁴⁶ Moeser, G. D.; Roach, K. A.; Green, W. H.; Laibinis, P. E.; Hatton, T. A. *Ind. Eng. Chem. Res.* **2002**, *41*, 4739-4749.

²⁴⁷ Wormuth, K. *Journal of Colloid and Interface Science* **2001**, *241*, 366-377.

²⁴⁸ Mendenhall, G. D.; Geng, Y.; Hwang, J. *Journal of Colloid and Interface Science* **1996**, *184*, 519-526.

²⁴⁹ Zaitsev, V. S.; Filimonov, D. S.; Presnyakov, I. A.; Gambino, R. J.; Chu, B. *J. Colloid Interface Sci.* **1999**, *212*, 49-57.

Block copolymers containing poly(meth)acrylic acid sequences have also been used for magnetite stabilization. Magnetite was prepared by chemical co-precipitation at 60 °C in the presence of poly(ethylene oxide-*b*-methacrylic acid) (PEO-*b*-PMAA) with a 3000 g mol⁻¹ PEO block and 700 g mol⁻¹ PMAA block, yielding a stable suspension. The coated magnetic particles were subsequently dispersed in a mixture of MAA and HEMA, emulsified into decane, and free radically polymerized to yield magnetic latex particles.²⁵⁰ Grafted block terpolymers comprised of PEO and poly(propylene oxide) grafted onto a poly(acrylic acid) backbone were used to prepare aqueous magnetite fluids. Magnetite was prepared by chemical co-precipitation in the presence of the terpolymer that contained approximately 84% of unreacted carboxylic acid groups. This process resulted in water-dispersible magnetic particles coated with an outer hydrophilic PEO shell and an inner hydrophobic PPO core that were suitable for organic extraction applications.²⁵¹

Carboxylic acid-functionalized polymers prepared without poly(meth)acrylic acids have been used to prepare aqueous magnetite fluids. Carboxylic acid-containing polyurethane central blocks were incorporated into PEO by the reaction of hydroxyl-terminated PEO with isophorone diisocyanate and bis(hydroxymethyl)propionic acid using a dibutyltin dilaurate catalyst in dimethylformamide.^{252,253} These reactions resulted in the formation of PEO-*b*-polyurethane(COOH)-*b*-PEO triblock copolymers. Magnetite nanoparticles were prepared by chemical co-precipitation and were subsequently reacted with a solution of the triblock copolymer in dichloromethane for thirty minutes. The dichloromethane was removed by evaporation aided by a strong flow of nitrogen, resulting in stable aqueous dispersions of magnetite.

Aqueous magnetite dispersions have also been prepared by chemical co-precipitation of magnetite in the presence of dextran,²⁵⁴ polyvinyl alcohol,²⁵⁵ and

²⁵⁰ Wormuth, K. *Journal of Colloid and Interface Science* **2001**, *241*, 366-377.

²⁵¹ Moeser, G. D.; Roach, K. A.; Green, W. H.; Laibinis, P. E.; Hatton, T. A. *Ind. Eng. Chem. Res.* **2002**, *41*, 4739-4749.

²⁵² Harris, L. A.; Goff, J. D.; Carmichael, A. Y.; Riffle, J. S.; Harburn, J. J.; St. Pierre, T. G.; Saunders, M. *Chemistry of Materials* **2003**, *15*, 1367-1377.

²⁵³ Harris, L. A. In *Ph. D. Thesis, Chemistry Department*; Virginia Tech: Blacksburg, 2002.

²⁵⁴ Pardoe, H.; Chua-anusorn, W.; St. Pierre, T. G.; Dobson, J. J. *Magn. Mater.* **2001**, *225*, 41-46.

²⁵⁵ Pardoe, H.; Chua-anusorn, W.; St. Pierre, T. G.; Dobson, J. J. *Magn. Mater.* **2001**, *225*, 41-46.

polyoxyalkylene diphosphonates,²⁵⁶ and by the reaction of magnetite with alkoxy silane-terminated poly(ethylene glycol).²⁵⁷

The synthesis of stable, hydrophobic, magnetite fluids has not been investigated as thoroughly as aqueous magnetite fluids. Most of the work has involved oleic acid as a stabilizing surfactant,^{258,259,260,261,262} but there have also been investigations with alkyl phosphonate surfactants.²⁶³ Oleic acid is an eighteen carbon surfactant chain with one terminal carboxylic acid group and is a suitable surfactant for preparing hydrocarbon-based magnetite fluids. Interestingly, stearic acid does not stabilize magnetite particles despite the fact that it is a similar eighteen-carbon surfactant. The difference between the two surfactants is that oleic acid contains a cis double bond that forms kinks whereas stearic acid contains no kinks. Researchers have concluded that the kink in oleic acid allows the eighteen-carbon chain to be better solubilized by hydrocarbon solvents, resulting in stable colloids.²⁶⁴

There are some examples in non-English patents and journals of polysiloxane-based magnetite fluids.^{265,266,267} According to translated summaries of these reports, the magnetite particles were stabilized in polysiloxane fluids using stabilizers such as oleic acid,²⁶⁸ anionic surfactants,²⁶⁹ or silane coupling agents.²⁷⁰ A European patent describes the use of a two-component surfactant system for stabilizing magnetite nanoparticles in

²⁵⁶ Dumazet-Bonnamour, I.; Le Perche, P. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2000**, *173*, 61-71.

²⁵⁷ Zhang, Y.; Kohler, N.; Zhang, M. *Biomaterials* **2002**, *23*, 1553-1561.

²⁵⁸ Miyazaki, M.; Yamamoto, K.; Nagayoshi, T.; Nishimura, M. In *Jap. Pat. JP51013995*; Matsumoto Yushi-Seiyaku Co., Ltd.: Japan, 1976; p 3.

²⁵⁹ Berkowitz, A. E.; Lahut, J. A.; VanBuren, C. E. *IEEE Trans. Magn.* **1980**, *16*, 184-190.

²⁶⁰ Tadmor, R.; Rosensweig, R. E.; Frey, J.; Klein, J. *Langmuir* **2000**, *16*, 9117-9120.

²⁶¹ Sahoo, Y.; Pizem, H.; Fried, T.; Golodnitsky, D.; Burstein, L.; Sukenik, C. N.; Markovich, G. *Langmuir* **2001**, *17*, 7907-7911.

²⁶² Rosensweig, R. E.; Nestor, J. W.; Timmins, R. S. *Materials Association for Direct Energy Conversion, Proc. Symp.* **1965**, *5*, 133-137.

²⁶³ Sahoo, Y.; Pizem, H.; Fried, T.; Golodnitsky, D.; Burstein, L.; Sukenik, C. N.; Markovich, G. *Langmuir* **2001**, *17*, 7907-7911.

²⁶⁴ Tadmor, R.; Rosensweig, R. E.; Frey, J.; Klein, J. *Langmuir* **2000**, *16*, 9117-9120.

²⁶⁵ Fujita, T.; Ito, R.; Kuzuno, E.; Kawada, K. *Funtai oyobi Funmatsu Yakin* **1996**, *43*, 757-760.

²⁶⁶ Grabovskii, Y. P.; Sokolenko, V. F.; Filippova, T. P. In *Russian pat. SU1090662*; All-Union Scientific-Research Institute for Gas Processing: U.S.S.R., 1984.

²⁶⁷ Yabe, S.; Yokochi, A. In *Jap. Pat. JP04108898*; Nippon Seiko K. K.: Japan, 1992.

²⁶⁸ Grabovskii, Y. P.; Sokolenko, V. F.; Filippova, T. P. In *Russian pat. SU1090662*; All-Union Scientific-Research Institute for Gas Processing: U.S.S.R., 1984.

²⁶⁹ Fujita, T.; Ito, R.; Kuzuno, E.; Kawada, K. *Funtai oyobi Funmatsu Yakin* **1996**, *43*, 757-760.

²⁷⁰ Yabe, S.; Yokochi, A. In *Jap. Pat. JP04108898*; Nippon Seiko K. K.: Japan, 1992.

polysiloxane carrier fluids.²⁷¹ In this system, the magnetite particles are first stabilized in a volatile solvent using a hydrocarbon stabilizer such as oleic acid. In the second step, a polysiloxane carrier fluid containing a functionalized polysiloxane stabilizer is added to the magnetic fluid at 50-60 °C with stirring. The volatile solvent was evaporated during this process, leaving behind a stable polysiloxane-based magnetite fluid.

²⁷¹ Raj, K.; Rosenzweig, R. E.; Aziz, L. M. In *Eur. Patent No. 0,859,379*, 1998.

2 Chapter 2. Poly(dimethylsiloxane)-Magnetite Nanoparticle Complexes and Dispersions

2.1 Introduction

Magnetic silicone fluids are comprised of magnetic nanoparticles sterically stabilized in a polydimethylsiloxane (PDMS) carrier fluid and may potentially be used for the treatment of retinal detachment.²⁷² There are at least three major obstacles that must be overcome to achieve magnetic fluids suitable for biomedical applications. The magnetic nanoparticles must be stable against oxidation so that the oxygen-rich environment of the body will not affect their magnetization. Magnetic transition metals (iron, cobalt, nickel) oxidize readily, whereas iron oxides such as magnetite (Fe_3O_4) are much more stable against oxidation. For this reason, magnetite may be a more appropriate magnetic material for biomedical applications. Materials that will disperse the magnetic nanoparticles in the PDMS carrier fluid and prevent particle aggregation are needed. These materials are typically polymers containing two segments: a functionalized segment that adheres to the nanoparticle surface and a nonpolar segment that extends into the PDMS fluid and prevents particle aggregation by steric repulsion. The magnetic fluids must be purified to avoid toxicity.

Most of the literature on magnetite stabilization involves the preparation of aqueous dispersions. Homopolymer stabilizers such as poly(methacrylic acid),²⁷³ dextran,²⁷⁴ poly(vinyl alcohol),²⁷⁵ carboxylic acid-functionalized poly(ethylene oxide),²⁷⁶ and sodium polyoxyalkylene diphosphonates,²⁷⁷ block copolymer stabilizers such as

²⁷² Dailey, J. P.; Phillips, J. P.; Riffle, J. S. *Journal of Magnetism and Magnetic Materials* **1999**, *194*, 140-148.

²⁷³ Mendenhall, G. D.; Geng, Y.; Hwang, J. *Journal of Colloid and Interface Science* **1996**, *184*, 519-526.

²⁷⁴ Pardoe, H.; Chua-anusorn, W.; St. Pierre, T. G.; Dobson, J. *J. Magn. Magn. Mater.* **2001**, *225*, 41-46.

²⁷⁵ Pardoe, H.; Chua-anusorn, W.; St. Pierre, T. G.; Dobson, J. *J. Magn. Magn. Mater.* **2001**, *225*, 41-46.

²⁷⁶ Harris, L. A.; Goff, J. D.; Carmichael, A. Y.; Riffle, J. S.; Harburn, J. J.; St. Pierre, T. G.; Saunders, M. *Chemistry of Materials* **2003**, *15*, 1367-1377.

²⁷⁷ Dumazet-Bonnamour, I.; Le Perche, P. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2000**, *173*, 61-71.

poly(ethylene oxide-*b*-methacrylic acid),²⁷⁸ and graft copolymers such as poly(alkylene oxide-*g*-acrylic acid)²⁷⁹ have been used to prepare aqueous magnetite dispersions. The preparation of magnetite dispersions in nonpolar fluids typically uses oleic acid as a stabilizer.^{280,281,282} Nonpolar magnetic silicone fluids containing cobalt nanoparticles have been prepared by the thermolysis of dicobalt octacarbonyl in the presence of PDMS-*b*-(3-cyanopropyl)methylsiloxane-*b*-PDMS.²⁸³ Magnetic silicone fluids containing magnetite nanoparticles have been previously prepared using a polysiloxane surfactant²⁸⁴ or a two-surfactant system in which the first was oleic acid and the second was a functionalized polysiloxane.²⁸⁵

The focus of this research was to prepare stable magnetic silicone fluids. The fluids were prepared by first complexing magnetite nanoparticles with carboxylic acid-functionalized PDMS stabilizers and then dispersing the PDMS-magnetite complexes in low molecular weight silicone fluids. By combining the oxidative stability of magnetite and the biocompatibility of PDMS, it is anticipated that these fluids will be suitable for biomedical applications.

2.2 Experimental

2.2.1 Materials

Hexamethylcyclotrisiloxane (Gelest, D₃) was dried over calcium hydride and sublimed under vacuum into pre-weighed, flame-dried round bottom flasks, each containing a magnetic stirbar. The flasks were purged with nitrogen and weighed again to determine the exact amount of D₃ in each flask. *N*-Butyllithium was generously donated by FMC as a solution in hexane (2.43 M) and was titrated with diphenylacetic

²⁷⁸ Wormuth, K. *Journal of Colloid and Interface Science* **2001**, *241*, 366-377.

²⁷⁹ Moeser, G. D.; Roach, K. A.; Green, W. H.; Laibinis, P. E.; Hatton, T. A. *Ind. Eng. Chem. Res.* **2002**, *41*, 4739-4749.

²⁸⁰ Rocchiccioli-Deltcheff, C.; Franck, R.; Cabuil, V.; Massart, R. *Journal of Chemical Research, Synopses* **1987**, *5*, 126-127.

²⁸¹ Raj, K.; Rosenzweig, R. E.; Aziz, L. M. In *Eur. Patent No. 0,859,379*, 1998.

²⁸² Sahoo, Y.; Pizem, H.; Fried, T.; Golodnitsky, D.; Burstein, L.; Sukenik, C. N.; Markovich, G. *Langmuir* **2001**, *17*, 7907-7911.

²⁸³ Rutnakornpituk, M.; Thompson, M. S.; Harris, L. A.; Farmer, K. E.; Esker, A. R.; Riffle, J. S.; Connolly, J.; St. Pierre, T. G. *Polymer* **2002**, *43*, 2337-2348.

²⁸⁴ Chagnon, M. S. In *US 4,356,098*; Ferrofluidics Corporation: United States, 1982.

²⁸⁵ Raj, K.; Rosenzweig, R. E.; Aziz, L. M. In *Eur. Patent No. 0,859,379*, 1998.

acid prior to use.²⁸⁶ Cyclohexane (EM Science, 99%) was stirred with concentrated sulfuric acid for one week, washed with deionized water until neutral, stirred over calcium hydride, distilled, stored over sodium under a nitrogen atmosphere, and distilled prior to use. Tetrahydrofuran (EM Science, 99.5%) was dried over calcium hydride, distilled, stored as a purple sodium/benzophenone dispersion under a nitrogen atmosphere, and distilled prior to use. Trivinylchlorosilane (Gelest) was distilled under reduced pressure prior to use. Toluene (Burdick & Jackson, 99.9%) was distilled from calcium hydride and deoxygenated by sparging with dry nitrogen prior to use. Ethyl acetate (Mallinckrodt, 99.9%) was deoxygenated by sparging with dry nitrogen prior to use. Ammonium hydroxide (Alfa Aesar, 50% v/v aqueous) was used as received. A 25 % by volume solution of aqueous HCl was prepared, for example, by adding 5 mL concentrated HCl (EM Science) to 15 mL deionized water in a graduated cylinder. Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), both from Aldrich, were stored under nitrogen in a desiccator and used as received. Mercaptoacetic acid (97%), mercaptosuccinic acid (97%), and 2,2'-azobisisobutyronitrile (AIBN, 98%) were all used as received from Aldrich.

2.2.2 Synthesis of Trivinylsilyl-Terminated PDMS

An exemplary procedure to prepare a 2100 g mol^{-1} PDMS oligomer with a trivinylsilyl group on one end is provided. The reaction was performed in a rigorously cleaned, flame-dried, nitrogen-purged round bottom flask containing a magnetic stirbar and enclosed with a rubber septum bound with copper wire. Cyclohexane (42 mL) was added via syringe to the flask containing the D₃ monomer (41.42 g) and the monomer was dissolved at room temperature. Next, *n*-butyllithium (7 mL, 18.8 mmol) was added via syringe. This solution was stirred for approximately one hour followed by the addition of THF (58 mL). The progress of the reaction was monitored by ¹H NMR. At 96% conversion of the monomer, the reaction was terminated with excess trivinylchlorosilane (4.4 mL, 28.2 mmol) and stirred overnight. The polymer solution was filtered and then concentrated by evaporating most of the solvent under reduced

²⁸⁶ Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879-1880.

pressure. The concentrated polymer solution was precipitated into methanol, stirred for 90 minutes, and washed a second time with methanol for 30-90 minutes. The PDMS was separated from the methanol in a separatory funnel, diluted with chloroform, and washed three times with deionized water. Finally, chloroform and any other residual solvents were removed by drying under reduced pressure at 80 °C for several hours. The products were clear, colorless liquids.

2.2.3 Thiol-ene Addition of Mercaptoacetic Acid to the Trivinylsilyl End group

These reactions were performed in either ethyl acetate or toluene. The 2350, 4270, and 7290 g mol⁻¹ trivinylsilyl-terminated polymers were functionalized in ethyl acetate according to the following representative procedure. The 2350 g mol⁻¹ PDMS (20 g, 8.5 mmol) was weighed into a round bottom flask equipped with a magnetic stirbar. Ethyl acetate (13 mL) was added via syringe and the solution was bubbled with dry nitrogen. AIBN (67.7 mg, 0.41 mmol) was added and the flask was purged with nitrogen. Mercaptoacetic acid (2.1 mL, 30.2 mmol) was added via syringe and the reaction flask was placed in an oil bath at 55 °C. The reactions were monitored via ¹H NMR by following the disappearance of the peaks corresponding to the vinyl protons. The solvent was removed under vacuum and the concentrated polymer solution was precipitated into water. The polymer was dissolved in chloroform and washed with water three times. Sodium chloride was added to break up emulsions formed during the washing process. The solutions were concentrated and filtered to remove salts. The remaining solvent was removed under reduced pressure at 60 °C.

The 1270 g mol⁻¹ trivinylsilyl-terminated PDMS was functionalized by the thiol-ene addition reaction in toluene. The 1270 g mol⁻¹ PDMS (20.0 g, 16 mmol) was added to a clean, nitrogen-purged round bottom flask equipped with a magnetic stirbar. Toluene (200 mL) was added via syringe. The polymer solution was bubbled with dry nitrogen to remove oxygen. AIBN (0.125 g, 0.76 mmol) and mercaptoacetic acid (10.6 mL, 0.152 mol) were added to the flask. The reaction was stirred at 80 °C for 45 minutes.

The polymer was purified by removing the toluene under reduced pressure at 30 °C. The polymer was dissolved in methanol and stirred 30 minutes. Water was added and the polymer coagulated. The polymer was collected and the dissolution/coagulation process was repeated. The polymer was collected, dissolved in methanol, and dried over magnesium sulfate. The solution was filtered once by vacuum filtration and twice through syringes equipped with 0.1 µm Whatman Anotop 25 mm filters. The polymer was dried under reduced pressure at 35 °C.

2.2.4 Thiol-ene Addition of Mercaptosuccinic Acid to the Trivinylsilyl End Group

These reactions were performed in ethyl acetate due to the insolubility of mercaptosuccinic acid in toluene. In a representative example, mercaptosuccinic acid (2.07 g, 13.8 mmol) was weighed into a round bottom flask containing a magnetic stirbar and ethyl acetate (29 mL) was added. Next, trivinylsilyl-terminated 2350 g mol⁻¹ PDMS (10 g, 4.3 mmol) was weighed into the flask. AIBN (70 mg, 0.4 mmol) was weighed separately and added to the solution. The flask was covered with a rubber septum and purged with dry nitrogen. The reaction was stirred in a 55 °C oil bath for 15 hours and conversion of the vinyls was monitored by ¹H NMR. The polymers were purified as described previously for the thiol-ene addition reactions performed in ethyl acetate.

2.2.5 Studies to Determine the Effect of Acidic Conditions on PDMS Molecular Weight Distribution

Two reaction conditions were modeled using 1270 g mol⁻¹ PDMS. PDMS (0.5 g), ethyl acetate (5 mL), and mercaptoacetic acid (0.28 mL) were added to a round bottom flask and stirred at 65 °C for 3.5 hours. In the second set of conditions, PDMS (0.5 g), toluene (5 mL), and mercaptoacetic acid (0.28 mL) were added to a round bottom flask and stirred at 80 °C for 45 minutes.

2.2.6 Preparation of PDMS-Magnetite Nanoparticle Complexes

A representative example for the preparation of a PDMS-nanomagnetite complex charged with 30 wt% magnetite is described. The magnetite (theoretically 0.86 g) was prepared by a chemical co-precipitation reaction. The iron chloride salts, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (2.0 g) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.736 g), were each dissolved separately in 20 mL of deoxygenated water and then combined in a 2-necked round bottom flask purged with dry nitrogen and equipped with a rubber septum and mechanical stirrer. The aqueous solution was vigorously stirred while adding ammonium hydroxide (~20 mL) until the solution reached pH 9-10. After 15-30 minutes, a solution containing the PDMS stabilizer (2.0 g) in dichloromethane (60 mL) was added to the aqueous solution. The two phases were vigorously stirred for 15-30 minutes. While stirring, aqueous HCl was added dropwise until the solution became slightly acidic (pH ~3) as determined with pH paper. The PDMS-nanomagnetite complexes were separated from the emulsion by evaporating the dichloromethane under reduced pressure using a rotary evaporator. If there existed any uncomplexed nanomagnetite, this remained in the aqueous phase while PDMS-nanomagnetite complexes congealed into a hydrophobic phase. The solid-rubbery, black, PDMS-nanomagnetite complex was washed with water once, washed with methanol twice, and collected with a permanent magnet. The complex was dissolved in chloroform and centrifuged until no significant amount of magnetite precipitated from the dispersion. The chloroform was removed under vacuum and the complex was washed three times with methanol, several times with water, and dried under reduced pressure at ~40 °C.

2.2.7 Preparation of Magnetic Poly(dimethylsiloxane) Fluids

An aliquot of 20,200 g mol^{-1} PDMS (0.5 g) was dissolved in chloroform (~20 mL) in a vial. The PDMS was synthesized by the living polymerization of D_3 using *n*-butyllithium as the initiator and was terminated with trimethylchlorosilane. A PDMS-nanomagnetite complex (0.5 g) containing a 1200 g mol^{-1} mercaptoacetic acid-functionalized PDMS stabilizer and 52 wt% magnetite nanoparticles was added to the

PDMS solution. The solution was ultrasonicated in intervals of two seconds for a total of approximately 20 seconds. The chloroform was removed under reduced pressure in a rotary evaporator. The dispersion was washed with methanol three times and then washed with water four times by mixing thoroughly with a spatula and collecting the dispersion with a magnet. The product, a magnetic fluid containing 50 wt% PDMS-magnetite complex, was dried under vacuum at 45 °C.

2.2.8 Rheometric Studies of Magnetic Fluids

A series of magnetic fluids were prepared in which the molecular weight of the carrier fluid (5140, 12,300, and 20,200 g mol⁻¹) and the concentration of PDMS-magnetite complex (10, 30, and 50 wt%) were varied. Magnetic fluids were prepared using these compositions according to the procedure described in the previous section.

2.2.9 Instrumentation

¹H NMR and ²⁹Si NMR spectra were obtained from a Varian Unity 400 NMR instrument operating at 400 and 80 MHz, respectively, using chloroform-*d* as the solvent. Quantitative ²⁹Si NMR analyses were obtained using inverse gated decoupling, approximately 500 scans, and chromium (III) acetylacetonate shift reagent to reduce the relaxation time. Polymer molecular weights and polydispersities were determined using a Waters 2690 GPC instrument equipped with Styragel columns HR-1, HR-2, HR-3 and HR-4, a viscosity detector (Viscotek model T60A) and an external refractive index concentration detector. Samples were run using chloroform as the solvent and a flow rate of 1 mL min⁻¹. TEM images of PDMS-magnetite complexes and dispersions were obtained using a Philips 420T transmission electron microscope with an accelerating voltage of 100 kV. The magnetite complexes and dispersions were diluted with toluene until a light brown color was achieved. A few drops of each were deposited onto carbon-coated copper grids (SPI Supplies, West Chester, PA) and the grids were allowed to air-dry. Vibrating sample magnetometry was performed using a LakeShore model 7300 magnetometer. The applied field was ramped from +8000 to -8000 Gauss and the

saturation magnetizations of the samples were recorded. Elemental analysis was performed by Desert Analytics Laboratory (Tucson, AZ) by treating the samples with hot concentrated nitric acid followed by concentrated perchloric acid until complete dissolution was achieved. The sample solution was analyzed by inductively coupled plasma (ICP) to determine the percent iron. The percent iron was calculated from sample response relative to standards and blanks. Viscosities of the magnetic dispersions were determined using a Brookfield Rheometer model DVIII with coaxial cylinder geometry operating at 20 rpm. Sample sizes ranged from 4-6 mL and values were reported in a temperature range from 22-50 °C. The samples were equilibrated at a given temperature for five minutes prior to recording the viscosity. FTIR spectra were obtained using a Nicolet Impact 400 instrument and OMNIC 3.1a software. Each sample was analyzed with thirty-two scans.

2.3 Results and Discussion

2.3.1 PDMS Stabilizer Synthesis

The living anionic ring opening polymerization of D_3 has been well documented.^{287,288,289,290,291,292,293} This technique was used to synthesize a series of trivinylsilyl-terminated poly(dimethylsiloxane)s in a range of molecular weights. The polymerizations were monitored using 1H NMR by following the disappearance of the D_3 methyl peak at 0.15 ppm and appearance of the methyl protons on the polymer repeat units at 0.05 ppm (Figure 2-1). The polymerizations were terminated with trivinylchlorosilane prior to 100% conversion to avoid backbiting reactions that may occur upon depletion of the monomer. When the terminating reagent was added, white

²⁸⁷ McGrath, J. E. In *Block Copolymers*; Meier, D. J., Ed.; MMI Press: New York, 1983; Vol. 3, pp 1-16.

²⁸⁸ McGrath, J. E. *Makromol. Chem., Macromol. Symp.* **1991**, *42/43*, 69-91.

²⁸⁹ Liu, Q.; Wilson, G. R.; Davis, R. M.; Riffle, J. S. *Polymer* **1993**, *34*, 3030-3036.

²⁹⁰ Peters, M. A.; Belu, A. M.; Linton, R. W.; Dupray, L.; Meyer, T. J.; DeSimone, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 3380-3388.

²⁹¹ Yilgor, I.; McGrath, J. E. In *Polysiloxane Copolymers/Anionic Polymerization*; Springer-Verlag: New York, 1988; pp 1-86.

²⁹² McGrath, J. E. In *Ring-Opening Polymerization: Kinetics, Mechanisms, and Synthesis*; McGrath, J. E., Ed.; American Chemical Society: Washington, D.C., 1985; Vol. 286, pp 1-22.

²⁹³ Kawakami, Y.; Yamashita, Y. In *Ring-Opening Polymerization: Kinetics, Mechanisms, and Synthesis*; McGrath, J. E., Ed.; American Chemical Society: Washington, D.C., 1985; Vol. 286, pp 245-261.

LiCl byproducts precipitated out of solution. ^1H NMR was used to determine number average molecular weight (M_n) by comparing the integrations of the butyl peaks at 1.25, 0.9, and 0.5 ppm to the integration of the methyl peaks of the PDMS repeat unit at 0.05 ppm (Figure 2-2). Quantitative termination with the trivinylsilyl end group was verified by comparing the integrations of the butyl peaks to the integrations of the vinyl peaks at 6.0 ppm. Similarly, ^{29}Si NMR was used to calculate M_n and verify complete functionalization with the trivinylsilyl group (Figure 2-3). Three peaks were observable in the ^{29}Si NMR spectra and were attributed to the two terminal silicon atoms, $\text{BuMe}_2\text{SiO-}$ (8 ppm) and $\text{Vi}_3\text{SiO-}$ (-27 ppm), and the silicon atoms of the polysiloxane repeat unit, $-\text{SiMe}_2\text{O-}$ (-22 ppm). GPC chromatograms showed sharp, unimodal peaks and narrow molecular weight distributions that are characteristic of polymers synthesized by living polymerizations. A summary of molecular weights calculated from ^1H NMR, ^{29}Si NMR, and GPC data for the series of trivinylsilyl-terminated polymers is shown in Table 2-1.

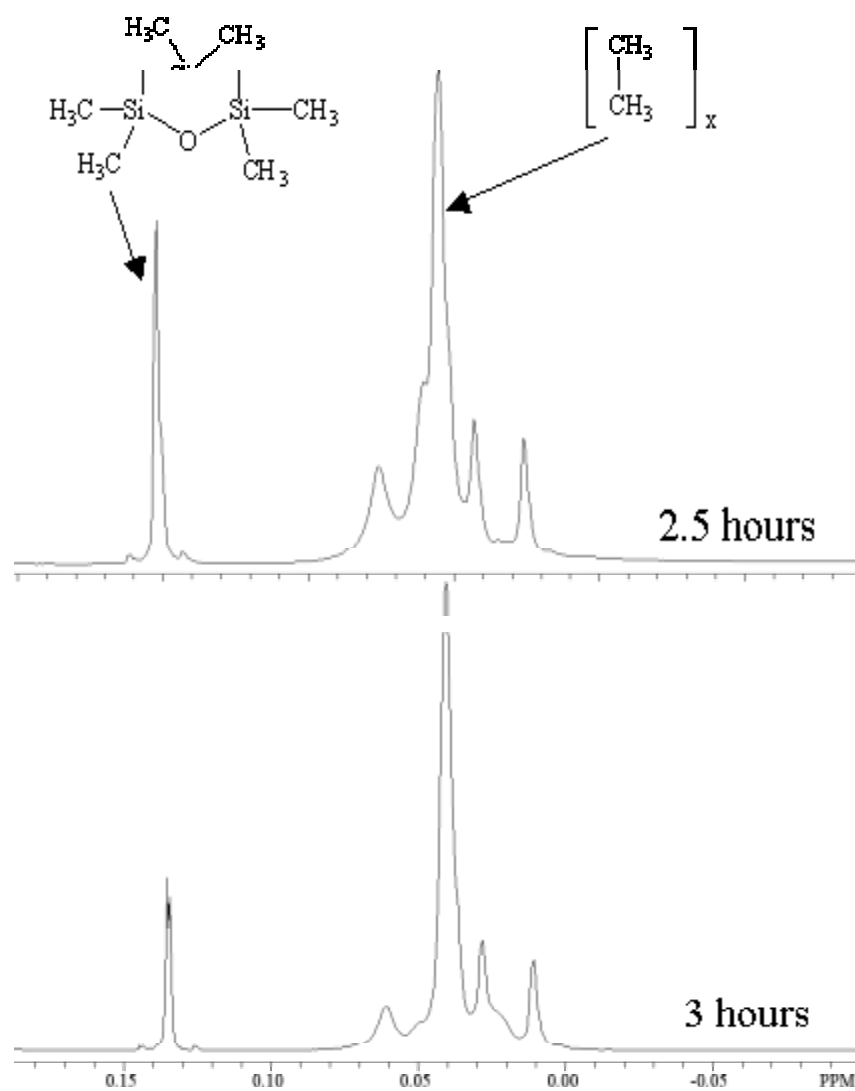


Figure 2-1. ^1H NMR spectra showing monomer depletion during the living ring opening polymerization of hexamethylcyclotrisiloxane at 25 °C.

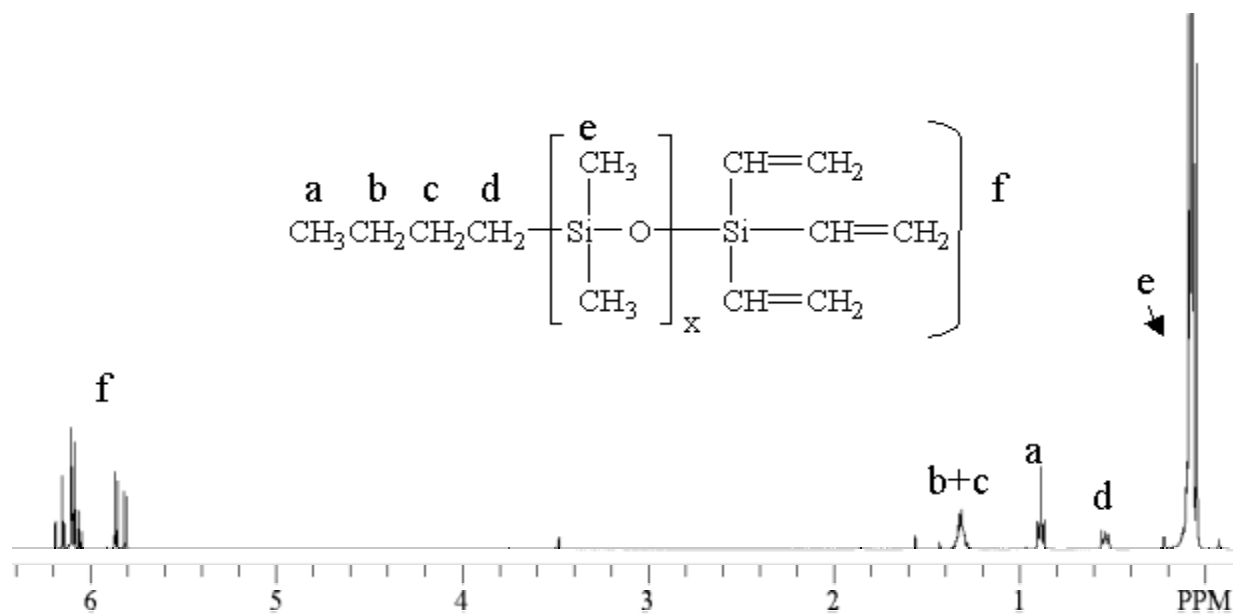


Figure 2-2. ^1H NMR spectra of a 1230 g mol^{-1} trivinylsilyl-terminated poly(dimethylsiloxane) oligomer.

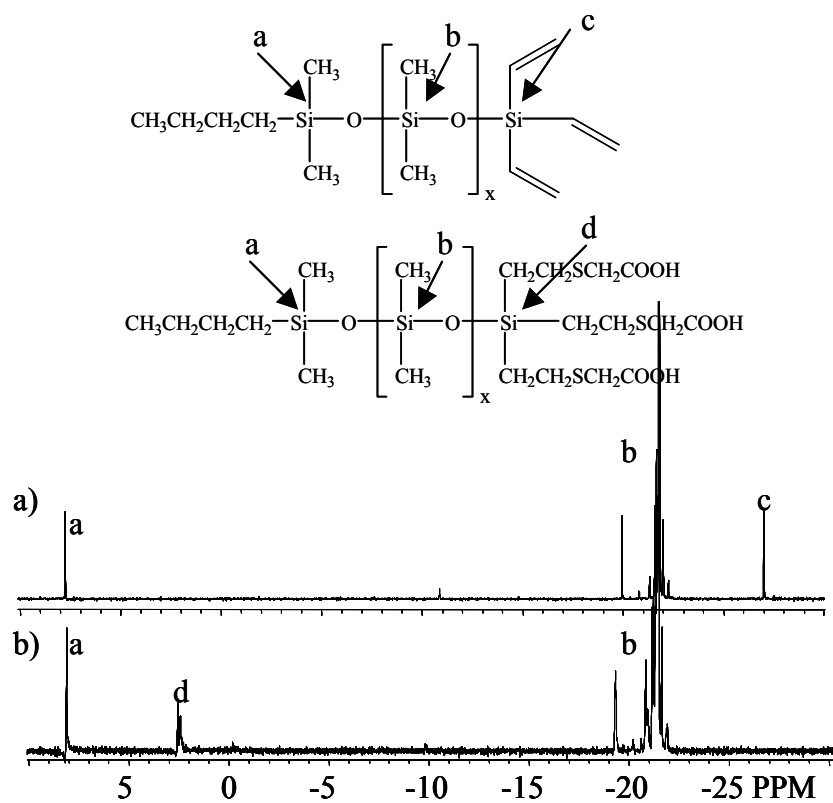


Figure 2-3. ^{29}Si NMR spectra showing a) 2200 g mol^{-1} trivinylsilyl-terminated PDMS and b) 2600 g mol^{-1} trimercaptoacetic acid-terminated PDMS.

Table 2-1. Number average molecular weights and polydispersities obtained from ^1H NMR, ^{29}Si NMR, and GPC for the trivinylsilyl-terminated PDMS series.

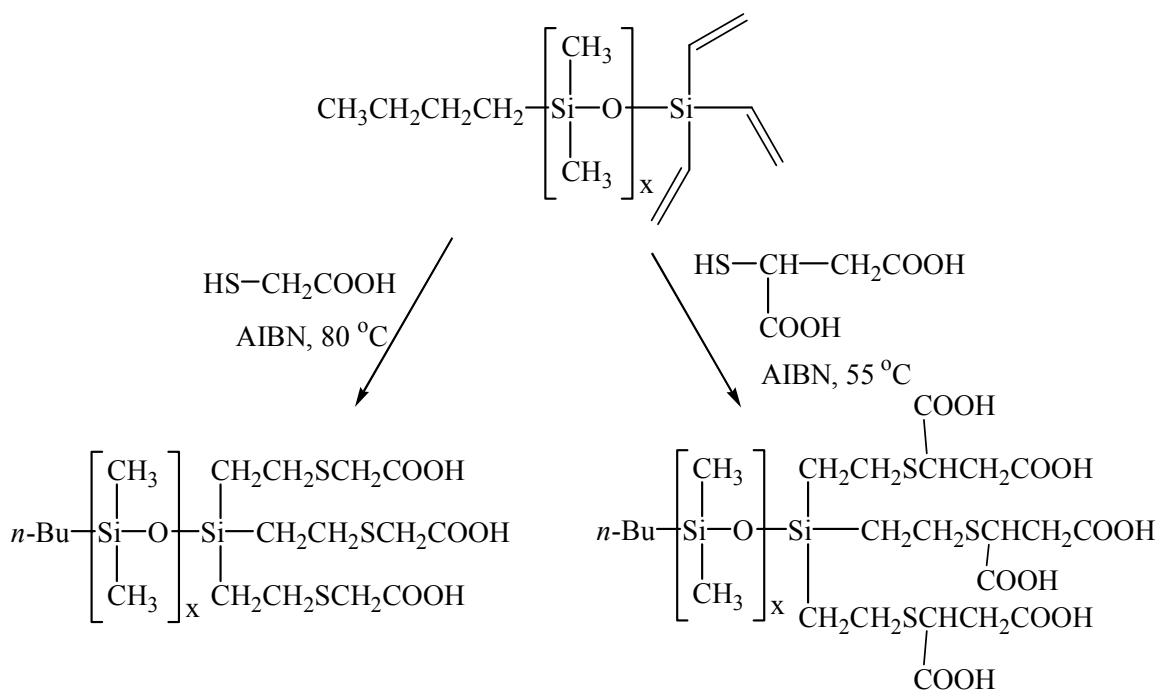
Target M_n (g mol^{-1})	M_n by ^1H NMR (g mol^{-1})	M_n by ^{29}Si NMR (g mol^{-1})	M_n by GPC (g mol^{-1})	M_w/M_n
1220	1180	1140	2170	1.06
2280	2350	2510	3080	1.04
4430	4270	4600	5770	1.03
7290	7290	7930	9150	1.01

The trivinylsilyl-terminated polymers were functionalized with a controlled number of terminal carboxylic acid groups using the thiol-ene addition reaction (Scheme 2-1). The thiol-ene addition reaction has been used previously by Chojnowski, et al. to add mercaptoacetic acid across the vinyl groups in PDMS-*b*-poly(methylvinylsiloxane) and poly(dimethylsiloxane-*co*-methylvinylsiloxane)-*b*-PDMS copolymers.²⁹⁴ Those reactions were conducted in toluene at 80 °C for five hours and 98% of the vinyl groups were converted to the β -addition product. The thiol-ene addition reaction has also been used to incorporate *t*-butyl²⁹⁵ and pyridinyl²⁹⁶ groups into polysiloxanes through the pendent vinyl groups. In the research presented here, carboxylic acid groups were added at one end of the polymer, resulting in the formation of PDMS surfactants with nonpolar PDMS tails and polar head groups containing between three (mercaptoacetic acid addition) and six (mercaptosuccinic acid addition) carboxylic acid groups. To our knowledge, the thiol-ene addition of mercaptosuccinic acid to polysiloxanes containing pendent vinyl groups has not been reported. The thiol-ene addition reactions were monitored via ^1H NMR by following the disappearance of the vinyl peaks at ~6.0 ppm (Figure 2-4). ^{29}Si NMR was used to verify that the vinyl groups had reacted (Figure 2-3).

²⁹⁴ Scibiorek, M.; Gładkova, N. K.; Chojnowski, J. *Polymer Bulletin* **2000**, *44*, 377-384.

²⁹⁵ Rozga-Wijas, K.; Chojnowski, J.; Zundel, T.; Boileau, S. *Macromolecules* **1996**, *29*, 2711-2720.

²⁹⁶ Herczynska, L.; Lestel, L.; Boileau, S.; Chojnowski, J.; Polowinski, S. *European Polymer Journal* **1999**, *35*, 1115-1122.



Scheme 2-1. Thiol-ene addition of mercaptocarboxylic acids to trivinylsilyl-terminated PDMS.

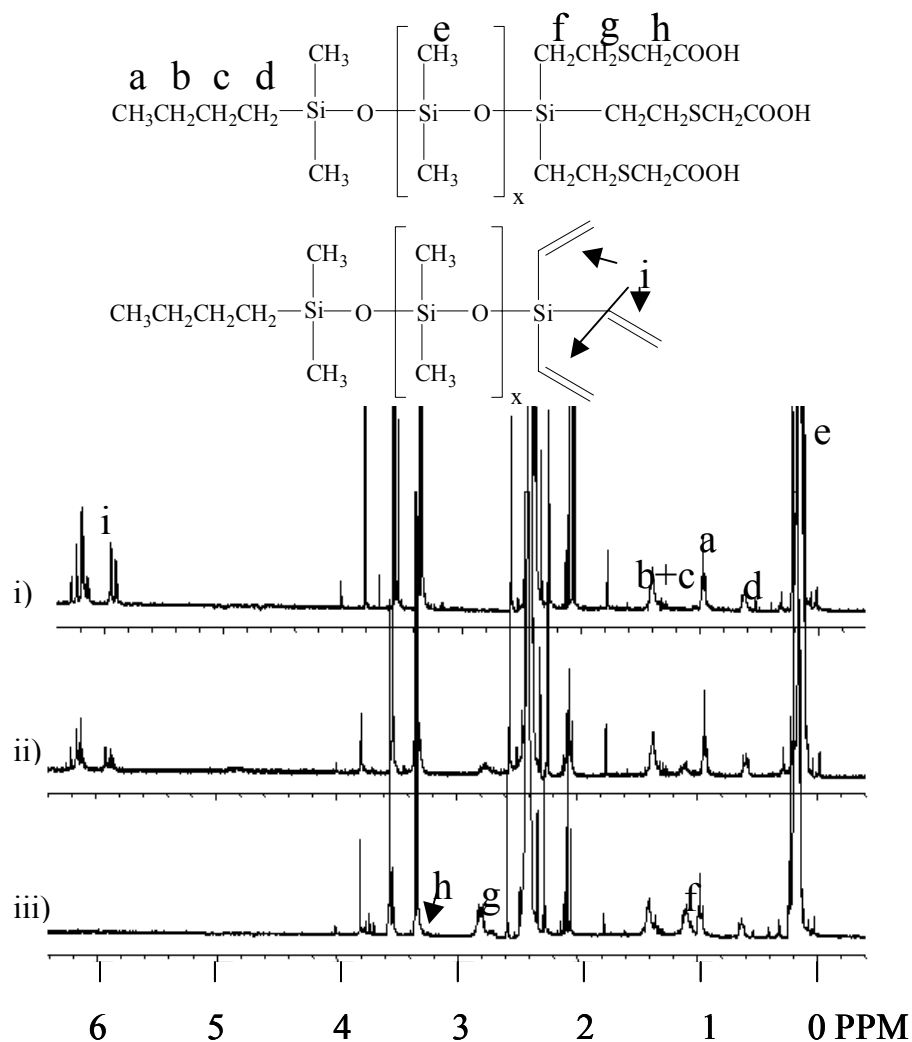


Figure 2-4. ^1H NMR spectra monitoring the thiol-ene addition of mercaptoacetic acid to a 2000 g mol^{-1} trivinylsilyl-terminated PDMS at i) 0 minutes ii) 15 minutes and iii) 45 minutes.

Table 2-2 summarizes the series of polymers that were prepared. The average number of carboxylic acid groups per butyl end group was determined by titrating the polymers in isopropanol with a methanolic solution of potassium hydroxide and phenolphthalein as an indicator. In all cases, the degree of functionalization that was achieved agreed with the targeted amounts.

Table 2-2. Characterization of the carboxylic acid-containing PDMS surfactant series.

M_n by ^1H NMR (g polymer/mole butyl end group)	M_n by ^{29}Si NMR (g polymer/mole butyl end group)	Targeted #COOH per butyl end group	#COOH per butyl end group (titration)
1400	1350	3	2.3
2620	2710	3	3.0
4540	4600	3	2.8
7560	8400	3	2.7
2800	---	6	5.7
4720	---	6	5.5
7740	---	6	5.5

The polymers were analyzed by GPC following the thiol-ene addition reactions (Figure 2-5). The addition reactions conducted in ethyl acetate used approximately 1.1 equivalents of acid per vinyl. Bimodal GPC chromatograms were obtained for the polysiloxanes functionalized under these conditions. One peak corresponded to the expected molecular weight of a single PDMS chain and the second peak (at lower elution volumes) appeared to represent two chains that had coupled. It is proposed that the coupling was caused by a free radical reaction between the vinyl end groups on two PDMS chains (Scheme 2-2). In step 2 of the reaction, the thiol radical of the mercaptoacetic acid adds across the vinyl group, as expected. In step 3, the newly formed radical species can either abstract a hydrogen radical from a second molecule of mercaptoacetic acid or add across a vinyl group on another PDMS chain. According to this proposed mechanism, the coupling reaction should become more prominent toward the end of the reaction when there is less mercaptoacetic acid available for hydrogen abstraction. The thiol-ene addition reactions conducted in toluene using the 1270 g mol^{-1} trivinylsilyl-terminated PDMS used 3.0 equivalents of mercaptoacetic acid per vinyl. GPC chromatograms of polymers functionalized under these conditions were monomodal, indicating that the excess mercaptoacetic acid may have prevented the coupling reactions by acting as a hydrogen radical source.

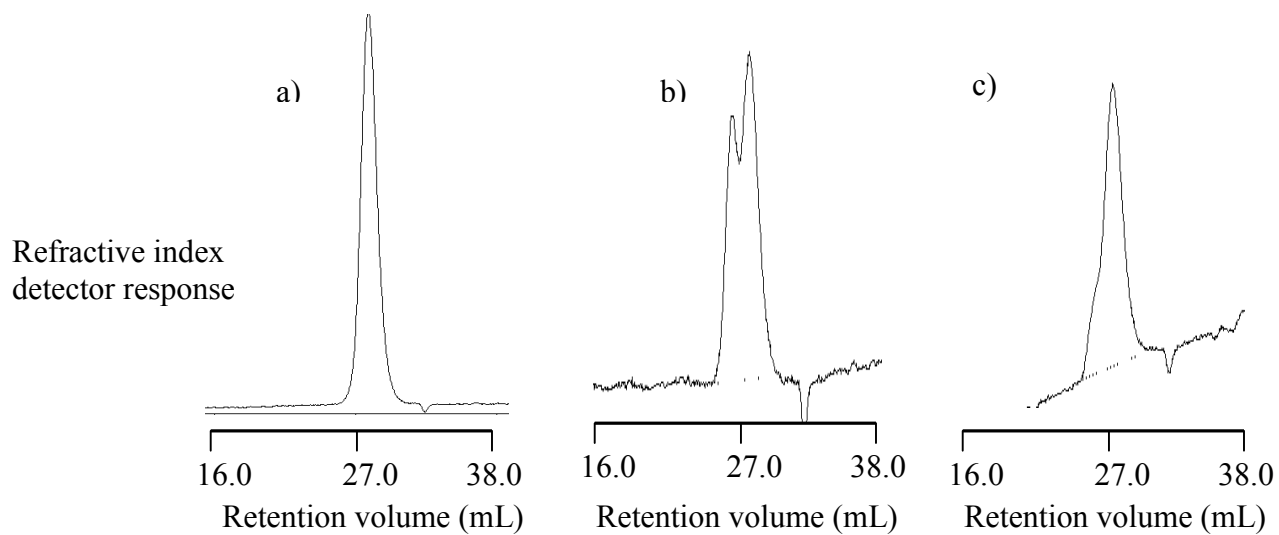
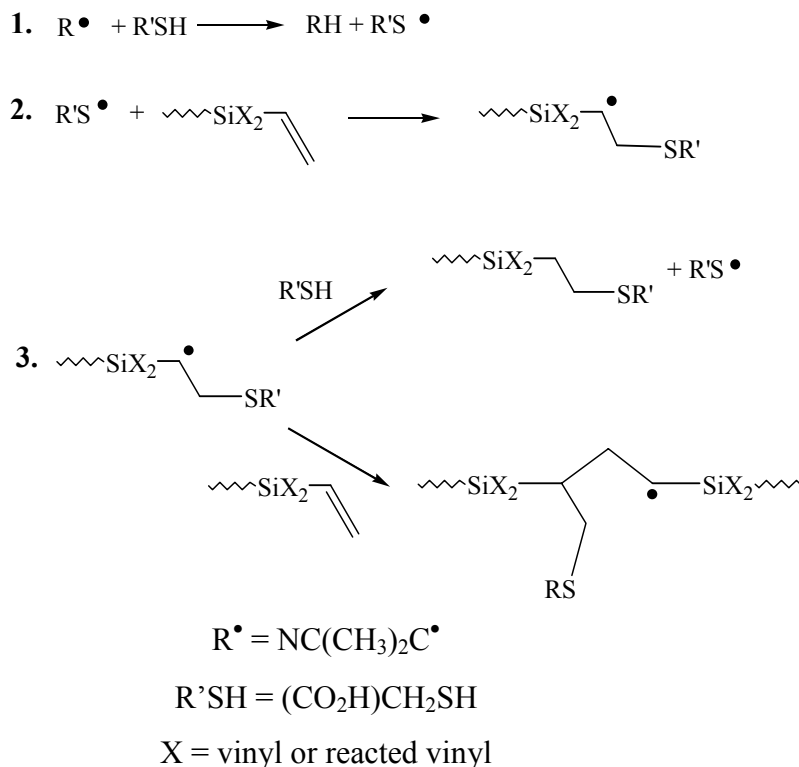


Figure 2-5. GPC chromatograms of 4270 g mol^{-1} PDMS a) trivinylsilyl-terminated b) after the thiol-ene addition of mercaptoacetic acid and c) after the thiol-ene addition of mercaptosuccinic acid suggest that some chain coupling occurs under these conditions.



Scheme 2-2. Proposed free radical mechanism involving PDMS-vinylsilyl chain coupling.

Siloxane bonds (Si-O) are susceptible to cleavage in the presence of acids and bases, resulting in a redistribution of polysiloxane molecular weights.^{297,298} During the thiol-ene addition reactions, the PDMS was exposed to acid (mercaptoacetic or mercaptosuccinic acid) at temperatures between 55 to 80 °C for forty-five minutes to several hours. A controlled study was performed to determine whether the acidic conditions of the thiol-ene addition reaction affected PDMS molecular weight distributions. In each of the two conditions studied, three moles of mercaptoacetic acid were used for every equivalent of vinyl. AIBN was not added to the solutions because the goal was to simulate the conditions of the thiol-ene addition reactions without executing the free radical addition reaction. One PDMS sample was exposed to mercaptoacetic acid in ethyl acetate at 65 °C for 3.5 hours and the other in toluene at 80

²⁹⁷ Noll, W. *Chemistry and Technology of Silicones*; Academic Press: New York, 1968.

²⁹⁸ Voronkov, M. G.; Mileshekevich, V. P.; Yuzhelevskii, Y. A. *The Siloxane Bond*; Consultants Bureau: New York, 1978.

°C for 45 minutes. GPC was used to analyze the polymers after exposure to the acidic conditions and the results were compared to the 1270 g mol⁻¹ trivinylsilyl-terminated PDMS control (Figure 2-6). No significant change was detected between the control ($M_n = 2330$ g mol⁻¹, $M_w/M_n = 1.04$), the PDMS exposed to acidic conditions in toluene ($M_n = 2340$ g mol⁻¹, $M_w/M_n = 1.06$), and the PDMS exposed to acidic conditions in ethyl acetate ($M_n = 2240$ g mol⁻¹, $M_w/M_n = 1.06$). These data suggested that both conditions were mild enough to avoid cleavage of the PDMS chains.

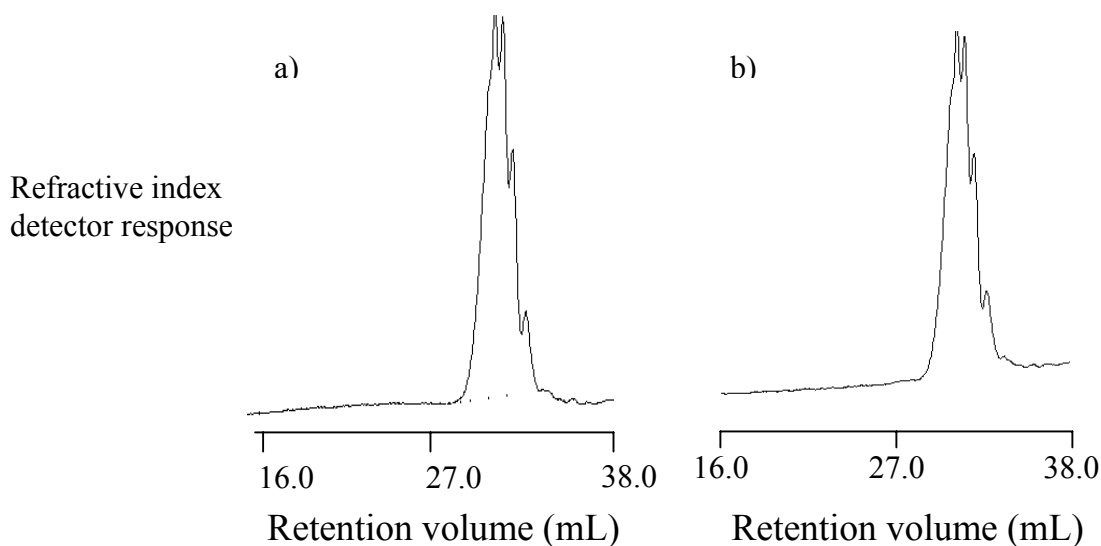


Figure 2-6. GPC chromatograms showing a) 1270 g mol⁻¹ trivinylsilyl-terminated PDMS and b) 1270 g mol⁻¹ trivinylsilyl-terminated PDMS after exposure to acidic conditions at 80 °C for 45 minutes.

2.3.2 PDMS-Magnetite Nanoparticle Complex Preparation

A series of PDMS surfactants having three to six terminal carboxylic acid groups was synthesized to establish the relationship between PDMS composition (molecular weight and number of carboxylic acid groups) and the amount of magnetite that could be complexed by the PDMS. One objective was to calculate the magnetite surface area occupied per PDMS chain, and to determine how the type of polar head group (mercaptoacetic acid or mercaptosuccinic acid) affected the surface area coverage. This

information was expected to provide an understanding of the relative efficiency of the mercaptocarboxylic acid binding groups.

PDMS-nanomagnetite complexes were prepared using the PDMS surfactants and the amount of nanomagnetite charged to the reactions was varied between 30, 50, and 60 wt%. The PDMS-nanomagnetite complexes were prepared in three steps. First, the nanomagnetite was synthesized in an aqueous chemical co-precipitation reaction at basic pH. Upon addition of hydroxide base, the initially clear yellow solution immediately turned black, indicating the precipitation of magnetite nanoparticles. Next, a solution of the PDMS in dichloromethane was added to the aqueous magnetite solution to adsorb onto the particle surface. The aqueous magnetite dispersion would completely separate from the organic phase if stirring was discontinued, suggesting that the carboxylic acid groups did not bind to the magnetite at the basic pH.

In the last step of the reaction, the pH was adjusted to neutral or slightly acidic. The change in acidity resulted in a transfer of the magnetite particles from the aqueous phase to the organic phase. In reactions where the magnetite complexation was highly effective, the final aqueous phases were clear and colorless with no observable traces of magnetite. The pH of the slightly acidic solution was below the reported isoelectric point of magnetite (pH 6.8)²⁹⁹ indicating that the majority of the magnetite surface was positively charged. It is proposed that at the slightly acidic pH (pH 3-6), PDMS carboxylate groups migrated to the dichloromethane/water interface and reacted with the cationic surface of the magnetite.

At a basic pH, the carboxylate groups were unable to bind to the anionic magnetite surface. Similar results were previously found by our research group in a study that used carboxylic acid-functionalized poly(ethylene oxide) to stabilize magnetite nanoparticles in aqueous solutions.³⁰⁰ It was found that the poly(ethylene oxide)-nanomagnetite complexes remained stable at a pH between 2 and 7 but became destabilized at a pH greater than or equal to 8. These results suggested that the carboxylate groups were bound to magnetite at a neutral to acidic pH, but not at a basic pH. In the current study, the surfaces of the nanomagnetite particles were effectively

²⁹⁹ Tewari, P. H.; McLean, A. W. *J. Colloid Interface Sci.* **1972**, *40*, 267.

³⁰⁰ Harris, L. A.; Goff, J. D.; Carmichael, A. Y.; Riffle, J. S.; Harburn, J. J.; St. Pierre, T. G.; Saunders, M. *Chemistry of Materials* **2003**, *15*, 1367-1377.

coated with PDMS at a neutral to slightly acidic pH, causing the particles to be dispersible in the dichloromethane phase but not in water.

Following purification, the PDMS-nanomagnetite complexes were solid, rubbery, or viscous liquid materials depending on the magnetite concentration. The complexes were studied by elemental analysis to determine the concentration of magnetite and by VSM to determine the saturation magnetization (Table 2-3). The complexes were also analyzed by TEM to verify particle size and shape (Figure 2-7). The average particle size was calculated to be 7.4 ± 1.7 nm and was determined by averaging the diameters of hundreds of particles, excluding particle clusters where individual particles could not be identified (Figure 2-8). The particles were approximately spherical in shape.

Table 2-3. Characterization of PDMS-magnetite complexes.

Stabilizer (g mol ⁻¹)	Wt% magnetite charged	Wt% Fe (elemental analysis)	Wt% Fe ₃ O ₄	Saturation magnetization (emu gram ⁻¹ complex)
1400 PDMS(COOH) ₃	30	45	63	45.7
	50	48	67	49.2
	60	48	67	51.6
2620 PDMS(COOH) ₃	30	32	45	35.8
	50	35	49	37.3
	60	40	56	38.6
4540 PDMS(COOH) ₃	30	27	37	25.0
	50	33	46	31.1
	60	37	51	34.1
7560 PDMS(COOH) ₃	30	17	24	15.3
	50	21	29	20.1
	30	30	42	27.9
2800 PDMS(COOH) ₆	50	37	51	38.5
	60	38	52	34.5
	30	27	37	27.7
4720 PDMS(COOH) ₆	50	32	44	36.2
	30	14	20	13.9
7740 PDMS(COOH) ₆	50	16	22	15.6

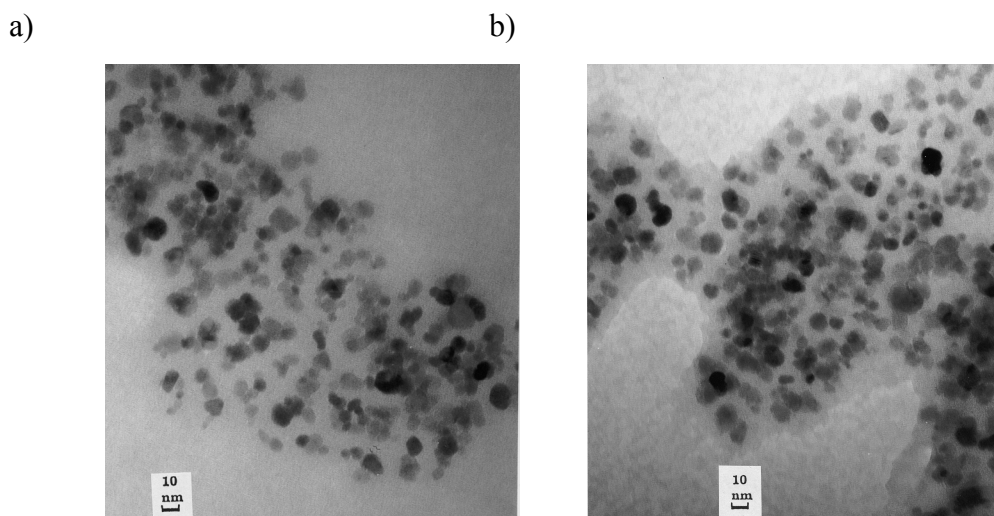


Figure 2-7. TEM images a) PDMS-magnetite complex containing 50 wt% magnetite and a 3500 g mol^{-1} PDMS(COOH)₃ stabilizer and b) the same complex dispersed in a 2000 g mol^{-1} PDMS carrier fluid.

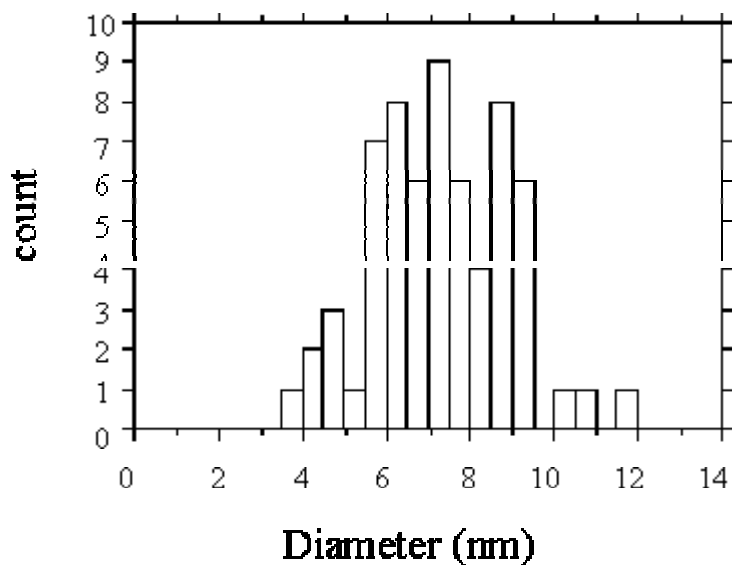


Figure 2-8. Histogram depicting the distribution of magnetite particle diameters.

Qualitatively, the results of these analyses suggest that PDMS molecular weight had a large influence on PDMS-nanomagnetite complex composition. For example, complexes were prepared with 7560 or 1400 g mol^{-1} PDMS that had three carboxylic acid

groups and were charged with 30 wt% magnetite. The concentration of magnetite in these PDMS-nanomagnetite complexes, as determined by elemental analysis, increased from 24 to 63%, respectively. These results are logical since the lower molecular weight polymers contained more carboxylic acid groups per gram than the higher molecular weight polymers, allowing for more magnetite to be complexed. The data also show that there was no difference between the mercaptoacetic acid and mercaptosuccinic acid-functionalized polymers in terms of the final PDMS-nanomagnetite complex compositions. For example, the 2620 g mol⁻¹ PDMS-(COOH)₃ and 2800 g mol⁻¹ PDMS-(COOH)₆ complexed 45 and 42 wt% magnetite, respectively, when charged with 30 wt% magnetite. Even though the PDMS-(COOH)₆ contains twice the amount of carboxylic acid groups per gram relative to the PDMS-(COOH)₃, it complexes a comparable amount of magnetite nanoparticles.

To obtain a more quantitative understanding of these results, the elemental analysis and TEM data were used to calculate the magnetite surface area coverage per PDMS chain (Figure 2-9) and also to compare the total number of PDMS carboxylate groups to the number of active binding sites on magnetite for each complex (Table 2-4). For example, in the complex that contained the 1400 g mol⁻¹ PDMS stabilizer with three carboxylic acid groups and 63 wt% magnetite as determined by elemental analysis, it was assumed that a 100-gram sample of this complex contained 63 grams of magnetite and 37 grams of PDMS. An example is shown below for calculating the number of PDMS carboxylate groups and the total number of magnetite binding sites in a 100-gram sample of this complex and for calculating the magnetite surface area coverage per PDMS chain. The volume per magnetite particle (212 nm³) and surface area per particle (172 nm²) were calculated using the particle diameter determined by TEM (7.4 nm), the density of magnetite (5.1 x 10⁻²¹ g nm⁻³) was taken from the literature,³⁰¹ and the number of active magnetite binding sites (5.2 per nm²) was also taken from the literature.³⁰²

³⁰¹ Weast, R. C., Ed. *CRC Handbook of Chemistry and Physics*; 56th ed.; CRC Press: Cleveland, 1975.

³⁰² Sun, Z. X.; Su, F. W.; Forsling, W.; Samskog, P. O. *Journal of Colloid and Interface Science* **1998**, *197*, 151-159.

carboxylates in 100 grams of the complex = 37 g PDMS * (1 mole/1400 g) * (3 COOH/mole PDMS) * (6.022 x 10²³ COOH/mole) = **4.77 x 10²²**

magnetite binding sites in 100 grams of the complex = 63 g magnetite * (1 nm³/5.1 x 10⁻²¹ g) * (1 particle/212 nm³) * (172 nm²/1 particle) * (5.2 binding sites/1 nm²) = **5.21 x 10²²**

surface area per PDMS chain = total magnetite surface area ÷ molecules of PDMS = 1.00 x 10²² nm² ÷ 1.59 x 10²² PDMS chains = **0.63 nm² per chain**

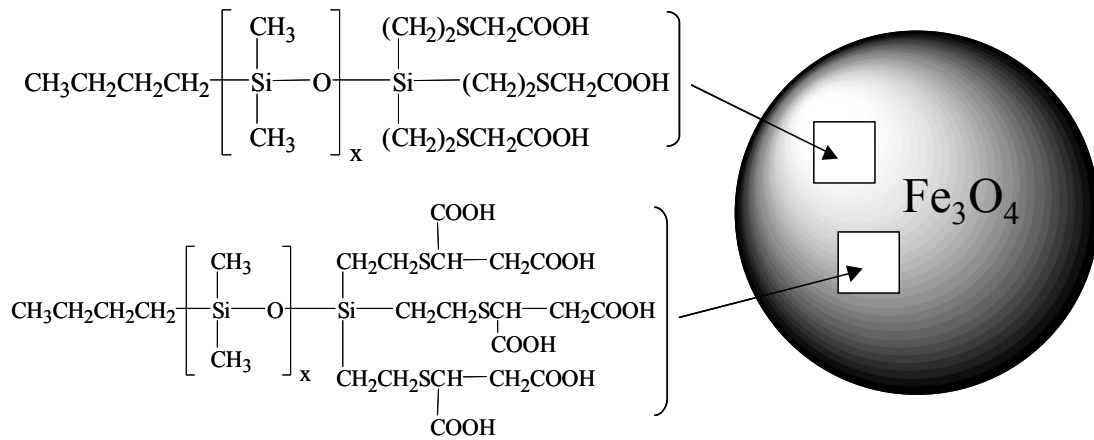


Figure 2-9. Schematic representation of the magnetite surface area covered by a PDMS chain functionalized with either mercaptoacetic acid or mercaptosuccinic acid.

Table 2-4. Results of calculations to determine the relationship between the number of COOH groups in the polymer and the number of active magnetite binding sites in the complexes. The calculations assume 100 grams of complex and the amount of magnetite and PDMS are taken from elemental analysis data.

PDMS Surfactant	Magnetite in the complex (g)	PDMS in the complex (g)	Number of polymer COOH groups	Number of active magnetite binding sites	Magnetite surface area (nm ²) per PDMS chain
1400-(COOH) ₃	63	37	4.77E+22	5.21E+22	0.63
	67	33	4.26E+22	5.54E+22	0.75
	67	33	4.26E+22	5.54E+22	0.75
2620-(COOH) ₃	45	55	3.81E+22	3.72E+22	0.56
	49	51	3.53E+22	4.05E+22	0.66
	56	44	3.05E+22	4.64E+22	0.88
4540-(COOH) ₃	37	63	2.50E+22	3.06E+22	0.71
	46	54	2.15E+22	3.81E+22	1.02
	51	49	1.95E+22	4.22E+22	1.25
7560-(COOH) ₃	24	76	1.83E+22	1.99E+22	0.63
	29	71	1.71E+22	2.40E+22	0.81
	42	58	7.47E+22	3.48E+22	0.54
2800-(COOH) ₆	51	49	6.31E+22	4.22E+22	0.77
	52	48	6.19E+22	4.30E+22	0.80
	37	63	4.82E+22	3.06E+22	0.73
4720-(COOH) ₆	44	56	4.28E+22	3.64E+22	0.98
	20	80	3.76E+22	1.65E+22	0.51
7740-(COOH) ₆	22	78	3.66E+22	1.82E+22	0.57

The average surface area coverage per PDMS chain for the mercaptoacetic acid and mercaptosuccinic acid-functionalized polymers was 0.8 ± 0.2 and 0.7 ± 0.2 nm², respectively. These data indicate that there was no significant difference in magnetite surface area coverage between the two types of functionalized PDMS surfactants, despite the fact that the mercaptosuccinic acid-functionalized PDMS contained twice the number of carboxylate groups. Furthermore, when comparing the number of PDMS carboxylates with the number of active magnetite binding sites, it is apparent that the mercaptoacetic acid-functionalized PDMS was more efficient at binding magnetite. For example,

Figure 2-10 shows a comparison of the data obtained for complexes prepared using PDMS-(COOH)₃ and PDMS-(COOH)₆ of comparable molecular weights. The

complexes prepared using the mercaptoacetic acid-functionalized PDMS contained a comparable number of magnetite binding sites and carboxylate groups, with a small excess of binding sites. According to the calculations, all of the carboxylate groups could have been bound to magnetite. In addition, these data indicate that full magnetite surface coverage was not required for the particles to be stabilized in an organic solvent. Therefore, the PDMS-(COOH)₃ served as an efficient stabilizer for magnetite. On the other hand, the complexes prepared using the mercaptosuccinic acid-functionalized PDMS contained a large excess of carboxylate groups relative to binding sites. This indicates that many of the carboxylate groups were not bound to magnetite. To reiterate, the PDMS-(COOH)₆ and PDMS-(COOH)₃ complex approximately the same amounts of magnetite but the PDMS-(COOH)₆ complexes in such a way that many of the carboxylates remain unbound.

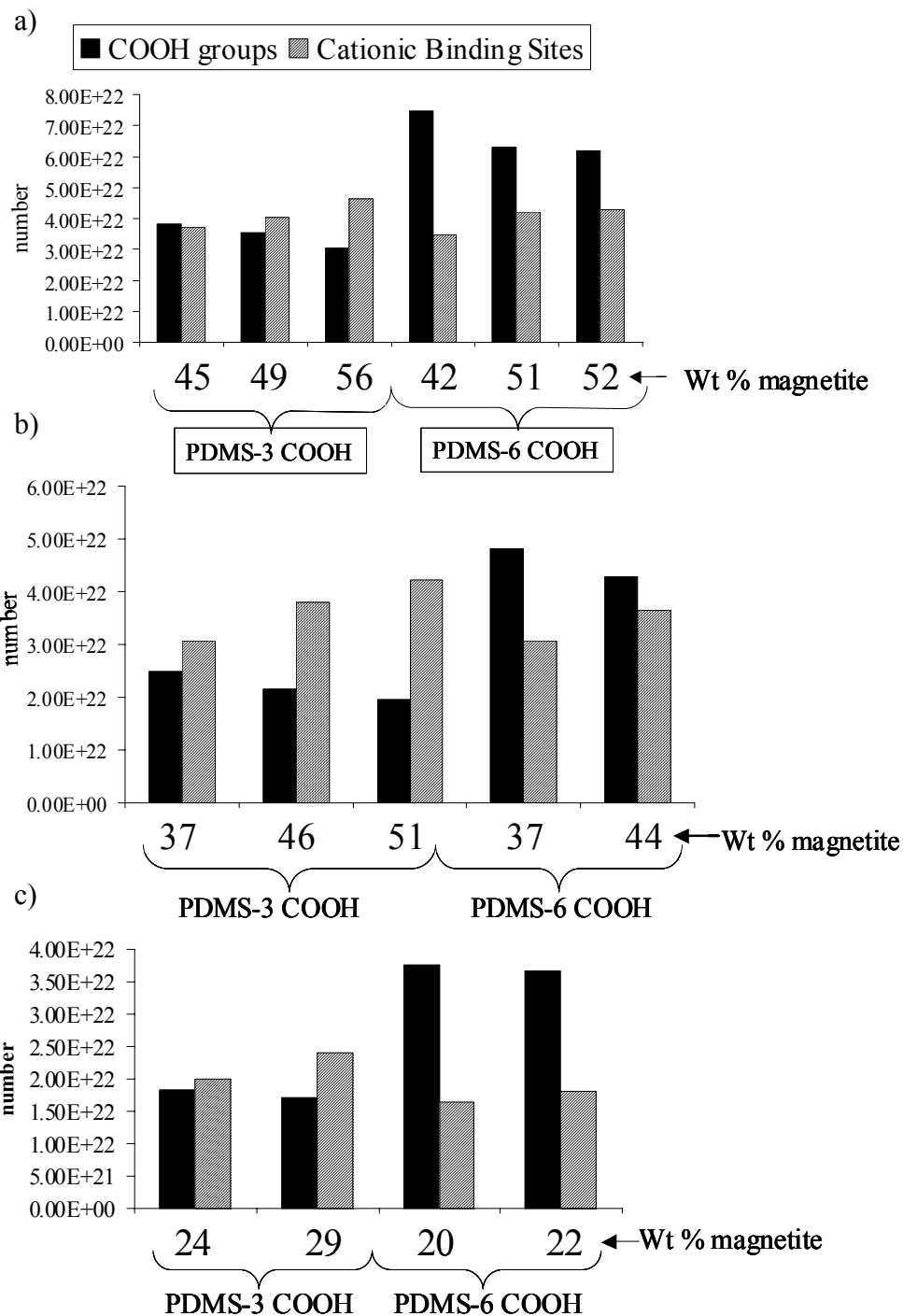


Figure 2-10. A comparison of the number of COOH groups and magnetite binding sites in PDMS-magnetite complexes prepared using a) 2620 g mol^{-1} PDMS-(COOH)₃ and 2800 g mol^{-1} PDMS-(COOH)₆. b) 4540 g mol^{-1} PDMS-(COOH)₃ and 4720 g mol^{-1} PDMS-(COOH)₆. c) 7560 g mol^{-1} PDMS-(COOH)₃ and 7740 g mol^{-1} PDMS-(COOH)₆.

To support these calculations, the mercaptocarboxylate groups and magnetite surface were modeled using Chem3D Pro software utilizing an MM2 energy model. The objective was to obtain a qualitative understanding of the behavior of the PDMS carboxylate groups in the presence of a cationic magnetite crystal surface (Figure 2-11). Iron oxide surfaces have been modeled previously to understand the effects of different crystal planes on surface hydration.³⁰³ In the current study, the magnetite surface was designed with approximately 5 cationic binding sites per nm² to keep the model consistent with the literature value of 5.2 sites per nm².³⁰⁴ Cationic sites were modeled as protonated hydroxyl groups. As a simplification, the PDMS carboxylates were modeled using a trimethylsilyl moiety to replace the long PDMS chain. The energies of the PDMS carboxylates were minimized in the presence of the magnetite surface while keeping the surface unchanged. This minimization allowed for an understanding of the electrostatic interactions between the carboxylate groups and the cationic magnetite surface, but did not provide insight into the binding mechanism.

According to the models, the surface area coverage of the mercaptoacetate and mercaptosuccinate groups was in agreement with the coverage derived from TEM and elemental analysis. The models in (Figure 2-11) predicted that there was a distance of 0.9 nm between certain carboxylate groups while the calculations indicated surface areas in the range of 0.7 nm². The models showed that there was not a significant difference between the magnetite surface areas covered by the mercaptoacetate and mercaptosuccinate groups under the given conditions. Interestingly, for the surface charge density that was modeled, the distance between two cationic binding sites on the magnetite surface was 0.6 nm, while the distance between two carboxylate groups on a mercaptosuccinate moiety was 0.3 – 0.4 nm. This suggested that it was unlikely for both of the mercaptosuccinate carboxylate groups to bind to magnetite. The model prediction that both mercaptosuccinate carboxylate groups cannot bind to magnetite was consistent with the surface area calculations that denoted an excess of mercaptosuccinate carboxylate groups relative to magnetite binding sites.

³⁰³ Jones, F.; Rohl, A. L.; Farrow, J. B.; van Bronswijk, W. *Phys. Chem. Chem. Phys.* **2000**, *2*, 3209-3216.

³⁰⁴ Sun, Z. X.; Su, F. W.; Forsling, W.; Samskog, P. O. *Journal of Colloid and Interface Science* **1998**, *197*, 151-159.

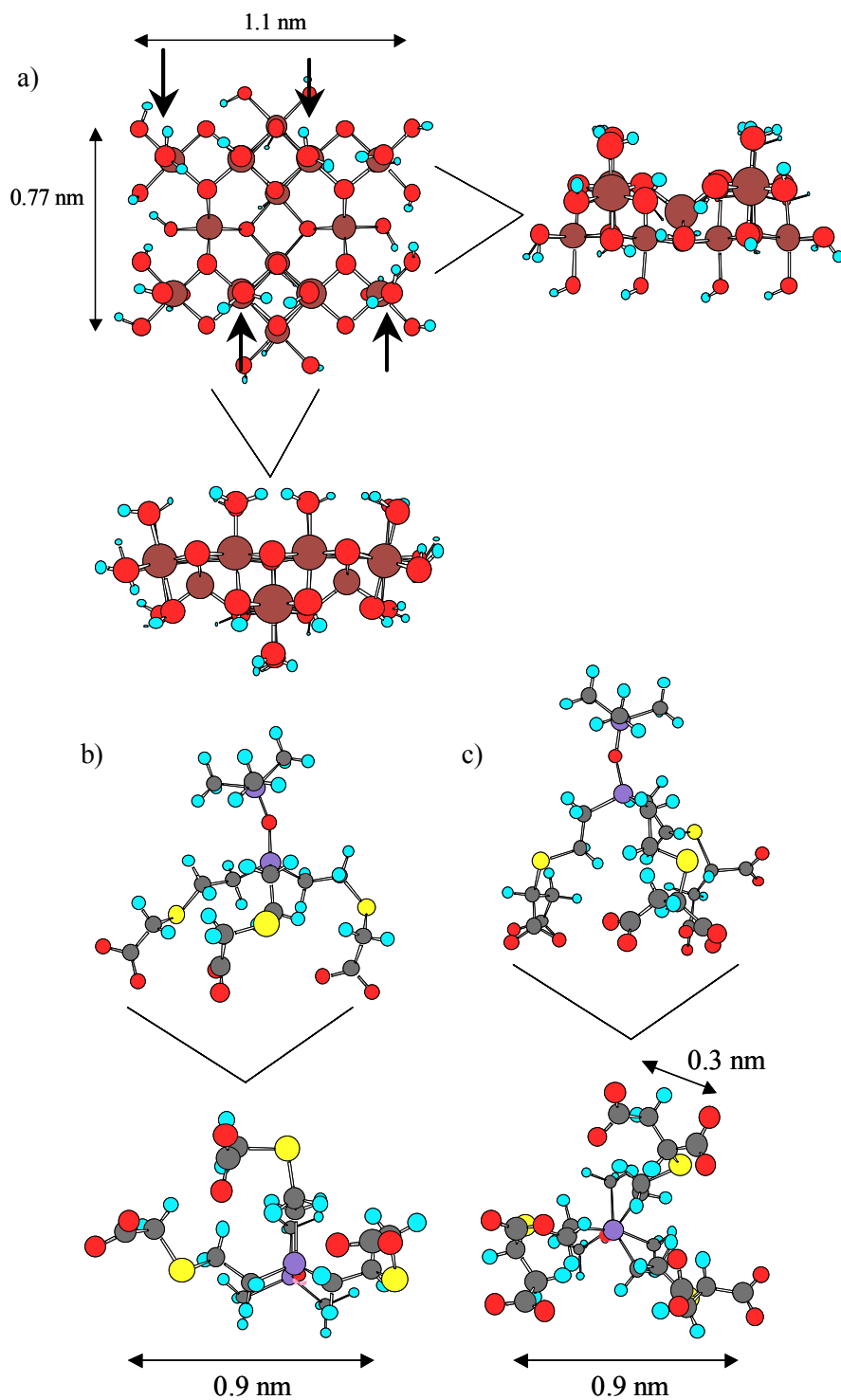


Figure 2-11. Molecular models generated using MM2 energy models and Chem3D Pro software a) magnetite surface (top and side views) b) PDMS mercaptoacetate end groups and c) PDMS mercaptosuccinate end groups after energy minimization near magnetite surface. Cationic surface sites are denoted with black arrows. Hydrogen = blue; carbon = gray; oxygen = red; silicon = purple; sulfur = yellow; iron = brown.

FTIR spectrometry was used to probe the interaction of the carboxylate groups on the magnetite surface (Figure 2-12). The potassium salt form of PDMS-(COOH)₃ was prepared by dissolving the polymer in methanol and adding a methanolic solution of potassium hydroxide until the solution was basic. The methanol was subsequently removed by heating under reduced pressure. The PDMS-(COOH)₃ and PDMS-(COO⁻K⁺)₃ were analyzed as neat samples and the PDMS-magnetite complexes were analyzed as pastes prepared by mixing with a minimal amount of cyclohexane. All samples were analyzed between salt plates.

In the spectral region shown in Figure 2-12, two absorbances are present in all four samples at ~1265 cm⁻¹ and 1382-1416 cm⁻¹. These peaks correspond to the C-H symmetrical and asymmetrical bending, respectively, of the Si-CH₃ groups in the PDMS backbone. The PDMS-(COOH)₃ spectrum contains an absorbance at 1712 cm⁻¹ corresponding to the C=O stretch of the acid functionality. The PDMS-(COO⁻K⁺)₃ spectrum shows a strong C=O asymmetrical stretching band at 1589 cm⁻¹ and a weaker C=O symmetrical stretching absorbance shoulder at 1449 cm⁻¹. Another weak absorbance is present at 1733 cm⁻¹ corresponding to the C=O stretch of some residual carboxylic acid functionality. The PDMS-(COOH)₃-magnetite complex spectrum contains a broad absorbance at 1608 cm⁻¹ and a very sharp absorbance at 1451 cm⁻¹. It is proposed that these bands correspond to the asymmetrical and symmetrical stretching of the carboxylate group bound to the surface of magnetite. Similar absorbances appear in the PDMS-(COOH)₆-magnetite complex spectrum in addition to a weak absorbance at 1716 cm⁻¹ that corresponds to the C=O stretching of the carboxylic acid.

The FTIR analyses yielded some significant results. The spectra of the two polymers demonstrated that the carboxylic acid and carboxylate end group absorbances were easily distinguished. The FTIR spectrum of the PDMS-(COOH)₃-magnetite complex indicated that the carboxylic acid groups were in their carboxylate form when bound to magnetite. This result agreed with the proposal that anionic carboxylate groups reacted with cationic magnetite surfaces at a slightly acidic pH. Also, the asymmetric C=O stretch was noticeably broader than the asymmetric C=O stretch associated with the PDMS-(COO⁻K⁺)₃. It was proposed that this broadening was a direct result of a specific

interaction between the carboxylate groups and the magnetite surface. On the other hand, the spectrum of the PDMS-(COOH)₆-magnetite complex revealed that there were at least two forms of the functionality present: the carboxylate bound to magnetite and the unbound carboxylic acid. This result was very important because it confirmed the accuracy of the calculations and molecular modeling results, both of which indicated that some of the carboxylic acid or carboxylate groups of mercaptosuccinic acid were not bound to magnetite. It was certain that some of the unbound functionality existed in the acid-form, however, some of it may also have been present in the salt-form. Although it was difficult to distinguish, the broad asymmetric absorbance appeared to be bimodal. The bimodality may have been due to the presence of both bound and unbound carboxylate groups.

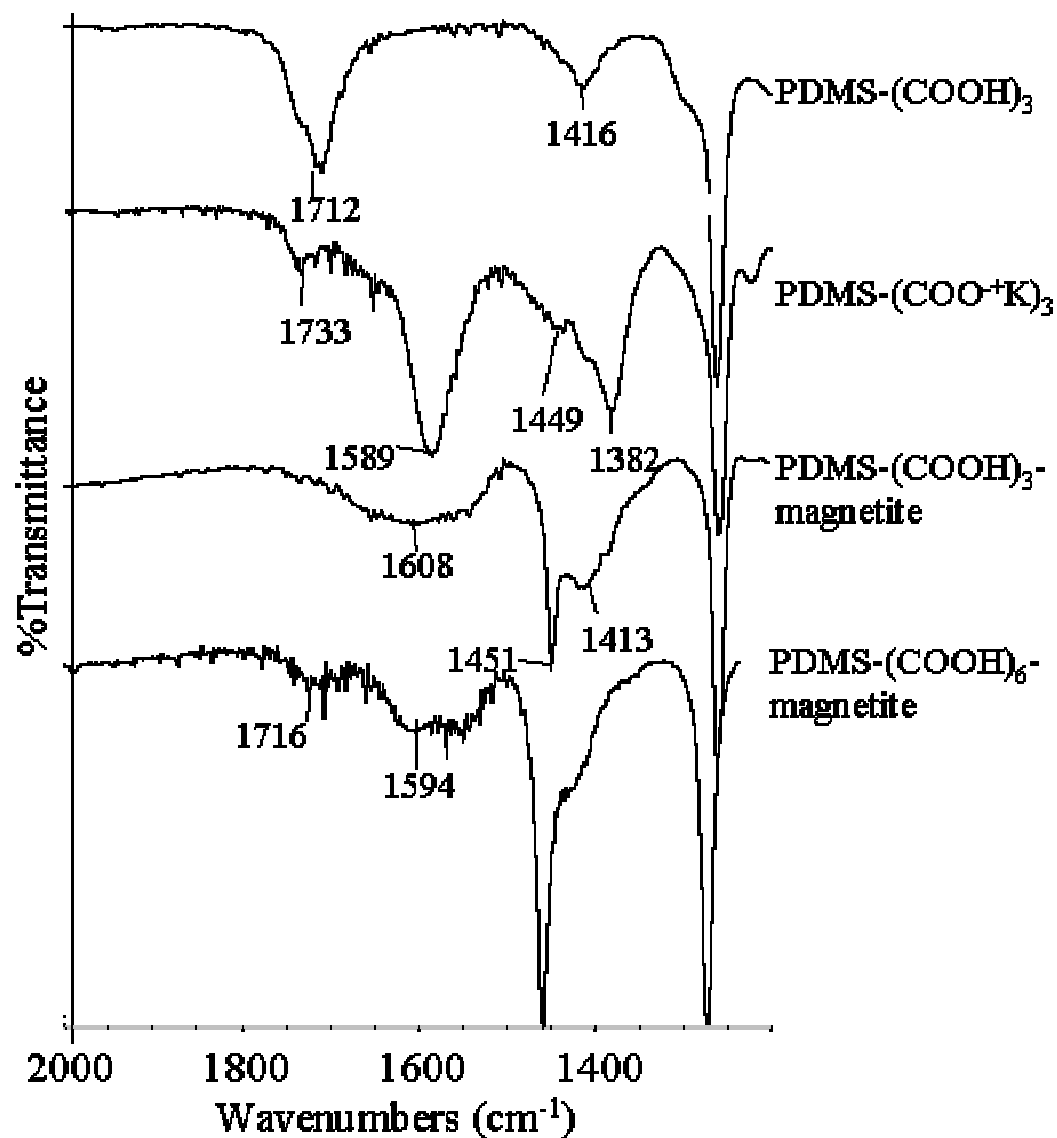


Figure 2-12. FTIR spectra showing PDMS-(COOH)₃, the same polymer in its salt-form, PDMS-(COO⁻K)₃, and PDMS-magnetite complexes prepared using PDMS-(COOH)₃ and PDMS-(COOH)₆.

2.3.3 Magnetic Silicone Fluid Preparation

Magnetic silicone fluids were prepared by ultrasonating the PDMS-nanomagnetite complexes in solutions containing a PDMS carrier fluid and chloroform followed by solvent removal and purification of the dispersions. It was necessary to

dilute the mixture in chloroform to reduce the viscosity and obtain a more even distribution of ultrasonic energy. The viscosities of these magnetic fluids were a function of the concentration of magnetite in the complex, the concentration of PDMS-nanomagnetite complex in the carrier fluid, and the molecular weight of the carrier fluid.

2.3.3.1 Rheometric Studies of Magnetic Fluids

The desired viscosity of the magnetic fluids depends on the specific application. For the medical treatment of retinal attachment, for example, a moderately viscous fluid was desirable. It was therefore important to study the effect of two variables on the viscosity of the fluids: carrier fluid molecular weight and the concentration of PDMS-magnetite nanoparticle complex in the fluid.

The three PDMS carrier fluids used in this study are summarized in Table 2-5. The viscosities of the PDMS carrier fluids and the magnetic PDMS fluids were measured at temperatures from 22-50 °C. The series of fluids and their viscosities at 37 °C (human body temperature) are shown in Table 2-6. There was an obvious trend of increasing viscosity with increasing molecular weight for the PDMS carrier fluids. This trend was an indication that, as expected, the number of chain entanglements was increasing with molecular weight. There was also a significant increase in viscosity with increasing concentration of PDMS-magnetite nanoparticle concentration. When comparing magnetic fluids containing the same concentration of PDMS-magnetite nanoparticle concentration but with different molecular weight carrier fluids an interesting result was observable. The magnetic fluids containing the 5000 g mol⁻¹ carrier fluid had significantly higher viscosities than the 15,000 and 25,000 g mol⁻¹ fluids. For example, for the 50 wt% compositions, the viscosities of the 25,000, 15,000, and 5000g mol⁻¹ fluids were 1.1, 1.5, and 12.1 Pa*s, respectively. The higher viscosities of the 30 and 50 wt% dispersions in 5000 g mol⁻¹ carrier fluid were likely the result of poor dispersion quality (particle aggregation). It was unclear why poor dispersions were obtained with the lower molecular weight carrier fluid.

Table 2-5. Characterization of PDMS carrier fluids used for rheometric studies.

M_n by ^1H NMR (g mol^{-1})	M_n by ^{29}Si NMR (g mol^{-1})	M_n by GPC (g mol^{-1})	PDI (M_w/M_n)
5140	5300	6710	1.01
12,300	11,600	14,200	1.01
20,200	15,300	22,600	1.15

Table 2-6. Magnetic fluid compositions and viscosities at 37 °C.

Fluid Composition	Viscosity at 37 °C (Pa*s)
20,200 g mol^{-1} PDMS	0.42
20,200 g mol^{-1} PDMS – 10 wt% complex	0.062
20,200 g mol^{-1} PDMS – 30 wt% complex	0.19
20,200 g mol^{-1} PDMS – 50 wt% complex	1.1
12,300 g mol^{-1} PDMS	0.075
12,300 g mol^{-1} PDMS – 10 wt% complex	0
12,300 g mol^{-1} PDMS – 30 wt% complex	0.050
12,300 g mol^{-1} PDMS – 50 wt% complex	1.5
5140 g mol^{-1} PDMS	0.012
5140 g mol^{-1} PDMS – 30 wt% complex	0.61
5140 g mol^{-1} PDMS – 50 wt% complex	12.1

The effect of temperature on viscosity was determined by plotting the data according to an Arrhenius plot of $\ln(\eta)$ vs T^{-1} (Figure 2-13). The slope of the lines was equal to E_a/R , where E_a was the activation energy to induce polymer flow and R was the ideal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$). The activation energies were therefore calculated using the slope. Since the activation energies for the dispersions were not significantly different, it was proposed that temperature had little effect on viscosity within this temperature range.

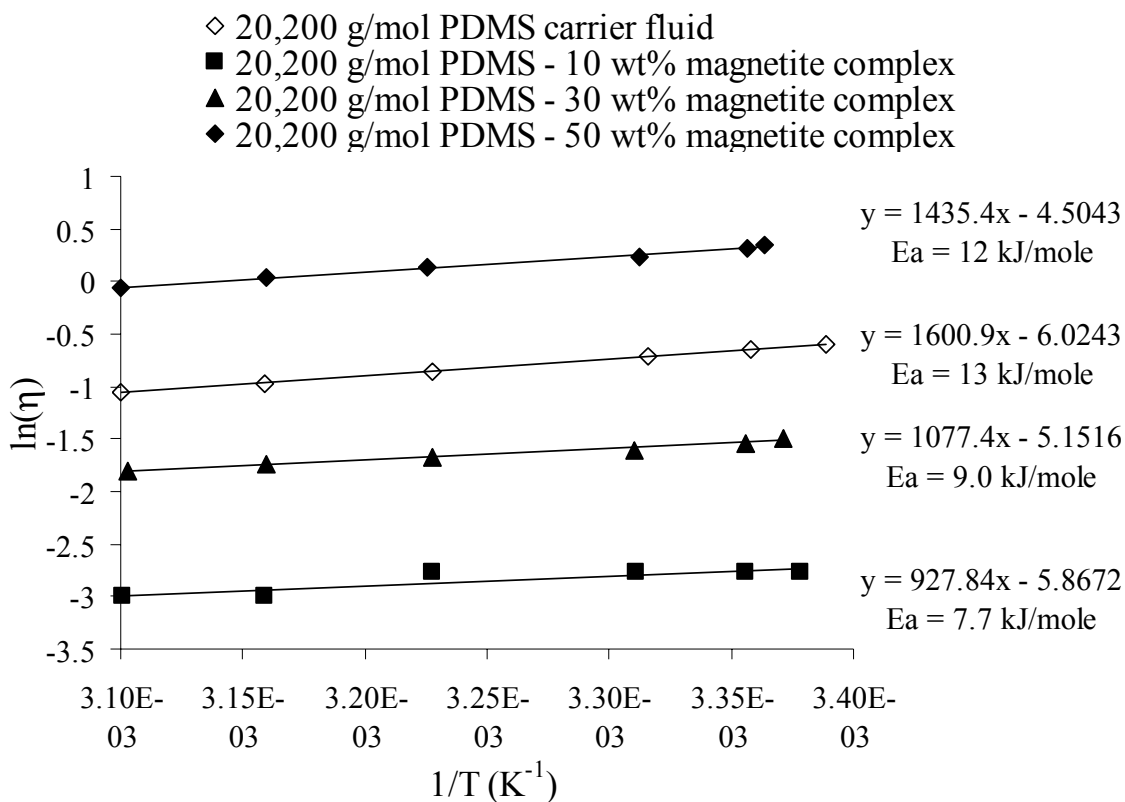


Figure 2-13. Arrhenius plot of $\ln \eta$ vs. $1/T$ for the magnetite dispersions in 20,200 g mol⁻¹ PDMS carrier fluid.

2.4 Conclusions

Methods were developed for the functionalization of PDMS with mercaptoacetic acid or mercaptosuccinic acid one end of the chain. In this way, the PDMS chains were tailored to contain either three or six terminal carboxylic acid groups. A technique was developed for the preparation of PDMS-magnetite complexes by the interfacial reaction of aqueous magnetite nanoparticles at a slightly acidic pH with organic solutions of the carboxylic acid-functionalized PDMS. Our studies suggested that the binding process involved the reaction of PDMS carboxylate groups with the positively charged magnetite surfaces. Calculations indicated that both the mercaptoacetic acid and mercaptosuccinic acid-functionalized PDMS chains covered the same magnetite surface area per chain.

However, the mercaptoacetic acid-functionalized PDMS proved to be a more efficient surfactant for magnetite complexation.

Molecular modeling of the electrostatic interaction of the functionalized end groups with a positively charged magnetite surface suggested that the mercaptoacetic acid functionalities could bind efficiently with magnetite. The models also suggested that not all of the acid groups of mercaptosuccinic acid functionality were able to bind to magnetite. These models helped to explain why the calculations indicated that the two functionalities occupied the same magnetite surface area. FTIR studies on the mercaptoacetic acid-functionalized PDMS, the polymer in its potassium salt form, and on the PDMS-magnetite complexes provided supporting information. Specifically, unbound carboxylic acid groups were observed in the PDMS-(COOH)₆-magnetite complex and were not observed in the PDMS-(COOH)₃-magnetite complex. PDMS-magnetite complexes were successfully dispersed in PDMS carrier fluids, resulting in magnetic PDMS fluids that have the potential to be used for biomedical applications.

3 Chapter 3. Preparation of Controlled-Size Magnetite Nanoparticles and Their Dispersibility in Vinyl Ester Resins

3.1 Introduction

Magnetite particles with diameters greater than ~100 nm display magnetic hysteresis because these particles are large enough to contain multiple magnetic domains.³⁰⁵ Particles in this size range are different from 10 nm magnetite particles which contain only one magnetic domain and do not display magnetic hysteresis. A magnetic hysteresis loop (Figure 3-1) is shown in a plot of applied magnetic field (H) versus sample magnetization (M). Hysteresis results when particles display remanence magnetization (M_R) and coercivity (H_C). Heat is generated as a result of hysteresis loss when an alternating magnetic field is applied to the magnetite particles. The amount of heat generated is proportional to the area within the hysteresis loop. This process is known as magnetic induction heating^{306,307} and has potential applications in cancer treatment therapies^{308,309,310,311,312} and in thermally-induced resin curing.

³⁰⁵ Kittel, C. *Phys. Rev.* **1946**, 70, 965.

³⁰⁶ Monovoukas, Y. A. In *US 5,378,879*; Raychem Corporation: United States, 1995.

³⁰⁷ McGaffigan, T. H. In *US 5,208,443*; Metcal, Inc.: United States, 1993.

³⁰⁸ Kawashita, M.; Tanaka, M.; Kokubo, T.; Yao, T.; Hamada, S.; Shinjo, T. *Key Eng. Mater.* **2002**, 218-220, 645-648.

³⁰⁹ Jordan, A.; Scholz, R.; Wust, P.; Fahling, H.; Felix, R. *J. Magn. Magn. Mater.* **1999**, 201, 413-419.

³¹⁰ Gilchrist, R. K.; Medal, R.; Shorey, W. D.; Hanselman, R. C.; Parrott, J. C.; Taylor, C. B. *Ann. Surg.* **1957**, 146, 596-606.

³¹¹ Brusentsov, N. A.; Brusentsova, T. N.; Sergeev, A. V.; Shumakov, L. I. *Pharmaceutical Chemistry Journal* **2000**, 34, 201-207.

³¹² Jordan, A.; Wust, P.; Fahling, H.; John, W.; Hinz, A.; Felix, R. *Int. J. Hyperthermia* **1993**, 9, 51-68.

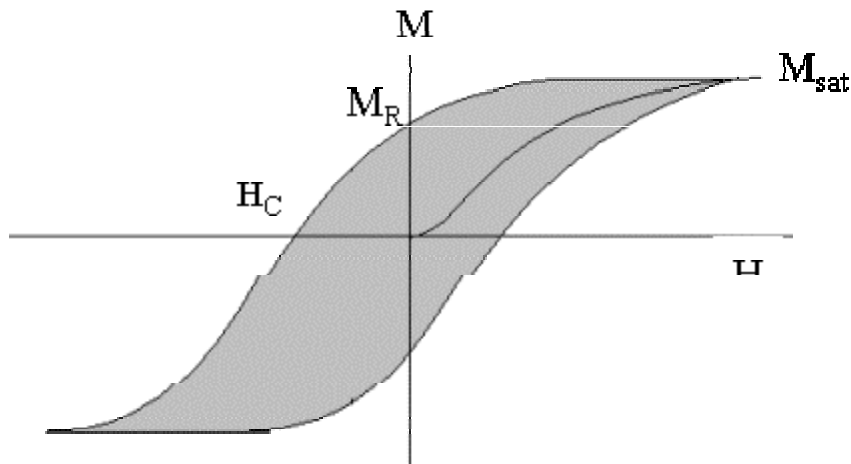


Figure 3-1. An exemplary magnetic hysteresis loop showing saturation magnetization (M_{sat}), remanence magnetization (M_R), and coercivity (H_C).

The focus of the research presented here is on the preparation of controlled-size magnetite nanoparticles (~100-500 nm in diameter) that display magnetic hysteresis and are dispersible in vinyl ester resins. By dispersing magnetite particles into vinyl ester resins, it is proposed that induction heating of the particles will result in thermal curing of the resin. The goal of this research is to determine the relationships between particle size and particle surface chemistry on the dispersibility of the particles in the vinyl ester resin and the time frame in which the particles remain well-dispersed. Good dispersions are necessary to ensure an even heat distribution within the resin during the cure procedure. It is also important that the particles remain dispersed for extended periods so that there is enough time to process the resins without the particles settling out of the dispersion. The magnetite particles are coated with an acid-functionalized poly(ϵ -caprolactone-*b*-methylvinylsiloxane-*b*- ϵ -caprolactone) (PCL-*b*-PMVS-*b*-PCL) copolymer to promote dispersibility in the resins.

This research describes the synthesis of the carboxylic acid-functionalized PCL-*b*-PMVS-*b*-PCL, the preparation of controlled-size magnetite nanoparticles, coating of the particles with the functionalized block copolymers, and the dispersibility of the particles in vinyl ester resins. Future research will be required to determine the variables necessary for effective resin curing (particle size, particle-resin composition, alternating current frequency, etc.).

3.2 Experimental

3.2.1 Materials

1,3,5,7-Tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (D₄vinyl, Gelest), 1,3-bis(hydroxybutyl)tetramethyldisiloxane (95%, Gelest), and trifluoromethanesulfonic acid (triflic acid, 99+%, Aldrich) were used as received. ε-Caprolactone (Aldrich, 99%) was vacuum distilled from calcium hydride and stored under a blanket of nitrogen. Ethyl acetate (Mallinckrodt, 99.9%) was deoxygenated by sparging with dry nitrogen prior to use. Mercaptoacetic acid (97%), 2,2'-azobisisobutyronitrile (AIBN, 98%), propylene glycol (1,2-propanediol), and itaconic acid (99+%) were all used as received from Aldrich. Ethylene glycol (J.T. Baker), stannous octoate (tin (II) ethyl-hexanoate, Sigma, 95%), hydrochloric acid (EM Science), and the vinyl ester resin (DERAKANE 441-400, The Dow Chemical Company) were used as received. DERAKANE 441-400 is comprised of a ~700 g mol⁻¹ vinyl ester oligomer (derived from epichlorohydrin and bisphenol A and capped with methacrylate groups on both ends) diluted with ~30 wt% styrene. Goethite (FeOOH) was generously donated by Dr. John Dillard of Virginia Tech.

3.2.2 Preparation of Controlled-Size Magnetite by Reduction of Goethite and Crystallization from Propylene Glycol-Water Solutions (designated Method 1)

A dispersion of goethite (1 g) in propylene glycol (60 mL) and water (1-5 mL) was prepared in a 100-mL beaker. This mixture was ultrasonicated with a 50:50 pulse sequence for five minutes. The mixture was then added to a Parr pressure reactor, the reactor was sealed, and the temperature was increased to 240 °C and stirred for 3-12 hours. The final magnetite mixture was poured into a beaker and the particles were collected at the bottom with a magnet. The particles were thoroughly washed with deionized water (50 mL x 4) and acetone (50 mL x 4) in that order, and then dried in a vacuum oven at ~60 °C.

3.2.3 Preparation of Controlled-Size Magnetite by Reduction of Goethite and Crystallization from Ethylene Glycol-Water Solutions in the Presence of Carboxylic Acids (designated Method 2)

A dispersion of goethite (1 g) and itaconic acid (0.6-2.0 g) in ethylene glycol (60 mL) and water (10 mL) was prepared in a 100-mL beaker. This mixture was ultrasonicated with a 50:50 pulse sequence for five minutes. The mixture was then added to a Parr pressure reactor, the reactor was sealed, and the temperature was increased to 230 °C and stirred for at least 12 hours. The final magnetite solution was poured into a beaker and the particles were collected at the bottom with a magnet. The particles were thoroughly washed with deionized water (50 mL x 4) and acetone (50 mL x 4) in that order, and then dried in a vacuum oven at ~60 °C.

3.2.4 Synthesis of Carboxylic Acid-Functionalized Triblock Copolymers for the Steric Stabilization of Magnetite Nanoparticles

3.2.4.1 Synthesis of α,ω -Dihydroxybutyl-Terminated Poly(methylvinylsiloxane)

The procedure for the synthesis of an 1150 g mol⁻¹ α,ω -dihydroxybutyl-terminated poly(methylvinylsiloxane) (PMVS) is given. D₄vinyl (50 g, 0.15 mole), 1,3-bis(hydroxybutyl)tetramethyldisiloxane (20.3 mL, 67.8 mmol), and 1.8 wt% triflic acid (0.073 mL) were added to a flame-dried, one-neck, round bottom flask equipped with a condensing tube and a magnetic stirbar. The condensing tube was closed with a wire-bound rubber septum. The reaction flask was placed in an oil bath at 65 °C and stirred for approximately 18 hours. The polymer solution was subsequently dissolved in diethylether and washed with deionized water in a separatory funnel until neutral. Diethylether, cyclics, and water were removed under vacuum at 100 °C for several hours.

3.2.4.2 Synthesis of Poly(ϵ -caprolactone-*b*-methylvinylsiloxane-*b*- ϵ -caprolactone) (PCL-*b*-PMVS-*b*-PCL) Utilizing the α,ω -Dihydroxybutyl-Functionalized Poly(methylvinylsiloxane) Oligomer as a Macroinitiator

The copolymerizations were conducted in bulk according to the following representative procedure for preparing a triblock copolymer containing 500 g mol^{-1} poly(ϵ -caprolactone) tail blocks. α,ω -Dihydroxybutyl-terminated PMVS (5.7 g, 5.0 mmol), ϵ -caprolactone (9.7 mL, 88 mmol), and stannous octoate ($\sim 0.05 \text{ mL}$) were added to a flame-dried and nitrogen-purged round bottom flask equipped with a magnetic stirbar. The flask was placed in an oil heating bath at $70 \text{ }^\circ\text{C}$ for 3 h. The temperature of the oil bath was then increased to $120 \text{ }^\circ\text{C}$ and the reaction mixture was stirred for another 21 h. Reaction progress was monitored by $^1\text{H NMR}$. After 21 hours the monomer had reacted to $\sim 95\%$ conversion. The copolymer was purified by precipitation into methanol followed by washing several times with methanol and then water. The copolymer was dried in a vacuum oven at $40 \text{ }^\circ\text{C}$.

3.2.4.3 Ene-Thiol Addition of Mercaptoacetic Acid to the PCL-*b*-PMVS-*b*-PCL Copolymer to Form Pendent Carboxylic Acid Groups (designated PCL-*b*-PMVSCOOH-*b*-PCL)

The 500 g mol^{-1} PCL-*b*- 1150 g mol^{-1} PMVS-*b*- 500 g mol^{-1} PCL triblock copolymer (5 g, 2.3 mmol) was added to a clean, dry, nitrogen-purged, round bottom flask equipped with a magnetic stirbar and sealed with a rubber septum. Ethyl acetate (20 mL) and mercaptoacetic acid (1.6 mL, 23 mmol) were added via syringe. AIBN (56 mg, 0.34 mmol) was added and then the flask was purged again with nitrogen. The flask was placed in an oil heating bath at $55 \text{ }^\circ\text{C}$ and stirred for three days. The reaction conversion was monitored by $^1\text{H NMR}$. The polymer was purified by precipitating into methanol followed by washing several times with methanol and then water. The polymer was dried overnight in a vacuum oven at $40 \text{ }^\circ\text{C}$. The molecular weight of the PCL-*b*-PMVSCOOH-*b*-PCL block copolymer was 2100 g mol^{-1} .

3.2.5 Adsorption of PCL-*b*-PMVSCOOH-*b*-PCL onto Magnetite Nanoparticles

The particles prepared using method 1 were coated with PCL-*b*-PMVSCOOH-*b*-PCL copolymers where the PCL tail block molecular weights were systematically varied and the central anchor block length was held constant at 2100 g mol⁻¹. The magnetite nanoparticles (0.6 g) were placed in a two-neck, round bottom flask equipped with a mechanical stirrer and a rubber septum. Deionized water (60 mL) containing sodium chloride (0.5) was added and the particles were stirred vigorously until they became well-dispersed. The PCL-*b*-PMVSCOOH-*b*-PCL (1.0 g) was dissolved in dichloromethane (50 mL) and added to the stirring aqueous magnetite dispersion. The pH of the resulting emulsion was adjusted to pH 5-6 using dilute HCl and was stirred for one hour. The particles were collected with a magnet, washed thoroughly with chloroform, water, and acetone and then dried under vacuum at 40 °C.

3.2.6 Preparation of Dispersions of Magnetite Nanoparticles in Vinyl Ester Resins

Dispersions containing 10 wt % magnetite nanoparticles in DERAKANE 441-400 vinyl ester resin were prepared. The vinyl ester resin (1.98 grams) was weighed into a small vial. The magnetite nanoparticles (0.22 g) were weighed separately and then added to the resin. This mixture was stirred with a spatula and then ultrasonicated for approximately seven one-minute intervals.

3.2.7 Instrumentation

¹H NMR spectra were obtained from a Varian Unity 400 NMR instrument operating at 400 MHz using chloroform-*d* as the solvent. Differential scanning calorimetry was performed using a TA Instruments calorimeter model Q1000 with a heating rate of 5 °C per minute. The samples were cooled to -150 °C and heated to 100

°C prior to recording data to erase the thermal history of the samples. The recorded data was obtained from the second heating cycles. Magnetite crystallizations were conducted in a Parr pressure reactor model 452 HC with a 300 mL volume capacity and a 3000 psi capacity at 350 °C. X-ray photoelectron spectroscopy was performed on a Perkin-Elmer 5400 spectroscope operating at 14 kV and 300 W. Scanning electron microscopy (SEM) was performed using a LEO 1550 Field Emission Scanning Electron Microscope at a voltage of 5 kV. SEM samples were prepared by first applying double-sided tape to metal stubs. The samples were then placed onto the tape. Excess sample was removed using pressurized air. The sample was then sputter-coated with a 10-nm gold layer using a Cressington 208 HR Sputter Coater. A Tekmar Sonic Disruptor model TM300 (sonicator) fitted with a microtip was used to disrupt nanoparticle aggregates in the magnetite-vinyl ester resin dispersions.

3.3 Results and Discussion

3.3.1 Preparation of Controlled-Size Magnetite

The preparation of magnetite particles of a controlled size is an important area of chemistry since the magnetic properties of the material will change with particle size. Magnetite particles have a wide variety of applications in fields such as medicine and data storage. Therefore, there has been much interest in controlling the size of magnetite nanoparticles. For example, controlled-size narrow-distribution magnetite particles have been prepared up to 16 nm in diameter by a seed-mediated growth method in a medium containing iron (III) acetylacetonate precursor material.³¹³

The procedures for controlled-size magnetite synthesis used in the current study utilized goethite (FeOOH) as a precursor material and were adapted from the patent literature.³¹⁴ Goethite is comprised of iron (III) atoms while magnetite contains both iron (III) and iron (II) atoms. Although the mechanism for controlling the size of the magnetite crystals is unknown, it is certain that the iron (III) atoms in goethite were partially reduced prior to crystallization. The reactions were conducted in a pressure

³¹³ Sun, S.; Zeng, H. *J. Am. Chem. Soc.* **2002**, *124*, 8204-8205.

³¹⁴ Han, K. S.; Bae, D. S.; Noh, J. S.; Choi, S. H.; Cho, S. B. In *US Pat. 6,203,774 B1*; Korea Institute of Science and Technology: United States, 2001.

reactor so that temperatures in the range of 230-240 °C could be maintained. It was interesting to note that at the start of the reactions pressures from ~700-1000 kPa were obtained and these decreased to ~550-800 kPa towards the end of the reactions. The differences between initial and final pressures depended upon the volumes of the mixtures. It was proposed that the drop in pressure was caused by the crystallization of high-density magnetite (5.18 g cm^{-3})³¹⁵ from the lower density goethite (4.28 g cm^{-3}).³¹⁶ The increased density of the mixture resulted in a volume decrease, thereby decreasing the pressure inside the reactor.

Scanning electron microscopy images of the particles prepared by method 1 showed that the amount of water added to the reaction medium had a strong influence on particle size and shape (Figure 3-2). When the least amount of water was added (1 mL), this resulted in highly saturated solutions that provided a large number of particle nucleating sites. In these cases, particle sizes were relatively small (100-400 nm) and approximately spherical in shape. It was found that increasing the amount of water in the reaction (up to 5 mL) decreased the supersaturation of the goethite solution. Decreasing the supersaturation decreased the number of nucleating sites for particle growth, resulting in particles with larger diameters (500 nm-1 μm) and well-defined octahedral shapes.

³¹⁵ Weast, R. C., Ed. *CRC Handbook of Chemistry and Physics*; 56th ed.; CRC Press: Cleveland, 1975.

³¹⁶ Weast, R. C., Ed. *CRC Handbook of Chemistry and Physics*; 56th ed.; CRC Press: Cleveland, 1975.

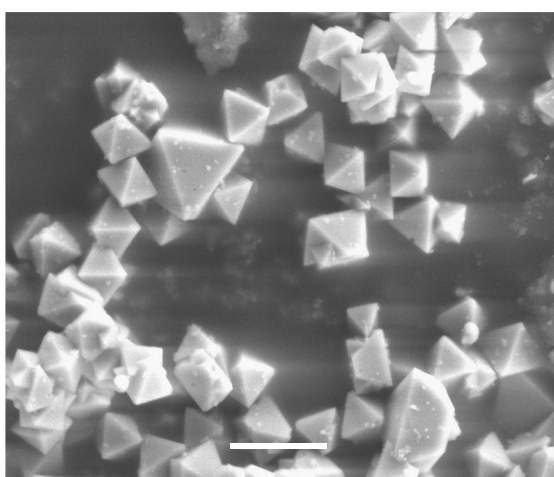
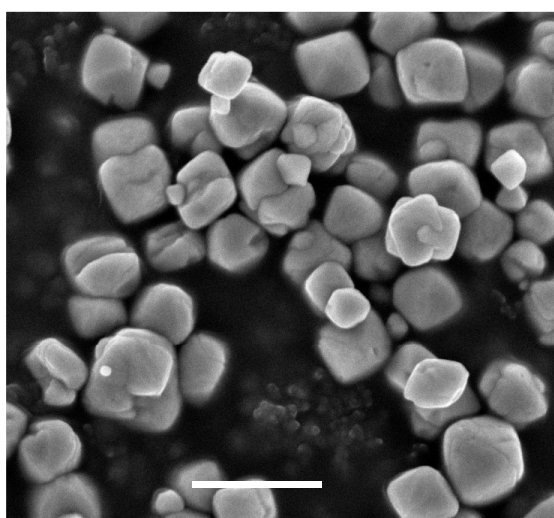
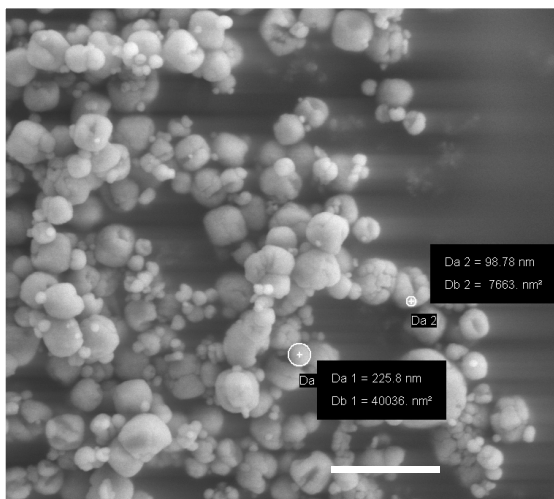


Figure 3-2. SEM images of magnetite nanoparticles prepared according to the reported procedure with 1 mL water (top), 3 mL water (middle), or 5 mL water (bottom). The white lines indicate 1 μm markers.

In method 2, ethylene glycol was used as the solvent instead of propylene glycol because itaconic acid was not soluble in propylene glycol. SEM images of magnetite particles prepared by method 2 indicated that the concentration of itaconic acid in the reaction medium influenced particle size (Figure 3-3). When no itaconic acid was added to the reaction mixture (50 mL ethylene glycol, 10 mL water, 1 g goethite), the particles resembled those prepared using method 1 with 5 mL of water. The particles were ~500 nm in diameter and were octahedral in shape. When itaconic acid was added to the reaction mixture, the particles became smaller in diameter and more spherical. The particle sizes decreased as itaconic acid concentration increased until the particles reached ~100 nm in diameter. This was the minimum diameter reached using method 2. It was hypothesized that the carboxylic acid binds to the magnetite and limits the size of the crystals.

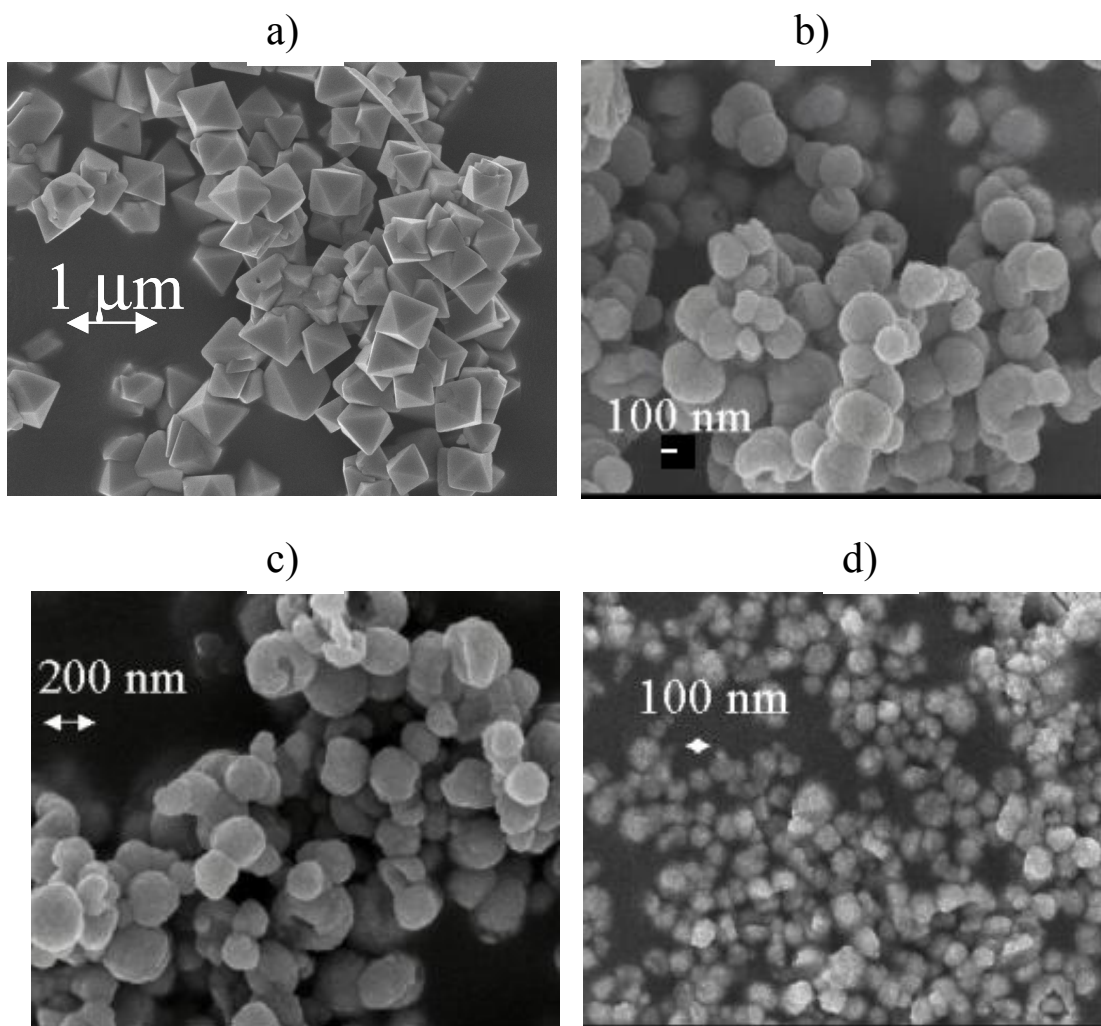


Figure 3-3. SEM images of magnetite nanoparticles prepared using method 2 according to the reported procedure with a) no itaconic acid b) 0.6 g itaconic acid c) 1.0 g itaconic acid and d) 1.4 g itaconic acid.

The magnetic properties of the coated magnetite nanoparticles were analyzed using vibrating sample magnetometry (Figure 3-4). Shown below is the magnetization curve for particles prepared using method 1 that were ~400 nm in diameter. The magnetization curve has been expanded to show only the region between -1000 and +1000 Gauss. It was obvious from this curve that the particles displayed hysteresis, as expected for magnetite nanoparticles in this size range.

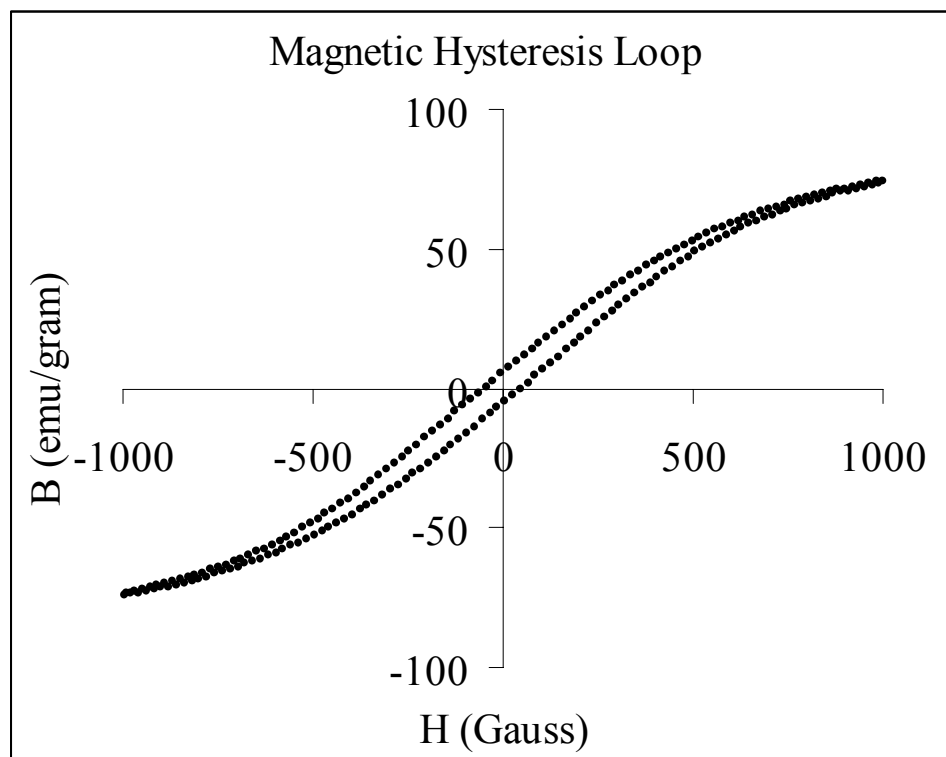


Figure 3-4. Magnetic hysteresis loop obtained by vibrating sample magnetometry for magnetite nanoparticles prepared using method 1 (~400 nm diameter).

3.3.2 Synthesis of Carboxylic Acid-Functionalized Triblock Copolymers for the Steric Stabilization of Magnetite Nanoparticles

3.3.2.1 Synthesis of α,ω -Dihydroxybutyl-Terminated Poly(methylvinylsiloxane)

The acid-catalyzed equilibrium polymerization of D₄vinyl in the presence of 1,3-bis(hydroxybutyl)tetramethyldisiloxane resulted in a α,ω -dihydroxybutyl-terminated poly(methylvinylsiloxane) (PMVS). If the reaction had converted 100% of the monomer to polymer, the molecular weight would have been 1480 g mol⁻¹. The experimental number average molecular weight as determined by ¹H NMR was 1150 g mol⁻¹, therefore, ~22% cyclics were present at equilibrium. ¹H NMR was used to verify the purity and functionality of the polymer (Figure 3-5).

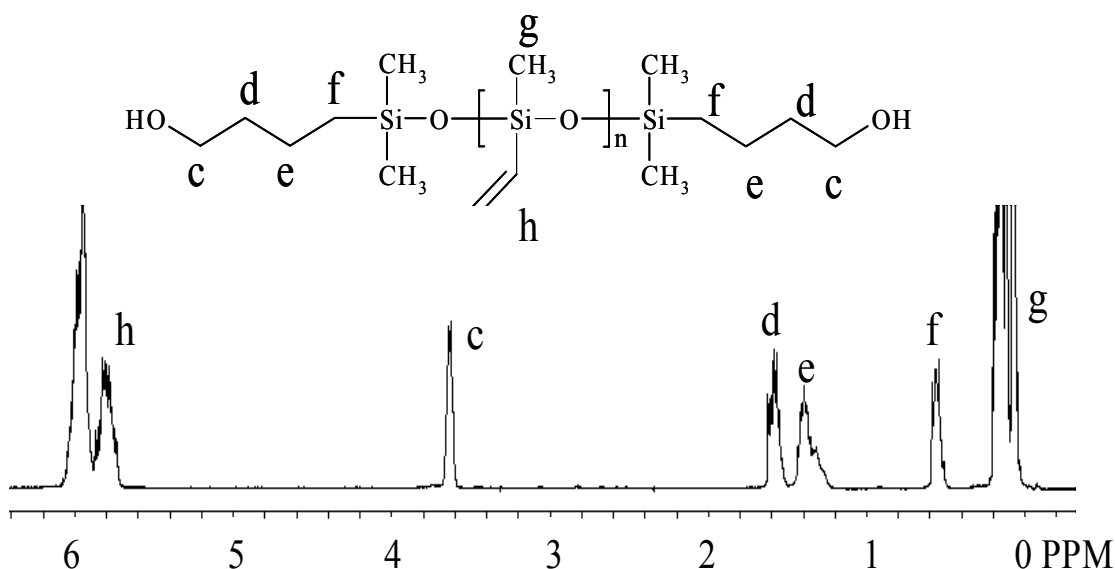


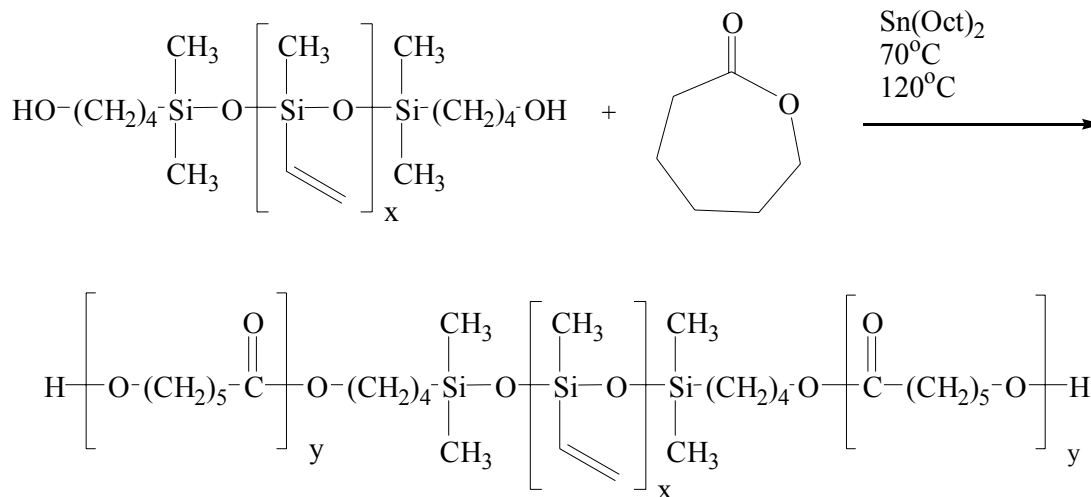
Figure 3-5. ^1H NMR spectrum of the 1150 g mol^{-1} α,ω -dihydroxybutyl-terminated PMVS.

3.3.2.2 Synthesis of Poly(ϵ -caprolactone-*b*-methylvinylsiloxane-*b*- ϵ -caprolactone) (PCL-*b*-PMVS-*b*-PCL) Utilizing the α,ω -Dihydroxybutyl-Functionalized Poly(methylvinylsiloxane) Oligomer as a Macroinitiator

The copolymerization procedure used in this study (Scheme 3-1) was adapted from a patented procedure in which poly(ϵ -caprolactone-*b*-dimethylsiloxane-*b*- ϵ -caprolactone) copolymers were polymerized from α,ω -dihydroxybutyl-functionalized poly(dimethylsiloxane) oligomers.³¹⁷ In the current study, the hydroxyl groups on the PMVS initiated the polymerization of ϵ -caprolactone. Stannous octoate served as a catalyst for the coordination-insertion polymerization. The PMVS and ϵ -caprolactone were initially immiscible but slowly became miscible while the temperature was maintained at $70 \text{ }^\circ\text{C}$. The temperature was then raised to $120 \text{ }^\circ\text{C}$ to increase the rate of the polymerization. The progress of the polymerizations were monitored by ^1H NMR.

³¹⁷ Ward, R. S.; Riffle, J. S. In *US Pat. 4,963,595*; Thoratec Laboratories Corp.: United States, 1990.

The monomer typically reacted to about 80-95% conversion. Higher conversions were not achievable because of the dramatic increase in viscosity at 120 °C.



Scheme 3-1. Copolymerization of ϵ -caprolactone using a α,ω -dihydroxybutyl-functionalized PMVS oligomer as a macroinitiator.

Differential scanning calorimetry (DSC) was used to investigate the thermal properties of the PCL-*b*-PMVS-*b*-PCL triblock copolymer and the PCL and PMVS homopolymers and oligomers (Figure 3-6). A 5000 g mol⁻¹ PCL semicrystalline homopolymer displayed a glass transition temperature (T_g) at -64 °C and a melting endotherm at ~50 °C. No crystallization exotherm was detected because the most of the PCL crystallized quickly as the sample was cooled to -150 °C after the first heating cycle. The 1150 g mol⁻¹ PMVS oligomer displayed a T_g at -121 °C. The triblock copolymer containing 500 g mol⁻¹ PCL tail blocks and a 1150 g mol⁻¹ PMVS central block displayed a T_g at ~105 °C and a melting endotherm at 40-50 °C. These data indicated that the amorphous phases of the PCL and PMVS blocks were miscible, resulting in a single T_g at a temperature intermediate between the T_g s of the two homopolymers. The data also indicated that the PMVS central block did not disrupt the crystallinity of the PCL tail blocks.

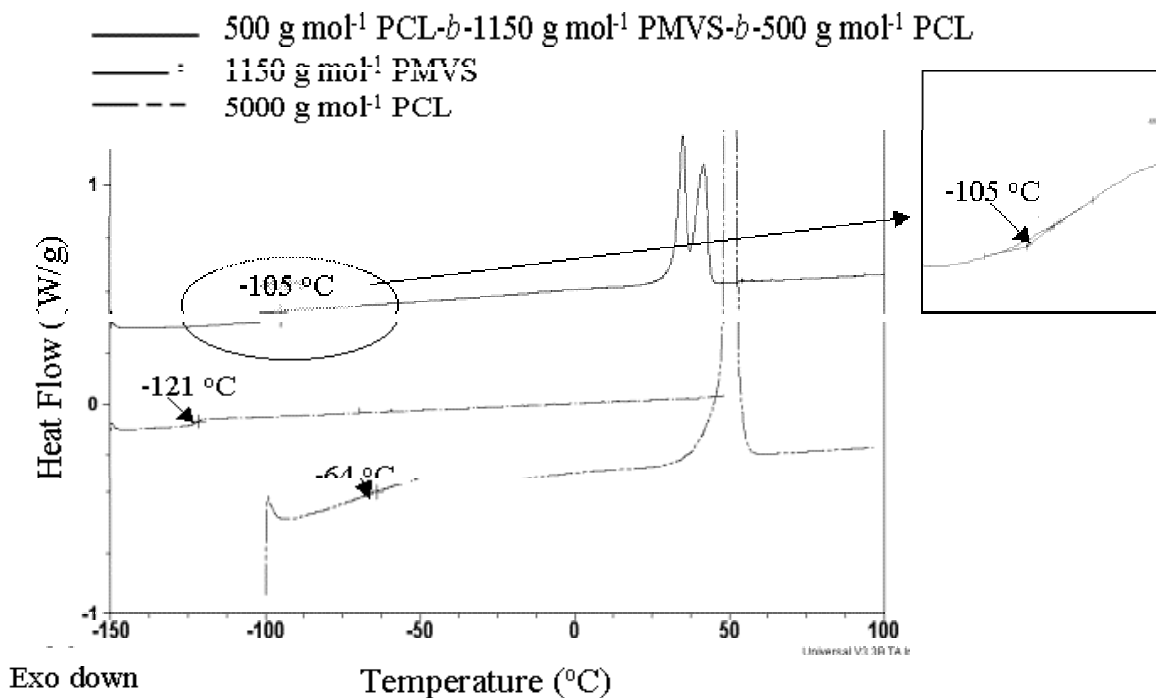
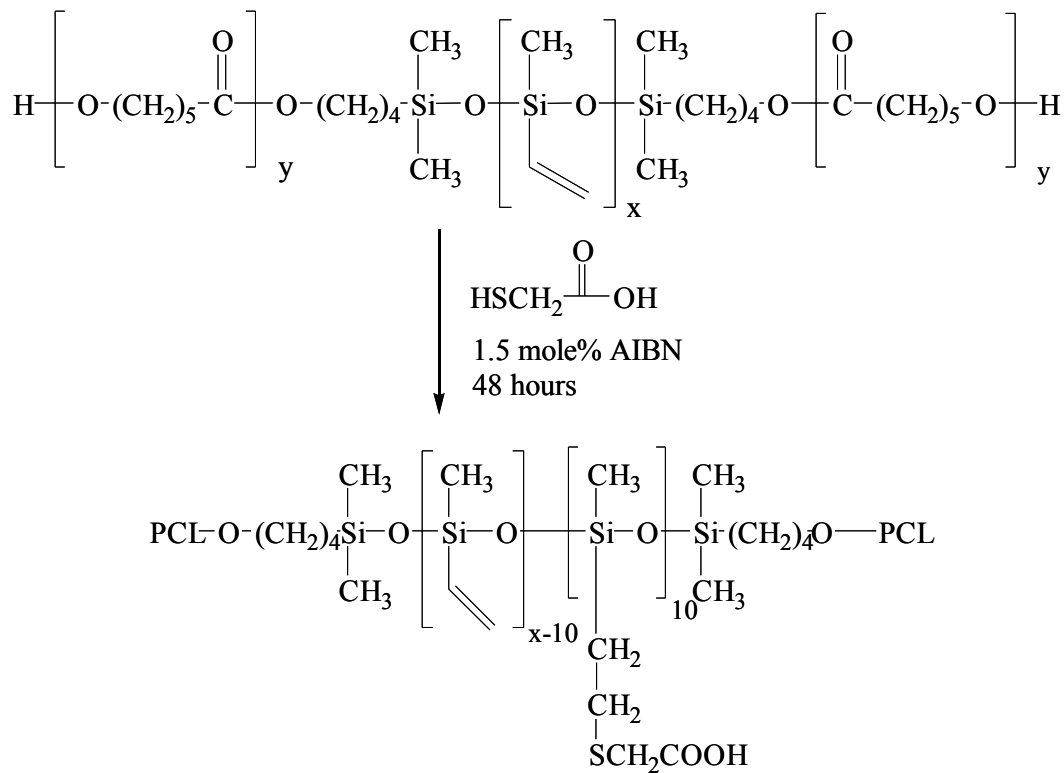


Figure 3-6. DSC thermograms for the PCL and PMVS copolymers and homopolymers.

3.3.2.3 Ene-Thiol Addition of Mercaptoacetic Acid to the PCL-*b*-PMVS-*b*-PCL Copolymer to Form Pendent Carboxylic Acid Groups

The ene-thiol addition reaction was utilized to incorporate pendent carboxylic acid functionalities onto the PMVS central block of the copolymer (Scheme 3-2). The number of acid groups added to the pendent vinyl groups could be adjusted by changing the amount of mercaptoacetic acid added to the reaction. In this study, ten acid groups per chain were targeted. The reactions were monitored by following the disappearance of the resonances associated with the vinyl groups in the ¹H NMR spectrum at ~6 ppm.



Scheme 3-2. Ene-thiol addition of mercaptoacetic acid to PCL-*b*-PMVS-*b*-PCL.

The number of carboxylic acid groups per polymer chain was verified by titration. For the titrations, the PCL-*b*-PVMSCOOH-*b*-PCL was dissolved in isopropanol and phenolphthalein was added as an indicator. A 1.0 M solution of potassium hydroxide in methanol was added via a microsyringe until the characteristic pink color was observed. A series of three PCL-*b*-PVMSCOOH-*b*-PCL copolymers was prepared (Table 3-1).

Table 3-1. Characterization of the PCL-*b*-PMVSCOOH-*b*-PCL copolymer series.

M _n by ¹ H NMR (g mol ⁻¹)	# COOH per chain (target)	# COOH per chain (titration)
500 PCL-1150 PMVS-500 PCL	10	10.3
5800 PCL-1150 PMVS-5800 PCL	10	4.0
13,660 PCL-1150 PMVS-13,660 PCL	10	10.3

3.3.3 Adsorption of PCL-*b*-PMVSCOOH-*b*-PCL onto Magnetite Nanoparticles

The magnetite nanoparticles prepared using method 1 were coated with the series of PCL-*b*-PVMSCOOH-*b*-PCL copolymers via an interfacial reaction. Sodium chloride was added to the aqueous dispersion of magnetite particles to increase the ionic strength of the water. This served to keep the aqueous and organic phases immiscible so that the block copolymer remained soluble in the organic phase. The pH was adjusted to pH 5-6 with dilute HCl. In this pH range, the magnetite surface was cationic (magnetite isoelectric point = pH 6.8) and the acid groups were partially ionized. Therefore, this pH promoted adsorption of the carboxylate groups onto the magnetite surface. Following the coating procedure, there was a noticeable difference in the dispersibility of the magnetite particles. The particles were no longer miscible with water, but were miscible with chloroform. This observation suggested that the particles were coated with an organic-soluble material, namely the PCL block copolymer.

3.3.4 Characterization of Magnetite Nanoparticles by X-Ray Photoelectron Spectroscopy

It was expected that the surface chemistry of the magnetite nanoparticles would strongly influence their dispersibility in vinyl ester resins. For this reason, it was important to analyze the surface properties of the particles using X-ray photoelectron spectroscopy. XPS analysis was performed on the ~500 nm octahedral magnetite

particles prepared using method 1, the same particles from method 1 after the adsorption of PCL-*b*-PVMSCOOH-*b*-PCL, and the ~100 nm particles from method 2 (Table 3-2).

Table 3-2. Elemental compositions on the surfaces of magnetite nanoparticles by XPS analysis.

Sample description	% Fe	% O	% C	% Si
500 nm octahedral particles	21	49	30	0
~500 nm octahedral particles coated with PCL- <i>b</i> -PVMSCOOH- <i>b</i> -PCL (500 g mol ⁻¹ PCL tails)	8	40	48	4
~500 nm octahedral particles coated with PCL- <i>b</i> -PVMSCOOH- <i>b</i> -PCL (5800 g mol ⁻¹ PCL tails)	0	26	61	12
~500 nm octahedral particles coated with PCL- <i>b</i> -PVMSCOOH- <i>b</i> -PCL (13,660 g mol ⁻¹ PCL tails)	1	28	64	7
~100 nm particles coated with itaconic acid	12	42	46	0

The high iron (21%) and oxygen (49%) contents on the surface of the iron oxide particles prepared using method 1 suggested that the surfaces were relatively clean. However, 30% carbon was also detected on the surface. It was proposed that the extra carbon and oxygen on the surface was due to adsorbed propylene glycol and water from the reaction mixture that were not removed during the particle cleaning process. After the particles were coated with the PCL-*b*-PVMSCOOH-*b*-PCL containing 500, 5800, and 13,660 g mol⁻¹ PCL tail blocks, there was a dramatic decrease in the amount of surface iron (8, 0, and 1%, respectively). Also, as the molecular weight of the PCL tail block increased, there was a corresponding increase in the concentration of carbon at the surface. It was proposed that the presence of silicon after the coating procedures was due to the PMVS central block of the PCL-*b*-PVMSCOOH-*b*-PCL. Interestingly, for the particles coated with the 5800 g mol⁻¹ PCL that showed 0% iron at the surface, the ratio of the percent carbon and oxygen was approximately equal to the ratio of carbon and oxygen in a PCL repeat unit. These data suggested that the PCL-*b*-PVMSCOOH-*b*-PCL had adsorbed onto the surface of the magnetite nanoparticles.

The binding energies for carbon on the surface of magnetite before and after the coating procedure were also inspected (Figure 3-7). Prior to the coating procedure, the magnetite particles prepared using method 1 displayed a single binding energy at 285 eV. However, after the coating procedure, two binding energies were observed at 289 and

285 eV. The peak at 289 eV corresponded specifically to carbonyl carbons.³¹⁸ It is proposed that the carbonyl carbon binding energy corresponded to ester carbonyl groups within the PCL backbone. Therefore, these data strongly suggest that the coating procedure was successful and the magnetite particles were well coated with PCL.

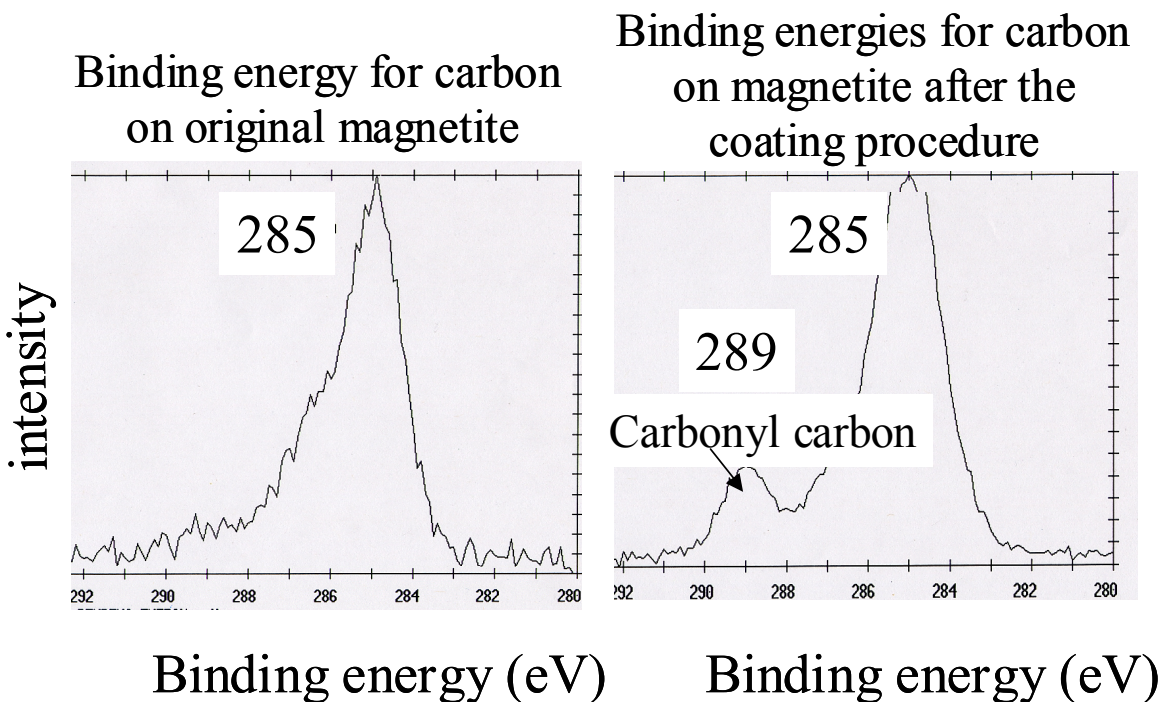


Figure 3-7. XPS binding energies for carbon on the surface of original magnetite prepared using method 1 (left) and magnetite after the adsorption of PCL-*b*-PVMSCOOH-*b*-PCL (right).

The XPS data for the magnetite particles prepared using method 2 in which itaconic acid was added to the crystallization medium (Table 3-2) were different from the data for the method 1 particles. The amount of iron (12%) was half that of the method 1 particles and the amount of surface carbon (46%) was significantly higher. This suggested that the particles were covered with a carbon-containing compound. In addition, it was noted that there were two binding energies for carbon at 285 and 289 eV (Figure 3-8). The presence of a 289 eV binding energy for a carbonyl carbon strongly suggested that the particles were coated with itaconic acid. It was proposed that the

³¹⁸ Wagner, C. D.; Naumkin, A. V.; Kraut-Vass, A.; Allison, J. W.; Powell, C. J.; Rumble, J. R. In; NIST X-Ray Photoelectron Spectroscopy Database: <http://srdata.nist.gov/xps/>, 2003.

carboxylic acid groups on the itaconic acid complexed with the surface of the magnetite during the crystallization reaction in the pressure reactor.

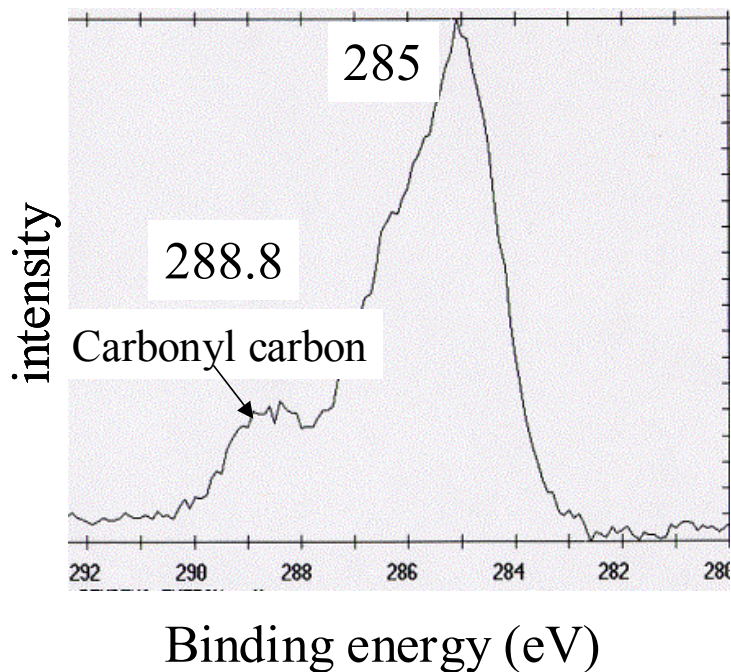


Figure 3-8. XPS binding energies of carbon on the surface of magnetite prepared using method 2 in which itaconic acid was added to the crystallization medium.

The surface analysis of the particles prepared using method 2 also provided some insight into the possible role of itaconic acid in the magnetite crystallization procedure. Since it was demonstrated that itaconic acid was on the surface of the magnetite and since it was known that carboxylic acid groups bind to magnetite, this suggested that itaconic acid complexed with the growing magnetite crystals. By complexing with the surface, the itaconic acid may have served to prevent further crystal growth and limit the particle size. With increasing concentrations of itaconic acid, the particle sizes decreased down to 100 nm because crystal growth was impeded to a greater extent.

3.3.5 Preparation of Dispersions of Magnetite Nanoparticles in Vinyl Ester Resins

The goal of this study was to prepare dispersions of magnetite nanoparticles in vinyl ester resins in which the particles were well-dispersed and remained dispersed for extended periods without agitation. To this end, dispersions containing 10 wt% magnetite nanoparticles in vinyl ester resin were prepared. It was necessary to ultrasonicate the particle dispersions to break up particle aggregates. The dispersions were monitored visually and the time for the onset of particle sedimentation was noted (Figure 3-9).

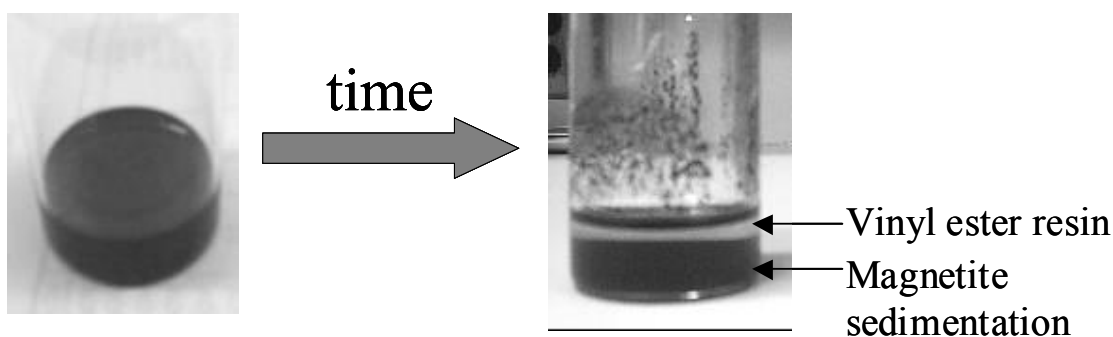


Figure 3-9. Variation in dispersion quality with time for 10 wt% dispersions of magnetite nanoparticles in vinyl ester resin.

The time for the onset of magnetite particle sedimentation from 10 wt% magnetite dispersions in vinyl ester resin was determined for particles prepared using method 1 that were coated with PCL-*b*-PVMSCOOH-*b*-PCL with 500, 5,800, and 13,660 g mol⁻¹ PCL tail blocks and the particles prepared using method 2 that were coated with itaconic acid (Figure 3-10). A noticeable trend was displayed by the PCL-*b*-PVMSCOOH-*b*-PCL-coated ~500 nm magnetite particle dispersions. The time for the onset of magnetite sedimentation increased with increasing PCL tail block length. It was also observed that the itaconic acid-coated 100 nm particles remained stable for the longest time (~3 days).

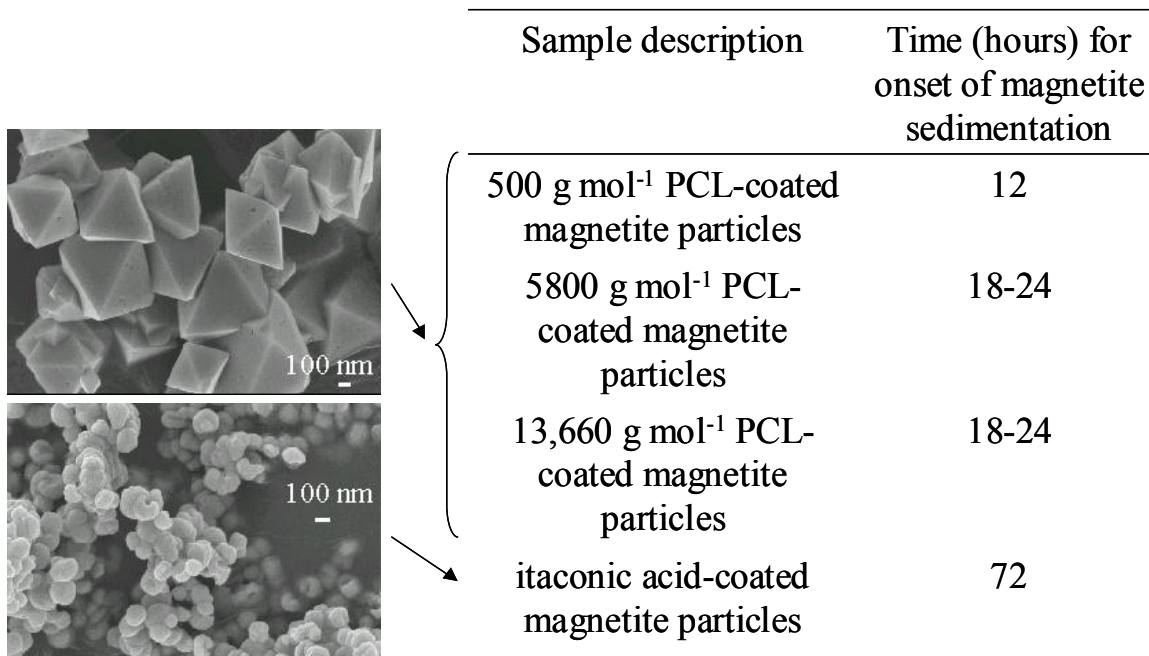


Figure 3-10. Time for the onset of magnetite nanoparticle sedimentation from 10 wt% dispersions in vinyl ester resins.

The longer PCL tail blocks provided a thicker barrier against particle aggregation. Steric stabilization occurs due to loss of polymer conformational entropy upon the approach of two polymer-coated particles. For the particles coated with the longer PCL chains, the entropic effect began at a greater distance compared to the particles coated with the shorter PCL chains. This made magnetite particle aggregation less favorable for the magnetite particles coated with long PCL tail blocks.

The difference between the stability of the PCL-coated particles from method 1 and the itaconic acid-coated particles from method 2 was based on the difference in particle mass. The more massive particles were more strongly affected by the force of gravity and, therefore, began falling out of the resin after 12-24 hours. The 100 nm magnetite particles were less massive and less affected by gravity and could remain dispersed for more time. Unfortunately, no conclusion could be made concerning the effect of the itaconic acid on particle stability since there were no 100 nm particles that were not coated with itaconic acid available for study. However, it was proposed that the

carbon-coating on the particles may also have enhanced the dispersibility of the magnetite nanoparticles in the vinyl ester resin.

3.4 Conclusions

A method was developed for the synthesis of PCL-*b*-PVMSCOOH-*b*-PCL triblock copolymers. Two methods were established for the preparation of controlled-size magnetite nanoparticles. The particles prepared using method 1 ranged from 1 μm to 400 nm in diameter and from octahedral to approximately spherical in shape. It was determined that increasing the amount of water in the reactions decreased supersaturation, decreased the number of nucleating sites, and resulted in larger particles. The PCL-*b*-PVMSCOOH-*b*-PCL copolymers could be subsequently adsorbed onto the magnetite nanoparticle surfaces via an interfacial reaction. The addition of itaconic acid to the reaction mixture resulted in smaller particle sizes (100-200 nm diameter). It was proposed that the function of itaconic acid was to nucleate particle growth and complex with the nanoparticle surfaces, preventing further crystal growth. The PCL-coated particles from method 1 were dispersible in vinyl ester resins and the extent of dispersibility was a function of PCL chain length. The itaconic acid-coated particles from method 2 remained dispersed in vinyl ester resins for extended periods without agitation. It was expected that these particles would be suitable for induction heating applications.

4 Chapter 4. Synthesis and Characterization of Monohydroxyalkyl-Functional Poly(dimethylsiloxane)

4.1 Introduction

Difunctional polydimethylsiloxane oligomers with terminal hydroxyalkyl groups can be prepared by the equilibrium polymerization of octamethylcyclotetrasiloxane (D₄) in the presence of a catalyst and an appropriate hydroxyl-functional disiloxane endcapping reagent.^{319,320} At equilibrium, a distribution of linear and cyclic species are present, with the concentration of cyclics being ~15% by weight.³²¹ Molecular weights of the linear species can be controlled by the ratio of endcapping reagent relative to D₄ monomer, and the distribution of molecular weights is approximately two. These difunctional polysiloxanes are commercially available. By contrast, investigations of the synthesis of monohydroxyalkyl-functionalized PDMS, which must be obtained via living polymerizations of hexamethylcyclotrisiloxane (D₃), have been limited.³²² These monofunctional oligomers are of interest since they can be employed in subsequent reactions to generate well-controlled block or graft copolymers by macro-initiation of ring-opening polymerizations, endcapping step-growth polymerizations, or grafting onto appropriately functionalized polymer backbones. Incorporation of PDMS blocks into other polymers is useful for imparting properties such as toughness,³²³ surface hydrophobicity,³²⁴ fire resistance,³²⁵ oxygen permeability,³²⁶ and biocompatibility.^{327,328}

³¹⁹ Matsukawa, K.; Inoue, H. *Polymer* **1992**, *33*, 667-670.

³²⁰ Chujo, Y.; McGrath, J. E. *J. Macromol. Sci. - Pure Appl. Chem.* **1995**, *A32*, 29-40.

³²¹ Yilgor, I.; McGrath, J. E. In *Polysiloxane Copolymers/Anionic Polymerization*; Springer-Verlag: New York, 1988; pp 1-86.

³²² Peters, M. A.; Belu, A. M.; Linton, R. W.; Dupray, L.; Meyer, T. J.; DeSimone, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 3380-3388.

³²³ Riffle, J. S.; Yilgor, I.; Tran, C.; Wilkes, G. L.; McGrath, J. E.; Banthia, A. K. In *Epoxy Resin Chemistry II*; Bauer, R. S., Ed.; American Chemical Society: Washington, D.C., 1983; Vol. 221, pp 21-54.

³²⁴ Kawakami, Y.; Yamashita, Y. In *Ring-Opening Polymerization: Kinetics, Mechanisms, and Synthesis*; McGrath, J. E., Ed.; American Chemical Society: Washington, D.C., 1985; Vol. 286, pp 245-261.

³²⁵ Wang, L. F.; Ji, Q.; Glass, T. E.; Ward, T. C.; McGrath, J. E.; Muggli, M.; Burns, G.; Sorathia, U. *Polymer* **2000**, *41*, 5083-5093.

³²⁶ Willis, S. L.; Court, J. L.; Redman, R. P.; Wang, J. H.; Leppard, S. W.; O'Byrne, V. J.; Small, S. A.; Lewis, A. L.; Jones, S. A.; Stratford, P. W. *Biomaterials* **2001**, *22*, 3261-3272.

In this paper, a two-step method for preparing monohydroxyalkyl-terminated PDMS with controlled molecular weights and narrow molecular weight distributions is described. First, hydrosilane-terminated PDMS was prepared by the living polymerization of hexamethylcyclotrisiloxane, and this was followed by termination with dimethylchlorosilane, phenylmethylchlorosilane or diisopropylchlorosilane. Second, allyloxyethanol was hydrosilated with the terminal silicon hydride in toluene using a platinum catalyst. This resulted in monohydroxyalkyl-terminated PDMS in most cases. A series of hydroxyalkyl-terminated polymers were synthesized and their chemical structures and molecular weights were characterized by ^1H NMR, ^{29}Si NMR and GPC. As supportive evidence for the presence of PDMS-hydroxyalkyl groups, the functionalized PDMS oligomers were utilized as macroinitiators for ring-opening polymerization of ϵ -caprolactone.

4.2 Experimental

4.2.1 Materials

Hexamethylcyclotrisiloxane (Gelest, D_3) was dried over calcium hydride and sublimed at ~ 80 °C under vacuum into pre-weighed, flame-dried round bottom flasks, each containing a magnetic stirbar. The flasks were purged with nitrogen and re-weighed to determine the amount of D_3 in each flask. *N*-Butyllithium initiators were generously donated by the Lithco Division of FMC as solutions in hexane (~ 2.45 M and ~ 1.48 M), were stored in a freezer under a blanket of nitrogen, and were titrated with diphenylacetic acid prior to use.³²⁷ Cyclohexane (EM Science, 99%) was stirred with concentrated sulfuric acid for one week, washed with deionized water until neutral, dried over MgSO_4 , decanted, stirred over calcium hydride, distilled, stored over sodium under a nitrogen atmosphere, and distilled again prior to use. Tetrahydrofuran (EM Science, 99.5%) was dried over calcium hydride, distilled, stored as a purple sodium/benzophenone dispersion under a nitrogen atmosphere, and distilled prior to use. Toluene (Burdick and Jackson,

³²⁷ Riffle, J. S.; Banthia, A. K.; Webster, D. C.; McGrath, J. E. *Organic Coatings and Plastics Chemistry* **1980**, *42*, 122-126.

³²⁸ Tang, L.; Sheu, M. S.; Chu, T.; Huang, Y. H. *Biomaterials* **1999**, *20*, 1365-1370.

³²⁹ Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879-1880.

99.9%) was washed with sulfuric acid, washed with water until neutral, dried over MgSO_4 , decanted, dried over calcium hydride, and distilled prior to use. Dimethylchlorosilane, diisopropylchlorosilane, and phenylmethylchlorosilane were obtained from Gelest, and stored in a freezer under a blanket of nitrogen. Phenylmethylchlorosilane was vacuum distilled just prior to use. Diisopropylchlorosilane and dimethylchlorosilane were used as received. ϵ -Caprolactone was vacuum distilled from calcium hydride and stored under a blanket of nitrogen. Platinum divinyltetramethyldisiloxane (2.3 wt% Pt° in xylene) was used as received from Gelest. Allyloxyethanol (Aldrich) and tin (II) ethyl hexanoate (stannous octoate: Aldrich) were used as received.

4.2.2 Synthesis of Dimethylhydrosilane-Terminated Poly(dimethylsiloxane)

An exemplary procedure for the synthesis of a 6200 g mol^{-1} dimethylsilane-terminated poly(dimethylsiloxane) is provided. Hexamethylcyclotrisiloxane (14.35 g) was dissolved in cyclohexane (14 mL) in a nitrogen-purged round bottom flask containing a magnetic stirbar. The solution was stirred at room temperature and *n*-BuLi (0.84 mL, 2.07 mmol) was added quickly via syringe. THF (21 mL) was added one hour later. At 90% conversion, dimethylchlorosilane (2.26 mL, 20.7 mmol) was added via glass syringe and the solution was stirred overnight. Most of the solvents were removed under reduced pressure on a rotary evaporator. The concentrated polymer solution was poured into methanol to precipitate the polymer and this mixture was stirred for at least thirty minutes. The polymer was separated from methanol in a separatory funnel, dissolved in chloroform, and washed with water three times. Excess solvents were removed from the polymer by stirring under vacuum at 100°C for several hours.

4.2.3 Synthesis of Diisopropylhydrosilane-Terminated PDMS

The diisopropylhydrosilane-terminated PDMS was synthesized according to the procedure described above. An exemplary synthesis of a 5100 g mol^{-1} PDMS utilized D_3 (11.87 g), cyclohexane (12 mL), 2.45 M *n*-BuLi (0.91 mL, 2.3 mmol) and THF (12 mL).

The reaction was terminated at 93% conversion with diisopropylchlorosilane (0.78 mL, 3.3 mmol) and purified as described previously.

4.2.4 Synthesis of Phenylmethylhydrosilane-Terminated PDMS

The phenylmethylhydrosilane-terminated PDMS was synthesized according to the procedure described above. An exemplary synthesis of a 15,000 g mol⁻¹ PDMS utilized D₃ (14.16 g), cyclohexane (20 mL), 1.48 M *n*-BuLi (0.6 mL, 0.9 mmol) and THF (12 mL). The reaction was terminated at 93% conversion with phenylmethylchlorosilane (0.6 mL, 4 mmol) and purified as described previously.

4.2.5 Synthesis of a Hydroxyalkyl-Terminated Poly(dimethylsiloxane) Oligomer

A representative procedure for functionalizing a 6200 g mol⁻¹ dimethylsilane-terminated PDMS is provided. The polymer (5.95 g, 0.96 mmol) was weighed into a dry round bottom flask equipped with a magnetic stirbar. The flask was closed with a rubber septum bound with copper wire and was purged with nitrogen. Toluene (6mL), allyloxyethanol (0.11 mL, 1.06 mmol), and platinum divinyltetramethyldisiloxane (4.1 μL) were added via syringes. The clear, colorless solution was stirred at room temperature for thirty minutes. The polymer solution was then poured into methanol to precipitate the polymer. The polymer was dried under vacuum at ~100 °C.

4.2.6 Synthesis of a Poly(dimethylsiloxane-*b*-ε-caprolactone) Diblock Copolymer Utilizing a Hydroxyalkyl-Functionalized Poly(dimethylsiloxane) Oligomer as a Macroinitiator

First, a stock solution of stannous octoate catalyst in toluene was prepared. Stannous octoate (0.25 mL) was diluted with toluene (1 mL) in a vial to prepare a 0.62 M solution. Hydroxyalkyl-terminated 7340 g mol⁻¹ PDMS (0.5 g) was weighed into a

separate vial equipped with a magnetic stirbar. The vial was then closed with a wire-bound rubber septum and purged with nitrogen. To the vial was added toluene (4 mL), ϵ -caprolactone (0.49 mL, 0.5 g), and stannous octoate catalyst stock solution (30 μ L, 500 ppm tin). The vial was placed in an oil bath maintained at 75 °C and the contents were stirred for two hours. The temperature of the oil bath was subsequently increased to 110 °C and the contents of the vial were stirred for another hour. After this time, another 30 μ L of the stannous octoate stock solution were added. The oil bath temperature was increased again to 116 °C and the reaction was stirred for another four hours at this temperature. The vial was removed from the oil bath and the polymer was precipitated into methanol. The methanol was removed with a pipette and fresh methanol was added to the polymer. The polymer was stirred in methanol at room temperature for 48 hours to remove residual ϵ -caprolactone.

4.2.7 Instrumentation

^1H NMR and ^{29}Si NMR spectra were obtained from a Varian Unity 400 NMR instrument operating at 400 and 80 MHz, respectively, using chloroform-*d* as the solvent. Quantitative ^{29}Si NMR analyses were obtained using inverse gated decoupling, approximately 500 scans, and chromium (III) acetylacetonate shift reagent to reduce the relaxation time. Polymer molecular weights and polydispersities were determined using a Waters 2690 GPC instrument equipped with Styragel columns HR-1, HR-2, HR-3 and HR-4, a viscosity detector (Viscotek model T60A) and an external refractive index concentration detector. Samples were run using chloroform as the solvent and a flow rate of 1 mL min⁻¹. FTIR spectra were obtained using a Nicolet Impact 400 instrument and OMNIC 3.1a software. Polymers were run neat between salt plates.

4.3 Results and Discussion

4.3.1 Synthesis of Dialkylhydrosilane-Terminated PDMS

The method of living anionic ring opening polymerization was used to generate a series of monofunctional hydrosilane-terminated PDMS (Table 4-2). The living

polymerization of hexamethylcyclotrisiloxane (D₃) has been well documented and results in the formation of well-defined PDMS with narrow molecular weight distributions.^{330,331,332,333,334,335,336} In this study, the polymerizations were terminated with dimethylchlorosilane (DMCS), diisopropylchlorosilane (DIPCS), or phenylmethylchlorosilane (PMCS) (Figure 4-1).

The polymerizations were monitored using ¹H NMR by following the disappearance of the D₃ methyl peak at 0.15 ppm and appearance of the methyl protons on the polymer repeat units at 0.05 ppm. The percent conversion of monomer was determined by examining the ratio of the integrations of these two peaks.

The Si-H proton at the end of the dimethylsilyl-terminated PDMS chain resonated at ~4.7 ppm in the ¹H NMR spectrum of the purified polymer (Figure 4-2). The Si-H protons of the DIPCS and PMCS-functionalized PDMS chains resonated at 4.2 and 5.1 ppm, respectively. The integration value for this peak was compared with the integration values of the peaks corresponding to the butyl end group to verify quantitative functionalization. High degrees of hydrosilane functionality (79-100% by ¹H NMR) were obtained using all three terminating reagents (Table 4-1). Quantitative hydrosilane functionalities were obtained using the PMCS terminating reagent.

³³⁰ McGrath, J. E. In *Block Copolymers*; Meier, D. J., Ed.; MMI Press: New York, 1983; Vol. 3, pp 1-16.

³³¹ McGrath, J. E. *Makromol. Chem., Macromol. Symp.* **1991**, *42/43*, 69-91.

³³² Liu, Q.; Wilson, G. R.; Davis, R. M.; Riffle, J. S. *Polymer* **1993**, *34*, 3030-3036.

³³³ Peters, M. A.; Belu, A. M.; Linton, R. W.; Dupray, L.; Meyer, T. J.; DeSimone, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 3380-3388.

³³⁴ Yilgor, I.; McGrath, J. E. In *Polysiloxane Copolymers/Anionic Polymerization*; Springer-Verlag: New York, 1988; pp 1-86.

³³⁵ McGrath, J. E. In *Ring-Opening Polymerization: Kinetics, Mechanisms, and Synthesis*; McGrath, J. E., Ed.; American Chemical Society: Washington, D.C., 1985; Vol. 286, pp 1-22.

³³⁶ Kawakami, Y.; Yamashita, Y. In *Ring-Opening Polymerization: Kinetics, Mechanisms, and Synthesis*; McGrath, J. E., Ed.; American Chemical Society: Washington, D.C., 1985; Vol. 286, pp 245-261.

Table 4-1. Degree of hydrosilane functionality determined by ^1H NMR and ^{29}Si NMR.

Endcapping reagent	M_n target (g mol $^{-1}$)	%Si-H functionality by ^1H NMR	%Si-H functionality by ^{29}Si NMR
DMCS	6400	90	94
DMCS	8720	96	100
DMCS	14,300	89	100
DIPCS	5110	79	100
DIPCS	13,900	82	90
PMCS	7620	100	100
PMCS	15,100	100	100

Number average molecular weights were calculated by comparing the ^1H NMR integrals of the protons on the repeat units to the average integrals for the butyl protons followed by adding the molecular weights of each end group. An example calculation is provided below:

$$\underline{\text{CH}_3}\text{CH}_2\text{CH}_2\text{CH}_2\text{- integration} = 0.60 \div 3 = 0.2$$

$$\text{CH}_3\underline{\text{CH}_2\text{CH}_2}\text{CH}_2\text{- integration} = 0.84 \div 4 = 0.21$$

$$\text{CH}_3\text{CH}_2\text{CH}_2\underline{\text{CH}_2}\text{- integration} = 0.38 \div 2 = 0.19$$

$$\text{Average of the butyl integrations} = (0.2 + 0.21 + 0.19) \div 3 = 0.20$$

$$\text{-Si}(\underline{\text{CH}_3})_2\text{O- integration} = 96.92 \div 6 = 16.15$$

$$M_n \text{ of the repeat units} = (16.15 \div 0.20) * 74 \text{ g mol}^{-1} = 5980 \text{ g mol}^{-1}$$

$$M_n \text{ of the polymer} = 5980 \text{ g mol}^{-1} + 115 \text{ g mol}^{-1} (\text{butyl}) + 59 \text{ g mol}^{-1} (\text{dimethylsilane}) = \mathbf{6150 \text{ g mol}^{-1}}$$

Table 4-2. Characterization of the hydrosilane-terminated PDMS series.

Endcapping reagent	M_n target (g mol $^{-1}$)	M_n by ^1H NMR (g mol $^{-1}$)	M_n by ^{29}Si NMR (g mol $^{-1}$)	M_n by GPC (g mol $^{-1}$)	M_w/M_n
DMCS	6400	6200	5980	9670	1.00
DMCS	8720	9190	7480	13,000	1.00
DMCS	14,300	21,800	26,900	26,900	1.00
DIPCS	5110	5420	4910	7360	1.01
DIPCS	13,900	14,400	16,900	18,700	1.01
PMCS	7620	9740	9660	12,000	1.02
PMCS	15,100	16,600	16,900	22,300	1.01

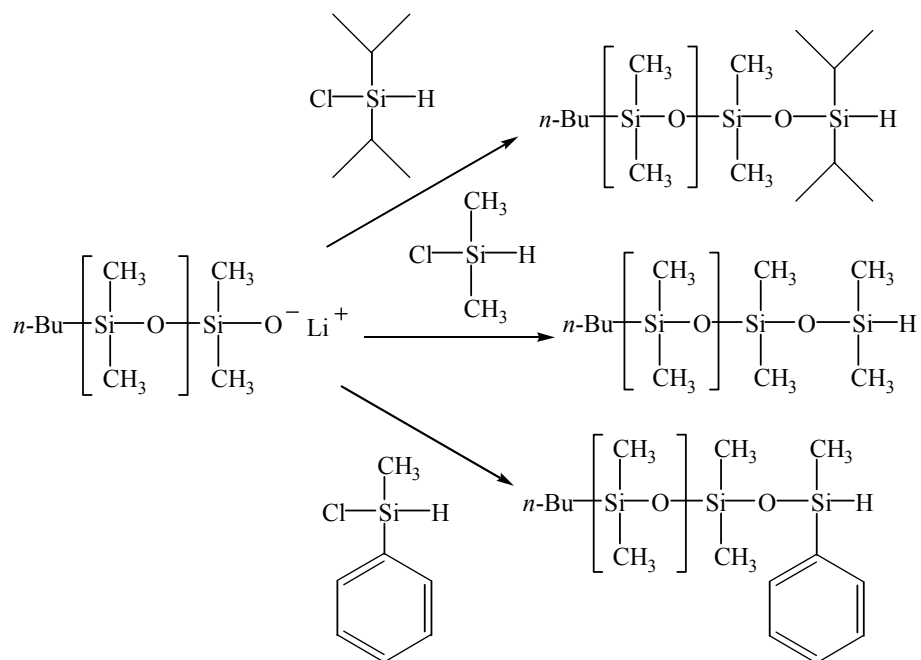


Figure 4-1. Terminating reactions with diisopropylchlorosilane, dimethylchlorosilane, and phenylmethylchlorosilane that were used to incorporate one hydrosilane functionality at the end of PDMS chains.

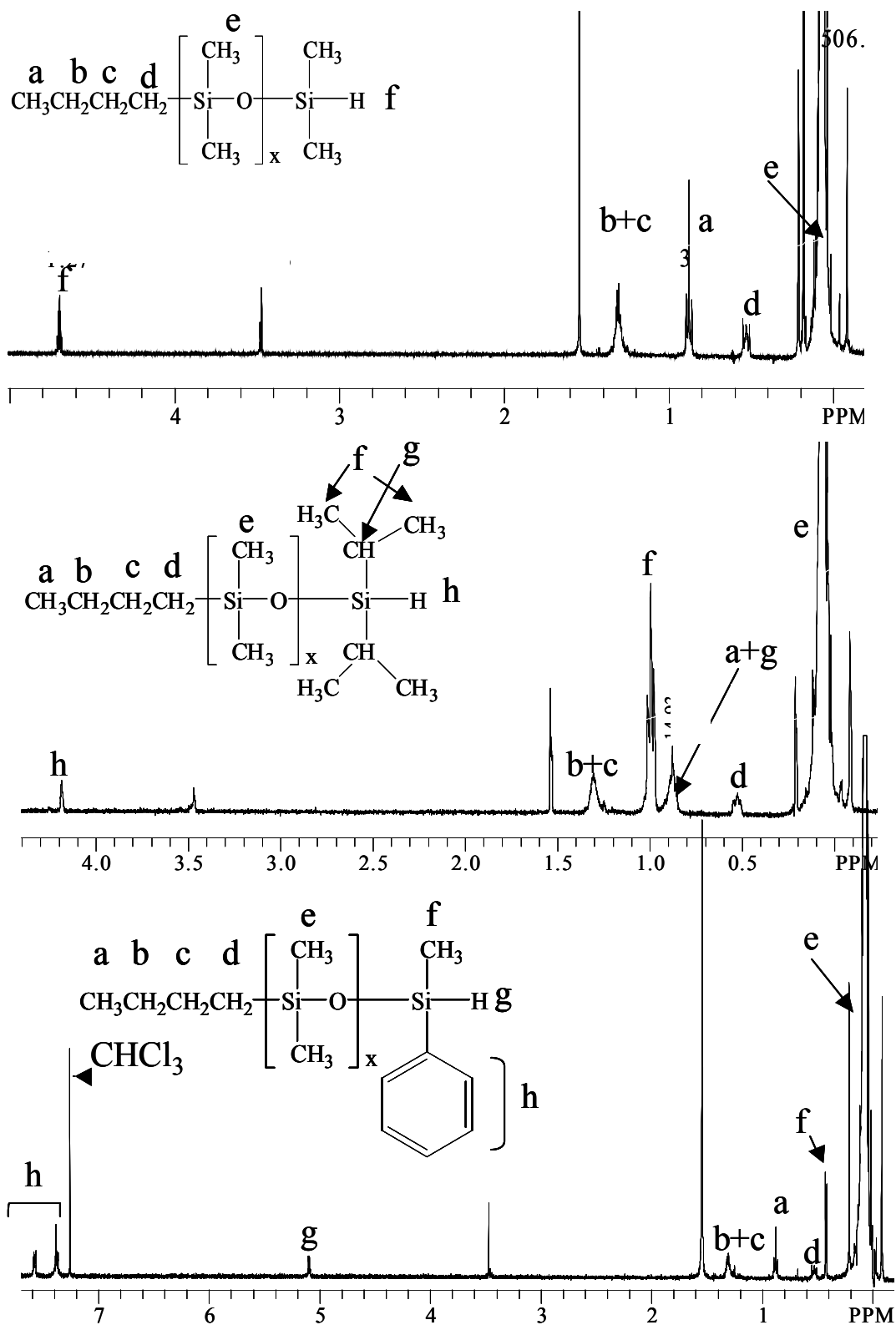


Figure 4-2. ^1H NMR spectra of dimethylsilane-terminated 6150 g mol^{-1} PDMS (top), diisopropylsilane-terminated $13,700 \text{ g mol}^{-1}$ PDMS (middle), and phenylmethylsilane-terminated $16,600 \text{ g mol}^{-1}$ PDMS (bottom).

Quantitative ^{29}Si NMR analyses (Figure 4-3) were utilized to support the molecular weight data derived from proton NMR, and to quantify the extent of Si-H functionalization (Table 4-1). For the DMCS-functionalized PDMS, the ^{29}Si NMR spectra displayed three resonances corresponding to the two terminal silicon atoms, $\text{Bu}(\text{Me})_2\text{SiO}-$ (8 ppm) and $\text{H}(\text{Me})_2\text{SiO}-$ (-7 ppm), and the silicon atoms of the repeat unit Me_2SiO_2- (-22 ppm). The ^{29}Si NMR spectra of the DIPCS and PMCS-functionalized PDMS were the same except for the Si-H silicon atoms that resonated at 3 and -14 ppm, respectively. By comparing the integrals of the terminal Si-H silicon atoms to the terminal $\text{Bu}(\text{Me})_2\text{SiO}-$ silicon atoms, it was determined that nearly one hundred percent Si-H functionality was achieved for these polymers under the given conditions.

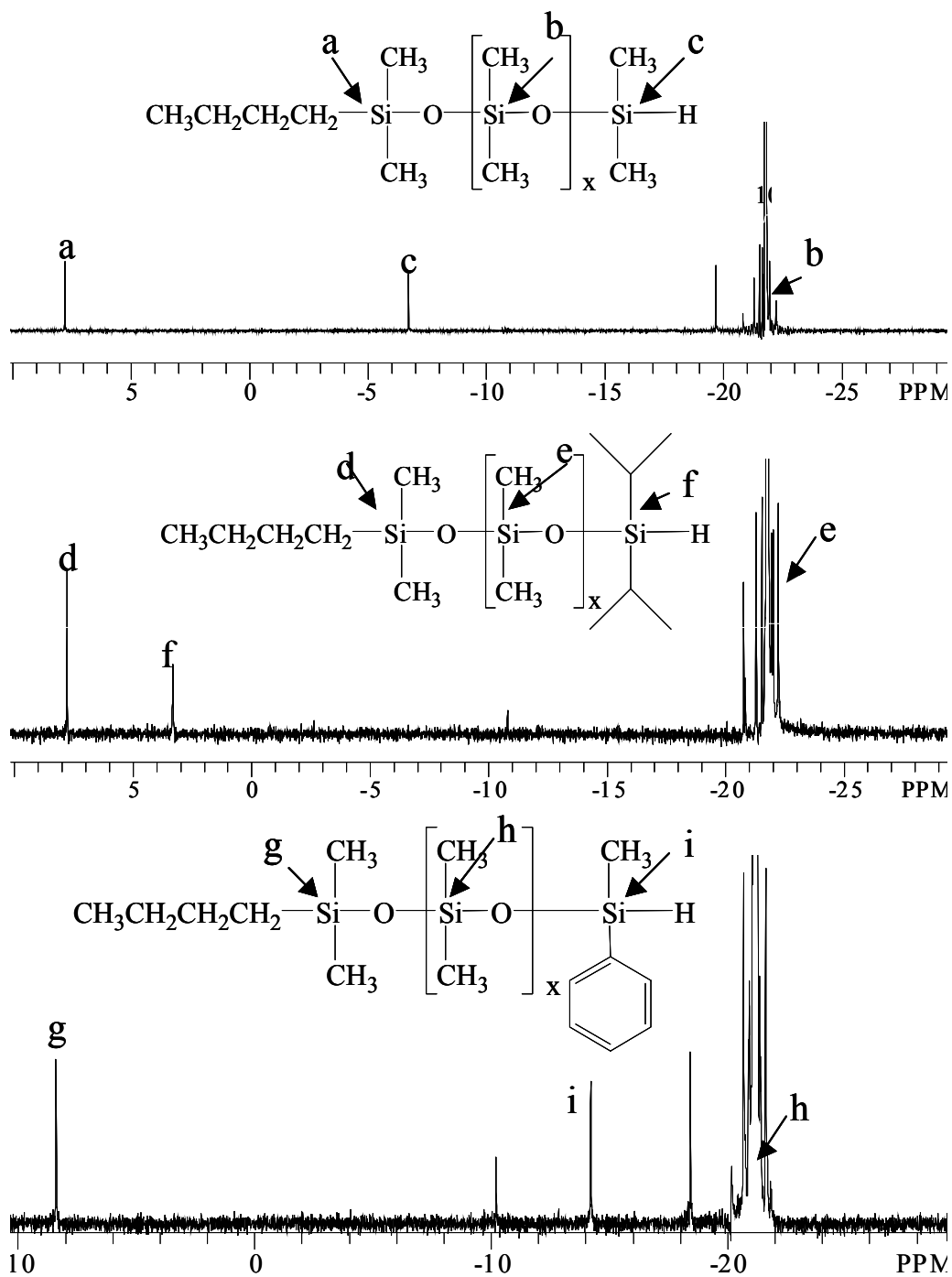


Figure 4-3. ^{29}Si NMR spectra of dimethylsilane-, diisopropylsilane-, and phenylmethylsilane-terminated PDMS.

The hydrosilane-functional polymers were also characterized by GPC. In all cases, narrow and unimodal molecular weight distributions were achieved, as was expected for living polymerizations (Figure 4-4). Since no chain coupling was observed, it was concluded that the reaction of lithium siloxanolate end groups with the Si-Cl bonds of the excess dialkylchlorosilane terminating reagents afforded quantitative termination. An effort was made to obtain absolute molecular weights by utilizing a viscosity detector in conjunction with a refractive index concentration detector. A Universal calibration curve was constructed from polystyrene standards. Although all of the peaks were narrow, the “absolute” values for M_n and M_w derived from the GPC did not match well with the NMR and targeted molecular weights (Table 4-2). This was attributed to the low viscosities of the PDMS oligomers that probably caused large errors in the on-line viscosities.

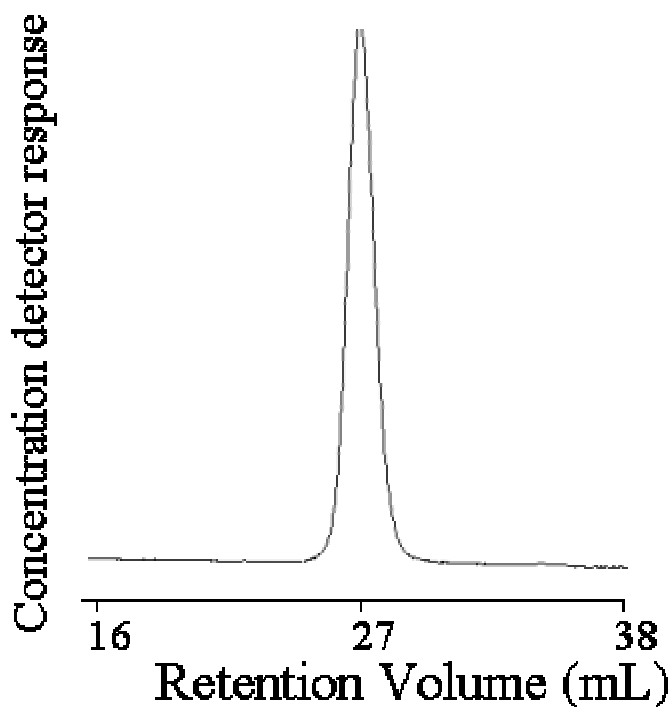


Figure 4-4. GPC chromatogram of 6150 g mol^{-1} dimethylhydrosilane-terminated PDMS.

The butyllithium initiators used for the living anionic polymerization of D_3 sometimes contain lithium hydroxide impurities in small quantities. This is because

butyllithium reacts very quickly with small amounts water over time to form lithium hydroxide and butane. This reaction decreases the concentration of active initiating species. To verify the butyllithium concentrations in the initiator solutions, they were periodically titrated using diphenylacetic acid via the method reported by Kofron and Baclawski.³³⁷ The titrations indicated that the butyllithium concentrations in hexane were consistent with the concentration reported by the supplier. However, it may be important to note that there was a small amount of white precipitate visible at the bottom of the otherwise clear yellow solution, and it was expected that this precipitate was lithium hydroxide. The agreement between the targeted molecular weights and those derived from ¹H and ²⁹Si NMR analyses reaffirms that the concentration of active butyllithium species was as expected.

It is known that the hydrosilane bond is very susceptible to base-catalyzed hydrolysis.^{338,339,340,341,342} In this reaction, one molecule of hydroxide base attacks the electropositive silicon atom, releasing a hydride ion that subsequently deprotonates a molecule of water forming hydrogen gas and reforming a molecule of hydroxide base. It has been determined that this hydrolysis reaction occurs by an S_N2 mechanism.³⁴³ For these reasons, it was necessary to prevent the interaction of the dialkylhydrosilane-terminated polymers with any type of base. Interestingly, the phenylmethylhydrosilane-terminated PDMS was less sensitive to base-catalyzed hydrolysis. This difference in reactivity was attributed to the electronegative nature of the silicon atom as a result of resonance in the phenyl ring (Figure 4-5).

³³⁷ Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879-1880.

³³⁸ Gilman, H.; Dunn, G. E. *J. Am. Chem. Soc.* **1951**, *73*, 3404-3407.

³³⁹ West, R. *J. Am. Chem. Soc.* **1954**, *76*, 6015-6017.

³⁴⁰ Noll, W. *Chemistry and Technology of Silicones*; Academic Press: New York, 1968.

³⁴¹ Pawlenko, S. *Organosilicon Chemistry*; de Gruyter: New York, 1986.

³⁴² Price, F. P. *J. Am. Chem. Soc.* **1947**, *69*, 2600-2604.

³⁴³ Price, F. P. *J. Am. Chem. Soc.* **1947**, *69*, 2600-2604.

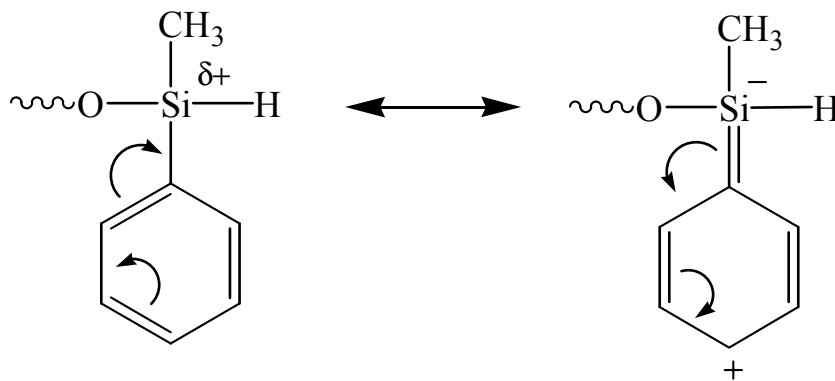


Figure 4-5. Proposed resonance structures for phenylmethylhydrosilane-terminated PDMS that illustrate the reduced sensitivity of the terminal silicon atom towards nucleophilic attack.

4.3.2 Synthesis of Hydroxyalkyl-Terminated Poly(dimethylsiloxane)

All the polymers in the series of hydrosilane-terminated PDMS with high degrees of functionality (Table 4-2) were reacted via hydrosilation reactions with allyloxyethanol (Table 4-3). These reactions were conducted in toluene at room temperature and proceeded to completion when the dimethylhydrosilane- and phenylmethylhydrosilane-functionalized polymers were used (Figure 4-6). The reactions were followed by monitoring the disappearance of the hydrosilane peak at ~ 4.7 (dimethylhydrosilane) or ~ 5.1 ppm (phenylmethylhydrosilane) in the ^1H NMR spectra as well as the appearance of new peaks corresponding to methylene groups in the hydroxyalkyl functional group (Figure 4-7). Completion of the reactions was also verified via ^{29}Si NMR by observing the disappearance of the peak corresponding to the hydrosilane silicon atom (Figure 4-8). Interestingly, following the addition of allyloxyethanol, the ^{29}Si NMR resonances of the two terminal silicon atoms overlap at 7 ppm.

Table 4-3. Characterization of hydroxyalkyl-terminated PDMS series.

Hydrosilane End Group	M _n by ¹ H NMR (g mol ⁻¹)	M _n by ²⁹ Si NMR (g mol ⁻¹)	M _n by GPC (g mol ⁻¹)	M _w /M _n
dimethyl	7340	6970	9740	1.00
dimethyl	9280	9360	13,000	1.00
dimethyl	22,600	27,200	27,400	1.01
phenylmethyl	9590	9640	12,100	1.03
phenylmethyl	18,400	21,200	20,600	1.01

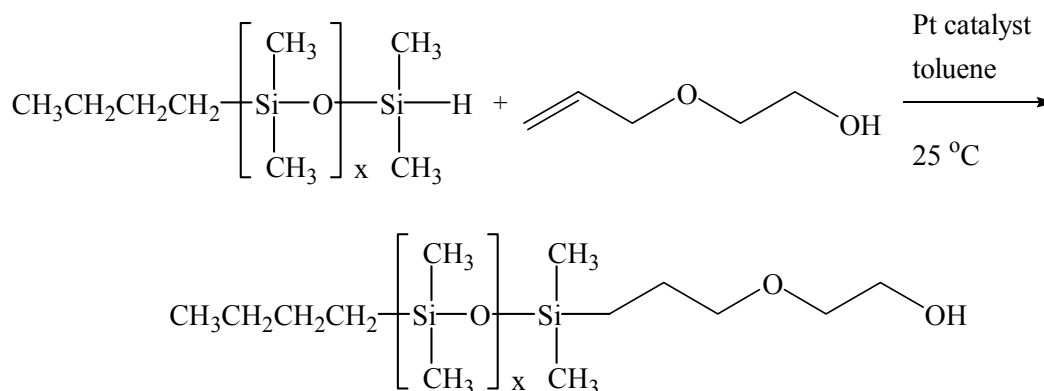


Figure 4-6. Reaction scheme for the synthesis of hydroxyalkyl-terminated PDMS by hydrosilylation of hydrosilane-terminated PDMS with allyloxyethanol.

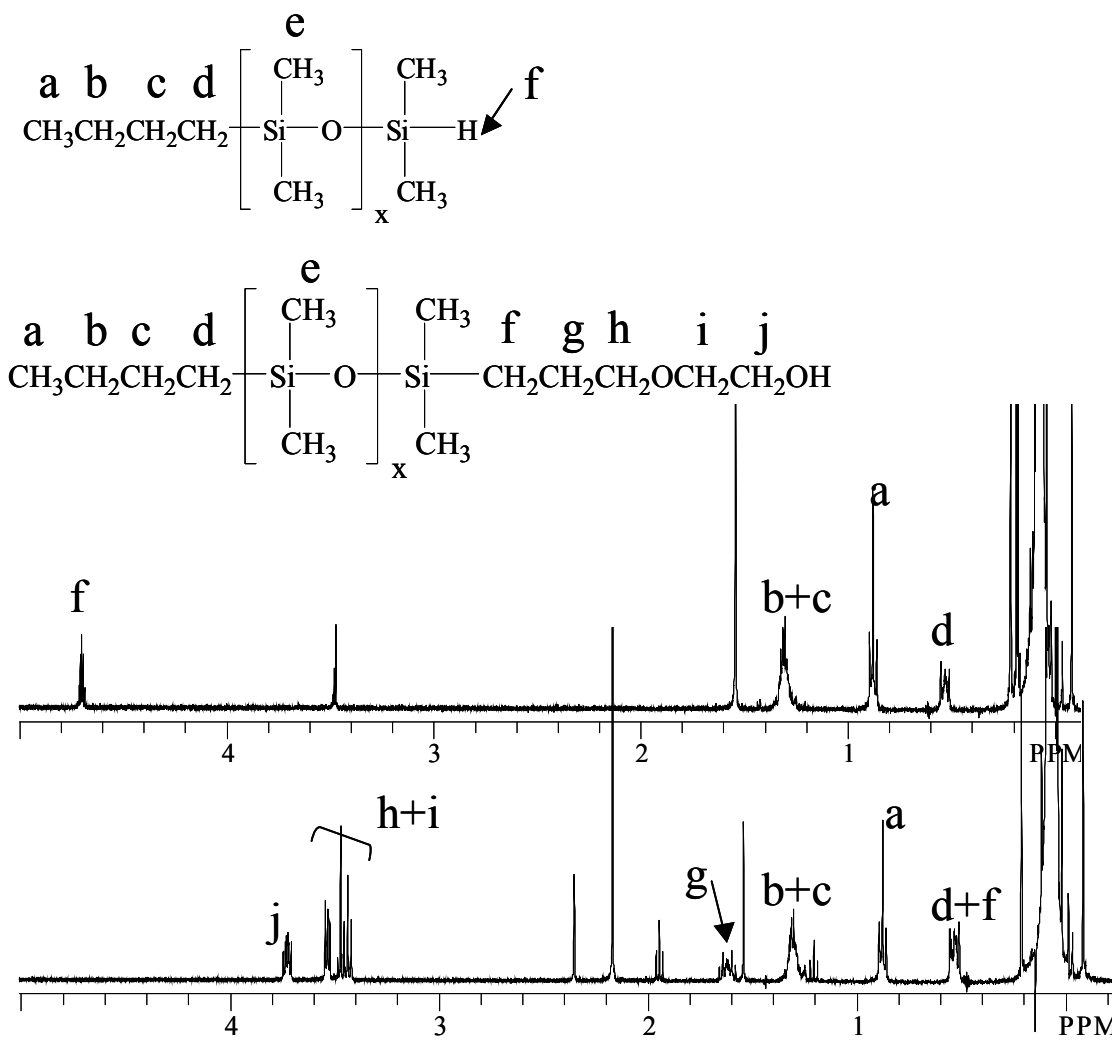


Figure 4-7. ^1H NMR spectra of 6150 g mol^{-1} dimethylhydrosilane-terminated PDMS before (top) and after (bottom) hydrosilation with allyloxyethanol.

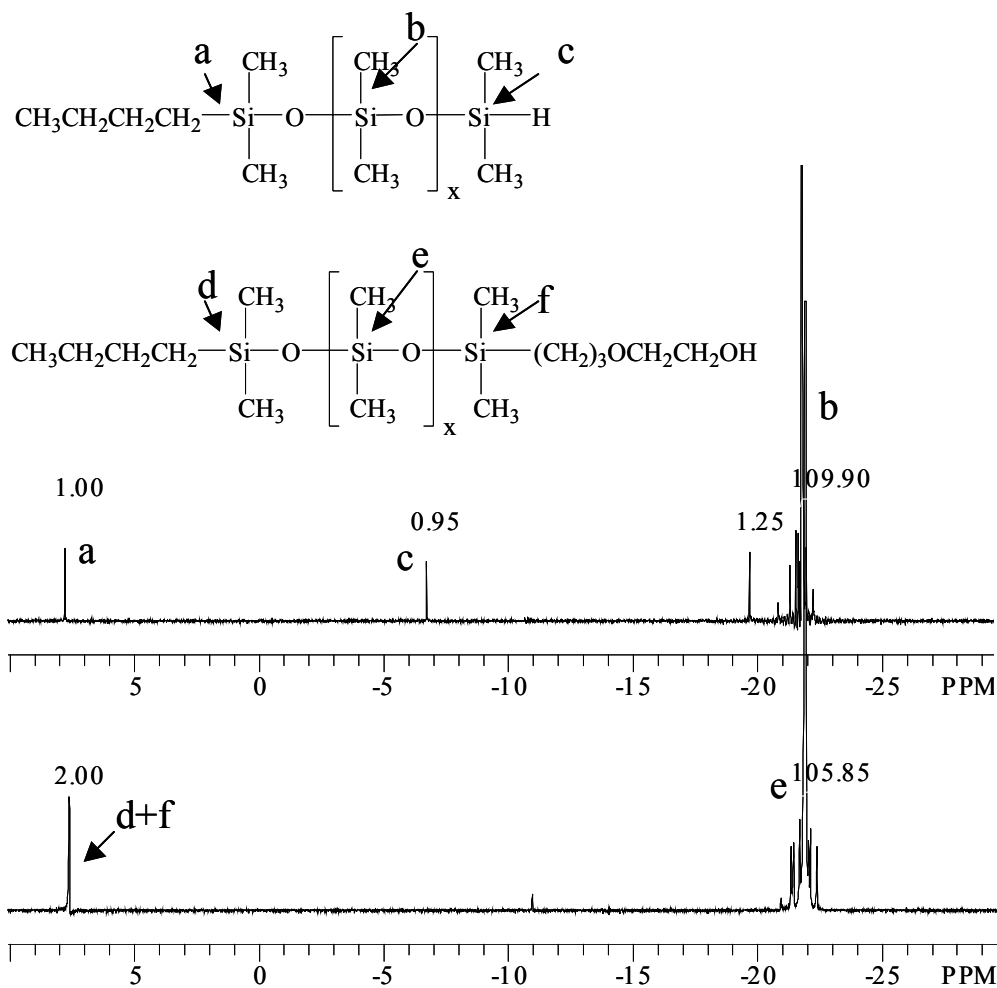


Figure 4-8. ^{29}Si NMR spectra of 6200 g mol $^{-1}$ dimethylsilane-terminated PDMS before and after hydrosilylation with allyloxyethanol showing integral values.

The PDMS was analyzed by FTIR spectroscopy before and after the hydrosilylation with allyloxyethanol (Figure 4-9). There was a distinct absorption band at 2126 cm^{-1} in the hydrosilane-terminated PDMS that corresponded to the Si-H stretching absorbance. Following hydrosilylation, this absorbance completely disappeared, providing further evidence that these hydrosilylation reactions proceeded to completion. There was no characteristic absorbance in the 3600 cm^{-1} region corresponding to $-\text{OH}$ stretching, however. The absence of this absorbance was attributed to the small quantity of hydroxyl groups relative to the polymer chain.

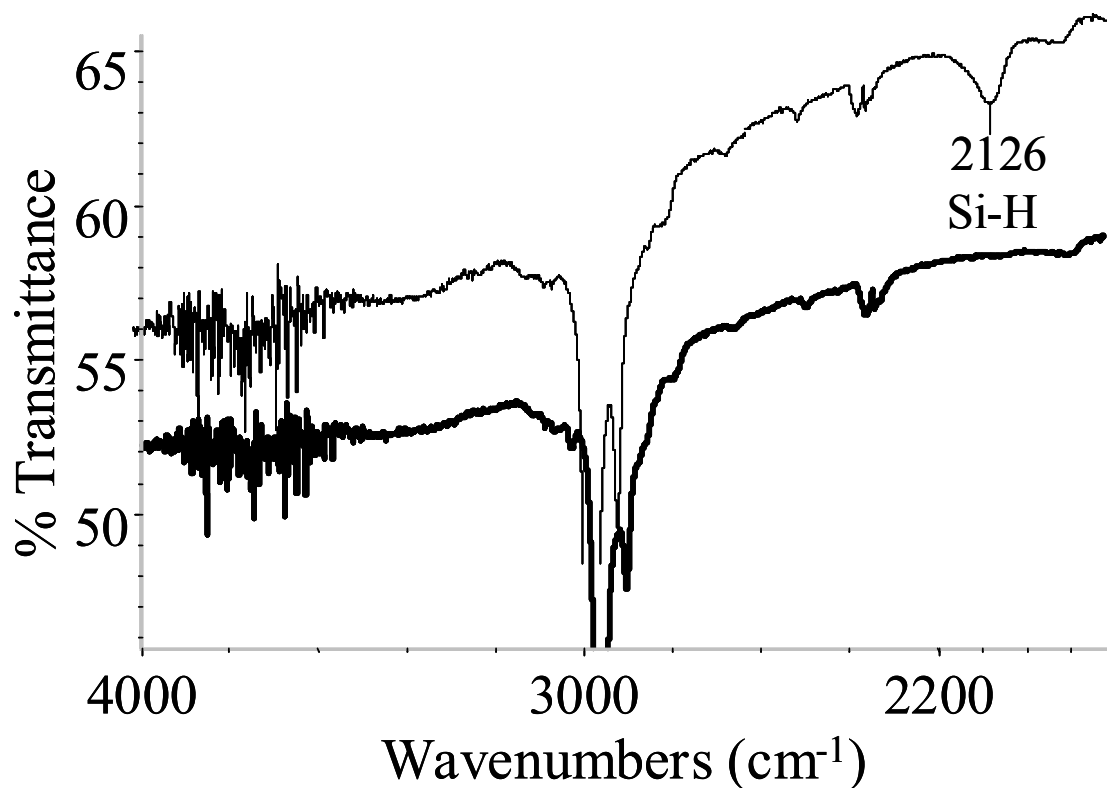


Figure 4-9. FTIR spectra of phenylmethylhydrosilane-terminated PDMS (top) and the same polymer following the hydrosilylation reaction with allyloxyethanol (bottom).

The hydrosilylation reactions with allyloxyethanol that were performed on the diisopropylhydrosilane-functionalized PDMS were unsuccessful. In an exemplary reaction, diisopropylhydrosilane-functionalized $13,660 \text{ g mol}^{-1}$ PDMS (0.5 g) was reacted in toluene (1 mL) with allyloxyethanol (4.3 μL , 40 μmol) using platinum divinyltetramethyldisiloxane catalyst (1 μL). There was no noticeable disappearance of the ^1H NMR hydrosilane peak at 4.2 ppm after stirring for 24 hours at room temperature. The reaction temperature was subsequently increased to 40 $^{\circ}\text{C}$ and stirred for another 24 hours after which time there was still no observable change in the ^1H NMR spectrum. It is proposed that the hydrosilylation reaction was obstructed by the steric bulk of the diisopropyl groups.

4.3.3 Copolymerization of ϵ -Caprolactone from a Hydroxyalkyl-Terminated Poly(dimethylsiloxane) Macroinitiator

The ring-opening polymerization of ϵ -caprolactone has been well documented.^{344,345,346} The first reported synthesis of ϵ -caprolactone monomer and its polymerization was in 1934 by Carothers.³⁴⁷ Poly(caprolactone) is particularly interesting because of its biodegradability^{348,349,350} and its propensity to form miscible blends with other polymers.^{351,352,353,354} Polymerization of ϵ -caprolactone can be initiated with carbanions, alkoxides, or hydroxyl groups.^{355,356} There have been several reports where hydroxyl-functionalized polymers have been successfully used to initiate the ring-opening polymerization of ϵ -caprolactone to produce block copolymers^{357,358} graft copolymers.³⁵⁹

In this study, hydroxyalkyl-terminated PDMS (PDMS-OH) oligomers were used as macroinitiators for the ring-opening polymerization of ϵ -caprolactone. The reactions were conducted using toluene as a solvent and were clear and colorless in appearance. The reactions were monitored by ¹H NMR by following the shift in the peaks associated with ϵ -caprolactone. Specifically, the peaks corresponding to the methylene adjacent to

³⁴⁴ Young, R. H.; Matzner, M.; Pilato, L. A. In *Ring-Opening Polymerization*; Gould, R. F., Ed.; American Chemical Society: Washington, D.C., 1977; Vol. 59, pp 152-164.

³⁴⁵ Lundberg, R. D.; Cox, E. F. In *Ring-Opening Polymerization*; Frisch, K. C., Reegen, S. L., Eds.; Marcel Dekker: New York, 1969; Vol. 2, pp 247-302.

³⁴⁶ van Natta, F. J.; Hill, J. W.; Carothers, W. H. *J. Am. Chem. Soc.* **1934**, *56*, 455.

³⁴⁷ van Natta, F. J.; Hill, J. W.; Carothers, W. H. *J. Am. Chem. Soc.* **1934**, *56*, 455.

³⁴⁸ Perrin, D. E.; English, J. P. In *Handbook of Biodegradable Polymers*; Domb, A. J., Kost, J., Wiseman, D. M., Eds.; Harwood: Amsterdam, 1997; pp 63-76.

³⁴⁹ Siparsky, G. L. In *Polymers from Renewable Resources: Biopolyesters and Biocatalysis*; Scholz, C., Gross, R. A., Eds.; American Chemical Society: Washington, D.C., 2000; Vol. 764, pp 230-251.

³⁵⁰ Tang, L.; Sheu, M. S.; Chu, T.; Huang, Y. H. *Biomaterials* **1999**, *20*, 1365-1370.

³⁵¹ Koleske, J. V. In *Polymer Blends*; Paul, D. R., Newman, S., Eds.; Academic Press: New York, 1978; Vol. 2, pp 369-389.

³⁵² Brode, G. L.; Koleske, J. V. *J. Macromol. Sci., Chem.* **1972**, *A6*, 1109-1144.

³⁵³ Kalfoglou, N. K. *J. Appl. Polym. Sci.* **1983**, *28*, 2541-2551.

³⁵⁴ Vion, J. M.; Jerome, R.; Teyssie, P.; Aubin, M.; Prudhomme, R. E. *Macromolecules* **1986**, *19*, 1828-1838.

³⁵⁵ McGrath, J. E. In *Ring-Opening Polymerization: Kinetics, Mechanisms, and Synthesis*; McGrath, J. E., Ed.; American Chemical Society: Washington, D.C., 1985; Vol. 286, pp 1-22.

³⁵⁶ Storey, R. F.; Taylor, A. E. *J.M.S. - Pure Appl. Chem.* **1998**, *35*, 723-750.

³⁵⁷ Han, C. J.; Lee, M. S.; Byun, D. J.; Kim, S. Y. *Macromolecules* **2002**, *35*, 8923-8925.

³⁵⁸ Ward, R. S.; Riffle, J. S. In *US Pat. 4,963,595*; Thoratec Laboratories Corp.: United States, 1990.

³⁵⁹ Chung, T. C.; Rhubright, D. *Macromolecules* **1994**, *27*, 1313-1319.

the ester oxygen in the monomer and polymer were used to calculate percent conversion. These two peaks were clearly separated and did not overlap with any other peaks. The monomer methylene peak at 4.25 ppm shifted upfield to 4.1 ppm upon polymerization. In one exemplary reaction, ϵ -caprolactone was copolymerized with a 7340 g mol^{-1} PDMS-OH oligomer and was reacted to 64% conversion (Figure 4-10). This reaction produced a PDMS-*b*-PCL copolymer with a targeted molecular weight of $12,040 \text{ g mol}^{-1}$ for the copolymer and 4700 g mol^{-1} for the PCL block. The copolymerization was stopped by cooling the reaction to room temperature.

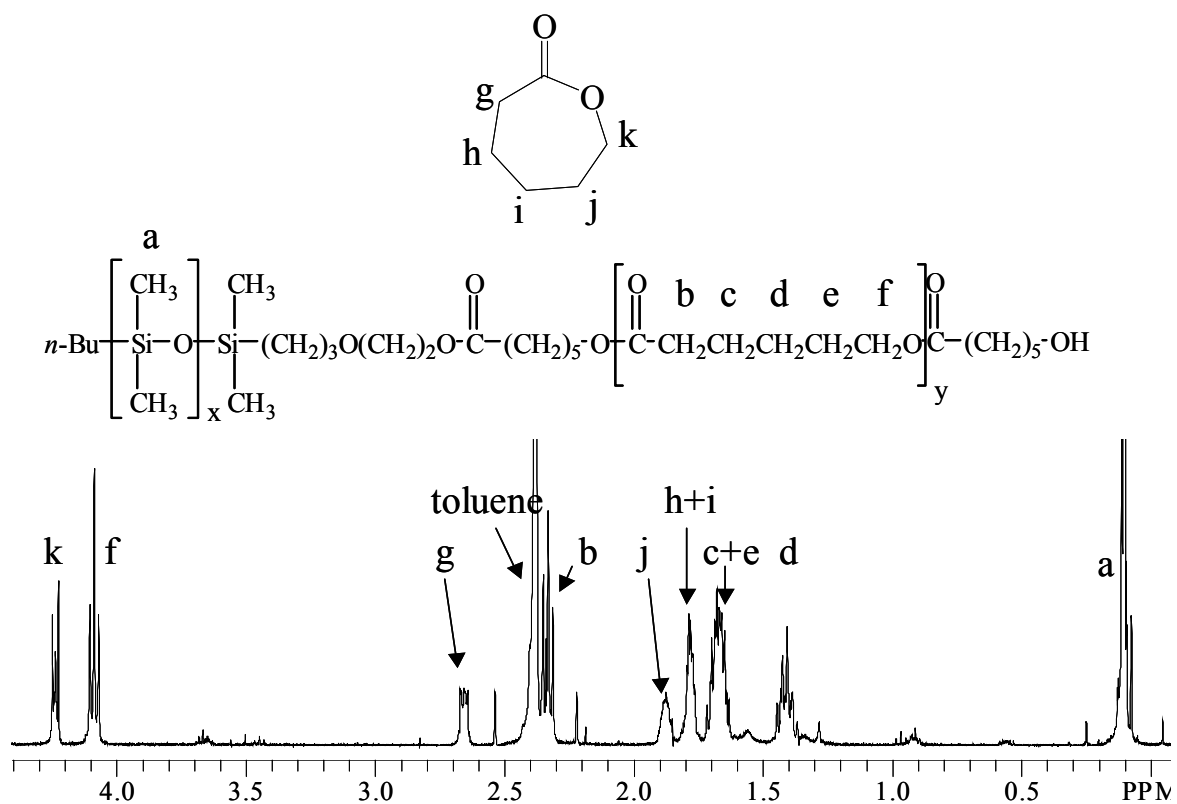


Figure 4-10. ^1H NMR spectrum of ϵ -caprolactone copolymerization reaction at ~64% monomer conversion.

^1H NMR analysis of the purified copolymer indicated that the copolymerization reaction was successful (Figure 4-11). The resonances corresponding to protons on the PCL repeat units were located at 4.0, 2.3, 1.6, and 1.4 ppm and the resonance corresponding to the protons on the PDMS repeat unit was located at 0.1 ppm. Small resonances due to the methylene groups in the ether linkage between the PDMS and PCL blocks (0.5, 3.4, 3.6, and 4.2 ppm) and the methylene group at the end of the PCL chain ($-\text{CH}_2\text{OH}$ at 3.6 ppm) were distinguishable. The most notable peak was labeled “j” in the ^1H NMR spectrum. Upon reaction with ϵ -caprolactone, this terminal methylene peak on the PDMS-OH shifted from ~3.8 ppm (Figure 4-7) to 4.2 ppm and no residual protons are notable at 3.8 ppm in the ^1H NMR spectrum of the copolymer. This information indicated that all of the available hydroxyl groups on PDMS were involved in the initiation of ϵ -caprolactone copolymerization. The experimental number average molecular weight of the PCL block (3640 g mol^{-1}) was calculated by comparison of the

PCL repeat unit peaks in the ^1H NMR spectrum to peaks “j”, “i”, “h”, and the terminal methylene peak on the PCL (Figure 4-11).

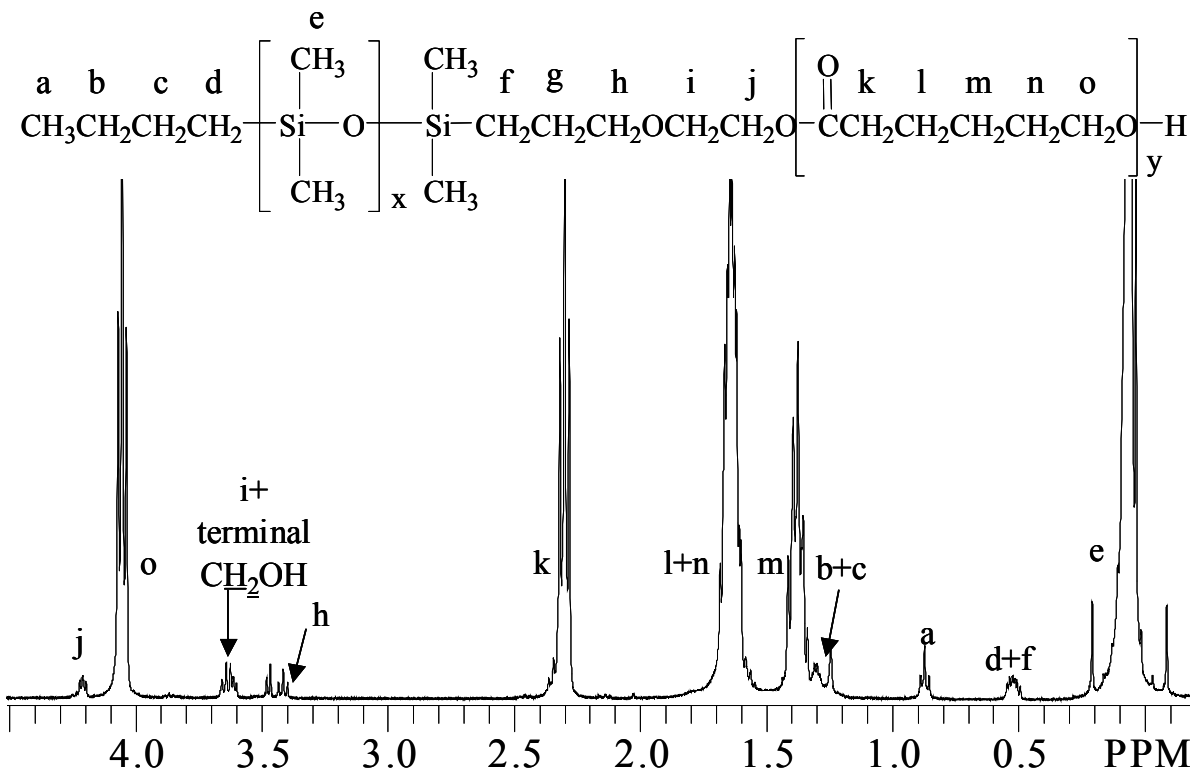


Figure 4-11. ^1H NMR spectrum of poly(dimethylsiloxane-*b*- ϵ -caprolactone).

GPC chromatograms of the PDMS-OH and the purified PDMS-*b*-PCL copolymer suggested that some PDMS macroinitiator remained after copolymerization (Figure 4-12). A small, low molecular weight shoulder on the GPC chromatogram of the diblock copolymer overlapped with the PDMS macroinitiator GPC chromatogram. This indicated that some of the PDMS chains did not initiate the polymerization of ϵ -caprolactone.

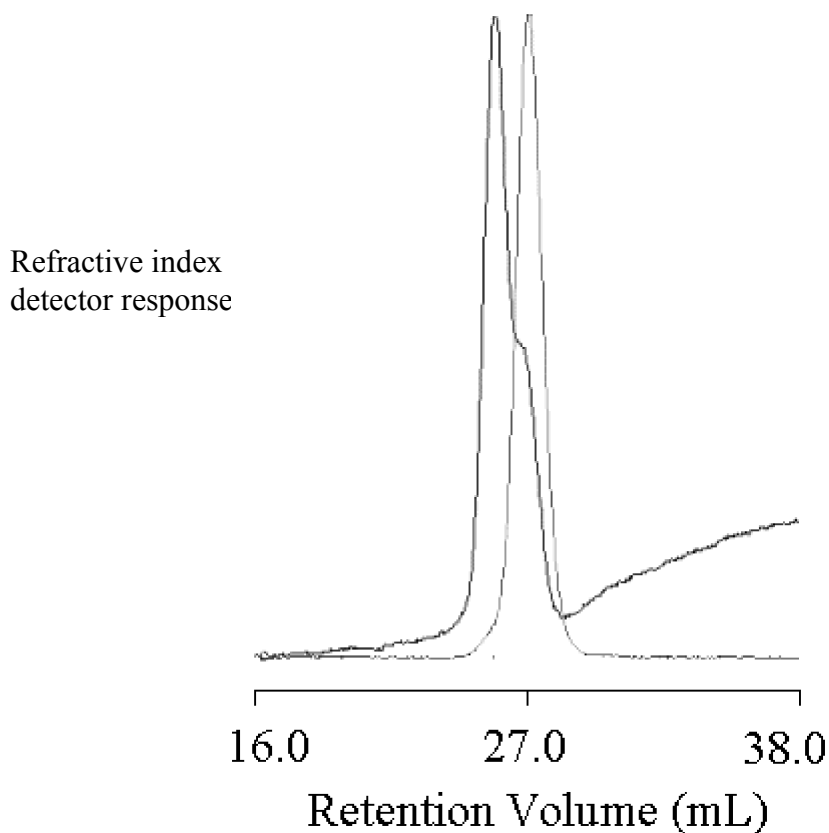


Figure 4-12. GPC chromatograms of hydroxyl-terminated PDMS (gray chromatogram) and PDMS-*b*-PCL (black chromatogram).

The number average weight for the copolymer determined by GPC was $12,300 \text{ g mol}^{-1}$, which is close to the molecular weight that was targeted ($12,040 \text{ g mol}^{-1}$). The number average molecular weight for the PCL block determined by $^1\text{H NMR}$ (3640 g mol^{-1}) was also within the targeted range (4700 g mol^{-1}). In addition, the $^1\text{H NMR}$ spectrum of the PDMS-*b*-PCL copolymer clearly showed that the terminal $\text{CH}_2\text{-OH}$ methylene group, originally at $\sim 3.8 \text{ ppm}$, was absent. These data suggested that the polymerization of ϵ -caprolactone was in fact initiated by the terminal $\text{CH}_2\text{-OH}$ group on PDMS, not by residual water. If residual water had initiated the polymerization, the molecular weight of PCL would not have been as close to the targeted molecular weight and the GPC chromatogram would have been broader. Previous work has shown that water-initiated ϵ -caprolactone polymerizations resulted in polymers with broad molecular

weight distributions.³⁶⁰ Initiation with water produced PCL chains with one carboxylic acid head group and one hydroxyl tail group. It was proposed that condensation polymerization of these two functional groups caused the broadening in the molecular weight distribution. In the present research, the GPC chromatogram suggested a narrow molecular weight distribution, disregarding the low molecular weight shoulder.

The small shoulder on the GPC chromatogram was probably from PDMS chains from the original D₃ polymerization terminated with DMCS that were not appropriately functionalized. The 7340 g mol⁻¹ hydroxyalkyl-terminated PDMS used in this copolymerization was prepared from a 6400 g mol⁻¹ dimethylhydrosilane-terminated PDMS that contained between 6-10% chains (as determined by ¹H and ²⁹Si NMR) that were not hydrosilane-functional. These PDMS chains did not participate in the hydrosilation reaction with allyloxyethanol. Therefore, these chains were not hydroxyalkyl-terminated and were incapable of initiating the polymerization of ε-caprolactone.

4.4 Conclusions

Methods were developed for preparing monohydroxyalkyl-terminated PDMS via a hydrosilation reaction of dimethyl- and phenylmethylhydrosilane-terminated PDMS with allyloxyethanol. The platinum-catalyzed hydrosilation reactions with allyloxyethanol were unsuccessful when diisopropylhydrosilane-terminated PDMS was used. The slower reactivity toward hydrosilation reactions in the diisopropylhydrosilane-PDMS was attributed to the steric bulk of the diisopropyl groups that impeded coordination with the platinum catalyst. Copolymerization of ε-caprolactone using the PDMS-hydroxyalkyl group as a macroinitiator further proved the practicality of this PDMS-functionalization method.

³⁶⁰ Storey, R. F.; Taylor, A. E. *J.M.S. - Pure Appl. Chem.* **1998**, *35*, 723-750.

5 Concluding Remarks and Recommendations for Future Work

A method was developed for the preparation of magnetic PDMS fluids. These fluids contain magnetite nanoparticles sterically stabilized with carboxylic acid-functionalized PDMS oligomers. PDMS-magnetite nanoparticle complexes were prepared by the interfacial reaction of PDMS-carboxylate groups in an organic phase with aqueous dispersions of cationic magnetite nanoparticles. The PDMS-magnetite complexes were characterized using transmission electron microscopy (TEM) to verify particle size and shape, elemental analysis to determine the concentration of magnetite, and vibrating sample magnetometry to determine the saturation magnetization. PDMS-magnetite complexes containing up to 67 wt% magnetite with magnetizations of ~ 52 emu gram⁻¹ were prepared. The magnetite nanoparticles were 7.4 ± 1.7 nm in diameter. Calculations using TEM and elemental analysis data suggested that the complexes prepared using mercaptosuccinic acid-functionalized PDMS (PDMS-6COOH) complexes contained unbound carboxylic acid groups whereas the mercaptoacetic acid-functionalized PDMS (PDMS-3COOH) complexes did not. Also, calculations showed that the PDMS-3COOH and PDMS-6COOH covered the same surface area per polymer chain on the surface of the magnetite nanoparticles. The calculations were supported by molecular models and FTIR analyses. Molecular models based on a magnetite binding site density of 5.2 sites nm⁻² suggested that the distance between carboxylic acids on a mercaptosuccinic acid group was too small to allow both acids to bind to magnetite. On the other hand, the models suggested that the mercaptoacetic acid-functionalized PDMS could cover all of the magnetite binding sites in a 1:1 ratio of acids:binding sites. The complexes were dispersed into PDMS carrier fluids by ultrasonication, resulting in magnetically-responsive PDMS fluids. These magnetic PDMS fluids could be formulated to be viscous fluids, displayed high magnetizations, and were biocompatible, which made them strong candidates for magnetic fluids to be used in the treatment of retinal detachment.

For the PDMS magnetic fluids to be safely used in retinal detachment treatment, their properties must be well-defined. Therefore, future research should be focused on clearly defining the relationships between PDMS carrier fluid molecular weight, concentration of PDMS-magnetite complex, viscosity of the fluids, and dispersion quality. Preliminary studies into these relationship suggested that there was a decrease in viscosity in going from pure PDMS carrier fluid to fluids containing 10 wt% PDMS-magnetite complex. The cause of this decreased viscosity was unknown. Initial studies also suggested that poor dispersions may have been prepared when lower molecular weight PDMS carrier fluids ($\sim 5000 \text{ g mol}^{-1}$) were used. Different methods for dispersing the complexes into the carrier fluids should be investigated since this may affect dispersion quality.

Additional future research should focus on studying dispersion quality in the PDMS magnetic fluids. Poor dispersions resulted when magnetite particles aggregated. As the particles aggregated, they began to sediment out of the PDMS carrier fluid. This process of sedimentation would be detrimental if it occurred within the eye since the PDMS carrier fluid would no longer be held in place with the permanent magnet. Therefore, the PDMS would be free to disperse throughout the vitreous region and would impair vision. Methods such as small angle neutron scattering may be useful in studying dispersion quality.

Magnetite particles ($\sim 100 \text{ nm}$ to $1 \text{ }\mu\text{m}$ in diameter) were synthesized by partial reduction of goethite (FeOOH) and crystallization from glycol/water solutions under pressure. Two methods for particle growth were investigated in which the crystallization medium was varied by adjusting the amount of water (method 1) or the concentration of itaconic acid (method 2) in the reaction mixture. Magnetite particles prepared by method 1 ranged in size from $\sim 400 \text{ nm}$ to $1 \text{ }\mu\text{m}$ in diameter where the larger particles were prepared from reactions that contained the most amount of water (8% water by volume). Method 2 afforded particles that were $\sim 100\text{-}200 \text{ nm}$ in diameter. The magnetite particle surfaces were analyzed by x-ray photoelectron spectroscopy (XPS) to determine the concentration of elements at the surface. Carboxylic acid-functionalized poly(ϵ -caprolactone) (PCL) stabilizers could be adsorbed onto the magnetite particles with moderately clean surfaces (30% carbon) that were prepared by method 1. The binding

energies for carbon on the surface of the magnetite verified that the method 1 particles were coated with PCL and the method 2 particles were coated with itaconic acid. The magnetite particles displayed magnetic hysteresis. The particles were dispersed into vinyl ester resins by ultrasonication. The PCL-coated particles prepared by method 1 remained dispersed for up to 24 hours and the degree of stability was dependant upon PCL molecular weight. It was demonstrated that the ~100 nm particles remained dispersed for three days without agitation. It was proposed that magnetic induction heating of the magnetite particles by the application of an AC magnetic field could be used to cure the vinyl ester resins. The ~100 nm itaconic acid-coated particles satisfied the three requirements for magnetic induction heating applications: 1) the magnetite particles displayed hysteresis 2) the particles were well-dispersed and 3) the particles remained dispersed for extended periods.

For magnetic induction heating applications, future work should focus on determining the relationships between magnetite particle size, concentration of magnetite in the dispersions, and the amount of heat that can be generated by application of an AC magnetic field. Ideally, an adequate concentration of magnetite should be added to the vinyl ester resins to allow for sufficient curing temperatures without compromising the mechanical properties of the resulting composite material.

Furthermore, the itaconic acid-coated 100 nm particles may provide an interesting avenue to the chemical modification of magnetite nanoparticles for various applications. The molecular models described in chapter 2 suggested that carboxylic acid groups separated by two carbons could not bind to two protonated magnetite surface sites because they were not separated by a sufficient distance. The carboxylic acid groups of itaconic acid are, in fact, separated by two carbon atoms, suggesting that only one of the acids may bind to magnetite. One carboxylic acid would, therefore, be left free on the surface of magnetite and potentially available for further chemical modification. For example, amine-terminated poly(ethylene oxide) could possibly be reacted with the particles affording water-dispersible 100 nm magnetite particles. Reactions with other amine- or hydroxyl-terminated polymers would allow for the preparation of magnetite particles with tailored surface properties.

A method was developed for the synthesis of monohydroxyalkyl-terminated PDMS. This was achieved by the living polymerization of D_3 and termination with dimethylchlorosilane, phenylmethylchlorosilane, or diisopropylchlorosilane (DIPCS). Platinum-catalyzed hydrosilation of the hydrosilane-terminated PDMS with allyloxyethanol afforded a systematic series of hydroxyalkyl-terminated PDMS. The reactions with DMCS- and PMCS-functionalized PDMS were successful, but the hydrosilation of sterically-hindered DIPCS-functionalized PDMS was unsuccessful since no reaction was observed. Hydroxyalkyl-terminated PDMS oligomers were successful in initiating the stannous octoate-catalyzed copolymerization of ϵ -caprolactone, which afforded PDMS-*b*-PCL diblock copolymers of controlled composition. Therefore, it was demonstrated that monohydroxyalkyl-terminated PDMS could be used as precursors for block copolymers.

Future work in this area should focus on studying the potential applications for the monohydroxyalkyl-functionalized PDMS oligomers. For example, the feasibility of using the functional oligomers for the preparation of graft copolymers and as endcapping reagents in step-growth polymerizations should be investigated. In addition, the platinum-catalyzed hydrosilation of allyloxyethanol with the hydrosilane-functionalized poly(siloxanes) could possibly be applied to poly(dimethylsiloxane-*co*-methylhydrosiloxane) random copolymers. This would result in polysiloxanes with hydroxyalkyl groups branching from the main siloxane backbone.

6 Vita

Kristen Wilson O'Brien was born Kristen Susanne Wilson on April 3, 1977 in Doylestown, Pennsylvania to parents Ed and Dot Wilson. She grew up in rural Quakertown, PA with her three older brothers Jonathan, Tom, and Joe Wilson where she spent much of her childhood playing soccer and climbing trees. She graduated from Quakertown High School in 1995. She enrolled in the Honors program at James Madison University in Harrisonburg, Virginia and graduated with a B.S. degree in Chemistry in 1999. While studying at JMU, Kristen obtained professional experience through summer internships at the U.S. Geological Survey in Reston, VA and at Merck and Co., Inc. in West Point, PA. She decided to follow an interest in polymer chemistry by pursuing a doctoral degree at Virginia Polytechnic Institute and State University in nearby Blacksburg, VA. She worked under the advisement of Dr. Judy Riffle and her work focused on functionalized poly(dimethylsiloxane) synthesis and the preparation of stable magnetic nanoparticle dispersions for biomedical applications. On May 16, 2003, Kristen married Emmett O'Brien, a chemical engineering graduate student of Dr. T.C. Ward at Virginia Tech. Upon completion of her work at Virginia Tech, Kristen will begin an NRC postdoctoral fellowship at the National Institute of Standards and Technology in Gaithersburg, Maryland where she will study nanocomposites for use in dental restorative materials.