Synthesis and Characterization of Novel Silicone Graft Copolymers

by

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ABSTRACT

Silicone compounds have a very low surface energy due to highly flexible Si-O-Si backbone and large number of $-CH_3$ groups, but these compounds are extremely hydrophobic and thus have limited applications in aqueous formulations. Modification of such silicone compounds by grafting hydrophilic chains provides a wide range of silicone products called "Silicone Surfactants". Silicone surfactants are surface active agents which get adsorbed at the air-water interface thereby, reducing the interfacial tension. Some of the larger applications of silicone surfactant are in the manufacture of plastic foams, in personal care products and as spreading and wetting agents (Hill, R.M, 2002).

In this thesis, a series of silicone surfactant graft copolymers were synthesized via hydrosilylation reaction. Poly(ethylene glycol) (PEG) of different chain length was grafted to a hydrophobic Poly(methylhydrosiloxane) (PMHS) backbone to improve the final hydrophilicity. Also, a positively charged quaternary ammonium salt (allyltriethylammonium bromide) was grafted to the PMHS backbone. The objective of this thesis was to synthesize polymers in predefined ratios of the above mentioned side groups and utilize these polymers to-

1) Study the effect of PEG chain length and its composition on the hydrophilicity of the polymer.

2) Study the effect of PEG: ammonium salt ratio on the surface tension of aqueous systems.

Analysis of FT-IR and ^{1}H NMR spectra of the polymers confirmed the predicted structure. The absence of characteristic Si-H absorbance peak at 2160 cm^{-1} in FT-IR spectra indicates consumption of silane groups along the polymer backbone. The actual moles of the side chain grafted on the backbone are calculated by ^{1}H NMR peak integration. The results of contact angle studies indicated an increase in hydrophilicity with an increase in the composition of PEG in molecule. A 2*2 factorial DOE analysis reported that the fraction of Si-H bonds converted to PEG grafts was the critical factor towards increasing the hydrophilicity (p value of 0.015). Surface tension studies report that the air-water interfacial tension of the synthesized polymers is between 28mN/m – 45mN/m. The amount of Si-H was concluded to be the deciding factor in lowering the surface tension.

DEDICATION

To my parents

S. S. Singh

Suchita Singh

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CHAPTER 1

INTRODUCTION

1.1 Motivation

Polymers are commonly used in the personal care and cosmetic industry, as surfactants, emulsifiers, rheology modifiers, film formers and thickeners. They can perform these functions while providing additional consumer benefits such as extended product wear, improved product aesthetics, ease of application, enhanced skin, hair and nail protection etc. Within a series of polymers, structural variations and modifications, such as, degree of polymerization, branching, type of substituent group, and ratio of different blocks within copolymers, highly affect the nature of the polymer and thus dictate the applications they are designed for.

Several articles have been published relating the advancements and structure–function relationship of polymers specific to personal care and cosmetic industry (Gruber, J. V, 1999; Lochhead, R. Y, 2007; Clarke, T. M, 1993; Butuc, G., Morrison, D. S, 2007). A book based on the international symposium on "Polymers for cosmetic and Personal care" provided significant motivation for this work (Patil, A., et al; 2013). The book covers multiple facets of the use of polymers in personal care industry and recent advances in how specific properties of polymers have been used to provide some unique benefits in personal care products. An understanding of the polymer structure-function relationship and the ability to alter these structures for specific applications translated into the present work.

As mentioned, polymers can be used for various functions in personal care industry. A large variety of polymers such as poly(α-olefins), acrylate copolymers, silicone-acrylate copolymers, polyester resins and polyurethanes are used as film formers, these polymers do not necessarily form a self-standing film but can improve the spreadability of cosmetic formulation. The films formed can serve various functions such as extend sunscreen protection, impart oil or water resistance and improve product aesthetics. Polymers are also used in cosmetic products such as lipsticks and lip-gloss as transfer resistance agents. When a cosmetic product does not deposit on food or cloth or when it resists removal, it is called "transfer- resistant". A trimethylsiloxysilicate polymer, due to its highly cross-linked structure is an extremely efficient

transfer resistant. In shampoos, soaps and detergents, polymers are used as surface active agents. Poly(ethylene oxide) (PEO), poly (propylene oxide) (PPO) and their copolymers are some examples of surface active polymers commonly used in personal care industry. Though PEO and PPO differ only in a single methyl group, this small difference has high implications. PEO homopolymers are soluble in water at all molecular weights; in contrast, PPO is hydrophobic. Block copolymerization of EO/PO produces an entire range of amphiphilic nonionic surfactants. Though such surfactants are conventionally used, they are less surface active as compared to a comparatively new class of surfactants called "silicone surfactants" which have low surface energy $-CH_3$ groups attached to a highly flexible Si-O-Si backbone. The above mentioned polymers along with additional examples are tabulated in Table 1.1 which relates functional properties of the polymers to the consumer benefits.

Table 1.1: Cosmetic Ingredient Functional Properties and Consumer benefits

(Patil, A., Sandewicz, R.W., 2013, p 17)

Functional Property	Consumer benefits	Polymeric examples
Film formation	Extended product wear; enhanced skin protection; improved product aesthetics	Nitrocellulose, polybutene, polyester resins, acrylates copolymers, silicone acrylate copolymers, polyurethanes
Transfer resistance	Tenacious product adhesion; enhanced skin protection; reduction in number of product application cycles	Trimethylsiloxysilicate (MQ resins), silicone elastomers
Surface activity	Ease of application; enhanced product shelf life	PEG/PPG block copolymers
Rheological control	Ease of application; enhanced product shelf life	Hydroxypropylmethylcellulose, hydroxyethyl cellulose, polyacrylic acid, polyamides

Gloss reduction	Mitigation of appearance of undesirable skin surface defects	Polyurethane crosspolymers
Pigment surface treatment	Ease of application; novel visual aesthetics	Reactive silanes

1.2 Silicone Polymers

Silicone polymers are a class of inorganic polymers with a Si-O-Si backbone. In the past, silicones frequently used in personal care applications were homopolymers of dimethylsiloxanes known as poly(dimethylsiloxane) (PDMS). The highly flexible silicone and oxygen backbone of PDMS has the ability to orient itself in such a way, so as to allow maximum adsorption of low surface energy methyl groups attached to it, thus having a very low surface tension. Moreover, due to a very low glass transition temperature (T_g) PDMS is liquid at room temperature and is thus not sticky, therefore, having a desired dry feel character associated with it. In order to take advantage of these numerous properties desirable for various personal care products, alternative silicone compounds for various applications were explored. The use silicone compound as surface active agents is one such application. These surface active agents called "surfactants" consist of a hydrophilic and hydrophobic part which when dissolved in liquid reduces its surface tension. The first silicone surfactant was introduced to the marketplace in 1950s for manufacturing of polyurethane foam (Herrington et al., 1991); the surface activity of silicones in a non-aqueous medium formed the basis of their use in polyurethane manufacture. Though silicones are surface active even in an aqueous medium, its strong hydrophobic nature limits its applications. Poly(ethylene glycol) is grafted to the silicone to form amphiphilic silicone surfactants. These silicone surfactants have certain unique properties, since their hydrophobic group is silicone; they are able to lower the surface tension to ≈20mN/m as compared with ≈30mN/m for conventional hydrocarbon surfactants causing them to be surface active in both aqueous and non-aqueous media. Though silicone surfactants are superior to hydrocarbon surfactants, the two show similarities in many common features of surfactants. For both types of

surfactants, micelle formation is represented by a break in their surface tension versus log concentration curve. Moreover, the variation in critical micelle concentration (cmc; defined as the concentration of surfactant above which micelles forms and there is no further decrease in surface tension) with molecular structure is similar for both types of surfactants, that is, within a homologous series larger hydrophobic groups lead to smaller cmc value.

1.3 Problem Statement

This thesis is focused on synthesizing silicone surfactant polymers. Poly(ethylene glycol)mono methyl ether(PEG_{11}, M_n 550) or triethylene glycol mono methyl ether (PEG_3) and a quaternary ammonium salt (*N,N,N*- triethylprop-2-en-1-ammonium bromide) is grafted on to the silicone backbone via hydrosilylation reaction. Poly(ethylene glycol)s and quaternary ammonium salt are attached to impart hydrophilic characteristics in a surfactant, also, the positive charge on the quaternary ammonium salt provides conditioning nature (Kollmeier, B. J, 1986).

Since, these polymers were designed for personal care products; the area of application for the polymers is skin and hair. The function of a conditioner is to improve the quality (condition) of the biological surface with which it interact thus reducing the surface damage. Cationic polymers such as quaternary ammonium silicones are very effective conditioning agents because of their substantivity to the respective substrate, directly attributable to electrostatic interactions between the negatively charged damaged sites on the hair shaft and positive charge on the polymer. Moreover, the germicidal properties associated with quaternary ammonium salts (Lu et al., 2007) and their ability to reduce surface tension made them a suitable source of positive ions. In the past, in order to take advantage of the various desirable properties offered by otherwise hydrophobic silicones, they were used as emulsion in aqueous medium in addition to conventional anionic surfactants being primary surfactants. However, the presence of anionic surfactants shifts the hydrophilic-lipophilic balance (HLB) and splits the emulsion thus reducing the shelf life of the product. Modification of silicone by grafting PEG results in a surfactant that is soluble in aqueous formulations and thus can be used with anionic surfactants. Moreover, since silicone surfactants have high surface activity they are used in lesser quantities in the formulations.

The objective of this thesis was to synthesize polymers in predefined ratios of the above mentioned side groups and utilize these polymers to-

1) Study the effect of PEG chain length and its composition on the hydrophilicity of the polymer.

2) Study the effect of PEG: ammonium salt ratio on the surface tension of aqueous systems.

1.4 Organization of Thesis

This thesis is structured into 5 chapters. Chapter 1 provides an introduction to the use of polymers in personal care industry, particularly silicone polymers and delivers an overview of the objective of this thesis. Then, chapter 2 delves deeper into silicone surfactants; it gives an overview of the commonly used methods to synthesize such polymers with special emphasis on hydrosilylation mechanism. The reaction scheme adopted to synthesize these polymers is discussed with detailed experimental procedure. Furthermore, the two series of polymers synthesized are introduced at the end of chapter 2.

Chapter 3 discusses the characterization techniques adopted to confirm the structure of the synthesized polymers. Fourier Transform Infrared spectroscopy (FT-IR) is utilized for qualitative analysis of the polymers. However, it is not sufficient to quantitatively analyze the structure. ^{1}H Nuclear Magnetic Resonance (NMR) Spectroscopy is used to calculate the actual number of repeating units in the backbone grafted with side chains. The combination of these analyses is used to calculate the molecular weight of the polymers and the composition of unreacted hydrosilane and grafted side chains.

Chapter 4 presents techniques of physical characterization of polymers. Contact angle and surface tension studies are conducted to determine the wettability and surface activity properties of the polymers. The theory of both these techniques is discussed along with laboratory procedures for sample preparation and measurement methods. Results are analyzed and discussed at the end of chapter 4.

Chapter 5 summarizes and concludes the results of this thesis and explores the future scope of research.

CHAPTER 2

SYNTHESIS OF POLYMERS

2.1 Introduction

Silicone surfactants are prepared by attaching one or more polar groups to the permethylated siloxane backbone. The three most widely used methods of attaching these polar groups are discussed below. However, the first step in the synthesis of siloxane surfactants is to prepare a siloxane backbone containing reactive sites such as SiOH, SiOR (where, R is usually $-CH_3$ or $-CH_2CH_3$) and SiH. Ionic and nonionic groups are then attached to these reactive sites by the techniques described below. Non-ionic surfactants are prepared usually by the direct synthesis routes of transesterification and hydrosilylation whereas, the indirect method involving a two step synthesis, is used for attaching ionic species to the backbone. The three routes are (Randal M.Hill, Silicone surfactants: Vol. 86; p 7-13):

1) Transesterification – Directly by reaction of $SiOR^1$ and R^2OH

The method of transesterification involves coupling of alkoxymethylsiloxane polymers and hydroxyl-terminated polyoxyalkylenes to form siloxane polymers. The following reaction represents the same;

$$SiOR_1 + R_2OH \longrightarrow SiOR_2 + R_1OH$$
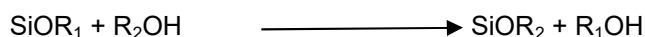
Where R_1 is usually $-CH_3$ or $-CH_2CH_3$ and R_2 is polyalkylene oxide.

Siloxane surfactants prepared by this method contain Si-O-C linkages, which hydrolyze in water to generate a silanol and alcohol. Therefore, the products of this reaction are suitable for non-aqueous applications such as polyurethane foam manufacturing. Since, in the current work, designing polymers for aqueous formulations was of interest, alternative approaches were explored.

2) Hydrosilylation – Directly by reaction of Si-H and $CH_2=CHCH_2R$; where R is a polar group

Hydrolytically stable siloxane surfactants can be prepared by hydrosilylation. This method involves the reaction of reactive Si-H bonds, such as; poly(methyl hydrosiloxane) with allyl-

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functionalized polar groups to form siloxane surfactants. Numerous works involving amphiphilic polymers with polar groups attached to siloxanes using hydrosilylation have been reported in past. These polymers are designed and modified for various applications. A poly(dimethyl siloxane) modified by grafting a poly(ethylene glycol) (PDMS-g-PEG), has the ability to form nano tanks of self-assembled vesicles for hydrophobic drugs (Li et al., 2010); novel synthesis techniques involving hydrosilylation are used to generate PMHS-g-PEG-co-PMVS copolymer membranes with enhanced water cohesion and lubrication properties (Ding et al. ,2012). Moreover, due to the extraordinary flexibility of siloxanes, synthesis of such polymers as solid polymer electrolytes has also been reported.

3) Two step synthesis using reactive intermediate- Indirectly by attaching a reactive group such as epoxy via hydrosilylation and then using that reactive group to attach the polar group.

Two step synthesis routes via formation of reactive intermediate are used to attach polar groups that are incompatible with hydrosilylation reaction conditions. This process involves the addition of a reactive group to the backbone and then a subsequent reaction to attach polar groups. A detailed literature review showed most of the work for attaching quaternary ammonium groups to the siloxanes followed this synthesis technique. Hou and Kan synthesized polysiloxanes with quaternary ammonium groups using allyl glycidyl ether as the reactive intermediate, followed by a ring opening reaction of the epoxide group with diethyl amine and quaternization with benzyl chloride (Hou, Z. and Kan, C., 2015). However, literature also supports the use of hydrosilylation for attaching such reactive ionic groups (Tong et al., 2003).

In this thesis, novel siloxane polymers were grafted with either allyl functionalized poly(ethylene glycol)mono methyl ether(PEG_{11}, M_n 550) or triethylene glycol mono methyl ether (PEG_3, M_n 164) and a quaternary ammonium salt (*N,N,N*- triethylprop-2-en-1-ammonium bromide) via hydrosilylation and, thus, this method is discussed in detail in the following section. To our knowledge, there have been no earlier attempts to simultaneously graft these groups to the PMHS backbone.

2.2 Hydrosilylation

Hydrosilylation describes the addition of hydrosilanes across carbon-carbon multiple bonds under catalysis by transition metal complexes. A simple model of this reaction is given below where heptamethyltrisiloxane is used to hydrosilylate allyl alcohol in presence of Pt catalyst.

$$(Me_3SiO)_2MeSiH_3 \ + \ CH_2 =\!\!=\!\!= CHCH_2OH \ \xrightarrow{\quad Pt \quad} \ (Me_3SiO)_2MeSi(CH_2)_3OH$$
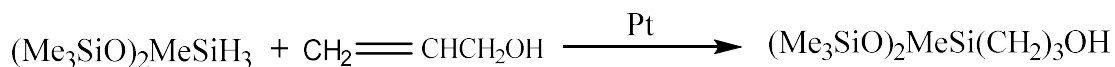
A group VIII transition metal complex is used to catalyze the hydrosilylation reaction. Numerous reports on hydrosilylation and various forms of catalysis have been published and summarized in articles (Patai, S. and Rappoport, Z., 1989). Complexes of Ni, Pt, Pd and Rh have been widely studied for hydrosilylation. A Pt compound such as hexachloroplatinic acid (H_2PtCl_6), platinumdicyclopentadienyldichloride [Pt(dcp)] and platinumdivinyltetramethyldisiloxane [Pt(dvs)] are most commonly used. Hydrosilylation is an exothermic reaction with heat of reaction of 117.15 KJ/mol. Various solvents, such as tetrahydrofuran (THF), isopropyl alcohol (IPA), and toluene, are used depending upon the compatibility of the reactants. These solvents act as heat sink for energy generated during the reaction. The work of Zhang and Laine provides a comparison between different combinations of the aforementioned Pt complexes and solvents for these reactions (Zhang, C., Laine, R.M., 2000).

The mechanism for hydrosilylation of unsaturated olefins or polyethers by homogenous catalysis using transition metal complex is described by Chalk and Harrod (Chalk, A.J., Harrod, J.F, 1964). Oxidative addition of the hydrosilane to a metal complex, which is low in oxidation state activates the hydrosilane and is the most important step in hydrosilylation. This leads to the formation of hydrido-silyl complex (I) coordinated with substrate alkene. The complex I undergoes insertion of alkene into M-H bond forming alkyl-silyl species (II) .Reductive elimination of the alkyl and silyl ligands from complex II results in the formation of final product. The following sequence shows elemental reactions in a transition metal complex catalyzed hydrosilylation.
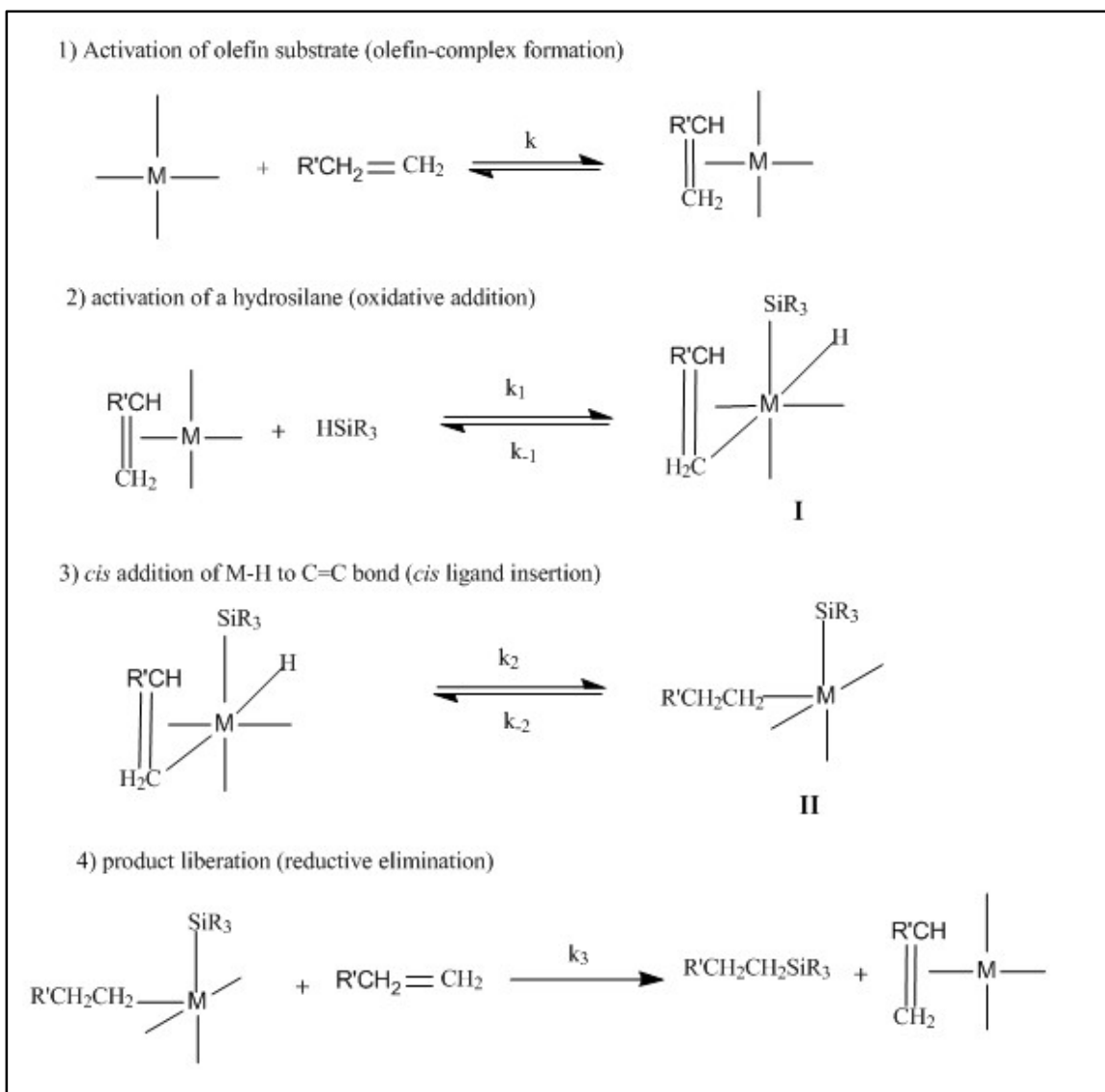
Figure 2.1.Hydrosilylation reaction mechanism

(Ojima, I, Yamamoto, K. ,Kumada, M. Aspects of homogeneous catalysis: A series of advance, 2012, Vol 3, p 188)

Although, the mechanism of the hydrosilylation reaction is usually depicted as shown in Figure 2.1, it is often accompanied with competing side reactions. Isomerization of the terminal olefinic groups is favored at high temperatures (> 80°C) resulting in retardation/termination of hydrosilylation reaction. Since, this reaction has been well studied over the years; it was determined that the addition of excess of allyl-containing compounds will reduce the propensity for the competing isomerization reaction. Another side reaction that can occur is silylation,

wherein the hydrosilane reacts with hydroxyl group on terminal carbons in polyethers to form alkoxysilane. This can be controlled by protecting the active hydrogen in unsaturated alcohols. For this work, methyl terminated poly(ethylene glycols) were used to eliminate the possibility of silylation byproducts. Furthermore, residual hydrosilane functionalities can lead to hydrolysis of Si-H in presence of moisture to form silanol and hydrogen gas.

2.3 Reaction Scheme and Polymers Synthesized.

The process of hydrosilylation requires three steps:

1) Preparation of hydrosilane intermediate

2) Preparation of allyl substituted derivatives of polar groups.

3) Hydrosilylation of second compound to first one to form final polymer

Hydrosilane intermediates can be synthesized by several different processes. The most popular method involves hydrolysis of hydridochlorosilanes. Hydridomethyl siloxanes are prepared commercially by hydrolysis of $HMeSiCl_2$ in presence of Me_3SiCl as shown in equation 2.1. Trimethylchlorosilane serves as end groups to control the molecular weight of the polymer during the polymerization reaction.

$$2Me_3SiCl + \ (w + x)HMeSiCl_2 \xrightarrow{\text{Excess } H_2O} Me_3SiO(HMeSiO)_xSiMe_3 + \ w(HMeSiO)_y$$

$$+2(w + 1 + x) \ HCl \quad \ldots\ldots\ldots\ldots\ldots\ldots.2.1$$
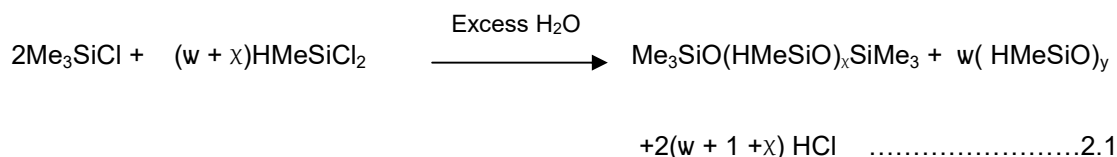
For the current work, poly(methylhydrosiloxane) (PMHS) end capped with trimethylsilane was directly obtained from Gelest. ^{1}H NMR spectroscopy (Figure 2.2) of the sample indicated 20 repeating units (n= 20). The allyl substituted derivatives of the polar groups were prepared in the laboratory, and then attached subsequently to the PMHS according to the procedure described in section 2.4. The overall reaction scheme is shown in figure 2.3.

Figure 2.2. ^{1}H NMR spectrum of PMHS

Figure 2.3. Overall Reaction scheme

2.4. Experimental Section

2.4.1 Materials

Poly(methylhydrosiloxane) (PMHS, M_n-1700-3200) was obtained from Gelest. Poly(ethyleneglycol)mono methyl ether(PEG_{11}, M_n 550) and triethylene glycol mono methyl ether were obtained from Sigma- Aldrich. Platinum divinyltetramethyldisiloxane [Pt(dvs)] (also known as Karstedt's catalyst 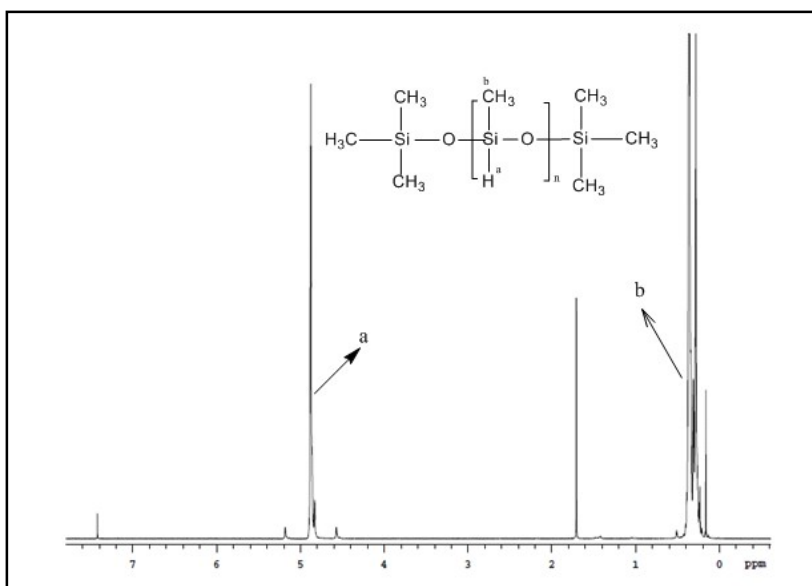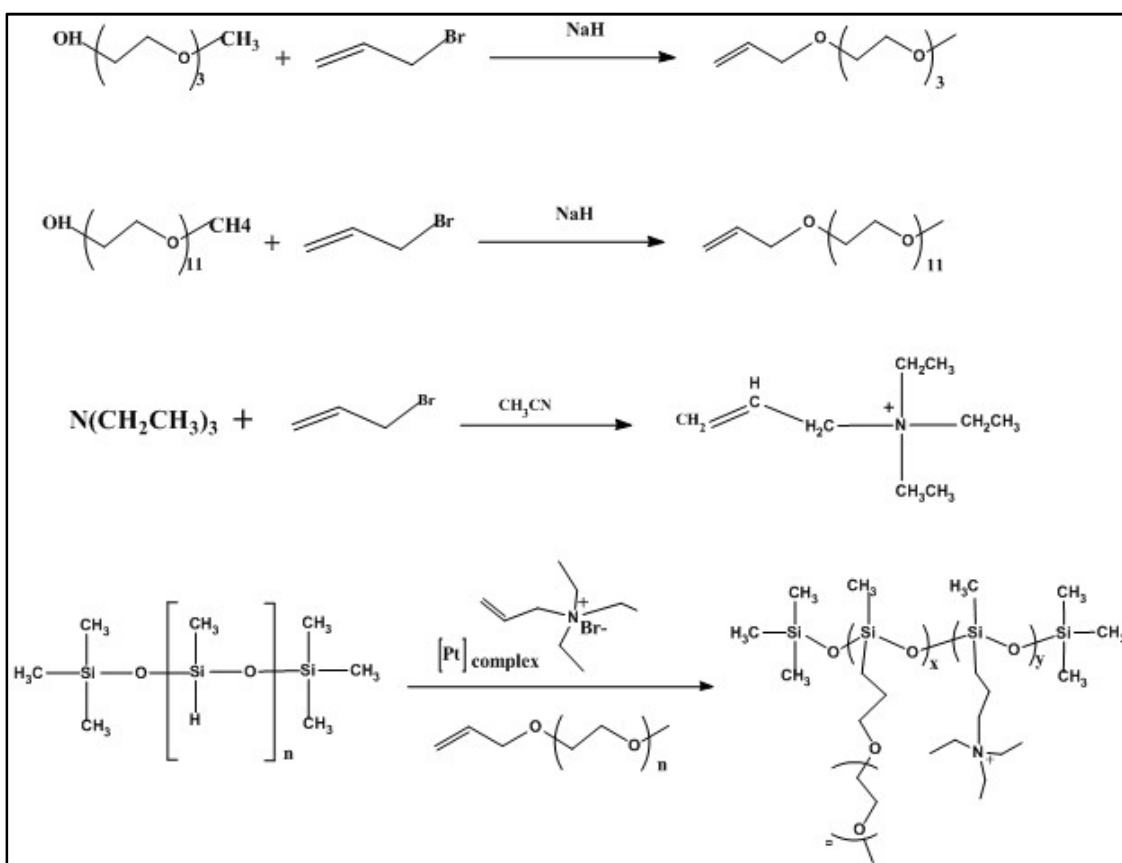), 3% in xylene solution, allyl bromide, 60% dispersion of sodium hydride (NaH) in mineral oil, triethylamine and NMR grade deuterated chloroform were also supplied by Sigma-Aldrich. Diethyl ether, chloroform, THF, toluene and acetone were ACS reagent grade, obtained from Fisher Scientific, and used without any further purification.

2.4.2 Synthesis of unsaturated polyethylene glycol (ALPEG)

Poly(ethylene glycol)allyl methyl ether ($ALPEG_{11}$) was synthesized according to literature protocol (Hooper et al.,2001). A solution of 0.06 mol of poly(ethylene glycol) methyl ether ($Mn=550$ g/mol) was added drop wise to a suspension of NaH (0.12 mol) in THF (50 mL) maintained at 0ºC. The mixture was stirred at 180 rpm for 3 h followed by dropwise addition of a solution of allyl bromide (0.06 mol) in THF (50 mL). The resulting mixture was warmed to room temperature and stirred for 18 h. The solution was concentrated using rotatory evaporation to yield an orange oil. This orange oil was then dissolved in water and unreacted PEG was removed by washing with 50 mL of toluene three times. The desired product was then extracted from the water layer using chloroform (3*200 mL). The organic layer was then dried with $MgSO_4$ and concentrated using rotatory evaporation followed by vacuum drying. 14.85 g of pale yellow colored product ($ALPEG_{11}$) was obtained.^{1}H NMR spectroscopy of the product confirmed the structure and the conversion of PEG_{11} to $ALPEG_{11}$ was determined to be 81%.

Triethylene glycol allyl methyl ether ($ALPEG_3$) was synthesized by the same procedure where 0.06 mol of triethylene glycol mono methyl ether was used instead of poly(ethylene glycol methyl ether). The final yield was11.32 g. ^{1}H NMR spectroscopy of the product confirmed the structure and the conversion was determined to be 78%. Figure 2.4 shows the ^{1}H NMR spectra for $ALPEG_3$ and $ALPEG_{11}$.

^{1}H NMR (CDCl$_3$),δ (ppm): 5.85 (m,1H) , 5.15 (dd,2H), 3.95(d,2H), 3.45-3.65(m,12 H), 3.35(s,3H).
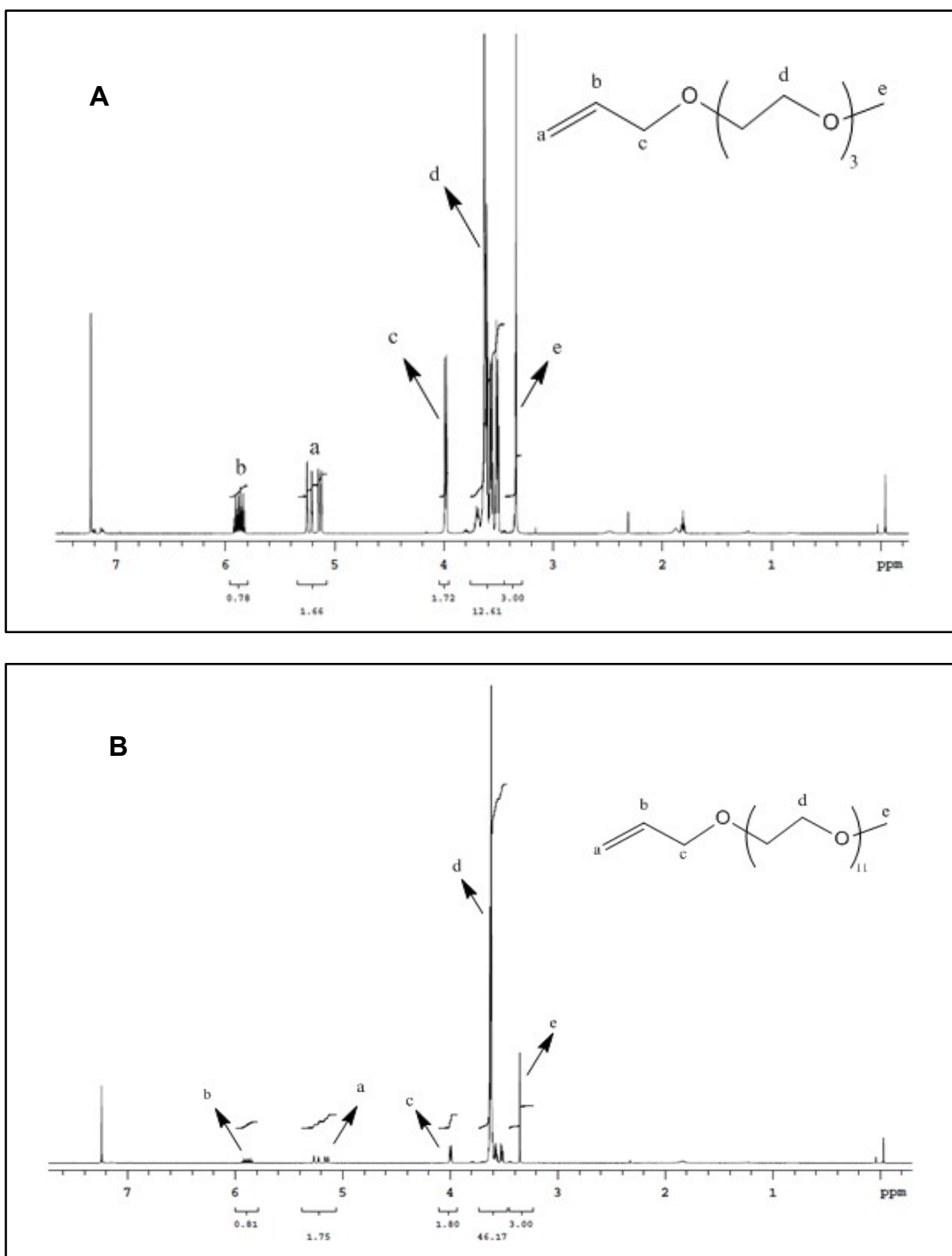
Figure 2.4. ^{1}H NMR spectra of A) ALPEG$_3$ and B) ALPEG $_{11}$

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2.4.3. Synthesis of Allyltriethylammonium bromide (ALQUAT)

ALQUAT was synthesized by the method described by Tong et al. (Tong et al., 2003). Allyl bromide (6.0 g, 0.05 mol) was added dropwise to a solution of triethylamine (10 g, 0.07 mol) in acetonitrile (70 mL). The mixture was allowed to reflux for 10 h. After the reaction was completed, the product was precipitated in 50 mL of diethylether. The precipitate was filtered and dried under vacuum to yield 9.28 g of white solid. The structure was confirmed by ^{1}H NMR spectroscopy and the spectrum of the product is shown in Figure 2.5.

^{1}H NMR (CDCl$_3$),δ (ppm):6 (m,1H) , 5.8 (dd,2H), 4.15(d,2H), 3.45(q,6 H), 1.4(t,9H).
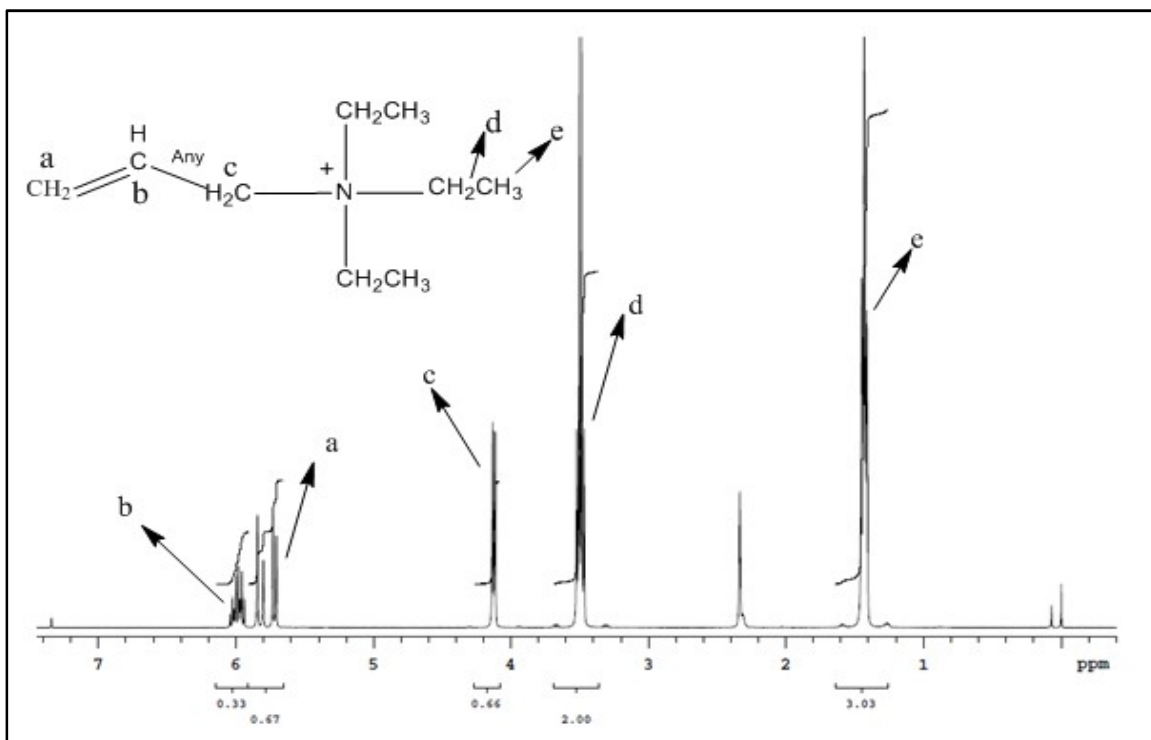
Figure 2.5. ^{1}H NMR spectrum of ALQUAT

2.4.4 Synthesis of polymers

Two series of polymers were synthesized. Series I include, ALPEG$_3$ or ALPEG$_{11}$ grafted to the PMHS backbone. Whereas, series II includes ALPEG$_3$ and ALQUAT or ALPEG$_{11}$ and ALQUAT attached to the PMHS backbone. Table 2.2 and 2.3 shows the amounts of these

reactants required to synthesize the polymers of the desired ratio. A general procedure for the synthesis of polymers is outlined here.

A solution of PMHS in toluene (10 mL) was placed in a two neck round bottomed flask equipped with a reflux condenser. The desired quantities of ALPEG$_3$, ALPEG$_{11}$ and ALQUAT was added to the reaction vessel. The contents of the reactor were mixed for 15 min to dissolve the reactants in solvent. The reactor was carefully degassed and backfilled with nitrogen three times using the freeze-pump-thaw cycle. Then, the reactor was heated to 75°C and 250 µL of Pt(dvs) catalyst was added via syringe. Hydrosilylation is an exothermic reaction and slight effervescence was observed following the addition of the catalyst. The reaction was allowed to run for 18 h under reflux. Volatiles were evaporated under vacuum to obtain final product. The structure of all synthesized copolymers was confirmed by ^{1}H NMR spectroscopy and fourier transform infrared spectroscopy (FT-IR). A detailed analysis of graft copolymer structures is given in chapter 3.Table 2.1 gives the nomenclature for both series of polymers. This nomenclature will be used throughout this thesis.

Table 2.1: Naming of synthesized polymers

Series	PMHS: Ammonium: PEG Ratio	Sample code	
	PEG Chain Length	PEG (3)	PEG (11)
Series I	1:0:10	1:10 (3)	1:10 (11)
	1:0:20	1:20 (3)	1:20 (11)
Series II	1:5:15	1:5:15 (3)	1:5:15 (11)
	1:10:10	1:10:10 (3)	1:10:10 (11)

Table 2.2: Synthesis of Series I polymers

Sample code	PMHS (mol)		ALPEG (mol)		ALPEG (g)	
	Req	M	Req	M	Req	M
1:10 (3)	0.0005	0.00055	0.005	0.0058	1.02	1.20
1:20 (3)	0.0005	0.00051	0.010	0.010	2.04	2.04
1:10 (11)	0.0005	0.00050	0.005	0.0051	2.78	2.80
1:20 (11)	0.0005	0.00053	0.010	0.0112	5.56	6.23

*Req = Required   *M= Measured

Table 2.3: Synthesis of Series II polymers

Sample code	PMHS (mmol)		ALPEG (mmol)		ALPEG (g)		ALQUAT (mmol)		ALQUAT (g)	
	Req	M	Req	M	Req	M	Req	M	Req	M
1:5:15 (3)	0.05	0.055	0.75	0.85	1.53	1.74	0.25	0.27	0.555	0.59
1:10:10 (3)	0.05	0.05	0.5	0.51	1.02	1.02	0.50	0.51	1.11	1.13
1:5:15 (11)	0.05	0.05	0.75	0.75	4.17	4.19	0.25	0.24	0.555	0.54
1:10:10 (11)	0.05	0.05	0.5	0.5	2.78	2.78	0.50	0.50	1.11	1.11

*Req = Required   *M= Measured

2.5. Synthesis challenges

Though literature reports hydrosilylation reaction conditions for attaching polar groups such as poly(ethylene glycol) or, separately, for attaching quaternary ammonium compounds, to our knowledge there have been no earlier attempts to simultaneously graft these groups to the PMHS backbone. Thus, the biggest challenge during the synthesis phase was the selection of the reaction conditions, including the amount of catalyst, temperature of the reaction and time

required for the reaction to go to completion. For the graft copolymers with the nomenclature 1:5:15 (3 or 11), the process conditions selected were similar to those reported in literature for grafting allyl PEG to the PMHS. Due to unavailability of in-situ FT-IR, the reaction was allowed to run for 24 h (i.e., the maximum duration reported in literature for similar hydrosilylation reactions). Lastly, it is required to follow laboratory safety protocols while dealing with hazardous chemicals such as NaH, triethylamine and allyl bromide. According to Globally Harmonized System (GHS) of classification these chemicals are highly flammable, corrosive and toxic. NaH reacts violently with moisture to produce hydrogen gas, which can ignite from the exothermic reaction. Thus, a good understanding of possible dangers and a thorough knowledge of the standard operating procedures while dealing with such chemicals are required.

Figure 2.6 - shows a schematic of the various challenges encountered during the synthesis of the PMHS graft copolymers.
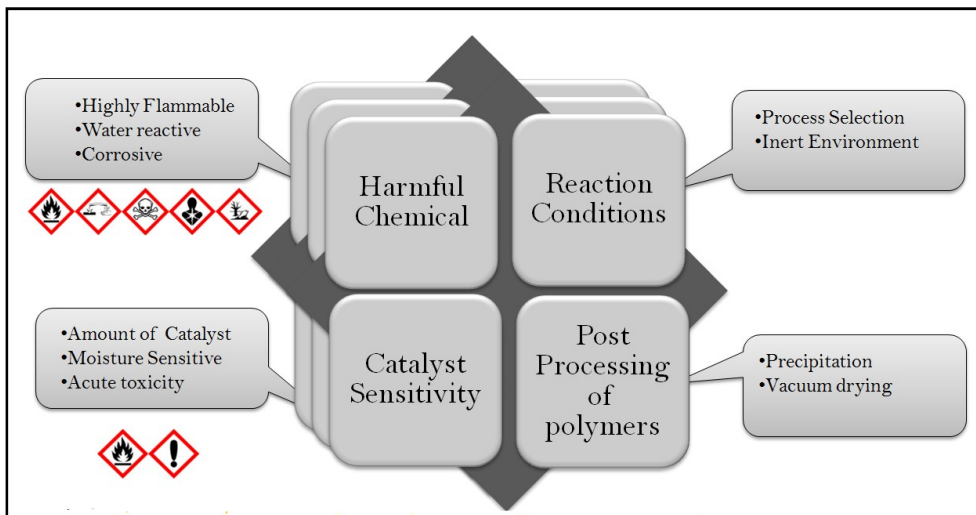
Figure 2.6. Schematic of synthesis challenges

CHAPTER 3

STRUCTURAL CHARACTERIZATION

3.1 ^{1}H NMR Spectroscopy

3.1.1. ^{1}H NMR Spectroscopy Introduction

An accurate quantitative analysis of polymers can be performed by elucidating molecular structures using nuclear magnetic resonance spectroscopy. NMR spectroscopy is a technique that studies the magnetic properties of the nuclei and thus provides useful information required for identifying organic molecules. The NMR spectrum is produced by absorption of electromagnetic radiations in radio–frequency region at frequencies defined by the structure of the sample. All nuclei carry a charge; however, in some nuclei this charge spins along the nuclear axis generating a magnetic dipole moment. During NMR spectroscopy experiments this magnetic dipole moment is analyzed. Isotopes such as ^{12}C, ^{16}O, ^{32}S have no spin and thus cannot be analyzed by NMR. Whereas, nuclei with positive or negative spin like ^{1}H, ^{13}C, ^{19}F, ^{29}Si can be easily studied.

Since almost all organic molecules have ^{1}H isotopes, ^{1}H is the most studied nucleus. Figure 3.1 shows the chemical shifts for common proton functional groups in ppm.
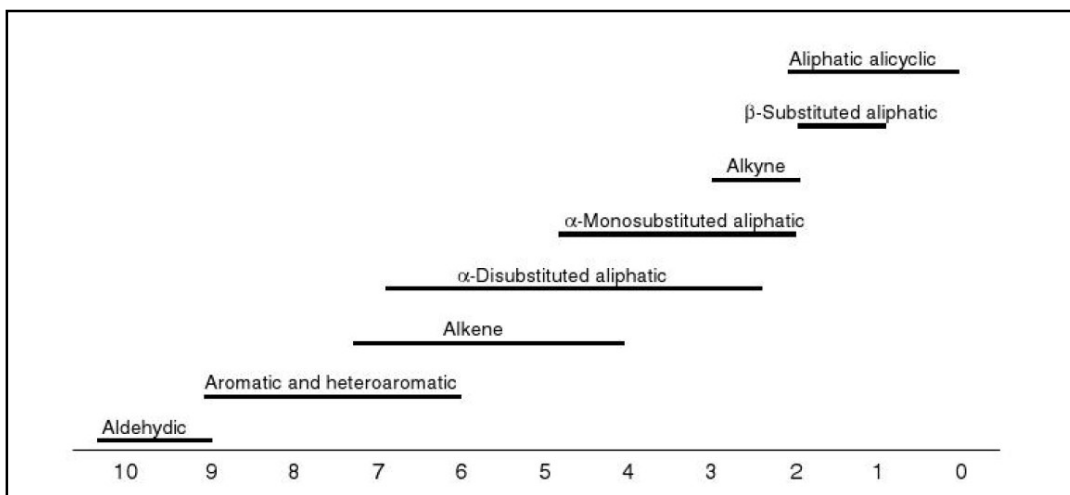
Figure 3.1.General region of ^{1}H chemical shift in organic molecules.

(Enrique, S.G; Eduardor, V.L . Handbook of Polymer Synthesis, Characterization, and Processing (1); Wiley: Somerset, 2013; p 344)

In this thesis, ^{1}H NMR spectroscopy was used to quantitatively analyze the two series of polymers synthesized. ^{1}H NMR spectra were obtained using a Bruker FT-NMR spectrometer (400 MHz) using CDCl$_3$ as the solvent. Tetramethylsilane (TMS) was used as reference for all reported NMR spectra.

3.1.2 Methods and measurement

^{1}H NMR spectroscopy samples were prepared by dissolving 20-22 mg of polymers in CDCl$_3$ solvent and introducing these polymer solutions in NMR tubes. Based on the molecular nature, some samples dissolved easily in the solvent while others were stirred for 30 min. All the samples prepared were clear solutions and free from suspended dust and impurities. These samples were injected into clean, dried NMR tubes through filters.

3.1.3. ^{1}H NMR analyses

3.1.3.1 Series I polymers

As described in Chapter 2, two series of polymers were synthesized. Polymers in series I include either PMHS-g-ALPEG$_3$ or PMHS-g-ALPEG$_{11}$ with predefined ratios of PMHS: PEG. ^{1}H NMR spectra were used to calculate the number of Si-H repeating units grafted with side chains. The calculations for sample 1:10(3) are discussed in detail below. Similar calculations were performed for all series I polymers, the results are listed in Table 3.1. Based on these analyses, the amount of hydrophilic poly(ethylene glycol) in the copolymer and number average molecular weight (M$_n$) of the synthesized polymers was calculated. This information was used for analyzing the contact angle and surface activity of the graft copolymers.

From table 2.2,

We have,

Actual moles of PMHS added= 0.00055 moles

Moles of ALPEG$_3$ added = 0.00588 moles

Also,

^{1}H NMR spectrum of ALPEG$_3$ (Figure 2.4- A) shows conversion of 78%

Thus,

actual moles of allyl PEG added = 0.78 (0.00588)

$$= 4.58 * 10^{-3}$$

Therefore,

The ratio of PMHS: Allyl PEG is 1:8.5 . It is worth noting here, that the target ratio for this polymer was 1:10.

According to the ^{1}H NMR spectrum of 1:10 (3) shown in Figure 3.2.

$$D * = \frac{16/2}{76.2/78} = 8.188$$

Where, 16 and 76.2 are the integration corresponding to peak *c* and *a* respectively.

$$D = 20 - D * = 11.81$$

^{1}H NMR spectra for 1:20(3), 1:10(11) and 1:20(11) are shown in figures 3.3, 3.4 and 3.5 respectively.

Table 3.1: Quantitative ^{1}H NMR spectroscopy analyses for Series I polymers

Sr. no.	Code	Structure of PMHS-PEG				PEG chain Length (n)	PEG Content (wt%)	Mn (g/mol)
		Target		Obtained				
		D*	D	D*	D			
1	1:10 (3)	10	10	8.18	11.81	3.2	55.63	3,010.0
2	1:20 (3)	20	0	16.97	3.03	3.2	72.35	4,810.0
3	1:10 (11)	10	10	7.9	12.91	11.1	76.03	5,790.0
4	1:20 (11)	20	0	15.6	4.4	11.1	86.72	10,020.0
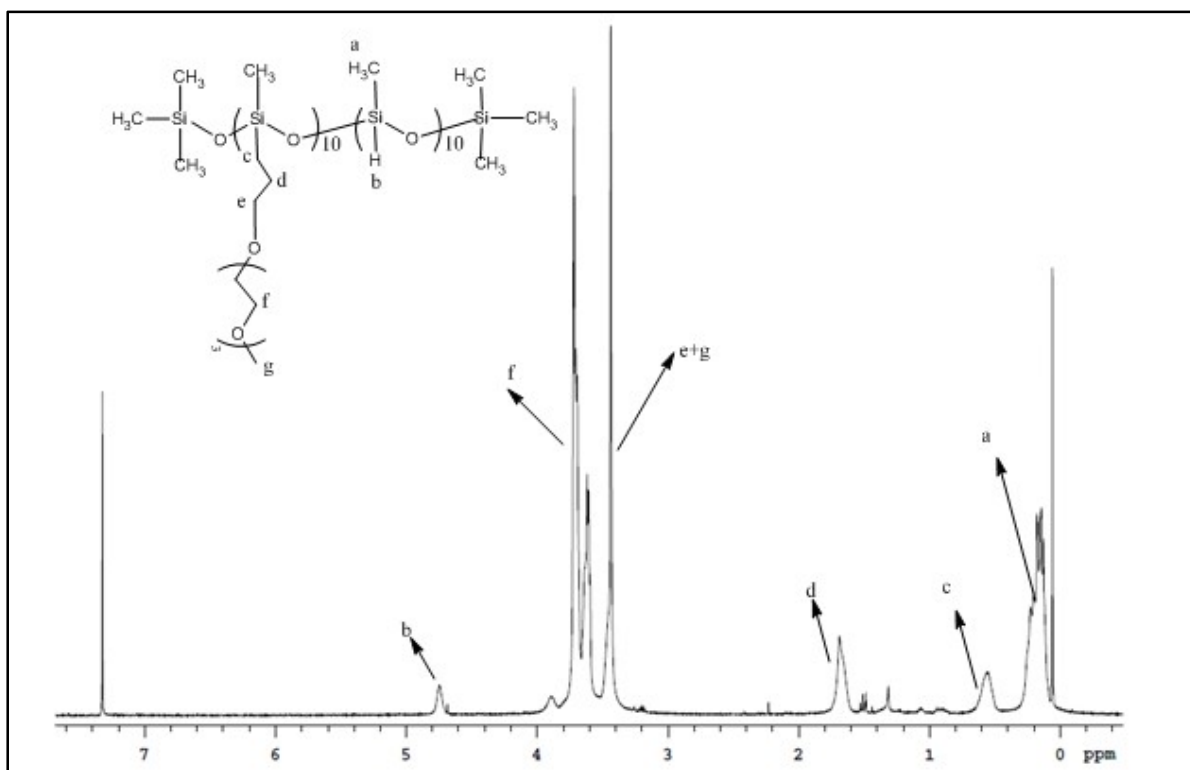
Figure 3.2. ^{1}H NMR Spectrum of 1:10(3)
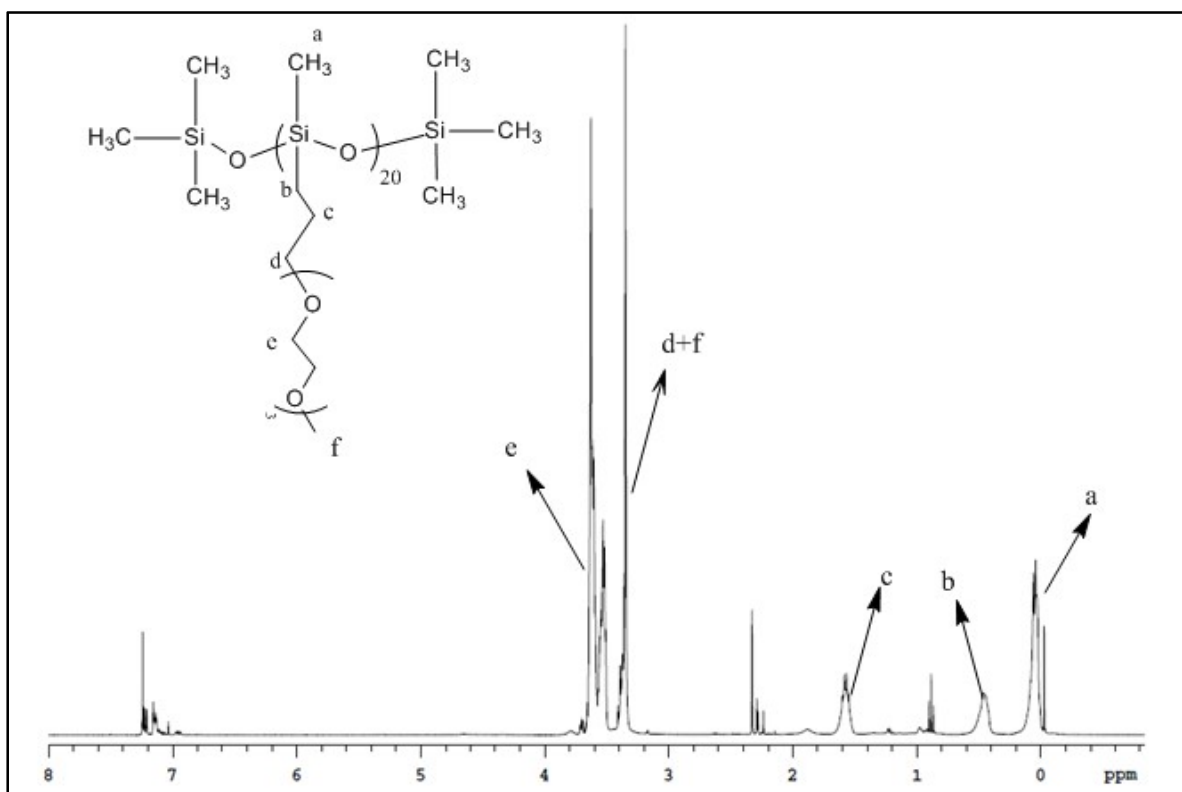
Figure 3.3. ^{1}H NMR spectrum of 1: 20(3)

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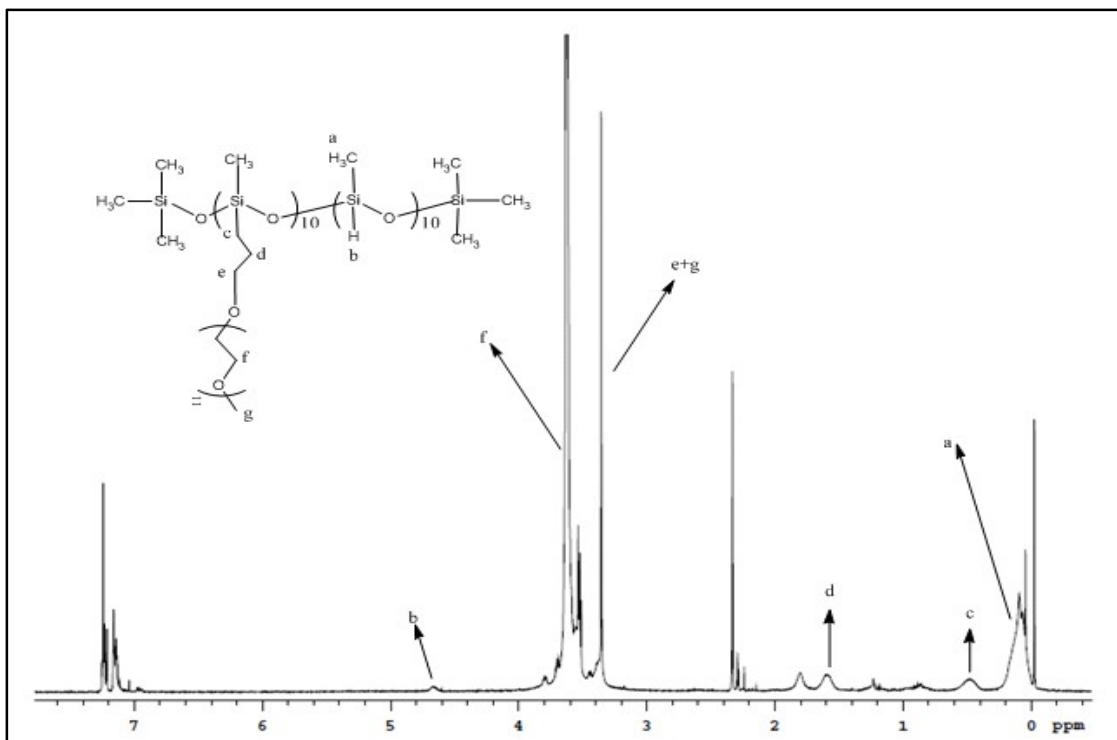
Figure 3.4.^{1}H NMR spectrum of 1:10 (11)
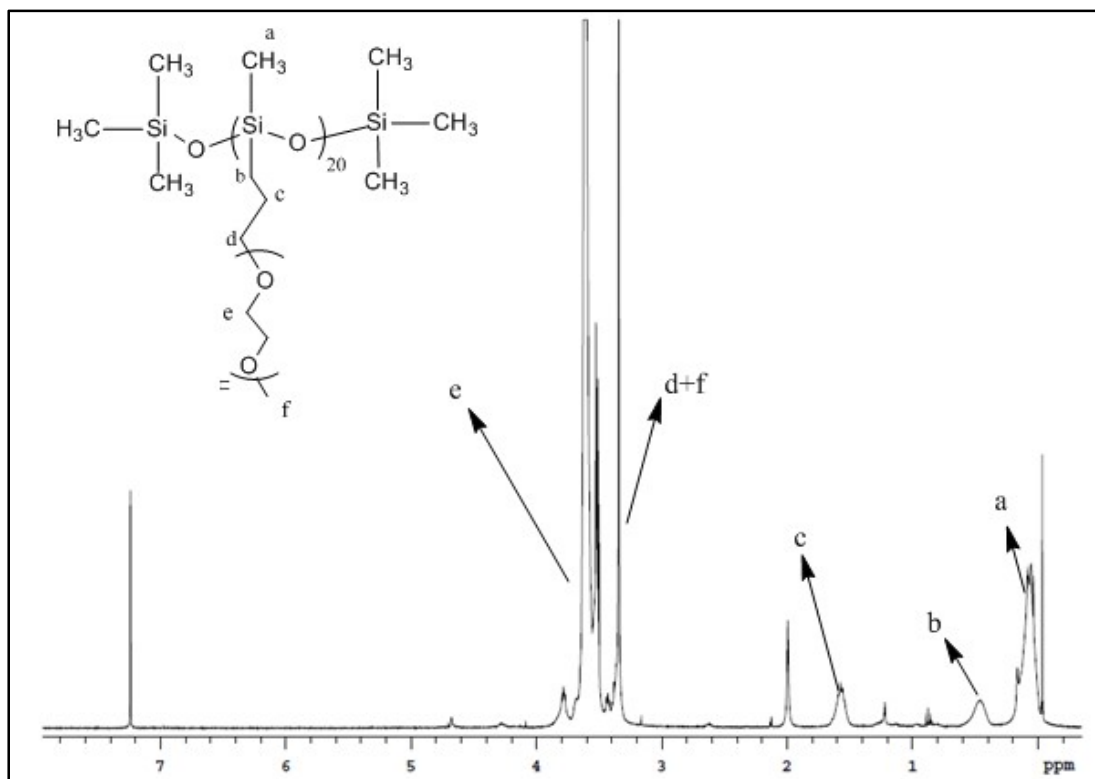
Figure 3.5. ^{1}H NMR spectrum of1:20(11)

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3.1.3.2 Series II Polymers

^{1}H NMR spectra for series II polymers were also studied. An analysis similar to series I

polymers was performed to obtain the values of D, D* and unreacted hydrosilane.

Detailed analysis for one of the series II graft copolymer (1:5:15(3)) is discussed below.

From table 2.3,

        Actual moles of PMHS added= 0.00055 moles

        Moles of ALPEG$_3$ added   = 0.0085 moles

        Moles of ALQUAT added   = 0.0027 moles

        ^{1}H NMR spectrum of ALPEG$_3$ (Figure 2.4- A) shows conversion of 78%

Thus, actual moles of allyl PEG added   = 0.78 (0.0085)

$$= 6.63*10^{-3}$$

Therefore, the ratio of PMHS : Allyl PEG is 1:12.03. It is worth noting here, that the target ratio

for this polymer was 1:15.

Also, ^{1}H NMR spectrum of ALQUAT (Figure 2.5) shows 99 % conversion,

Thus, actual moles of quaternary ammonium added = 0.99 (0.0027)

$$= 2.66*10^{-3}$$

Therefore, the ratio of PMHS: Allyl Substituted quaternary ammonium salt is 1:5.3. The desired

ratio here was 1:5.

According to the ^{1}H NMR spectra of 1:5:15 (3) shown in figure 3.6.

$$D* = \frac{12.61/12}{6.81/78} = 12.035$$

Where, 12.61 and 6.81 are the integration corresponding to peak *b* and *a* respectively.

Also,

$$D = \frac{2.09/6}{6.81/78} = 3.98$$

Where, 2.09 is the integration corresponding to peak *d*.

Similar analyses were performed for all the series II copolymers and the results are listed in

table 3.2.
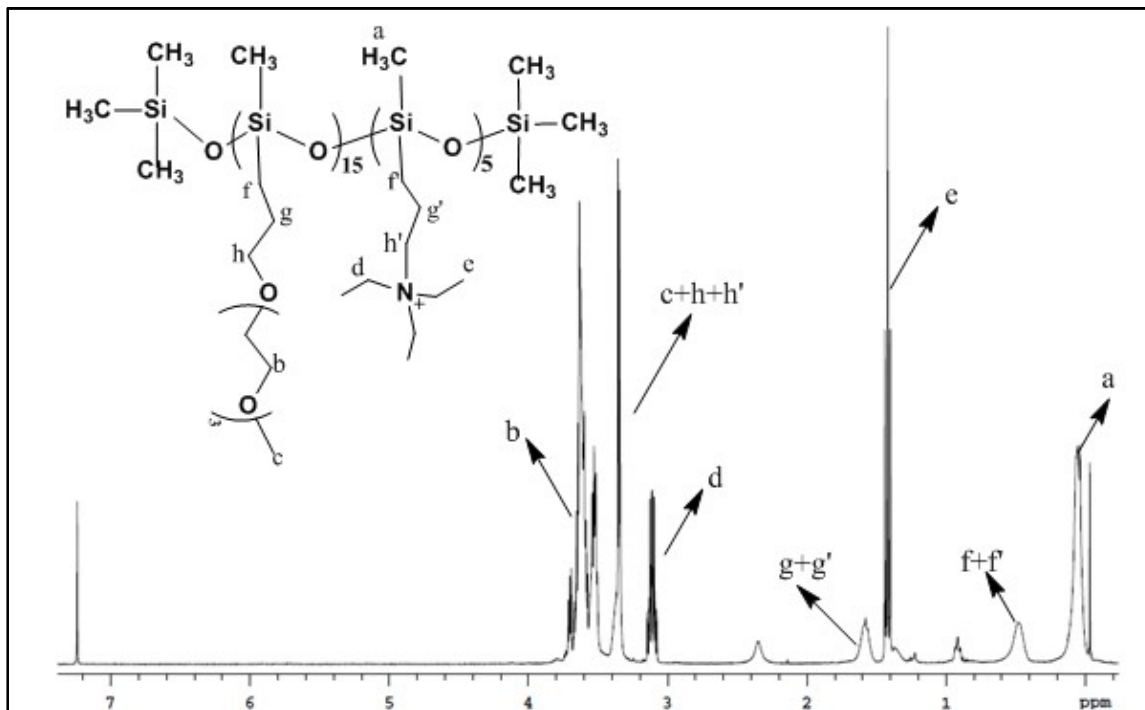
Figure 3.6. ^{1}H NMR spectrum of of 1:5:15(3)

Table 3.2: Quantitative ^{1}H NMR spectroscopy analysis for Series II polymers

Code	Structure of PMHS-PEG					* (n)	*X	*Y	Si-H	Mn
	Target		Obtained				(wt%)	(wt%)	content	(g/mol)
	D*	D	D*	D	Si-H					
1:10:10 (3)	10	10	9.1	6.5	4.4	3.2	46.92	23.37	29.71	3976.0
1:5:15 (3)	15	5	12.0	3.98	3.98	3.2	51.27	8.8	39.93	3826.0
1:10:10 (11)	10	10	8.1	5.6	6.3	11.1	68.32	12.12	19.56	6603.0
1:5:15 (11)	15	5	11.0	2.15	6.85	11.1	70.32	2.83	26.85	7550.0

*X= PEG content   *Y = Ammonium content   *n= PEG Chain length

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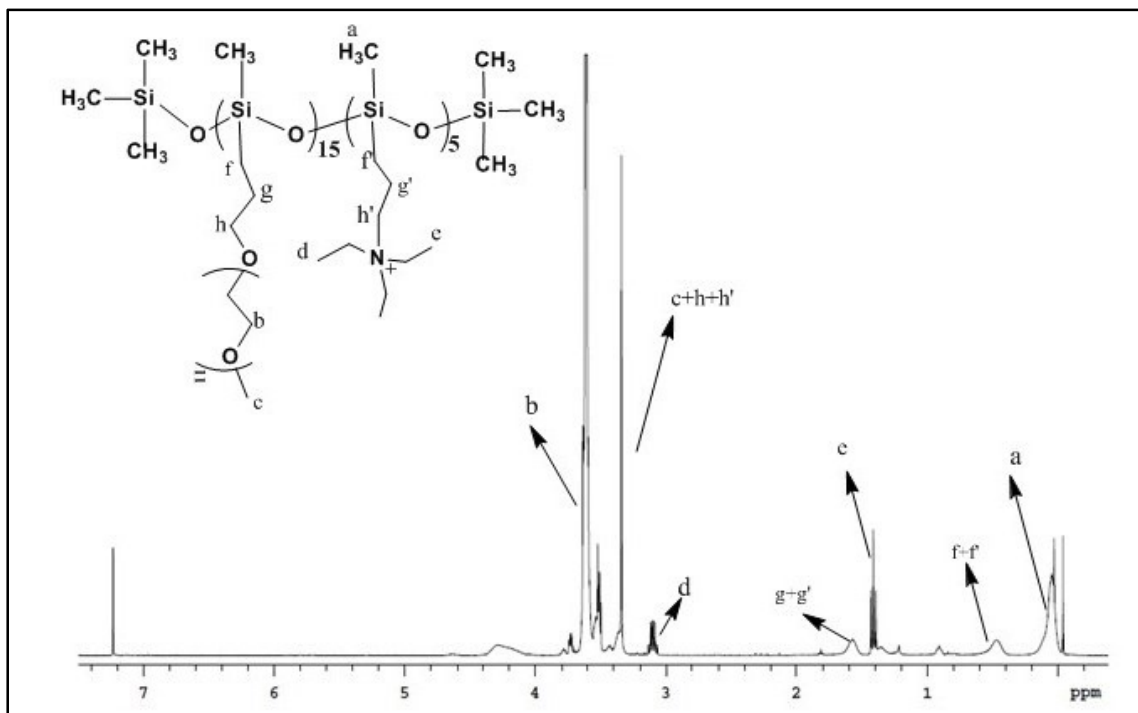
Figure 3.7. ^{1}H NMR spectrum of 1:5:15(11)
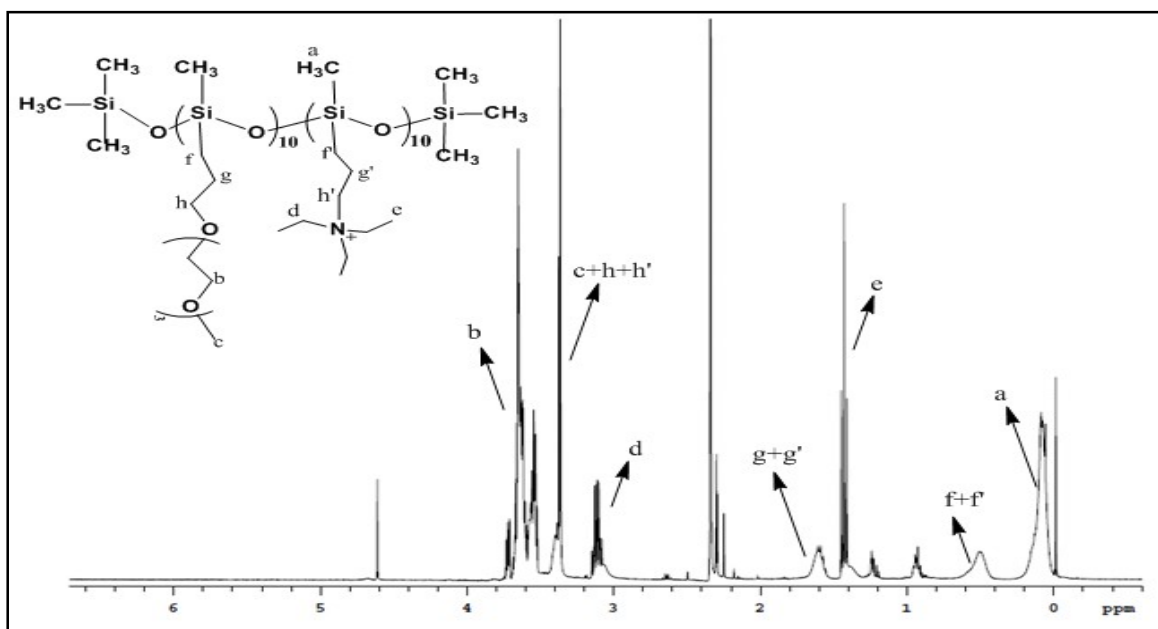
Figure 3.8. ^{1}H NMR spectrum of 1:10:10 (3)
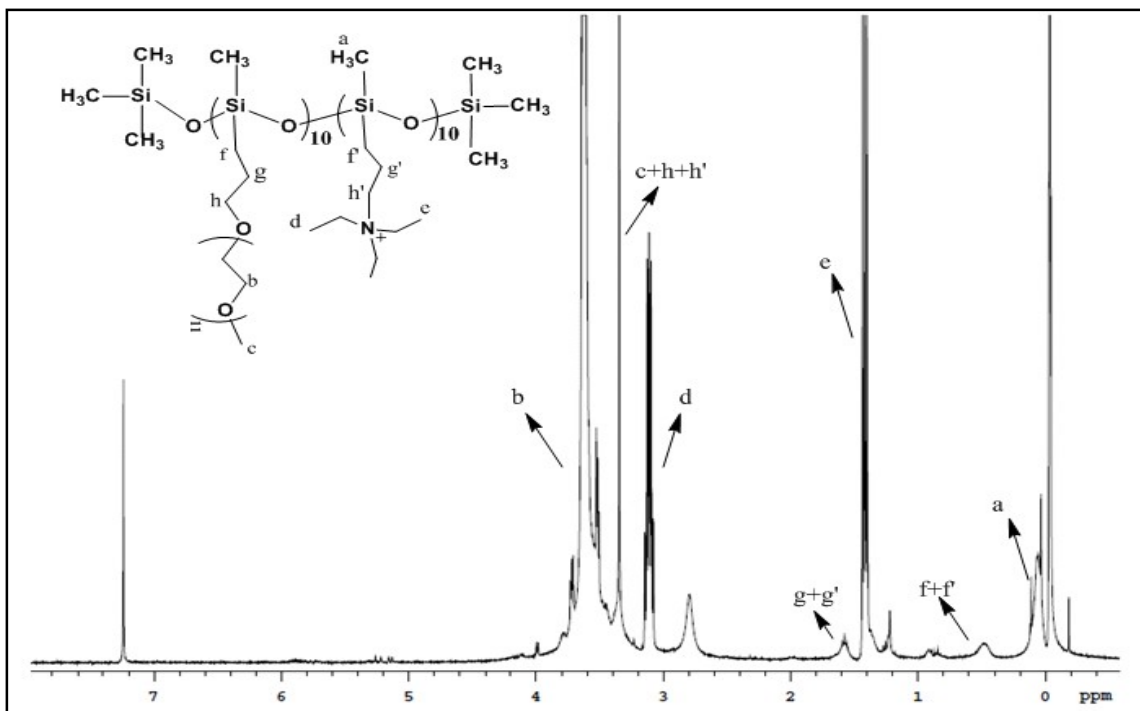
Figure 3.9. ^{1}H NMR spectrum of for 1:10:10(11)

3.2 Fourier Transform Infrared spectroscopy (FT-IR)

3.2.1. Introduction

Infrared spectroscopy is a technique used for the structural characterization of samples based on the absorbance of the IR-frequency energy by the bonds between the atoms. In this technique, the sample is placed in a sample holder and infrared rays are passed through it. The sample absorbs energy at a frequency specific to the structure of the molecule. The use of Fourier transform to process the results of interferogram led to the development of FT-IR. For most organic molecules, infrared rays interact with atoms in a chemical bond in mid IR region (4000 cm^{-1}-400 cm^{-1}) to give an absorption band. These interactions involve changes in molecular dipoles associated with vibrations and rotations.

3.2.2. Methods and measurement

The product of hydrosilylation was vacuum dried for 12 h at 40ºC to obtain completely dry white solid polymer. Mortar and pestle was used to obtain fine powder of the sample which was then placed in a sample holder filled to the brim. Thermal Fisher 1S50 FT-IR Nicolet was used to

obtain FT-IR spectrum at room temperature in the range of 4000 cm^{-1} to 400 cm^{-1} and averaged over 16 scans.

3.2.3. Results

FT-IR absorption spectra were obtained for both series I and series II polymers. For samples 1:10(3) and 1:10(11) a characteristic Si-H stretching peak was observed at 2160 cm^{-1}, however no such peak was observed for 1:20 type polymers .The O—HO stretching from water at 3480 cm^{-1}, asymmetric C-H$_3$ stretching at 2906 cm^{-1}, Si-CH$_3$ stretching at 1960 cm^{-1} and C-O-C bending at 1100 cm^{-1} were visible in both series I and series II polymers. In addition, series II polymers also showed C-H$_2$ stretching from amine at 2492 cm^{-1} indicating the presence of ammonium groups. Qualitative analysis of the samples was done using FT-IR to better understand the structural composition of the synthesized polymers.
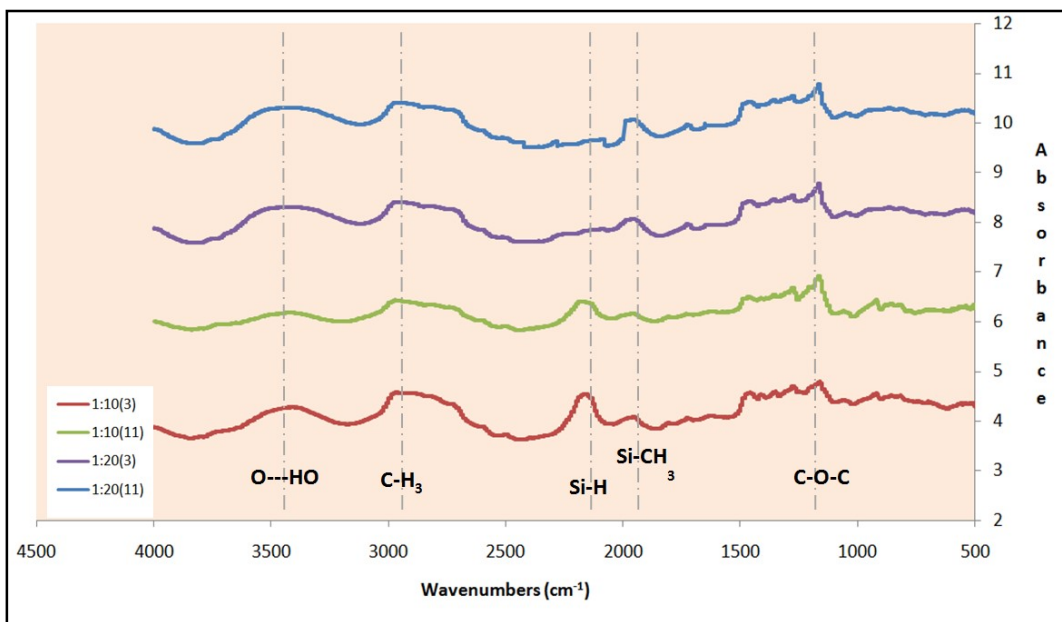
Figure 3.10. FT-IR spectrum of series I polymer
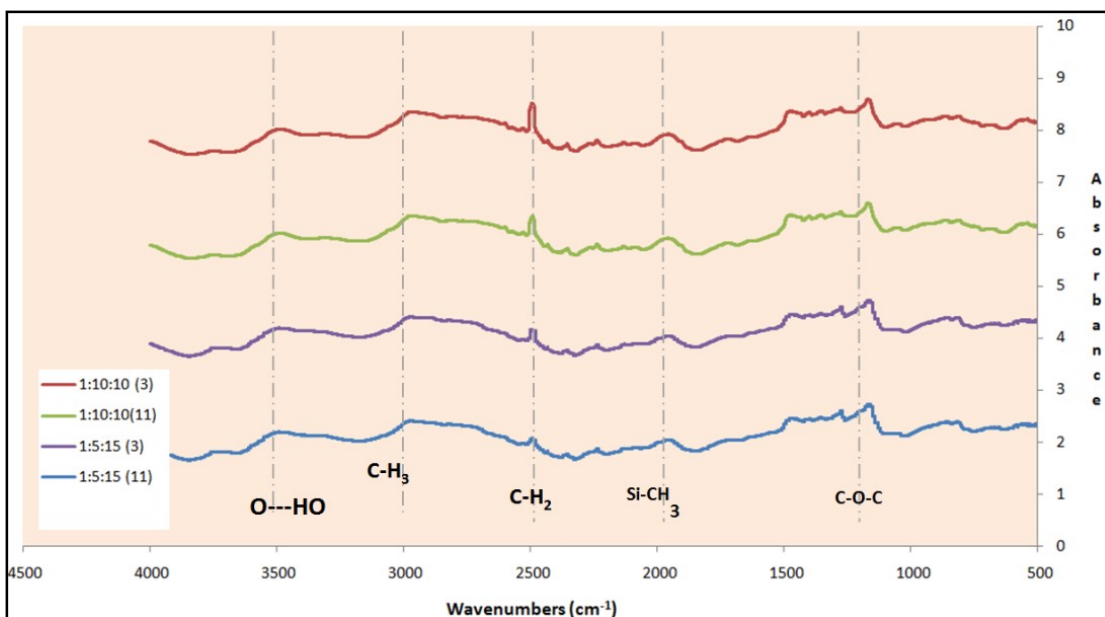
Figure 3.11. FT-IR spectrum of series II polymer

Table 3.3. FT-IR peak assignment

Frequency(cm^{-1})	Assignment
2160	Si-H bending
1957	CH_3 deformation in $SiMe_2$
1160	C-O-C stretching
2967	Asym CH_3 stretching
2492	CH_2 stretching in amine
3480	OH---O stretching from water

CHAPTER 4

PHYSICAL CHARACTERIZATION

4.1 Contact angle Study

4.1.1 Introduction

Contact angle is the measure of wettability of solid surface by a liquid. For a drop of liquid resting on a flat horizontal solid surface, the contact angle (θ) is defined as the angle formed by the intersection of liquid–vapor interface and liquid-solid interface. If a liquid spread over the solid surface, the measured contact angle is small and the wetting of the solid surface is favorable, such surfaces for which $\theta < 90^0$ are considered hydrophilic surfaces. Whereas, for hydrophobic surfaces with $\theta > 90^0$ wetting of the surface by liquids is unfavorable, therefore; the liquid minimizes its contact with solid by forming compact liquid droplets on the surface.

Contact angle is determined by a combination of surface tension and external forces (usually gravity) acting on the liquid drop. The phenomenon of surface tension or surface free energy is discussed in detail in section 4.2. Thomas Young in 1805 first defined the contact angle of a liquid drop on a solid surface as the mechanical equilibrium of drop under three interfacial tensions (Young, T, 1805). Equation 4.1 shown below is referred to as Young's equation.

$$\gamma_{lv} \cos \theta_\gamma = \gamma_{sv} - \gamma_{sl} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \ 4.1$$

Where,

γlv = liquid vapor interfacial tension

γsv = solid-vapor interfacial tension

γsl = solid-liquid interfacial tension

$\theta\gamma$ = Young's contact angle

PMHS is extremely hydrophobic with the water contact angle of 103º, whereas the C-O-C ether linkages present on the poly(ethylene glycol) form hydrogen bonds with water resulting in complete spreading and consequently very low contact angle. In this work, PEG chains were grafted on the PMHS backbone to impart hydrophilicity to the designed polymer and the effect of two factors a) concentration of PEG and b) PEG chain length, on the hydrophilicity of the

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copolyme were studied by measuring contact angle. Similar studies performed in the past by Ding et al. and Chung & Lim, reported an increase in hydrophilicity with an increase in the concentration of PEG attached to the molecule when the PEG chain length is kept constant. Ding et al. studied these effects using a shorter PEG (n=7) whereas, Chung & Lim studied a longer PEG of 16 repeating units. No work in literature was found where both these factors were altered simultaneously. A 2^2 full factorial experiment was performed on series I polymers to study the effects of main factors and their interaction. The results are discussed in detail in the section 4.1.4.

4.1.2 Sample Preparation

The polymeric products obtained from the hydrosilylation reaction were in the form of white solid powder. Since a smooth continuous solid film is required for contact angle measurements, thin films of these polymeric samples were prepared over glass substrate. To cast a typical film, 0.05 g of each sample was dissolved in 0.66 g of THF to obtain 7 wt% solution of sample in THF which were then stirred at 320 rpm for 24 h to ensure maximum dissolution. Table 4.1 below shows the exact quantities measured while preparing the samples. Air free drops of these solutions were deposited very carefully by pipette, on to the thin glass cover slip. The THF was evaporated by drying in air for 12 h, leaving thin, smooth polymeric films. These films were then used as solid surface for contact angle measurements. Easy drop from Kruss was used to measure contact angle.

Table 4.1: Contact angle sample preparation

Sample code	Sample measured (g)	Sample + THF (g)	Sample Wt%
1:10(3)	0.049	0.690	7.10
1:20(3)	0.054	0.722	7.47
1:10(11)	0.051	0.687	7.42
1:20(11)	0.048	0.646	7.43
1:5:15 (3)	0.054	0.701	7..70
1:5:15 (11)	0.052	0.697	7.46
1:10:10 (3)	0.050	0.714	7.00
1:10:10(3)	0.049	0.706	6.94

4.1.3 Contact angle Measurement

The interface where liquid, solid and vapor coexist is called a three phase contact line. Depending on the nature of the contact line, contact angle can be defined as static or dynamic. If the contact line is stationary, Young's equation can be directly applied to determine the unique contact angle called Young's contact angle (θ_Y). However, in practice, the phenomenon of wetting is dynamic in nature and a single contact angle is no longer entirely sufficient to characterize the wetting behavior of the solid, though it is still considered a good approximation for smooth homogenous surfaces (Yuan,Y.; Lee, T.R. 2013).

In such case, when the three phase contact line is in motion, dynamic contact angle in the form of advancing and receding contact angles are usually measured. Advancing and receding contact angles are represented as θ_a and θ_r respectively and are determined by expanding or contracting the liquid drop on the solid surface. The difference between θ_a & θ_r is called hysteresis and is the measure of surface roughness and heterogeneity of the sample. Ideally, dynamic contact angles should be measured to completely characterize the wetting behavior of the solid surface. Advancing contact angle is a good approximation of θ_Y for rough or chemically homogenous surfaces, while the receding contact angle has low reproducibility due to solid swelling or liquid sorption (Sedev et al., 1996).However, in this thesis, due to the limitations of the instrument, static contact angles were measured for a drop of pure water resting on the polymeric film. As mentioned earlier, advancing and receding contact angles are measured by expanding and contracting the liquid drop while the needle is still in contact with the drop. Kruss's Easy Drop limits such measurements and is designed to report a value of static contact angle when needle is out of the liquid drop. Due to such limitations, utmost care was taken while preparing the solid polymeric films, such that the films were free from air bubbles and cracks and, thus, had the least surface roughness possible.

The measurement of contact angle relies significantly on the consistency of the operator. To reduce experimental errors due to such factors, a standard operating procedure for contact angle measurement was determined. A 3 μL sessile drop was formed on the polymer surface and a live image of the drop was obtained. Initially, the solid polymeric film was focused to

determine the baseline of the drop image which is the boundary between solid surface and the drop. The focus was then shifted to the drop image and *Tangent Method 1* was used to calculate the contact angle which involves aligning a tangent line to the sessile drop profile at solid-liquid interface. The complete profile of the sessile drop is then fitted to a general conic section equation and the derivative of this equation at the baseline gives the slope at three phase contact point and thus the contact angle. For every sample, contact angle was measured at 3 locations on the sample surface at the end of 10 seconds. The measured values of contact angle given in the last column of the table 4.2 & 4.6 represent an average of the contact angle measured at three locations for each sample.

4.1.4 Results and Discussion

Grafting PEG to PMHS backbone is a technique to improve hydrophilicity of the resulting copolymer. Contact angle studies for both series I polymers and series II polymers were performed according to the procedure described above. Tables 4.2 & 4.6 show the average value of static contact angle for series I and series II copolymers respectively.

Table 4.2: Static Contact angle for series I copolymers

Code	Structure of PMHS-PEG Obtained		PEG chain Length (n)	PEG Content (wt%)	Mn (g/mol)	Static Contact angle
	D*	D				
1:10 (3)	8.18	11.81	3.2	55.63	3,010.0	45.3
1:20 (3)	16.97	3.03	3.2	72.35	4,810.0	38
1:10 (11)	7.9	12.91	11.1	76.03	5,790.0	41
1:20 (11)	15.6	4.4	11.1	86.72	10,020.0	38.5

The primary objective of the contact angle study for series I polymers was to determine the effect of PEG chain length and number of repeating units in the copolymer containing PEG on the hydrophilicity of the polymers. Since PEG is polar in nature, an overall increase in its

composition is expected to increase the hydrophilicity of the polymer. However, the individual effect of the contributing factors on the water contact angle is not much studied.

In this work, principles of design of experiments and analysis software like JMP were used to study the individual factor effects. A 2^2 full factorial design was constructed with two factors A and B each at two levels. These levels are arbitrarily called low and high levels. The +1 and -1 represent high and low level of the factors respectively. PEG chain length was selected as Factor A, whereas, the number of repeating units in the copolymer containing PEG was factor B. Table 4.3 shows low and high levels of these factors. For factor B, the values of the target structure were taken as low and high level. A full factorial 2^2 design consists of 4 runs at all possible combinations of low and high level of both factors. The four treatment combinations are shown in table 4.4. Series I polymers are the polymers generated from these treatment combinations. For example, in sample 1:10(3), both factor A and factor B are at their low levels of 3 and 10, respectively.

Table 4.3: High and low levels of factors

Factor	Low	High
A	3	11
B	10	20

Table 4.4: Treatment combinations and contact angle data for Series I polymers

S no	A (PEG length)	B(PEG composition)	A*B	Run 1	Run 2
1	-1	-1	+1	44.6	46
2	-1	+1	-1	40	36
3	+1	-1	-1	42	40
4	+1	+1	+1	38	39

Since the polymers obtained were solid powders, they were dissolved in THF to obtain 7 wt% solutions which were then used to prepare films. Two films were prepared for each sample from the same 7 wt% solution of the sample. Contact angles were measured at 3 different points at the end of 10 seconds for both films of every sample. The data given in run 1 and run 2

columns of the table 4.4- is the average of contact angle measured at three points on each film. Two runs were performed for each sample to reduce variability of the system. Effect estimates of the main factors A and B and their interaction AB were calculated. The magnitude of the effect estimate identifies significant factor whereas the sign (+ or -) indicates increase or decrease in response variable with change in factor levels. These estimates are reported in table 4.5.

Table 4.5: Effect estimates for factors

Factor	Effect
A	-1.9
B	-4.9
A*B	2.4

Since the magnitude of factor B (4.9) is larger than that of factor A and AB, the number of repeating units grafted with PEG has larger effect on the hydrophilicity than the PEG chain length. The Negative sign indicates that the contact angle decreases with the increase in the number of repeating units grafted. In other words, hydrophilicity increases considerably if the increase in PEG content in the polymer is due to the increase in number of Si-H units grafted with PEG rather than due to an increase in the PEG chain length. This important conclusion gives immense power to control the wettability of siloxane polyether copolymers.

Figure 4.1 shows the main factor plots and interaction plots from JMP. A low P value of 0.015 for factor B indicates that it is highly significant.
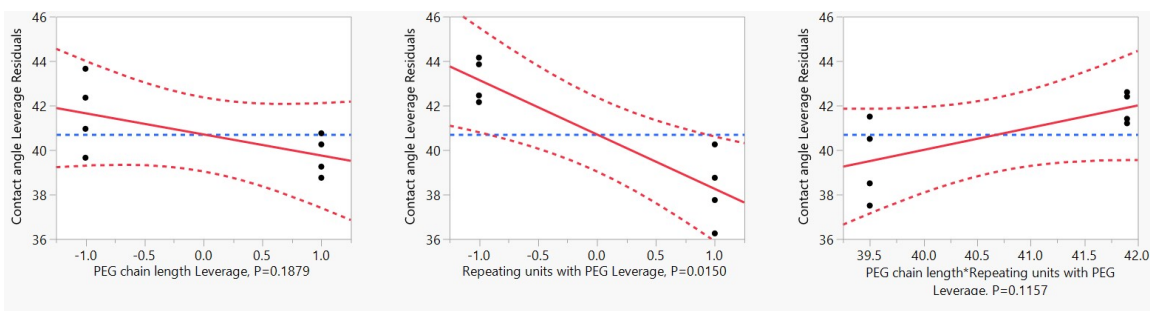

Figure 4.1: Main effect s and Interaction plots from JMP

Also, static contact angles were measured for series II polymers, and these results are shown in Table 4.6. It was observed that for pairs of copolymers with same chain length, the

contact angle increased in spite of an increase in PEG content. This unexpected effect can be attributed to the simultaneous increase in SiH content for both pairs of copolymers. For example between 1:10:10(3) and 1:5:15(3), in spite of a 5% increase in PEG content, the contact angle increases by 4^0 ; this may be attributed to a 10% increase in Si-H (from 29.71 to 39.93). This suggests that between the following two factors: a) amount of PEG   and b) amount of Si-H hydrophobe; the second factor determines the hydrophilicity of the copolymer.

Table 4.6: Static Contact angle for series II copolymers

Code	Structure of PMHS-PEG					*X	*Y	*Z (wt%)	Static
	Target		Obtained			(wt%)	(wt%)		Contact
	D*	D	D*	D	Si-H				angle
1:10:10 (3)	10	10	9.1	6.5	4.4	46.92	23.37	29.71	38
1:5:15 (3)	15	5	12.0	4.0	4.0	51.27	8.8	39.93	42
1:10:10 (11)	10	10	8.1	5.6	6.3	68.32	12.12	19.56	33
1:5:15 (11)	15	5	11.0	2.15	6.85	70.32	2.83	26.85	37.5

*X= PEG Content   *Y= Ammonium Content   *Z= Si-H content

4.2 Surface Tension

4.2.1 Introduction

Contact angle depends upon the shape of liquid droplet on solid surface which in turn is a function of unbalanced intermolecular forces. Every molecule in the bulk of the liquid, experiences equal amount of pull in all the directions resulting in net zero force. However due to unbalanced intermolecular forces, the molecules on the surface are pulled inward thereby attaining a state of minimum energy. This intermolecular force which leads to contraction of liquid surface is called surface tension of the liquid.

Surfactants are the surface active agents consisting of a hydrophilic and hydrophobic part which when dissolved in a liquid reduces its surface tension. For a surfactant dissolved in water,

the hydrophilic group of surfactant is solvated by water molecules while the hydrophobic group is forced towards air-water interface (away from the water molecules), this is called the hydrophobe effect and is the reason for strong adsorption of surfactant on the water surface. According to Gibb's adsorption isotherm, given in equation 4.2, the adsorption of any molecule on the surface leads to a decrease in surface tension.

$$-d\sigma = \Gamma RT \ln C$$ ……………………………………..…4.2

Where,

σ = Surface tension of the solution

Γ = Surface concentration of adsorbed molecules

C = Concentration of adsorbed sample in the bulk phase

Initially, an increase in the bulk concentration of the surfactant (C) decreases surface tension until a point when no further decrease in surface tension is observed with increase in surfactant concentration. This is known as the critical micelle concentration (cmc) and defines the effectiveness of the surfactant.

Silicone surfactant solutions can have very low surface tension between 20-30 mN/m due to the large number of methyl groups and small intermolecular attraction between the siloxane hydrophobe. The siloxane backbone is highly flexible and can lie flat on the surface, allowing maximum orientation of the $-CH_3$ groups at the interface, leading to a very dense packing of low surface energy methylene groups on the surface. Since surface energy is mostly dependent on the composition of the hydrophobe, for silicone surfactants (silicones modified with hydrophilic groups) an increase in the composition of the hydrophilic group in the molecule is expected to increase the surface tension. Specifically, for this work, an increase in PEG composition in PMHS-g-PEG was hypothesized to increase the air-water interfacial tension. Furthermore, depending upon the type of the grafted group and size of the PEG chain, different packing densities can be obtained which can also affect surface tension.

4.2.2. Sample preparation

The polymers obtained from hydrosilylation reaction were dissolved in water to form a 2 wt% aqueous solution of samples. 0.02 g of each sample was dissolved in 1.2 g of water. Table 4.7-, shows the actual measurements for the samples prepared. All solutions were mixed for 12 h at 280 rpm to ensure formation of a homogenous solution. Samples with a higher concentration of PEG formed clear solution in water; whereas, samples with a lower PEG composition, or higher number of unreacted Si-H (non polar) groups and quaternary ammonium groups formed a white turbid suspension. These 2 wt% aqueous solutions were used to analyze the air-water interfacial tension using Kruss Easy Drop. The values obtained were compared with the surface tension of pure water (without surfactant).

Table 4.7: Surface tension sample preparation

Sample code	Sample measured (g)	Sample + Water (g)	Sample Wt%
1:10(3)	0.024	1.219	1.97
1:20(3)	0.025	1.260	1.98
1:10(11)	0.023	1.156	1.99
1:20(11)	0.023	1.120	2.05
1:5:15 (3)	0.022	1.120	1.96
1:5:15 (11)	0.027	1.340	2.01
1:10:10 (3)	0.024	1.210	1.98
1:10:10(3)	0.023	1.20	1.92

4.2.3 Measurement Method

Surface tension of the 2 wt% aqueous solution was obtained by fitting the Young-Laplace equation to the contour profile of a pendant drop. A 3 µL pendant drop was formed at the tip of the syringe needle. The drop assumes a characteristic shape and size which is used to calculate surface tension. A requirement is that the drop is in hydromechanical equilibrium. In such an equilibrium, the force of gravity acting on the drop equals the Laplace pressure drop below and above the curved section of the drop. This is represented mathematically as:

$$\Delta P = \sigma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) = z \Delta \rho \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 4.3$$

Where,

r1 *and* r2 are the principle radii of curvature

$\Delta\rho$ = density difference between liquid drop and its surroundings

g = acceleration due to gravity

The contour profile of the drop was extracted and the Young-Laplace equation was fitted to the profile. An inbuilt model from *Easy Drop* directly computes the air- water interfacial tension for each surfactant solution. Four drops were formed for every sample and the error of fit between the actual drop curvature and the model was found to be very small. The small values of fit error are indicative of this method as an efficient method for measuring surface tension.

4.2.4 Results and discussion

Low surface energy is a characteristic of the siloxane backbone. The methyl groups attached to the siloxane chain has lower surface energy as compared to the $-(CH_2)$- moiety in the surfactant having hydrocarbon chain. Moreover, the siloxane backbone is highly flexible due to the easy rotation of Si-O-Si bonds resulting in improved film forming properties at the air- water interface. Due to such advantages, the use of silicone backbone is gaining importance over the conventional hydrocarbon backbone. Poly(ethylene glycol)s are attached as hydrophilic part of the siloxane surfactants forming silicone polyether copolymers mentioned in chapter 2.However, it has been previously reported that the surface tension of air-water interface increases with an increase in PEG concentration in the molecule (Ding et al.,2012).

Quaternary ammonium derivatives of siloxanes have also been reported to have surface active properties. Vaidhya and Kumar studied the surface active properties of olefinic quaternary amino siloxanes and concluded that lowering in surface tension by oligomeric quaternary siloxane for air-water interface was more than that observed for monomeric quaternary siloxanes. Furthermore, because of the positive charge, these surfactants have excellent binding properties to negatively charged substrates like hair and skin, thus, providing the conditioning effect.

In this thesis, surface active properties of the synthesized polymers were studied. Air-water interfacial tension (IFT) for the polymers was measured according to the procedure

discussed above. Table 4.8 and 4.9 shows the IFT values for series I and series II polymers respectively.

Table 4.8: Surface tension for series I polymers

Code	PEG Content (wt%)	Ammonium Content (wt%)	PMHS content	Mn (g/mol)	Avg. IFT
1:10 (3)	55.63	-----	44.37	3,010.0	28
1:20 (3)	72.35	-----	27.65	4,810.0	32
1:10 (11)	76.03	-----	23.97	5,790.0	44.95
1:20 (11)	86.72	-----	13.28	10,020.0	38

Table 4.9: Surface tension for series II polymers

Code	PEG Content (wt%)	Ammonium Content (wt%)	PMHS content	Mn (g/mol)	Avg. IFT
1:10:10(3)	46.92	23.37	30	3976.0	38
1:5:15 (3)	51.27	8.8	39.93	3826.0	33
1:10:10 (11)	68.32	12.12	20	6603.0	44
1:5:15 (11)	70.32	2.83	26.85	7550.0	40

Considering table 4.8, the PEG content increases while the PMHS content decreases (moving down the table). Since both these trends favor an increase in surface tension, the average value of IFT (last column of table 4.8) was expected to increase. Though this value increases from 28 mN/m to 44.95 mN/m for 1:10(3) to 1:10(11), there is a decrease in IFT for 1:20(11) in spite of a 10% favorable change in PEG and PMHS content as compared to 1:10(11). The reason for this unusual behavior is not completely understood.

For series II polymers, (last column of table 4.9) the IFT value increases with decrease in PMHS content. This means that less lowering in surface tension is obtained for small amount of

PMHS in the molecule. For easy comparison, the data from table 4.9 is reproduced below in table 4.10 in decreasing order of PMHS composition.

Table 4.10: Trend analysis for series II polymers with respect to PMHS content

Code	PMHS content	Avg. IFT (mN/m)
1:5:15 (3)	39.93	33
1:10:10 (3)	30	38
1:5:15 (11)	26.85	40
1:10:10 (11)	20	44

In order to determine the effect of PEG concentration on IFT for series II polymers, the data was arranged as shown in table 4.11.

The comparison between two pairs of samples having same PEG chain length (i.e. [1:10:10(3) & 1:5:15(3)] and [1:10:10(11) & 1:5:15(11)] shows an increase in air- water interfacial tension in spite of a decrease in PEG content. This observation suggests that the PMHS composition of a molecule is the deciding factor for IFT calculations.

Table 4.11: Trend analysis for series II polymers with respect to PEG content

Code	PEG content	Avg. IFT (mN/m)
1:5:15 (3)	51.27	33
1:10:10 (3)	46.92	38
1:5:15 (11)	70.32	40
1:10:10 (11)	68.32	44

Figure 4.2 and 4.3 plots the IFT value as a function of PMHS content and PEG content for both series I and series II polymers. Ideal behavior was observed for series II polymers where the IFT values decreases with decrease in PMHS content.
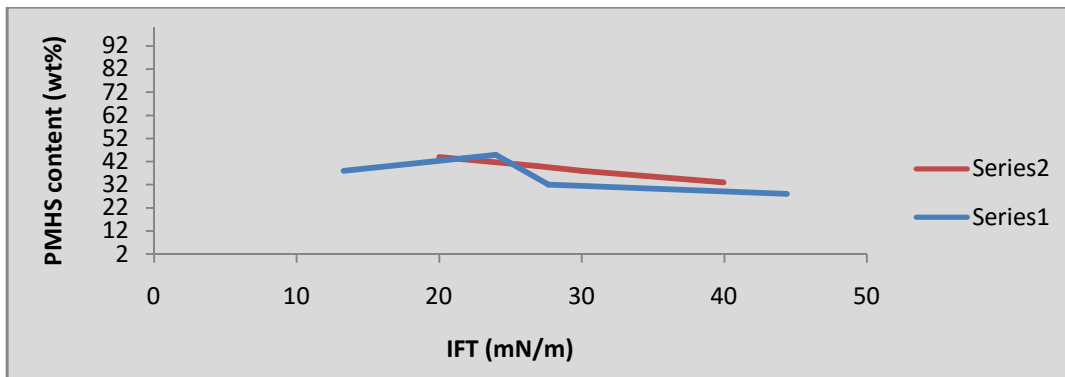
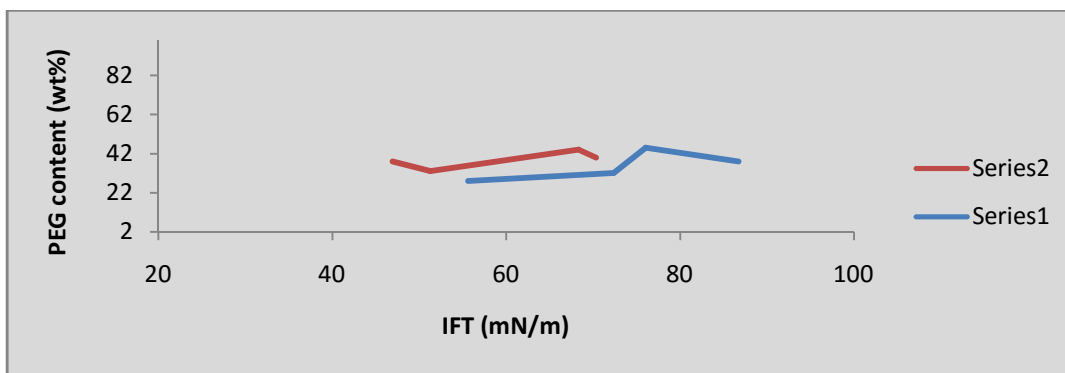Figure 4.2. Air- water interfacial tension (IFT) as a function of PMHS content

Figure 4.3. Air- water interfacial tension (IFT) as a function of PEG content

CHAPTER 5

CONCLUSION AND FUTURE WORK

In this thesis, series of silicone graft copolymers were successfully synthesized by hydrosilylation. Two series of polymers were synthesized. Series I include, allyl-PEG of different chain length grafted to the PMHS backbone. Whereas, series II includes allyl-PEG and a quaternary ammonium salt attached to the PMHS backbone. The structure of the polymer was characterized by ^{1}H NMR spectroscopy and FT-IR, and the contact angle and air-water interfacial tension of the polymers was studied.

Principles of *Design of Experiment* were used to determine the effect of two factors ; a) PEG chain length b) number of repeating units in the copolymer containing PEG; and their interaction on the hydrophilicity for series I polymers . Analyses of the results show an expected increase in the hydrophilicity with increase in PEG content. However, the increase in hydrophilicity is considerably larger if the increase in PEG content in the polymer is due to the higher number of Si-H units grafted with the poly(ethylene glycol) rather than due to increase in PEG chain length. Similar results were obtained for series II polymers.

Since lowering in surface tension is a characteristic of silicone backbone, the IFT value decreases with decrease in PMHS content. Results of the study were suggestive of hydrophobe content to be the deciding factor in IFT calculations as compared to the PEG content.
These important conclusions give a good control over surface properties (wettability and spreadability) while designing such polymers.

Polymers synthesis and structural characterization formed a major fraction of the current work. Though some surface characterization techniques like contact angle and surface tension studies were conducted, a lot can still be done to fully understand the nature of these polymers .The thermal and rheological behavior of the polymers can be studied to characterize the physical properties of polymers. The glass transition temperature (T_g) and melting points of the polymers can be obtained from Differential Scanning Calorimetry (DSC) curves in order to study polymer morphologies.

Also, solution rheology can be studied to obtain the viscosity of the polymers which depends upon molecular weight and level of crosslinking within the polymer. Since such polymers usually constitute 1%- 2% by weight of cosmetic formulation which have water as major component (around 85%), knowledge of rheological behavior of 1 wt% -2 wt% aqueous solutions of these polymers helps in determining the flow behavior of the final product. Also, the charge density on the polymer can be determined, as a measure of the conditioning effect provided by the polymer.

From a consumer's point of view, the ability to form foam is perceived as a test for good surfactant. In silicone polymers, foam forming ability depends upon the balance of Si composition in the polymer and the amount of water in the formulation. In order, to test the consumer appeal of the synthesized polymers, such foam forming tests can be performed. Also, as these polymers are designed for personal care products, they are required to be gentle to sensitive organs like skin and eyes. Smaller molecular weight polymers can penetrate in the eyes and cause irritation; therefore larger molecular weight polymers are preferred. However, as molecular weight of the polymer increases its ability to function in different capacities changes, thus a good understanding of all these factors is required while designing polymers for specific applications. Table 5.1 relates molecular weight of the polymer to the function they are most suitable for.

Table 5.1 General relationship between molecular weight of polymer and its function.
(Patil, A., Sandewicz, R.W, 2013, p 17)

Molecular weight (Daltons)	Function
500	Wetting
2,500	Emulsification
10,000	Conditioning
50,000	Water proofing

In conclusion, in this work, an attempt was made to design and synthesize novel polymers for specific applications, though the target structures were obtained and important structure-function relationships discovered, further analyses are required to completely comment on the utility and future of these polymers.

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