

# **SYNTHESIS OF FUNCTIONALIZED POLYSILOXANES AND INVESTIGATION OF HIGHLY FILLED THERMALLY CONDUCTIVE MICROCOMPOSITES**

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# Synthesis of Functionalized Polysiloxanes and Investigation of Highly Filled Thermally Conductive Microcomposites

Jennifer K. Hoyt-Lalli

(ABSTRACT)

The scope of this research entailed the synthesis of novel polyorganosiloxanes with pendent phosphine, phosphine oxide, nitrile and carboxylic acid moieties. Such polysiloxanes were prepared with controlled concentrations of both the polar moieties and hydrido or vinyl pendent crosslinkable sites to afford precursor materials for well-defined networks. The intention was to generate stable microcomposite dispersions with very high concentrations of polar thermally conductive fillers. Lightly crosslinked elastomeric networks with controlled amounts of polar moieties were prepared via a hydrosilation curing mechanism. High concentrations of thermally conductive microfillers were dispersed throughout the resins and the microcomposites were investigated as thermally conductive adhesives.

Random polysiloxane copolymers containing controlled number average molecular weights ( $M_n$ s) and compositions with systematically varied concentrations of hydridomethylsiloxy- or vinylmethylsiloxy- units were prepared via ring-opening equilibrations of cyclosiloxane tetramers. These precursors were functionalized with precise concentrations of polar pendent moieties via hydrosilation (nitrile) or free radical addition reactions (phosphine and carboxylic acids). Valuable additions to the family of polysiloxanes were prepared by oxidizing the phosphine moieties to form phosphine oxide containing polysiloxanes. Defined concentrations of residual hydrido- or vinyl-reactive sites were crosslinked via hydrosilation to yield elastomeric adhesives.

Specific interactions between the nitrile and phosphine oxide substituted polysiloxanes and the acidic proton of chloroform were shown using  $^1\text{H}$  NMR. The magnitude of the shift for the deshielded chloroform proton increased with the degree of hydrogen bonding, and was larger for the phosphine oxide species.

The polar polysiloxane resins were filled with high concentrations of thermally conductive fillers including silica-coated AlN, Al spheres, BN and Ag flake, then hydrosilated to form microcomposite networks. Microcomposite adhesive strengths,

thermal properties (glass transition temperature ( $T_g$ ) and high temperature stability), and thermal conductivities were studied. An unfilled polysiloxane network containing only 15 mole percent phosphine oxide exhibited a dramatic improvement (46 N/m) in adhesive strength to Al adherends relative to a control polydimethylsiloxane network (2.5 N/m). Importantly, stable polysiloxane micro-dispersions were obtained with up to 67 volume percent (86 weight percent) silica-coated AlN. TEM data confirmed the dispersion homogeneity and XPS demonstrated that the particle surfaces were well-coated with the functionalized polysiloxanes. A microcomposite comprised of 67 volume percent silica-coated AlN and a polysiloxane containing only 9 molar percent nitrile groups had a thermal conductivity of 1.42 W/mK. The glass transition temperatures of the microcomposites were controlled by the amounts of polar functional moieties on the resins and the network crosslink densities. All of the microcomposites exhibited  $T_g$ s lower than  $-44$  °C and the materials remained stable in dynamic TGA measurements to approximately 400 °C in both air and nitrogen.

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## Chapter 1. Introduction

Polysiloxanes with flexible polymer backbones and strongly electron donating groups were synthesized and yielded promising candidates for thermally conductive adhesive resins. Polymers are inherently insulating materials and consequently have low thermal conductivity values, 0.1 – 0.3 W/mK.<sup>1,2</sup> Thermally conductive adhesives are prepared by dispersing high concentrations of thermally conductive metal (e.g. Ag) or ceramic (AlN) particulate fillers in an organic resin. Such fillers have respective thermal conductivities of ~ 400 W/mK and 150 W/mK. Currently, the best thermally conductive adhesives are based on Ag filled epoxies and exhibit thermal conductivities of ~ 4 W/mK. Optimized oxide filled epoxies and adhesives prepared with AlN exhibit lower thermal conductivities of 0.07 – 1.0 and 1.8 – 2.2 W/mK, respectively.<sup>2</sup> A high value reported for a polysiloxane based thermally conductive adhesive was 1.5 W/mK.<sup>1</sup>

Polysiloxanes have low glass transition temperatures ( $T_g$ s ~ -125 °C), remain flexible at subambient temperatures and are more thermally stable at higher temperatures relative to most organic polymers. Networks prepared from polysiloxanes offer a wide service temperature range and are therefore useful for applications where repeated thermal cycling is involved.  $T_g$ s of polysiloxane networks are well below use temperatures for typical microelectronic components. Additionally, low modulus polysiloxane elastomers can compensate for thermal expansion differences between the power source, e.g. semiconductor chip, and metal adherend line (heat sink) opposed to more brittle epoxy or acrylate thermosetting adhesives.<sup>1</sup>

The thermal conductivity of an adhesive depends on the amount and type of filler that can be dispersed in the adhesive resin. A goal of this research was to improve the dispersion quality of functionalized polyorganosiloxanes with polar conductive fillers. High concentrations of polar microfillers result in poor microcomposite dispersions with

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1. R. P. Cross, "Thermally Conductive Silicone Adhesives as an Alternative to Fasteners, Pads, and Greases for Thermal Management in Electronics",
  2. J. C. Bolger, "Prediction and Measurement of Thermal Conductivity of Diamond Filled Adhesives", *Proc. Electron. Compon. Technol. Conf.*, 42nd, 219-224, 1992.

nonpolar polydimethylsiloxanes (filler aggregation occurs). Functionalized polyorganosiloxanes with strongly electron donating pendent groups were synthesized to form complexes or hydrogen bond with metal or oxide fillers. Phosphines form complexes with metals; while phosphine oxide, nitrile and carboxylic acid groups are three strongly hydrogen bonding groups that interacted particularly well with oxide surfaces. Stronger interactions between the functional polysiloxane matrix with dispersed conductive fillers resulted in stable polyorganosiloxane microcomposites with higher concentrations of filler, and consequently higher thermal conductivities than currently available for PDMS resins.

Four different families of polar siloxanes were synthesized with controlled concentrations of nitrile, phosphine, phosphine oxide and carboxylic acid pendent moieties (Figure 1.1). Model siloxane monomers were prepared to investigate organophosphorus chemistry, including the Michaelis-Arbuzov rearrangement and free radical addition reactions with vinylsilyl species. Phosphine oxide substituted siloxane monomers were investigated for the ability to hydrogen bond and to participate in hydrosilation curing reactions. Another attribute of both silicon- and phosphorus-containing materials is that they yield large amounts of char upon burning. Integrating phosphorus into the polymer backbone or as a pendent sidechain group is one approach to forming flame retardant materials.

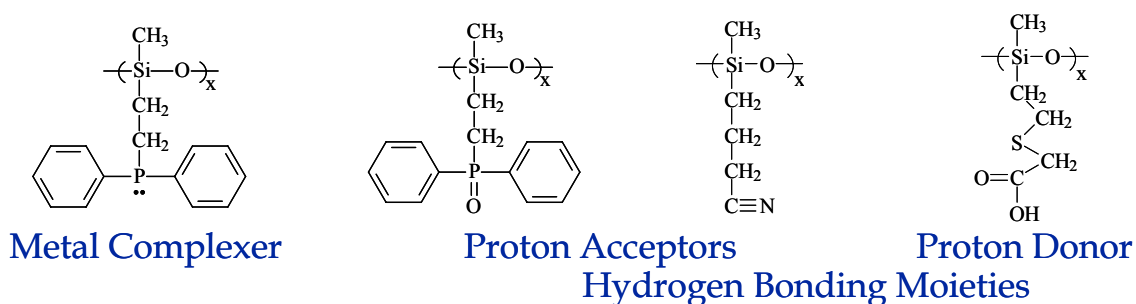


Figure 1.1. Polysiloxane Pendent Functional Groups Capable of Strongly Hydrogen Bonding or Complexing Metals

Model studies led to the syntheses of four new polyorganosiloxanes with precise concentrations of pendent polar moieties and crosslinkable groups. Concentrations of polar groups were tailored to control the  $T_g$ s and dispersion quality with polar microfillers. The molar fraction of crosslink sites controlled the crosslink densities of the respective networks. Ring opening co-equilibrations of cyclosiloxane tetramers yielded random polysiloxane copolymers with well-defined  $M_n$ s and concentrations of methylhydrosiloxy- or methylvinylsiloxy- repeat units. Allyl cyanide was hydrosilated with poly(dimethyl-co-methylhydrido)siloxanes to yield poly(dimethyl-co-methylhydrido-3-cyanopropylmethyl)siloxane random copolymers. Free radical addition reactions of diphenylphosphine or mercaptoacetic acid with vinyl substituted copolysiloxanes yielded phosphine or carboxylic acid substituted polysiloxanes with controlled amounts of vinyl groups left intact. Phosphine oxide substituted polysiloxanes were also synthesized by oxidizing the phosphine substituted polysiloxanes with bis(trimethylsilyl)peroxide.

Incorporation of strongly hydrogen bonding pendent moieties into polysiloxanes imparts significantly greater adhesive strength to a variety of metal and other oxide surfaces. Previous work showed that poly(3-cyanopropylmethyl)siloxanes exhibited adhesive peel strengths twice those of nonpolar polydimethylsiloxanes on aluminum adherends.<sup>3</sup> This improvement was attributed to secondary interactions between the lone pair of electrons on pendent nitrile groups with hydroxyl groups on the oxide layer of the aluminum. Consistent with this propensity for hydrogen bonding, transmission electron micrographs also suggested a strong interaction between the nitrile groups of the polysiloxane resin with surface silanols on fumed silica.<sup>4</sup>

Lightly crosslinked polyorganosiloxane networks with systematically varied crosslink densities and polarity were prepared via hydrosilation curing reactions of the vinyl- or hydrido- crosslink sites available after functionalization. The present study has

- 
3. J. K. Hoyt, P. Phillips, G. H. Li and J. S. Riffle, "Valuable Properties", *Adhesives Age*, 43: (5) 28-+ May 2000.
  4. J. K. Hoyt, C. H. Li, P. Phillips and J. S. Riffle, "Nitrile Containing Polysiloxanes as Novel Adhesive and Sealant Materials", *Abstr. Pap. Am. Chem. Soc., PMSE*, Aug. 2000.

shown that phosphine oxide and nitrile substituted polysiloxane networks exhibited much higher adhesive strengths with Al relative to nonpolar PDMS networks. Hydrogen bonding characterization via  $^1\text{H}$  NMR studies substantiated the adhesion data. A downfield shift was observed for the deshielded proton of chloroform when mixed in equivalent ratios with the functional groups on the resins.

Nitrile and phosphine oxide functional polyorganosiloxane resins were filled with very high volume percentages of various thermally conductive fillers and crosslinked to yield thermally conductive microcomposite networks. Both X-Ray Photoelectron Spectroscopy (XPS) and Transmission Electron Microscopy (TEM) data exhibited the importance of specific interactions between the resins and silica-coated AlN for stable microcomposites. Thermal conductivities of thin film (5 - 8 mils) microcomposites were measured for nitrile containing polysiloxanes filled with: silica-coated AlN, Al spheres, BN and Ag flake. A microcomposite comprised of a 9 molar % nitrile substituted polysiloxane and 67 volume % silica coated AlN had a thermal conductivity value of 1.42 W/mK, a  $T_g$  of  $-115$  °C and exhibited thermal stability in dynamic Thermogravimetric Analysis (TGA) measurements above 400 °C in both air and  $\text{N}_2$ . This low modulus ( $\sim 19$  MPa) microcomposite was the best thermally conductive adhesive candidate.

## Chapter 2. Literature Review

### 2.1. Historical Background of Phosphorus Chemistry

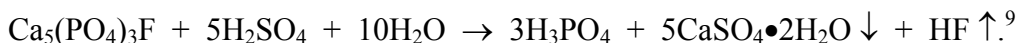
Phosphorus compounds represent a significant branch of chemistry and biochemistry due to a significant increase in knowledge during the last few decades. The bonding and structural versatility of phosphorus may be observed by its conflicting roles. While certain phosphorus compounds [deoxyribonucleic acid (DNA) and ribonucleic acid (RNA)] are essential to the life process, others (nerve gases and phosphine derivatives) can prove fatal in minute quantities. Moreover, elemental white phosphorus spontaneously ignites, yet certain phosphorus containing derivatives are among the best flame-retardant additives for materials today.<sup>5,6,7,8</sup>

Historically, in 1669, alchemist Hennig Brandt of Hamburg first obtained phosphorus by distilling urine in an attempt to make gold. However, Arabian alchemists may have been responsible for its discovery much earlier. The substance produced by Brandt burst into flames in open air and glowed in the dark; hence, it was given the name phosphorus, meaning "light bearing". Today, many materials that "glow" are said to "phosphoresce", yet may not contain the element phosphorus. The combustion product of phosphorus, phosphorus pentoxide, was discovered in 1694 by Boyle, who then dissolved his product in water to yield phosphoric acid. Scheele in 1770 recognized

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5. D. E. C. Corbridge, ed., Phosphorus: An Outline of its Chemistry, Biochemistry and Technology, Fourth Edition, Elsevier Scientific Publishing Company, Amsterdam, The Netherlands, 1990.
  6. E. N. Walsch, E. J. Griffith, R. W. Parry and L. D. Quin; eds., Phosphorus Chemistry, Developments in American Science, ACS Symposium Series **486**, American Chemical Society, Washington D. C., 1992.
  7. A. D. F. Toy, ed., Phosphorus Chemistry in Everyday Living, American Chemical Society, Washington D. C., 1976.
  8. A. D. F. Toy and E. N. Walsh, eds., Phosphorus Chemistry in Everyday Living, Second Edition, American Chemical Society, Washington D.C., 1987.

phosphorus as an essential component of animal bones and teeth. In 1779 Gahn identified one of the first phosphorus-containing compounds, pyromorphite.<sup>5,8</sup>

One of today's most industrially important families of phosphorus based products, fertilizers, was recognized as early as the latter portion of the 18<sup>th</sup> century. Liebig and Lawes recognized the value of phosphates as fertilizers as advances were made in the science of plant nutrition. Lawes and Murray were granted British patents in 1842 for the manufacture of fertilizers from bones and sulfuric acid.<sup>5</sup> An alternate source of phosphorus other than from urine and bones was needed and was found in calcium phosphate mineral deposits. This led to serious commercial production in Europe ~ 1850 of phosphorus compounds directly from the ores via the "wet process" production of phosphoric acid:



The electric furnace method, a major development, was subsequently invented by Readman in 1888 for the continuous production of phosphorus directly from phosphate ores. This chemistry,<sup>8</sup>  $2\text{Ca}_3(\text{PO}_4)_2 + 6\text{SiO}_2 + 10\text{C} \rightarrow \text{P}_4 \uparrow + 10\text{CO} \uparrow + 6\text{CaSiO}_3$ , is similar to that of Brandt's distillation of urine.<sup>9</sup> A mixture of phosphate rock, sand and coke are heated to ~ 1500°C in an electric furnace. Phosphorus yields of ~90% are collected after the phosphorus vapors and CO gas are first passed through an electrostatic precipitator, to remove particulate matter, and then through water condensers. Today, most phosphorus is converted to more useful reagents:  $\text{PCl}_3$ ,  $\text{POCl}_3$ ,  $\text{P}_4\text{S}_{10}$  and phosphoric acid,  $\text{H}_3\text{PO}_4$ . Typical ammonium phosphate fertilizers,  $(\text{NH}_4)\text{H}_2\text{PO}_4$  and  $(\text{NH}_4)_2\text{HPO}_4$ , are made from ammonia and  $\text{H}_3\text{PO}_4$ .<sup>9</sup>

The most ubiquitous phosphorus chemistry is encountered in its firemaking ability in the match. The earliest known French "ethereal match" was expensive and in vogue in 1780. A four-inch glass tube containing a thin wax taper dipped in white phosphorus would burst into flame upon introducing air to oxidize the phosphorus by breaking the tube. Precursors to the wooden "strike anywhere" match may be attributed to the white

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9. J. Emsley and D. Hall, eds., The Chemistry of Phosphorus, Environmental, organic, inorganic, biochemical and spectroscopic aspects, John Wiley & Sons, Inc., New York, 1976.

phosphorus-tipped splint matches made by Sauria in 1830, and the "strike on the (red phosphorus coated) box safety match" by J. E. Lundstrom in 1855.

White phosphorus causes a disease known as phosphorus necrosis or "phossy jaw", a serious illness of workers in the match factories. White phosphorus was prohibited from the formulation of matches in 1939 by Egyptian law. Phosphorus sesquisulfide ( $P_4S_3$ ) replaced it as a fuel along with potassium chlorate as the oxidizer, and the formulation was patented in 1898. The patent was subsequently deeded to the public in 1911 by the Diamond Match Company.<sup>5,6,8,10</sup> It was also during this era that simple inorganic phosphorus compounds were characterized: phosphine by Gengembre in 1783 and Kirwan in 1786, and  $PCl_3$ ,  $PCl_5$  and probably  $PF_3$  by Gay Lussac in 1808, and also by Thenard and Davy.<sup>5,11</sup>

Orthophosphoric acid,  $H_3PO_4$ , is the starting material for most industrially important phosphorus based materials. It is manufactured by either the "wet process" described above or the thermal process:<sup>8</sup>  $P_4 + 5O_2 \rightarrow P_4O_{10}$ ,  $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$ . Over 75% of the world's phosphate rock is converted to phosphoric acid using the dry thermal method.<sup>5</sup> In fact, the ever popular soft drinks, such as Coca Cola<sup>®</sup>, are basically sweetened, flavored and carbonated dilute phosphoric acid solutions. They are packaged in glass bottle containers cleaned in an alkaline bath with sodium phosphates, and sealed with a metal cap that has been phosphated in a phosphoric acid solution to prevent the cola from rusting through the enamel coating.<sup>8</sup> Other notable phosphorus compounds include plasticizers, fire retardants and toxic war gases. Major phosphorus based applications are fertilizers, the largest single use, followed by detergents and animal foodstuffs.<sup>5</sup>

Phosphorus was first associated with living tissues after the discoveries of the first organic phosphorus compounds. Lethicin, found in brain fat, was one of the first organic phosphorus compounds discovered by Vauquelin in 1811. It was characterized as a

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10. J. R. Van Wazer, ed., Phosphorus and its Compounds, Volume II: Technology, Biological Functions, and Applications, Interscience Publishers, Inc., New York, 1961.
  11. J. R. Van Wazer, ed., Phosphorus and its Compounds, Volume I: Chemistry, Interscience Publishers, Inc., New York, 1958.

phosphorus containing lipid by Gobley in 1850, followed soon thereafter in 1868 by the isolation of "nuclein" from debris on surgical bandages by Miescher. The first synthetic organic phosphorus compounds are attributed to Lassaigne, who reacted alcohols with phosphoric acid to yield crude alkyl phosphates in 1820. By 1840, Thenard had synthesized phosphine derivatives. Many more phosphorus-carbon-containing compounds were produced before the turn of the century that are mostly credited to the so-called "founders of organophosphorus chemistry", Michaelis and Arbuzov.<sup>5</sup>

Phosphorus-carbon-containing compounds are related to the most significant advances in biology and biochemistry in the 20<sup>th</sup> century. In 1929, Fiske and Subarrow isolated the "universal energy transfer compound," adenosine triphosphate (ATP) from muscle. This compound was later synthesized by Todd and co-workers in ~1950. The discovery of two significant biological processes soon followed: glycolysis in 1932 by Embden and Mayerhof and glucose oxidation in 1937 by Krebs. Lipman soon thereafter in 1941 formulated the concept of high energy phosphate bonds. It was near the end of World War II that Schrader and Saunders independently discovered the toxic properties of several phosphate esters (leading to their development as insecticides and nerve gases).<sup>5</sup>

Interestingly, the reported net worth of a 150 lb. human body in 1984 was ~\$9.00 and only 98¢ during the depression in 1936.<sup>7</sup> Typical chemical composition of the body consists of 65% O, 18% C, 10% H, 3% N, 1.5% Ca, 1% P and 1.5% other. This ≈ 1% body weight of phosphorus is crucial. While human teeth and bones are basically calcium phosphates, the remainder of phosphorus plays a vital role in controlling genetic makeup and biological functions.<sup>8</sup> In 1940, highly polymerized phosphate esters were established as nucleic acids, the normal constituents of all cells and essential constituents of chromosomes.<sup>6</sup> This led to the definition of molecular structures for the nucleic acids, DNA and RNA, by Crick and Watson in 1953. The possibilities for genetic engineering became evident in 1973 with the techniques for DNA cloning.<sup>5</sup> A sheep named Dolly was the first successfully cloned mammal, and human cloning technology was publicly documented in 1996 at the Roslin Institute in Scotland.

Phosphorus is not found free in nature, but typically in its fully oxidized state as phosphate. It exists widely in soils, rocks, oceans, living cells, most foods and many man-made materials, but not in the atmosphere. Of the major life elements (H, C, N, O, P and S), phosphorus is the least plentiful in the ocean, second to carbon in the earth's crust, and 12<sup>th</sup> in abundance. The United States (Florida), Morocco and the U.S.S.R. are the largest producers of phosphate rock with over 150 million tons produced annually, of which over 90% is used for fertilizers. Guano, a deposit from decayed bones and excreta, is the second most abundant source of phosphorus, accounting for less than 10% of the world's phosphate. A third and minor source is "slag", the by-product of furnaces processing iron ores containing significant phosphorus content. It should be noted that unduly high phosphate concentrations in lakes promote excessive algae growth, causing severe oxygen depletion. This unwelcome environmental effect is known as eutrophication and is believed to be the direct result of increased polyphosphate detergents introduced into domestic sewage.<sup>5</sup>

In addition to the liquid and vapor states, elemental solid phosphorus may be obtained in more allotropic forms than any other element. While the three major allotropes, white, red and black have been recognized for over fifty years, many polymeric forms have also been discovered. Although their interconversion is not well understood, heat, X-rays or light can typically initiate the conversions.<sup>12</sup>

White phosphorus is the most volatile and reactive allotrope, and is consequently highly toxic. It spontaneously ignites in air or oxygen. The slow oxidation of its emitted vapor gives phosphorus its characteristic "phosphorescent glow". This soft waxy white colored (yellow when impure) form of phosphorus is readily soluble in a number of organic solvents. Pure white phosphorus exists in a cubic ( $\alpha$ ) crystalline form at room temperature with the following properties:  $\rho = 1.82 \text{ g/mL @ } 20 \text{ }^\circ\text{C}$ , m.p. =  $44.1^\circ\text{C}$ , b.p. =  $280^\circ\text{C}$  and a vapor pressure of 0.181 mm at RT ( $20 \text{ }^\circ\text{C}$ ). A hexagonal ( $\beta$ ) crystalline form of white phosphorus with a slightly higher density of 1.88 g/mL is formed at  $-77 \text{ }^\circ\text{C}$  and which transforms reversibly to the cubic form.<sup>12</sup>

The black and red allotropes exist as a few different polymeric crystalline allotropes along with one amorphous form each. Black phosphorus is the most thermodynamically stable form. The dark colored allotropes ranging in density between

2.25 and 3.88 g/mL are highly polymeric, insoluble forms of phosphorus with low vapor pressures. Red phosphorus is found as a variety of reddish forms whose densities and melting points vary between 2.0 and 2.4 g/mL at 585 and 610 °C, respectively. Color variations are formed that depend upon particle size variations or types of impurities present. The stabilities and reactivities of red phosphorus allotropes lie between those of white and black, although red allotropes exhibit a greater resemblance to the latter. They are insoluble polymers which do not ignite spontaneously in air, although they do ignite more easily than black phosphorus.<sup>12</sup>

## 2.2. Chemistry of Phosphorus

The element phosphorus, P, atomic number 15, is a nonmetal with an atomic weight of 30.98 g/mol. It is the second lightest element in Group V (referred to as the Pnicogens or Pnictides) directly below nitrogen and above arsenic in the periodic table. The major phosphorus isotope, <sup>31</sup>P, has a nuclear spin of ½, making it a good element for NMR measurements. Six other unstable isotopes with various half-lives are known: <sup>28</sup>P: 0.3 sec., <sup>29</sup>P: 4.4 sec., <sup>30</sup>P: 2.5 min., <sup>32</sup>P: 14.3 sec., <sup>33</sup>P: 25 days, <sup>34</sup>P: 12.4 sec. The electronic atomic structure of P is 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>3</sup> with 3 unpaired electrons in the outer 3p orbitals available for bonding.<sup>5</sup> Phosphorus may form chemical linkages with as many as ten close neighbors, as is the case for coordinated metallic phosphides where the bonds are either part metallic or largely ionic. Phosphorus may be formally trivalent or pentavalent when using its 3 electrons from the outer p orbitals or all 5 electrons from the outermost shell, respectively.<sup>5,9,12</sup>

Phosphorus chemistry resembles arsenic, a metalloid, and the heavier Group V elements more closely than it does the nonmetal nitrogen. Phosphorus has readily available d orbitals resulting in a larger atom with a higher polarizability, thereby making its lone pair of electrons more reactive than nitrogen. The energy gap from 3s → 3d (16.5 eV) is small enough that its vacant d orbitals may participate in bonding, allowing for pentavalency and hybridized orbitals with special orientations (Figure 2.1).<sup>5</sup>

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12. D. E. C. Corbridge, ed., The Structural Chemistry of Phosphorus, Elsevier Scientific Publishing Co., Amsterdam, 1974.

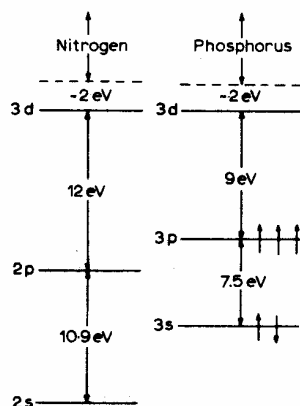


Figure 2.1. Energy Gap from 3s to 3d for Nitrogen and Phosphorus<sup>5</sup>

Effective d orbital bonding is not available for nitrogen and other first row elements as the transition energy required for  $2s \rightarrow 3d$  (22.9 eV) is too great.<sup>5,12</sup> For this reason, amine oxides ( $R_3N^+-O^-$ ) which lack accessible d orbitals cannot form double bonds and are consequently much less stable than phosphoryl ( $R_3P=O$ ) compounds. Nitrogen also lacks the ability to form stable tetrahedral oxyanions like phosphorus and arsenic,  $PO_4^{3-}$  and  $AsO_4^{3-}$ .<sup>5</sup>

The Pauling electronegativity value of phosphorus (2.1) is also closer to arsenic (2.0) than nitrogen (3.0). In fact, only oxygen (3.5) and fluorine (4.0) have higher values than nitrogen. The electronegativity of phosphorus (2.1) is less than carbon (2.5), greater than silicon (1.8) and approximately equal to hydrogen (2.1). Nitrogen, a small first row element, forms very strong hydrogen bonds, while those involving the much larger phosphorus atoms are very weak. Heavier atoms such as S, As, Sb (1.8) and Bi (1.8) are incapable of forming hydrogen bonds.<sup>5</sup> Phosphorus and the heavier pnictides also form continuous chains of single bonds (e.g. -P-P-P-P-P-) similarly to S. The pnictides, excluding nitrogen, may be found in this highly polymerized form. Nitrogen is the only pnictide that preferentially forms double bonds.<sup>5</sup>

Trivalent phosphorus compounds are pyramidal and are characterized by their unshared lone pairs of electrons. The apex angles of the pyramidal conformation are closer to  $100^\circ$  than  $90^\circ$  and may be regarded as tetrahedral with the lone pair electrons

residing in the fourth position. The two unshared 3s electrons along with the three 3p electrons which form covalent bonds complete the outer octet. The lone pair of electrons on trivalent phosphorus confers a high degree of chemical reactivity that leads to a high propensity to polymerize or oxidize to the pentavalent state.<sup>5</sup> For example, pyramidal phosphorus trichloride readily oxidizes to become tetrahedral, pentavalent phosphorus oxytrichloride (Figure 2.2).<sup>5</sup>

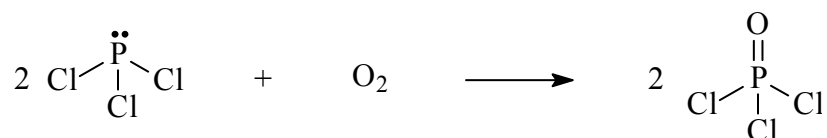


Figure 2.2. Oxidation of Phosphorus Trichloride<sup>5</sup>

The typical spatial arrangements of pentavalent phosphorus compounds may be either tetrahedral or trigonal bipyramidal (Figure 2.3).<sup>5</sup> The phosphoryl moiety, P=O, in the pentavalent compound phosphorus oxytrichloride may be referred to as a donor type covalent bond. This "double" bond is formed by the donation of the unshared lone electron pair on phosphorus to an oxygen atom, thereby giving this bond partial ionic properties. It may be written as P<sup>+</sup>—O<sup>-</sup>, P→O or as P=O, a "double" bond, completing the formal pentavalency on the central phosphorus atom.<sup>12</sup> When phosphorus acquires three extra electrons, it may form four of these "donor" type P→O bonds as in the very stable orthophosphate anion, PO<sub>4</sub><sup>3-</sup>. Alternatively, four single covalent P-Cl bonds are formed when phosphorus loses one electron, as in PCl<sub>4</sub><sup>+</sup>, the tetrachlorophosphonium cation.<sup>5</sup>

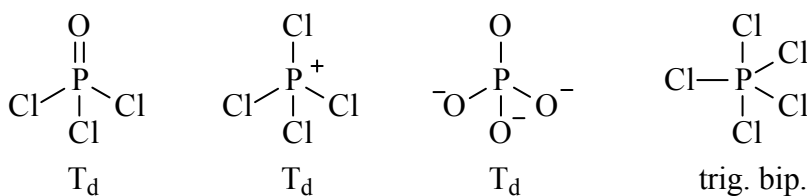


Figure 2.3. Typical Spatial Arrangements of Pentavalent Phosphorus<sup>5</sup>

Phosphorus utilizes its d rather than p orbitals in compounds having  $\pi$  or multiple bonds. It does not often form stable  $p\pi$ - $p\pi$  double bonds with C, N, O or S. This situation is similar to cases with other second row elements such as Si and S. The nature of the atoms bound to phosphorus control the degree of d orbital  $\pi$  bonding available. Bound atoms which are very electronegative increase the effective positive charge on phosphorus, thereby favoring  $\pi$  bonding with its  $d_z^2$  and  $d_{x^2-y^2}$  orbitals. Back-donation also occurs when the atoms bound to phosphorus have unshared electron pairs that are available to fill the empty phosphorus d orbitals. For example, the oxygen electrons in  $\text{POCl}_3$  back-donate to yield  $3d_\pi(\text{P})$ - $2p_\pi(\text{O})$  bonding in addition to  $\sigma$  bonding. Although  $\pi$  bonding is typically weak for trivalent phosphorus compounds, it is a significant addition to  $\sigma$  bonding in tetrahedral compounds.<sup>5</sup> The symmetric tetrahedral orthophosphate anion,  $\text{PO}_4^{3-}$  is probably the most commonly encountered resonance structure in phosphorus chemistry (Figure 2.4). It is comprised of a  $\pi$  bond equally distributed, which resonates among four linkages. In contrast, the  $\pi$  bonding in  $\text{POCl}_3$  resides almost completely in the phosphoryl bond, more representative of a fixed "double" bond.<sup>5</sup>

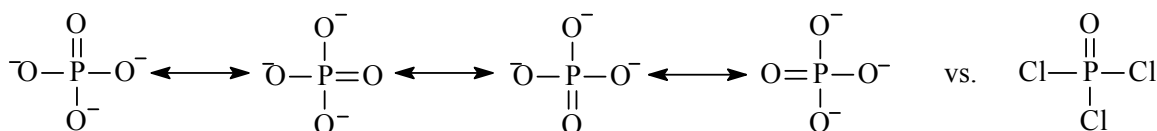


Figure 2.4. Resonance Structures of the Orthophosphate Anion<sup>5</sup>

The phosphoryl moiety,  $\text{P}=\text{O}$ , in symmetrical  $\text{R}_3\text{P}=\text{O}$  compounds is extremely stable. This special stability is attributed to the two lone electron pairs on oxygen that back-donate to overlap with two separate d orbitals of phosphorus. This formation of two mutually perpendicular  $d_\pi$ - $p_\pi$  orbitals offers the symmetry (although not the strength) of a triple bond. The  $p_z^2$ - $d_{x^2-y^2}$  orbital overlap scheme for  $\text{POCl}_3$  is represented as follows (Figure 2.5).<sup>12</sup>

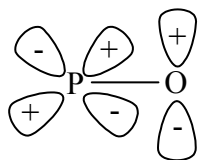


Figure 2.5. Orbital Overlap for  $\text{POCl}_3$ <sup>12</sup>

The extent of d orbital participation depends on the bond character of phosphorus linkages.<sup>5</sup> High bond strengths characterized by unusually short interatomic distances and absorption at high infrared frequencies are all evidence for multiple bonding involving d orbitals. Bond strengths for selected phosphorus compounds have been reported (Table 2.1).<sup>5</sup>

Table 2.1. Relative Strengths of Phosphorus Bonds and Related Atoms<sup>5</sup>

<b>Heteropolar Bond Energies (kcal/mol)</b>						
P-H 77	N-H 93	As-H 59	Sb-H 70	C-H 99	Si-H 70	S-H 81
P-F 126	N-F 65	As-F 116	Sb-F 108	C-F 105	Si-F 135	
P-Cl 79	N-Cl 46	As-Cl 69	Sb-Cl 74	C-Cl 78	Si-Cl 86	S-Cl 60
P-Br 63		As-Br 58				
P-I 44		As-I 43				
P-C 65	N-C 73	As-C 48	Sb-C 47			
P-N 55				C-N 73	Si-N 77	
P-O 86	N-O 50			C-O 85	Si-O 88	
P=O 130	N=O 145			C=O 174		
<b>Comparison of Bond Energies for Carbon, Nitrogen and Phosphorus (kcal/mol)</b>						
	P-P 50		N-N 39		C-C 83	
	P=P 84		N=N 104		C=C 146	
	P≡P 117		N≡N 226		C≡C 200	

It is generally found that:<sup>5</sup>

- 1) P-H bonds are weaker than N-H or C-H and are comparable to Si-H or S-H.
- 2) P-X (X = halogen) bonds are about as strong as C-X and stronger than N-X.
- 3) P-O bonds are stronger than both N-O and C-O.
- 4) P-C bonds are  $\approx$  C-C and N-C.
- 5) P=O bonds are stronger than P=S and much stronger than P-O, but somewhat weaker than C=O or N=O.

The stability of phosphorus compounds depends on the bonds and their environments. The P-C bond is very resistant against hydrolysis or oxidation and is considered more stable than C-C bonds under these conditions.<sup>5</sup> The corresponding P-Si bonds are typically less stable. The P=O phosphoryl donor type bond governs a great majority of phosphorus chemistry due to its exceptional strength and stability. It should be cautioned that when the oxygen is involved in a bridge, such as P-O-P or P-O-C, its hydrolytic stability is greatly diminished. When hydrolytic stability is desired, a P-O-P bridge is more resistant to hydrolysis than a P-O-Si bond. The P=O and P-O bonds have better hydrolytic and thermal stability than the sulfur analogues.<sup>5</sup>

The interatomic distance between atoms for  $\sigma$  bonds may be estimated by the simple addition of the single bond covalent radii of the two atoms. However, experimentally determined bond lengths between unlike atoms are typically shorter than expected. Both partial ionic bond character (related to the electronegativities of the bound atoms) and  $\pi$  bonding are responsible for the shorter bond lengths.<sup>5</sup> Representative bond lengths for phosphorus compounds are provided in Table 2.2.<sup>5</sup> The very short bond length, 1.45 Å, of the P=O linkage, in  $\text{POCl}_3$  is second only to the short P-H bond of 1.44 Å in phosphines. The special stability of the phosphoryl linkage is attributed to the  $\pi$  character of the bond. In fact, P-O bond lengths are linearly dependant on the  $\pi$ -bond order and are significantly longer as the  $\pi$  character is decreased.<sup>5</sup>

Table 2.2. Interatomic Distances for Phosphorus and Related Bonds<sup>5</sup>

<b><u>Representative Bond Lengths for Phosphorus Compounds</u></b>		
<b>Bond</b>	<b>Length (Å)</b>	<b>Compound</b>
P-H	1.44	PH <sub>3</sub>
P-F	1.57	PF <sub>3</sub>
P-Cl	2.04	PCl <sub>3</sub>
P-Br	2.22	PBr <sub>3</sub>
P-I	2.52	PI <sub>3</sub>
P-B	1.96	PB
P=B	1.83	(Mes) <sub>2</sub> B=PMes
P-C	1.85	PMe <sub>3</sub>
P=C	1.66	Ph <sub>3</sub> P=CH <sub>2</sub>
P≡C	1.54	HCP
P-N	1.77	NaHPO <sub>3</sub> NH <sub>2</sub>
P=N	1.57	Ph <sub>3</sub> PNC <sub>6</sub> H <sub>4</sub> Br
P≡N	1.49	PN
P-O	1.64	P <sub>4</sub> O <sub>6</sub>
P-O <sup>-</sup>	1.54	LiMnPO <sub>4</sub>
P=O	1.45	POCl <sub>3</sub>

The characteristic lone pair electrons on trivalent phosphorus lends both nucleophilic and basic activity, which parallel nitrogen chemistry. Phosphorus is larger than N and has more polarizable electron pairs, making it more nucleophilic than nitrogen.<sup>9</sup> For example, Et<sub>3</sub>P is more reactive toward MeI than Et<sub>3</sub>N.<sup>5</sup> Phosphorus compounds typically react by electron pair mechanisms. In general, trivalent phosphorus derivatives are nucleophilic and pentavalent phosphorus exhibits electrophilic behavior.<sup>5,9</sup>

The trivalent pyramidal configuration, where a lone pair occupies what would be the fourth substituent of a tetrahedron is the most reactive for phosphorus compounds. As a nucleophile, it reacts rapidly with electron deficient centers (a), alkyl halides (b), and commonly substitutes at halogen centers (c) (Figure 2.6). When phosphorus boasts a complete outer octet with three electron withdrawing halide substituents, it may exhibit electrophilic behavior, accepting electrons from halides (Figure 2.6 d).<sup>5</sup>

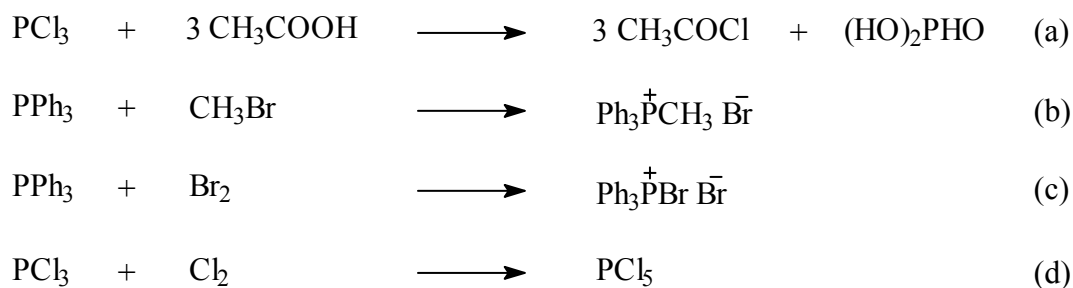


Figure 2.6. Representative Reactions of Trivalent Phosphorus Compounds<sup>5</sup>

Trivalent phosphorus having alkoxy substituents are nucleophilic and react with alkyl halides to yield carbon-phosphorus bonds (Figure 2.7).<sup>9</sup> This extremely important reaction known as the Michaelis-Arbuzov rearrangement will be discussed in detail later.

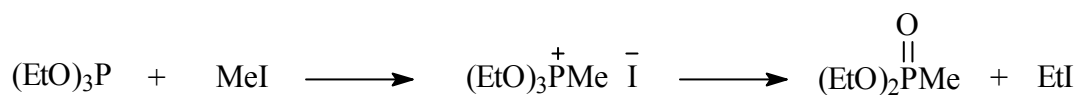


Figure 2.7. The Michaelis-Arbuzov Rearrangement<sup>9</sup>

Phosphorus exhibits biphilic reactivity (nucleophilic and electrophilic behavior in the same reaction) during the formation of phosphoryl reagents  $\text{R}_3\text{P}=\text{O}$ . It acts as a nucleophile in forming  $\sigma$  bonds and as an electrophile in forming  $\pi$  bonds by accepting electrons via back-donation. Phosphorus will in fact rearrange intramolecularly to a phosphoryl when possible in the absence of catalysts or other reagents. A complete review of uncatalyzed rearrangements of trivalent phosphorus esters to phosphoryls was published by Victor Mark.<sup>13</sup> The driving force (D) for the formation of the very strong phosphoryl group often dominates phosphorus chemistry ( $D_{\text{P}=\text{O}} = 523\text{-}631 \text{ kJ/mol}$  vs.  $D_{\text{N}^+-\text{O}^-} = 210\text{-}290 \text{ kJ/mol}$ ) and is generally the final, irreversible step in any reaction sequence.<sup>5</sup> This final rearrangement occurs in Michaelis-Arbuzov reactions between alkyl halides and phosphites.

13. B. S. Thyagarajan, ed., V. Mark, "The Uncatalyzed Rearrangement of Trivalent Phosphorus Esters", in Mechanisms of Molecular Migrations, Volume 2, John Wiley & Sons, Inc., New York, 1969.

Both trivalent and pentavalent phosphorus compounds undergo nucleophilic substitution reactions. Phosphine oxides,  $R_3P=O$ , are a significant exception due to the exceptional stability of the phosphoryl moiety. In this respect, phosphorus chemistry does not parallel the reactive carbon ketone analogue,  $R_2C=O$ . Carbon and phosphorus substitution reactions both form the trigonal bipyramidal intermediate in a one-step  $S_N2$  mechanism. A major difference is that the phosphorus intermediate has a finite existence ( $> 10^{-13}$  s), which can be observed and in some cases isolated, whereas the transition state involving carbon has only a transient existence ( $< 10^{-13}$  s). The intermediate phosphorus trigonal bipyramid is observed especially when the substituents are not "good leaving groups". This scenario is not the case when the driving force is present to form a phosphoryl group where substitution proceeds readily.<sup>5,9</sup>

Optically active tetrahedral compounds demonstrate another difference observed in the  $S_N2$  mechanism (pentacoordinate intermediate) between carbon and phosphorus chemistry. Carbon  $S_N2$  reactions are stereospecific and yield products with inversion of the molecular configuration. Stereospecificity is not always observed for phosphorus where pseudorotation of the trigonal bipyramid may occur before the leaving group is eliminated. The phosphorus  $S_N1$  (ionic intermediate, two-step mechanism) also occurs and is analogous to that for carbon chemistry. Substitution reactions at initially pentavalent phosphorus atoms certainly have no resemblance to carbon chemistry. Of the limited knowledge describing these reactions, it is known that they proceed with octahedral or tetrahedral phosphonium ion transition states, each of which can coexist in equilibrium with trigonal bipyramidal configurations.<sup>5,9</sup>

### **2.3. Phosphorus Nomenclature**

Phosphorus nomenclature can be ambiguous as there is no complete and universally accepted system. In 1952, a joint committee formed by the British and American Chemical Societies attempted to make formal recommendations on naming compounds with one phosphorus atom.<sup>14</sup> As international agreement has yet to occur,

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14. Editorial Report on Nomenclature, Appendix 3, "Nomenclature for Compounds based on One P Atom", *J. Chem Soc.*, pp. 5122-5131, 1952.

other sources may be used as guides.<sup>15,16</sup> Many common phosphorus compounds may be referred to by two or more widely accepted names:<sup>5</sup>

1)	PH <sub>3</sub>	phosphine	phosphane
2)	PPh <sub>3</sub>	triphenylphosphine	phosphorus triphenyl
3)	HP(O)(OH) <sub>2</sub>	phosphorus acid	phosphonic acid
4)	H <sub>2</sub> P(O)OH	hypophosphorus acid	phosphinic acid
5)	Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	sodium pyrophosphate	sodium diphosphate
6)	POCl <sub>3</sub>	phosphorus oxychloride	phosphoryl chloride
7)	PO(NH <sub>2</sub> ) <sub>3</sub>	phosphoryl triamide	phosphoric triamide
8)	H <sub>2</sub> N-PH <sub>2</sub>	phosphazane	aminophosphine
9)	HN=PN	phosphazene	iminophosphine
10)	H <sub>3</sub> P=CH <sub>2</sub>	phosponium methylide	phosphine methylene

The nomenclature for organophosphorus compounds based on phosphinic derivatives, R<sub>2</sub>P(O)-, and phosphonic derivatives,  $\text{R}_2\text{P}(\text{O})\begin{matrix} \diagup \\ \diagdown \end{matrix}$ , has proved very convenient. This style has in fact found its way into most branches of phosphorus chemistry, e.g. POCl<sub>3</sub> is phosphoryl chloride, MePOCl<sub>2</sub> is methylphosphonic dichloride and Me<sub>2</sub>POCl is dimethylphosphinic chloride.<sup>9</sup> Organophosphorus compounds may be based on the four organophosphorus acids (Figures 2.8 and 2.9).<sup>17</sup>

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15. F. G. Mann, The Heterocyclic Derivatives of P, As, Sb & Bi, Wiley, New York, 1970.
  16. Int. Union of Pure and Applied Chemistry, IUPAC 1957 Rules, "Convention for Naming Ring Compounds IUPAC", *J. Am. Chem. Soc.*, **82**, 5566, 1960.
  17. M. Sander and E. Steininger, "Phosphorus-Containing Polymers: Introduction", *J. Macromol. Sci. (Revs.)*, **C1**(1), pp. 1-5, 1967.

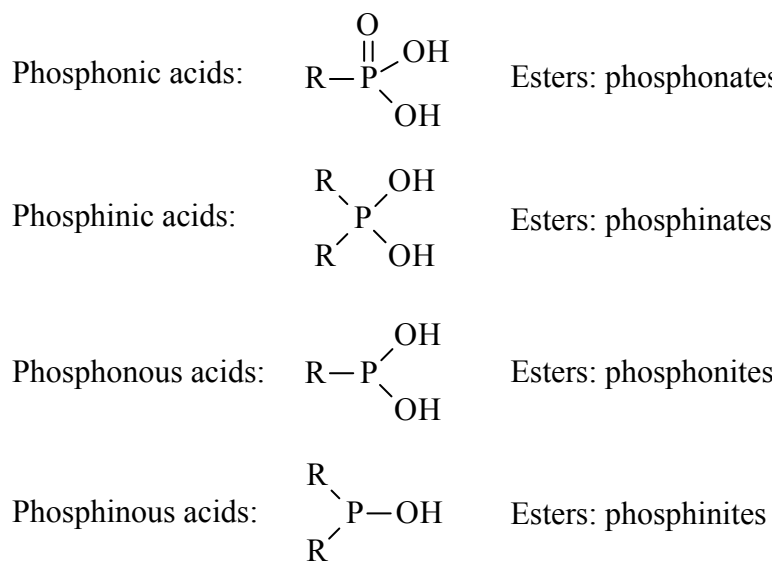


Figure 2.8. Organophosphorus Acids<sup>5</sup>

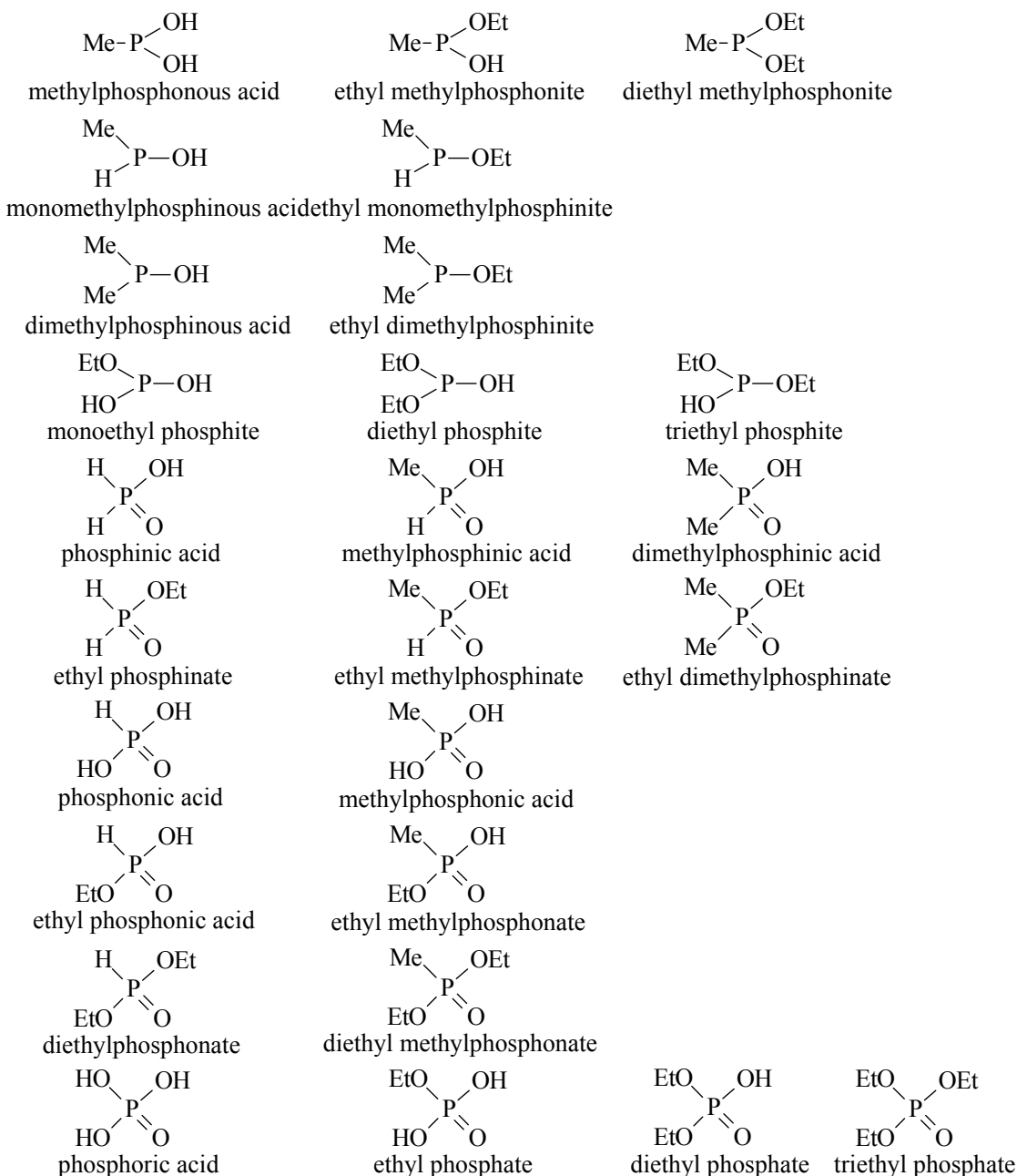


Figure 2.9. Organophosphorus Nomenclature<sup>5</sup>

## 2.4. Phosphorus- Containing Polymers

Two main limitations of typical organic polymers are thermal instability and lack of flame resistance. Flame and thermal resistance of polymers may be improved by the combined incorporation of aromatic rings along with certain chemical elements such as

phosphorus.<sup>18</sup> Double strand aromatic polymers, e.g. polyimides with heterocyclic ring systems in the backbone improve thermal stability. The high aromatic compositions of typical polyimides also lead to improved flame resistance.<sup>18</sup> Novel volatile-free phenolic-epoxy networks<sup>19</sup> and phenolic-epoxy matrix composites<sup>20</sup> have also shown significant potential as flame retardant materials for adhesives and structural composites.

Phosphorus may be incorporated into organic resins to improve the flame resistance of polymeric materials. One approach is to blend organophosphorus flame retardant additives into the resinous matrix. Several drawbacks are associated with this method. There is often poor compatibility with the base polymer, especially since high amounts of the additive may be necessary. The resultant polymer blend may also yield a high amount of volatiles upon burning, and adverse effects on the mechanical properties and processability of the polymer blend occur. Phosphorus may be strategically integrated into the polymer to overcome these undesirable properties.<sup>18</sup> Several approaches to this method exist. Phosphorus may be incorporated into the side chains via modification of polymers.<sup>21</sup> Linear chains may be synthesized with phosphorus in the backbone and these linear polymers can also contain cyclic structures.<sup>22</sup> The phosphorus containing- polymer chain structure, e.g. (aliphatic or aromatic) influences the flame

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18. S. Maiti, S. Banerjee and S. K. Palit, "Phosphorus-Containing Polymers", *Prog. Polym. Sci.*, Vol. 18, pp. 227-261, 1993.
  19. H. Ghassemi, H. K. Shobha, M. Sankarapandian, A. Shultz, C. L. Sensenich, J. S. Riffle, J. J. Lesko, J. E. McGrath and U. Sorathia, "Volatile-free Phenolic Networks for Infrastructure", pp. 46-56, in Fiber Compos. Infrastruct., Proc. Int. Conf. Compos. Infrastruct., 2<sup>nd</sup>, Vol. 1, Saadatmanesh and Hamid, eds., University of Arizona, Engineering Professional Development, Tuscon, Az., 1998.
  20. C. S. Tyberg, P. Shih., K. N. E. Verghese, A. C. Loos, J. J. Lesko and J. S. Riffle, "Latent Nucleophilic Initiators for Melt Processing Phenolic-Epoxy Matrix Composites", *Polmer*, 41(26), pp. 9033-9048, 2000.
  21. M. Sander and E. Steininger, "Chapter 1: Linear Polymers with Phosphorus in Side Chains", *J. Macromol. Sci. (Revs.)*, C1(1), pp. 7-89, 1967.
  22. M. Sander and E. Steininger, "Chapter 2: Linear Polymers with Phosphorus and Carbon in the Main Chain", *J. Macromol. Sci. (Revs.)*, C1(1), pp. 91-177, 1967.

retardancy of the final product.<sup>18</sup> Low molecular weight compounds containing phosphorus combined with nitrogen (e.g. polyphosphoric amides) or halogens can yield synergistic effects on flame retardance. Phosphazenes represent the oldest known synthetic polymer and one of the most intensely studied inorganic macromolecules in terms of flame retardance.<sup>23</sup>

Phosphorylation is one approach for incorporating phosphorus into linear thermoplastics<sup>24</sup> as high molecular weight phosphorus-containing thermoplastic materials are difficult to synthesize. Phosphorus may cause chain termination or radical transfer during polymerizations.<sup>25</sup> Copolymers produced from a combination of phosphorus and non-phosphorus containing monomers typically have lower molecular weights than homopolymers void of phosphorus. In fact, the molecular weights of copolymers decrease as the percentage of phosphorus-containing monomers is increased. However, higher molecular weight copolymers may be obtained when relatively low percentages of phosphorus-containing monomers are used.

Copolymerization reactivity ratios have been investigated for a large number of combinations of phosphorus and nonphosphorus containing monomers. The relative inertness of unsaturated phosphorus monomers to polymerize is made evident by their typically lower copolymerization parameter values. Trivalent phosphorus compounds display the greatest polymerization inhibiting effects. Primary and secondary phosphines are pronounced inhibitors that rapidly transfer their hydrogens to radicals. Tertiary phosphines and trialkyl or triaryl phosphites also represent effective radical scavengers, or radical chain transfer reagents. It has also been reported that P(III) monomers reduce oxidizing initiators (such as peroxides) thereby deactivating them.<sup>21</sup> Interestingly, a high degree of polymerization (from radical or spontaneous initiation) occurs when the

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23. M. Sander and E. Steininger, "Chapter 4: Inorganic Phosphorus Polymers", *J. Macromol. Sci. (Revs.)*, **C2**(1), pp.33-56, 1968.

24. M. Sander and E. Steininger, "Chapter 5: Phosphorylation of Polymers", *J. Macromol. Sci. (Revs.)*, **C2**(1), pp. 52-72, 1968.

25. M. Sander and E. Steininger, "Chapter 3: Phosphorus-Containing Resins", *J. Macromol. Sci. (Revs.)*, **C2**(1), pp. 1-31, 1968.

phosphorus atom of the monomer is bound to several electron attracting (and bulky) groups. For example, a triphenylphosphine containing vinyl monomer polymerizes relatively faster than styrene (Figure 2.10).<sup>21</sup>

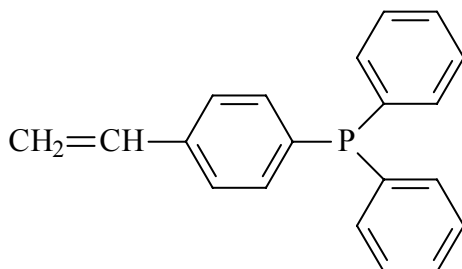


Figure 2.10. Triphenylphosphine Containing Vinyl Monomer<sup>21</sup>

Tricoordinated and tetracoordinated phosphorus monomers are typically incapable of cationic polymerization. The highly electron donating phosphonyl moieties form strong complexes with Lewis acids and Ziegler-Natta catalysts. However, the complexes formed are weak enough to allow limited degrees of polymerization when the phosphorus atom is bound to bulky groups (Figure 2.10). Conversely, anionic polymerizations of phosphorus-containing monomers typically prevail over radical polymerization methods as long as the monomer has no phosphine oxide activated methylene groups which act as active charge carriers (Figure 2.11).<sup>21</sup>

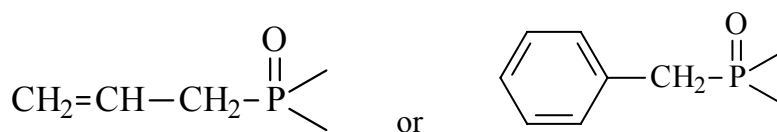


Figure 2.11. Phosphine Oxide Activated Methylene Groups<sup>21</sup>

Vinyl phosphine oxides and vinylphosphonium salts have been polymerized via X-rays, electrons or  $\gamma$  rays to yield macromolecules without crosslinking side reactions. Conversely, esters of vinylphosphonic acids have a tendency to crosslink.<sup>21</sup> Disadvantages are also present in polycondensation reactions involving phosphorus

containing monomers, because side reactions occur. High phosphorus contents may be obtained, although molecular weights greater than 10,000 g/mol are difficult to obtain. Hydrolysis and solvolysis interferences commonly occur which prevent quantitative conversion of phosphorus- containing monomers in condensation reactions. The P-O-C and P-N-C compounds and the esters and amides of trivalent phosphorus are particularly sensitive to hydrolysis. Copolycondensation and copolyaddition of phosphorus-containing monomers are acceptable methods for the modification of three dimensional polymers to yield thermosetting resins. In these cases, linear chain segment precursors are relatively short with irregular crosslinking sites; therefore side reactions and chain termination are treated as insignificant (for non-model networks).<sup>25</sup>

Phosphorus incorporation offers many advantageous properties in addition to flame resistance. Notable advantages of phosphorus- containing polymers include significantly improved dyeability and adhesion to polar solids including glass, ceramic materials, metals or cellulose (for the phosphoryl, P=O group). Trivalent phosphorus(III) imparts strong forces of association, and the unshared lone pair of electrons can also act as a nucleophile.<sup>17</sup> Phosphorus- containing polymers exhibit higher anti-static properties, enhanced hydrophilic solubility properties, as well as the capability for ion exchange.<sup>18,24</sup> These qualities influenced the synthesis of novel phosphorus containing polyorganosiloxanes as dispersing resins for metal particulates to yield thermally conductive adhesive microcomposite networks.

Recent advances in novel flame retardant polymers and organophosphorus containing polysiloxanes were established by Ji et al.<sup>26</sup> Amine terminated polydimethylsiloxane oligomers and bis(hydroxypropyl)isobutylphosphine oxide were introduced into polyurethanes as soft segments and chain extenders, respectively. Phosphate- and silicate- like char production were expected to improve the fire resistance. A 67% decrease in the heat release rate was observed for siloxane containing polyurethanes relative to conventional polyurethanes, and self-extinguishing

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26. Q. Ji, M. Muggli, F. Weng, T. C. Ward, G. Burns, U. Sorathia and J. E. McGrath, "Synthesis and Characterization of Modified Segmented Polyurethanes displaying Improved Fire Resistance", *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **38**(1), pp. 219-220, 1997.

characteristics were observed for the phosphorus- containing polyurethanes.<sup>26</sup> An earlier publication described the synthesis of randomly segmented poly(arylamide)-poly(dimethylsiloxane) copolymers formed by a one-step imidization process in o-dichlorobenzene/N-methylpyrrolidone.<sup>27</sup> A hydrolytically stable chain extender, bis(3-amino-phenoxy-4'-phenyl)phenylphosphine oxide in conjunction with oxydiphthalic anhydride yielded the hard segment of the copolymers. Controlled molecular weight alpha,omega-aminopropyl polydimethylsiloxane oligomers formed the soft segment. High molecular weight copolymers with controlled concentrations of polysiloxane soft segments were prepared. The copolymers with 40-60 wt.% siloxane exhibited T<sub>g</sub>s in the range of 130 °C - 180 °C, and substantial char yields in air at 750 °C (as the siloxane content was increased).<sup>27</sup>

Current work by McGrath's group involves the synthesis of perfectly alternating poly(arylene ether phosphine oxide)-poly(dimethylsiloxane) segmented copolymers.<sup>28,29</sup> These novel materials served as candidates for ordered nanocomposites as the block copolymer matrix is capable of forming uniform dispersions with fine silica particles.<sup>28,29</sup> Phosphine oxide- containing poly(arylene ethers) were also investigated as candidate polymeric resins for advanced composites and formed stable dispersions with both nano silica particles and metal salts.<sup>30</sup> The uniform dispersions were due to strong specific

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27. J. W. Wescott, T.-H. Yoon, D. Rodrigues, L. A. Kiefer, G. L. Wilkes and J. E. McGrath, "Synthesis and Characterization of Triphenylphosphine oxide-containing Poly(arylimine)-poly(dimethylsiloxane) Randomly Segmented Copolymers", *J. Macromol. Sci., Pure Appl. Chem.*, A31(8), pp. 1071-1085, 1994.
  28. W. D. Polk, S. J. Mecham, S. Wang, M. Sankarapandian, T. E. Glass and J. E. McGrath, "Segmented Poly(arylene ether phosphine oxide)-poly(dimethylsiloxane) Copolymers", *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 40(2), p. 929, 1999.
  29. W. D. Polk, S. Wang, Y. Kim, M. Sankarapandian, T. E. Glass and J. E. McGrath, "Perfectly Alternating Poly(arylene ether phosphine oxide)-poly(dimethylsiloxane) Copolymers", *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 41(2), p. 1385, 2000.
  30. S. Wang, H. Zhuang, M. Sanakrapandian, H. K. Shobha, Q. Ji, A. R. Shultz and J. E. McGrath, "Phosphine Oxide-Containing Polymer-Based Metal Salts/Polymer

interactions between the phosphoryl moieties on the resinous matrix with the surface silanols of the silica, and the metal ions of the salts.<sup>30</sup>

## **2.5. Introduction to Silanes and Polysiloxanes with Pendent Organophosphorus Moieties**

Numerous advantageous properties of polysiloxanes are due to the nature of the siloxane bond. The siloxane bond is one the most thermodynamically stable bonds. The Si-O bond length of  $1.64 \pm 0.03 \text{ \AA}$  is much shorter than the expected interatomic bond length of  $1.8 \text{ \AA}$  (calculated from the addition of  $1.17 \text{ \AA}$  and  $0.66 \text{ \AA}$ ). This  $0.2 \text{ \AA}$  difference can be attributed to both its substantial ionic character ( $\sim 40\%$ ) and partial double bond character.

The longer Si-O bond length of  $1.64 \text{ \AA}$  of polydimethylsiloxanes (PDMS) (relative to typical organic bonds C-C,  $1.54 \text{ \AA}$ ) allows for a wider range of valence angles.<sup>31</sup> For PDMS, the valence angles around the Si-O-Si and O-Si-O bonds are  $\sim 143^\circ$  and  $110^\circ \pm 10^\circ$ , respectively which is much wider than the typical tetrahedral bond angle of  $\sim 111^\circ$ .<sup>31,78</sup> Wide bond angles coupled with a very low energy barrier for rotation (Si-O  $< 0.8 \text{ kcal/mol}$  versus C-O  $\sim 11.3 \text{ kcal/mol}$ ) lead to highly flexible polysiloxane chains. Polysiloxanes exhibit low  $T_g$ s of  $\sim -123 \text{ }^\circ\text{C}$  and the corresponding networks offer flexibility at temperatures well below sub-ambient.<sup>78</sup> Consequently, the tensile properties of siloxane elastomers are not as temperature dependent as those of to most organic polymers. The inorganic character of the siloxane backbone (which does not absorb UV radiation due to the lack of unsaturation) makes polysiloxanes resistant to UV radiation and ozone.<sup>32</sup>

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and Silica/Polymer Hybrid Nanocomposites", *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 41(2), p. 1350, 2000.

31. M.G. Voronkov, "The Siloxane Bond", Consultants Bureau, New York, 1987.
32. S. J. Clarson, J. J. Fitzgerald, M. J. Owen and S. D. Smith, eds., "Silicones and Silicone-Modified Materials", ACS Symposium Series 729, American Chemical Society, Washington D. C., 2000.

The goal of this research was to synthesize high performance polyorganosiloxanes capable of yielding stable microcomposites (specifically with thermally conductive microfillers) for use in a wide range of thermal, environmental and mechanical conditions. PDMS, with two nonpolar methyl groups on every silicon atom, is not a suitable medium for polar fillers. The siloxane chain must be modified to yield a more polar resin suitable for various polar fillers to yield composites with enhanced properties. Polysiloxane networks with pendent nitrile groups capable of hydrogen bonding exhibited improved adhesion to metal oxide substrates and increased chemical resistance toward nonpolar fuels.<sup>33</sup>

Polysiloxanes with strongly electron donating organophosphorus groups, which can complex metal, are of interest. Phosphine and phosphine oxide (phosphoryl) groups were introduced to polysiloxanes as sidechain moieties rather than along the chain (where R, R', Y and Y' = organic substituents) for two reasons (Figure 2.12). First, the desirable properties of polysiloxanes attributed to the siloxane bond, Si-O-Si, should be maintained. Second, pendent Si-(C)<sub>n</sub>-P groups are much more stable than Si-P and Si-O-P bonds (Table 2.1). P-X bonds (where X = Si, Ge or Sn) are almost all unstable in air and water, and are typically much less stable than a P-C bond.<sup>5</sup> Similarly, the Si-O-P bonds of silyl esters<sup>34</sup> are more susceptible to hydrolysis than carbon analogues, i.e., C-O-P.<sup>5,35,36</sup>

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33. J. K. Hoyt, Synthesis and Characterization of Nitrile Containing Polysiloxanes and their Corresponding Networks as Aircraft Sealant Materials, M.S. Thesis, J. S. Riffle, J. E. McGrath and A. R. Shultz, eds., Virginia Tech, 1999.
  34. R. Engel, ed., Handbook of Organophosphorus Chemistry, Marcel Dekker, Inc., New York, 1992.
  35. S. N. Borisov, M. G. Voronkov and E. Ya. Lukevits, eds., Organosilicon Derivatives of Phosphorus and Sulfur, Plenum Press, New York, 1971.
  36. L. Wozniak and J. Chojnowski, "Silyl Esters of Phosphorus – Common Intermediates in Synthesis", *Tetrahedron*, Vol. 45, No. 9, pp. 2465 – 2524, 1989.

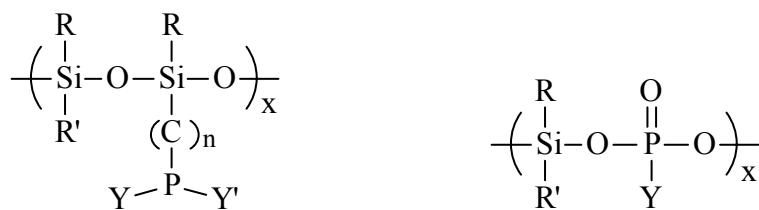


Figure 2.12. Polysiloxanes with Organophosphorus Groups Incorporated Pendent to and Within the Backbone

The organophosphorus linkage to a silicon atom (the Si-(C)<sub>n</sub>-P bond) can be formed via several mechanisms. For this research, phosphorus was added to silanes and siloxanes via the Arbuzov rearrangement and via free radical additions, respectively. Several reactions which yield the Si-(C)<sub>n</sub>-P bond are discussed.

Generally, organosilicon Grignard reagents react with halogen containing phosphorus compounds in a dry solvent (THF or THF/ether), where n = 1 – 3, R = an organic group and X = Br or Cl (Figure 2.13).<sup>35</sup>

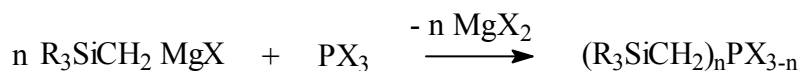


Figure 2.13. Reaction of Grignard Reagents with Halogenated Phosphorus Compounds<sup>35</sup>

Grignard reactions may also be performed on organohalophosphines, where the number of silicon containing groups in the product is determined by the number of halogen groups on the organohalophosphine starting reagent, where n = 1-2, and m = 1 or 3 (Figure 2.14). Replacement of two halogens on phosphorus yields halogen-free products. When POCl<sub>3</sub>, phosphoryl trichloride, was used rather than PX<sub>3</sub>, phosphine oxide-containing products, [R<sub>3</sub>Si(CH<sub>2</sub>)<sub>n</sub>]<sub>3</sub>PO, were obtained. Phosphorus and silicon substituted aryl compounds, [(CH<sub>3</sub>)<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>]<sub>3</sub>P, have also been synthesized by reacting silicon substituted arylmagnesium halides with PX<sub>3</sub>, POCl<sub>3</sub> or (RO)<sub>2</sub>POCl compounds.<sup>35</sup>

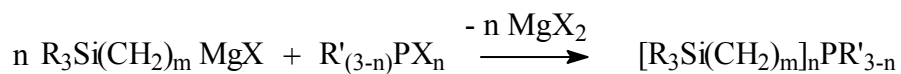


Figure 2.14. Grignard Reaction of Organohalophosphines<sup>35</sup>

Acid chlorides of silicon containing alkylphosphinic acids have been synthesized using the Clayton-Soborovski reaction (Figure 2.15).<sup>35</sup> This reaction starts at room temperature and proceeds with the evolution of heat. Alkylsilanes do not react with  $\text{PBr}_3$  or  $\text{C}_6\text{H}_5\text{PCl}_2$  in this type of reaction.  $\text{PBr}_3$  reportedly remains unchanged while phenyldichlorophosphine is oxidized to  $\text{C}_6\text{H}_5\text{P}(\text{O})\text{Cl}_2$ . Typical yields for this reaction are low ( $\sim 30 - 35\%$ ) due to side reactions that include disproportionation, dehydrochlorination, cleavage of the Si-C bond and hydrolysis of the P-Cl bond.<sup>35</sup>



Figure 2.15. Clayton-Soborovski reaction<sup>35</sup>

Organosilicon ylides of phosphorus can be obtained upon dehydrohalogenation of organosilicon phosphonium halides. Quaternary phosphonium salts are first formed (Figure 2.16 (a and b)).<sup>35</sup> The quaternary phosphonium salts are subsequently treated with butyllithium or phenyllithium (Figure 2.17 (1)) or may be decomposed thermally under vacuum (Figure 2.17 (2)) to yield the organosilicon ylides of phosphorus (in yields of  $\sim 90\%$  for the former).<sup>35</sup>

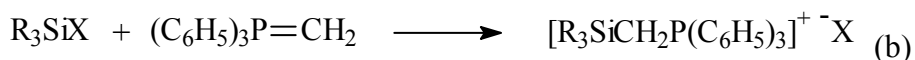
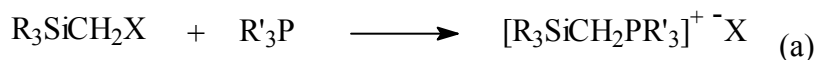


Figure 2.16. Formation of Quaternary Phosphonium Salts<sup>35</sup>

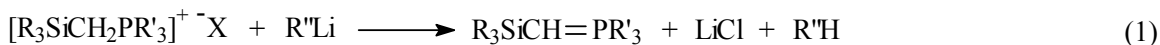


Figure 2.17. Synthesis of Organosilicon Ylides of Phosphorus<sup>35</sup>

Reactions similar to the Arbuzov rearrangement were initiated by Keeber and Post in 1955, who reacted a haloalkylsilane with a phosphoric acid salt (Figure 2.18), where Y = O or S to yield an organosilane with a pendent phosphonate.<sup>35</sup> This reaction is analogous to the Michaelis reaction of an alkyl halide with a metal dialkylphosphite to yield a dialkyl ester of an alkyl phosphonate (Figure 2.19). The Michaelis reaction typically gives lower yields than Michaelis-Arbuzov reactions.<sup>5</sup>

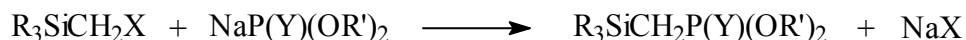


Figure 2.18. Reaction of a Phosphoric Acid Salt with A Haloalkylsilane<sup>35</sup>

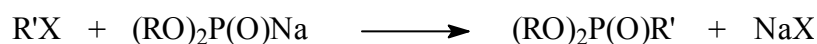


Figure 2.19. The Michaelis Reaction<sup>5</sup>

Variations of the Keeber/Post reaction soon followed with diverse R and R' groups, along with replacement of the haloalkylsilane by  $\text{XZ(R}_2\text{SiO)}_n\text{ZX}$ , (X = halide and Z = alkylene or phenylene) or bifunctional organosilicon compounds, e.g.  $\text{ClCH}_2\text{Si(CH}_3)_2\text{Cl}$ . These reactions yield linear polymers with terminal phosphonate groups or compounds with phosphorus bound to silicon with carbon and oxygen bridges, respectively. When the phosphoric acid salt is replaced with a metal phosphide, a phosphine analogue (a triorganosilylalkyldiorganophosphine) may be obtained (Figure 2.20).<sup>35</sup> These reactions lead to the Arbuzov rearrangement, which was first observed between haloalkylsilanes and triethylphosphite.<sup>35</sup>

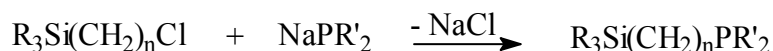


Figure 2.20. Synthesis of a Triorganosilylalkyldiorganophosphine<sup>35</sup>

### 2.5.1. Michaelis-Arbuzov Rearrangement

The Michaelis-Arbuzov rearrangement is an important and versatile method for forming carbon bridges between phosphorus and another atom (in this case, Si). It is also referred to as the Arbuzov rearrangement, Arbuzov reaction or Arbuzov transformation. The Arbuzov pathway for carbon-phosphorus bond formation proceeds via reaction of an alkyl halide with an ester moiety on a trivalent phosphorus compound. The reaction was first discovered by the German chemist, A. Michaelis, in 1898. Subsequently, A. E. Arbuzov, a Russian chemist, led extensive investigations of this reaction.<sup>8,37</sup> This rearrangement, primarily used to synthesize phosphonates, phosphinites, and tertiary phosphine oxides (Figure 2.21) is one of the most widely studied reactions in organophosphorus chemistry.<sup>37</sup>

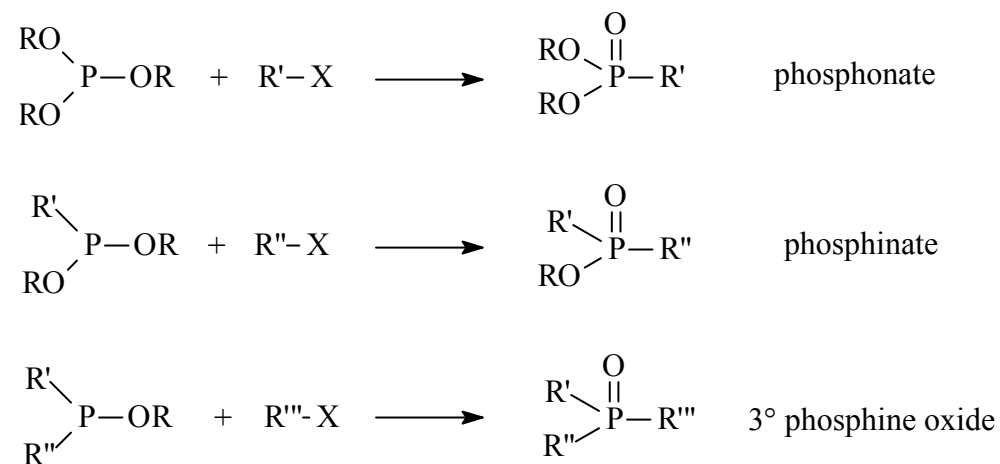


Figure 2.21. Synthesis of Phosphonates, Phosphinites and Phosphine Oxides via the Michaelis-Arbuzov Rearrangement<sup>37</sup>

In general, the Michaelis-Arbuzov rearrangement is a two-step mechanism involving the reaction of a trivalent phosphorus (P<sub>III</sub>) (e.g., a trialkyl phosphite) with an alkyl halide to yield a pentavalent phosphorus (P<sub>V</sub>) dialkylphosphonate (Figure 2.22).<sup>37</sup> The first step involves attack of the phosphite lone pair of electrons on the alkyl halide to

37. A. K. Bhattacharya and G. Thyagarajan, "The Michaelis-Arbuzov Reaction", *Chemical Reviews*, Vol. 81, No. 4, pp. 415-430, 1981.

form a salt. This is followed by dissociation of one of the alkyl groups from the phosphite, and rearrangement to form the phosphoryl, P=O, bond. The driving force for this rearrangement has been attributed to the net gain of either 32 or 65 kcal/mol energy to form the stable phosphoryl group, provided an accessible path for the redistribution of electron densities is present. The eliminated alkyl group will form a new alkyl halide that may also be attacked by the phosphite.<sup>37</sup> This volatile alkyl halide formed in situ is typically distilled continually to increase the yield of the desired Michaelis-Arbuzov product. A small excess of phosphite is typically employed to compensate for this side reaction.<sup>38</sup>

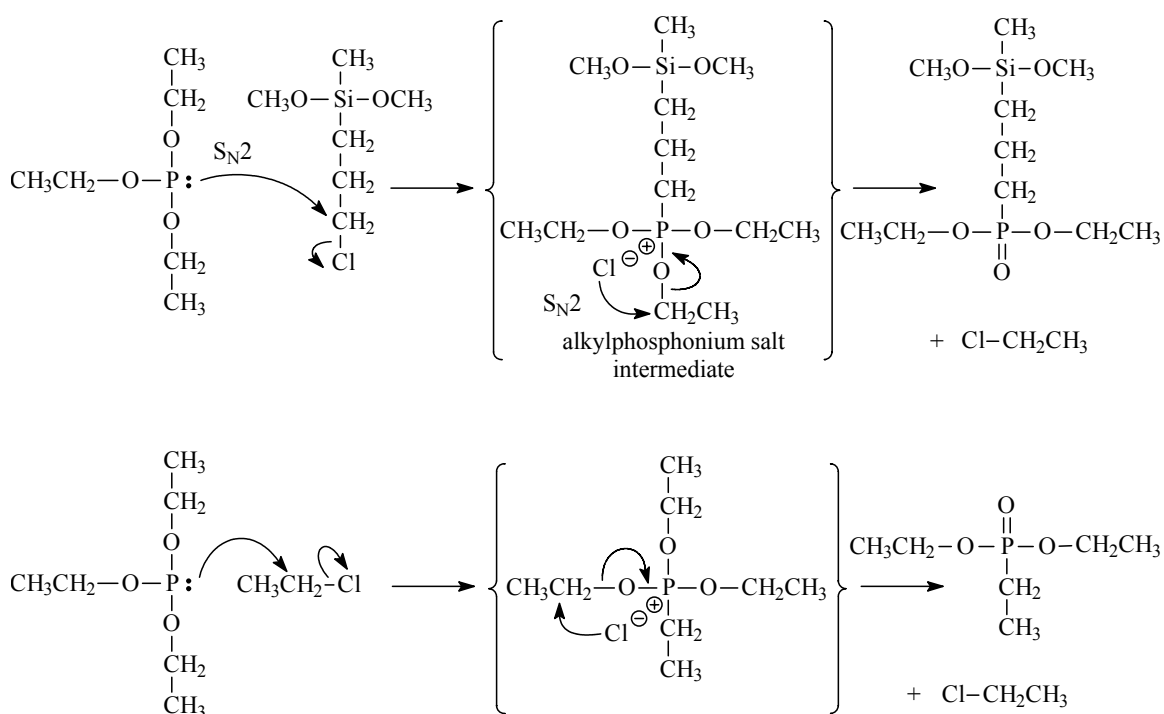


Figure 2.22. Mechanism of the Michaelis-Arbuzov Rearrangement and Side Reaction<sup>37,61</sup>

38. G. M. Kosolapoff, "Isomerization of Alkyl Phosphites. IV. The Synthesis of Some Alkaryl Phosphonic Acids and Esters", *J. Am. Chem. Soc.*, **67**, pp. 2259-2260, 1945.

Interestingly, intramolecular rearrangement to the phosphoryl group will occur for a halogen containing phosphite upon heating, e.g. tris( $\beta$ -chloroethyl)phosphite (Figure 2.23).<sup>37</sup>

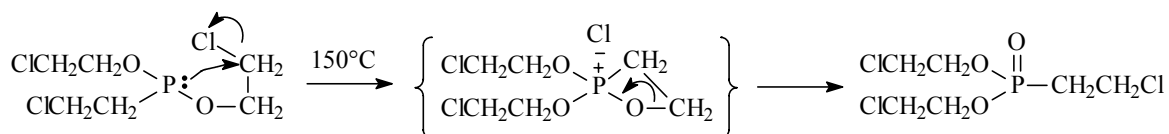


Figure 2.23. Intramolecular Rearrangement to the Phosphoryl Group<sup>37</sup>

Arbuzov formed the quaternary phosphonium crystalline salts (Figure 2.24) as intermediates to the phosphonate rearrangement products.<sup>37</sup> Others have formed these salts as products and refer to them as "quasiphosphonium salts".<sup>39,40,41</sup> The bonding nature of P-X was partially ionic and partially covalent.<sup>42</sup> Tetraalkyl phosphonium salts may undergo a wider variety of reactions relative to tetraalkyl ammonium salts. The phosphonium salts have longer bond radii due to the larger phosphorus atom and may also have possibilities for d-orbital participation.<sup>43</sup>

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39. R. G. Harvey and E. R. DeSombre, "The Michaelis-Arbuzov and Related Reactions", pp. 57-111 in Topics in Phosphorus Chemistry, Vol. 1, M. Grayson and E. J. Griffith, Eds., Interscience, New York, 1964.
40. R. G. Harvey and E. R. DeSombre, "The Michaelis-Arbuzov and Related Reactions", pp. 57-111 in Topics in Phosphorus Chemistry, Vol. 1, M. Grayson and E. J. Griffith, Eds., Interscience, New York, 1964.
41. H. R. Hudson, A. T. Kow and K. Henrick, "Structure and Reactivity of Quasiphosphonium Intermediates", pp. 517-520, in Phosphorus Chemistry, Proceedings of the 1981 International Conference, L. D. Quin and J. G. Verkade, eds., ACS Symposium Series **171**, American Chemical Society, Washington D. C., 1981.
42. H. R. Hudson, A. T. Kow and K. Henrick, "Structure and Reactivity of Quasiphosphonium Intermediates", pp. 517-520, in Phosphorus Chemistry, Proceedings of the 1981 International Conference, L. D. Quin and J. G. Verkade, eds., ACS Symposium Series **171**, American Chemical Society, Washington D. C., 1981.
43. R. F. Hudson, Structure and Mechanism in Organo-Phosphorus Chemistry, Academic Press, Inc., London, 1965.

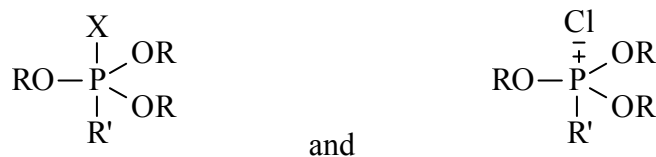


Figure 2.24. Quaternary Phosphonium Salts<sup>37</sup>

The rate determining step in the Michaelis-Arbuzov rearrangement is formation of the phosphonium salt (Figure 2.25).<sup>44</sup> The distribution of products depends on the manner in which the salt decomposes. Typically, decomposition of alkylphosphonium salts takes place as  $\text{X}^-$  attacks R from the back side. Simultaneous O-R bond breaking, R-X bond formation and inversion of configuration on the product are characteristic of an  $\text{S}_{\text{N}}2$  reaction mechanism.<sup>45</sup> Furthermore, the reactivity of the trialkyl phosphite,  $\text{P}(\text{OR})_3$ , is dependent on the size of the R group, where  $\text{Me} > \text{Et} > i\text{-Pr}$ . This also suggests an  $\text{S}_{\text{N}}2$  type mechanism.<sup>42</sup> However, support for a carbonium ion  $\text{S}_{\text{N}}1$  mechanism has been shown for phosphinite esters with tertiary alkyl substituents which may also rearrange.<sup>39,46</sup> The R group first dissociates from the phosphonium salt which is subsequently attacked by  $\text{X}^-$ .<sup>37</sup>

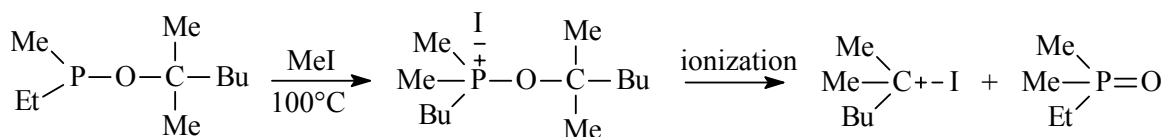


Figure 2.25. Formation of the Phosphonium Salt<sup>44</sup>

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44. R. R. Holmes, ed., Pentacoordinated Phosphorus, Volume II, Reaction Mechanisms, pp. 168, ACS Monograph **176**, American Chemical Society, Washington, D. C., 1980.
45. W. Gerrard and W. J. Green, "Mechanism of the Formation of Dialkyl Alkylphosphonates", *J. Chem. Soc.*, pp. 2550-2553, 1951.
46. J. E. Griffiths and A. B. Burg, "Oxygen Chemistry of the  $(\text{CF}_3)_2\text{P}$  Group: the Diphosphoxane; the Phosphinous Acid, Esters and Related Phosphine Oxides: Phosphinyl Halides and Infrared Spectra", *J. Am. Chem. Soc.*, **84**, pp. 3442-3450, 1962.

Any alkyl halide that can react with nucleophilic reagents by an  $S_N2$  pathway and not containing inhibiting groups (carbonyl or nitro) is suitable for the Michaelis-Arbuzov rearrangement with a phosphite. The reactivity for alkyl halides generally follows as:  $RCO-X > RCH_2-X > RR'CH-X > RR'R'C-X$  and; for the X group as:  $R-I > R-Br > R-Cl$ .<sup>47</sup> Primary alkyl-, benzyl-, diphenylmethyl- and triphenylmethyl- halides react normally to yield the expected normal rearrangement products, while tertiary alkyl-, simple aryl- and vinyl- halides are unreactive toward trialkyl phosphites.<sup>37</sup>

Certain alkyl halides will yield the "normal" Arbuzov rearrangement P-C product as a minor component along with the major product having a P-O bond, an enol phosphate ester.<sup>5</sup> This anomalous reaction which yields the "abnormal" product is known as the Perkow reaction. Saturated  $\alpha$ -chloro/bromo ketones and aldehydes react with trialkyl phosphites to yield mostly dialkyl vinyl phosphates. For example, substituted  $\alpha$ -bromo acetophenone reacts with trialkyl phosphites to yield both Arbuzov (ketophosphonates) and Perkow products (vinyl phosphates) (Figure 2.26).<sup>48</sup> Yields of the Arbuzov product decreased for a more deactivated ring in the following order:  $R' = MeO > Me > H > F > Cl > Br > NO_2$ .<sup>49</sup>

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47. K. H. Worms and M. Schmidt-Dunker, "Phosphonic Acids and Derivatives", p. 24, in Organic Phosphorus Compounds, G. M. Kosolapoff and L. Maier, eds., Vol. 7, John Wiley and Sons, Inc., New York, 1976.

48. I. Pethehazy, G. Szakal and L. Toke, "The Synthesis of Enolphosphonates and Ketophosphonates. The examination of Perkow and Arbuzov Reactions", pp. 555-560, in First International Congress on Phosphorus Compounds Proceedings, M. V. Rabat, Marocco, 1977.

49. E. M. Gaydou and J.-P. Bianchini, "Kinetics and Mechanism of Ketophosphonate Formation from Triethyl Phosphite and Aryl Substituted  $\alpha$ -Bromoacetophenones", *Chem. Commun.*, **14**, pp. 541-542, 1975.

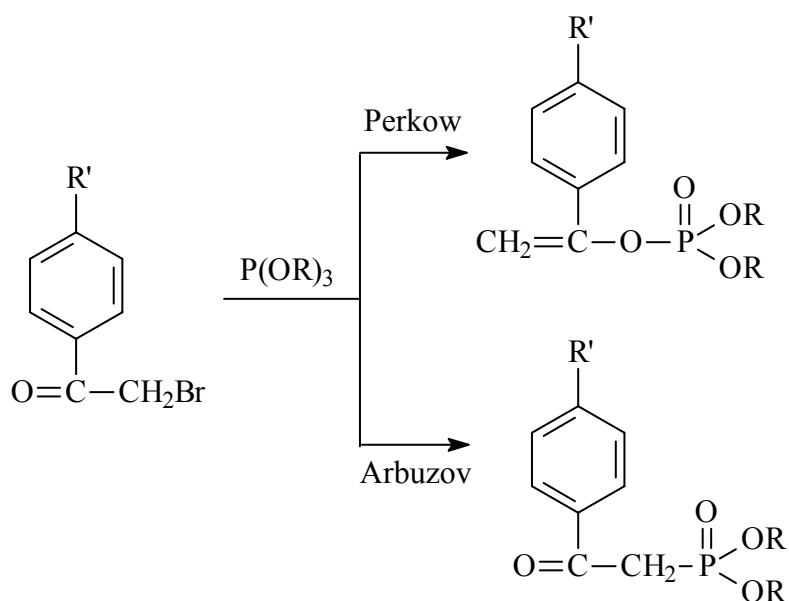


Figure 2.26. Comparison of the Perkow and Arbuzov Reactions<sup>37</sup>

Phosphates are not formed as a result of the Perkow reaction for  $\alpha$ -iodo ketones as iodine alkyl halides favor a greater reactivity toward simple S<sub>N</sub>2 displacement. Iodine, being less electronegative exerts a smaller polarization effect on the carbonyl group relative to  $\alpha$ -chloro and  $\alpha$ -bromo ketones.<sup>50</sup> Formation of the Arbuzov phosphonate product is also favored at higher reaction temperatures.<sup>37</sup> Iodobenzenes yield Arbuzov products through other mechanisms, rather than rearrangement. Iodobenzene reacts with either trimethylphosphite at 60°C via a free radical "photo Arbuzov" mechanism<sup>51</sup> or with potassium dialkyl phosphites in liquid ammonia under 350 nm irradiation<sup>52</sup> to yield dialkyl arylphosphonates. The photochemical Arbuzov free radical rearrangement yields

50. H. I. Jacobsen, M. J. Griffin, S. Preis and E. V. Jensen, *J. Am. Chem. Soc.*, **79**, 1608, 1957.

51. J. J. L. Fu, W. G. Bentrude and C. E. Griffin, *J. Am. Chem. Soc.*, **94**, 7717, 1972.

52. J. F. Bunnett and X. Creary, "Photosimulated Condensation of Aryl Iodides with Potassium Dialkyl Phosphites to Form Dialkyl Arylphosphonates", *J. Org. Chem.*, **39**, pp. 3612-3614, 1974.

substantial amounts of isomeric phosphonates when trialkyl phosphites are subjected to ultraviolet radiation.<sup>53</sup>

The reactivity of phosphorus esters, ABP-OR, depends on the alkyl groups A and B which may be 1° alkoxy, 2° alkoxy, aryloxy, alkyl, aryl or dialkylamino groups. The ease of nucleophilic attack by the lone pair of electrons of the phosphite on the alkyl halide is increased for more electron-repelling A and B groups. Electron attracting groups, A and B, will retard the reaction. The ease of reaction increases as A, B = aryloxy < alkoxy < aryl < alkyl < dialkylamino. The R group of the ester also affects the reactivity of the phosphite and should be aliphatic for the reaction to proceed smoothly. Reactions with CH<sub>3</sub>I exhibit increased ease of rearrangement for smaller R groups: Me > Et > *i*-Pr.<sup>42</sup>

An interesting recent development in the synthesis of Arbuzov products was reported by Han et. al.<sup>54</sup> They studied a novel synthetic route to Arbuzov products eliminating the production of an alkyl halide side product (which occurs for classic Arbuzov reactions described above). Transition metal-catalyzed addition reactions across unsaturated carbon bonds are an attractively clean and versatile way of forming carbon-hetero atom bonds with no evolution of side products. Palladium catalyzed hydrophosphorylation reactions of a highly reactive five membered cyclic hydrogen phosphonate over terminal and cyclic alkenes were investigated. The five membered cyclic phosphonate, (4,4,5,5-tetramethyl-1,3,2-dioxaphospholane 2-oxide), was reacted with 1-octene in the presence of *cis*-PdMe<sub>2</sub>(PPh<sub>2</sub>Me<sub>2</sub>) for 3 hours at 110 °C in toluene to yield 63% of the Arbuzov product (Figure 2.27).

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53. R. B. LaCount and C. E. Griffin, *Tetrahedron Lett.*, 3071, 1965.

54. L.-B. Han, F. Mirzaei, C.-Q. Zhao and M. Tanaka, "High Reactivity of a Five-Membered Cyclic Hydrogen Phosphonate Leading to Development of Facile Palladium-Catalyzed Hydrophosphorylation of Alkenes", *J. Am. Chem. Soc.*, **122**, pp. 5407-5408, 2000.

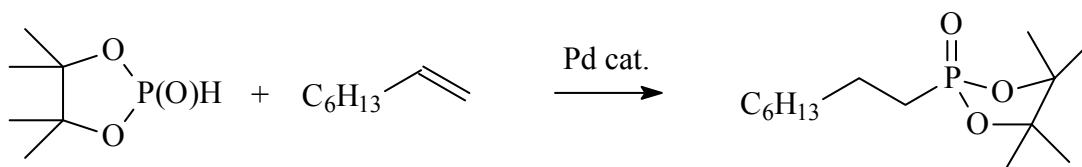


Figure 2.27. Pd Catalyzed Addition of a Five Membered Cyclic Hydrogen Phosphonate to an Alkene<sup>54</sup>

The hydrophosphorylation was described by (i) the oxidative addition of the H-P bond, followed by (ii) addition of the H-Pd bond of **3** to an alkene (hydropalladation) and finally (iii) the reductive elimination of the adduct **2** from **4** (Figure 2.28).<sup>54</sup> Higher product yields (~ 93%) were obtained when PdMe<sub>2</sub>[Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>4</sub>PPh<sub>2</sub>] was utilized as the catalyst, which demonstrated the importance of the transition metal catalyst ligands. Other transition metal complexes were investigated. Lower yields of 49% and 26% were found using RhCl(PPh<sub>3</sub>)<sub>4</sub> and Ni(PPh<sub>3</sub>)<sub>4</sub>, respectively; and Pt(CH=CH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub> was virtually inactive. Product yields were nearly quantitative when ethene or propene were used as the terminal alkene. Han et al's work has shown that only the highly reactive, ring-strained, five member hydrogen phosphonates would produce high yields of Arbuzov products, while noncyclic and six membered rings were unreactive. The authors hypothesized that the higher reactivity of the five membered cyclic was associated with the reductive elimination process.<sup>54</sup>

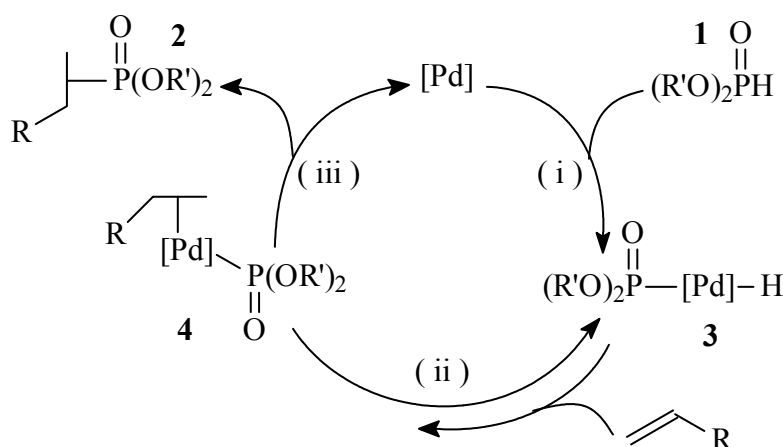


Figure 2.28. Pd Catalyzed Hydrophosphorylation<sup>54</sup>

One objective of my dissertation research was to synthesize novel alkylphosphonate silanes and siloxanes (Si-C-P bonds) for high performance adhesive materials. Materials with Si-O-C<sub>n</sub>-P bonds are typically unstable and will undergo thermally initiated reverse Arbuzov reactions;<sup>55</sup> and those containing Si-O-P bonds are hydrolytically unstable.<sup>5</sup> Earlier work on coupling silicon to carbon-phosphorus bonds via the Michaelis-Arbuzov rearrangement was pioneered in the U.S. by A. R. Gilbert (General Electric Co.) in the 1950s.<sup>56,57</sup> Typical reactions involved haloalkylsilanes and trialkyl phosphites with reaction conditions varying from 6 - 15 hours at ~ 150 °C – 200 °C to obtain satisfactory yields of dialkyl silylalkylphosphonates, where n = 1-3 and X = Cl (Figure 2.29).<sup>35</sup>

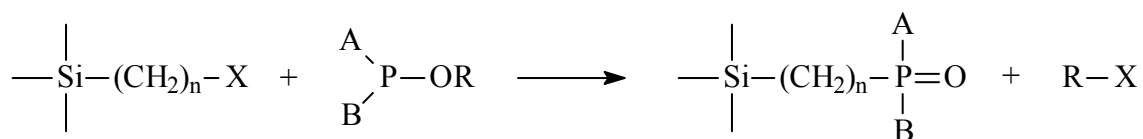


Figure 2.29. Reaction of Haloalkylsilanes with Trialkyl Phosphites to Yield Dialkyl Silylalkylphosphonates<sup>35</sup>

Replacement of A and B alkoxy groups with phenyl considerably increases the product yield using relatively milder reaction conditions. For example, heating trimethyl(chloro)methylsilane, (Me)<sub>3</sub>-Si-CH<sub>2</sub>-Cl, with triethyl phosphite, P(OEt)<sub>3</sub>, at 175 °C for 6 hours and at 185 °C for 3 days yielded the Arbuzov product (Me)<sub>3</sub>-Si-CH<sub>2</sub>-P(O)(OEt)<sub>2</sub> with respective yields of 32% and 62%. When the ethoxy groups of triethylphosphite were replaced by one and two phenyl groups, Ph(P)(OEt)<sub>2</sub> and

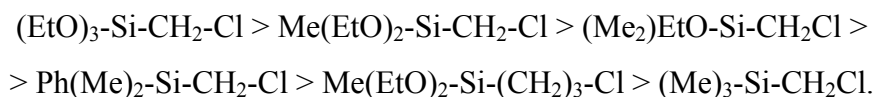
55. G. A. Kuttyrev and R. A. Cherkasov, "The Reactivity of Organosilicon Derivatives of Phosphorus in Addition Reactions", *Russian Chemical Reviews*, **53**(10), pp. 971-988, 1984.

56. A. R. Gilbert, General Electric Co., New York, "Organosilicon Compounds Containing Phosphorus", US Patent, 2,768,193, 1956.

57. A. R. Gilbert and F. M. Precopio, "Organophosphorus Silicon Compounds", Abstracts of Papers to the 125<sup>th</sup> Meeting of the Am. Chem. Soc., p. 16, 1954.

(Ph)<sub>2</sub>POEt, and heated at ~120 °C for 10 hours, the respective Arbuzov yields were increased to 80% and 95%.<sup>35</sup>

The haloalkylsilane, (Me)<sub>3</sub>SiCH<sub>2</sub>Cl may also be modified to increase the reaction rate. Replacement of methyl groups with alkoxy or aromatic groups on the silicon atom increased the reaction rate with triethyl phosphite or phenyl phosphinates. The following reactivity series for haloalkylsilanes has been established for strict reaction conditions between a 1.5 : 1 molar ratio of haloalkylsilane : phosphite at 140 ± 2°C as:<sup>35</sup>



When a triorganosilyl halide (e.g. Me<sub>3</sub>Si-I) is reacted with trialkyl phosphites, silyl esters of alkylphosphonic acids are formed rather than the Arbuzov silylalkylphosphonates.<sup>58</sup>

The synthesis of novel phosphonate containing polysiloxanes via Michaelis-Arbuzov rearrangements is currently being investigated by several groups. C. D. Yeungst and W. P. Weber investigated two routes to prepare dimethyl phosphonomethyl methylsiloxane-dimethylsiloxane copolymers.<sup>59</sup> Cyclic tetramers, chloro- and bromo-(methylheptamethylcyclotetrasiloxane) were prepared via free radical halogenation reactions of octamethylcyclotetrasiloxane (D<sub>4</sub>) with bromine or chlorine; and were isolated in a 25% yield as a central boiling fraction (brominated D<sub>4</sub> 125°C / 12mm) (Figure 2.30).<sup>59</sup> Arbuzov reactions were subsequently carried out on the halogenated cyclic siloxanes with a five-fold excess of trimethyl phosphite, and refluxed for 24 hours to yield the dimethyl phosphonomethylheptamethyl-cyclotetrasiloxane monomer. The

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58. J. Chojnowski, M. Cypryk, J. Michalski and L. Wozniak, "Reactions of Triorganosilyl Halides with Esters of Tricoordinated and Tetracoordinated Phosphorus", pp. 521-524, in Phosphorus Chemistry, Proceedings of the 1981 International Conference, L. D. Quin and J. G. Verkade, eds., ACS Symposium Series **171**, American Chemical Society, Washington D. C., 1981.

59. C. D. Yeungst and W. P. Weber, "Preparation and Properties of Dimethyl Phosphonomethyl Methylsiloxane Dimethylsiloxane Copolymers", *Journal of Polymer Science: Part A: Polymer Chemistry*, Vol. 25, pp. 1967-1978, 1987.

monomer was isolated in a 97% yield and separated from the dimethyl methylphosphonate byproduct under high vacuum ( $10^{-4}$  mm) (Figure 2.31).

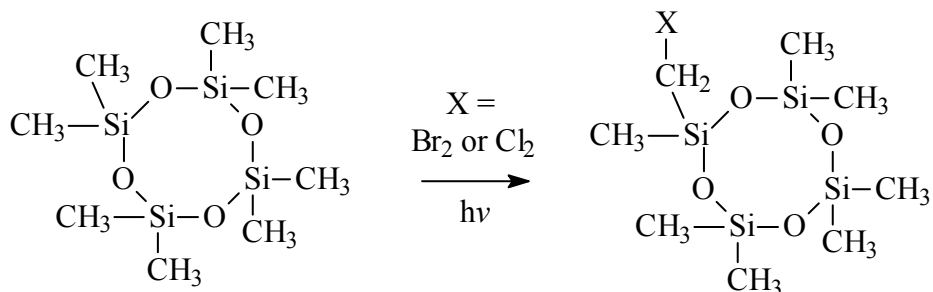


Figure 2.30. Free Radical Halogenation of Octamethylcyclotetrasiloxane<sup>59</sup>

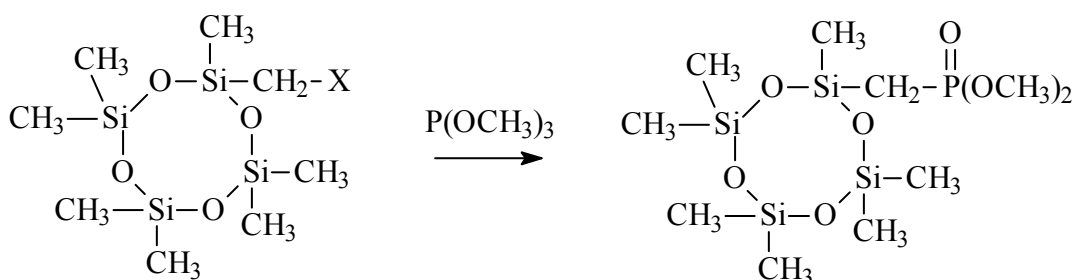


Figure 2.31. Arbuzov Reaction with Halogenated Cyclosiloxane<sup>54</sup>

A siloxane dimer was halogenated and phosphonylated to synthesize a 1,3-bis(dimethyl phosphonomethyl)tetramethylsiloxane endcapping reagent.<sup>59</sup> The brominated siloxane analogues required milder reaction conditions and did not produce side products upon phosphonylation. Anionic polymerization of the phosphonate tetramers resulted in varying degrees of hydrolysis of the methyl phosphonate ester groups.<sup>59</sup> Acid catalysts were employed for base sensitive groups, e.g. Si-H and Si-CH<sub>2</sub>-X.<sup>60</sup> Therefore, sulfuric acid promoted copolymerizations were carried out with D<sub>4</sub> : phosphonate dimer in molar ratios of 40:1 and 1:1 to yield linear polydimethylsiloxanes with  $M_n = 36000$  g/mol and an oligomer endcapped with diethylmethylphosphonate.<sup>59</sup>

60. W. Simmler, "Studien zur Äquilibrierung von Methylsiloxanen", *Makromol. Chem.*, **57**, pp. 12-24, 1962.

Undesirable hydrolysis of the methyl phosphonate ester groups persisted for the polymers during aqueous recovery. Therefore, acid catalyzed copolymerizations were also carried out on the phosphonate tetramer with various endcapping reagents (MM) (Figure 2.32).<sup>59</sup> Low yields of 14% of low  $M_n$  linear phosphonylated polymers (7100 and 12700 g/mol) were obtained with complicated  $^{31}\text{P}$  NMR spectra indicative of side reactions.

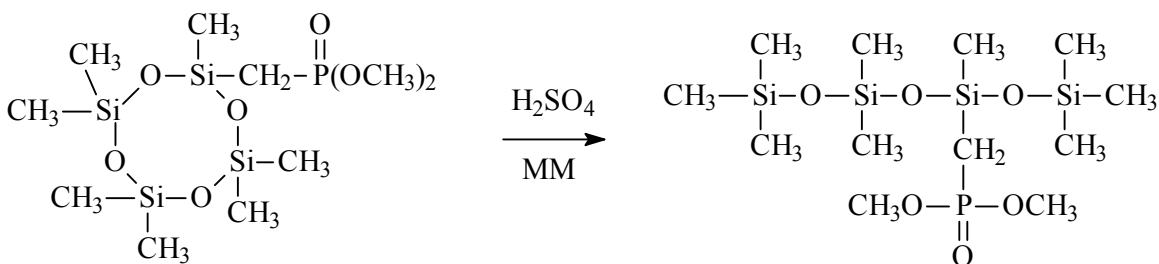


Figure 2.32. Acid Catalyzed Polymerization of a Cyclosiloxane Tetramer Substituted with One Phosphine Oxide Moiety<sup>59</sup>

In an attempt to circumvent the hydrolysis issues, an Arbuzov reaction of triethylphosphite with a linear bromomethylmethylsiloxane-dimethylsiloxane copolymer endcapped with trimethylsilyl groups was conducted ( $M_n$  of 14600 g/mol) (Figure 2.33).<sup>59</sup> Methyl bromide was continually distilled, and a phosphonylated polymer was formed quantitatively without degradation. This synthetic route to the phosphine containing polymer gave respective  $M_n$  and  $M_w$  values of 15610 g/mol and 45700 g/mol via GPC. Each of the phosphonate containing polysiloxane copolymers were thermally stable to  $\sim 190$  °C via dynamic thermogravimetric analysis, where 95% weight loss was exhibited at  $\sim 300$  °C. A number of monomeric dimethyl phosphonomethylsilanes decomposed at  $\sim 200$  °C yielding dimethyl methylphosphonate and a methoxy-substituted silane as the major degradation products.<sup>59</sup>

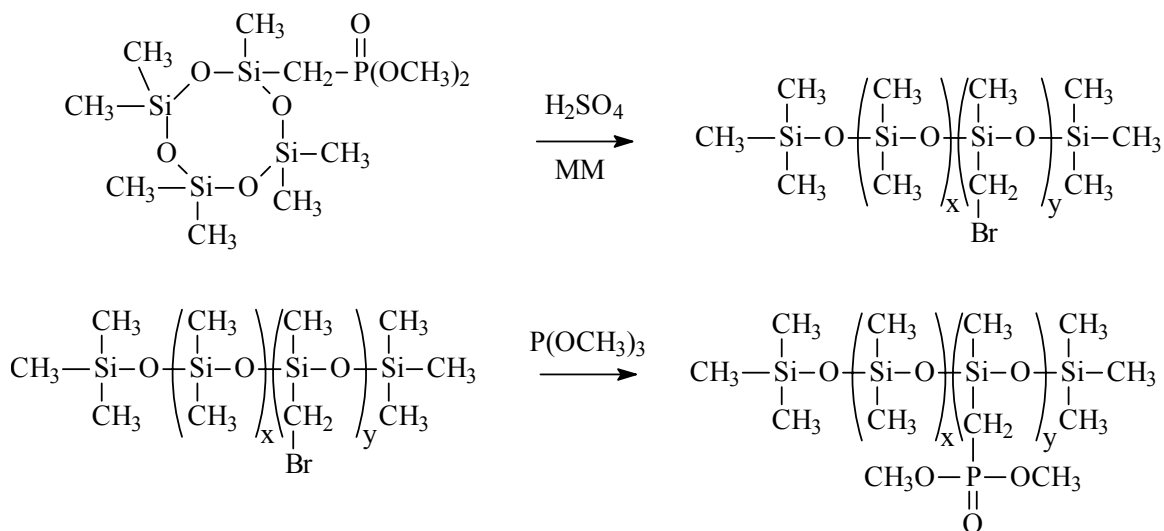


Figure 2.33. Arbusov Reaction with a Bromine Containing Polysiloxane<sup>59</sup>

Recently, similar procedures were conducted by S. Gallagher to yield siloxanes with pendent alkylphosphonate substituents.<sup>61</sup> Two different (chloromethyl)-methylsiloxane-dimethylsiloxane copolymers, each containing 33 mol % of chloromethyl and chloropropyl functional groups, were reacted with triethylphosphite at 156 °C for 48 hours and 18 days, respectively. A second route involved the reaction of 3-chloropropylmethyldimethoxysilane with triethyl phosphite for 5 days. The alkylphosphonate silane monomer was subsequently polymerized at room temperature with dimethyldimethoxysilane (catalyzed by NaOH) and endcapped with trimethylsilane.<sup>61</sup>

An interesting synthesis of a poly(phosphonosiloxane) was carried out by S. Lin and I. Cabasso Figure 2.34.<sup>62</sup> A 2130 g/mol poly(methylhydrosiloxane) was hydrosilated with vinylbenzyl chloride (70% meta, 30% para) using a Pt<sup>0</sup> catalyst complexed with 1,3-

61. S. Gallagher, "Synthesis and Characterization of Phosphonate Containing Polysiloxanes", *Polymer Preprints*, 41(1), pp. 70-71, 2000.

62. S. Lin and I. Cabasso, "Synthesis of Poly(phosphonosiloxane) and its Cyclic Monomer Via Hydrosilation and Phosphonoloylation of Vinylbenzyl Chloride", *Journal of Polymer Science: Part A: Polymer Chemistry*, Vol. 37(22), pp. 4034-4053, 1999.

divinyltetramethyldisiloxane. Hydrosilation of the hydrido functional polymer was complete in ~ 48 h, relative to 3 h for the D<sub>4</sub>H cyclic tetramer. The longer reaction time was attributed to steric hindrance of the polymer backbone during the final stages of the reaction. Both  $\alpha$  and  $\beta$  addition products were formed (48:52) in toluene. This product ratio was considered normal for hydrosilation of vinylbenzyl chloride. Phosphonylation of the vinylbenzyl chloride residue was then conducted upon refluxing with an excess triethylphosphite for 7 hours at 156 °C under N<sub>2</sub>.<sup>62</sup>

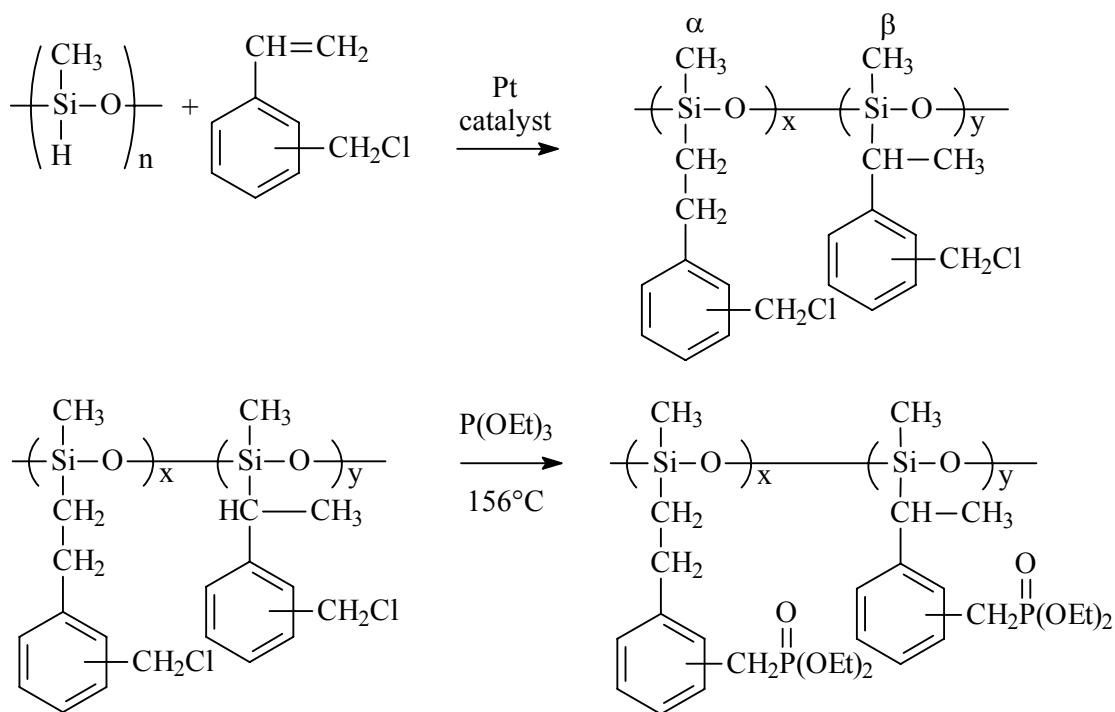


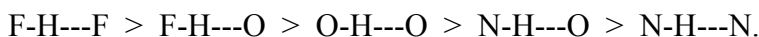
Figure 2.34. Synthesis of a Poly(phosphono)siloxane<sup>62</sup>

The Arbuzov polymer, poly(diethylphosphonobenzyl $\alpha,\beta$ -ethylmethylsiloxane) isolated in ~70-80% yield (after vacuum stripping unreacted triethylphosphite and volatile byproducts) exhibited a  $T_g$  of -38 °C. The authors had not found a method or catalyst capable of polymerizing the corresponding phosphonosiloxane cyclic tetramer. Attempts were also made to hydrosilate the poly(methylhydrosiloxane) directly with a vinylbenzylphosphonate ester to yield the Arbuzov product. Although it was proposed that the strongly electron donating phosphoryl group might have complexed with the

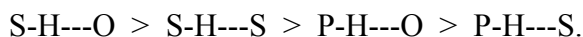
platinum catalyst.<sup>62</sup> Similar behavior has been previously noted by Spier on the hydrosilation of styrene in the presence of a strong electron donor.<sup>63</sup>

### 2.5.2. Hydrogen Bonding and Complexation of Phosphylyl Containing Compounds

Hydrogen bonding occurs when a hydrogen atom is bonded to a strongly electronegative atom. The bond,  $A^{\delta-}-H^{\delta+}$ , with an induced dipole, allows for a second electronegative atom to be attracted to it:  $A^{\delta-}-H^{\delta+} \cdots B^{\delta-}$ . Evidence for this phenomenon is commonly observed by a shift in the infrared stretching frequency of  $\nu$  (A-H) to a lower value. X-ray diffraction or electron diffraction can also provide evidence for the hydrogen bonding of A-H $\cdots$ B by a considerably less than expected interatomic bond distance  $d_{A-B}$  (less than the sum of the two single bond covalent radii). The strengths of hydrogen bonds are greater than van der Waals type attractions ( $\sim 4$  kJ/mol) and weaker than typical covalent bond strengths ( $\sim 40$  kJ/mol). The generally accepted order of hydrogen bond strength is dependent on the electronegativity of the atoms, A and B, as follows:

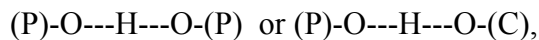


While second row elements can participate in hydrogen bonding in the order:

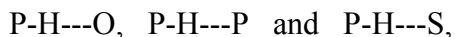


Hydrogen bonds formed with second row elements are much weaker relative to those formed with first row electronegative atoms. In fact, large atoms such as arsenic, antimony and bismuth (atoms below P) do not exhibit direct hydrogen bonding.<sup>5</sup>

The most common hydrogen bonding for phosphorus compounds takes place between an oxygen atom bound to either a phosphorus or a carbon atom:



while the hydrogen bonding for a phosphorus atom (not attached to an oxygen atom):

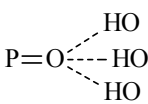


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63. J. L. Spier, "Homogenous Catalysis of Hydrosilation by Transition Metals", in Advances in Organometallic Chemistry, F. G. A. Stone and R. West, eds., Academic Press, New York, Vol. 17, pp. 407-447, 1979.

is characterized as either extremely weak or nonexistent.<sup>5</sup>

The phosphoryl group, P=O, is an excellent hydrogen bonding acceptor moiety (from -OH or -NH<sub>2</sub> groups), where X---OH acts as the donor. Typically large infrared hydrogen bonding stretching frequency shifts of ~ 50 cm<sup>-1</sup> to a lower value occur with a corresponding increase in the intensity of the phosphoryl absorption, ν (P=O). The P=O group can accept up to 3 hydrogen bonds commonly from P-OH, C-OH or N-H donor

moieties, , with little effect on its bond length. Evidence for hydrogen bonding of P-H--- is conflicting, and at best is weak. This is evident by the much lower melting and boiling points (~ 75 ° lower) of phosphine, PH<sub>3</sub>, relative to ammonia, NH<sub>3</sub>, due to a drastically reduced amount of hydrogen bonding.<sup>5</sup>

In contrast to the strongly hydrogen bonding phosphine oxide group, phosphine compounds with an unshared pair of electrons may form covalent bonds or act as complexation species. Alkylphosphines may be prepared by replacing one, two or three of the hydrogen atoms of phosphine to yield primary, secondary or tertiary organic phosphines. An example of this is the reaction of phosphine with triphenylmethyl sodium in ether, followed by a reaction with an alkyl halide (Figure 2.35). The degree of substitution on phosphine is controlled by varying the proportions of the metal to phosphine.<sup>11,64</sup> A convenient method for the preparation of tertiary phosphines in the laboratory may be conducted by refluxing a Grignard reagent with a phosphorus trihalide or its organic derivatives in ether (Figure 2.36).<sup>11,64</sup>

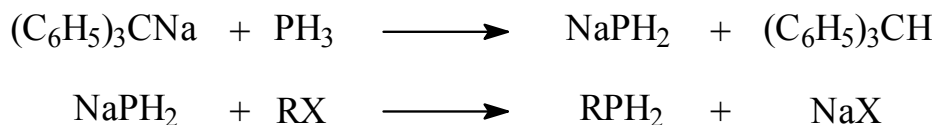


Figure 2.35. Synthesis of Alkylphosphines<sup>11</sup>

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64. G. M. Kosolapoff, Organophosphorus Compounds, John Wiley & Sons, Inc., New York, pp. 10-41, 1950.

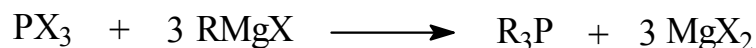


Figure 2.36. Synthesis of Tertiary Phosphines<sup>11</sup>

Organic phosphines are extremely reactive and quite toxic substances with a garlic type odor. Their reactivity and toxicity tend to decrease with substitution, while their basicity increases (PH<sub>3</sub> itself is not basic). Organic phosphines react readily with oxygen, sulfur, and halogens, and form complexes with certain metals. Oxidation occurs readily in air at room temperature for primary and secondary phosphines substituted with lower aliphatic groups. Aromatic and tertiary phosphines are relatively stable to ambient atmospheric oxidation although are susceptible to attack by certain oxidizing agents.<sup>64</sup>

Phosphine (and its organic derivatives) displays inorganic behavior acting as a ligand in coordination compounds.<sup>65,66,67,68</sup> Phosphine ligands are capable of stabilizing many unusual oxidation states of transition metals. Typical resultant complexes may be isolated and characterized as organo ( $\sigma$ - and  $\pi$ - bonded), hydrido, carbonyl and nitrosyl

65. F. J. Hollander and D. Coucouvanis, "Metal Complexes as Ligands. V. The Crystal and Molecular Structure of Tris(bis(triphenylphosphine)silver(I)) Tris(dithiooxalato)iron(III) and -aluminum(III), [Ag(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>]<sub>3</sub>M(O<sub>2</sub>C<sub>2</sub>S<sub>2</sub>)<sub>3</sub>, M = Fe(III) and Al(III)", *Inorganic Chemistry*, Vol. 13, No. 10, pp. 2381-2386, 1974.
66. J. E. Shade and A. Wojcicki, "Chiral Iron Complexes ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>CH(Ph)Me)Fe(CO)(L)X (L = Phosphine, Phosphite; X = Acyl, Alkyl, Halide, Hydride)", *Journal of Organometallic Chemistry*, 319, pp. 391-406, 1987.
67. M. Yoshifuji, "Coordination Chemistry of Some Low Coordinate Organophosphorus Compounds of Coordination Number 2", *Bull. Chem. Soc. Jpn.*, **70**, pp. 2881-2893, 1997.
68. E. C. Constable, C. E. Housecroft, M. Neuburger, A. G. Schneider and M. Zehnder, "The Diatopic Ligands 4'-(diphenylphosphino)-2,2':6',2"-terpyridine L<sup>1</sup> and 4'(oxodiphenylphosphanyl)-2,2':6',2"-terpyridine L<sup>2</sup>: Coordination to Iron(II), Ruthenium(II), Cobalt(II) and Palladium(II); Crystal Structures of [RuL<sup>2</sup>]<sub>2</sub>[PF<sub>6</sub>]<sub>2</sub>•H<sub>2</sub>O•MeCN and *trans*-[PdCl<sub>2</sub>L<sup>1</sup>]<sub>2</sub>•2.5CH<sub>2</sub>Cl<sub>2</sub>", *J. Chem. Soc., Dalton Trans.*, pp. 2427-2434, 1997.

derivatives along with nitrogen, acyl, nitrene and carbene complexes. Representative phosphorus-metal complexes serve as catalysts for various types of reactions and as model compounds in kinetic and metal surface simulation studies.<sup>69</sup> The first reported phosphine complex,  $\text{H}_3\text{P}\cdot\text{TiCl}_4$ , was discovered in 1832 by Rose. Phosphine ligands,  $-\text{PH}_3$ , as complexes are relatively rare in comparison with the number of organophosphine  $-\text{PR}_3$  complexes possible, particularly  $-\text{PPh}_3$ . The complexes containing at least one M-P bond are generally non-ionic and soluble in organic solvents (opposed to the salt-like complexes of amine derivatives). Standard organophosphine complex preparation simply involves mixing stoichiometric ratios of metal to phosphine ligands (A-C), or displacement reactions (D) (Figure 2.37).<sup>5</sup>

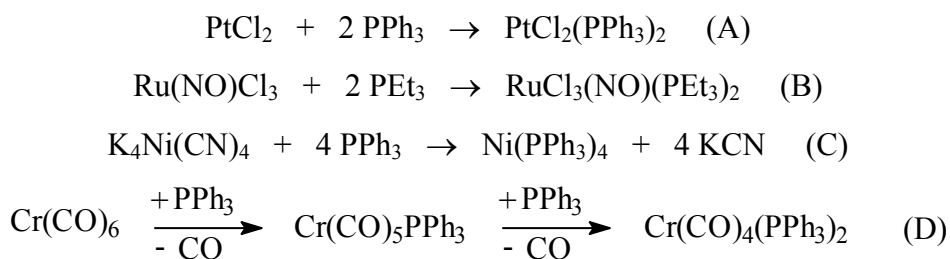


Figure 2.37. Preparation of Metal-Organophosphine Complexes<sup>5</sup>

The stereochemical structures of the metal complexes are dependent on both the metal and the ligand. Various stereochemical configurations are possible and are illustrated in the following common complexes as: linear (A), trigonal planar (B), tetrahedral (C), planar (D), trigonal bipyramidal (E), tetragonal pyramidal (F) and octahedral (G) (Figure 2.38).<sup>5</sup> It should be noted that complexes containing only  $-\text{PPh}_3$  are unstable and will undergo reactions where more ligands are added or exchanged with  $-\text{PPh}_3$  ligands.<sup>5</sup> For example,  $\text{Ni}(\text{PPh}_3)_4$  is known, but dissociates substantially to  $\text{Ni}(\text{PPh}_3)_3$  at room temperature. Similarly,  $\text{Pt}(\text{PPh}_3)_4$  dissociates into  $\text{Pt}(\text{PPh}_3)_3$  and  $\text{PPh}_3$

69. G. Booth, "Phosphine Complexes with Metals", chapter 3a, pp. 433-545, in Organic Phosphorus Compounds, Vol. 1, G. M. Kosolapoff and L. Maier, eds., John Wiley and Sons, Inc., New York, 1972.

in solution. A general trend for the complexing strengths of organo- and phosphine (III) ligands follows:  $P(OR)_3 > PF_3 > PH_3 > PR_3 > P(OPh)_3 > PPh_3 \approx PBu_3$ .<sup>9</sup>

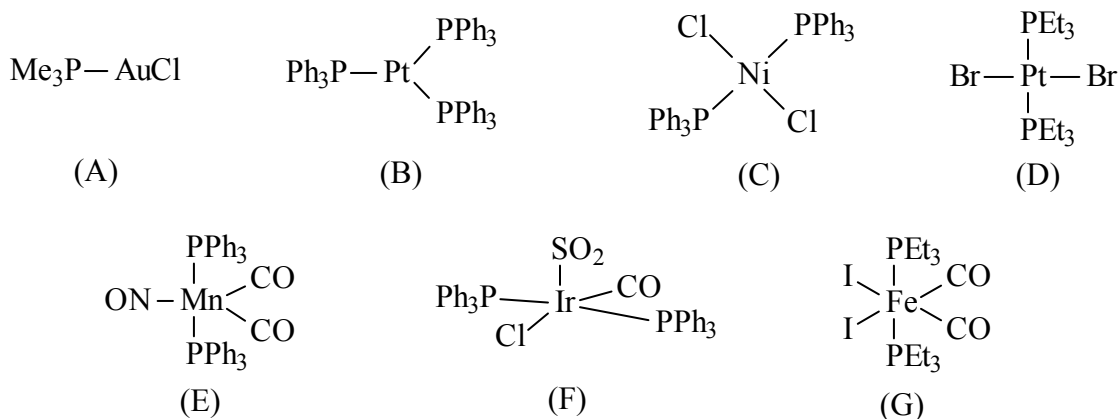


Figure 2.38. Stereochemical Configurations Possible for M-P Complexes<sup>5</sup>

Polysiloxanes with pendent diphenylphosphine moieties are of special interest as high performance dispersants for particulate metals and oxide fillers. The combination of particulate metals with macromolecules may yield novel polymeric materials capable of electron transport and heat transfer. Any extended ordering from the polymeric matrix could potentially impart interesting association<sup>70</sup> and mechanical properties on the dispersed metal. A number of macromolecular metal complexes, based on a diphenylphosphine substituted polystyrene, are possible.<sup>71</sup>

70. C. Pathmamanoharan, P. Wijkens, D. M. Grove and A. P. Philipse, "Paramagnetic Silica Particles: Synthesis and Grafting of a Silane Coupling Agent Containing Nickel Ions onto Colloidal Silica Particles", *Langmuir*, **12**, pp. 4372-4377, 1996.

71. F. Ciardelli, E. Tsuchida and D. Wöhrle, eds., Macromolecule-Metal Complexes, Springer-Verlag, Berlin Heidelberg, 1996.

### 2.5.3. Free Radical Addition of Phosphines

Another important route for the synthesis of materials containing Si-C-P bonds involves the free radical addition of alkylphosphines containing a P-H bond to alkenylsilane groups. This method is especially desirable for producing novel phosphine containing polysiloxanes capable of forming complexes with certain metals. The previous focus was on the synthesis of the strongly hydrogen bonding and extremely stable phosphoryl moiety via Michaelis-Arbuzov rearrangements. Below, the free radical chemistry involving organophosphorus reagents will be discussed with an emphasis on the synthesis of siloxanes with organophosphorus moieties, having an unshared pair of electrons.

Two main types of phosphorus radicals exist. The first class includes seven electron species: phosphinyl radicals,  $R_2P\cdot$  or  $(RO)_2P\cdot$ , phosphoryl radicals,  $R_2\dot{P}=O$ , and the phosphinium radical cation,  $R_3P\cdot^+$  (each with one unpaired electron in the valence shell of P). The second class contains nine electron phosphorus radicals (one unpaired), represented by the phosphoranyl radical,  $R_4P\cdot$  or  $(RO)_4P\cdot$  and the phosphonium radical anion,  $R_3P\cdot^-$ .<sup>72</sup> Sometimes, the phosphoryl radicals may be regarded as nine electron radical species due to the certain degree of double bond character that they possess. This radical could be represented as a resonance hybrid (Figure 2.39), and is commonly denoted as the middle species. This radical is usually included in the  $7 e^-$  radical class as it exhibits reactivity more similar to the phosphinyl rather than the phosphoranyl radicals.<sup>5,9,73</sup>

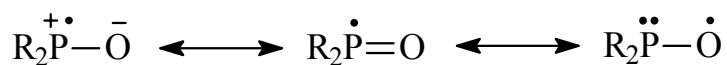


Figure 2.39. Resonance of the Phosphonyl Radical<sup>5</sup>

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72. B. J. Walker, Organophosphorus Chemistry, William Clowes and Sons Limited, Great Britain, 1972.
73. W. G. Bentrude, J.-J. L. Fu and P. E. Rogers, "Free-Radical Chemistry of Organophosphorus Compounds. Polar, Bond Strength, and Resonance Effects on Phosphoranyl Radical Formation", *J. Am. Chem. Soc.*, **95**(11), pp. 3625-3635, 1973.

Phosphinyl radicals,  $R_2P\cdot$ , are fairly stable radicals (e.g.  $Ph_2P\cdot$  has a half-life of 20 minutes at 173 K). This radical species is generally formed by either homolytic fission of a diphosphine via thermal or photochemical dissociation (A), or by radical abstraction from a phosphine (B) (Figure 2.40).<sup>5</sup> Once formed, the phosphinyl radical typically undergoes two types of reactions, either addition (C) or abstraction (D) (Figure 2.41).<sup>5,9</sup>

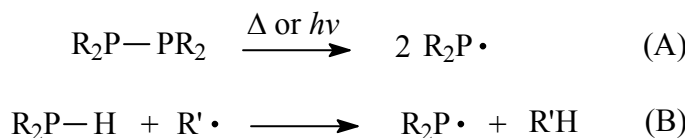


Figure 2.40. Formation of Phosphinyl Radical<sup>5</sup>

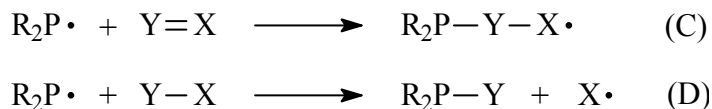


Figure 2.41. Reactions of the Phosphinyl Radical<sup>5</sup>

The phosphinyl radicals from primary or secondary organic phosphines add rapidly to olefins. Derivatives with more than one P-H can react with more than one mole of the alkene when promoted with a free radical initiator such as 2,2'-azobisisobutyronitrile (AIBN). Therefore, phosphine can react with alkenes to yield a mixture of primary, secondary and tertiary phosphines (Figure 2.42).<sup>5,9</sup> Anti-Markovnikov products are formed as phosphorus radicals add to the least-substituted end of the double-bond to yield the most highly substituted radical (similarly to organic radical reactions) (Figure 2.43).<sup>9</sup> The  $R\cdot$  initiator typically evolves from organic peroxides.<sup>35,74</sup>

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74. V. I. Yudelevich, L. B. Sokolov and B. I. Ionin, "Phosphinates (Hypophosphites) and Their Reactivity", *Russian Chemical Reviews*, **49** (1), pp. 46-58, 1980.

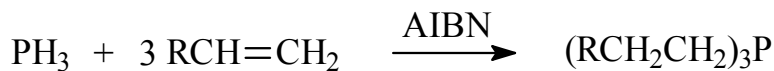


Figure 2.42. Free Radical Addition of Phosphine to Vinyl<sup>9</sup>

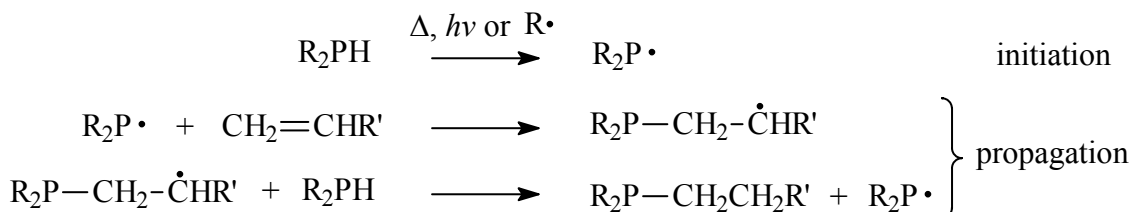


Figure 2.43. Free Radical Addition of Secondary Phosphine to Vinyl<sup>9</sup>

The addition reactions of organic phosphines across silanes with pendent vinyl groups may be initiated with ultraviolet radiation or organic peroxides, such as azobisisobutyronitrile and tert-butyl peroxide. Although, the reaction may also be conducted by heating the alkene / phosphine mixture to 160 °C in the absence of initiating species (Figure 2.44).<sup>35</sup> The R group on the silane may be an alkyl, alkoxy, siloxy or a halide radical, and x = 0-3 and y = 0-2. The R' group on phosphorus may be either a hydrogen or an organic group, and R'' may be an organic group.<sup>35</sup>



Figure 2.44. Free Radical Addition of an Organophosphine to Vinyl Sans Initiator<sup>35</sup>

An exemplary study on the synthesis of siloxanes with electron-donating organophosphorus moieties via free radical addition reactions was carried out by Chojnowski and Rózga.<sup>75</sup> Three siloxane trimers were synthesized, D<sub>3</sub>R, each with a

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75. J. Chojnowski and K. Rózga, "Synthesis of Linear Polysiloxanes with Electron-Donating Organophosphorus Pendent Groups by Kinetically Controlled Ring-Opening Polymerization", *Journal of Inorganic and Organometallic Polymers*, Vol. 2, No.3, pp. 297-317, 1992.

different organophosphorus pendent group on one of the three silicon atoms: R =  $-\text{CH}_2\text{CH}_2\text{PPh}_2$ ,  $-\text{CH}_2\text{CH}_2\text{P(S)Ph}_2$  and  $-\text{CH}_2\text{CH}_2\text{P(O)Ph}_2$ . The addition reaction of diphenylphosphine with the cyclic siloxane trimers containing one pendent vinyl group, 1-vinylpentamethylcyclotrisiloxane, was carried out and promoted with azobisisobutyronitrile (AIBN) (Figure 2.5). A total of 0.155 mol% of AIBN (based on the moles of vinyl) was added in two portions: the first, 0.055 mol% at room temperature prior to the addition of diphenylphosphine, and the second 0.1 mol% was added after the complete addition of diphenylphosphine to the vinyl siloxane trimer at 115 °C. The reaction proceeded at 115 °C for 15 hours and was monitored using  $^{31}\text{P}$  NMR to yield ~ 75% pure [2-(diphenylphosphino)ethyl]pentamethylcyclotrisiloxane after purification via distillation and column chromatography. The sulfur ( $-\text{P(S)Ph}_2$ ) substituent was prepared by the addition of sulfur.<sup>75</sup> The phosphoryl ( $-\text{P(O)Ph}_2$ ) analogues were formed by oxidation of the phosphine substituted siloxane with bis(trimethylsilyl)peroxide (BSPO) monomer (Figure 2.45).<sup>76</sup>

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76. L. Woz'niak, J. Kowalski, and J. Chojnowski, "Bis(trimethylsilyl)peroxide as a Versatile Reagent for Selective Generation of Oxyphosphoryl Group", *Tetrahedron Letters*, Vol. 26, No. 40, pp. 4965-4968, 1985.

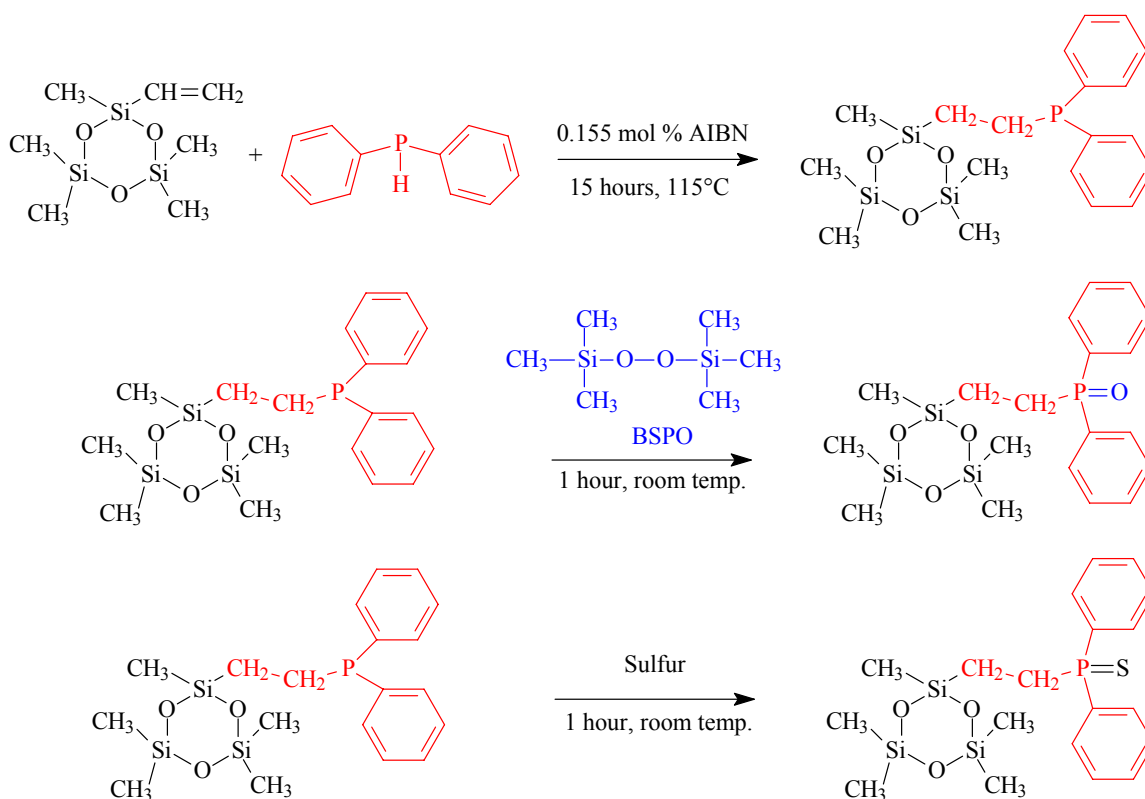


Figure 2.45. Free Radical Addition of Diphenylphosphine and Subsequent Oxidation to Yield a Phosphine Oxide Containing Cyclic Siloxane Trimer<sup>75</sup>

The corresponding series of linear polysiloxanes containing phosphonyl pendent groups were prepared by kinetically controlled ring-opening polymerizations of the phosphine containing siloxane trimers.<sup>75</sup> Exemplary reactions were promoted with lithium silanolate initiators and carried out in 50 volume % tetrahydrofuran at 40 °C. The weight average molecular weights,  $M_w$ , for most of the polymers were ~10000 g/mol. Microstructure compositions with a regular arrangement of the pendent phosphine containing substituents would be expected if one of the siloxy groups in the cyclosiloxane trimer were significantly more reactive.

The authors found that the presence of phosphorus enhanced cyclization and broadened the molecular weight distributions ( $M_w/M_n$ ) of the resultant polymers.<sup>75</sup> Moreover, this effect was relatively weak for the thiophosphinoyl analogue. The  $M_w/M_n$  values for the phosphine containing polysiloxanes were >2 and between 1.3 and 1.7 for

the thiophosphine polymers, relatively higher than expected for typical living anionic polymerizations of cyclosiloxane trimers (where  $M_w/M_n \sim 1.1$ ). The lower polydispersity values for the sulfur containing trimers was attributed to the thiophosphoryl group being a poor and soft base, imparting relatively weak interactions with the hard alkali metal cation. Conversely, the strong interactions of both pendent phosphine and phosphine oxide groups with the counterion, led to the formation of a proposed chelate structure (Figure 2.46).<sup>75</sup> The microstructural arrangement of sulfur containing polysiloxanes was also more regular than for the phosphonyl substituted polysiloxanes.

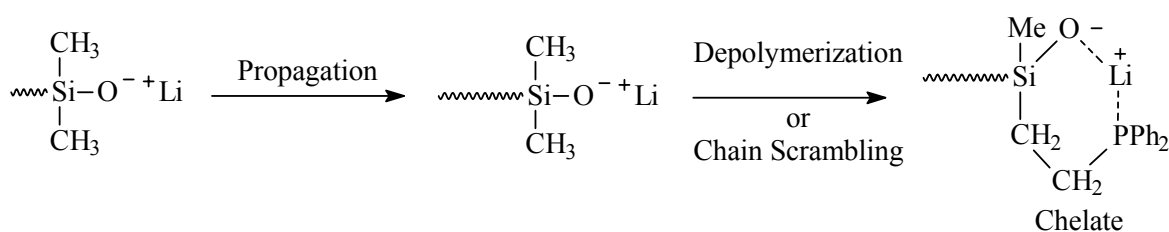


Figure 2.46. Formation of Proposed Phosphine Lithium Siloxanolate Chelate<sup>75</sup>

A current facile synthesis of carbon-phosphorus bonds mediated by a palladium catalyst was investigated by Allen et. al.<sup>77</sup> Functional bisphosphonates were isolated in good yields via palladium catalyzed bis-phosphorylation reactions of terminal alkynes with dialkyl phosphites. Vicinal bisphosphonates were formed by the bis-addition of P-H bonds across the triple bonds of terminal alkynes (Figure 2.47).<sup>77</sup> The reactions proceeded only with electron deficient terminal alkynes. Also, higher yields (72 – 90%) were obtained for R = ethyl compared to those of (55 – 86%) for R = isopropyl groups. Dimethylphosphite reacted to give only the mono-addition products, alkenylphosphonates, opposed to the bis-addition products.<sup>77</sup>

77. A. Allen Jr., D. R. Manke and W. Lin, "Synthesis of Functional Bisphosphonates Via New Palladium-Catalyzed Bis-hydrophosphorylation Reactions", *Tetrahedron Letters*, **41**, pp. 151-154, 2000.

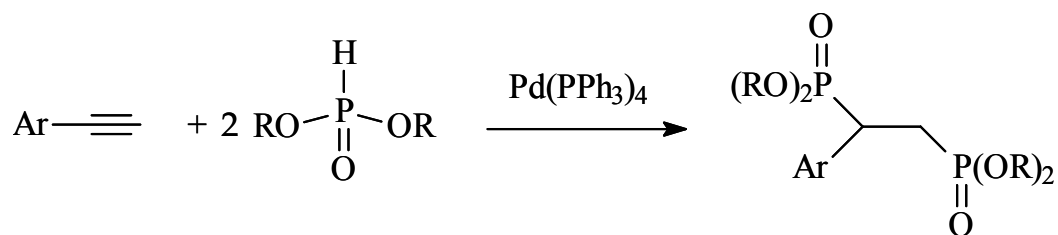


Figure 2.47. Synthesis of Vicinal Bisphosphonates<sup>77</sup>

#### 2.5.4. Synthesis of Polysiloxanes via Anionic Ring Opening Polymerization Methods

The synthesis and characterization of polyorganosiloxanes has been extensively reviewed.<sup>(31,78,79,80,81,82,83,84,85,86,87,88,89,90,91,92)</sup> Polysiloxanes are typically synthesized by

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78. W. Noll, "Chemistry and Technology of Silicones", Academic Press, New York, 1968.
  79. K. J. Saunders, "Organic Polymer Chemistry An Introduction to the Organic Chemistry of Adhesives, Fibres, Paints, Plastics, and Rubbers, 2<sup>nd</sup> Ed.", Chapman and Hall, New York, 1988.
  80. H. A. Liebhafsky, "Silicones Under the Monogram, A Story of Industrial Research", John Wiley & Sons, Inc., New York, 1978.
  81. Stephen J. Clarson and J. Anthony Semlyen, "Siloxane Polymers", PTR Prentice Hall, Inc., New Jersey, 1993.
  82. I. Yilgor, J. S. Riffle, and J. E. McGrath, in "Reactive Oligomers", F. W. Harris, Editor, ACS Symp. Series 1985.
  83. I. Yilgor, D. Tyagi, A. Sha'ban, W. S. Steckle Jr., G. L. Wilkes, and J. E. McGrath, *Polymer (London)*, **25**, 1800-1806, 1984.
  84. J. E. McGrath, "Ring-Opening Polymerization", pp. 1-22 in Ring Opening Polymerization Kinetics, Mechanisms, & Synthesis, Vol. 286, ACS Symposium Series, ACS, Washington, D. C., 1985.
  85. J. E. McGrath, Synthetic Importance and Industrial Applications of Ring-Opening Polymerization, *Makromol. Chem., Macromol. Symp.* **42/43**, 69-91 (1991).

the hydrolysis of bifunctional silanols or via ring opening polymerizations of lower cyclosiloxanes. Typical monomers, hexamethylcyclotrisiloxane (D<sub>3</sub>) or D<sub>4</sub>, are polymerized into high molecular weight polyorganosiloxanes by cleaving the Si-O bond and reforming new siloxane bonds. These polymerizations may be done using acidic or basic catalysts. For anionic polymerizations, activation energies increase as a function of the ring strain of the cyclic siloxane monomer.

Cyclosiloxane trimers are less stable due to a larger degree of ring strain, and have lower activation energies for ring-opening,  $\sim 16.5 \pm 1.0$  kcal/mole. Conversely, more stable cyclic siloxanes with greater than 3 siloxane units have activation energies of  $\sim 19.5 \pm 1.0$  kcal/mole. This activation energies difference of  $\sim 3$  kcal/mole is about equal to the energy value for the ring strain of trimeric cyclosiloxanes.<sup>31</sup> Polymerizations of cyclosiloxane trimers ( $\Delta H =$  exothermic) are enthalpically driven, whereas polymerizations of higher cyclics (most commonly D<sub>4</sub> with  $\Delta H \cong 0$ ) are entropically controlled equilibrations.<sup>92</sup> The polyorganosiloxanes prepared for this research were

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86. M. Szwarc, in "Anionic Polymerization: Kinetics, Mechanisms, and Synthesis", J. E. McGrath, editor, ACS Symposium Series, No. **166**, 1981.
  87. K. J. Ivan, and T. Saegusa, Editors, "Ring Opening Polymerization" (in three volumes), Elsevier, 1984.
  88. P. V. Wright, Chapter 14, in Reference 27.
  89. E. E. Bostick, Chapter 8, "Cyclic Siloxanes and Silazanes" pp. 327-357, in Ring Opening Polymerization, K. C. Frisch and S. C. Reegen, Eds., Marcel Dekker, New York, 1969.
  90. J. E. McGrath, J. S. Riffle, A. K. Banthia, I. Yilgor, and G. L. Wilkes "Ring Opening Polymerization of Siloxanes", in "Initiation of Polymerization", F. E. Bailey, Jr., Editor, ACS Symposium Series No. **212**, 1983.
  91. J. S. Riffle, I. Yilgor, A. K. Banthia, C. Trans, G. L. Wilkes, and J. E. McGrath, in "Epoxy Resin Chemistry II", R.S. Bauer, Editor, ACS Symposium Series No. **221**, Chapter 2, Washington D.C., 1983.
  92. D. J. Brunell, Ring Opening Polymerization Mechanisms, Catalysis, Structure, Utility, Hanser Publishers, New York, 1993.



PDMS is commonly synthesized using the more stable D<sub>4</sub> tetramer since it is a less expensive and more readily available monomer. D<sub>4</sub> has essentially no ring strain, whereas D<sub>3</sub> has a ring strain of about 3.2 kcal/mole (12 – 15 kJ/mole).<sup>(31,78,84,85)</sup> Ring-opening polymerizations of D<sub>4</sub> are entropically driven, where  $\Delta S \cong +6.7$  J/moleK. The stable tetramer opens to form a large number of highly flexible chains with greater degrees of freedom (relative to the tetramer) due to the large silicon atoms and long Si-O bonds along the siloxane backbone. A positive entropy for polymerization is unusual since most monomers are more disordered than their corresponding polymers.<sup>31</sup>

A thermodynamic equilibrium is established between the cyclics and linear chains for the polymerization of cyclic siloxanes with greater than three units. The size and type of sidechain chemical structures on the cyclosiloxane influences the concentration of equilibrates. Oligomers with controlled average molecular weights can be prepared when D<sub>4</sub> is polymerized in the presence of a small linear disiloxane endcapping reagent. Kinetics of the equilibration of D<sub>4</sub> in the presence of hexamethyldisiloxane were demonstrated as first order with respect to D<sub>4</sub> and had a square root dependence on either KOH or the siloxanolate. The vapor pressures were monitored above the equilibrating mixtures and compared to the vapor pressures above known concentrations of D<sub>4</sub> in PDMS.<sup>93</sup>

The Si-O bond is resistant to homolytic cleavage, therefore an acid or base catalyst is required to heterolytically cleave the Si-O bond to form ionic active centers, R<sub>3</sub>Si-O<sup>-</sup>, necessary for propagation. The activation energy for ring opening D<sub>4</sub> is higher than for D<sub>3</sub>, and requires more basic reactive centers than tightly associated lithium siloxanolate (for D<sub>3</sub>) for polymerization.<sup>(31,84,85)</sup> The catalyst strength determines the rate at which the equilibrates (linear chains and cyclics) are formed.<sup>(31,88)</sup> Catalyst choice is based on the types of sidechain chemical structures on the silicon atoms of the monomer and the endgroups on the endcapping reagent. Generally, groups susceptible to attack by acid are polymerized via a basic catalyst, and vice versa.<sup>90</sup>

The initiation step for base catalyzed polymerizations involves attack of the base on the electropositive silicon atom in the cyclic siloxane tetramer to yield reactive siloxanolate centers,  $\equiv\text{Si-O}^-$ . Base reactivity towards lower cyclic and linear siloxanes is greatest for strained difunctional siloxanes (D type units, a difunctional Si atom bonded

to two oxygen atoms), and least reactive towards unstrained monofunctional (M type units, a Si atom bonded to three oxygen atoms), where:  $D_3 > D_4 > MD_2M > MDM > MM$ . This phenomenon illustrates how the reactivity of the siloxane bond towards base increases with the number of electronegative oxygen atoms which effectively increase the positive character of the silicon atom.<sup>(93,94)</sup> It also supports the observation that  $D_4$  requires a stronger base than  $D_3$  for ring-opening polymerization, and that an MM type linear siloxane will function as an effective endcapping reagent.

The most active anionic catalysts include: hydroxides, alcoholates, phenolates, silanolates or siloxanolates, mercaptides of the alkali metals, quaternary ammonium and phosphonium bases and their siloxanolates, organo(-lithium, -sodium, and -potassium) compounds, hydrocarbon radicals ( $R\bullet$ ) or RM type compounds.<sup>31</sup> Many catalysts have been extensively studied.<sup>(31,78,88,95)</sup> Catalysts commonly used for the thermodynamic, anionic, ring opening of the stable cyclic tetramer  $D_4$ , will be focused on here.

Polymerizations of  $D_4$  with a series of strong bases was carried out to investigate the nature of the silicon-oxygen-alkali bond.<sup>95</sup> Alkali metal hydroxides (commonly anhydrous KOH) are more basic than the organolithiums, and frequently used to ring-open  $D_4$  at common polymerization temperatures  $\sim 140\text{ }^\circ\text{C} - 160\text{ }^\circ\text{C}$ .<sup>(85,95)</sup> Both the solubility in  $D_4$  and reactivity of the alkali metal hydroxides depend on the size of the cation. Cesium hydroxide dissolves below  $100\text{ }^\circ\text{C}$ , potassium hydroxide at  $\sim 150\text{ }^\circ\text{C}$ , while the weaker sodium and lithium hydroxide bases do not dissolve even above  $150\text{ }^\circ\text{C}$ . Polymerization temperatures can be decreased by using a more reactive base. Base reactivity increases with increasing size of the cation:  $\text{CsOH} > \text{RbOH} > \text{KOH} >$

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93. S. W. Kantor, W. T. Grubb, R. C. Osthoff, *J. Am. Chem. Soc.*, **76**, 5190, 1954.

94. C. L. Frye, R. M. Salinger, W. G. Fearon, J. M. Klosowski, and T. DeYoung, Reactions of Organolithium Reagents with Siloxane Substrates, *The Journal of Organic Chemistry*, **35**, 1308-1314 (1970).

95. D. T. Hurd, R. C. Osthoff, and M. L. Corrin, The Mechanism of the Base-catalyzed Rearrangement of Organopolysiloxanes, *Journal of the American Chemical Society*, **76**, 249-252 (1954).

NaOH > LiOH.<sup>(78,95)</sup> Tetramethylammonium<sup>(31,95,96)</sup> and tetrabutylphosphonium<sup>(31,95,97)</sup> siloxanolate react at rates similar to that of cesium siloxanolate.

Thermally labile catalysts<sup>(31,91,95,96,97,98,99)</sup> such as quaternary ammonium (R<sub>4</sub>NOH) and phosphonium hydroxides (R<sub>4</sub>POH) are known as transient catalysts. The catalyst species decompose when heated (above 100 °C) into inert, volatile products that can be distilled away from the product. Extra steps required for alkali metal hydroxides of washing or neutralizing the solution are eliminated.<sup>(31,91)</sup> Tetramethylammonium siloxanolate decomposes slowly above ~ 90 °C and quickly above 130 °C to yield methanol (or a trimethoxysiloxy- endgroup) and trimethylamine (activation energy of ~ 42 kcal/mole): (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup> OR + Δ → (CH<sub>3</sub>)<sub>3</sub>N + CH<sub>3</sub>OR, where R = H or (-Si(CH<sub>3</sub>)<sub>2</sub>O-)n.<sup>(95,99)</sup> Quaternary phosphonium siloxanolate degrades at a slightly lower temperature of ~ 110 °C to yield gaseous hydrocarbons and triorganylphosphine oxides: R<sub>4</sub>POH + Δ → RH + R<sub>3</sub>PO.<sup>97</sup> Activation energy for equilibration of D<sub>4</sub> (between 60 – 100 °C) is reported as ~ 20.0 kcal/mole when catalyzed with tetramethylammonium hydroxide.<sup>(31,98)</sup> Tetramethylammonium hydroxide was the basic catalyst chosen for this study to polymerize D<sub>4</sub> and tetramethyltetravinylcyclotetrasiloxane (D<sub>4</sub>Vi) in the bulk.

Tetramethylammonium hydroxide reacts with D<sub>4</sub> to yield silanols that condense to form longer anionic disiloxanolate anionic species. The tetramethylammonium siloxanolate anionic centers react by attacking its own chain, or by attacking another growing chain (Figure 2.49).<sup>100</sup> Moisture free catalysts are required to yield high molecular weight polymers. Water is a known impurity that reacts to form silanols and decreases the molecular weight.<sup>88</sup> The water of hydration and reaction are first removed from the tetramethylammonium disiloxanolate catalyst. Propagation of D<sub>4</sub> then proceeds with a large initial increase in the molecular weight and the viscosity of the solution

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96. J. F. Hyde, U. S. Patent 2,443,353, June 16, 1948.

97. A. R. Gilbert, S. W. Kantor, *J. Polym. Sci.* **40**, 35, 1959.

98. Z. Laita, P. Hlozek, B. Bucek, M. Jelinek, *J. Polym. Sci.*, **C16**, 669, 1967.

99. K. Kawazumi, H. Matusami, and K. Hashi, *Kogyo Kagaku Zasshi*, **66**, 628, 1963.

100. M. Mazurek and J. Chojnowski, *Makromol. Chem.*, **178**, 1005, 1977.

(Figure 2.49).<sup>93</sup> Studies suggest that the propagation step involves successive additions of discrete tetrameric dimethylsiloxane increments.<sup>93,101</sup> The quick and steady increase in molecular weight typically occurs until about 60 –70% conversion of the cyclics to linear chains, whereupon the molecular weight decreases by a series of redistribution reactions until an equilibrium plateau is reached.<sup>84,85</sup>

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101. J. B. Carmichael and J. Heffel, *J. Phys. Chem.*, **69**, 2213, 1965.

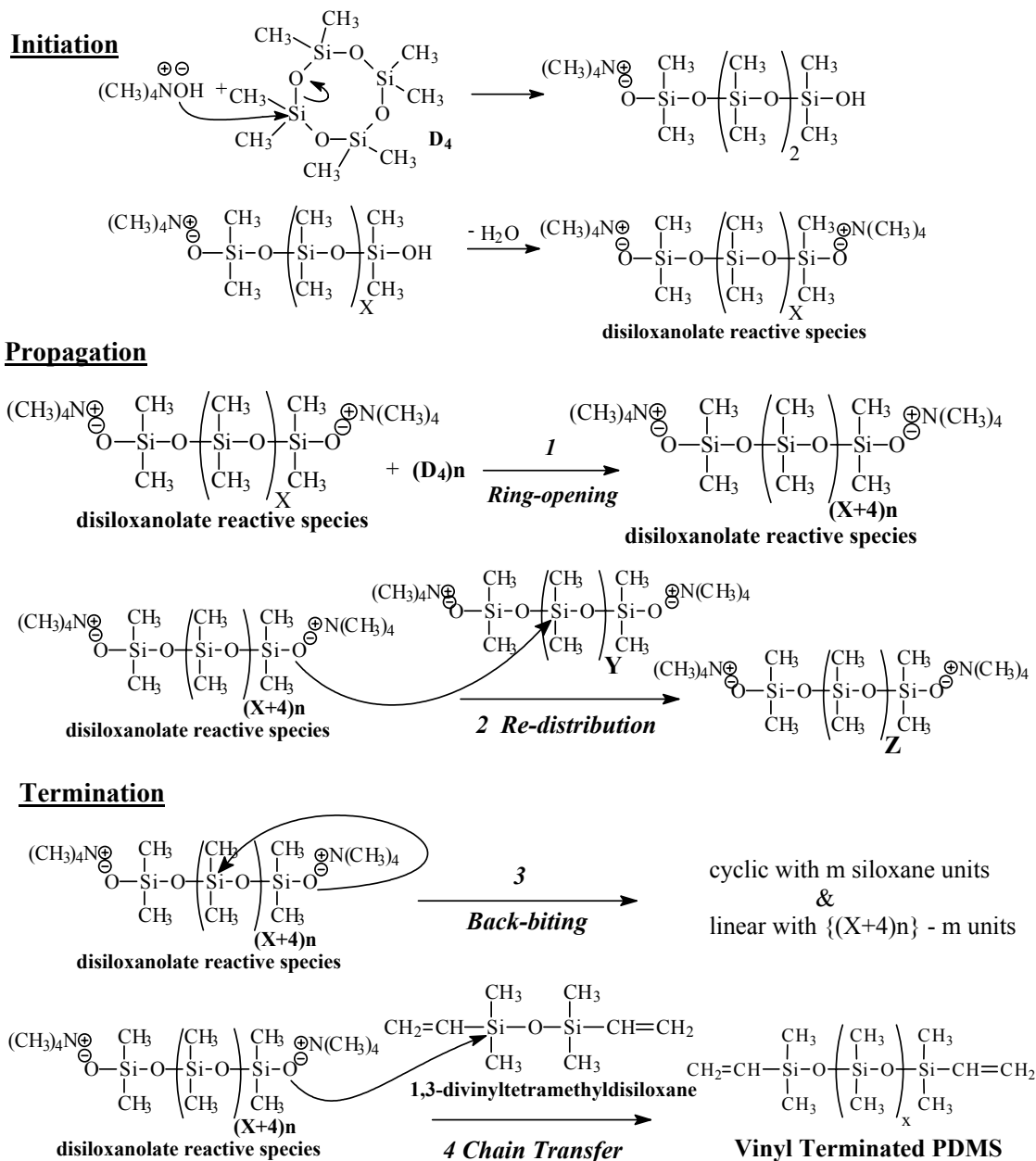


Figure 2.49. Mechanism for the Anionic Ring Opening Polymerization of a Cyclosiloxane Tetramer

A small dimeric unit (typically hexamethyldisiloxane) may be introduced at the beginning of the polymerization to serve as a chain transfer reagent and effectively endcap the siloxane chains (Figure 2.49). Siloxane bonds have partial ionic character, while Si-C bonds are mostly covalent. The siloxanolate reactive species attacks the

siloxane bond of the dimer and will not react with the Si-C bond of the endcapping reagent under normal equilibration conditions. Controlled molecular weight polymers are therefore predicted by the molar concentration ratio of D<sub>4</sub> to the endcapping reagent, taking into account the equilibrium concentration of cyclics.<sup>85</sup>

The propagation mechanism (Figure 2.49) involves attack of the siloxanolate anion on 1) the electropositive silicon atom of a cyclic tetramer (*ring-opening*) followed by a series of redistribution reactions involving the attack of the siloxanolate anion on: 2) the silicon atom of a growing chain (*re-distribution*), 3) a silicon atom within its own chain to form a new cyclic (*backbiting*), or 4) the silicon atom in the dimeric endcapping reagent (*chain transfer*). After the initial increase in molecular weight, steps 2 through 4 (which only affects the longer chains) become increasingly important until an equilibrium between the rings and chains is established. The reaction is terminated by removing the reactive species once equilibrium is confirmed. In this case, the transient catalyst tetramethylammonium siloxanolate, is decomposed by heating the solution above 130°C and bubbling N<sub>2</sub> through to remove the inert, volatile decomposition products. It is important to establish when thermodynamic equilibrium is attained to avoid removal of the reactive species too early during the equilibration.

Gel Permeation Chromatography, GPC, is an effective method to monitor equilibrations since the concentrations of small cyclics and the Gaussian distribution of linear chains can be established. GPC separates molecules based on their hydrodynamic volumes in a solvent by passing them through porous, polymeric beads. The larger molecules (linear chains) pass through the column first. The smaller species (cyclics) elute last since they first travel through the smaller pores inside the beads and therefore travel a longer path.<sup>102</sup> This method for monitoring equilibrations of D<sub>4</sub> was first established by Brown and Slusarczuk.<sup>103</sup> The concentration of cyclics present at equilibrium generally does not depend on the target molecular weight of the newly

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102. P. C. Painter and M. M. Coleman, "Fundamentals of Polymer Science", Technomic Publishing Co., Inc., Lancaster, 1994.

103. J. F. Brown and G. M. J. Slusarczuk, *J. Am. Chem. Soc.*, **87**, 931, 1965.

formed chains, and is typically ~ 17% for PDMS.<sup>(85,104,105)</sup> Knowing how the equilibrium conditions are affected by the starting conditions (type of monomer, etc.) is of substantial importance for the highest yield of polymer.<sup>106</sup>

The work of Brown and Slusarczuk was used as the basis for extensive studies of the cyclic populations in equilibrated polymeric systems. Semlyen and coworkers made use of Jacobson and Stockmayer's equilibrium theory of macrocyclization<sup>107</sup> by relating the concentration of cyclics at equilibrium to the statistical conformations of their respective open chains.<sup>88</sup> Jacobson and Stockmayer's theory showed that the concentration of cyclics increases with dilution, and that 100% cyclics will result beyond a critical dilution.<sup>107</sup> Later, this theory was revised by Semlyen and Flory<sup>108</sup> who accounted for the larger than predicted amounts of unstrained cyclics, D<sub>4</sub> and D<sub>5</sub> at equilibrium. The rotational isomeric state theory, of Flory, Crescenzi, and Mark has been used to interpret the conformation dependent properties of many synthetic polymers.<sup>(104,105)</sup>

The percentage of cyclics remaining at equilibrium depends on both the size of the monomer, and also the size and polarity of the substituents. The concentration of cyclics at equilibrium does not depend on the target M<sub>n</sub>. A study supporting this was conducted by Wright and Semlyen.<sup>109</sup> A series of unstrained substituted R-methylcyclotetrasiloxanes (R = H-, CH<sub>3</sub>-, CH<sub>3</sub>CH<sub>2</sub>-, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>-, and CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>-) were equilibrated in the presence of base. The only difference in the polymerizations was a lower equilibration temperature (273 K) for hydrogenmethyltetracyclosiloxane than the

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104. J. A. Semlyen and P. V. Wright, *Polymer*, **10**, 543-553, 1969.

105. P. V. Wright, *J. Polym. Sci., Polym. Phys.*, **11**, 51-64, 1973.

106. M. A. Buese, *Macromolecules*, **20**, 694-696, 1987.

107. H. Jacobson and W. H. Stockmayer, *J. Chem. Phys.*, **18**, 1600, 1950.

108. P. J. Flory and J. A. Semlyen, Macrocyclization Equilibrium Constants and the Statistical Configuration of Polydimethylsiloxane Chains, *Journal of the American Chemical Society*, **88**, 3209-3212 (1966).

109. P. V. Wright and J. A. Semlyen, *Polymer*, **11**, 462, 1970.

others (383 K). Cyclization data corresponded to an earlier study using intrinsic viscosities.<sup>88</sup> The percentage of small cyclics ( $x = 3 - 6$ ) at equilibrium increased with the size and polarity of the substituent on the monomer as: R = H- (~ 6%), CH<sub>3</sub>- (~ 12%), CH<sub>3</sub>CH<sub>2</sub>- (~ 20%), CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>- (~ 30%), and CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>- (~ 78%). The equilibrium shifted toward higher concentrations of cyclics with larger or more polar substituted monomers. This data suggested that the conformational freedom of polysiloxane chains decreased as the size and/or polarity of the substituent on the monomer increased.<sup>(109,110)</sup>

### 2.5.5. Synthesis of Polysiloxanes with Pendent Vinyl Groups

For this research, poly(methylvinyl)siloxane homopolymers and poly(dimethyl-co-methylvinyl)siloxane oligomers served as reactive precursors for siloxanes containing organophosphorus and carboxylic acid moieties. Free radical addition reactions of the pendent vinyl groups were performed to yield novel polyorganosiloxanes. Various synthetic routes to yield vinyl containing polysiloxanes have been investigated. Typical cyclic monomers are tetrameric or trimeric cyclosiloxanes with one to four, or one to three pendent vinyl groups, respectively, on the silicon atoms. The poly(dimethyl-co-methylvinyl)siloxane- copolymers may be synthesized using a cyclic that is not completely substituted with methylvinyl- groups, or by copolymerization of two siloxane cyclics with all methyl and all methylvinyl- groups. Alternatively, acyclic organosilicon monomers<sup>111</sup> with pendent vinyl groups may be polymerized.

Cyclic and linear siloxane precursors for polyorganosiloxanes are synthesized from organohalosiloxanes.<sup>80</sup> The direct, Grignard, olefin addition, and redistribution processes are all important commercial methods for synthesizing chlorosilanes and

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110. J. A. Semlyen, "Ring-Chain Equilibria and the Conformations of Polymer Chains", in "Advances in Polymer Science", **21**, H. -J. Cantow, Editor, New York, 1976.

111. A. D. Petrov, B. F. Mironov, V. A. Ponomarenko and E. A. Chernyshev, eds., Synthesis of Organosilicon Monomers, Consultants Bureau Enterprises, Inc., New York, 1964.

organochlorosilanes. Commercially, chlorosilanes are synthesized from Si (derived from SiO<sub>2</sub>): SiO<sub>2</sub> + 2C → Si + 2CO, and Si + 2Cl<sub>2</sub> → SiCl<sub>4</sub>.<sup>79</sup>

Precursors for polyorganosiloxanes are synthesized by the hydrolysis of organochlorosilanes to yield unstable organosilanols that spontaneously condense to form a mixture of linear and cyclic siloxanes (Figure 2.50). The type of siloxane formed depends on the functionality of the halosilane and the reaction conditions. For example, hydrolysis of dimethylchlorosilane reacts to form the dimer, hexamethyldisiloxane (Figure 2.51).

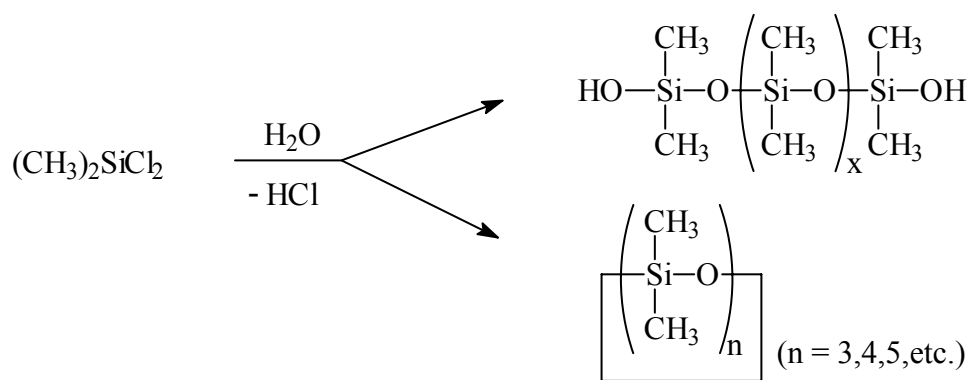


Figure 2.50. Hydrolysis of Dichlorosilane to Yield a Mixture of Linear and Cyclosiloxanes<sup>78</sup>

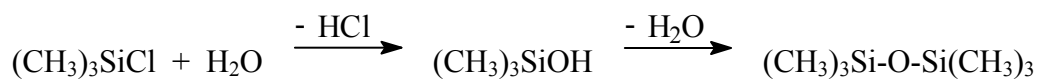


Figure 2.51. Synthesis of Hexamethyldisiloxane<sup>78</sup>

Hexamethyldisiloxane can act as a chain transfer reagent and used to control molecular weights of polyorganosiloxanes. Hydrolysis of the difunctional halosilane, dimethyldichlorosilane leads to a mixture of linear and cyclic oligomers (Figure 2.50), where the percentage of the linear and cyclic siloxanes produced depends on the reaction conditions. When hydrolysis is carried out exclusively with water, yields of 50 – 80% of

linear polydimethylsiloxane- $\alpha,\omega$ -diols and 50 – 20% polydimethylcyclorosiloxanes are obtained. The oligomeric proportion of cyclorosiloxanes is increased to ~ 70% when hydrolysis is carried out using 6N HCl instead of water.<sup>78</sup> By contrast, when 50 – 85% sulfuric acid is present during the hydrolysis, high molecular weight linear polymers are preferentially formed with only a small percentage of cyclorosiloxanes.

When preferential formation of lower cyclorosiloxanes is desired, hydrolysis with water is carried out interfacially in the presence of solvents such as toluene, xylene, or diethyl ether. Intramolecular condensation is favored over intermolecular condensation due to the reduction in concentration of the organochlorosilanes in the aqueous phase. Since the cyclorosiloxane products are soluble in the organic phase, they are protected from the attack of the aqueous HCl acid. Finally, hydrolysis of the trifunctional, methyltrichlorosilane, yields highly crosslinked gel-like or powdery polymers (Figure 2.52).<sup>79</sup> The linear silanol and cyclorosiloxane products of the hydrolysis reactions may be catalyzed by either acids or bases. When organochlorosilanes are hydrolysed (in the absence of an organic solvent), the acidic HCl formed in situ typically acts as the catalyst leading to rapid condensation.<sup>79</sup>

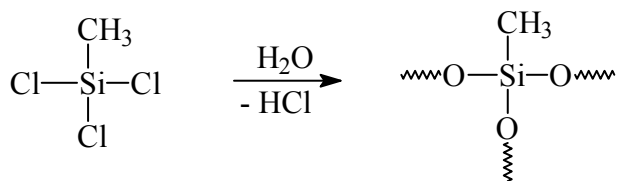


Figure 2.52. Formation of Siloxane Crosslinks<sup>79</sup>

An exemplary synthesis of siloxane cyclic trimers with one pendent vinyl group was performed by the heterofunctional polycondensation of a dichloromethylsilane<sup>111</sup> with an organosilane diol in the presence of excess pyridine<sup>75</sup> or triethylamine as the HCl

acceptor.<sup>112</sup> Higher yields of the trimer have been reported by using a catalytic amount of 4-(N-N-dimethylamine)pyridine (DMAP) together with triethylamine as the HCl accepting system (Figure 2.53).<sup>113</sup> The starting material, 1,3-dihydroxytetramethyldisiloxane, is synthesized by the hydrolysis (5-6 moles of water) of 1,3-dichlorotetramethyldisiloxane (4 moles) in an aqueous solution of ammonium carbonate saturated with NaCl for 2 days at  $-5\text{ }^{\circ}\text{C}$ .<sup>114</sup> Organosiloxane tetramers are typically easier to synthesize by a variety of synthetic routes and isolated due to their lack of ring strain relative to the cyclic trimers. A complete review of their synthesis is covered by Johansson and Lee.<sup>115</sup>

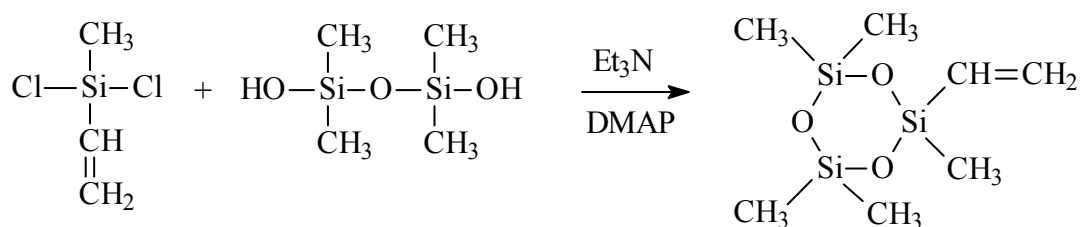


Figure 2.53. Synthesis of a Cyclosiloxane Trimer Containing One Vinyl Moiety<sup>113</sup>

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112. A. I. Nogaideli, L. I. Nakaidze, and V. S. Tskhovrebashvili, "Synthesis of Organosiloxanes with Aralkyl and Aralkenyl Groups on Silicon", *Zhurnal Obshchei Khimii*, Vol. 48, No. 6, pp. 1344-1347, 1978.
113. S. Rubinsztajn, M. Cypryk and J. Chojnowski, "Condensation of Model Linear Siloxane Oligomers Possessing Silanol and Silyl Chloride End Groups. The Mechanism of Silanol Silylation by a Chlorosilane in the Presence of Neutral Nucleophiles", *Journal of Organometallic Chemistry*, Vol. 367, pp. 27-37, 1989.
114. G. I. Harris, "A Study of Hydrogen Bonding in Poly(diorganosiloxane)- $\alpha\omega$ -diols", *Journal of the American Chemical Society*, pp. 5978-5982, 1963.
115. K. Johansson and C.-L. Lee, "Cyclic Siloxanes and Silazanes", pp. 459-686, in *Cyclic Monomers*, K. C. Frisch, ed., John Wiley and Sons, Inc., New York, 1972.

## 2.6. Thermally Conductive Adhesives

As the demand for smaller electrical components grows, adhesives that can effectively dissipate heat are needed.<sup>116</sup> Polymers are generally insulating materials and are inherently poor conductors with very low thermal conductivity (k) values in the range of 0.2 – 0.3 W/mK. Thermally conductive adhesive microcomposites are prepared by dispersing high concentrations of thermally conductive microfillers in adhesive binding resins. The thermal conductivity depends on the type and amount of filler which can be loaded into the organic resin without significant and detrimental effects on the final microcomposite.<sup>1</sup>

Organic polymers are typically filled with thermally conductive particulate metals such as Ag, Cu, Au or Al (respective k values ~ 420, 400, 290 and 200 W/mK). Thermally conductive ceramic particles, such as AlN,<sup>117</sup> BN, Al<sub>2</sub>O<sub>3</sub> or Kovar (respective k values ~150, 36, 31 and 16 W/mK) are also commonly used to improve the thermal conductivity of the resultant microcomposites. Sn-coated Cu powders have also recently been investigated.<sup>118,119</sup> Presently, the best conductive adhesive materials have thermal conductivity values of ~ 3 – 4 W/mK. This value is still less than 1% of the k value for pure silver or copper. Certain types of diamond, with k values in the bulk state as high as 2000 W/mK are also currently under investigation. Although the particulate form of diamond powder exhibits a much lower k value of ~ 300 W/mK (less than particulate Ag).<sup>2</sup> Silver is known as an isotropic material (conductive in all directions), and is

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116. R. D. Hermansen and S. A. Tunick, "Formulating Custom-Tailored Thermal Transfer Adhesives", *Organic Chip Pkg.*, pp. x-x, March 2000.
  117. X. Chen and K. E. Gonsalves, "Synthesis and Properties of an Aluminum Nitride/Polyimide Nanocomposite Prepared by a Nonaqueous Suspension Process", *J. Mater. Res.*, Vol. 12, No. 5, pp. 1274 – 1286, 1997.
  118. S. K. Kang and P. Purushothaman, "Development of Low Cost, Low Temperature Conductive Adhesives", *Electronic Components and Technology Conference*, pp.1031 – 1035, 1998.
  119. S. K. Kang and P. Purushothaman, "Development of Conducting Adhesive Materials for Microelectronic Applications", *Electronic Materials*, Vol. 28, No. 11, pp.1314 – 1318, 1999.

commonly used to yield electrically and thermally conductive microcomposite adhesive materials.<sup>119,120,121,122</sup> Higher costs result from resins filled with high concentrations of diamond or precious metals.

This research involves the synthesis of novel polyorganosiloxanes with strongly hydrogen bonding or complexing pendent groups as resins for thermally conductive microcomposites. Nitrile and phosphonyl groups are expected to interact strongly with particulate metals and oxides, and may yield systems with increased concentrations of filler. Highly filled polyorganosiloxane microcomposites should yield adhesives with higher  $k$  values (than previously reported for typical nonpolar siloxanes).

Volume fractions are necessary for thermal conductivity data interpretation and are calculated using:  $\phi_F = (w_F/\rho_F) / [(w_F/\rho_F) + (w_R/\rho_R)]$ .<sup>2</sup> The  $\phi_F$  is the volume fraction of filler (F);  $w_F$  and  $w_R$  are the weight fractions of filler (F) and resin (R) in the cured adhesive (always accurately known); and  $\rho_F$  and  $\rho_R$  are the densities ( $\text{g}/\text{cm}^3$ ) of the pure filler material (F) and unfilled base resin (R).<sup>2</sup> Resins filled with thermally conductive microparticles were studied as potential candidates for thermally conductive adhesive materials. Many variables determine the validity of the equations used to predict the thermal conductivity of composites. The shape of filler particulates (spherical or irregular) is one major variable that makes theoretical estimates of thermal conductivity difficult.<sup>2,123</sup>

The current resins of choice for thermally conductive adhesives are epoxies, acrylates, polyimides and polysiloxanes. The binding resin is chosen on the basis of the

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120. J. M. Pujol, C. Prud'Homme, M. E. Quenneson and R. Cassat, "Electroconductive Adhesives: Comparison of Three Different Polymer Matrices. Epoxy, Polyimide and Silicone", *J. Adhesion*, Vol. 27, pp. 213-229, 1989.
  121. J. C. Jagt, "Joints for Surface Mount Applications: A Summary of the State of the Art", *IEEE, Part A*, Vol. 21, No. 2, pp. 215-225, 1998.
  122. E. Sancaktar and N. Dilsiz, "Pressure-Dependent Conduction Behavior of Various Particles for Conductive Adhesive Applications", *J. Adhes. Sci. Technol.*, Vo. 13, No. 6, pp. 679-693, 1999.
  123. Y. Agari, A. Ueda and S. Nagai, "Thermal Conductivity of a Polymer Composite", *Journal of Applied Polymer Science*, Vol. 49, pp. 1625 – 1634, 1993.

targeted final product, with a bias on either thermal mechanical stability or strength at high temperatures. Silicones are advantageous adhesive materials that can undergo repeated thermal cycling. Phosphine oxides and siloxanes that exhibit high char yields upon burning are also well known for imparting flame retardant properties.<sup>26</sup> The siloxane backbone remains flexible, even at temperatures well below subambient, and does not go through its glass transition during the typical thermal cycles of small electrical components. Therefore, polyorganosiloxanes offer a higher resistance to repeated thermal cycling compared to epoxy and acrylate resins with much higher  $T_g$ s. The latter two materials are advantageous when a structural adhesive is required, due to higher characteristic tensile strengths. Another advantage of siloxanes is the ability to compensate for thermal expansion differences between the component (e.g. semiconductor chip) and the metal line (heat sink). This again is attributed to the flexible siloxane backbone. Polysiloxanes can yield void-free elastomeric networks with very thin bond lines.<sup>1</sup> These qualities are important in maximizing heat dissipation, where thin void-free films of ~ 2-15 mils are required.<sup>1,2</sup>

Polysiloxanes typically adhere poorly to most substrates. The adhesion strength to metal and oxide substrates should greatly improve by exploiting the pendent electron donating moieties of nitrile-, phosphoryl- and phosphine- containing polyorganosiloxanes. Previous work has shown that the adhesive strength to metal substrates was doubled using a nitrile containing polysiloxane network relative to nonpolar PDMS networks.<sup>33</sup>

Recent work on thermally conductive adhesive siloxane containing resins was conducted by Rolland et. al.<sup>124</sup> Thermoplastic polyurethane-urea polydimethylsiloxane copolymeric elastomers were investigated. An aminopropyl- terminated 2000 g/mol polysiloxane was reacted with bis(hydroxypropyl) isobutyl phosphine, and subsequently was reacted with polyurethanes. Incorporation of this polar phosphine oxide containing

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124. J. Rolland, D. L. Dunson, S. Wang and J. E. McGrath, "Thermally Conductive Polydimethylsiloxane Adhesives Containing Polyurethanes & Polyureas with Phosphine Oxide Hard Segments", *Proc. Of the 24<sup>th</sup> Annual Meeting of the Adhesion Society*, Williamsburg, VA, Feb., 214-216 , 2001.

group is expected to improve the quality of the dispersions with AlN. The resultant microcomposites are expected to have improved thermal conductivity values as a result of the improved dispersions.<sup>124</sup>

## Chapter 3. Experimental

### 3.1. Reagents and Purification Procedures

Triethyl phosphite (Aldrich, 98%), diphenylphosphine (Aldrich) and 2,2'-azobisisobutyronitrile (AIBN) (Aldrich, 98%) were used as received and stored under a blanket of N<sub>2</sub> to prevent oxidation. Chloroform (Aldrich, 99.9+%) was used without further purification. Bis(trimethylsilyl)peroxide (BSPO) and 3-chloropropylmethyldimethoxysilane, purchased from Gelest, Inc., were stored at 0° C and used without further purification. Octamethylcyclotetrasiloxane (D<sub>4</sub>) (donated by the Dow Corning Corp.), 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (D<sub>4</sub>Vi) (Gelest, Inc.) and 1,3,5,7-tetramethyltetracyclosiloxane (D<sub>4</sub>H) (Gelest, Inc.) were distilled under vacuum (500 mTorr) from CaH<sub>2</sub>. Polydimethylsiloxane (PDMS), poly(3-cyanopropylmethyl)siloxane (PCPMS) oligomers and their corresponding networks, and the nitrile containing crosslinking reagent 1,3,5,7-tetramethyl-1,3,5-trihydro-7-(3-cyanopropylmethyl)cyclotetrasiloxane (D<sub>4</sub>CNH<sub>3</sub>) were prepared according to previously published methods.<sup>33</sup> Tetramethylammonium hydroxide pentahydrate (TMAH•5H<sub>2</sub>O) (Aldrich 99%) was used as received. A platinum divinyltetramethyldisiloxane complex catalyst in xylene, 2.1–2.4% Pt conc. (Karstedt's catalyst), was purchased from Gelest, Inc. and used without further purification. Hexamethylcyclotrisiloxane (D<sub>3</sub>) and trimethyltrivinylcyclotrisiloxane (D<sub>3</sub>Vi) (Gelest, Inc.) cyclics were distilled under vacuum from CaH<sub>2</sub>. Mercaptoacetic acid (Aldrich 97+%), trifluoromethanesulfonic acid (triflic acid) (Aldrich 99+%) and butyllithium, 2.0 M (n-BuLi) in solvent, were used as received. Trimethylchlorosilane (99+%, Gelest, Inc.) was distilled under N<sub>2</sub> prior to use. The endcapping reagents 1,3-bis(3-aminopropyl)tetramethyldisiloxane and 1,3-bis(3-carboxypropyl)tetramethyldisiloxane (Gelest, Inc.) were used as received. Anhydrous diethyl ether (99%) and dichloromethane (Merck, HPLC grade) were used as received. Tetrahydrofuran (THF) (Merck) was distilled from CaH<sub>2</sub> under Ar. Cyclohexane (Merck) was stirred over conc. H<sub>2</sub>SO<sub>4</sub> and washed with water until neutral, dried over CaH<sub>2</sub> and distilled under Ar. Pre-dried cyclohexane was subsequently distilled from Na under N<sub>2</sub>. Isophorone diisocyanate (98%) and tetrakis(dimethyldisiloxy)silane (Aldrich)

were used as received. Hexamethyldisiloxane (Aldrich 99.9%) and 1,3-divinyltetramethyldisiloxane (Gelest, Inc.) were distilled under N<sub>2</sub> prior to use. Allyl cyanide (Aldrich, 98%) (first dried with 4Å molecular sieves) and 1,3-divinyltetramethyldisiloxane (Gelest, Inc.) were distilled under N<sub>2</sub> prior to use. Toluene (Fisher) was washed twice with concentrated sulfuric acid, and several times with water until neutral, predried with anhydrous magnesium sulfate, and dried overnight with calcium hydride powder and distilled under N<sub>2</sub>.

A variety of conductive fillers were kindly donated by IBM and used as received. Each of the following fillers was stored in a desiccator prior to use: silica coated AlN, Al spheres, Ag flakes and BN powder.

## **3.2. Synthesis of Phosphonyl Containing Siloxane Model Monomers**

### **3.2.1. Synthesis of 1,3,5,7-tetra(2-diphenylphosphineethyl)-1,3,5,7-tetramethylcyclotetrasiloxane (D<sub>4</sub>P) Cyclic Model Monomer**

A flame-dried 3-neck flask with a magnetic stir bar was fitted with a nitrogen needle inlet through a rubber septum, a condenser connected to a bubbler and an addition funnel sealed with a rubber septum. D<sub>4</sub>Vi (5.5 g, 0.016 mol) and 0.0015 g crystalline AIBN were charged to the flask and heated to 40 °C. Diphenylphosphine (10.1 ml, 0.058 mol) was added dropwise through the septum on the addition funnel and the flask contents were stirred for 1 hr. A 3.6:1 molar ratio of diphenylphosphine:D<sub>4</sub>Vi (rather than a 4:1 ratio) was used to insure complete reaction of the diphenylphosphine (which would theoretically react with 90% of the vinyl groups). This was done as a safety precaution since diphenylphosphine is a pyrophoric reagent. The mixture was heated to 115 °C and a second portion of AIBN (0.002 g dissolved in 0.2 ml CHCl<sub>3</sub>) was added through the addition funnel. The reaction was allowed to stir for no longer than 8 days and monitored using <sup>31</sup>P NMR to evaluate the extent of the reaction of the diphenylphosphine. As diphenylphosphine reacts, the peak for the phosphorus atom on

diphenylphosphine (~ -40 ppm) disappeared and a new peak was observed at (~ 9.3 ppm) which is indicative of the newly formed  $-\text{CH}_2\text{-P}(\text{Ph}_2)$  moiety. A clear viscous liquid, 1,3,5,7-tetra(2-diphenylphosphineethyl)-1,3,5,7-tetramethylcyclotetrasiloxane ( $\text{D}_4\text{P}$ ) was obtained after 4 days. A small percentage (typically ~ 10%) of diphenylphosphine remained unreacted after 8 days.

### **3.2.2. Synthesis of 1,3,5,7-tetra(2-diphenylphosphine oxideethyl)-1,3,5,7-tetramethylcyclotetrasiloxane ( $\text{D}_4\text{PO}$ ) Cyclic Model Monomer**

$\text{D}_4\text{P}$  (1g, 0.00090 mol), described above, and 10 ml dichloromethane were charged to a flame-dried 2-neck flask with a magnetic stir bar and fitted with an addition funnel.  $\text{N}_2$  was passed through a rubber septum on the funnel through a needle inlet. The second neck of the flask was fitted with a rubber septum connected to a bubbler to vent the  $\text{N}_2$ . Oxidizing reagent, BSPO, (0.79 ml, 0.0037 mol) was added to the addition funnel via syringe and was very slowly dripped from the addition funnel (1 drop/ 10 seconds) to control the exotherm. A 10% molar excess over a 4:1 ratio of BSPO: $\text{D}_4\text{P}$  was used to ensure complete oxidation of the  $\text{D}_4\text{P}$ . The boiling point of BSPO is 35° C/35 mm and vaporized before reacting if added too quickly. The mixture was stirred at room temperature until the resonant peak of the phosphorus atom in  $\text{D}_4\text{P}$  (~ -9.3 ppm) disappeared in the  $^{31}\text{P}$  NMR spectrum. The newly formed phosphorus peak for  $\text{D}_4\text{PO}$  occurs at ~ 33 ppm. Residual diphenylphosphine, observed at ~ -40 ppm, was also oxidized to yield diphenylphosphine oxide at ~ 22 ppm. This reaction was typically complete in ~ 1 h. Dichloromethane and the hexamethyldisiloxane byproduct were distilled off at 100 °C / 500 mTorr. BSPO quantitatively oxidized  $\text{D}_4\text{P}$  and yielded 1,3,5,7-tetra(2-diphenylphosphine oxideethyl)-1,3,5,7-tetramethylcyclotetrasiloxane ( $\text{D}_4\text{PO}$ ), a clear and more viscous liquid relative to  $\text{D}_4\text{P}$ .

### **3.2.3. Synthesis of 3-diethylphosphonatopropylmethyl-dimethoxysilane Model Monomer**

A flame-dried 2-necked flask with a magnetic stir bar was fitted with a nitrogen needle inlet through a rubber septum and a condenser connected to a bubbler and purged

with N<sub>2</sub>. Triethyl phosphite (50.2 ml, 0.293 mol) and 3-chloropropylmethyldimethoxysilane (25.2 ml, 0.140 mol) were charged to the flask and heated to 160 °C in a silicone oil bath. A 2.1:1 molar ratio of triethyl phosphite:3-chloropropylmethyldimethoxysilane was used to compensate for a side reaction which readily occurred between triethyl phosphite and the ethylchloride byproduct from the desired reaction. The byproduct of the side reaction, diethyl ethylphosphonate, (the oxidized form of triethylphosphite) does not undergo Michaelis-Arbuzov reactions. Nitrogen was continuously bubbled through the solution to facilitate the removal of the ethyl chloride byproduct formed in situ and thereby minimize the formation of diethyl ethylphosphonate. The mixture was stirred until the methylene protons on the –CH<sub>2</sub>Cl (~ 3.48 ppm) group disappeared, and the newly formed –CH<sub>2</sub>PO(OCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> methylene protons were observed at ~ 1.7 ppm via <sup>1</sup>H NMR. An 85 % yield, ~ 86 g, of pure 3-diethylphosphonatopropylmethyldimethoxysilane was typically obtained after ~ 4 days. The clear liquid was recovered by fractional vacuum distillation at ~122 °C / ~1 Torr.

### ***3.3. Base Catalyzed Equilibrations to Yield Polysiloxane Homopolymers and Prepolymers to Functionalization and Crosslinking Reactions with Methylvinylsiloxy- Moieties***

#### **3.3.1. Synthesis of Tetramethylammonium Disiloxanolate Basic Catalyst via a Novel Modified Dean Stark Apparatus**

For a typical reaction, 13.7g (0.046 mole) octamethylcyclotetrasiloxane (D<sub>4</sub>) and 0.685g (0.0038 mole) tetramethylammonium hydroxide pentahydrate (TMAH·5H<sub>2</sub>O) were added to a flask equipped with an overhead mechanical stirrer and a modified attached Dean Stark trap with condenser linked to a drying tube (Figures 3.1 and 3.2).<sup>(11,20)</sup> This represents a 5 weight % (TMAH·5H<sub>2</sub>O) solution. The mixture was reacted by heating the reactor in an 80 °C silicone oil bath for 24 hours under a stream of nitrogen bubbling through the reaction mixture to aid the removal of condensed water and water of hydration. The stream of N<sub>2</sub> was rapid during the first few hours, and lowered to 1 bubble/5 seconds overnight to prevent gelation. TMAH·5H<sub>2</sub>O was initially

insoluble in  $D_4$ , but above  $70\text{ }^\circ\text{C}$  it gradually dissolved as it reacted with  $D_4$ . The solution became homogeneous within  $\sim 2\text{ h}$ . After  $24\text{ h}$ , a few milliliters of water collected in the modified Dean Stark trap. After this  $24\text{ h}$  reaction period, the tetramethylammonium disiloxanolate catalyst was syringed immediately from the reactor into the desired equilibration solution.



Figure 3.1. Dean Stark Apparatus for Preparing Tetramethylammonium Disiloxanolate Catalyst

Water removal during preparation of the tetramethylammonium disiloxanolate catalyst is not trivial. The temperature of the reaction must be maintained at  $80\text{ }^\circ\text{C}$  since the catalyst begins to slowly degrade at  $90\text{ }^\circ\text{C}$ . The  $N_2$  stream and stirring speed were monitored so that the water was effectively removed from the tetramethylammonium pentahydrate without causing gelation. The original Dean Stark apparatus (Figure 3.1) required the use of a heat gun every few hours to assist the removal of the  $H_2O$  byproduct. Water vapor often became trapped above the flask bulb, condensing and

dripping back into the catalyst solution. This was due in part to the upward slope of the attached condenser tube. The author designed a modified reactor which was kindly constructed by Mr. Van Damme of the Virginia Tech glass shop (Figure 3.2). The condenser tube was designed with a downward slope and with the addition of a water cooling jacket to assist the removal of the H<sub>2</sub>O from the reaction. A vertical condenser was attached to the original apparatus, which was too far from the reactor vessel (and therefore required a rapid stream of N<sub>2</sub> to remove the water) (Figure 3.1). This improvisation eliminated the need for a heat gun and continuous attention to the reaction over a 24 h period. A lower N<sub>2</sub> flow rate could also be used to remove water. This prevented the common problem of gelation associated with preparing this catalyst. A round bottom 2-neck flask with a Drierite filled drying tube was attached to the modified reactor to collect the water.



Figure 3.2. Modified Dean Stark Catalyst Apparatus

### **3.3.2. Vinyl Terminated Poly(methylvinyl)siloxanes**

For a typical synthesis of 50 g of a 1500 g/mol vinyl terminated poly(methylvinyl)siloxane, 1,3-divinyltetramethyldisiloxane (9.32 g, 0.05 mol) and D<sub>4</sub>Vi (50 g, 0.145 mol) were added via syringe to a flame-dried flask having a stirbar and capped with a septum. The clear solution was heated in an oil bath to 80 °C while stirring. At 80 °C, 0.3 g of the tetramethylammonium disiloxanolate catalyst (0.6 wt. % of the solution) was syringed into the solution through the septum. The solution was initially cloudy and became clear after ~ 1h. An increase in viscosity was observed during the first few hours due to the fast propagation and initial large increase in molecular weight. Equilibration was allowed to continue for 72 h. The oil bath temperature was raised to 135 °C and a strong nitrogen purge was bubbled through the solution with a 12 gauge needle for 4 hours to decompose and remove the transient catalyst. Litmus paper was used to confirm the removal of base. The equilibrated cyclics were distilled off under vacuum at 130 °C/500 mTorr to yield ~40 g of a transparent oily vinyl terminated poly(methylvinyl)siloxane.

### **3.3.3. Aminopropyl Terminated Poly(methylvinyl)siloxanes**

For a typical synthesis of 50 g of a 1500 g/mol aminopropyl terminated poly(methylvinyl)siloxane, 1,3-bis(3-aminopropyl)tetramethyldisiloxane (12.67 g, 0.051 mol) and D<sub>4</sub>Vi (60 g, 0.174 mol) were charged through a septum to a flame-dried flask having a stirbar. The clear solution was heated in an oil bath to 80 °C while stirring; then 0.18 g of tetramethylammonium disiloxanolate catalyst was syringed into the solution and allowed to equilibrate for 72 h. The oil bath temperature was raised to 135 °C and a strong N<sub>2</sub> purge was bubbled through the solution for 4 hours to decompose and remove the transient catalyst. Cyclics remaining at equilibrium were distilled off at 130 °C/500 mTorr to yield ~40 g of a transparent oily aminopropyl terminated poly(methylvinyl)siloxane.

### 3.3.4. Random Vinyl Terminated Poly(dimethyl-co-methylvinyl)siloxanes

A typical synthesis of a vinyl terminated poly(dimethyl-co-methylvinyl)siloxane with 20 molar % random methylvinylsiloxyl- repeat units and target  $M_n$  of 2500 g/mol follows.  $D_4$  (120 g, 0.405 mol),  $D_4Vi$  (35.0 g, 0.101 mol) and 1,3-divinyltetramethyldisiloxane (13.0 g, 0.069 mol) were charged to a flame-dried round bottom flask having a stir bar and sealed with a septum. The molar ratio of methylvinyl-repeat units to methylvinyl units was tailored by controlling the molar ratio of  $D_4:D_4Vi$ . An example calculation for a random polysiloxane with 20 molar % methylvinylsiloxyl-repeat units follows:

$$\left(\frac{120 \text{ g } D_4}{\text{mol}}\right)\left(\frac{\text{mol}}{296.61 \text{ g}}\right)=0.40457 \text{ mol } D_4 \quad (1)$$

$$\left(\frac{0.40457 \text{ mol } D_4}{x}\right)=\frac{80 \text{ molar } \% D_4}{100 \text{ total molar } \% \text{ monomer}} \quad (2)$$

$$(x=0.50575 \text{ total mols monomer})(0.20 \text{ mol } D_4Vi/1 \text{ mol monomer})=0.10115 \text{ mol } D_4Vi \quad (3)$$

$$\left(\frac{0.10115 \text{ mol } D_4Vi}{\text{mol}}\right)\left(\frac{344.66 \text{ g}}{\text{mol}}\right)=34.9 \text{ g } D_4Vi \quad (4)$$

The mixture was heated to 80 °C, whereupon 0.93 g (0.6 wt. %) TMAH disiloxanolate catalyst was added via syringe through the septum. The reaction mixture was stirred and equilibrated for 72 h. A strong  $N_2$  purge (~ 3 bubbles/second) was bubbled through the solution and the temperature was raised to 130 °C for 4 h to decompose and remove the transient catalyst.<sup>91</sup> Base removal was confirmed using litmus paper. Small cyclics remaining at equilibrium were distilled off under vacuum at 130 °C/500 mTorr. A colorless oily poly(dimethyl-co-methylvinyl)siloxane, ~ 125 g, with a  $M_n$  of 3100 g/mol was isolated.

### **3.3.5. Random Aminopropyl Terminated Poly(dimethyl-co-methylvinyl)siloxanes**

A typical synthesis of a 5000 g/mol aminopropyl terminated poly(dimethyl-co-methylvinyl)siloxane with 50 molar % random methylvinylsiloxyl- repeat units follows. D<sub>4</sub> (17.2 g, 0.058 mol), D<sub>4</sub>Vi (20 g, 0.058 mol) and 1,3-bis(3-aminopropyl)tetramethyldisiloxane (1.57 g, 0.0063 mol) were charged to a flame-dried round bottom flask having a stir bar. A 1:1 molar ratio of D<sub>4</sub>:D<sub>4</sub>Vi was used to yield a copolymer with 50 molar % methylvinylsiloxyl- groups. The mixture was heated to 80 °C, whereupon 0.22 g tetramethylammonium disiloxanolate catalyst (0.6 wt. %) was added via syringe. The reaction mixture was stirred and allowed to equilibrate for 72 h. A strong N<sub>2</sub> purge was bubbled through the solution and the temperature was raised to 130 °C for 4 h to decompose and remove the transient catalyst.<sup>91</sup> Small cyclics remaining at equilibrium were distilled off under vacuum at 130 °C/500 mTorr and ~18 g of a clear amine terminated poly(dimethyl-co-methylvinyl)siloxane was isolated.

## ***3.4. Acid Catalyzed Equilibrations to Yield Polysiloxane Homopolymers and Prepolymers to Functionalization and Crosslinking Reactions with Methylhydrosiloxyl- Moieties***

### **3.4.1. Random Poly(dimethyl-co-methylhydrido)siloxanes**

A typical synthesis of a poly(dimethyl-co-methylhydrido)siloxane with 20% random methylhydrosiloxyl- repeat units and a target M<sub>n</sub> of 4162 g/mol follows. D<sub>4</sub> (120 g, 0.405 mol), D<sub>4</sub>H (24.0 g, 0.10 mol) and hexamethyldisiloxane (5.3 g, 0.033 mol) were charged to a flame-dried round bottom flask with a stir bar through a septum. The mixture was heated to 35 °C while stirring. The molar ratio of D<sub>4</sub>:D<sub>4</sub>H was controlled as described above in equations 1-4 to control the amount of methylhydrosiloxyl- repeat units incorporated into the polysiloxane backbone. Triflic acid (0.29 g) was carefully syringed into the solution through the septum. The reaction was heated to 65 °C while stirring, and allowed to equilibrate for 72 h. The oligomer was cooled to room temperature and diluted in 100 mL of diethyl ether followed by neutralization with 6

extractions with 300 ml H<sub>2</sub>O each. Solvent was initially removed via rotavap and the small cyclics were distilled under vacuum at 140 °C/500 mTorr for 5 h. A clear poly(dimethyl-co-methylhydrido)siloxane, ~ 106 g, was isolated with an M<sub>n</sub> of 4144 g/mol.

### **3.5. Synthesis of Random Polysiloxanes Functionalized with Controlled Concentrations of Pendent Hydrogen Bonding Substituents and Crosslinkable Moieties**

#### **3.5.1. Poly(dimethyl-co-methylvinyl-co-methyl,2-diphenylphosphineethyl)siloxanes**

The model cyclic monomer, D<sub>4</sub>P, was prepared to investigate the free radical reaction of diphenylphosphine with vinylsilyl species. The following procedure was optimized as the result of a design experiment performed to determine the optimal reaction temperature and mol % of AIBN catalyst.

Polysiloxane prepolymers with systematically varied concentrations of methylvinylsiloxy- units were reacted with controlled amounts of diphenylphosphine; an example follows. N<sub>2</sub> was bubbled through a vinyl terminated 2600 g/mol poly(dimethyl-co-methylvinyl)siloxane (100 g, 0.311 mol vinyl groups) for 4 h at 25 °C to deoxygenate the oligomer in a septum sealed flame-dried round bottom flask with a stir bar. The prepolymer contained 8.11 methylvinylsiloxy- repeat units (20 molar % random) and 2 vinyl endgroups for a total of 24 mol % vinyl moieties. AIBN (0.13 g) was quickly added to the solution and the flask was rapidly refitted with a rubber septum. N<sub>2</sub> was flushed through the flask for 10 additional minutes and the needle was removed leaving a blanket of N<sub>2</sub> over the solution. The success of this free radical reaction depends on an oxygen free environment. Diphenylphosphine (28.9 g, 0.1925 mol) was syringed into the solution through the septum. A deficiency of diphenylphosphine was used to leave 3 of the 8 initial vinyl groups intact for further reactions. The mixture was heated to 50 °C and was initially cloudy during the first few hours. As diphenylphosphine reacted, the solution gradually became clear. The reaction was stirred until <sup>31</sup>P NMR confirmed the

disappearance of the phosphorus peak characteristic of diphenylphosphine ( $\sim -40$  ppm) and the appearance of the diphenylphosphine substituted siloxane repeat unit  $-\text{CH}_2-\text{P}(\text{Ph})_2$  ( $\sim -9.33$  ppm). Typically, a small percentage ( $\sim 1\%$ ) of diphenylphosphine remained unreacted after 24 h. The polymer was diluted in  $\text{CHCl}_3$  and precipitated in 500 mL of methanol twice to remove the diphenylphosphine. Solvents were removed via rotavap and subsequently distilled at  $100\text{ }^\circ\text{C}/500\text{ mTorr}$ . A clear viscous poly(dimethyl-co-methylvinyl-co-methyl,2-diphenylphosphineethyl)siloxane was isolated with 15 molar % random diphenylphosphine containing and 9 molar % random methylhydridosiloxy-repeat units with an  $M_n$  of 3576 g/mol.

### **3.5.2. Poly(dimethyl-co-methylvinyl-co-methyl,2-diphenylphosphine oxideethyl)siloxanes**

Phosphine containing polysiloxanes were oxidized to yield phosphine oxide containing polysiloxanes. Oxidizing reagent BSPO (34.3 g, 0.1925 mol) was added dropwise (1 drop/10 sec to control the exotherm) to 90 g of a phosphine containing polysiloxane,  $M_n = 3576$  g/mol, with 15 molar % diphenylphosphine containing repeat units diluted in 130 mL  $\text{CH}_2\text{Cl}_2$ . The mixture was stirred  $\sim 1$  h at room temperature until  $^{31}\text{P}$  NMR confirmed the complete oxidation of the phosphine groups. This was indicated by the complete disappearance of the phosphorus peak at  $-9.3$  ppm and the appearance of the oxidized phosphorus at  $\sim 22$  ppm. Hexamethyldisiloxane and  $\text{CH}_2\text{Cl}_2$  were removed by distillation under vacuum at  $100\text{ }^\circ\text{C}/500\text{ mTorr}$ . The oxidation occurred quantitatively to yield a clear, viscous poly(dimethyl-co-methylvinyl-co-methyl,2-diphenylphosphine oxideethyl)siloxane with a  $M_n$  of 3659 g/mol.

### **3.5.3. Poly(dimethyl-co-methylvinyl-co-[2-(carboxymethylthio)ethyl]methyl)siloxanes**

Controlled concentrations of mercaptoacetic acid were added to poly(methylvinyl)siloxane prepolymers with systematically varied amounts of vinyl groups as per the following example.  $\text{N}_2$  was bubbled through a 2550 g/mol random poly(dimethyl-co-methylvinyl)siloxane containing 24 molar % random methylvinyl-repeat units (10 g, 0.031 mol vinyl) for 4 h at  $25\text{ }^\circ\text{C}$  to deoxygenate the oligomer. AIBN

(0.038 g) was added to the solution. The flask was quickly refitted with a rubber septum, purged with N<sub>2</sub> for 10 minutes and sealed under a blanket of N<sub>2</sub>. Mercaptoacetic acid (1.43 g, 0.016 mol) was charged to the solution through the septum, (a deficiency) allowing 50% vinyl groups available for further reactions. The mixture was stirred and heated to 50 °C. The solution was initially cloudy during the first few hours and cleared as the mercaptoacetic acid reacted. The reaction was stirred until <sup>1</sup>H NMR confirmed the disappearance of the thiol proton of mercaptoacetic acid, H-S-, (~ 2.2 ppm) and the appearance of the methylene protons on sulfur from the newly formed Si-CH<sub>2</sub>-CH<sub>2</sub>-S-linkage (~ 2.75 ppm). This typically occurred in 24 - 48 h. The oligomer was heated to 100 °C/1 torr overnight to remove any unreacted mercaptoacetic acid. A clear, viscous poly(dimethyl-co-methylvinyl-co-[2-(carboxy-methylthio)ethyl]methyl)siloxane was isolated with a M<sub>n</sub> of 2848 g/mol containing 11 molar % thioacetic acid containing repeat units and 11 molar % methylvinylsiloxyl- repeat units.

#### **3.5.4. Poly(dimethyl-co-methylhydrido-co-3-cyanopropylmethyl)siloxanes**

Poly(dimethyl-co-methylhydrido)siloxane prepolymers with systematically varied amounts of methylhydridosiloxy- units were reacted with controlled concentrations of allyl cyanide to yield 3-cyanopropylmethylsiloxy- units. A 4100 g/mol poly(dimethyl-co-methylhydrido)siloxane with 17 molar % random methylhydridosiloxy- repeat units (50 g, 0.115 mol hydride), allyl cyanide (4.6 mL, 0.058 mol), Karstedt's catalyst (0.15 mL, 0.2 wt. % of the solution (allyl cyanide and oligomer) and 10 ml purified toluene were added to a flame-dried flask with stir bar and condenser attached to a Drierite filled drying tube. It should be noted that the amount of catalyst added for this reaction was 2.5 g Karstedt's catalyst/mol allyl cyanide and should be optimized for a lower amount to minimize residual catalyst (and possible crosslinking) during the following purification process. The mixture was heated to 130 °C and allowed to reflux until <sup>1</sup>H NMR confirmed the disappearance of the vinyl protons from allyl cyanide, ~ 5.5 ppm. A typical reaction was completed in 12 h - 24 h. Excess toluene was distilled off under vacuum at 140 °C/500 mTorr 2 h - 4 h until no more was observed while collecting. A clear poly(dimethyl-co-methylhydrido-co-3-cyanopropylmethyl)siloxane was isolated

with a  $M_n$  of 4465 containing 10 molar % 3-cyanopropylmethylsiloxy- units and 7 molar % methylhydridosiloxy- units. The allyl cyanide added quantitatively and the newly formed nitrile containing siloxane repeat units were verified via  $^{29}\text{Si}$  NMR at  $\sim -24$  ppm.

### **3.6. Preparation of Lightly Crosslinked Polyorganosiloxane Networks Functionalized with Systematically Varied Molar Fractions of Different Polar Moieties**

A series of vinyl and hydrido functional polysiloxanes with controlled concentrations of polar groups were crosslinked to form lightly crosslinked elastomeric networks with varied types and degrees of polarity. This series of networks was prepared to elucidate an optimal balance of polarity, viscosity and  $T_g$  as binding resins for thermally conductive fillers. Each of the networks was formed using hydrosilation curing chemistry. Stoichiometric amounts of vinyl:silane (oligomers and crosslinking reagents) were reacted in the presence of Karstedt's catalyst, a  $\text{Pt}^0$  catalyst complexed with 1,3-divinyltetramethyldisiloxane in xylene. The amount of Karstedt's catalyst and temperature controlled the curing rate. More polar functional polyorganosiloxanes required relatively higher amounts of catalyst. This was due to partial complexation between Pt and polar moieties which somewhat inhibit the curing reaction. A set of equations that were used to determine the amounts of curing reagents and catalyst follows.

The following example is presented for the hydrosilation of 2 g of a 4465 g/mol nitrile containing polysiloxane containing 3.73 hydrido groups on average per chain. The number of nitrile groups is relevant to the polarity and, therefore, to the choice of a miscible crosslinking reagent; and to consider the amount of Pt catalyst necessary to overcome any complexation.

1<sup>st</sup>: Multiply grams of polymer by the average number of reactive groups per chain and divide by  $M_n$

$$\left( \frac{2.0 \text{ g oligomer}}{4465 \text{ g/mol}} \right) \left( \frac{3.73 \text{ hydrido groups}}{\text{oligomer}} \right) = 0.00167 \text{ mol hydrido groups} \quad (1)$$

2<sup>nd</sup>: Multiply mol of reactive groups by grams of Pt catalyst solution/mol reactive group necessary to yield a network within an hour at 80 °C. This amount determines the rate.

For polysiloxanes containing 10 – 55 molar % nitrile, 5.0 g Pt catalyst solution/mol functional groups was used; whereas 6.0 g Pt catalyst solution/mol functional groups was necessary to hydrosilate polysiloxanes containing 10 - 15 molar % phosphine oxide (more polar) moieties.

$$\left( \frac{0.00167 \text{ mol hydrido}}{\text{mol hydrido groups}} \right) \left( \frac{5 \text{ g Pt catalyst solution}}{\text{mol hydrido groups}} \right) = 0.0084 \text{ g Pt catalyst solution} \quad (2)$$

3<sup>rd</sup>: Calculate the g crosslinking reagent required to crosslink 1 g of polymer.

Determine the equivalent  $M_n$  of the polymer:

$$\frac{4465 \text{ g/mol}}{3.73 \text{ hydrido groups}} = \frac{1203.5 \text{ g/mol}}{\text{hydrido groups}} \quad (3a)$$

Determine the equivalent molecular weight of the crosslinking reagent:

$$\frac{186.4 \text{ g/mol}}{2 \text{ vinyl groups}} = \frac{93.2 \text{ g/mol}}{\text{vinyl groups}} \quad (3b)$$

Determine the g crosslinking reagent required to crosslink 1 g of polymer:

$$\frac{93.2 \text{ g / mol vinyl groups}}{1203.5 \text{ g / mol hydrido groups}} = \frac{X \text{ g crosslinking reagent}}{1 \text{ g polymer}} \quad (3c)$$

$X = 0.07744$  g of 1,3 – divinyltetramethyldisiloxane required per g of polymer

Therefore, 0.1549 g of 1,3-divinyltetramethyldisiloxane was used.

This general set of equations was used to crosslink all of the functional polysiloxanes.

### 3.6.1. Hydrosilation of Phosphine Oxide Substituted Polyorganosiloxane Oligomers to Yield Networks

A series of vinyl functional polysiloxane oligomers was synthesized with controlled amounts of polar phosphine oxide repeat units. Phosphine oxide containing polysiloxanes with pendent vinyl moieties were crosslinked with the silane functional crosslinking reagent tetrakis(dimethylsiloxy)silane. The vinyl components for the two-component addition cure were first mixed thoroughly. A 3659 g/mol polysiloxane containing 15 molar % phosphine oxide containing repeat units and 9 molar % methylvinylsiloxy- repeat units (1 g,  $7.9 \times 10^{-4}$  mol vinyl) and Karstedt's catalyst (0.005 g,

6 g catalyst/mol vinyl) were mixed thoroughly. Tetrakis(dimethylsiloxy)silane, (0.065 g,  $7.9 \times 10^{-4}$  mol silane) was subsequently added and mixed thoroughly. The resin was cured in an 80 °C oven typically for less than 1 h until FTIR confirmed the disappearance of the characteristic absorbance for silane at  $2170 \text{ cm}^{-1}$ . The phosphine oxide containing polysiloxane network containing 6 wt. % crosslinking reagent was transparent, flexible and slightly tacky.

### **3.6.2. Hydrosilation of Nitrile Substituted Polyorganosiloxane Oligomers to Yield Networks**

Vinyl terminated poly(3-cyanopropylmethyl)siloxane homopolysiloxanes were not miscible with tetrakis(dimethylsiloxy)silane and required novel polar hydride crosslinking reagents,  $\text{D}_4\text{CNH}_3$  and  $\text{D}_4(\text{CN})_2\text{H}_2$ .<sup>33</sup> The hydride functional polysiloxanes substituted with 9%, 27% and 54% 3-cyanopropylmethyl- groups were crosslinked using the nonpolar vinyl functional crosslinking reagent, 1,3-divinyltetramethyldisiloxane.

The vinyl components must be mixed together prior to the addition of the hydride functional polysiloxane for the two-component addition cure. When Karstedt's catalyst was initially added to the hydride functional polysiloxane, an undesirable and instantaneous crosslinking reaction occurred between the hydride oligomer and the 1,3-divinyltetramethyldisiloxane that is complexed with the Pt in Karstedt's catalyst. This resulted in black speckles throughout the resin, indicative of decomposed Pt due to the fast and highly exothermic curing reaction. This also prevented a uniform dispersion of the catalyst throughout the resin and an uneven cure after addition of the hydride containing polysiloxane.

A typical curing reaction for a poly(dimethyl-co-methylhydride-co-3-cyanopropylmethyl)siloxane with a  $M_n$  of 4465 g/mol, containing 6.7 molar % hydride and 9.4 molar % 3-cyanopropyl- groups, follows. Karstedt's catalyst (0.00835 g, 5 g catalyst/mol hydride) was diluted in the vinyl crosslinking reagent (rather than an oligomer to be crosslinked) 1,3-divinyltetramethyldisiloxane (0.1549 g, 0.00167 mol hydride) and mixed thoroughly. The hydride containing polysiloxane (2 g, 0.00167 mol hydride) was added to the catalyst/crosslinking reagent solution and mixed thoroughly. The resin was cured in an 80 °C oven typically in less than 1 h FTIR confirmed the

disappearance of the characteristic absorbance for silane at  $2170\text{ cm}^{-1}$ . The resultant nitrile containing polysiloxane network containing 7.2 wt. % crosslinking reagent was transparent, tack-free and semi-rigid.

### **3.6.3. Formation of a Phosphine Substituted Polyorganosiloxane Thermoplastic Polyurea**

Network formation using phosphine containing polysiloxanes was investigated. It is well known that phosphines complex with Pt, thereby prohibiting Pt catalyzed hydrosilation curing reactions.<sup>32</sup> In an attempt to circumvent this problem, an aminopropyl terminated poly(dimethyl-co-methylvinyl-co-methyl,2-diphenylphosphineethyl)siloxane was reacted with an epoxypropoxypropyl terminated tetramethyldisiloxane. The oligomer did not crosslink, but rather underwent the Wittig reaction. A thermoplastic polyurea was formed when the amine endgroups were reacted with isophorone diisocyanate. A poly(dimethyl-co-methylvinyl-co-methyl,2-diphenylphosphineethyl)siloxane with an  $M_n$  of 15054 g/mol containing 42 mol % diphenylphosphine repeat units (0.054 g,  $3.58 \times 10^{-6}$  mol) was mixed with isophorone diisocyanate (0.0008 g,  $3.58 \times 10^{-6}$  mol) on a glass slide. The sample was heated in an  $80\text{ }^\circ\text{C}$  oven until the disappearances of characteristic peak for isocyanate ( $\sim 2270\text{ cm}^{-1}$ ) was observed via FTIR. A clear brittle chain extended polyurea was formed within  $\sim 15$  minutes. Multifunctional isocyanates could alternatively be used to yield phosphine containing polysiloxane networks.

### **3.7. Preparation of Thermally Conductive Microcomposite Networks**

Nonpolar polydimethylsiloxanes do not form stable microcomposite dispersions with polar fillers and precipitation was observed visually within  $\sim 24$  h. Polysiloxanes capable of hydrogen bonding or complexing with fillers were designed and synthesized to maximize the potential amount of filler incorporated into the polysiloxane adhesives, while maintaining a stable microcomposite dispersion.

Microcomposite networks were prepared in a similar manner to the unfilled networks described above, with the addition of the conductive filler. The volume percentage of the filler was incorporated according to the following equation:

$$\frac{\frac{\text{g filler}}{\rho \text{ filler (g/mL)}}}{\left(\frac{\text{g filler}}{\rho \text{ filler (g/mL)}}\right) + \left(\frac{\text{g polymer}}{\rho \text{ polymer (g/mL)}}\right)} = \text{volume \% filler}$$

Several examples follow describing the order of addition and mixing conditions that were used to prepare the functional polysiloxane microcomposite networks.

### **3.7.1. Preparation of a 67 Volume % Silica Coated AlN Filled / 10 Mol % Nitrile Substituted Polyorganosiloxane Microcomposite Network**

Karstedt's catalyst (0.0084 g, 5 g catalyst/mol hydrido) was diluted in 1,3-divinyltetramethyldisiloxane, (0.1557 g, 0.00167 mol vinyl) and mixed thoroughly in a 50 mL beaker. Poly(dimethyl-co-methylhydrido-co-3-cyanopropylmethyl)siloxane (2 g, 0.00167 mol hydrido) with a  $M_n$  of 4465 g/mol, containing 6.7 molar % hydrido and 9.4 molar % 3-cyanopropyl- was added to the catalyst/crosslinking reagent solution and mixed thoroughly. Silica coated AlN (12 g, 67 volume %, 86 wt.%) was added to the uncured resin and mixed thoroughly with a metal spatula for ~ 5 min. The beaker was transferred to a high shear vacuum mixer and the microcomposite was mixed for 15 minutes under vacuum. Vacuum was released and the mixing blade was removed from the microcomposite. Vacuum was applied to the mixture for an additional 15 min to remove any air entrapped during the mixing process. The microcomposite was cured in an 80 °C oven in an aluminum weighing dish mold. Microcomposite samples were also cured between Al thermal conductivity test plates and between glass slides (to determine that the microcomposite was void-free). The silica coated AlN microcomposite network containing 7.2 wt. % crosslinking reagent was uniformly gray in color, tack-free and rigid. The samples were cured a few hours longer than the conditions determined for the unfilled networks to overcome any possible catalyst/filler interactions.

Thermal conductivity measurements were made at IBM on samples that were prepared by the author on site at IBM and in the Virginia Tech laboratory. Two thermal conductivity Al test plates were aligned together with a space for a probe. The thickness of the 2 plates was measured (before the application of microcomposite) on its 4 corners and in the center using a digital caliper. The thermal conductivity samples were prepared by applying the microcomposite to the bottom Al plate in the shape of an X. A spatula or an air compressor attached to a plastic syringe was used to apply the microcomposite to the Al plate to yield an air-free sample. The top Al plate was placed on top of the microcomposite with the spaces for probes aligned. The Al-microcomposite-Al bond was placed on a 4 mil spacer (provided by IBM). A heavy metal plate was pressed on the top Al plate to yield a 4 mil bondline. The microcomposite overflowed on all 4 sides (the entire surface of the Al plates were in contact with the microcomposite, rather than air). The bonded sample was carefully set on an inverted metal weighing dish (to prevent curing onto the oven floor) and transferred to an 80 °C oven. After the microcomposite was cured, the bonded thermal conductivity specimen was measured in the same 5 locations to determine the average bondline thickness.

Four different thermally conductive fillers were investigated with the polysiloxanes containing controlled concentrations of nitrile moieties. The microcomposite thickness varied between 4 – 10 mils depending on the type of filler and the amount of pressure applied to the specimen (therefore the spacer was not effective in controlling the thickness precisely). This data will be discussed in Chapter 6.

### **3.7.2. Preparation of a 65 Volume % Silica Coated AlN Filled / 27 Mol % Nitrile Substituted Polyorganosiloxane Microcomposite Network**

Karstedt's catalyst (0.0208 g, 5 g catalyst/mol hydrido) was diluted in 1,3-divinyltetramethyldisiloxane, (0.3622 g, 0.0042 mol vinyl) and mixed thoroughly in a 50 mL beaker. Poly(dimethyl-co-methylhydrido-co-3-cyanopropylmethyl)siloxane (2 g, 0.0042 mol hydrido) with a  $M_n$  of 3340 g/mol, containing 17.5 molar % hydrido and 26.9 molar % 3-cyanopropyl- was added to the catalyst/crosslinking reagent solution and mixed thoroughly. Silica coated AlN (11 g, 65 volume %, 85 wt.%) was added to the

uncured resin. The mixture was initially mixed thoroughly with a metal spatula, then mixed in a high shear mixer for 15 minutes. The mixing blade was removed from the beaker and vacuum was applied to the mixture for 15 min. The microcomposite samples were cured in an 80 °C oven.

### **3.7.3. Preparation of a 63 Volume % Silica Coated AlN Filled / 54 Mol % Nitrile Substituted Polyorganosiloxane Microcomposite Network**

Karstedt's catalyst (0.0170 g, 5 g catalyst/mol hydrido) was diluted in 1,3-divinyltetramethyldisiloxane, (0.320 g, 0.0034 mol vinyl) and mixed thoroughly in a 50 mL beaker. Poly(dimethyl-co-methylhydrido-co-3-cyanopropylmethyl)siloxane (2 g, 0.0034 mol hydrido) with a  $M_n$  of 3410 g/mol, containing 18.1 molar % hydrido and 54.0 molar % 3-cyanopropyl- was added to the catalyst/crosslinking reagent solution and mixed thoroughly. Silica coated AlN (10.13 g, 63 volume %, 84 wt.%) was added to the uncured resin. The mixture was mixed as described above and cured in an 80 °C oven.

### **3.7.4. Preparation of a 50 Volume % Silica Coated AlN Filled / 15 Mol % Phosphine Oxide Substituted Polyorganosiloxane Microcomposite Network**

A 3700 g/mol polysiloxane with 15% molar phosphine oxide, and 10% molar vinyl (1 g,  $7.9 \times 10^{-4}$  mol vinyl) and Karstedt's catalyst (0.005 g, 6 g catalyst/mol vinyl) were mixed together thoroughly in a 50 mL beaker with a spatula for 10 min. Tetrakis(dimethylsiloxy)silane (0.065 g,  $7.9 \times 10^{-4}$  mol silane) was added and mixed thoroughly for an additional 5 minutes. Silica coated AlN (3 g, 50 vol.%, 75 wt.%) was added and mixed thoroughly first with a spatula, then in a high shear mixer under vacuum for 15 min. The mixing blade was removed and the sample was held under vacuum for an additional 15 min. The microcomposite molds, glass slide bonds and thermal conductivity specimens were cured at 80 °C for 12 h.

### **3.7.5. Preparation of a 50 Volume % Silica Coated AlN Filled / PCPMS Network**

Trivinyl terminated poly(3-cyanopropylmethyl)siloxane homopolymer (PCPMS) (24,200 g/mol, 5.5 g,  $1.4 \times 10^{-3}$  mol vinyl) and Karstedt's catalyst ( $6.8 \times 10^{-3}$  g, 5 g catalyst/mol vinyl) were mixed with a spatula for 10 min in a 50 mL beaker. Polar crosslinking reagent,  $D_4CNH_3$ ,<sup>33</sup> (0.14g,  $1.4 \times 10^{-3}$  mol silane) was added to the mixture and mixed thoroughly for 5 min. Silica coated AlN (16.5 g, 50 vol.%, 75 wt.%) was added and mixed thoroughly with a spatula and then in a high shear mixer under vacuum for 15 minutes. Vacuum was applied to the sample for an additional 15 minutes in the absence of the mixing blade. The microcomposite was cured at 80 °C for 12 h.

### **3.7.6. Preparation of a 66 Volume % Al Sphere Filled / 10 Mol % Nitrile Substituted Polyorganosiloxane Microcomposite Network**

Karstedt's catalyst (0.0084 g, 5 g catalyst/mol hydrido) was diluted in 1,3-divinyltetramethyldisiloxane, (0.1635 g, 0.00175 mol vinyl) and mixed thoroughly in a 50 mL beaker. Poly(dimethyl-co-methylhydrido-co-3-cyanopropylmethyl)siloxane (2.1 g, 0.00175 mol hydrido) with a  $M_n$  of 4465 g/mol, containing 6.7 molar % hydrido and 9.4 molar % 3-cyanopropyl- was added to the catalyst/crosslinking reagent solution and mixed thoroughly. Al spheres (9.9 g, 66 volume %, 83 wt.%) were added to the uncured resin. The mixture was mixed thoroughly with a metal spatula, followed by 15 minutes in a high shear mixer. Vacuum was applied to the sample for 15 min prior to curing the microcomposite in an 80 °C oven.

### **3.7.7. Preparation of a 37 Volume % BN Filled / 10 Mol % Nitrile Substituted Polyorganosiloxane Microcomposite Network**

Karstedt's catalyst (0.0121 g, 5 g catalyst/mol hydrido) was diluted in 1,3-divinyltetramethyldisiloxane, (0.2258 g, 0.00242 mol vinyl) and mixed thoroughly in a 50 mL beaker. Poly(dimethyl-co-methylhydrido-co-3-cyanopropylmethyl)siloxane (2.9 g, 0.00242 mol hydrido) with a  $M_n$  of 4465 g/mol, containing 6.7 molar % hydrido and

9.4 molar % 3-cyanopropyl- was added to the catalyst/crosslinking reagent solution and mixed thoroughly. BN powder (3.5 g, 37 volume %, 55 wt.%) was added to the uncured resin. The mixture was mixed thoroughly with a metal spatula, followed by 15 minutes in a high shear mixer. Vacuum was applied to the sample for 15 min, although the sample was too "fluffy" for the air to be removed effectively. The BN microcomposite was packed into a 10 mL disposable syringe and centrifuged for 35 min at 3500 rpm. The microcomposite sample was cured in an 80 °C oven to yield a uniformly white network. The air was effectively removed using the centrifuge as indicated by the air free sample cured between the glass slides.

### **3.7.8. Preparation of 30 Volume % Ag Filled / 10 Mol % Nitrile Substituted Polyorganosiloxane Microcomposite Network**

Karstedt's catalyst (0.0084 g, 5 g catalyst/mol hydrido) was diluted in 1,3-divinyltetramethyldisiloxane, (0.1573 g, 0.00169 mol vinyl) and mixed thoroughly in a 50 mL beaker. Poly(dimethyl-co-methylhydrido-co-3-cyanopropylmethyl)siloxane (2.02 g, 0.00169 mol hydrido) with a  $M_n$  of 4465 g/mol, containing 6.7 molar % hydrido and 9.4 molar % 3-cyanopropyl- was added to the catalyst/crosslinking reagent solution and mixed thoroughly. Ag flake powder (8.08 g, 30 volume %, 80 wt.%) was added to the uncured resin. The mixture was mixed thoroughly with a metal spatula, followed by 15 minutes in a high shear mixer. Vacuum was applied to the sample for 15 min. This sample also had a "fluffy" appearance and was centrifuged to remove all of the air. The microcomposite was cured in an 80 °C oven for 12 h.

## **3.8. Characterization Methods for Monitoring Reactions and Purity of Reagents**

### **3.8.1. $^1\text{H}$ , $^{13}\text{C}$ , $^{29}\text{Si}$ and $^{31}\text{P}$ Nuclear Magnetic Resonance Spectroscopy**

Proton ( $^1\text{H}$ ), carbon ( $^{13}\text{C}$ ), silicon ( $^{29}\text{Si}$ ) and phosphorus ( $^{31}\text{P}$ ) Nuclear Magnetic Resonance Spectroscopy (NMR) are powerful characterization tools which were employed to monitor reactions and characterize products.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR data

were used to monitor hydrosilation reactions, determine the number average molecular weights ( $M_n$ ), characterize the percent of functionalization on polysiloxane precursors, and to confirm complete endcapping on polymers. Organophosphorus addition reactions and oxidation of phosphine containing monomers and polysiloxanes were monitored using  $^{31}\text{P}$  NMR.

$^1\text{H}$  NMR data were obtained on a Varian Unity 400 NMR spectrometer operating at 399.9 MHz with a spectral width of 5000 Hz,  $22^\circ$  pulse with a width of 25  $\mu\text{sec}$  and 64 scans with  $\pm 2\%$  error. The samples were prepared by dissolving  $\sim 100$  mg of sample in 1.0 mL deuterated chloroform ( $\text{CDCl}_3$ ). Polymer  $M_n$ s were calculated from endgroup analyses, by ratioing the area of one proton in a repeat unit to the area of one proton on an endgroup.

Organophosphorus reactions were monitored using  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 85%  $\text{H}_3\text{PO}_4$  external reference) on a Bruker 360 NMR spectrometer.

$^{29}\text{Si}$  NMR was used to quickly and accurately determine % functionalization on polysiloxane precursors. The number of reactive vinyl or hydrido functional groups of polysiloxane prepolymers were first determined using  $^{29}\text{Si}$  NMR. Diphenylphosphine, mercaptoacetic acid and allyl cyanide were reacted with the prepolymers and the number of newly formed silicon repeat units was established using  $^{29}\text{Si}$  NMR. Confirmation of complete endcapping and assurance that no silanol groups were present were also determined using  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR data obtained on a Varian Unity 400 NMR spectrometer. Quantitative  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR data were kindly obtained by Mr. Tom Glass.

For quantitative  $^{29}\text{Si}$  NMR, the instrument was operated at 79.46 MHz with a spectral width of 25000.0 Hz,  $45^\circ$  angle with a relaxation delay of 11.2 sec. and inverse gated decoupling was used with  $\sim 500$  scans with  $\pm 5\%$  error at most. For quantitative  $^{13}\text{C}$  NMR, the instrument was operated at 100.6 MHz with a sweep width of 25000.0 Hz and a  $90^\circ$  pulse angle with a relaxation delay of 6 sec and  $\sim 500$  scans with  $\pm 5\%$  error at most. Polymer samples for both  $^{29}\text{Si}$  and  $^{13}\text{C}$  NMR were prepared by dissolving 0.630 g of polymer in 2.4 mL  $\text{CDCl}_3$ , and doping with 0.0519 g tris(acetylacetonato)chromium (III),  $\text{Cr}(\text{acac})_3$  to decrease spin-lattice relaxation times ( $T_1$ ). The relaxation delay time in quantitative  $^{29}\text{Si}$  and  $^{13}\text{C}$  NMR was set to five times  $T_1$  for each sample.

### **3.8.2. Fourier Transform Infrared Spectroscopy**

FTIR spectra were obtained using a Midac GRAMS/32 Spectrometer model M2004. For the synthesis of thioacetic acid functional polysiloxanes, 2 drops of solution were placed on a NaCl plate to verify the disappearance of the thiol functional group (stretching band at  $2850\text{ cm}^{-1}$ ). Hydrosilation curing samples were prepared by placing two drops of the uncured resin mixture on NaCl plates. Samples were placed in a  $90\text{ }^{\circ}\text{C}$  oven and removed at hourly intervals for scanning. The FTIR samples for the  $180^{\circ}$  peel adhesion tests were prepared by scraping a thin piece of the network with a razor and placing it between NaCl salt plates. Transmission data were obtained by acquiring 8 scans with a resolution of  $8\text{ cm}^{-1}$  at room temperature from  $4000\text{ cm}^{-1}$  to  $900\text{ cm}^{-1}$  with background subtraction for each analysis.

### **3.8.3. Gel Permeation Chromatography**

Molecular weights were determined at  $40\text{ }^{\circ}\text{C}$  in THF (ACS grade) at  $1\text{ mL/min}$  using polystyrene standards on a Waters SEC equipped with 3 in-line PLgel  $5\text{ }\mu\text{m}$  MIXED-C columns with an autosampler and a 410 RI detector. Molecular weight distributions of polymer chains/small cyclics compositions at equilibrium and final polymers after removal of cyclics were evaluated. Samples were prepared by dissolving  $10 - 15\text{ mg}$  of sample in  $10\text{ mL}$  THF (ACS grade); and then filtered through a  $4.5\text{ }\mu$  filter before loading into the GPC autosampler. All GPC results were kindly acquired by Mark Flynn and Jeremy Lizotte.

### **3.8.4. Transmission Electron Microscopy**

Transmission electron micrographs of the dispersed silica coated AlN in the resins were obtained using a Philips 420T TEM run at  $100\text{ kV}$ . Uncured microcomposites were diluted in  $\text{CH}_2\text{Cl}_2$  to yield a light gray cloudy suspension and cast onto a copper TEM grid having a  $200\text{-}300\text{ \AA}$  thick carbon over-layer.  $\text{CH}_2\text{Cl}_2$  was allowed to evaporate before imaging.

Imaging of the dispersed Ag and silica coated AlN in the networks was performed by first cryotomizing the network samples. Samples were cryotomized on a Reichert-Jung

Ultracut-4E Ultramicrotome with an FC-4D cryoattachment at  $-100\text{ }^{\circ}\text{C}$  and imaged without staining.

### **3.8.5. Thermal Analysis**

Thermogravimetric analysis (TGA) and subambient differential scanning calorimetry (DSC) were performed on a TGA Q 1000 and DSC Q 500, respectively, from TA Instruments, Inc. TGA samples were ramped from  $25\text{ }^{\circ}$  to  $900\text{ }^{\circ}\text{C}$  at  $10\text{ }^{\circ}\text{C}$  in both air and  $\text{N}_2$  environments. DSC samples were heated from  $-170\text{ }^{\circ}\text{C}$  to  $25\text{ }^{\circ}\text{C}$  at a rate of  $10\text{ }^{\circ}\text{C}/\text{min}$  and held above their melt temperatures for 1 min.; then quenched to  $-170\text{ }^{\circ}\text{C}$  prior to the second heating cycle (from  $-170\text{ }^{\circ}\text{C}$  to  $25\text{ }^{\circ}\text{C}$ ,  $10\text{ }^{\circ}\text{C}/\text{min}$ ). Reported  $T_g$ s were taken from the midpoint of the transition in the second heat scans. Phosphine oxide containing polysiloxanes were also run at a slower heating rate of  $2.5\text{ }^{\circ}\text{C}/\text{min}$ . to clarify broad transitions.

### **3.8.6. Thermal Conductivity Measurements**

Thermal conductivity measurements were kindly conducted by our colleagues at IBM under the direction of Mr. Mike Gaynes using a modified procedure of ASTM 5470-01: "Standard Test Methods for Thermal Transmission Properties of Thin Thermally Conductive Solid Electrical Insulation Materials". This test was used to measure the thermal impedance of thin film functional polyorganosiloxane microcomposite networks. Steady state heat-flux was measured through the flat networks of known dimensions and thicknesses measured using a digital caliper. The networks were assumed to be homogenous. Since thermal impedance is influenced by pressure, three measurements were taken for each specimen with three different applied pressures.

### **3.8.7. Tensile Measurements**

Tensile measurements (ASTM D 412) were performed on networks to determine % elongation, strength, and Young's modulus. Tensile specimens with gauge dimensions of  $10\text{ mm} \times 2.65\text{ mm}$  were stamped out from networks  $\sim 2\text{ mm}$  thick using a dogbone die. The specimens were pulled at a rate of  $1\text{ mm}/\text{min}$  at  $25\text{ }^{\circ}\text{C}$  using a TA.XT2 Texture Analyzer (Texture Technologies Corp., Scarsdale, NY/Stable Micro Systems, Godalming, Surrey, UK).

### **3.8.8. X-Ray Photoelectron Spectroscopy**

Surface analysis of uncured microcomposites were investigated for dispersion quality or coating ability of the polyorganosiloxanes on thermally conductive particles via X-Ray Photoelectron Spectroscopy (XPS). The data were obtained on a Perkin Elmer X-Ray Photoelectron Spectrometer 5400 Series using a Mg anode operating at 300 watts (14 kV) with the pressure of the system below  $5 \times 10^{-6}$  Pa. Spectra were acquired off of a 1 cm x 1 cm area at a 90 ° take-off angle. The powder samples were prepared by applying the powder to double-sided tape on a 1 cm x 1 cm Al substrate. The microcomposites were applied directly to the Al substrate.

### **3.8.9. Adhesive Strength Analysis: 180° Peel Test**

Adhesive strengths of networks were tested using 180° metal-to-metal peel tests (ASTM D 903) conducted on a model 1123 Instron 5500R using a 200 lb reversible load cell at a rate of 6 "/min at 25 °C. The adherends, Al(7075-T6) alloy and TiAl<sub>4</sub>V<sub>6</sub> alloy panels (1 " x 8 " x 0.125 "), were used in conjunction with Al (1100 grade) foil (2 mil thick) substrates. Adherend surfaces were degreased with soapy water and a Scotchbrite® scrub, then abraded with acetone saturated Scotchbrite®, mechanically abraded with coarse grain sandpaper, and rinsed free of particulates with acetone and water. The adherends were conditioned in a 100 °C oven for a minimum of 1 h to ensure removal of residual solvent. The Al foil substrate sheet (~ 12 " x 16 ") was prepared similarly except without the initial degreasing treatment. The substrate sheet was placed on a smooth, stable, metal plate for support and the uncured resin was drawn down onto the foil (~ 12 " x 8 "), leaving about 4 " of space for an adhesive-free peel tab. Consistent sealant drawdown thicknesses of 10 - 15 mils, measured with a caliper (after cure), were achieved using a 19 mil (wet thickness) drawdown rod. Adherend panels were placed on top of the uncured resin mixture on the aluminum foil substrate. The entire sheet was placed in an oven at 90 °C until FTIR confirmed the disappearance of any hydride functional groups from network samples cut from an adherend edge. This typically required ~ 12 h to achieve complete reaction. Once cured, a roller type razor was employed to cut precisely along the edges of the substrate/adherend bonds, leaving one

inch adherend panels bonded to one inch pieces of foil substrates. The extra tab of foil and adherend were clamped in opposed grips of the Instron and separated at a 180° peel angle at a rate of 6 "/minute (Figure 3.3).

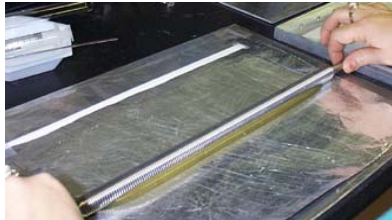


<b>1) Drawdown</b>	<b>2) Cure &amp; Cut</b>	<b>3) 180° Peel</b>
		
<p><b><u>Surface Preparation</u></b> Substrate &amp; Adherend: Degreasing Mechanical abrasion Acetone/H<sub>2</sub>O rinse 120° oven &gt; 1 hr</p>	<p>Al panel substrate 7075-T6 alloy 1" x 8" x 0.125" Al foil adherend 1145 grade (0.002") cut to fit 1" strip</p>	<p><b>Instron available at VA Tech</b></p>

Figure 3.3. ASTM D 903 Used to Evaluate the 180° Adhesive Peel Strengths of Polyorganosiloxane Networks on Aluminum Substrates

## Chapter 4. Results and Discussion

### ***4.1. Synthetic Overview of Functional Polysiloxanes as Thermally Conductive Adhesives***

Low modulus resins paired with highly thermally conductive fillers can yield thermally conductive adhesives. Such materials can effectively conduct heat away from silicon power substrates through conductive metal lines (heat sinks).<sup>125</sup> Polysiloxanes are especially desirable resins due to their extremely low moduli which aid in minimizing the effects of CTE mismatching between the adhesive and adherends.<sup>120,126</sup> Polysiloxanes can undergo repeated thermal cycling and perform consistently over a wider service temperature range (-60 °C to 250 °C) than typical organic polymers.<sup>78</sup> Networks based on polysiloxanes are elastic materials that maintain their flexibility at subambient conditions ( $T_g = -123$  °C for polydimethylsiloxane).<sup>81</sup> Hydrosilation curing reactions can yield void free adhesives with thin bondlines; two characteristics necessary for obtaining elevated thermal conductivity (k).<sup>2</sup> Highly filled thin films are critical for superior conductivity as  $Q = kA\Delta T/d$ : where Q is the heat flow, k is the thermal conductivity of the filler, A is the adhesive surface area,  $\Delta T$  is the change in temperature across the adhesive, and d is the microcomposite thickness.<sup>126</sup>

Polar polysiloxanes exhibit greatly improved specific adhesion to a variety of oxide particulates and adherends relative to nonpolar polydimethylsiloxanes (PDMS).<sup>3</sup> Nitrile and phosphine oxide containing siloxanes are capable of hydrogen bonding with the acidic proton of chloroform verified via <sup>1</sup>H NMR studies<sup>4</sup>, and the coordination of phosphines with metals is well documented.<sup>5</sup> Functionalized polysiloxanes containing such groups can disperse high volume fractions of polar conductive fillers, leading to microcomposite adhesive networks with correspondingly superior thermal conductivities. McGrath's group has demonstrated that novel linear copolymers comprised of a

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125. C. P. Wong, IEEE Transactions on Components, Packaging, and Manufacturing Technology, 1995, A, **18**(2), 270-273.

126. R. L. Dietz, D. Peck and P. J. Robinson, IMC Proc. Omiya, 1996, 304-308.

polydimethylsiloxane soft segment coupled with phosphine oxide containing polyurethane-urea hard segments can disperse high fractions of conductive fillers.<sup>124</sup>

This chapter first describes syntheses of model phosphine and phosphine oxide containing siloxane monomers. The model species were prepared to assess the potential for hydrogen bonding interactions with polar species. Series of polymers were then prepared as potential adhesive binders for thermally conductive particulate fillers. In general, a three-step procedure was performed to yield lightly crosslinked polysiloxane networks with controlled molar percentages of pendent polar substituents.

First, polysiloxane prepolymers containing controlled concentrations of vinyl or hydrido groups were synthesized via ring opening co-equilibration polymerizations of cyclic siloxane monomers, D<sub>4</sub>Vi (base catalyzed) or D<sub>4</sub>H (acid catalyzed), respectively. The second step involved functionalization of the prepolymers. Random poly(dimethyl-co-methylvinyl)siloxane prepolymers were free radically reacted with diphenylphosphine or mercaptoacetic acid, leaving a controlled amount of vinyl groups intact to be used for network formation. Phosphine oxide containing polysiloxanes were prepared by simply oxidizing phosphine containing oligomers. Random poly(dimethyl-co-methylhydrido)siloxane prepolymers were hydrosilated with allyl cyanide, leaving a controlled amount of hydrido groups unreacted. The final step involved hydrosilation of the residual reactive groups (hydrido or vinyl) with an appropriate crosslinking reagent to form networks.

## **4.2. Model Phosphonyl Containing Siloxanes**

Novel phosphonyl containing siloxane monomers were prepared as model compounds to investigate organophosphorus chemistry with chlorosilane and vinylsilyl species. An alkylphosphonate silane monomer was synthesized via the Michaelis-Arbuzov rearrangement.<sup>37</sup> This monomer was prepared to assess the viability of performing hydrosilation reactions in the presence of phosphine oxides (since phosphines inhibit Pt catalyzed hydrosilation reactions).<sup>81</sup> This model silane was investigated to evaluate hydrogen bonding with polar conductive fillers. The intention was to prepare polysiloxanes with controlled concentrations of phosphine oxide that could participate in hydrosilation reactions to yield lightly crosslinked networks. Cyclic siloxane tetramers

with organophosphorus moieties were also prepared and studied as model compounds (prior to synthesizing the oligomers). This provided a means for studying free radical addition reactions of diphenylphosphine with vinylsilyl species on precise model structures.

#### 4.2.1. Synthesis of 3-diethylphosphonatopropylmethyl-dimethoxysilane via the Michaelis-Arbuzov Rearrangement

Novel siloxanes with organophosphorus moieties were investigated as high performance adhesive components and as dispersants for metal particulates. The electronegativity of the oxygen in the phosphoryl bond (P=O) is well documented and is capable of binding strongly with electrophiles.<sup>5,12</sup> An alkylphosphonate silane monomer, 3-diethylphosphonatopropylmethyl-dimethoxysilane, was prepared via the Michaelis-Arbuzov rearrangement (Figure 4.1).<sup>37,61</sup>

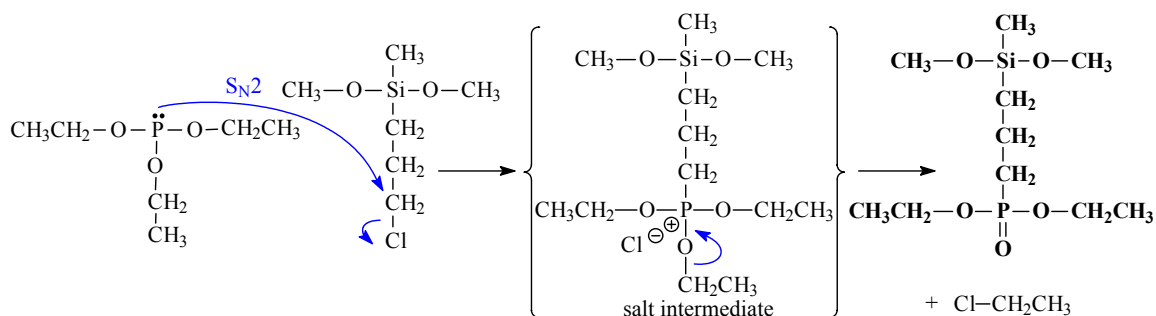


Figure 4.1. Michaelis-Arbuzov Rearrangement Mechanism to Yield 3-diethylphosphonatopropylmethyl-dimethoxysilane

The Michaelis-Arbuzov rearrangement involves the reaction between a phosphite,  $P(OR)_3$ , with an alkyl halide to yield the more stable phosphine oxide. In this case, triethyl phosphite was reacted with 3-chloropropylmethyl-dimethoxysilane to yield 3-diethylphosphonatopropylmethyl-dimethoxysilane. An excess of triethyl phosphite was required to completely react the alkyl halide since a side reaction between triethyl phosphite and the ethylchloride byproduct consumes some of the triethyl phosphite

(Figures 4.1 and 4.2). A steady N<sub>2</sub> purge aids in removing ethylchloride formed in situ to minimize this side reaction.

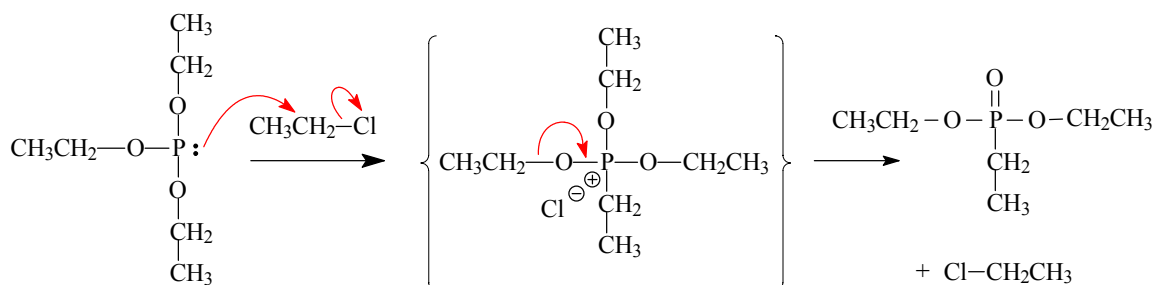


Figure 4.2. Mechanism for the Major Side Reaction of the Michaelis-Arbuzov Reaction

The reaction was monitored via <sup>1</sup>H NMR until the methylene protons on the –CH<sub>2</sub>Cl (~ 3.48 ppm) group disappeared, and newly formed –CH<sub>2</sub>PO(OCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> methylene protons were observed at ~ 1.7 ppm (Figure 4.3). The peak for the methylene protons (c) from the alkyl halide overlapped with the methoxy protons (f) for a total integral area of 8 at the beginning of the reaction. This integral area decreased to 6 after the reaction was complete, ~ 4 days. The methylene protons with the newly attached phosphate group shifted to ~ 1.7 ppm (e) which slightly overlapped the methylene peak (d). The integral area of peak d (2) correspondingly increased to a total area of 4 when all of the 3-chloropropylmethyldimethoxysilane had reacted. Peaks from less than 5% of the byproduct, diethyl ethylphosphonate, appeared at ~1.15 ppm, ~ 3.75 ppm and 3.85 ppm.

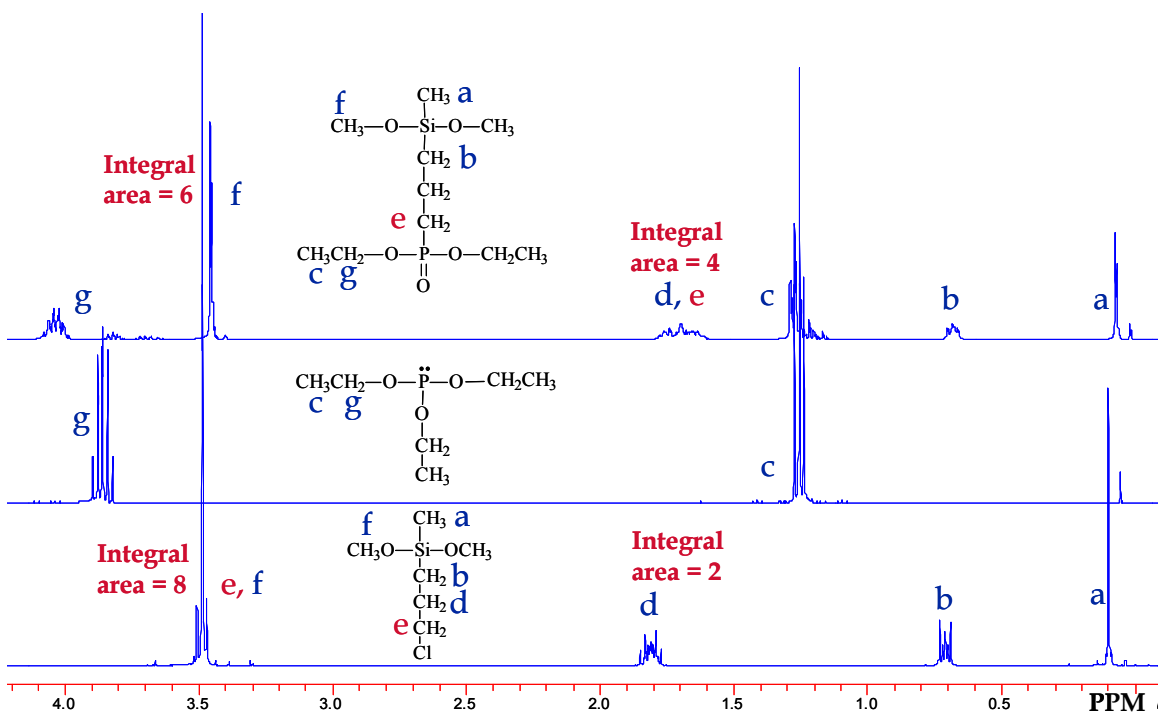


Figure 4.3. Monitoring the Synthesis of 3-diethylphosphonatopropylmethyldimethoxysilane via  $^1\text{H}$  NMR

The alkylphosphonate silane coupling and crosslinking reagent was expected to improve adhesion strength, enhance dispersion quality of metal or metal oxide fillers and inhibit corrosion at the metal/siloxane interface based on its ability to hydrogen bond. Previous work performed by the author on polar polysiloxane networks with pendent nitrile groups (PCPMS) has shown the importance of electron donating moieties.<sup>127</sup> PCPMS exhibited at least doubled  $180^\circ$  peel strengths on metal adherends over nonpolar PDMS networks, independent of crosslink density. The nitrile networks also exhibited greatly improved nonpolar solvent resistance (by an order of magnitude or less), yet they swelled considerably in chloroform. These results were attributed to hydrogen bonding between the nitrogen unshared electrons and the acidic hydrogen on the solvent.

127. J. K. Hoyt, C. H. Li, P. Phillips and J. S. Riffle, Proc. Of the 23<sup>rd</sup> Annual Meeting of the Adhesion Society, Myrtle Beach, SC, Feb., 2000.

Transmission electron micrographs also suggested a strong hydrogen bonding interaction between the nitrile groups and acidic silanols on fumed silica.<sup>4</sup>

The capacity for hydrogen bonding of 3-diethylphosphonatopropylmethyldimethoxysilane was investigated by <sup>1</sup>H NMR by observing the shift of the acidic proton on chloroform in 1:1 and 2:1 eq:eq chloroform:phosphine oxide mixtures (Figure 4.4). The downfield shift of the deshielded chloroform proton in the presence of the phosphoryl group suggested strong secondary specific interactions. Interestingly, the magnitude of the shift for the chloroform proton approximately corresponded to the equivalence ratio of chloroform:phosphine oxide (Figure 4.4). Analogous experiments were conducted with the nitrile containing siloxanes, D<sub>4</sub>CN (tetramer) and PCPMS (oligomer) using a 1:1 equivalent mixture of chloroform:nitrile. A similar downfield shift was observed, although the magnitude was much less. The magnitude of the chloroform proton shift was the same for the nitrile containing monomer and oligomer. It should be noted that the characteristic pentet d<sub>6</sub>-acetone solvent peaks strictly coincided (Figure 4.4).<sup>128</sup> The downfield shifts of the chloroform protons in the presence of phosphine oxide or nitrile groups in d<sub>6</sub>-acetone provided clear evidence of these secondary interactions. This experiment was also performed in d<sub>6</sub>-DMSO, a non hydrogen-bonding solvent<sup>128</sup> to further substantiate this data. The same trend and magnitude of chloroform proton shifts were observed while the d<sub>6</sub>-DMSO solvent peaks coincided.

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128. R. M. Silverstein, G. C. Bassler, T. C. Morrill, Spectrometric Identification of Organic Compounds, Fifth Ed., John Wiley and Sons, Inc., New York, 1991.

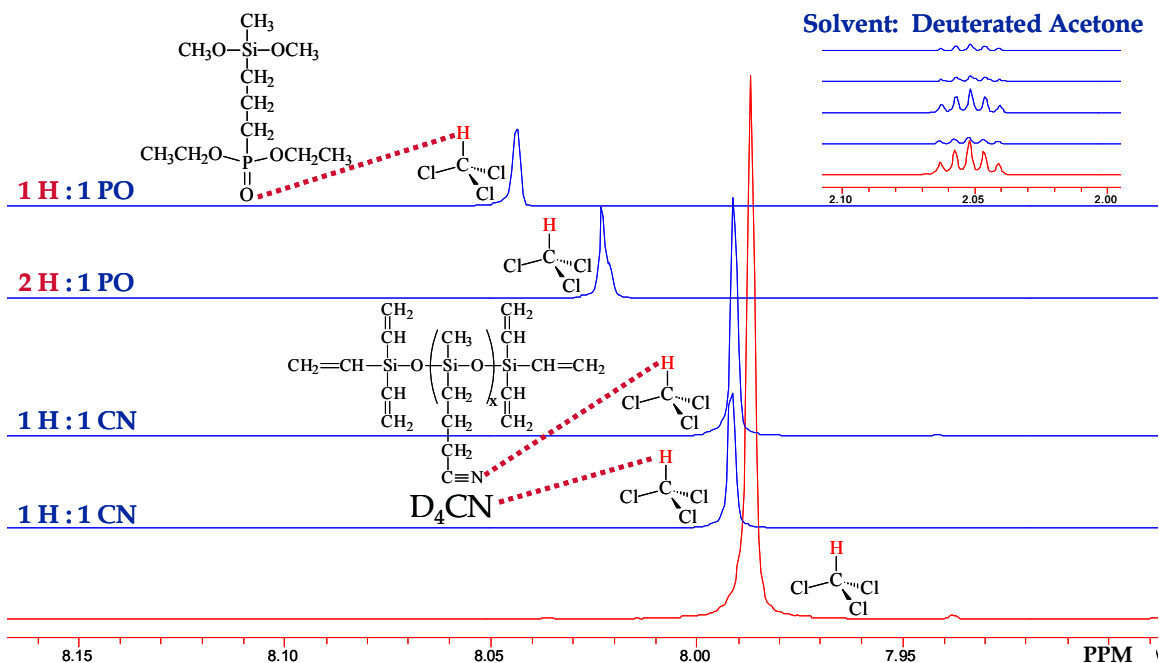


Figure 4.4. Hydrogen Bonding of 3-diethylphosphonatopropylmethyldimethoxysilane and Nitrile Containing Siloxanes with  $\text{CHCl}_3$  via  $^1\text{H}$  NMR in Deuterated Acetone

The  $^1\text{H}$  NMR hydrogen bonding study with chloroform suggested that the phosphine oxide groups should also hydrogen bond with electropositive metal oxide surface hydroxyls. This ethoxy functional silane may thus serve as an adhesion promoting crosslinking reagent. Moreover, the ethoxy groups on the phosphorus atom could presumably condense with hydroxyl groups on oxide surfaces to form covalent bonds (Figure 4.5).

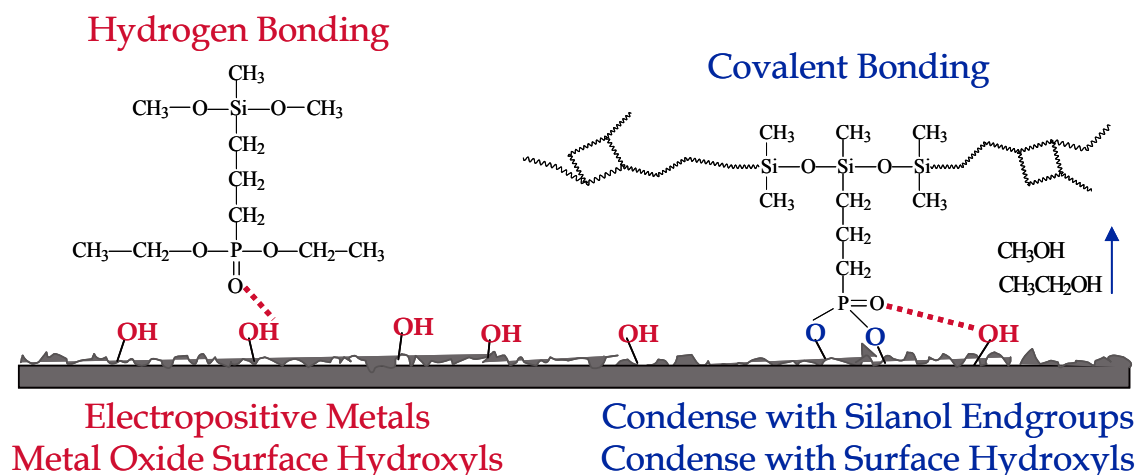


Figure 4.5. Ethoxy Functional Alkylphosphonate Silane as an Adhesion Promoting Crosslinking Reagent has Primary and Secondary Bonding Sites Available for Strong Interactions with Metal Oxide Surfaces

It was of interest to investigate hydrosilation crosslinking reactions in the presence of possible adhesion promoters such as 3-diethylphosphonatopropylmethyldimethoxysilane. Phosphines prohibit Pt catalyzed hydrosilation reactions, while phosphoryl species may not.<sup>35</sup> Controlled concentrations of 3-diethylphosphonatopropylmethyldimethoxysilane were added to Pt catalyzed hydrosilation reaction mixtures based on vinyl terminated PCPMS oligomers and a hydride functional crosslinking reagent, D<sub>4</sub>CNH<sub>3</sub> (stoichiometric amount of vinyl:silane). The resin mixtures were cured at 80 °C, which is well below the boiling point of the phosphine oxide monomer (120 °C/500 mTorr). Mixtures containing 1 and 5 wt % of the phosphine oxide monomer cured efficiently. FTIR confirmed the complete disappearance of the ≡Si-H groups at ~ 2170 cm<sup>-1</sup> in both cases (5 wt % shown in Figure 4.6). The characteristic peak for vinyl groups at ~ 1650 cm<sup>-1</sup> also disappear. It should also be noted that the phosphine oxide monomer was observed throughout the entire reaction indicated by the characteristic P=O FTIR stretching frequency at ~ 1200 cm<sup>-1</sup>.<sup>128</sup> It was concluded that phosphine oxide containing polysiloxanes should also cure via Pt catalyzed hydrosilation mechanisms.

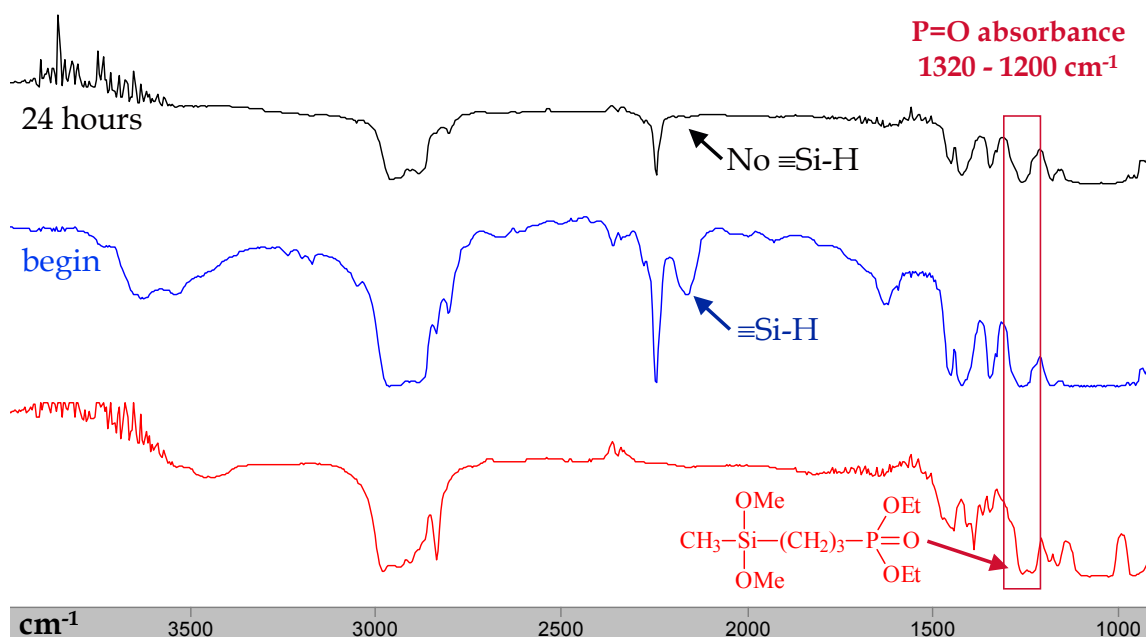


Figure 4.6. Monitoring a Pt Catalyzed Hydrosilylation Network Formation in the Presence of 5 wt % of a Phosphine Oxide Containing Silane Monomer via FTIR

#### 4.2.2. Free Radical Addition of Diphenylphosphine with D<sub>4</sub>Vi to Yield D<sub>4</sub>P

One major goal of this research was to prepare polysiloxanes with controlled concentrations of pendent phosphonyl moieties as candidate materials for binding to a wide range of polar fillers. The ability of phosphine containing siloxanes to complex metals such as Ag (both electrically and thermally conductive), ceramics such as AlN or BN (thermally conductive), or Co and Fe (magnetic nanoparticles) is of great interest. Both pendent electron donating phosphine and phosphonyl moieties are expected to complex metals and strongly hydrogen bond with oxide surfaces, respectively (and interact with soft and hard electrophiles, respectively).<sup>5</sup>

The free radical addition reaction of diphenylphosphine with vinylsilyl reagents was studied using the cyclic tetramer D<sub>4</sub>Vi. Novel organophosphorus siloxane cyclic tetramers were synthesized according to reaction conditions previously reported for

similar materials.<sup>75</sup> Reaction conditions were later optimized using the vinyl containing oligomers.

Free radical addition of diphenylphosphine over 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (D<sub>4</sub>Vi) promoted with 2,2'-azo-bis-isobutyronitrile (AIBN) yielded 1,3,5,7-tetra(2-diphenylphosphineethyl)-1,3,5,7-tetramethylcyclotetrasiloxane (D<sub>4</sub>P) with pendent phosphines (Figure 4.7).<sup>5,75</sup> The free radical mechanism for this reaction is shown in Figure 4.8. Initiation, involving homolytic bond cleavage occurs as AIBN decomposes via thermolysis to yield 2 free radical fragments and N<sub>2</sub>. The highly reactive radical fragments abstract a hydrogen atom from the relatively weak P-H bond (see Table 2.1) in diphenylphosphine to yield a diphenylphosphinyl radical.<sup>5</sup> Once formed, diphenylphosphinyl radicals may either 1) abstract a hydrogen atom (via the reverse reaction or from a neighboring diphenylphosphine), 2) add to another diphenylphosphinyl radical to yield the diphosphine species (also a relatively weak bond) (Figure 4.8), or 3) add rapidly to the unsaturated groups of D<sub>4</sub>Vi (Figure 4.9).

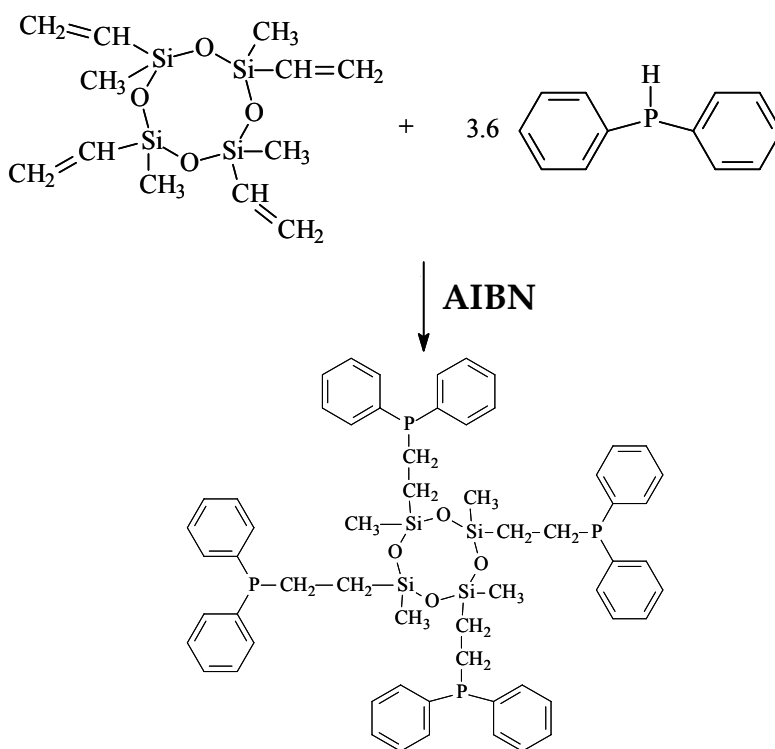


Figure 4.7. Free Radical Addition of Diphenylphosphine to Yield D<sub>4</sub>P

## Initiation

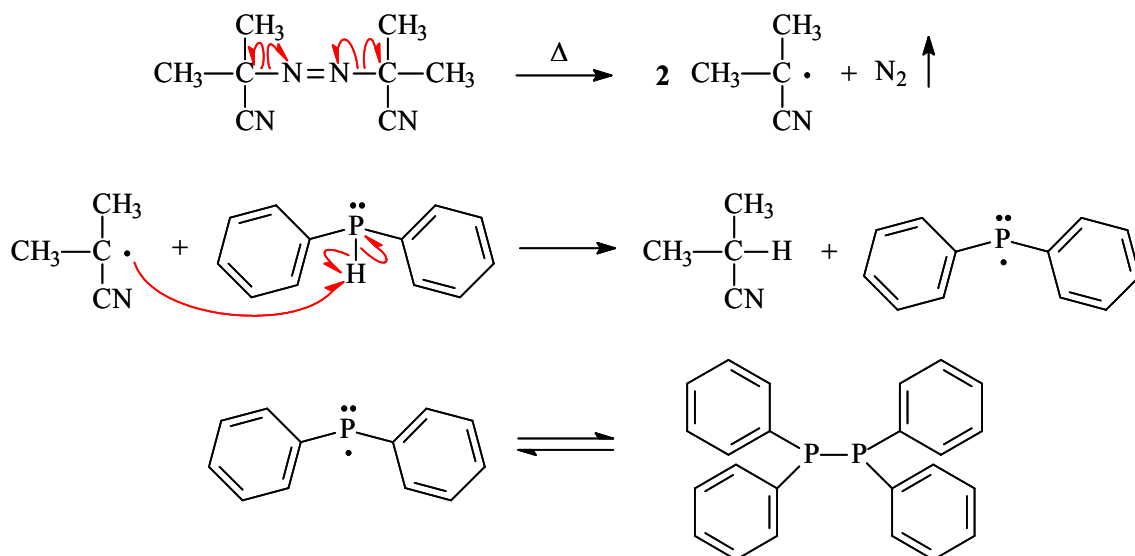


Figure 4.8. Mechanism for the Initiation of the AIBN Promoted Free Radical Addition of Diphenylphosphine to D<sub>4</sub>Vi

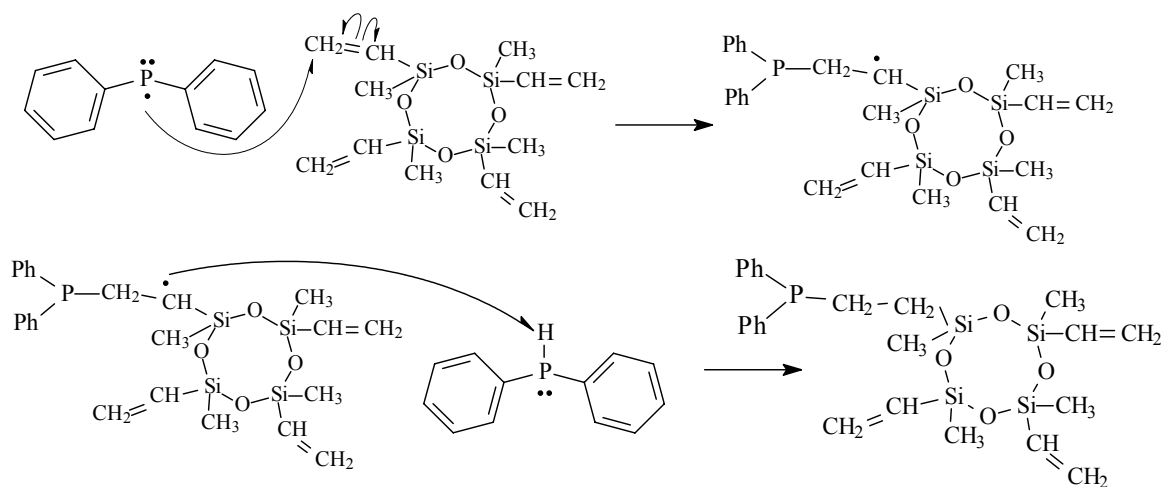


Figure 4.9. Addition of Diphenylphosphine to D<sub>4</sub>Vi

The diphenylphosphinyl radical adds to the least substituted carbon (with the most hydrogen atoms) to yield the more stable secondary radical.<sup>5</sup> The carbon radical subsequently abstracts a hydrogen atom from diphenylphosphine (Figure 4.9) to yield the newly formed diphenylphosphineethyl- substituent on the D<sub>4</sub>Vi monomer.

Syntheses of the organophosphorus siloxane cyclics were monitored using <sup>31</sup>P NMR (Figure 4.10). Progress of diphenylphosphine addition was easily monitored. During the initial study, a 10% equivalent molar excess of D<sub>4</sub>Vi was used to exhaust the pyrophoric diphenylphosphine (for safety reasons). The diphenylphosphine starting material had ~ 5% diphenylphosphine oxide impurity that also added to D<sub>4</sub>Vi to yield D<sub>4</sub>PO (Figure 4.10). The bottom spectrum (Figure 4.10) identifies the shifts for the phosphorus atoms in diphenylphosphine (~ -40 ppm) and diphenylphosphine oxide (~ 22 ppm). After 2 hours, 39% of the diphenylphosphine had added to D<sub>4</sub>Vi to yield the addition product indicated by the phosphorus peak at ~ -9.3 ppm.

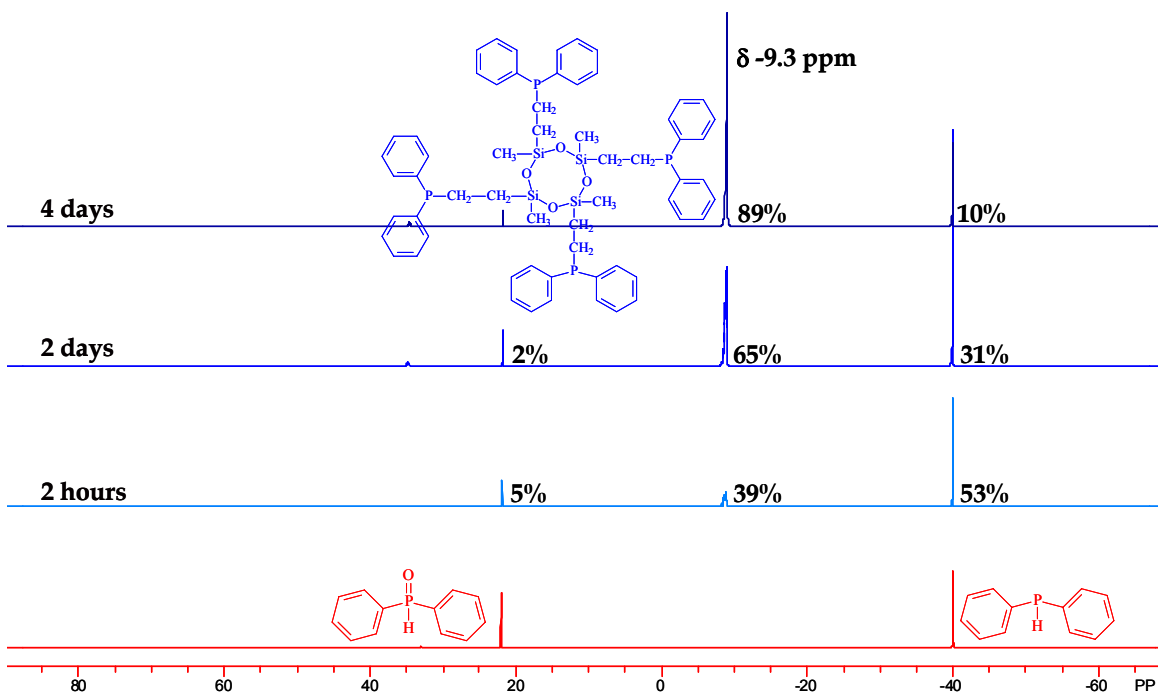


Figure 4.10. Monitoring the Progress of Phosphine Substitution on D<sub>4</sub>Vi via <sup>31</sup>P NMR

The stacked  $^{31}\text{P}$  NMR spectra (Figure 4.10) show that after 2 and 4 days of stirring at 115 °C, 65% and 89% of diphenylphosphine had added, respectively. This reaction was stirred for 7 days and no significant increase of addition product was observed although a 10 mol % excess of vinyl groups was present. For the model reaction described above, 0.15 mol % AIBN based on moles of vinyl was used. It seemed reasonable that increasing the amount of AIBN and using a lower reaction temperature would expedite the free radical addition of diphenylphosphine to vinylsilyl species. Importantly, the  $t_{1/2}$  of AIBN is only  $\sim 8$  min at 100 °C, and 21 h at 60 °C. The temperature and catalyst issues will be addressed later to optimize this addition reaction with vinyl containing polysiloxanes.

$^{29}\text{Si}$  NMR was also used to monitor the diphenylphosphine addition reaction with  $\text{D}_4\text{Vi}$  (Figure 4.11). The  $^{29}\text{Si}$  NMR spectrum (Figure 4.11) represents a sample taken at 49 hrs. It substantiated the amount of addition product formed after 48 hr as determined by  $^{31}\text{P}$  NMR (Figure 4.10).  $^{29}\text{Si}$  NMR spectra were interpreted by the types of silicon in the repeat units. The characteristic peak for a silicon atom of a methylvinylsiloxy- repeat unit is observed at  $\sim 32$  ppm. The newly formed repeat unit,  $\text{Si-CH}_2\text{-CH}_2\text{-P(Ph)}_2$ , on the cyclic siloxane is observed at  $\sim 20$  ppm. It should be noted that this peak is near the characteristic peak for a dimethylsiloxy- repeat unit in  $\text{D}_4$ , since the  $\text{Si-CH}_2$  bond of the diphenylphosphine repeat unit is what the NMR detects.

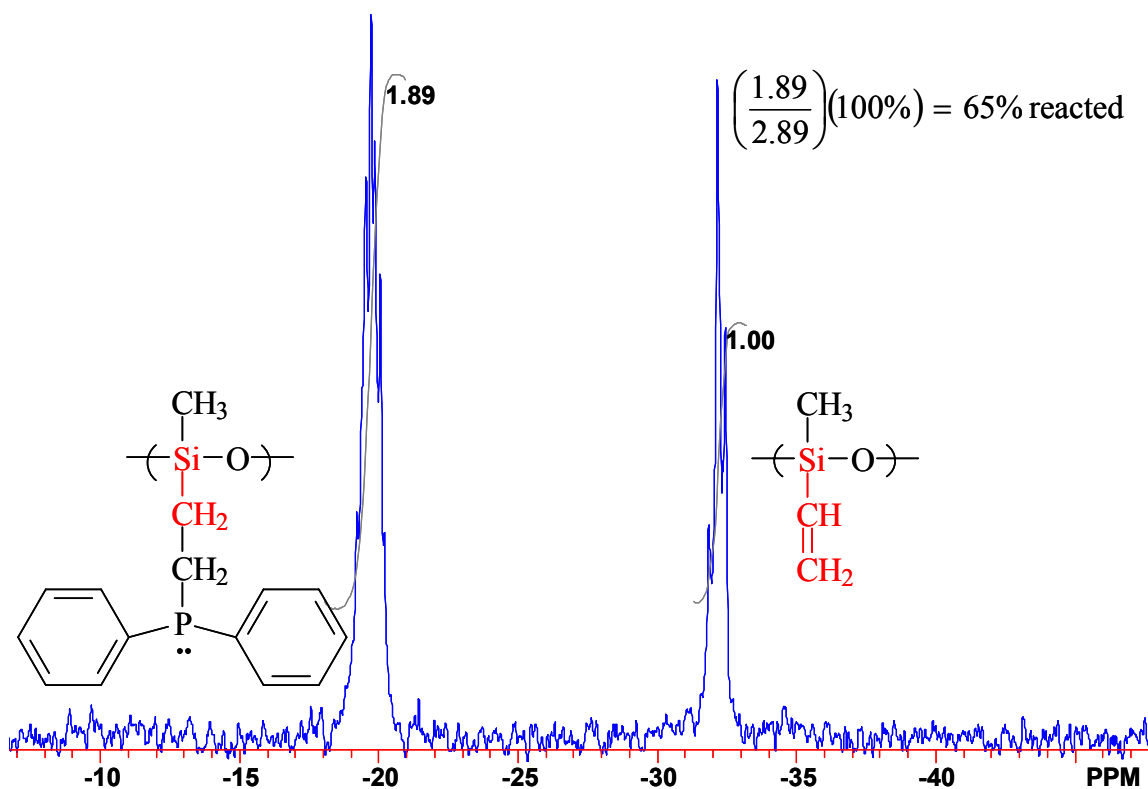


Figure 4.11.  $^{29}\text{Si}$  NMR Spectrum of a Phosphine Substituted Siloxane Tetramer

$^{29}\text{Si}$  NMR substantiated that  $^{31}\text{P}$  NMR could be used efficiently to quantitatively follow the addition reaction; therefore  $^{31}\text{P}$  NMR was primarily used. The reaction could also be monitored via  $^1\text{H}$  NMR (Figure 4.12), although the peaks and calculations were not as straightforward as those obtained with phosphorus NMR.

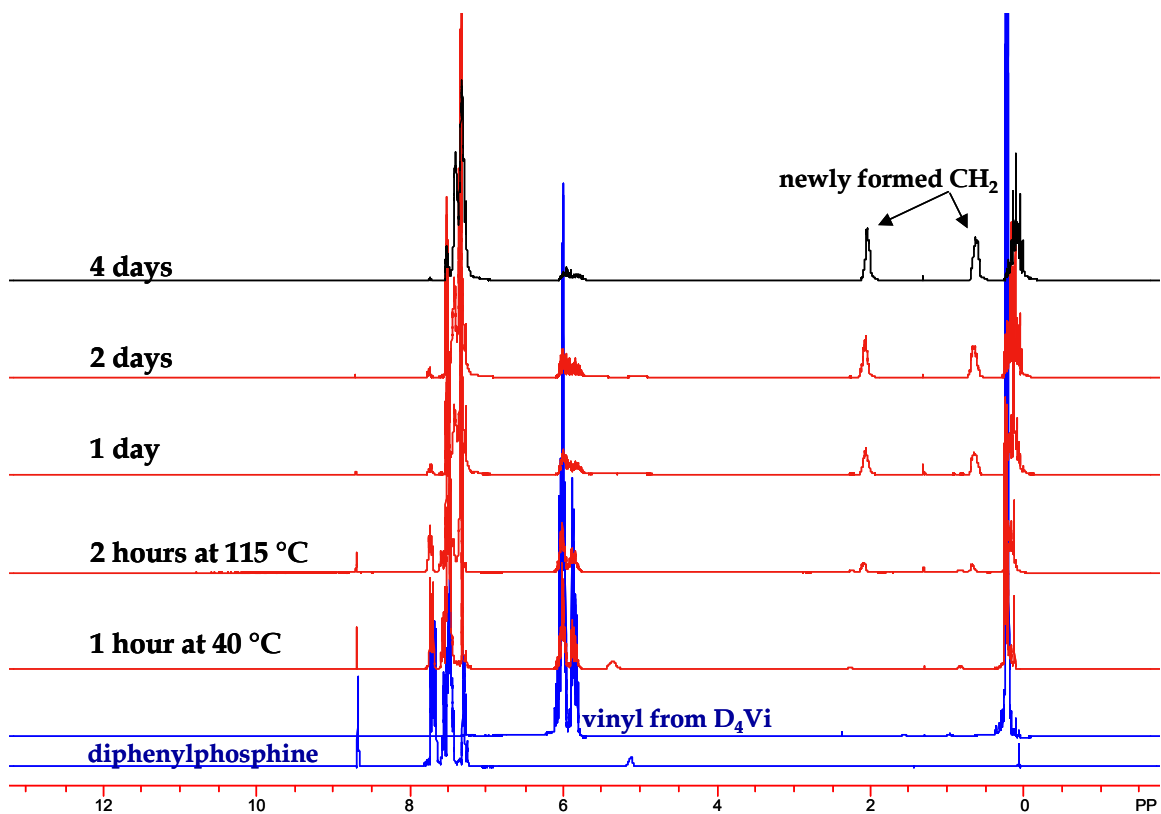


Figure 4.12. Progress of the Diphenylphosphine Addition Reaction to  $D_4Vi$  via  $^1H$  NMR

A  $^{13}C$  NMR spectrum of the crude product, 1,3,5,7-tetra(2-diphenylphosphineethyl)-1,3,5,7-tetramethylcyclotetrasiloxane ( $D_4P$ ) (Figure 4.13) indicated incomplete substitution. The characteristic peak (a) for the carbon atom of the methyl groups on  $D_4Vi$  at  $\sim 0$  ppm was set to an integral area of 1.0. Peaks for the methylene carbon atoms (b and c) as a result of diphenylphosphine substitution were observed at  $\sim 12$  ppm and  $\sim 20$  ppm and each integrated to an area of 0.77. These data showed that for every 1 methyl group, there were 0.77 diphenylphosphine substituents. For a cyclic tetramer, a 1:1 ratio would be required to yield the desired product  $D_4P$ . The final products for typical reactions yielded between 0.77 and 0.89 of the addition product and would be more appropriately called  $D_{3.08}P$  or  $D_{3.56}P$ , respectively. Optimization of the reaction parameters was pursued with the vinyl containing polysiloxane oligomers.

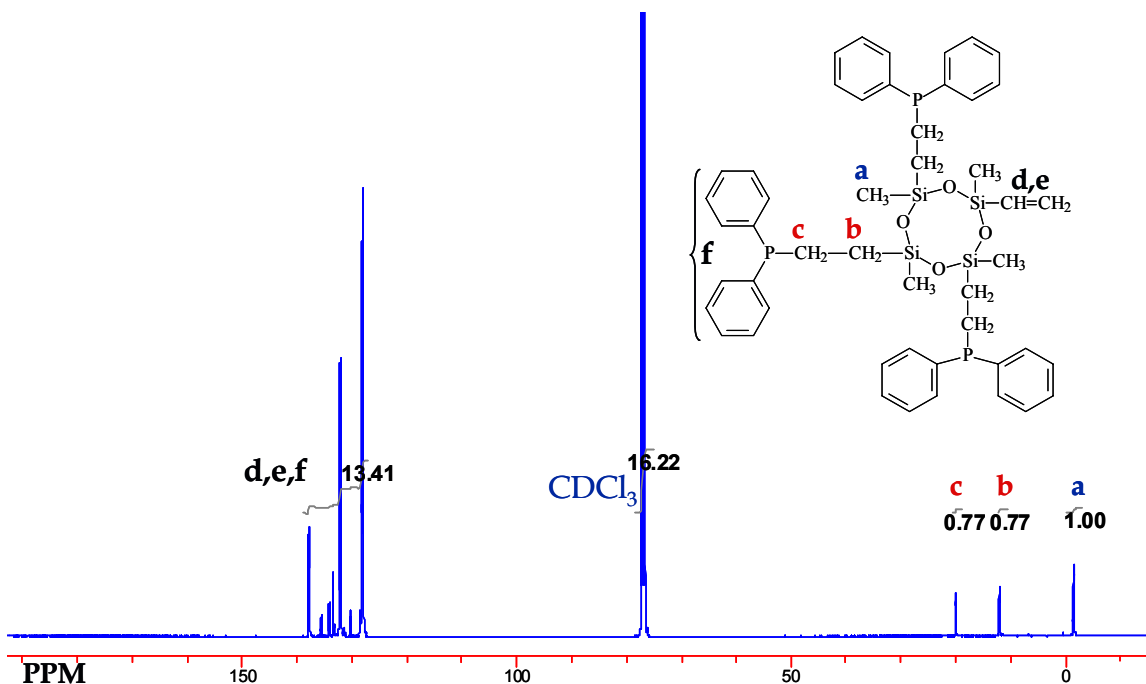


Figure 4.13.  $^{13}\text{C}$  NMR of the Incomplete Diphenylphosphine Addition Product

It is well known that ring-opening equilibrations of siloxane monomers with large or polar substituents preferentially yield cyclic products over the desired linear chains.<sup>81</sup> Therefore, the addition reaction of diphenylphosphine with cyclic  $\text{D}_4\text{Vi}$  was not intended to yield a novel monomer for ring opening equilibrations. It was also difficult to synthesize a pure  $\text{D}_4\text{P}$  monomer possibly due to steric hindrance between 4 bulky diphenylphosphine substituents on the tetramer. Thus, the phosphonyl containing polysiloxane oligomers described later herein were synthesized by direct reactions on pendent vinyl groups of vinyl containing polysiloxanes. Phosphonyl containing polysiloxanes with controlled amounts of phosphine substitution and free of byproducts were obtained in this manner.

#### 4.2.3. Oxidation of Diphenylphosphine ( $\text{D}_4\text{P}$ ) to Yield Diphenylphosphine Oxide ( $\text{D}_4\text{PO}$ )

The oxidation reaction of the " $\text{D}_4\text{P}$ " monomer described above was investigated. The intention was to prepare extremely polar polysiloxanes capable of strongly interacting with metals and oxides, while not prohibiting Pt catalyzed hydrosilation

curing reactions. A model D<sub>4</sub>P monomer was oxidized to investigate the optimum reaction conditions and methods for monitoring and characterizing the phosphine oxide containing siloxane species.

Oxidation of D<sub>4</sub>P was carried out with bis(trimethylsilyl)peroxide (BSPO) to yield 1,3,5,7-tetra(2-diphenylphosphine oxideethyl)-1,3,5,7-tetramethylcyclotetrasiloxane (D<sub>4</sub>PO) with phosphine oxide substituents (Figure 4.14).<sup>75,76</sup> The silyl peroxide reagent was chosen based on its ability to quantitatively oxidize phosphines within an hour at room temperature and in the absence of side reactions.<sup>76</sup> The only byproduct produced is hexamethyldisiloxane, which has a low enough boiling point (99 °C at 760 torr) to be easily vacuum distilled and separated from the desired product. A stoichiometric ratio of BSPO:phosphine is required to completely oxidize the phosphines.

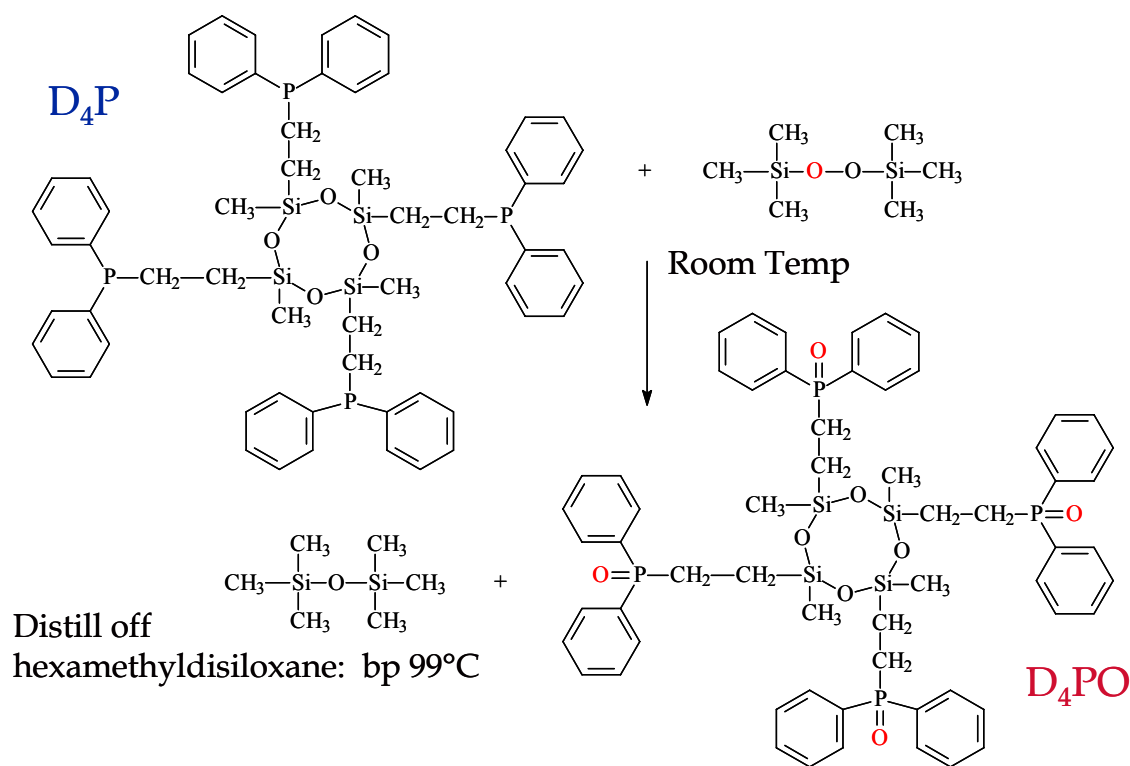


Figure 4.14. Oxidation of D<sub>4</sub>P to Yield D<sub>4</sub>PO

The phosphine oxidation involves attack of the phosphine on an oxygen atom in BSPO (Figure 4.15).<sup>76</sup> An oxygen atom is effectively transferred to the trivalent

phosphorus atom, P(III)  $\rightarrow$  P(V).<sup>76</sup> The reaction in general is proposed to be ionic, rather than free radical, due to the fast oxygen transfer and high stereospecificity.<sup>76</sup> It is suggested that the phosphorus atom acts as a nucleophilic center based on 1) retention of configuration at the phosphorus atom and on the observation that 2) phosphines,  $\text{PR}_3$ , are oxidized faster relative to phosphites,  $\text{P(OR)}_3$  (less effective nucleophiles).<sup>76</sup>

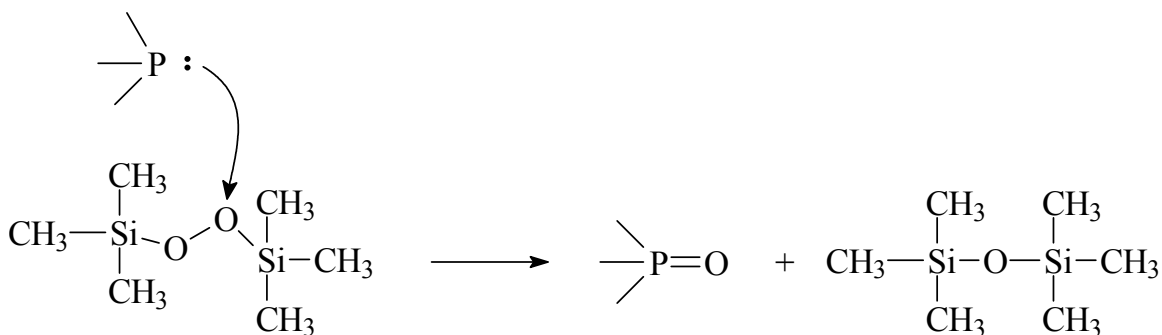


Figure 4.15. Oxidation of a Trivalent Phosphine via BSPO<sup>76</sup>

Oxidation of the  $\text{D}_4\text{P}$  cyclic proceeded smoothly at room temperature and was easily monitored via  $^{31}\text{P}$  NMR (Figure 4.16). The reaction was quite exothermic and a small excess ( $\sim 10\%$ ) of BSPO was used to overcome any loss of the reagent due to vaporization. This reaction could alternatively be performed in an ice bath. The stacked spectra in Figure 4.16 exhibit the oxidation of crude  $\text{D}_4\text{P}$  which had 10% unreacted diphenylphosphine remaining in the solution. The characteristic peak of the phosphine atoms in the  $\text{D}_4\text{P}$  at  $\sim -9.3$  ppm shifted to  $\sim 30$  ppm after quantitative oxidation. In fact, the 10% of diphenylphosphine ( $\sim -40$  ppm) that remained in the  $\text{D}_4\text{P}$  also oxidized to yield diphenylphosphine oxide ( $\sim 23$  ppm).

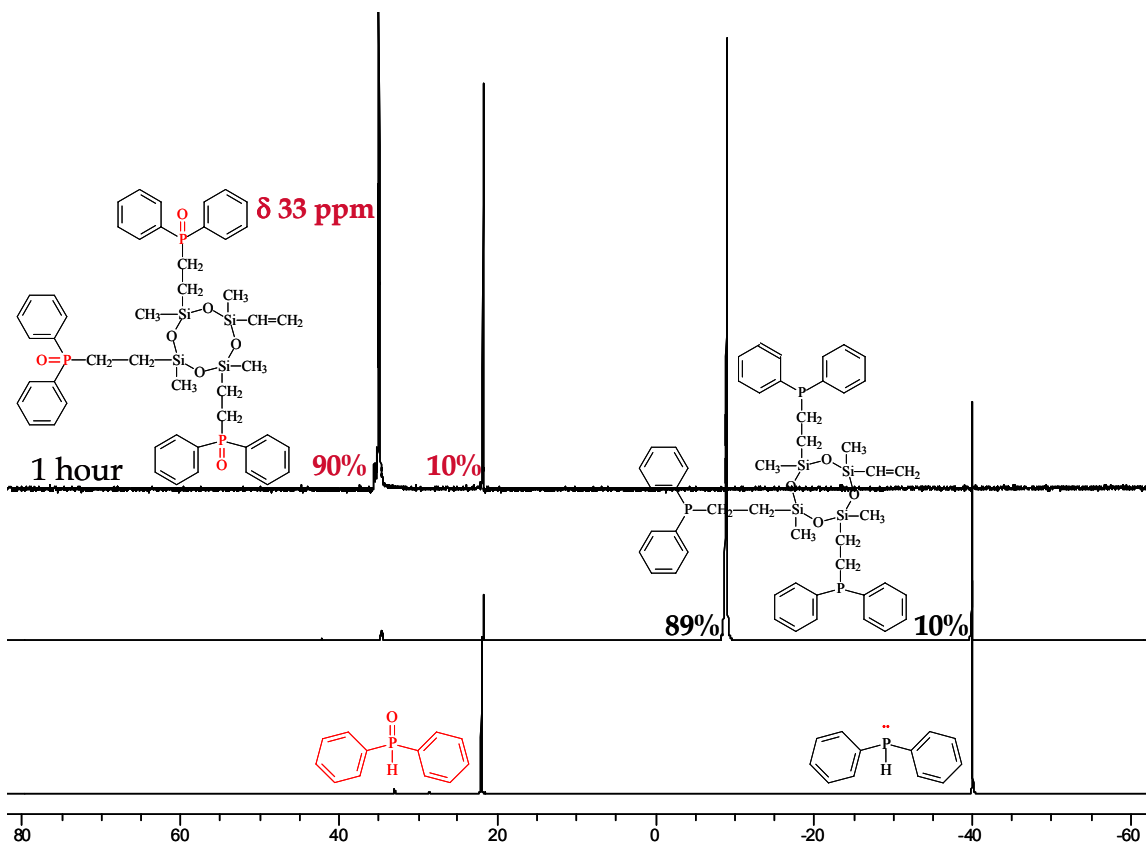


Figure 4.16. Monitoring the Oxidation of Phosphine Substituents on a Siloxane to Yield a Phosphine Oxide Containing Cyclosiloxane Tetramer via  $^{31}\text{P}$  NMR

### 4.3. Synthesis of Polysiloxane Precursors with Reactive Pendent Groups for Functionalization and Crosslinking Reactions

Four families of polysiloxanes were synthesized with systematically controlled amounts of different pendent functional groups: nitrile, phosphine, phosphine oxide, and thioacetic acid (Figure 1.1). Each of the functionalized polysiloxanes was evaluated as candidates for novel thermally conductive adhesive binders and/or stabilizers for metal nanoparticles. The polysiloxane backbone was chosen on the basis that wide service temperature range, low modulus, void free and weatherable networks with thin bond lines could be prepared. Nonpolar PDMS resins do not form stable microcomposite

dispersions with polar fillers. Pendent electron donating groups were introduced to overcome this problem and to enhance the adhesion strength with metal substrates.

Base catalyzed ring opening equilibrations were conducted to yield vinyl terminated, controlled  $M_n$  poly(3-cyanopropylmethyl)siloxane (PCPMS)<sup>3</sup>, poly(methylvinyl)siloxane and poly(dimethyl-co-methylvinyl)siloxane oligomers. Acid catalyzed equilibration reactions were also investigated to yield a series of random hydrido functional polysiloxanes, and carboxylic acid terminated polydimethylsiloxane homopolymers.

Figure 4.17 exhibits a scheme detailing the rationale for carrying out the intended synthetic plan. It should be noted that functionalization reactions were performed on oligomeric precursors. Direct ring opening polymerizations of siloxane cyclics with large and electron withdrawing substituents are typically not efficient. The equilibrium lies towards the side of the cyclics as the size of substituents on siloxane cyclics increases or becomes polar enough to complex with catalysts.<sup>81</sup>

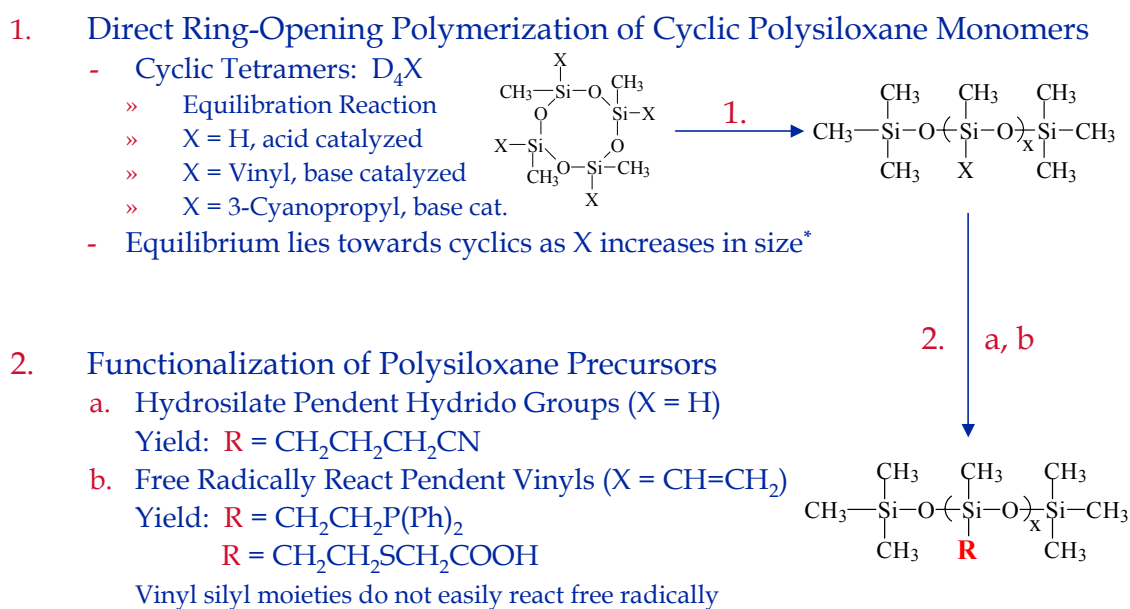


Figure 4.17. Rationale for the Synthetic Plan to Synthesize Polysiloxanes with Controlled Amounts of Pendent Polar Functional Moieties

A general 3-step method was carried out to yield the desired products: lightly crosslinked polysiloxane elastomers with controlled concentrations of pendent polar moieties. First, a series of well defined polysiloxane precursors with controlled molar percentages of pendent vinyl or hydrido groups were synthesized. Secondly, controlled fractions of the reactive repeat units were functionalized with polar moieties. Finally, the residual vinyl or hydrido groups were hydrosilated with appropriate crosslinking reagents to yield elastomeric networks. The network formation reactions and properties will be addressed in Chapter 5.

#### **4.3.1. Synthesis of Polysiloxane with Controlled Concentrations of Methylvinylsiloxy- Repeat Units via Base Catalyzed Equilibration Reactions**

A series of polysiloxanes with controlled amounts of pendent reactive vinyl groups randomly arranged along the backbone were prepared. Poly(methylvinyl)siloxane homopolymers with tailored endgroups were synthesized by base catalyzed equilibration reactions of  $D_4Vi$  (Figures 4.18). Random poly(dimethyl-co-methylvinyl)siloxane copolymers with controlled mole fractions of pendent vinyl groups were prepared by the base catalyzed copolymerization of  $D_4Vi$  and  $D_4$  (Figure 4.19). The molar ratio of methylvinylsiloxy:dimethylsiloxy repeat units was controlled by adjusting the molar ratio of  $D_4Vi:D_4$ . Each of the polymerizations were conducted in the presence of a disiloxane endcapping reagent containing the desired vinyl or aminopropyl endgroups.



The mechanism for the base catalyzed equilibration of D<sub>4</sub>Vi is similar to D<sub>4</sub> (Figure 2.50). The transient catalyst tetramethylammonium disiloxanolate<sup>91</sup> was chosen to initiate the polymerization. It was thermally decomposed and the byproducts were removed with a stream of N<sub>2</sub> bubbling through the solution at 130 °C. The tetramethylammonium disiloxanolate catalyst was prepared by reacting D<sub>4</sub> with tetramethylammonium hydroxide pentahydrate until all of the water of hydration and of reaction was removed (Figure 2.50). Vinyl groups on siloxanes withdraw electron density from the silicon atoms increasing the partial positive charge on silicon, making it more susceptible to attack by base (relative to D<sub>4</sub>).<sup>81</sup> While D<sub>4</sub> is less reactive than D<sub>4</sub>Vi, the reverse is true for the siloxanolate species.<sup>129,130</sup> A dimethyl siloxanolate is reportedly more reactive than a methylvinyl siloxanolate species<sup>31</sup>, therefore D<sub>4</sub>Vi was not used to prepare the catalyst. Tetramethylammonium disiloxanolate catalysts have approximately the same reactivity as CsOH (larger cation, less tightly associated ion pair).<sup>93</sup>

The disiloxanolate catalyst reacts with methylvinylsiloxane species via one of three routes. It may ring open D<sub>4</sub>Vi. This occurs rapidly to yield high molecular weight oligomers early in the equilibration, similar to analogous polymerizations of D<sub>4</sub>.<sup>84</sup> Secondly, the anion may attack another growing chain or attack itself (backbiting). This process occurs throughout the equilibration process until an equilibrium concentration between the cyclic species and linear oligomers forms. For D<sub>4</sub>, ~ 17% cyclics are present at equilibrium.<sup>31</sup> Mixed cyclic species are produced during co-equilibrations, and the equilibrium concentration depends on the molar ratio of the co-monomers. A polydispersity (M<sub>w</sub>/M<sub>n</sub>) of ~ 2.0 is established after the small cyclosiloxanes are removed via vacuum distillation. Finally, the anionic species can attack the Si-O bond of the siloxane dimeric endcapping reagents. The Si-C groups on the endcapping reagents are stable during the equilibration process.

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129. J. K. Paulasaari and W. P. Weber, "Preparation of Highly Regular Poly(1-hydrido-1,3,3,5,5-pentamethyltrisiloxane) and Its Chemical Modification by Hydrosilation, *Macromolecules*, **32**, 6574-6577, 1999.
130. K. Rozga-Wijas, J. Chojnowski, T. Zunfel, S. Boileau, "Controlled Synthesis of Siloxane Copolymers Having an Organosulfur Group by Polymerization of Cyclotrisiloxanes with Mixed Units", *Macromolecules*, **29**, 2711-2720, 1996.

Quantitative  $^{29}\text{Si}$  NMR is a powerful tool that was used to determine number average molecular weights, the random nature of the sequences and the chemical structures of organic moieties attached to silicon atoms. Molecular weight control of the oligomers was obtained by using a stoichiometric amount of endcapping reagent per mole of oligomer. Each peak in the  $^{29}\text{Si}$  NMR spectrum represents a silicon atom with organic substituents corresponding to a silicon endgroup or a siloxane repeat unit in the polymer backbone. The integral areas of the endgroup peaks were normalized to an area of 2 (to represent 2 endgroups per mole), then the areas of the internal silicon peaks were used to define the molecular weights.

Polysiloxanes with two different endgroups were investigated in this research. Aminopropyl terminated poly(methylvinyl)siloxanes were prepared for functionalization with phosphines. The terminal amines were subsequently reacted with isocyanates to yield networks. Platinum catalyzed hydrosilation reactions were prohibited by phosphine groups. Vinyl terminated poly(methylvinyl)siloxanes were prepared for functionalizing with phosphine oxide. Networks from these materials were formed via Pt catalyzed hydrosilation reactions.

$^{29}\text{Si}$  NMR spectra for poly(methylvinyl)siloxane homopolymers terminated on each end with aminopropyldimethylsiloxy- or dimethylvinylsiloxy- groups confirm the characteristic peaks for silicon endgroups (Figure 4.20). The silicon atom for the aminopropyldimethylsiloxy- endgroup is observed at  $\sim 10$  ppm. The dimethylvinylsiloxy- silicon atom, having a vinyl group rather than three saturated aliphatic groups, is observed further upfield at  $\sim -3$  ppm. These chemical shifts parallel shifts for the internal silicons. A methylvinylsiloxy- repeat unit is observed at  $\sim -34$  ppm, further upfield from a dimethylsiloxy- repeat unit ( $\sim -21$  ppm). The bottom spectrum represents the  $\text{D}_4\text{Vi}$  monomer with the characteristic silicon peak at  $\sim -31$  ppm. This was provided to show that the equilibrium cyclics were effectively removed from the two homopolymers. Very small peaks were observed at  $\sim -21.5$  ppm, which are due to dimethylsiloxy- repeat units incorporated into the backbone from the oligomeric tetramethylammonium disiloxanolate catalyst.

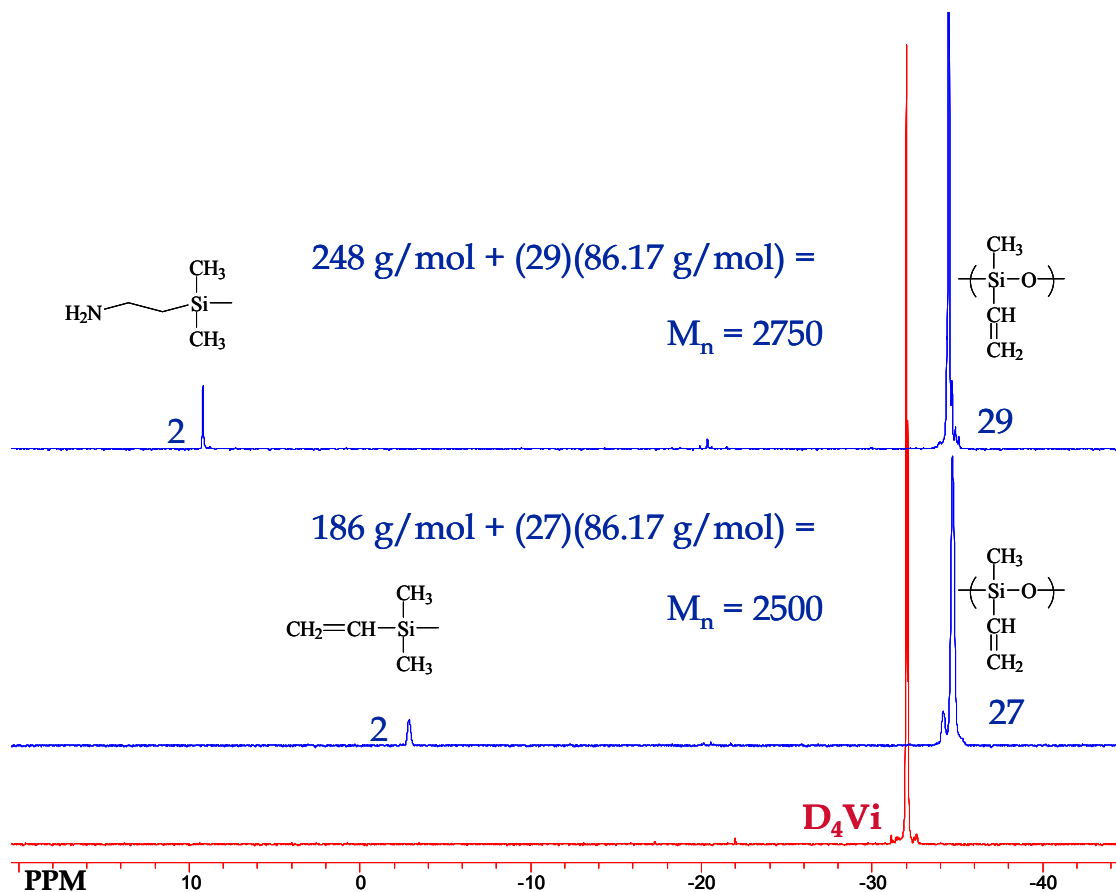


Figure 4.20.  $^{29}\text{Si}$  NMR for Aminopropyl and Vinyl Terminated Poly(methylvinyl)siloxanes and  $\text{D}_4\text{Vi}$

The endgroups from co-equilibrations of  $\text{D}_4$  with  $\text{D}_4\text{Vi}$  were observed in the  $^{29}\text{Si}$  NMR spectra. The bottom spectrum (Figure 4.21) represents a vinyl terminated poly(methylvinyl)siloxane homopolymer with 17 methylvinylsiloxo- repeat units at  $\sim -34$  ppm. Only one endgroup peak was observed for the two dimethylvinylsiloxo- endgroups at  $\sim -3$  ppm. The two upper spectra correspond to vinyl terminated poly(dimethyl-co-methylvinyl)siloxane copolymers with 80 and 54 mol % methylvinylsiloxo- repeat units. Each of the silicon repeat units has several peaks corresponding to the random nature of the microstructures. The copolymers exhibit characteristic silicon peaks for dimethylsiloxo- ( $\sim -21$  ppm) and methylvinylsiloxo- repeat units ( $\sim -34$  ppm). Each of the copolymer spectra exhibits 2 peaks for the 2 dimethylvinylsiloxo- endgroups. These correspond to an endgroup adjacent to a dimethylsiloxo- repeat unit ( $\sim -4$  ppm) or a

methylvinylsiloxo- repeat unit ( $\sim -3$  ppm). The integral areas of the endgroup peaks correspond to the mol fractions of each of the two repeat units in the oligomer chains.

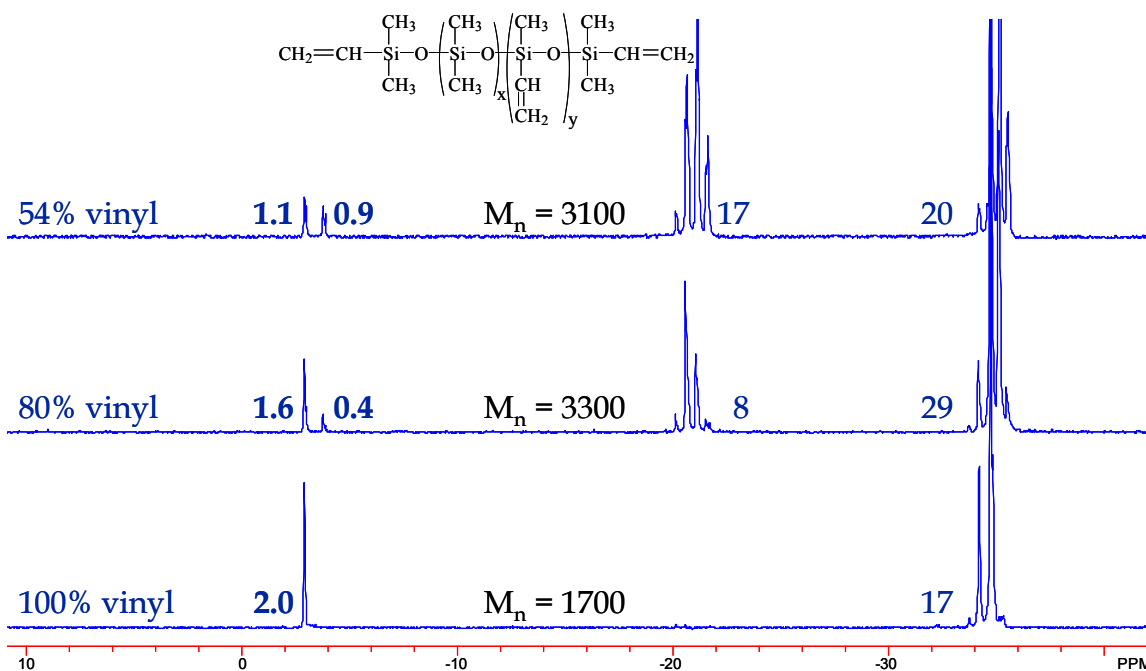


Figure 4.21. Polysiloxanes with Controlled Concentrations of Pendent Vinyl Groups Characterized via  $^{29}\text{Si}$  NMR

A series of poly(methylvinyl)siloxanes and poly(dimethyl-co-methylvinyl)siloxanes were prepared with varied  $M_n$ s (Tables 4.1 and 4.2). The data describe the chemical structures of the endgroups, the composition distributions of the linear chains after removing the equilibrium cyclics, and degrees of polymerization ( $n$ ). The desired copolymer compositions after removing the cyclics were achieved in every case. This indicated that the chemical composition distribution of the linear and the cyclic species in the equilibrates was the same.

Table 4.1. Methylvinylsiloxo- Containing Polysiloxanes with Controlled Mol Fractions of Methylvinylsiloxo- Repeat Units and Characterization Data via  $^{29}\text{Si}$  NMR

Target Composition	Experimental Composition*	Si-29 NMR Analysis for # and Types of Units			
		2 endgroups	vinyl	dimethyl	n
100% vinyl	100% vinyl	2 aminopropyl	29	0	29
50% vinyl	50% vinyl	2 aminopropyl	44	44	88
20% vinyl	19% vinyl	2 vinyl	6	25.5	31.6
35% vinyl	34% vinyl	2 vinyl	10.4	19.6	30.2
100% vinyl	100% vinyl	2 vinyl	26.3	0.3	26.6
20% vinyl	20% vinyl	2 vinyl	7.6	31	38.6
20% vinyl	20% vinyl	2 vinyl	14.2	58	72.1
20% vinyl	20% vinyl	2 vinyl	28.4	114	142.4
100% vinyl	100% vinyl	2 vinyl	17.4	0	17.4
80% vinyl	79% vinyl	2 vinyl	29.3	7.7	36.5
55% vinyl	54% vinyl	2 vinyl	19.7	16.8	37.0

\*Chemical compositions were calculated via  $^{29}\text{Si}$  NMR. The error was  $\pm 8-10\%$ .

Table 4.2. Molecular Weight Control of the Methylvinylsiloxo- Containing Polysiloxanes

Chemical Composition	Endgroups	g monomer/mol dimer	Mn*
100% vinyl	Aminopropyl	1180	2750
50% vinyl	Aminopropyl	5910	7300
19% vinyl	Vinyl	2220	2580
34% vinyl	Vinyl	2220	2520
100% vinyl	Vinyl	1580	2470
20% vinyl	Vinyl	2780	3120
20% vinyl	Vinyl	5550	5690
20% vinyl	Vinyl	11110	11070
100% vinyl	Vinyl	1000	1690
79% vinyl	Vinyl	3000	3130
54% vinyl	Vinyl	3100	3280

\*M<sub>n</sub>s were calculated via  $^{29}\text{Si}$  NMR. The error was  $\pm 8-10\%$ .

Molecular weights of the equilibrates were controlled by the ratios of endblocking reagents to cyclic monomers (Table 4.2). All of the molecular weights obtained after

removing the cyclics were within experimental error of the targeted values with the exception of the poly(methylvinyl)siloxane homopolymers. It has been established that ~17 % cyclics are present at equilibrium for D<sub>4</sub>.<sup>33</sup> The equilibrium concentration of cyclomethylvinylsiloxanes has not yet been established (Figure 4.22). GPC was used to verify M<sub>n</sub>s and qualitative equilibrate distributions. M<sub>n</sub> of a poly(dimethyl-co-methylvinyl)siloxane via GPC was 2410 g/mol and 2850 g/mol at equilibrium and after distillation, respectively, with an error of ± 500 g/mol. It is recommended that the cyclic distribution be investigated throughout these equilibrations to better understand the effects on the ability to control molecular weight. After vacuum distillation, a small percentage of small linear and/or larger vinyl cyclosiloxanes remain. This mixture of cyclic species with different amounts of methylvinylsiloxy- and dimethylsiloxy-substituents form throughout the equilibration process, therefore the amount of cyclics should change with varied copolymer compositions.

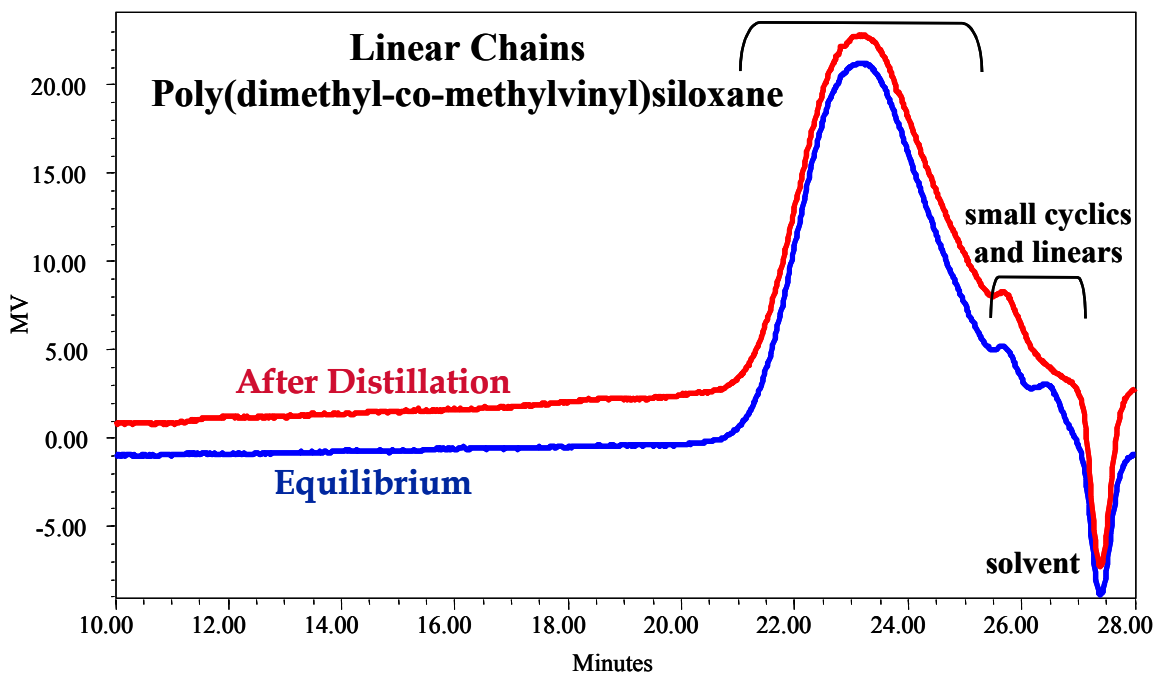
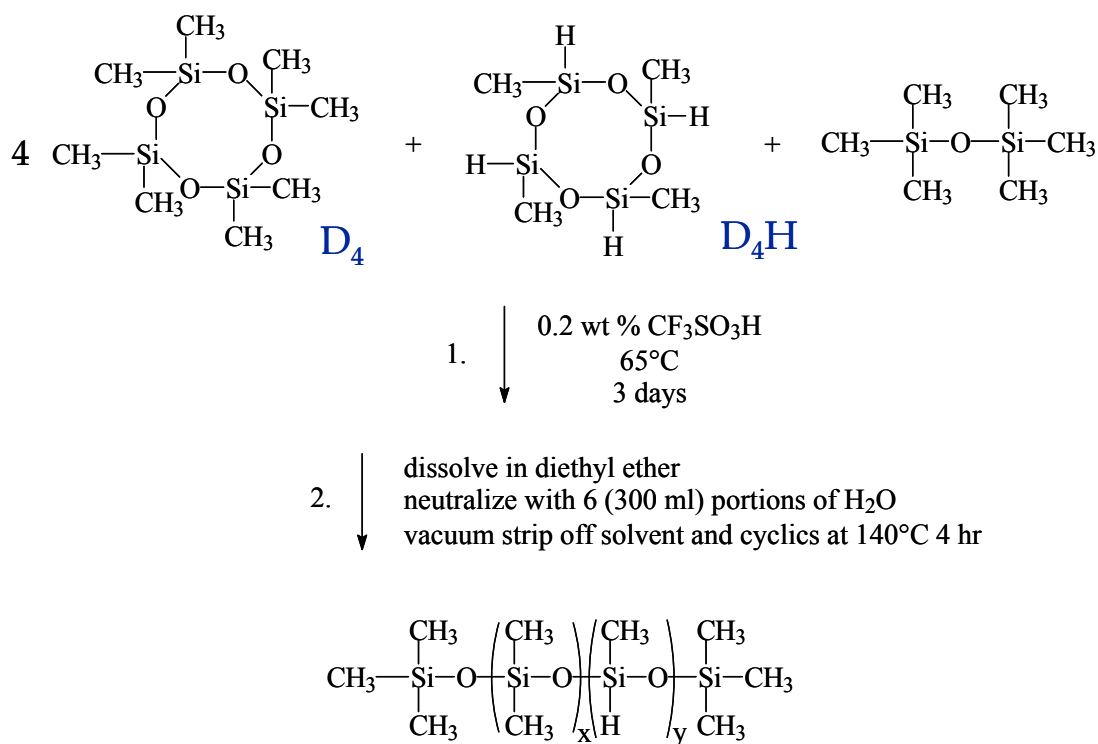


Figure 4.22. GPC Curves at Equilibrium and After Distillation for a Random Poly(dimethyl-co-methylvinyl)siloxane with 20% Methylvinylsiloxy- Repeat Units

### 4.3.2. Acid Catalyzed Equilibration Reactions to Yield Polysiloxanes with Controlled Concentrations of Methylhydridosiloxy- Repeat Units

A series of poly(dimethyl-co-methylhydrido)siloxanes was synthesized by the acid catalyzed co-equilibrations of  $D_4$  with  $D_4H$  (Figure 4.23). The mol fractions of methylhydridosiloxy- repeat units were controlled by adjusting the molar ratio of the cyclic tetramers. These materials were subsequently functionalized with allyl cyanide and crosslinked to form networks.



### Poly(dimethyl-co-methylhydrido)siloxane

Figure 4.23. Synthesis of a Trimethylsiloxy- Terminated Poly(dimethyl-co-methylhydrido)siloxane

Acid catalyzed co-equilibrations of  $D_4$  with  $D_4H$  were performed with triflic acid (Figure 4.23). An acid catalyst was used because an Si-H bond is susceptible to attack by base. The Si-H bonds react with hydroxide in 95% ethanol to yield silanols, which will

condense to form siloxane bonds.<sup>131</sup> Molecular weights were controlled by adjusting the weights of the cyclic monomers per mol of hexamethyldisiloxane endcapping reagent.

A proposed mechanism for an acid catalyzed equilibration of D<sub>4</sub> involves protonation of the partially negative oxygen with the strong acid, followed by propagation through the oxonium ion active species (Figure 4.24).<sup>132</sup>

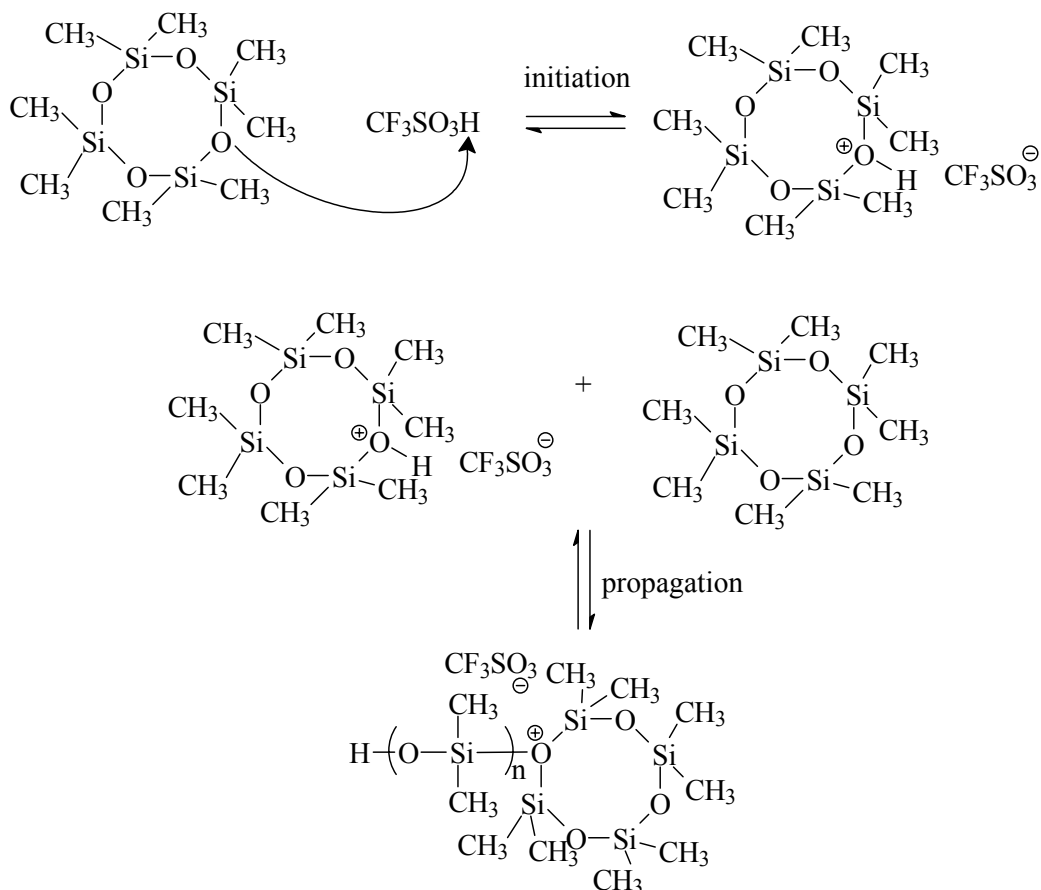


Figure 4.24. Initiation and Propagation for the Acid Catalyzed Ring Opening Polymerization of D<sub>4</sub>

131. J. K. Paulasaari and W. P. Weber, "Preparation and Orthogonal Polymerizations of 1-Hydrido-1-vinyldimethylsiloxy-3,3,5,5-tetramethylcyclotrisiloxane", *Macromolecules*, **32**, 5217-5221, 1999.

132. S. W. Kantor, W. T. Grubb and R. C. Osthoff, *J. Am. Chem. Soc.*, **76**, 5190, 1954.

$^{29}\text{Si}$  NMR was used to characterize the poly(dimethyl-co-methylhydrido)siloxanes with controlled compositions of methylhydridosiloxy- repeat units (Figure 4.25). The silicon atoms of the internal methylhydridosiloxy- units are observed at  $\sim 35 - 38$  ppm, depending on the adjacent microstructures. The dimethylsiloxy- repeat unit silicon atoms are observed between  $\sim 18-22$  ppm. The multiple peaks within each group are indicative that the microstructures of the materials were random in nature as opposed to having blocky structures. The characteristic peaks for the silicon atoms of the trimethylsiloxy-endgroups are observed at  $\sim 10$  ppm (adjacent to a methylhydridosiloxy- repeat unit) and  $\sim 8$  ppm (adjacent to a dimethylsiloxy- repeat unit). The integral areas for these peaks corresponded well to the targeted chemical compositions.

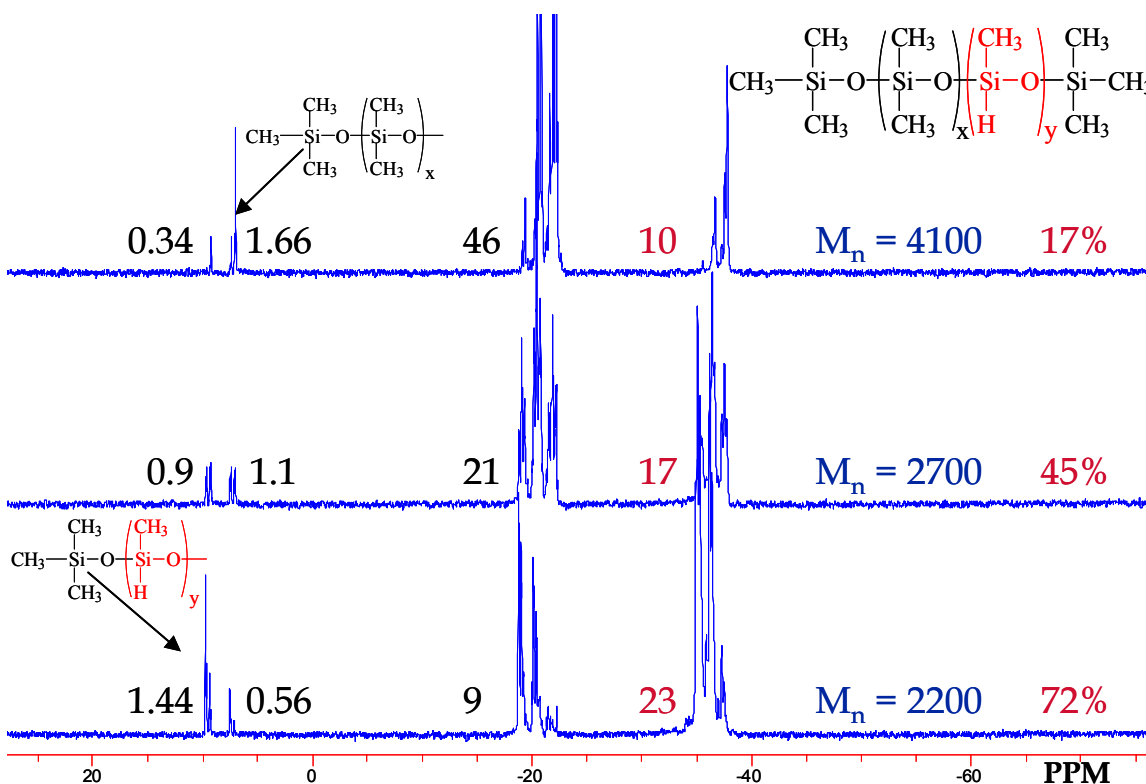


Figure 4.25. Poly(dimethyl-co-methylhydrido)siloxanes with Controlled Mol Fractions of Hydrido Groups Analyzed via  $^{29}\text{Si}$  NMR

Carboxylic acid containing polysiloxanes were also of interest to investigate the potential of stabilizing magnetic nanoparticles, specifically magnetite. Carboxylic acid

terminated polydimethylsiloxanes were prepared by the triflic acid equilibration of D<sub>4</sub> in the presence of 1,3-bis(carboxypropyl)tetramethyldisiloxane as the endcapping reagent (Figure 4.26).<sup>133</sup> The silicon atoms of the carboxypropylsiloxyl- endgroups are observed at ~ 7 ppm (Figure 4.27).<sup>134,135</sup>

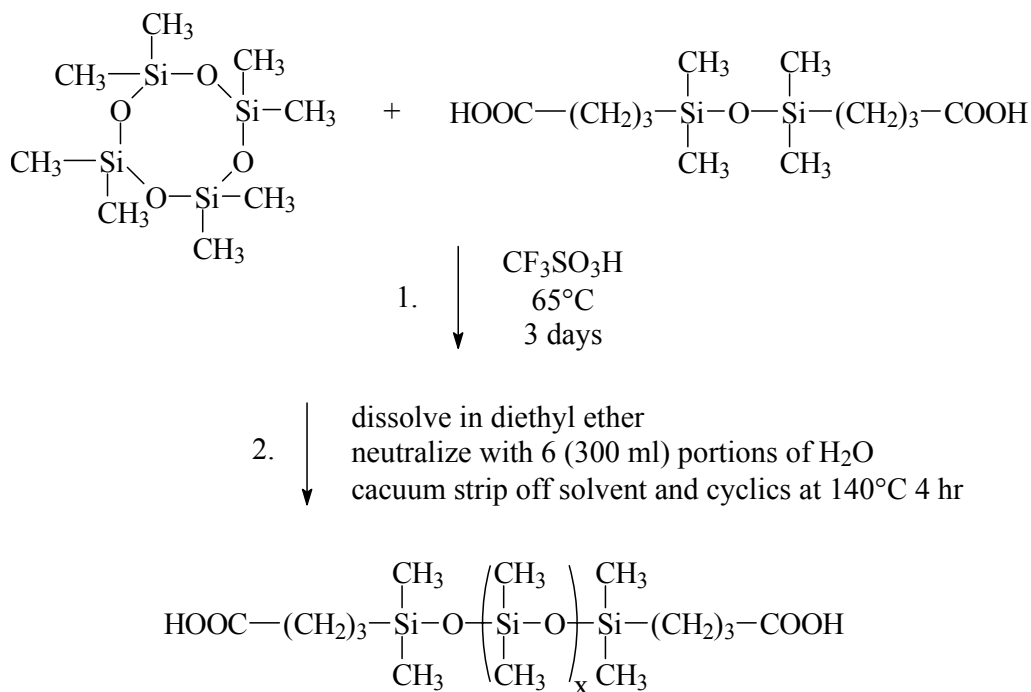


Figure 4.26. Synthesis of a Carboxylic Acid Terminated Polydimethylsiloxane

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133. B. S. Jewel, J. S. Riffle, D. Allison and J. E. McGrath, *Polym. Prepr.*, 30(1), 295, 1989.
134. E. A. Williams, "Recent advances in Silicon-29 NMR Spectroscopy", in *Annual Reports on NMR Spectroscopy*, Vol. 15, 235-289, Academic Press, London, 1983.
135. R. K. Harris and M. L. Robins, "<sup>29</sup>Si nuclear magnetic resonance studies of oligomeric and polymeric siloxanes: 4. Chemical shift effects of end-groups", *Polymer*, **19**, 1123-1132, 1978.

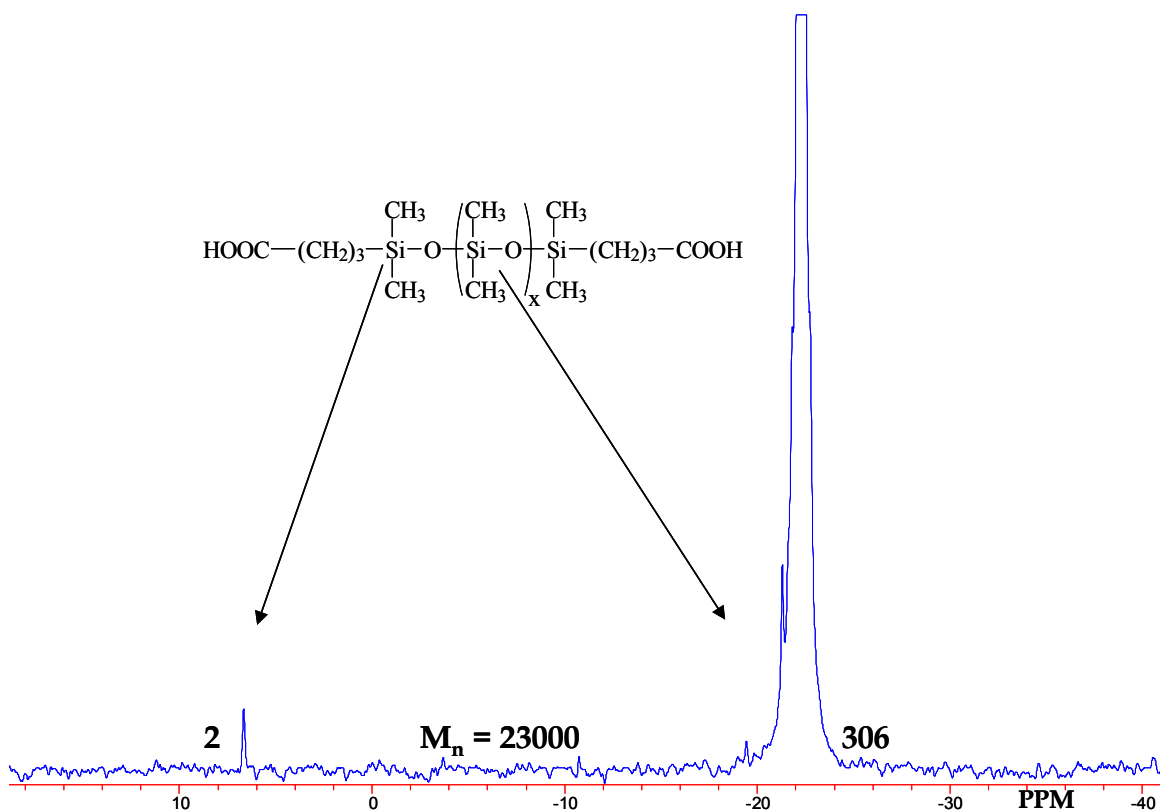


Figure 4.27.  $^{29}\text{Si}$  NMR of a Carboxylic Acid Terminated Polydimethylsiloxane

A series of poly(methylhydrido)siloxanes and a carboxylic acid terminated polydimethylsiloxane were prepared with varied  $M_n$ s (Tables 4.3 and 4.4). The data describe the chemical structures of the endgroups, the composition distributions of the linear chains after removing the equilibrium cyclics, and degrees of polymerization ( $n$ ) via  $^{29}\text{Si}$  NMR. The desired copolymer compositions were achieved in every case. This indicated that the chemical composition distribution of the linear and the cyclic species in the equilibrates was the same.

Molecular weights of the equilibrates were controlled by the ratios of endblocking reagents to cyclic monomers (Table 4.4). Each of the equilibrations was performed with 0.2 wt.% of triflic acid. Molecular weight control has not yet been established and will be addressed via GPC studies which can determine the point at which equilibrium occurs and when the polydispersity reaches  $\sim 2.0$ , characteristic for polysiloxanes equilibrations.

Table 4.3. Poly(dimethyl-co-methylhydrido)siloxanes with Controlled Concentrations of Methylhydridosiloxy- Repeat Units and  $^{29}\text{Si}$  NMR Data Analysis

Target Composition	*Experimental Composition	Si-29 NMR Analysis of # and Type of Units		
		Hydrido	Dimethyl	n
75% hydrido	72% hydrido	23	9	32.1
50% hydrido	45% hydrido	16.8	20.5	37.3
20% hydrido	17% hydrido	9.6	46.2	55.7
20% hydrido	19% hydrido	11.8	55.4	67.2

\*Chemical compositions were calculated via  $^{29}\text{Si}$  NMR. The error was  $\pm 8-10\%$ .

Table 4.4. Molecular Weight Control of the Methylhydridosiloxy- Containing Polysiloxanes

Chemical Composition	Endgroups	g monomer/mol dimer	Mn
72% hydrido	methyl	4450	2200
45% hydrido	methyl	4440	2680
17% hydrido	methyl	4440	4140
19% hydrido	methyl	4610	4980

\*M<sub>n</sub>s were calculated via  $^{29}\text{Si}$  NMR. The error was  $\pm 8-10\%$ .

#### 4.4. Introduction to Functionalized Polyorganosiloxanes

Four families of polysiloxanes were synthesized with different pendent functional groups: nitrile, phosphine, phosphine oxide, and thioacetic acid. Each of the functionalized oligomers were evaluated as candidates for thermally conductive adhesive binders. Dispersion quality as a function of the concentration of silica-coated AlN was studied with the polyorganosiloxanes to yield stable microcomposites. The minimum percentage of the best functional pendent group to afford good adhesion and yield stable microcomposite dispersions was considered. The polar functional polysiloxane microcomposites offered higher thermal conductivities than previously reported for nonpolar polysiloxanes,<sup>1</sup> and provide promise as new materials for thermally conductive adhesives.

A series of phosphine containing polysiloxanes were synthesized by the free radical addition of diphenylphosphine onto pendent vinyl groups of random poly(dimethyl-co-methylvinyl)siloxane precursors. Phosphine oxide containing polysiloxanes were prepared by oxidizing the pendent phosphine groups on polysiloxanes.<sup>76</sup> Thioacetic acid substituted polysiloxanes were prepared by the ene-thiol addition<sup>136,137,138</sup> of mercaptoacetic acid onto random poly(dimethyl-co-methylvinyl)siloxane precursors. Random poly(dimethyl-co-methylhydrido)siloxanes were functionalized with nitrile groups by hydrosilation with allyl cyanide.

#### 4.4.1. Synthesis of Polysiloxanes with Controlled Concentrations of Pendent Phosphine Moieties

A novel method was used to synthesize polysiloxanes with systematically controlled concentrations of pendent diphenylphosphine containing substituents. Polysiloxane precursors with precisely controlled mol fractions of pendent vinyl groups predetermined the maximum amount of phosphine substitution. Free radical addition reactions of diphenylphosphine onto pendent vinyl groups of vinyl containing polysiloxane homo- and copolymers were performed to yield a series of poly(dimethyl-co-methylvinyl-co-methyl,2-diphenylphosphineethyl)siloxanes (Figure 4.28). This synthesis paralleled an excellent study by J. Chojnowski and K. Rózga for the investigation of diphenylphosphine substitution onto a cyclosiloxane trimer containing one vinyl group (described in detail in Chapter 2).<sup>75</sup>

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136. E. L. Jenner and R. V. Lindsey Jr., *J. Am. Chem Soc.*, **83**, 1911-1915, 1961.
137. G. A. Gornowicz, J. W. Ryan and J. L. Speier, *J. Org. Chem.*, **33**(7), 2918-2924.
138. M. Ścibiorek, N. K. Gladkova, J. Chojnowski, *Polymer Bulletin*, **44**, 377-384, 2000.

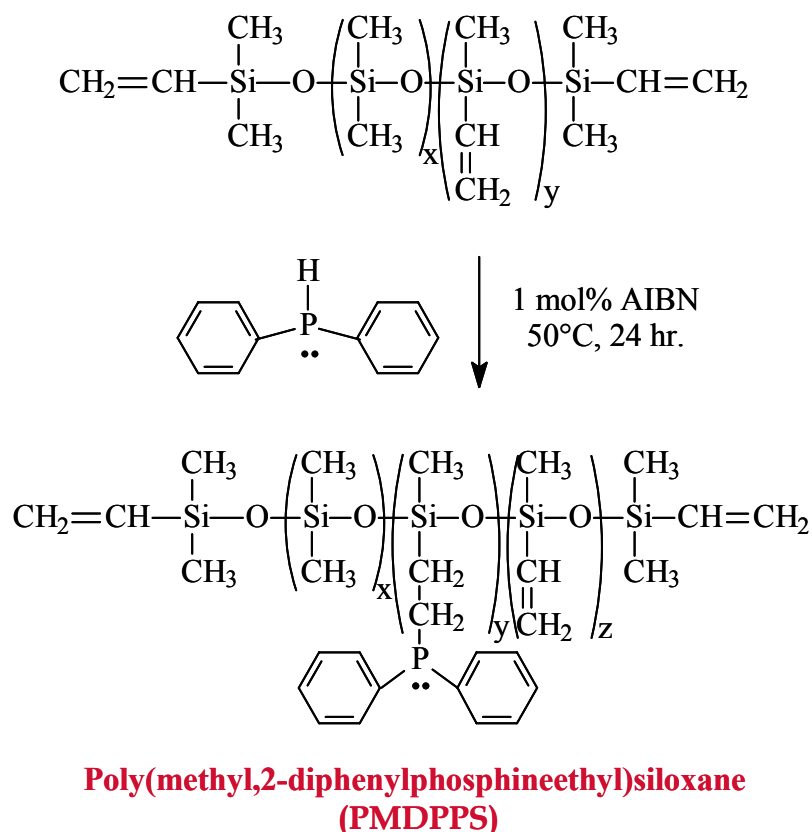


Figure 4.28. Synthesis of Poly(dimethyl-co-methylvinyl-co-methyl,2-diphenylphosphineethyl)siloxane

Phosphine containing polysiloxanes were prepared by Chojnowski and Rózga via anionic ring-opening polymerizations of phosphonyl containing cyclotrisiloxanes.<sup>75</sup> Diphenylphosphine readily oxidizes to yield diphenylphosphonious acid (Figure 4.29).<sup>75</sup> Trace amounts of this side product reportedly caused side reactions and varied kinetics to occur in these reactions. Repeated fractional recrystallizations and column chromatography were required to isolate a pure trimer suitable for anionic ring opening polymerization.<sup>75</sup>

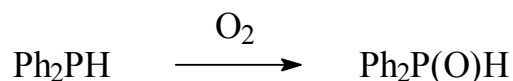


Figure 4.29. Oxidation of Diphenylphosphine<sup>75</sup>

Direct ring opening polymerization of siloxanes with large or very polar substituents is inefficient and sometimes impossible.<sup>81,139</sup> Oligomers ( $M_w$  in most cases  $\sim 10000$  g/mol) with an irregular arrangement of phosphine groups and broad polydispersity ( $M_w/M_n > 2$ ) were obtained.<sup>75</sup> Specifically, phosphine atoms on the diphenylphosphine substituents interacted very strongly with electrophiles. A stable chelate was proposed to form between the phosphine atoms and the cation associated with the anionic propagation center (Figure 2.47).<sup>75</sup> This was reasoned to account for the relatively low yields of polymers with larger than expected heterogeneity indices for living anionic polymerizations of cyclosiloxane trimers.<sup>75</sup> Interestingly, oligomers with more regular microstructural compositions and lower polydispersities were obtained when the sulfur containing cyclosiloxane trimer was polymerized.<sup>75</sup>

The procedure for synthesizing the D<sub>4</sub>P cyclic model tetramer corresponded with the literature method for successful addition of diphenylphosphine substitution onto a cyclosiloxane trimer with one vinyl group.<sup>75</sup> AIBN was added to D<sub>4</sub>Vi in two portions: 0.1 mol % based on vinyl equivalents (eq.) at 40 °C, and 0.05 mol % based on vinyl eq. at 115 °C. Typically, 39 % reacted after 2 days, and 89% after 4 days. No more than 90% of the addition product was obtained after 7 days of stirring at 115 °C, presumably due to steric hindrance between the 4 bulky methyl,2-diphenylphosphineethyl-substituents. The % conversion of vinyl groups from diphenylphosphine addition for a representative reaction was monitored graphically (Figure 4.30).

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139. J. Chojnowski, M. Cypriak, W. Fortuniak, K. Rózga-Wijas and M. Ścibiorek, "Controlled Synthesis of vinylmethylsiloxane-dimethylsiloxane gradient, block and alternate copolymers by anionic ROP of cyclotrisiloxanes", *Polymer*, **43**, 1993-2001, 2002.

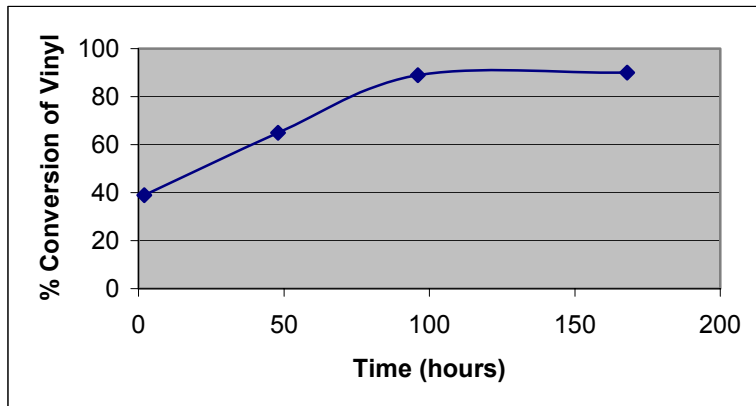


Figure 4.30. Percent Conversion of Vinyl Groups by the Diphenylphosphine Addition to D<sub>4</sub>Vi Versus Time at 155 °C Using 0.15 Mol % AIBN Based on Equivalents of Vinyl

A design experiment was performed using a poly(methylvinyl)siloxane precursor ( $M_n = 2470$  g/mol) to elucidate optimal reaction conditions to yield 100% of the addition product with minimum reaction time. Variables for the experiment were reaction temperature and mol % of AIBN based on equivalents of vinyl (Table 4.5). The temperature was lowered from 115 °C (from the original experiment) and only one portion of AIBN was added to the solution at the beginning of the reaction under a blanket of N<sub>2</sub>. This was done to minimize exposure of the reaction to the environment that occurred during addition of the second AIBN portion.

Table 4.5. Design Experiment for the Optimization of Diphenylphosphine Addition Reactions with Poly(methylvinyl)siloxanes

Temperature	Mol % AIBN	Deoxygenated	Vinyl % Conversion	Conversion Time
100 °C	3	no	82%	7 days
80 °C	3	no	85%	7 days
50 °C	3	no	89%	4 days
50 °C	0.3	no	87%	8 days
50 °C	1	no	93%	5 days
<b>50 °C</b>	<b>0.1</b>	<b>yes</b>	<b>99%</b>	<b>1 day</b>

Reaction temperatures strongly affected the rate of vinyl conversion. As the temperature was lowered from 100 °C to 80 °C to 50 °C, the % conversion of vinyl groups increased from 82% - 89% using 3 mol % AIBN based on equivalents of vinyl (Table 4.5). The reaction performed at 50 °C yielded 89% conversion in 4 days, compared to 7 days for the higher temperature reactions. Lower temperatures proved beneficial as expected when considering the  $t_{1/2}$  of AIBN  $\sim$  8 min at 115 °C and  $\sim$  21 hr at 60 °C.

The amount of AIBN was also adjusted for reactions performed at 50 °C to maximize the % conversion of vinyl groups. An important discovery was established by deoxygenating the reaction mixture. When polysiloxane precursors were deoxygenated and maintained in an oxygen free environment during the addition of diphenylphosphine and AIBN,  $\sim$  100 % conversion was obtained. More than 99% conversion of the vinyl groups was achieved for the addition of 80 mol % diphenylphosphine to a 2473 g/mol poly(methylvinyl)siloxane with only 0.1 mol % AIBN based on eq. of vinyl. All functionalization reactions performed thereafter were done using 0.1 mol % AIBN at 50 °C. Percent conversions for vinyl groups on poly(methylvinyl)siloxanes with and without deoxygenation are portrayed graphically (Figures 4.31 and 4.32).

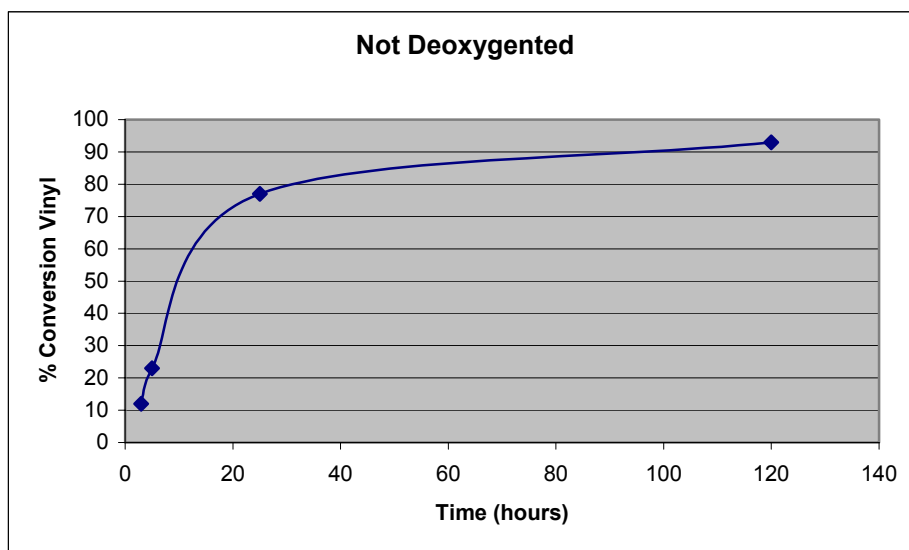


Figure 4.31. Percent Conversion of Vinyl Groups by the Diphenylphosphine Addition to Poly(methylvinyl)siloxane ( $M_n = 2470$  g/mol) Versus Time at 50 °C With Deoxygenation of the Oligomeric Precursor

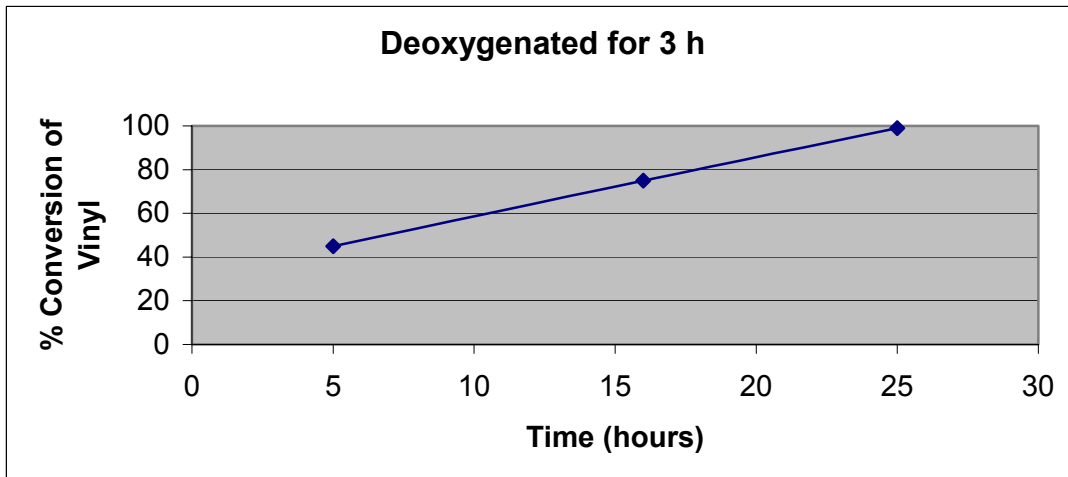


Figure 4.32. Percent Conversion of Vinyl Groups by the Diphenylphosphine Addition to Poly(methylvinyl)siloxane ( $M_n = 2470$  g/mol) Versus Time at 50 °C Without Deoxygenation of the Oligomeric Precursor

Vinyl containing polysiloxane precursors were reacted with diphenylphosphine to yield well-defined poly(dimethyl-co-methylvinyl-co-methyl,2-diphenylphosphineethyl)siloxanes with tailored concentrations of diphenylphosphine substituents statistically arranged in the microstructure.  $^{29}\text{Si}$  NMR was used to determine the percent of functionalization before and after diphenylphosphine substitution (Figure 4.33). Diphenylphosphine was added to an aminopropyl terminated poly(dimethyl-co-methylvinyl)siloxane precursor ( $M_n = 7300$  g/mol) with 50 mol % methylvinylsiloxyl-repeat units ( $\sim -35$  ppm). The silicon atoms of the newly formed methyl,2-diphenylphosphineethylsiloxyl-repeat units are observed at  $\sim -23$  ppm. This indicated that the phosphine moiety is far enough away from the silicon atom to not affect the characteristic position of a  $\text{CH}_3\text{SiCH}_2$  repeat unit. The two aminopropylsiloxyl-endgroups ( $\sim 8$  ppm and 9 ppm) were unaffected during the free radical addition reaction. Two endgroup peaks are observed since the endgroups may be adjacent to either a dimethylsiloxyl- or methyl,2-diphenylphosphineethylsiloxyl-repeat unit.



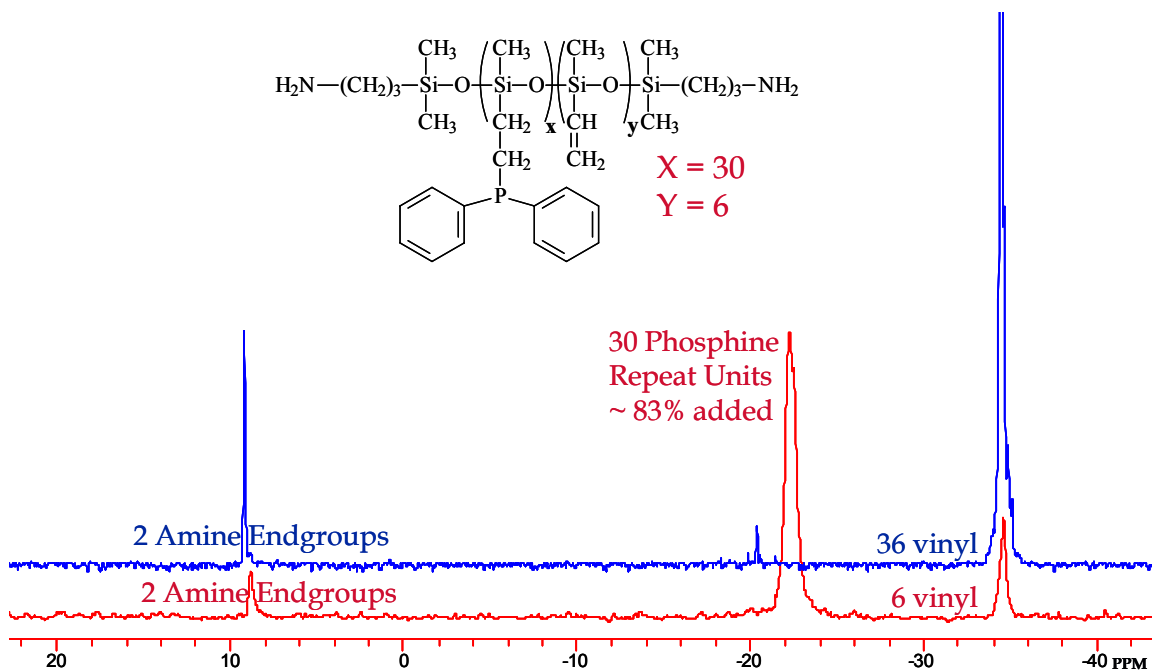


Figure 4.34.  $^{29}\text{Si}$  NMR for an Aminopropyl Terminated Poly(dimethyl-co-methylvinyl-co-methyl,2-diphenylphosphineethyl)siloxane with 80 Mol % Methyl,2-diphenylphosphineethylsiloxo- Repeat Units

Interestingly, when a vinyl terminated poly(dimethyl-co-methylvinyl)siloxane was reacted with diphenylphosphine, more than 2 endgroup peaks were observed in the  $^{29}\text{Si}$  NMR spectrum (Figure 4.35). Diphenylphosphine was added to react with one half of the vinyl groups of a poly(dimethyl-co-methylvinyl)siloxane ( $M_n = 2584$ ) containing 20 mol % vinylmethylsiloxo- repeat units. The two original dimethylvinylsiloxo-endgroups ( $\sim -3$  ppm and  $-4$  ppm) are adjacent to dimethylsiloxo- or methylvinylsiloxo-repeat units. The vinyl endgroups are equally as reactive as the pendent vinyl groups along the chain. Both 50 % of the pendent vinyl groups and 50 % of the vinyl endgroups reacted to yield methyl,2-diphenylphosphineethylsiloxo- repeat units and methyl,2-diphenylphosphineethylsilyl- endgroups, respectively. The original dimethylvinylsiloxo-endgroups ( $\sim -3$  ppm) adjacent to methylvinylsiloxo- repeat units had reacted completely. Two peaks were observed for the silicon atoms of the newly formed methyl,2-diphenylphosphineethylsiloxo- endgroups ( $\sim 7.5$  ppm and  $\sim 8.5$  ppm) adjacent to dimethylsiloxo- or methylvinylsiloxo- repeat units.

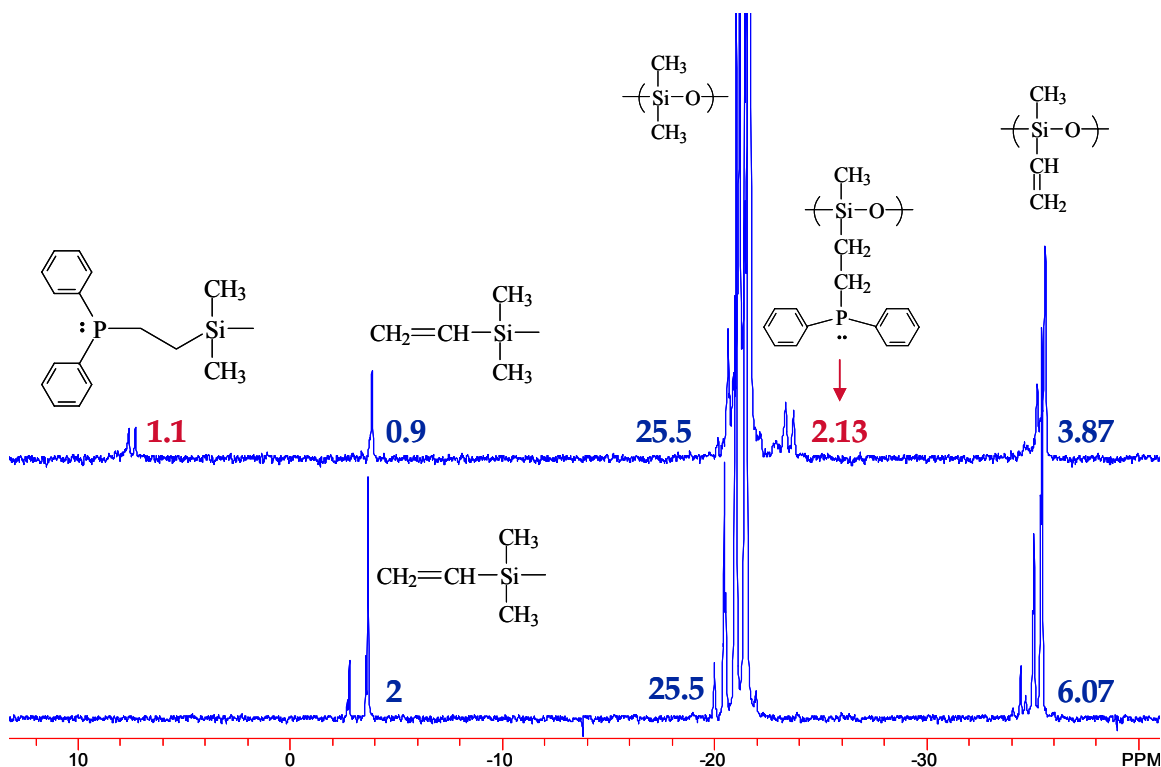


Figure 4.35.  $^{29}\text{Si}$  NMR of a Vinyl Terminated Poly(dimethyl-co-methylvinyl-co-methyl,2-diphenylphosphineethyl)siloxane with 10 Mol % Methyl,2-diphenylphosphineethylsiloxyl- Repeat Units

$^1\text{H}$  NMR confirmed the expected terminal adduct<sup>5</sup> via the addition of diphenylphosphine to poly(methylvinyl)siloxanes (Figure 4.36). The diphenylphosphinyl free radical attacks the least substituted carbon (with the most hydrogens) to form the more stable secondary radical.<sup>5,140</sup> This radical subsequently abstracts an available hydrogen atom to yield the  $\alpha$ -addition product. Both of the newly formed methylene protons  $\sim 0.65$  ppm and  $\sim 2.05$  ppm were formed as a result of the  $\alpha$ -addition product. The  $\beta$ -addition product was not observed for any of the phosphine containing polysiloxanes.<sup>5</sup> The 10 diphenylphosphine protons integrated to a slightly larger area of 10.5 as a small amount of unreacted diphenylphosphine was present. Unreacted

140. J. Pellon, *J. Am. Chem. Soc.*, **83**, 1915 – 1916, 1961.

diphenylphosphine was effectively removed by precipitating the oligomer in methanol (Figure 4.37).  $^1\text{H}$  NMR revealed that the polymer had a controlled concentration of vinyl groups available for subsequent crosslinking with a silane crosslinking reagent (with the oxidized form of the oligomer).

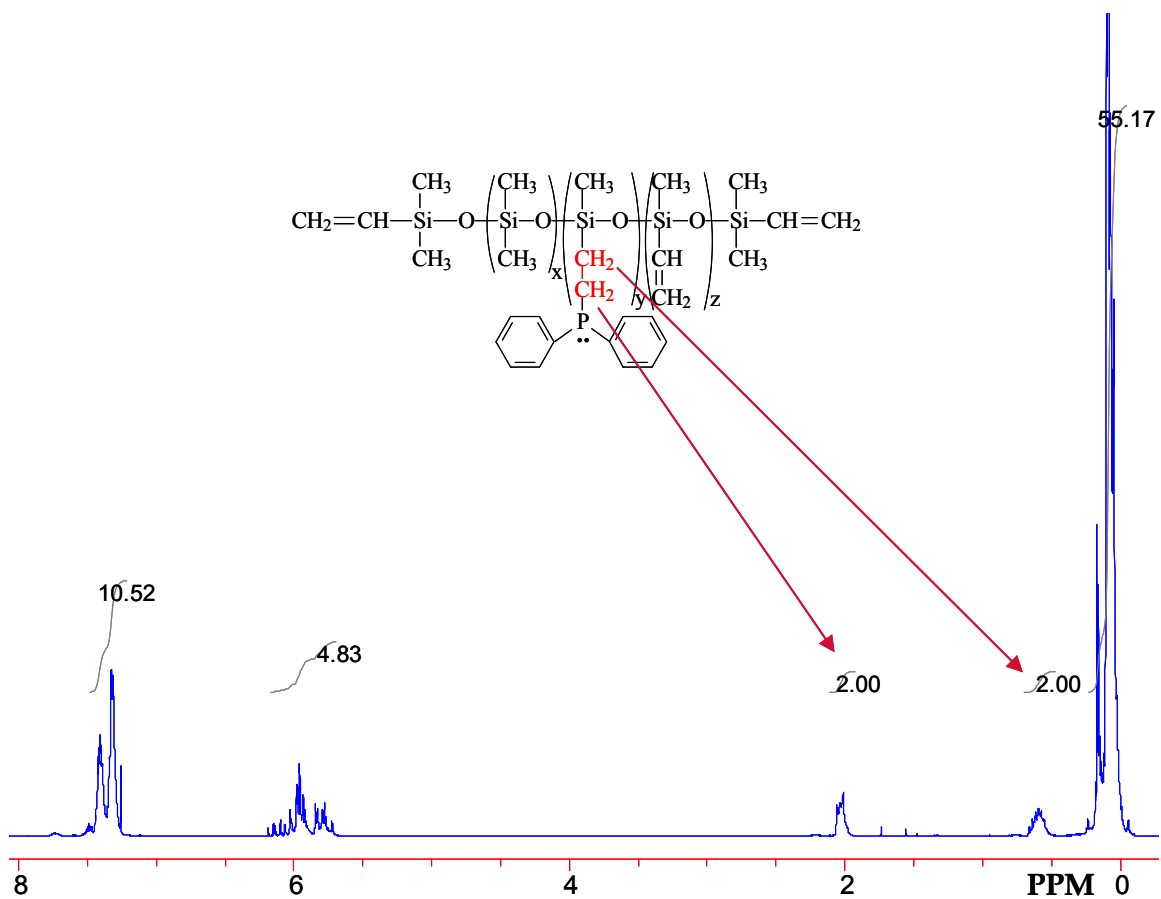


Figure 4.36.  $^1\text{H}$  NMR of a 3200 g/mol Vinyl Functional Polysiloxane Containing 10 Mol % Phosphine Containing Pendent Moieties from the  $\alpha$ -Addition of Diphenylphosphine

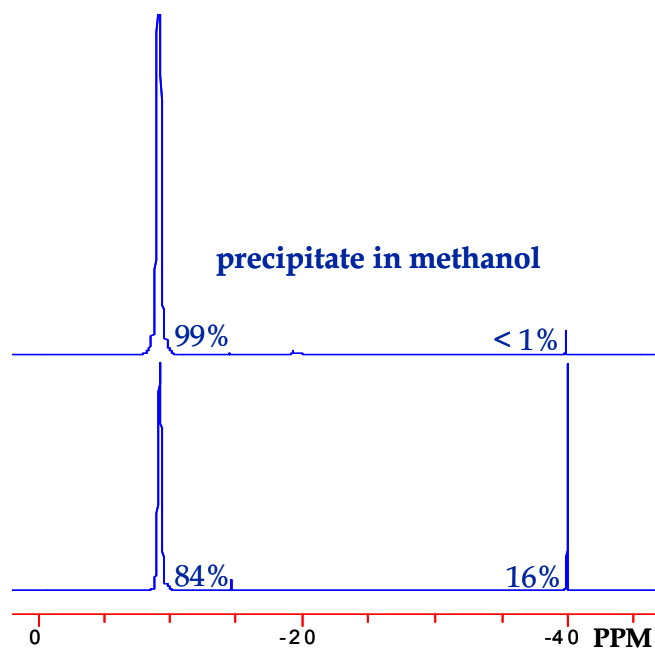


Figure 4.37.  $^{31}\text{P}$  NMR After (upper) and Before (lower) the Precipitation of a Phosphine Containing Polysiloxane in Methanol to Remove Diphenylphosphine

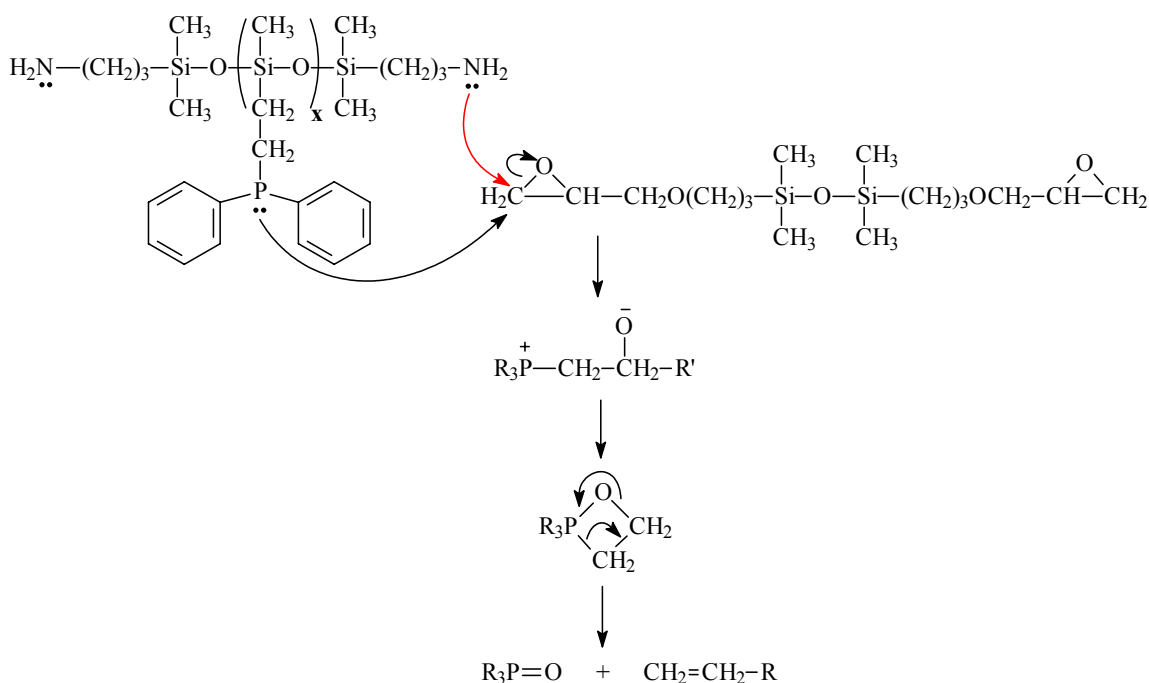
A series of poly(dimethyl-co-methylvinyl-co-methyl,2-diphenylphosphineethyl)siloxanes with controlled concentrations of methylvinylsiloxo- and methyl,2-diphenylphosphineethylsiloxo- repeat units were prepared and characterized via  $^{29}\text{Si}$  NMR (Table 4.6). The data describes the chemical structures of the endgroups, the composition distributions and degrees of polymerization ( $n$ ).

Table 4.6. Series of Poly(dimethyl-co-methylvinyl-co-methyl,2-diphenylphosphineethyl)siloxanes with Controlled Concentrations of Vinyl and Phosphine Substitution Characterized via  $^{29}\text{Si}$  NMR Data Analysis

Mol % Repeat Unit			Silicon-29 NMR Analysis					
Phosphine	Vinyl	Dimethyl	Endgroups	Phosphine	Vinyl	Dimethyl	$n$	Mn
83%	15%	2%	2 aminopropyl	29.6	6.2	2.3	36.7	9320
44%	6%	50%	2 aminopropyl	38.5	5.2	43.7	87.5	15050
77%	20%	3%	2 phosphine	20	5.8	1	28.7	6570
10%	14%	76%	1.1 phosphine, 0.9 vinyl	2.4	3.8	25.5	31.5	3200
15%	9%	76%	1.7 phosphine, 0.3 vinyl	3.5	2.6	25.5	31.6	3580

Phosphine prohibits Pt catalyzed hydrosilation reactions; therefore the amine terminated oligomers were reacted with 1,3-bis-(epoxypropyl)tetramethyldisiloxane in an attempt to yield networks. The Wittig reaction occurred preferentially (Figure 4.38) and network formation was unsuccessful.<sup>43</sup> The amine endgroups did react with isophorone diisocyanate to form a thermoplastic chain extended linear urea (Figure 4.39).

Figure 4.38. Wittig Reaction of a Phosphine Substituted Polyorganosiloxane with an Epoxy Terminated Polysiloxane<sup>43</sup>



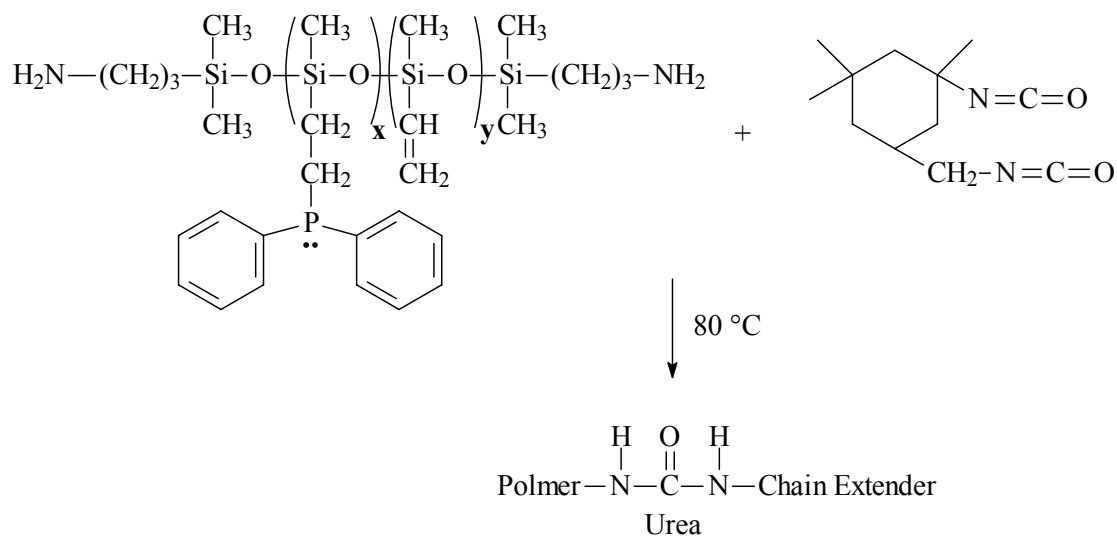


Figure 4.39. Preparation of a Phosphine Containing Polysiloxane Urea Thermoplastic

Thermoset (rather than thermoplastic), elastomeric networks were desired for this research. Therefore, the majority of the vinyl containing polysiloxane prepolymers were synthesized with vinyl endgroups. Importantly, free radical reactions of vinylsilyl groups can be controlled to leave residual vinyl groups for hydrosilation crosslinking reactions since vinylsilyl groups are not highly reactive under the free radical functionalization conditions used.<sup>75</sup> The vinyl containing prepolymers were reacted with controlled mol fractions of diphenylphosphine to leave a precise concentration of vinyl groups intact. These phosphine and vinyl substituted polysiloxanes were used to prepare phosphine oxide containing polysiloxanes to participate in hydrosilation reactions to yield novel polyorganosiloxane networks.

#### 4.4.2. Synthesis of Polysiloxanes with Controlled Concentrations of Pendent Phosphine Oxide Moieties

Phosphine oxide containing polysiloxanes were synthesized by oxidation of the poly(dimethyl-co-methylvinyl-co-methyl,2-diphenylphosphineethyl)siloxanes with bis(trimethylsilyl)peroxide (BSPO) (Figure 4.40). The proposed ionic mechanism and reaction conditions were described in detail for the preparation of the D<sub>4</sub>PO monomer.

No side reactions occurred during oxidation of the phosphine containing oligomers. The series of polysiloxanes with controlled concentrations of phosphine oxide moieties was characterized via  $^{29}\text{Si}$  NMR (Table 4.7). These oligomers were a very valuable addition to the family of novel polysiloxanes since the phosphine oxide groups did not inhibit Pt catalyzed hydrosilation reactions. Conversely, the phosphine containing polysiloxanes did complex with Pt and prohibit network formation. Vinyl moieties of the phosphine oxide substituted polysiloxanes were reacted with tetrakis(dimethylsiloxy)silane to prepare networks and will be described in detail later.

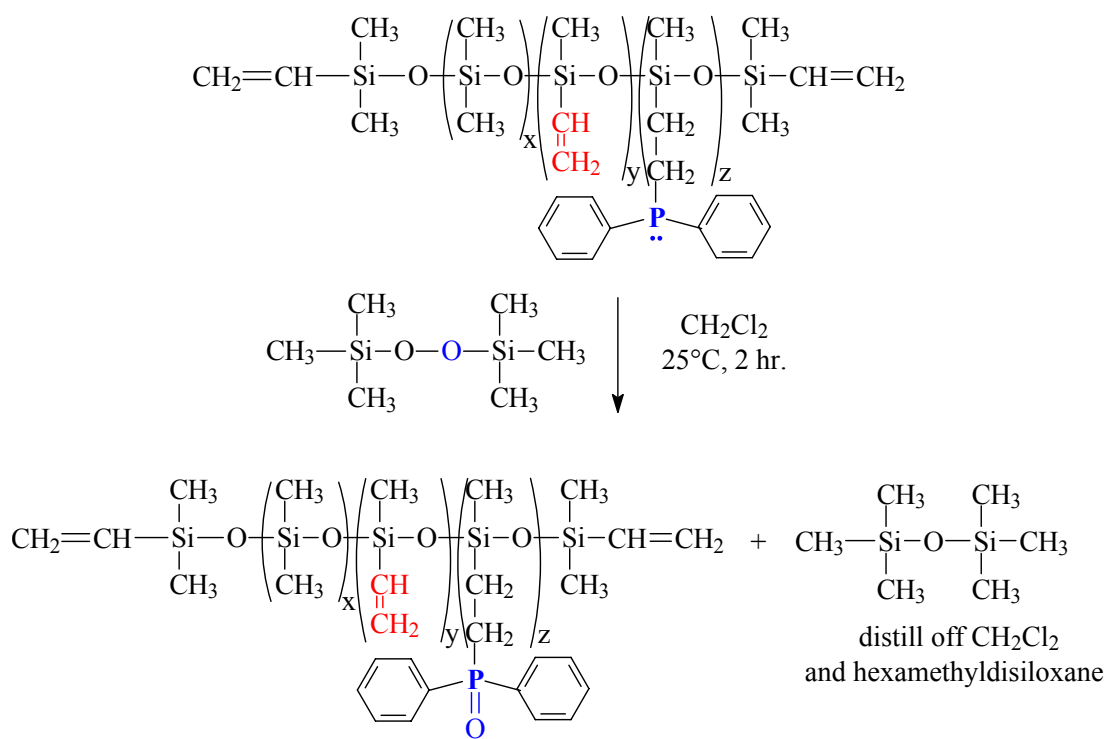


Figure 4.40. Synthesis of Poly(dimethyl-co-methylvinyl-co-methyl,2-diphenylphosphine oxideethyl)siloxane

Table 4.7. Series of Poly(dimethyl-co-methylvinyl-co-methyl,2-diphenylphosphine oxideethyl)siloxanes with Controlled Concentrations of Vinyl and Phosphine Oxide Substitution Characterized via  $^{29}\text{Si}$  NMR, where P=O is Phosphine Oxide

Mol % Repeat Unit			Silicon-29 NMR Analysis					n	Mn
P=O	Vinyl	Dimethyl	Endgroups	P=O	Vinyl	Dimethyl			
83%	15%	2%	2 aminopropyl	29.6	6.2	2.3	36.7	9760	
77%	20%	3%	2 P=O	20.0	5.8	1	28.7	6920	
10%	14%	76%	1.1 P=O, 0.9 vinyl	2.4	3.8	25.5	31.5	3200	
15%	9%	76%	1.7 P=O, 0.3 vinyl	3.5	2.60	25.5	31.6	3580	

Oxidation of the phosphine containing polysiloxane oligomers was performed using the same procedure described for oxidation of the D<sub>4</sub>P monomer. A 1:1 equivalent ratio of BSPO:phosphine was reacted in dichloromethane at room temperature and monitored via  $^{31}\text{P}$  NMR (Figure 4.41). Residual diphenylphosphine  $\sim 1\%$  remaining at the end of the addition reaction is also oxidized to diphenylphosphine oxide with BSPO.

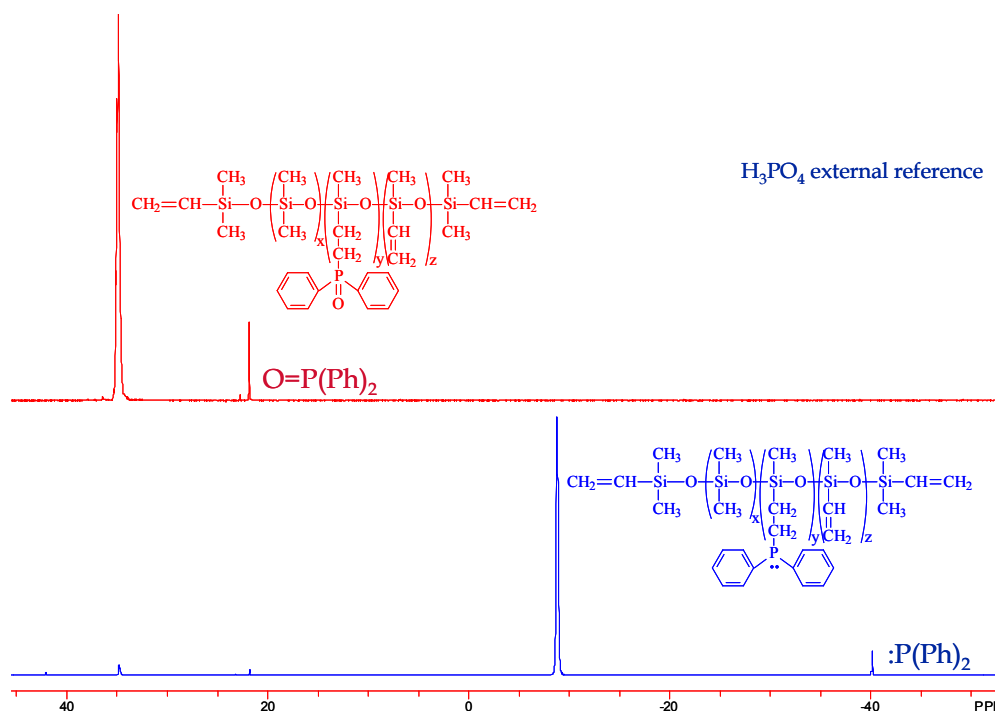


Figure 4.41. Monitoring the Oxidation of a Poly(dimethyl-co-methylvinyl-co-methyl,2-diphenylphosphineethyl)siloxane via  $^{31}\text{P}$  NMR

Quantitative  $^{29}\text{Si}$  NMR was used to follow the percent phosphine functionalization of a vinyl containing polysiloxane and subsequent oxidation (Figure 4.42). The middle spectrum showed that one half of the 6 vinyl groups were reacted to yield 2 new diphenylphosphine repeat units and 1 new diphenylphosphine-containing endgroup (since vinyl endgroups are equally as reactive). The top spectrum verified that all of the repeat units were intact with no side reactions taking place after oxidation of the phosphine groups. This spectrum represents a 3200 g/mol random polysiloxane containing 10 mol % phosphine oxide containing substituents (3 of 33 total repeat units and endgroups).  $^{31}\text{P}$  NMR was also used to verify the newly formed phosphine oxide containing substituents.

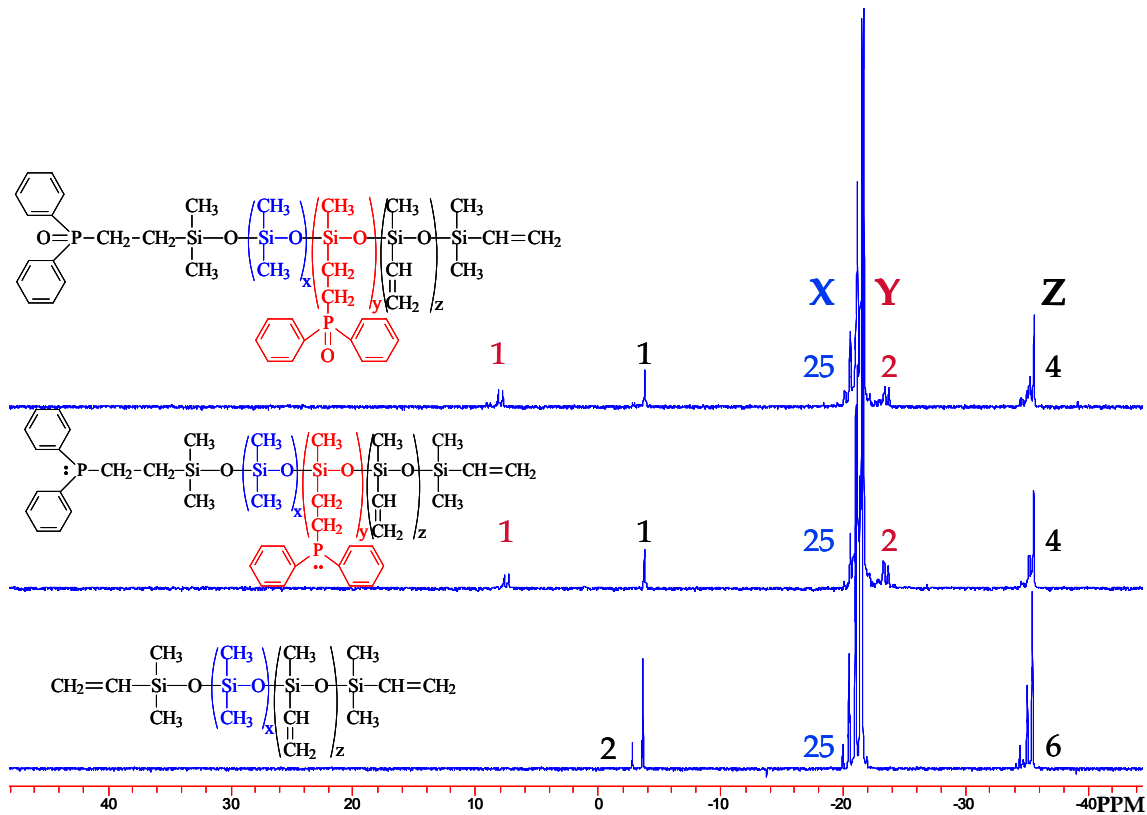


Figure 4.42. Monitoring the Phosphine Functionalization and Oxidation of a Random Vinyl Containing Polysiloxane Precursor via  $^{29}\text{Si}$  NMR

These phosphine oxide containing polysiloxanes were expected to adsorb strongly to metal or oxide fillers based on the ability to strongly hydrogen bond.<sup>5</sup> The capacity for hydrogen bonding was elucidated via <sup>1</sup>H NMR by monitoring the shift of the deshielded proton on chloroform in 1:1 equivalent phosphine oxide:chloroform mixtures (Figure 4.43). The downfield shift of the deshielded chloroform proton in the presence of the phosphine oxide containing polysiloxane suggested strong secondary specific interactions. The area of the peak for the chloroform proton that is hydrogen bonded with the phosphine oxide polysiloxane is much smaller (relative to the nitrile mixture) due to the concentration difference. Much less chloroform is required for a 1:1 molar ratio since there were only 10 mol % phosphine oxide groups on the polyorganosiloxane. The NMR samples were comprised of 0.1 g mixture in 1 mL of d-acetone (opposed to 0.1 g of chloroform). Analogous experiments were conducted with the nitrile containing polysiloxane. A similar downfield shift was observed, although the magnitude was much less.

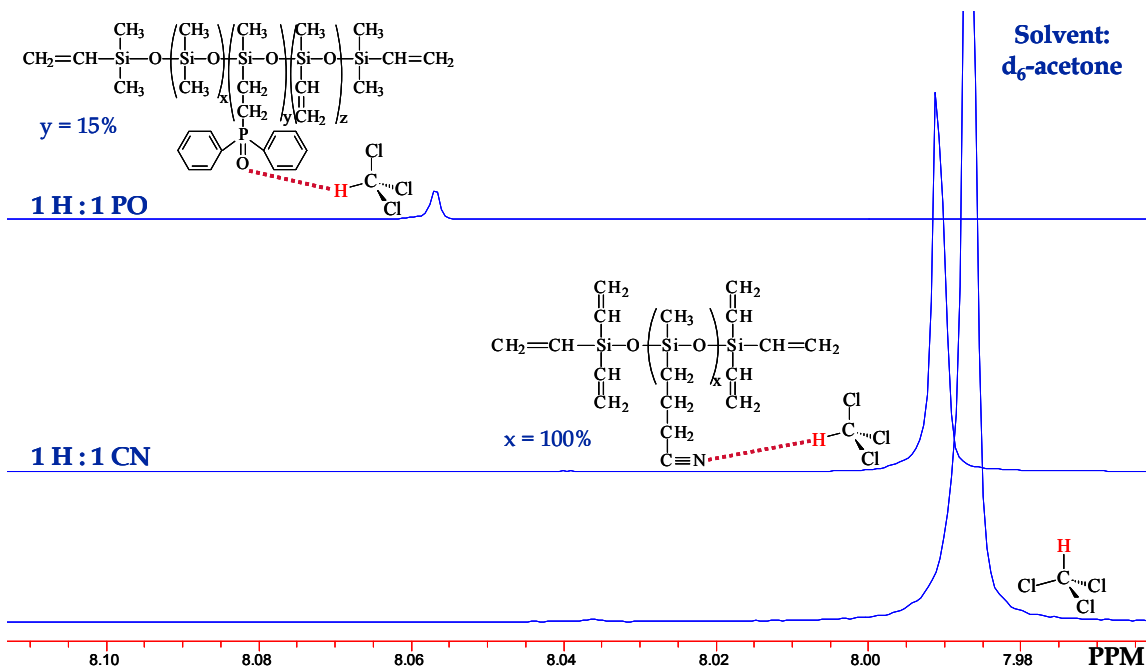


Figure 4.43. Evidence of Hydrogen Bonding Between the Deshielded Proton of CHCl<sub>3</sub> with Nitrile and Phosphine Oxide Pendent Moieties on Polyorganosiloxanes

Interestingly, the diphenyl groups also influence the strength of hydrogen bonds formed with acidic chloroform protons. The chloroform proton was not deshielded as strongly by the 3-diethylphosphonatepropylmethyldimethoxysilane monomer, and consequently, the magnitude of the proton shift was not as great (Figure 4.44). In contrast, the literature suggests that phosphines coordinate to electropositive metals instead of hydrogen bonding.<sup>5</sup> Consistent with this, analogous <sup>1</sup>H NMR experiments with diphenylphosphine containing polysiloxanes and chloroform did not exhibit any downfield shifts (Figure 4.45).

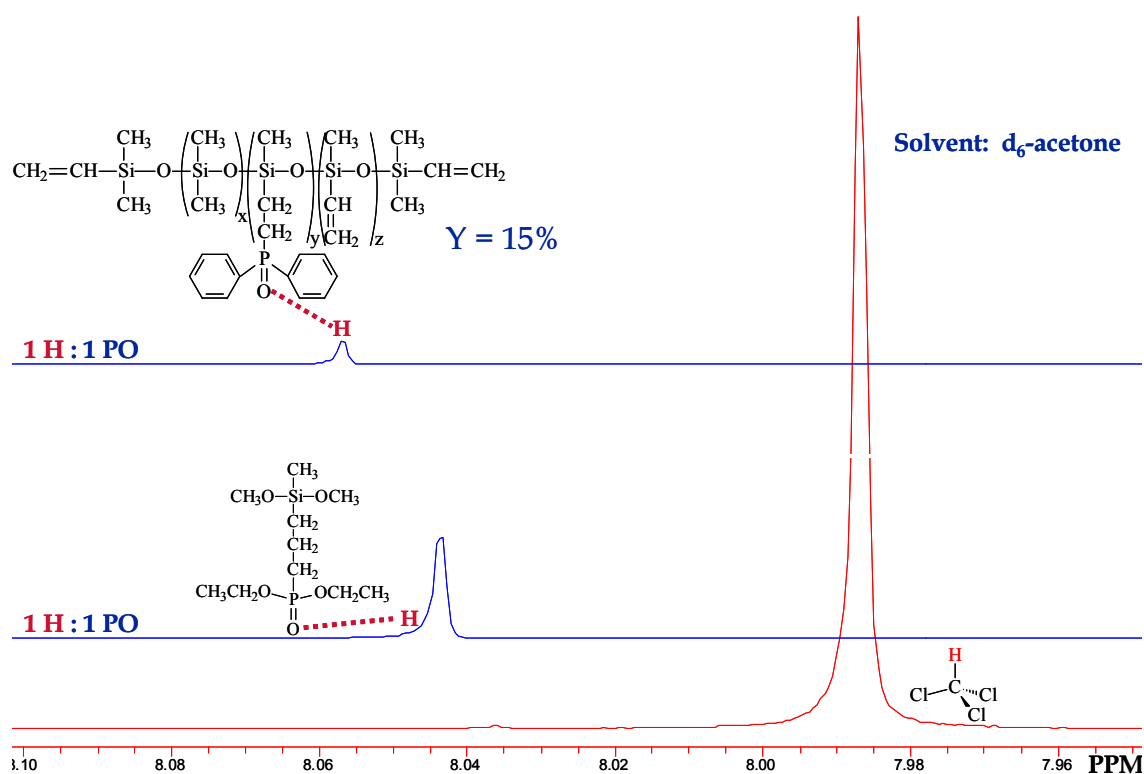


Figure 4.44. Investigation of Hydrogen Bonding Between the Acidic Proton of Chloroform with Two Types of Phosphine Oxide Siloxane Species via <sup>1</sup>H NMR

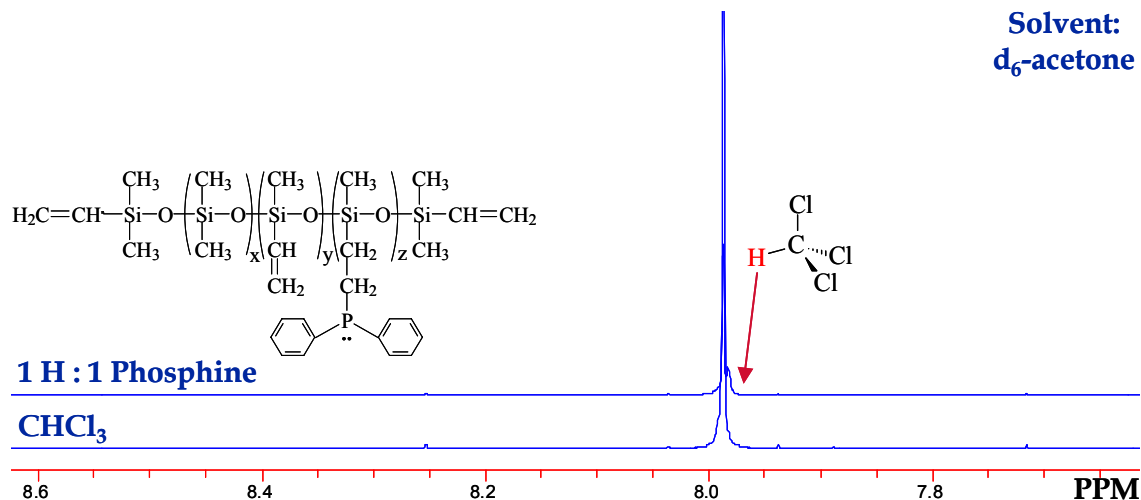


Figure 4.45 No Hydrogen Bonding Observed via  $^1\text{H}$  NMR Between a Phosphine Substituted Polysiloxane with Chloroform

#### 4.4.3. Synthesis of Polysiloxanes with Controlled Concentrations of Pendent Carboxylic Acid Moieties

Polysiloxane backbones serve as highly flexible platforms upon which chemical moieties can impart tailored surface properties.<sup>141</sup> The pronounced conformational freedom around the siloxane bond also allows for very interesting behavior in solution.<sup>141</sup> Surface activity and solubility depend on the chemical nature of the side chain moieties and the chain average molecular weight.<sup>141</sup> Polydimethylsiloxanes are extremely hydrophobic, and have low surface energies due to the methyl-rich exteriors.<sup>141</sup> Novel polysiloxane surfactants or dispersants have been synthesized when the methyl groups were systematically replaced with pendent electron donating or acidic groups.<sup>138,142</sup>

Carboxylic acid functional groups impart hydrophilicity to inherently hydrophobic polysiloxane materials. The combination of hydrophobic and hydrophilic groups may yield special surface properties. This approach with other materials has

141. R. M. Hill, *Silicone Surfactants*, Surfactant Science Series, v. 86, Marcel Dekker, Inc., New York, 1999.

142. J. K. Hoyt, Y. Kim, J. E. McGrath and J. S. Riffle, *Adh. Age*, **45**(1), 19-22, 2002.

resulted in emulsifiers, lubricants, steric stabilizers and precursors for further reactions.<sup>138,141,143</sup> It has been shown that the carboxylic acid functionality on oleic acid can stabilize magnetite nanoparticle dispersions.<sup>144,145,146</sup> One major focus is to synthesize chemically stable and biologically compatible stabilizers for magnetic-field directed drug delivery suites.<sup>147</sup>

Three different methods were performed to introduce pendent carboxylic acid functional groups onto polysiloxanes. A carboxylic acid terminated polydimethylsiloxane (PDMS) was synthesized by equilibrating octamethylcyclotetrasiloxane (D<sub>4</sub>) in the presence of 1,3-bis(3-carboxypropyl)tetramethyldisiloxane (described earlier).<sup>133</sup> Well-defined poly(dimethyl)-block-(methylvinyl)siloxanes were synthesized via sequential anionic polymerization of hexamethylcyclotrisiloxane (D<sub>3</sub>), then trimethyltrivinylcyclotrisiloxane (D<sub>3</sub>Vi).<sup>147</sup> Vinyl substituted block prepolymers were reacted with mercaptoacetic acid to yield carboxylic acid amphiphilic block copolysiloxanes. A series of random poly(dimethyl-co-[2-(carboxymethylthio)ethyl]methyl)siloxanes were synthesized by the free radical ene-thiol addition<sup>138</sup> reaction of mercaptoacetic acid with random poly(dimethyl-co-methylvinyl)siloxane prepolymers (Figure 4.46).

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143. V. M. Djinovic, V. V. Antic, J. Djonlagic and M. N. Govedarica, *Reactive and Functional Polymers*, 44, 299-306, 2000.
  144. P. C. Scholten, *Chem. Eng. Comm.*, 67, 331-340, 1988.
  145. S. S. Papell, O. C. Faber, *NASA Technical Note* 1968, (NASA-TN-D-4676), 25pp.
  146. R. E. Rosensweig, *Ferrohydrodynamics*, Cambridge University Press, Cambridge, 1985.
  147. K. Wilson, L. A. Harris, M. Rutnakornpituk, and J. S. Riffle, *Poly. Prepr.*, 43(1) 732, 2002.



poly(dimethyl-co-methylvinyl)siloxane precursors. Reactive vinyl moieties were incorporated into the backbone by controlling the ratio of D<sub>4</sub>:D<sub>4</sub>Vi during the initial ring-opening co-equilibrations.<sup>148</sup> Similarly, the percentage of vinyl groups in the block copolymers was controlled by the degree of polymerization of the second poly(methylvinyl)siloxane block.<sup>147</sup>

Vinyl silyl moieties do not react easily with each other to crosslink under the AIBN promoted functionalization conditions used herein.<sup>81</sup> The  $t_{1/2}$  of AIBN is only ~ 8 minutes at 100 °C. A lower reaction temperature of 50 °C (where  $t_{1/2}$  ~ 21 hr at 60 °C) allowed for near quantitative addition of mercaptoacetic acid in ~ 24 h. Consequently, this addition process can be performed to intentionally leave precise concentrations of vinyl groups intact for further crosslinking reactions. Future work will involve energetically crosslinking (UV or electron-beam) the residual vinyl groups of poly(methylvinyl-co-[2-(carboxymethylthio)ethyl]-methyl)-siloxane-*block*-(dimethyl)-siloxanes to yield lightly crosslinked elastomeric networks with controlled polarity. Another objective is to prepare polysiloxanes with high contents of carboxylic acid moieties as potential hydrogels.

Quantitative <sup>29</sup>Si NMR was primarily used to monitor ene-thiol functionalization reactions, establish chemical composition, and M<sub>n</sub> of carboxylic acid functionalized polyorganosiloxanes (Figure 4.47). The lower spectrum represents a 2500g/mol vinyl polysiloxane with 20 mol % vinylmethylsiloxy- repeat units (6 at ~ -35 ppm) and 2 dimethylvinylsiloxy- endgroups at ~ 3 ppm. The upper spectrum was obtained after reacting one-half of the vinyl groups. One-half of the 6 vinylmethyl repeat units reacted to yield a 2850 g/mol polysiloxane with 10 mol % (3 at ~ -25 ppm) carboxylic acid repeat units. The vinyl endgroups are equally as reactive toward substitution yielding 1.2 (~ 6 ppm) carboxylic acid functional siloxy endgroups. No side reactions or crosslinking occurred, and the 25 dimethylsiloxy- repeat units remained intact.

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148. J. K. Hoyt, Y. Kim, J. E. McGrath and J. S. Riffle, *Poly. Prepr.*, 43(1) 350, 2002.

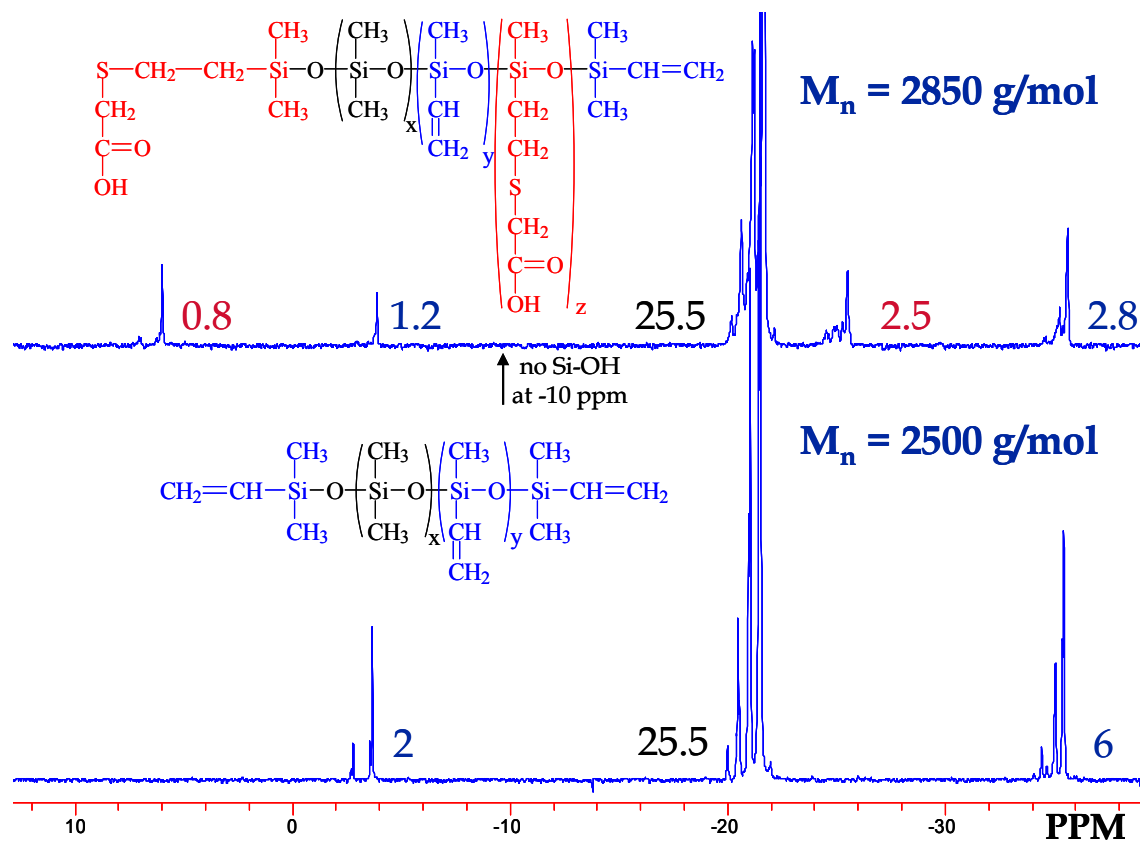


Figure 4.47. Monitoring the Thioacetic Acid Functionalization of a Vinyl Terminated Poly(dimethyl-co-methylvinyl)siloxane Precursor Containing 20 Mol % Methylvinylsiloxy- Repeat Units via  $^{29}\text{Si}$  NMR

A 4010 g/mol poly(dimethyl-co-methylvinyl-co-[2-(carboxy-methylthio)ethyl]-methyl)siloxane containing 60 molar % pendent thioacetic acid groups was also synthesized. The carboxylic acid functional random copolysiloxanes were analyzed via  $^{29}\text{Si}$  NMR (Table 4.8).

Table 4.8. Poly(dimethyl-co-methylvinyl-co-[2-(carboxy-methylthio)ethyl]methyl)siloxanes with Controlled Molar Amounts of Vinyl Groups and Carboxylic Acid Substitution Characterized via  $^{29}\text{Si}$  NMR

Mol % Repeat Unit			Silicon-29 NMR Analysis					n	Mn
COOH	Vinyl	Dimethyl	Endgroups	COOH	Vinyl	Dimethyl			
11	11	78	1.2 COOH, 0.8 Vinyl	2.5	2.9	25.5	32.9	2850	
61	35	4	2 COOH	15.4	10	1	28.3	4010	

The mechanism for the ene-thiol addition reaction of mercaptoacetic acid to poly(dimethyl-co-methylvinyl)siloxane proceeds through a free radical pathway (Figure 4.48).<sup>136,137</sup> Initiation begins via thermolysis of AIBN to yield 2 free radical fragments. The highly reactive AIBN radical fragments subsequently abstract a hydrogen atom from mercaptoacetic acid to yield a thionyl radical. Propagation occurs by thionyl radical attack on either of the unsaturated carbons on the polysiloxane to form a primary or secondary radical intermediate. The reactive intermediates are terminated by abstracting a neighboring hydrogen from mercaptoacetic acid. Therefore, both terminal and nonterminal adducts are formed via respective  $\alpha$ - or  $\beta$ - addition of mercaptoacetic acid to the poly(dimethyl-co-methylvinyl)siloxane chain, where terminal addition primarily occurs.<sup>137</sup>

Initiation:



Propagation:

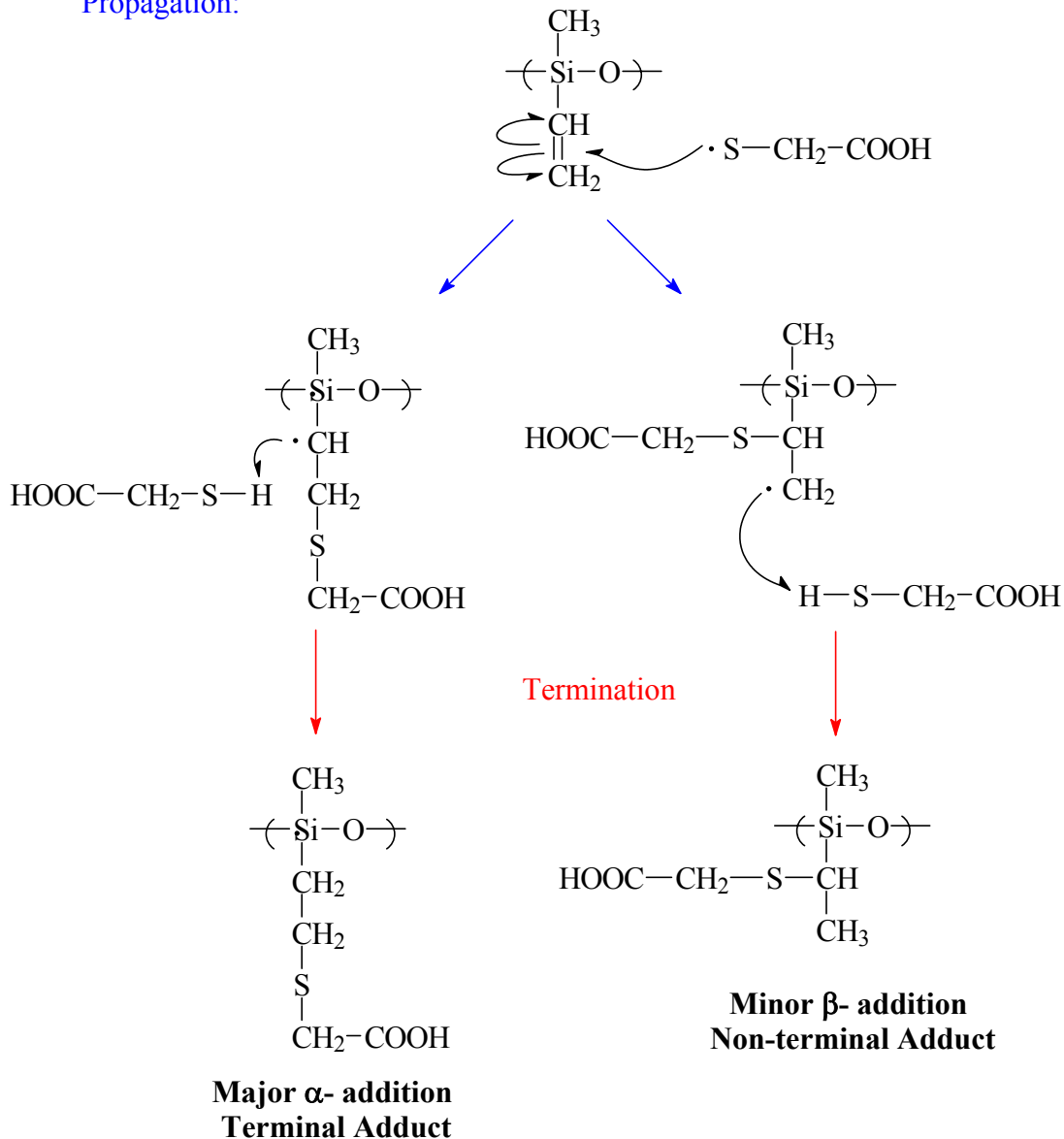


Figure 4.48. Mechanism of the AIBN Promoted Free Radical Ene-Thiol Addition Reaction of Mercaptoacetic acid with Poly(dimethyl-co-methylvinyl)siloxane

$^1\text{H}$  NMR was also used to follow the ene-thiol addition of mercaptoacetic acid with poly(dimethyl-co-methylvinyl)siloxanes (Figure 4.49). The reaction was monitored

for the disappearance of the thiol, H-S bond, at  $\sim 2.0$  ppm. The stacked spectra also show the decrease of the area for the vinyl groups on the poly(dimethyl-co-methylvinyl)siloxane.

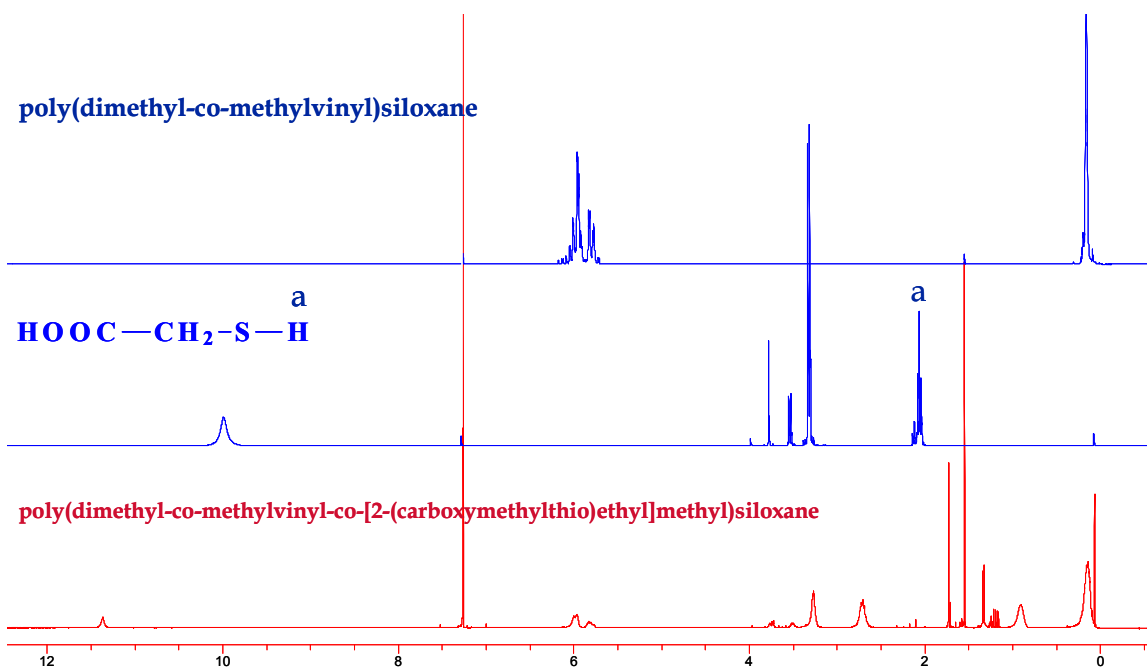


Figure 4.49. Monitoring the Ene-Thiol Free Radical Addition Reaction with a Poly(dimethyl-co-methylvinyl)siloxane via  $^1\text{H}$  NMR

$^1\text{H}$  NMR revealed that the major addition product was the  $\alpha$ -addition adduct, as expected (Figure 4.50).<sup>137</sup> The spectrum represents a 2850 g/mol poly(dimethyl-co-methylvinyl-co-[2-(carboxy-methylthio)ethyl]-methyl)siloxane. One half of the 20 mol % pendent vinyl groups of a poly(dimethyl-co-methylvinyl)siloxane precursor were reacted. The methylene protons next to the carboxylic acid (peak c  $\sim 3.25$  ppm) were normalized to an integral area of 2.0 and the carboxylic acid proton (peak f  $\sim 11$  ppm) integrated to an area of 1.04. The newly formed methylene protons on the major  $\alpha$ -addition terminal adduct (peaks a and b) were observed at  $\sim 0.9$  ppm and  $\sim 2.2$  ppm. The minor  $\beta$ -addition, non-terminal adduct was observed by the methyne and methyl protons, peaks d and e, respectively at  $\sim 2.3$  (overlaps with peak b) and  $\sim 1.3$  ppm. These two peaks integrated to areas of 0.12 and 0.36, the expected 1:3 ratio for a methyne:methyl.

This corresponded to 5.7 % of the minor  $\beta$ -addition adduct. The reaction yielded 50 mol % of the newly formed thioacetic acid functional groups. The integral area of the methylene peak (a), was a normalized area of 2; and the remaining vinyl groups integrated to an area of 3. This represented a 1:1 ratio of methylene:vinyl or one 2-(carboxy-methylthio)ethyl]-methylsiloxy- repeat unit for every one methylvinylsiloxy-repeat unit.

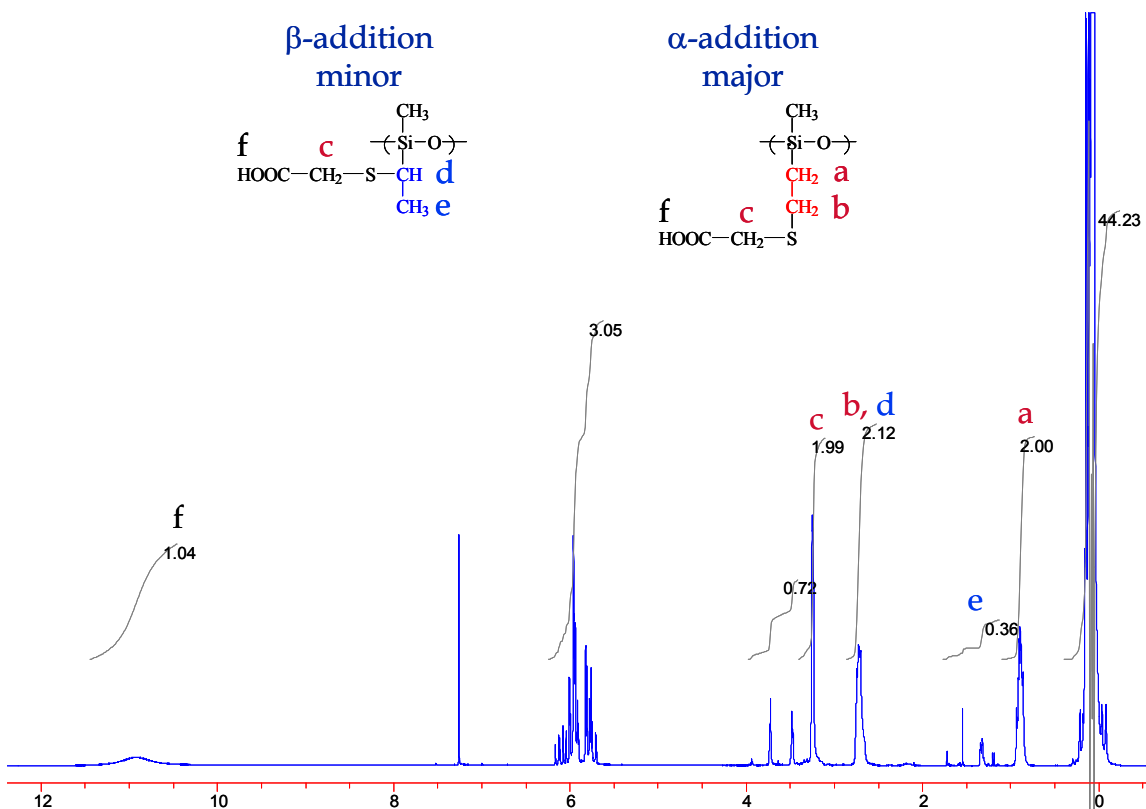


Figure 4.50.  $^1\text{H}$  NMR used to Elucidate the % of Minor Non-terminal  $\beta$ -Adduct as a Result of the Ene-Thiol Free Radical Addition of Mercaptoacetic Acid to a Poly(dimethyl-co-methylvinyl)siloxane

$^1\text{H}$  NMR also established that a thermoreversible network was formed when a 4013 g/mol poly(dimethyl-co-methylvinyl-co-[2-(carboxy-methylthio)ethyl]-methyl)siloxane containing 60 molar % carboxylic acid groups was dehydrated during a

rigorous purification process (100 °C/500 mTorr overnight). One half of the carboxylic acid groups condensed to yield the anhydride (Figure 4.51). The methyl groups on the polysiloxane were normalized to an integral area of 3. The 2 newly formed anhydride peaks (b and c) each integrate to an area of ~ 0.50. This represented one half of the methylene peaks which integrated to an area of ~ 1.0. The one carboxylic acid proton, peak d, would normally integrate to an area of 0.5, were it completely present. After dehydration, the carboxylic acid proton (~ 11.4 ppm) integrated to 0.26 (half of its expected value). Therefore 50% of the carboxylic acid groups had condensed. This material, behaved as a thermoreversible network, where it existed as a linear carboxylic acid containing polysiloxane at room temperature, and as a crosslinked anhydride after exposure to high enough temperatures to dehydrate the system.

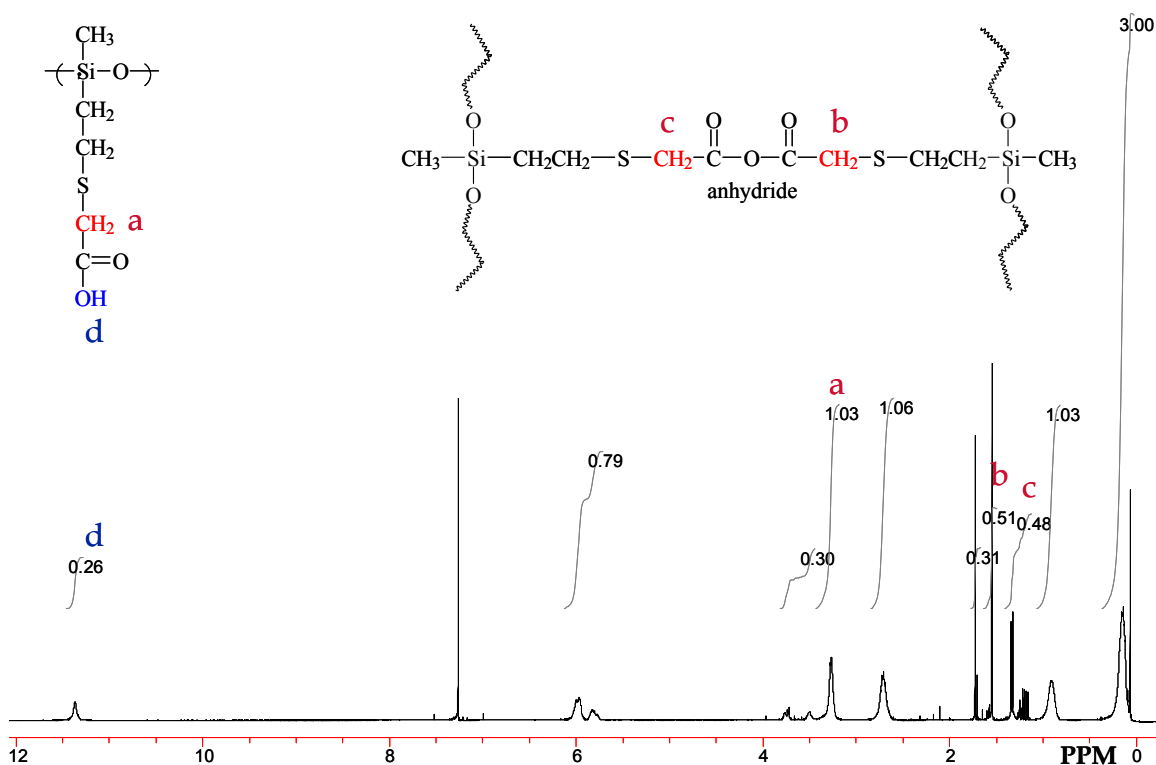


Figure 4.51. Dehydration of a Polysiloxane Containing Pendent Carboxylic Acid Moieties to Form an Anhydride Characterized via <sup>1</sup>H NMR

One current objective of Dr. Riffle's research group is to exploit carboxylic acid functional polysiloxanes as steric stabilizers for magnetite nanoparticles. The carboxylic acid functional polysiloxanes would serve as nontoxic materials for magnetic site specific drug delivery suites.<sup>147</sup> The research presented in this dissertation was the first to introduce carboxylic acid groups pendent to the polysiloxanes. Interesting morphological characteristics are possible by varying the polysiloxane microstructure and sidechain chemical structure. The random copolymers were prepared with varying degrees of carboxylic acid moieties to alter the overall acidity of the polysiloxane chain. These materials yield network structures with the magnetite nanoparticles having controlled crosslink densities based on the percentage of carboxylic acid repeat units. Amphiphilic block copolymers can effectively stabilize discrete nanoparticles. The methylated tail blocks serve as steric stabilizers whereas the carboxylic acid anchor moieties should stabilize the magnetite particles by reacting with the hydroxyl groups on the Fe<sub>3</sub>O<sub>4</sub> surface.<sup>144</sup> Transmission electron microscopy (TEM) and vibrating sample magnetometry (VSM) are currently being used to verify the well defined nature of the nanoparticles and the magnetic properties of stabilized dispersions.

#### **4.4.4. Synthesis of Polysiloxanes with Controlled Concentrations of Pendent Nitrile Moieties**

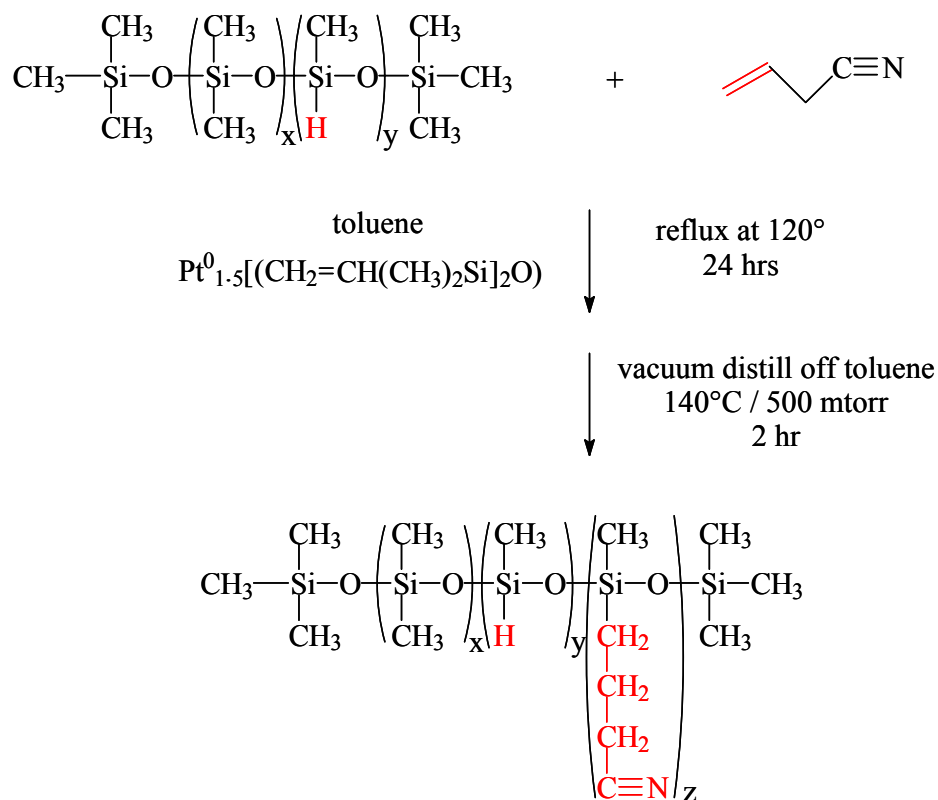
Synthetic procedures were discovered that yielded novel nitrile containing polysiloxane adhesive networks.<sup>33</sup> Tetramethyltetrahydrocyclotetrasiloxane (D<sub>4</sub>H) was hydrosilated with controlled amounts of allyl cyanide to yield a 3-cyanopropylmethylcyclotetrasiloxane monomer (D<sub>4</sub>CN)<sup>149,150</sup> and novel polar silane

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149. J. P. Stevenson, M. Rutnakornpituk, M. Vadala, A. Esker, J. S. Riffle, S. W. Charles, S. Wells, and J. P. Dailey, "Magnetic Cobalt Dispersions in Poly(dimethylsiloxane) Fluids," *J. Magn. Magn. Mater.*, **225**(1-2), 47-58, 2001.
150. M. Rutnakornpituk, M. S. Thompson, L. A. Harris, K. E. Farmer, A. R Esker, J. S. Riffle, J. Connolly and T. G. St. Pierre, "Formation of cobalt nanoparticle dispersions in the presence of polysiloxane block copolymers," *Polymer*, **43**, 2337-2348, 2002.

cyclic crosslinking reagents,  $D_4(CN)_2(H)_2$  and  $D_4CNH_3$ <sup>3,33</sup>. Ring opening equilibrations of  $D_4CN$  with LiOH were performed to yield controlled  $M_n$  poly(3-cyanopropylmethyl)siloxane (PCPMS) oligomers.<sup>33</sup>

It was established that the secondary interactions between nitrile and hydroxyl groups greatly influenced the adhesion, tensile and dispersion qualities of poly(3-cyanopropyl,methyl)siloxane (PCPMS) adhesives. A series of model networks with controlled crosslink densities prepared from PCPMS oligomers and nitrile-containing silane crosslinking reagents exhibited 180° peel adhesion strengths on Al and Ti double those for PDMS networks.<sup>33</sup> This was attributed to the nitrile groups strongly hydrogen bonding with the hydroxyl groups in the oxide layer of metal adherends. TEM data also suggested strong interactions between nitrile resin groups with surface silanols on fumed silica.<sup>4</sup> A much more uniform dispersion was observed for a PCPMS network with 5 wt. % untreated silica (2.5 OH/nm<sup>2</sup>). Networks filled with both 5 and 10 wt. % treated silica with less surface silanols (0.7 OH/nm<sup>2</sup>) exhibited pronounced aggregation of the silica particles.<sup>4</sup>

These previous studies motivated the preparation of a series of polysiloxanes with tailored amounts of nitrile moieties and reactive hydrido groups to yield networks. Poly(dimethyl-co-methylhydrido)siloxane precursors were hydrosilated with allyl cyanide to yield the pendent 3-cyanopropyl substituents (Figure 4.52). These oligomers were synthesized to assess the minimum amount of nitrile groups necessary to yield a stable microcomposite dispersion with high volume percentages of conductive fillers while remaining processable. A series of poly(dimethyl-co-methylhydrido-co-3-cyanopropyl,methyl)siloxanes and a PCPMS homopolymer control were prepared and characterized via <sup>29</sup>Si NMR (Table 4.9)



**Poly(dimethyl-co-methylhydrido-co-3-cyanopropylmethyl)siloxane**

Figure 4.52. Synthesis of Poly(dimethyl-co-methylhydrido-co-3-cyanopropyl,methyl)siloxane

Table 4.9. Poly(dimethyl-co-methylhydrido-co-3-cyanopropyl,methyl)siloxanes with Controlled Concentrations of Reactive Hydrido Groups and Nitrile Substitution Characterized via  $^{29}\text{Si}$  NMR

Mol % Repeat Unit			Silicon-29 NMR Analysis					n	Mn
Nitrile	Hydrido	Dimethyl	Endgroups	Nitrile	Hydrido	Dimethyl			
9.4	6.7	84	2 trimethyl	5.2	3.7	46.1	55.0	4470	
9.1	8.5	82.4	2 trimethyl	6.1	5.7	55.4	67.3	5600	
26.9	17.5	55.5	2 trimethyl	10	6.5	20.5	37	3340	
54	18.1	27.8	2 trimethyl	17.5	5.9	9	32.4	3410	
100	0	0	2 vinyl	81	0	0	81	10480	

Poly(dimethyl-co-methylhydrido-co-3-cyanopropyl,methyl)siloxanes were synthesized by hydrosilating equivalent ratios of allyl cyanide:hydrido groups in toluene (a heat sink) in the presence of platinum(0) complexed with 1,3-divinyltetramethyldisiloxane in xylene (Karstedt's catalyst) (Figure 4.53). Care was taken not to add excess allyl cyanide to ensure that the product would have no less than 3 hydrido groups,  $\equiv\text{Si-H}$ , on average per oligomer left intact. Karstedt's catalyst was chosen as the catalyst to initiate the hydrosilation due to its miscibility with the allyl cyanide, and also to avoid possible side reactions. Siloxane cleavage could occur with Speier's catalyst ( $\text{H}_2\text{PtCl}_6$ ), an acid that generates  $\text{HCl}$ .<sup>151</sup> Karstedt's catalyst solution is a complex of divinyltetramethyldisiloxane<sup>152,153</sup> with the active species being  $\text{Pt}(0)$  (2.1 – 2.4 %  $\text{Pt}$  in xylene).

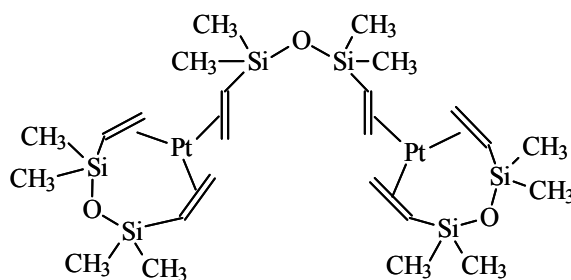


Figure 4.53 Karstedt's Catalyst

The mechanism for the hydrosilation process is not well understood. However, Figure 4.54 represents a proposed mechanism for a platinum catalyzed hydrosilation catalytic cycle.<sup>154,155,156,157</sup> An important side reaction to consider occurs between water

151. P. R. Dvornic and V. V. Gerov, *Macromolecules*, **27**(4), 1068-1070, 1994.

152. L. N. Lewis, *J. Amer. Chem. Soc.*, **112**, 5998-6004, 1990.

153. B. D. Karstedt, U. S. Patent, 3,775,452, 1973.

154. A. J. Chalk and J. F. Harrod, *Journal of the American Chemical Society*, **87**(1), 16-21 (1965).

and hydrido groups:  $\equiv\text{Si-H} + \text{H}_2\text{O} + \text{Pt} \rightarrow \equiv\text{Si-OH} + \text{H}_2\uparrow$ .<sup>81</sup> This reaction typically is a concern when the concentration of the desired reactant silane is relatively low.<sup>81</sup>

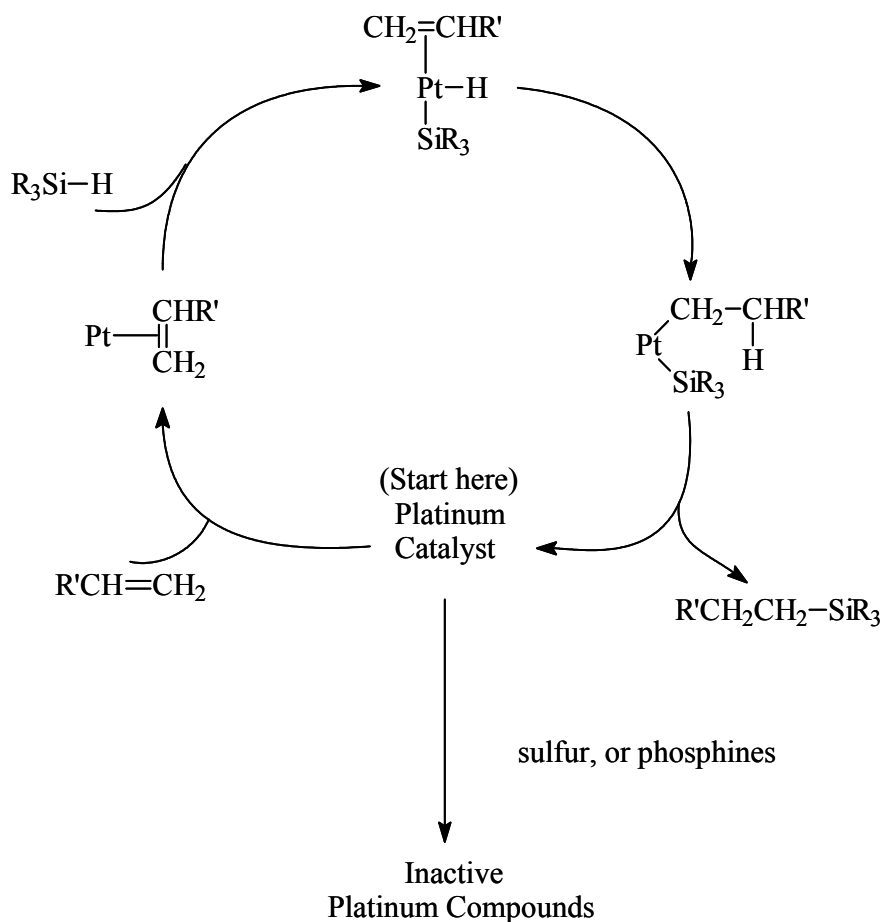


Figure 4.54. Proposed Mechanism for a Catalytic Cycle for Platinum Catalyzed Hydrosilation<sup>157</sup>

The reactions were monitored with  $^1\text{H}$  NMR to determine complete reaction of allyl cyanide via the disappearance of the characteristic vinyl protons at  $\sim 5.5$  ppm

155. L. N. Lewis and C. A. Sumpter, *Journal of Molecular Catalysis A: Chemical*, **104**, 293-297 (1996).

156. L. N. Lewis, *Journal of the American Chemical Society*, **112**, 5998-6004, 1990.

157. 3M Dental Products, <http://www.mmm.com/dental/prod imprintII chem.html>.

(Figure 4.55). The integral area of the characteristic silane peak  $\sim 4.8$  ppm decreases, and three newly formed methylene protons attached to the polysiloxane siloxane chain are observed in the final spectrum.

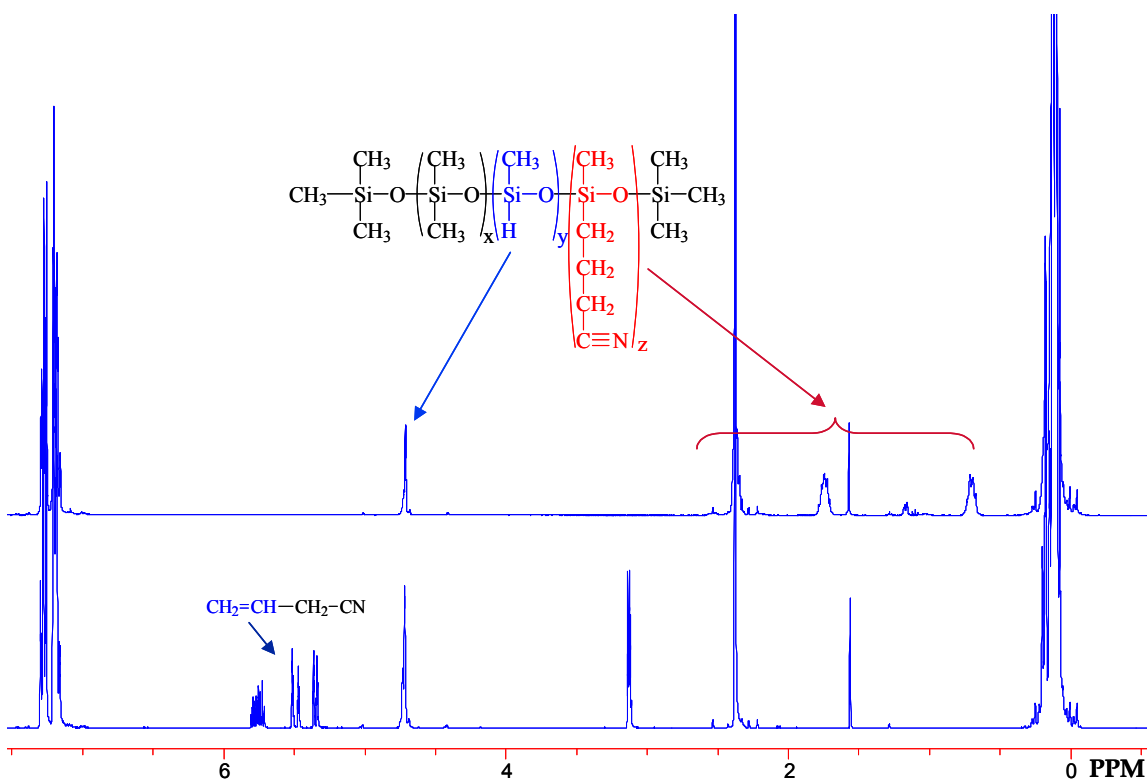


Figure 4.55. Monitoring the Hydrosilylation of Allyl Cyanide with Poly(dimethyl-co-methylhydrido)siloxane for the Disappearance of Vinyl Groups via  $^1\text{H}$  NMR

$^1\text{H}$  NMR spectra of a purified 3410 g/mol poly(dimethyl-co-methylhydrido-co-3-cyanopropyl,methyl)siloxane with 54 mol % nitrile substitution revealed both normal and reverse addition occurred, as expected (Figure 4.56).<sup>81</sup> The  $\alpha$ -addition adduct is a result of Markownikov addition, the major product. Pt catalyzed hydrosilylation addition reactions also yield the anti-Markownikov  $\beta$ -addition side product.<sup>81</sup> This was observed in previous work for the synthesis of the nitrile substituted monomer,  $\text{D}_4\text{CN}$ ; where  $\text{D}_4\text{H}$  was hydrosilated with allyl cyanide.<sup>33</sup> Typically, 10-15 % of the reverse addition product was formed for the monomer.<sup>33</sup> Here,  $\sim 13$  % occurred. This was observed by the methyne and methyl groups (peaks a and b at  $\sim 1.0$  ppm and 1.8 ppm) in a 1:3 ratio. In

this case, there are 2.75 3-cyanopropylmethyl- repeat units (peak f at ~ 4.7 ppm) for every 1.0 hydrido group which corresponds well (within 9%) with the  $^{29}\text{Si}$  NMR results. A 5-10% error is typically associated with  $^{29}\text{Si}$  NMR and ~ 1-2% for  $^1\text{H}$  NMR.<sup>128</sup>

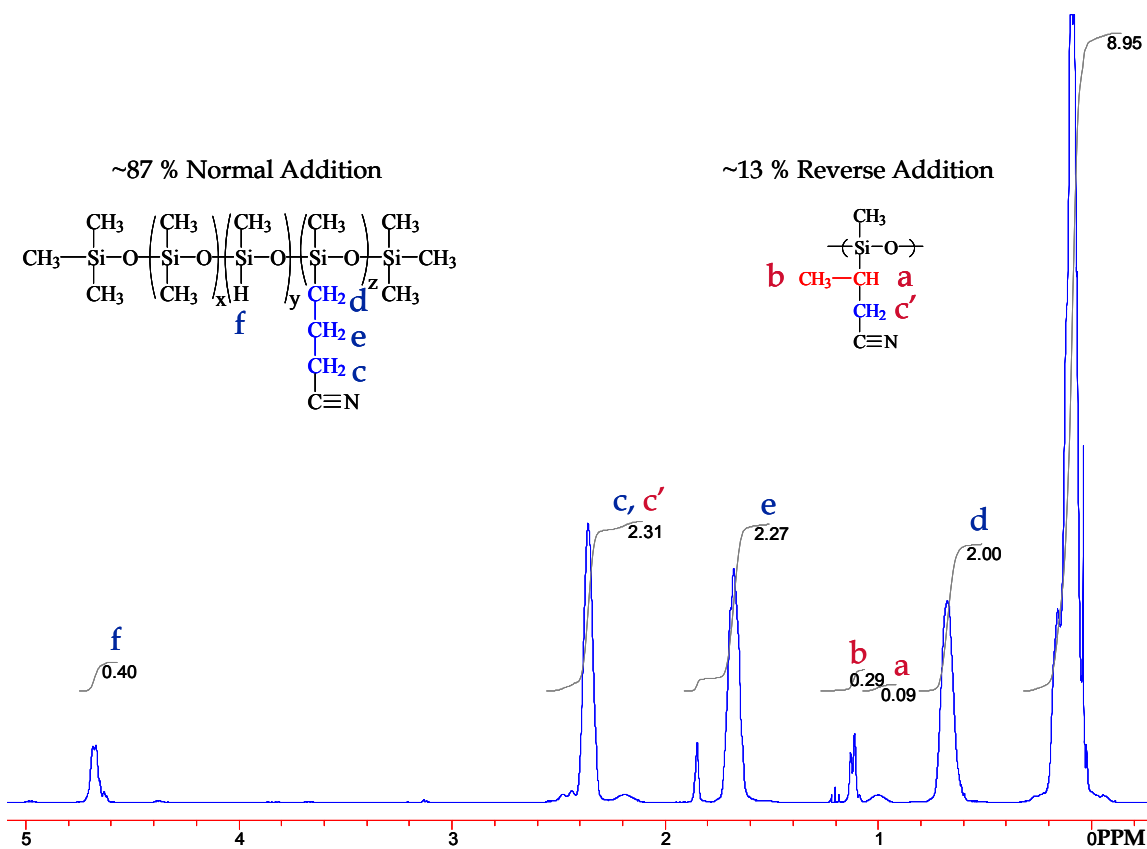


Figure 4.56.  $^1\text{H}$  NMR Confirmed the Percentage of Normal and Reverse Addition Hydrosilation Adducts for a 3410 g/mol Poly(dimethyl-co-methylhydrido-co-3-cyanopropyl,methyl)siloxane Containing 54 Mol % Nitrile Moieties

$^{29}\text{Si}$  NMR was used to confirm the number of newly substituted 3-cyanopropyl-units (Figure 4.57). It was shown earlier that the silicon atoms of new functional groups pendent to a polysiloxane chain attached by a methylene group are observed slightly upfield relative to the dimethylsiloxy- repeat units (~ 20 – 22.5 ppm). Multiple peaks were observed due to the statistical nature of the poly(dimethyl-co-methylhydrido)siloxane precursor. The silicon atoms of the 3-cyanopropyl,methylsiloxy-repeat units were observed at ~ 22.5 – 24 ppm. The precursor polysiloxane had 10

methylhydrosiloxy- repeat units (~ 36 – 38 ppm) before functionalization, whereas the product contains 4 methylhydrosiloxy- groups available for crosslinking reactions.

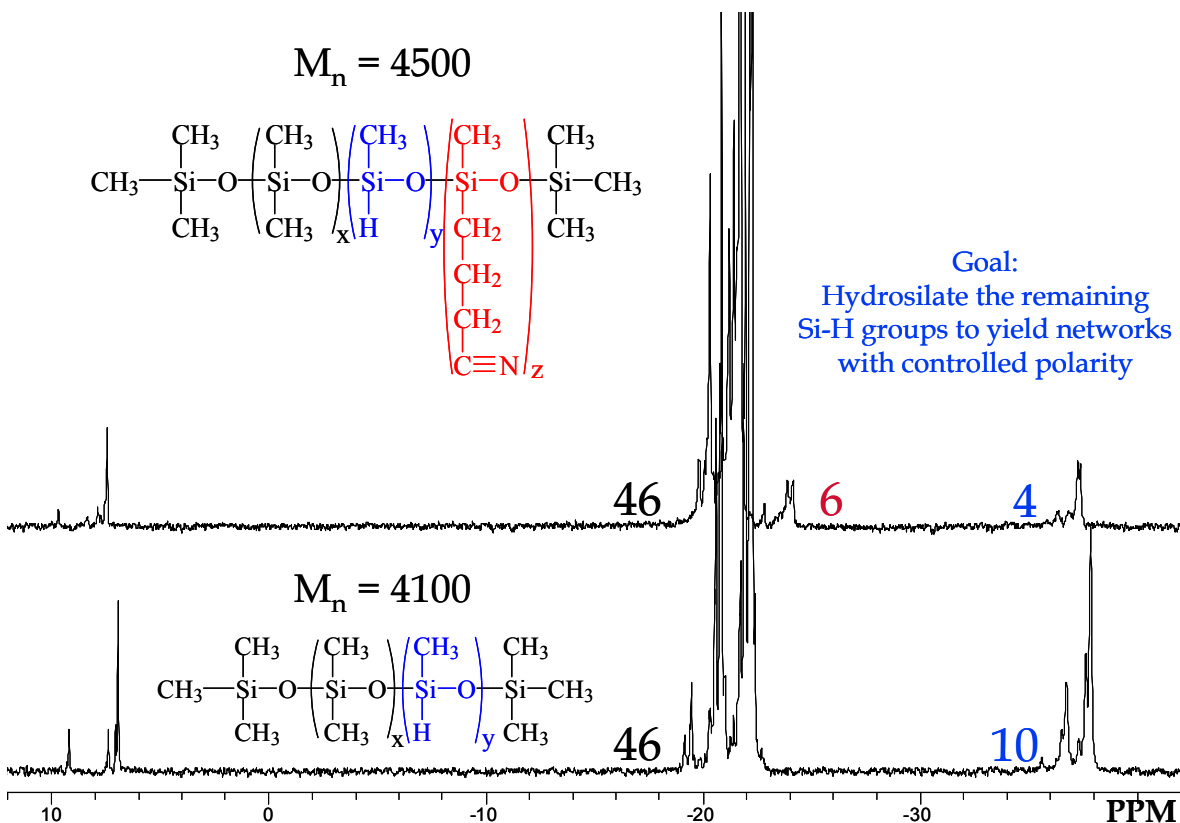


Figure 4.57.  $^{29}\text{Si}$  NMR Used to Follow the Hydrosilylation of a Poly(dimethyl-co-methylhydrido)siloxane with Allyl Cyanide to Yield a Poly(dimethyl-co-methylhydrido-co-3-cyanopropyl,methyl)siloxanes with 9 Mol % Nitrile Substitution

The goal for each of the functionalization reactions described herein was to leave controlled concentrations of hydrido (or vinyl described previously) unreacted. Network formation requires at least one of the reactants to have a functionality greater than 2.<sup>102</sup> Consequently, all of the reactions were performed to intentionally leave ~ 4 reactive hydrido or vinyl moieties. This was achieved for each synthesis (Tables 4.7 and 4.9).

## **Chapter 5. Investigation of Functionalized Polyorganosiloxanes and Corresponding Networks with Controlled Concentrations of Polar Moieties**

### ***5.1. Effects of Concentration and Type of Polar Pendent Moiety on Functionalized Polyorganosiloxanes and Respective Networks***

Novel polyorganosiloxanes with controlled concentrations of nitrile, phosphine oxide, phosphine, and carboxylic acid pendent moieties were synthesized. Each of the sidechain chemical structures is capable of strongly hydrogen bonding or complexing metals. This section details the effects of the molar fraction and type of substituent on the thermal and adhesion properties of the polysiloxane backbone. The typical glass transition temperature of polydimethylsiloxane ( $-125\text{ }^{\circ}\text{C}$ )<sup>81</sup> is strongly affected as bulky and strongly hydrogen bonding substituents are substituted for methyl- groups. Adhesion strength to metal oxides increased for the functional polysiloxanes as more polar substituents, capable of hydrogen bonding with surface hydroxyls, were added.

Lightly crosslinked polyorganosiloxane networks were prepared with controlled concentrations of nitrile (Figure 5.1) and phosphine oxide (Figure 5.2) pendent moieties. Network formation reactions and conditions were described in detail in Chapter 3. Each of the polyorganosiloxanes was crosslinked via two-component addition cures. Hydrido functional polysiloxanes were hydrosilated with vinyl functional crosslinking reagents whereas a hydrido crosslinking reagent was used to crosslink the vinyl functional polysiloxanes. Hydrosilation curing reactions were catalyzed with Karstedt's catalyst, platinum (0) complexed with 1,3-divinyltetramethyldisiloxane in xylene. Stoichiometric amounts of hydride to vinyl functional groups were used for all cures, and monitored via FTIR for the disappearance of the silane,  $\equiv\text{Si-H}$ , functional group absorbance at  $\sim 2160\text{ cm}^{-1}$ . All networks were fully cured at  $80\text{ }^{\circ}\text{C}$  either in molds or directly on metal adherends depending on the testing to be conducted.



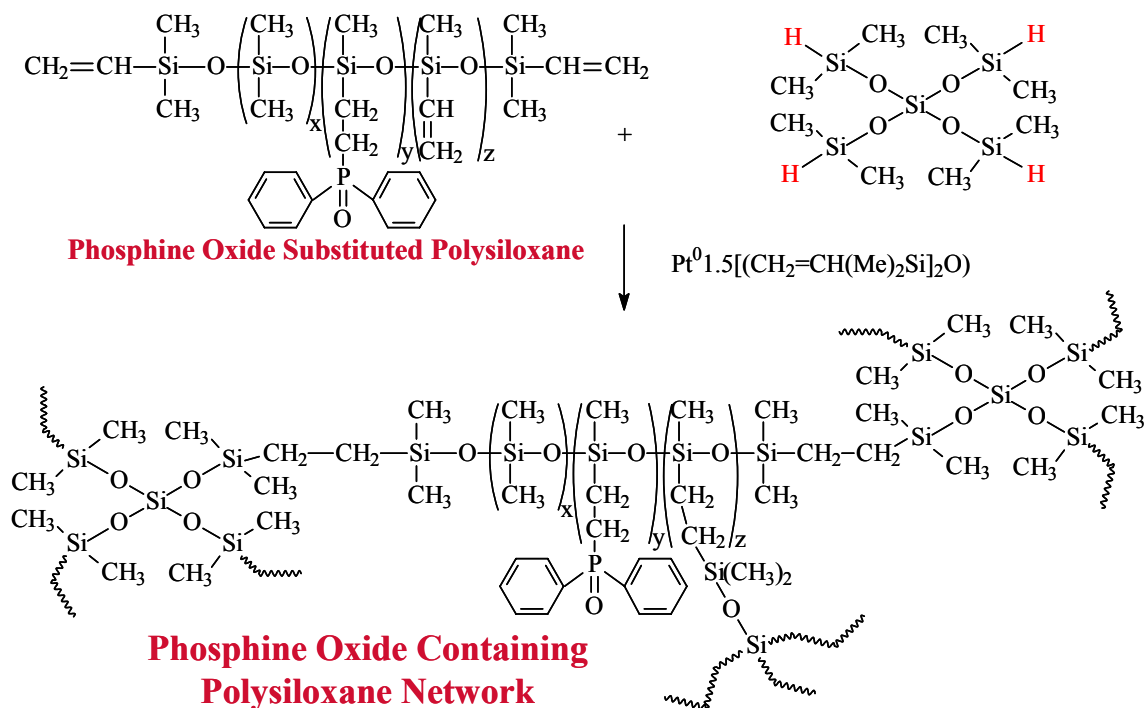


Figure 5.2. Hydrosilylation of a Polyorganosiloxane with Pendent 2-Diphenylphosphineethyl- Substituents and Reactive Vinyl Moieties to Yield Lightly Crosslinked Networks with Controlled Concentrations of Phosphine Oxide Moieties

Thermal analysis via differential scanning calorimetry (DSC) was performed to analyze the effects of crosslinking on the thermal properties of uncured oligomers. Adhesion strength measurements were conducted via 180° peel tests on Al substrates (ASTM D 903) with the polar polyorganosiloxane networks. These properties were important considerations for evaluating the materials as potential thermally conductive adhesives. The adhesives should maintain bond integrity between silicon (power device) and metal (heat sink) substrates while undergoing repeated thermal cycling.

## 5.2. Thermal Analysis: Differential Scanning Calorimetry

Polysiloxanes typically offer the lowest  $T_g$ s and subambient network flexibility relative to common organic thermally conductive adhesive resins (epoxies or methacrylates).<sup>1</sup> The glass transition ( $T_g$ ) is the reversible change in an amorphous

polymer or in amorphous regions of a partially crystalline polymer from, or to, a highly viscous or a rubbery condition.<sup>102</sup> Differential Scanning Calorimetry (DSC) is the measurement of energy absorbed (endotherm) or produced (exotherm), and may be applied to energy changes such as melting, crystallization, resin curing, loss of solvent; and to processes involving a change in heat capacity, such as the glass transition. DSC was used to measure the  $T_g$ s for all materials in this study.

Sample sizes between 5 – 10 mg of the polysiloxanes and networks were heated at a rate of 10 °C/min, and  $T_g$ s were recorded from their 2<sup>nd</sup> heat scans. Each sample was quenched from room temperature to –170 °C, scanned from –170 °C to 0 °C, quenched again (500 °C/min), and scanned again at 10 °C/min. The strongly hydrogen bonding phosphine oxide and carboxylic acid containing polysiloxanes required heating cycles above ambient. This procedure eliminated any crystallinity which might have been present before obtaining the  $T_g$ . This allowed totally amorphous samples to be tested, and possible crystallization to be observed during the second heat scan. The  $T_g$ s were measured before and after functionalization with polar moieties of the polysiloxane precursors (Table 5.1).  $T_g$  data were also compared for the functionalized polyorganosiloxane oligomers and their corresponding networks (Table 5.2). Each table provides the oligomer  $M_n$  (g/mol),  $n$  (degree of polymerization), type and % of functional moieties, % XL (wt. % crosslinking reagent for the networks) and  $T_g$ s.

Table 5.1. T<sub>g</sub> Data for Polysiloxane Precursors and Functionalized Polyorganosiloxanes

Chemical Composition			T <sub>g</sub>	Mn	n
<b>Polysiloxane Precursor</b>					
100% PDMS			<b>-125</b>	17460	234
<b>Polysiloxane Precursor</b>			<b>Tg</b>	<b>Mn</b>	<b>n</b>
20% vinyl, 80% dimethyl			<b>-131</b>	3120	38.6
20% vinyl, 80% dimethyl			<b>-129</b>	5690	72.1
20% vinyl, 80% dimethyl			<b>-127</b>	11070	142.4
100% vinyl			<b>-137</b>	1690	17.4
80% vinyl, 20% dimethyl			<b>-133</b>	3280	37.0
55% vinyl, 45% dimethyl			<b>-133</b>	3130	36.5
<b>Polysiloxane Precursor</b>	<b>Functionalized</b>		<b>Tg</b>	<b>Mn</b>	<b>n</b>
100% hydrido			<b>-141</b>	4410	70.9
72% hydrido, 28% dimethyl			<b>-137</b>	2200	32.1
45% hydrido, 55% dimethyl			<b>-133</b>	2680	37.3
17% hydrido, 83% dimethyl			<b>-129</b>	4140	55.7
6.7% hydrido, 84% dimethyl			<b>-120</b>	4470	55.0
17.5% hydrido, 55.5% dimethyl			<b>-102</b>	3340	37.0
18.1% hydrido, 27.8% dimethyl			<b>-84</b>	3410	32.4
100% nitrile			<b>-65</b>	10480	81
<b>Polysiloxane Precursor</b>	<b>Functionalized</b>		<b>Tg</b>	<b>Mn</b>	<b>n</b>
100% vinyl, aminopropyl terminated			<b>-127</b>	2750	29
100% vinyl, vinyl terminated			<b>-135</b>	2470	26.6
35% vinyl, 65% dimethyl			<b>-132</b>	2520	30.2
20% vinyl, 80% dimethyl			<b>-131</b>	2580	31.6
20% vinyl			<b>-5</b>	9320	40.0
50% Vinyl			<b>-31</b>	15050	93.5
9% vinyl, 76% dimethyl			<b>-90</b>	3580	31.6
16% vinyl, 3% dm			<b>+35</b>	6800	26.3
9% vinyl, 76% dimethyl			<b>-48</b>	3660	31.5
35% vinyl, 4% dimethyl			<b>-25</b>	4010	28.4
11% vinyl, 78% dimethyl			<b>-112</b>	2850	32.9
100% PDMS, COOH terminated			<b>-125</b>	23000	306.2

Table 5.2. Effect of Crosslinking on T<sub>g</sub> for Functionalized Polysiloxane Networks

% Functional Group	Mn	N	T <sub>g</sub> (°C) Polymer	T <sub>g</sub> (°C) Network	Wt. % XL
9% nitrile	4470	55.0	<b>-120</b>	<b>-111</b>	7
27% nitrile	3340	37.0	<b>-102</b>	<b>-89</b>	15
54% nitrile	3410	32.4	<b>-84</b>	<b>-68</b>	14
100% nitrile	10480	81	<b>-65</b>	<b>-60</b>	4
15% Phosphine Oxide	3660	31.5	<b>-48</b>	<b>-44</b>	6

### 5.2.1. Evaluation of $T_g$ s for the Polysiloxane Precursors, Functionalized Polyorganosiloxane Oligomers and Corresponding Networks

The  $T_g$ s for all of the polyorganosiloxanes and networks were below  $-25\text{ }^\circ\text{C}$  (with the exception of the 80 molar % phosphine oxide polysiloxane) making them good potential candidates for thermally conductive adhesives which may experience service temperatures in this range (Table 5.1). Each of the polyorganosiloxanes followed the expected trends for glass transitions.  $T_g$ s of polysiloxanes increased with increasing  $M_n$  and increasing size and/or polarity of the substituents on the polysiloxane backbone. These factors decreased the mobility of the polysiloxane chains relative to PDMS oligomers. Smaller or more mobile substituents such as hydrido or vinyl groups increased the flexibility of the polysiloxane chains and thereby resulted in materials with lower  $T_g$ s.<sup>81</sup> Crosslinking the oligomers resulted in 3-dimensional networks with decreased mobility, hence higher  $T_g$ s (Table 5.2).

The poly(dimethyl-co-methylvinyl)siloxane and poly(dimethyl-co-methylhydrido)siloxane polymers exhibit lower  $T_g$ s than PDMS ( $-125\text{ }^\circ\text{C}$ ). The hydrido containing polysiloxanes exhibited the lowest  $T_g$ s ( $-141\text{ }^\circ\text{C}$  to  $-129\text{ }^\circ\text{C}$ ), and decreased with increasing hydrido concentration. The vinyl terminated poly(dimethyl-co-methylvinyl)siloxanes with mol % vinyl decreasing from 100% to 35% to 20% (for very similar  $M_n$  oligomers, 2470 g/mol, 2520 g/mol, and 2580 g/mol) exhibited the same trend with a  $T_g$  increase from  $-135\text{ }^\circ\text{C}$  to  $-131\text{ }^\circ\text{C}$ . The size and polarity of endgroups also influenced the  $T_g$ s. An aminopropyl terminated poly(methylvinyl)siloxane exhibited a higher  $T_g$  of  $-127\text{ }^\circ\text{C}$  than the vinyl terminated homopolymer of  $-137\text{ }^\circ\text{C}$ . The glass transition temperatures of poly(dimethyl-co-methylvinyl)siloxanes containing 20 mol % methylvinylsiloxyl- repeat units increased (from  $-131\text{ }^\circ\text{C}$  to  $-127\text{ }^\circ\text{C}$ ) with  $M_n$  increasing from 3120 g/mol to 11070 g/mol.

Polyorganosiloxanes with increasing concentrations of pendent polar moieties were much more viscous than PDMS oligomers presumably due to hydrogen bonding. Each of the functionalized polyorganosiloxanes exhibited the expected trends for  $T_g$ s. Within each type of functional group, the  $T_g$ s increased with increased concentration of the substituent (Figures 5.3 - 5.5). The  $T_g$ s also increased as the size and hydrogen

bonding capability of the substituent increased for polysiloxanes with similar mol fractions of different types of functional group (Figure 5.6).

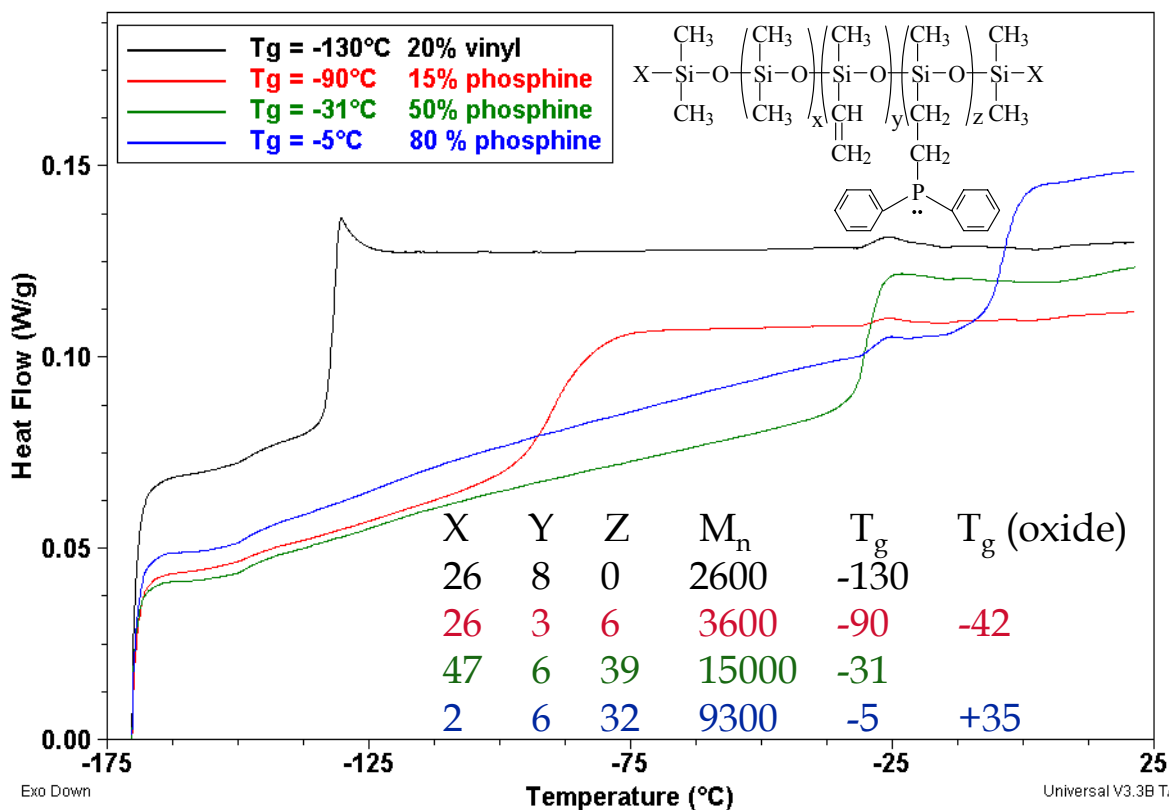


Figure 5.3. T<sub>g</sub>s of a Poly(dimethyl-co-methylvinyl)siloxane Precursor and Polyorganosiloxanes with Varied Concentrations of Pendent Phosphonyl Moieties (All DSC data shown are 2<sup>nd</sup> heat thermograms run at 10 °/min.)

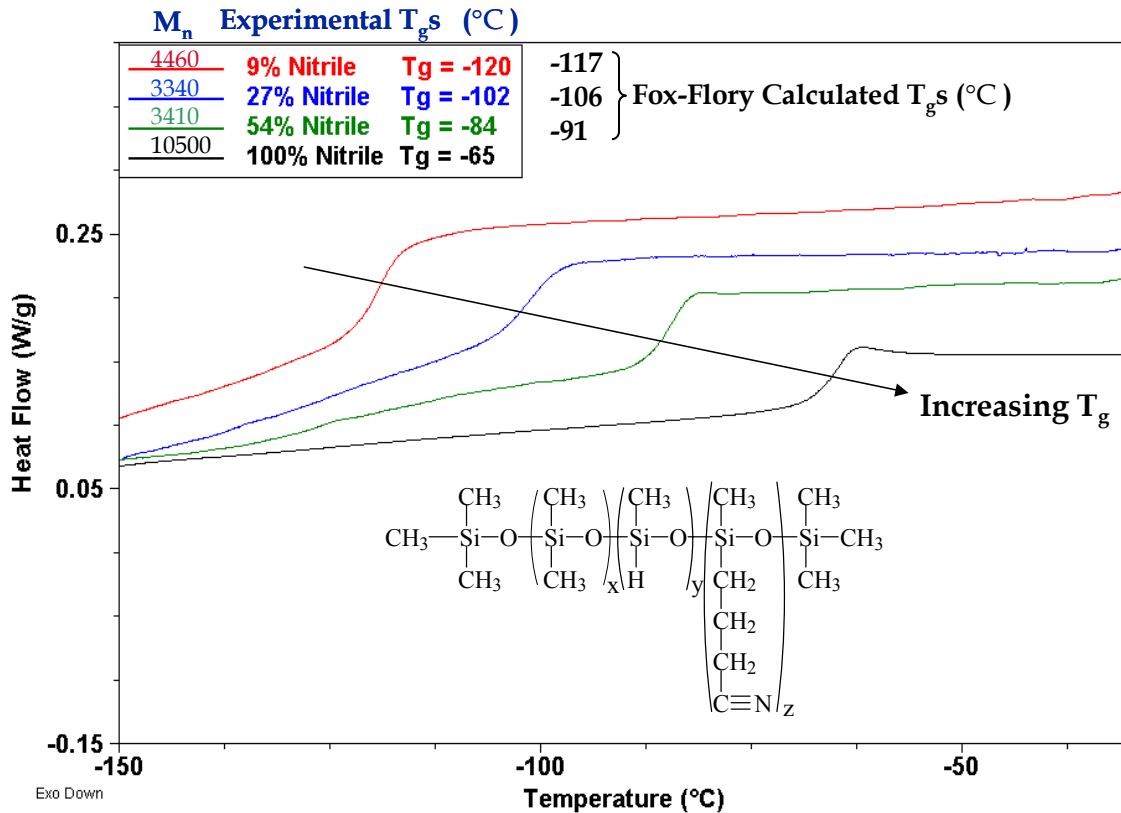


Figure 5.4. Effect of Increasing Nitrile Substitution on Polyorganosiloxane  $T_g$ s

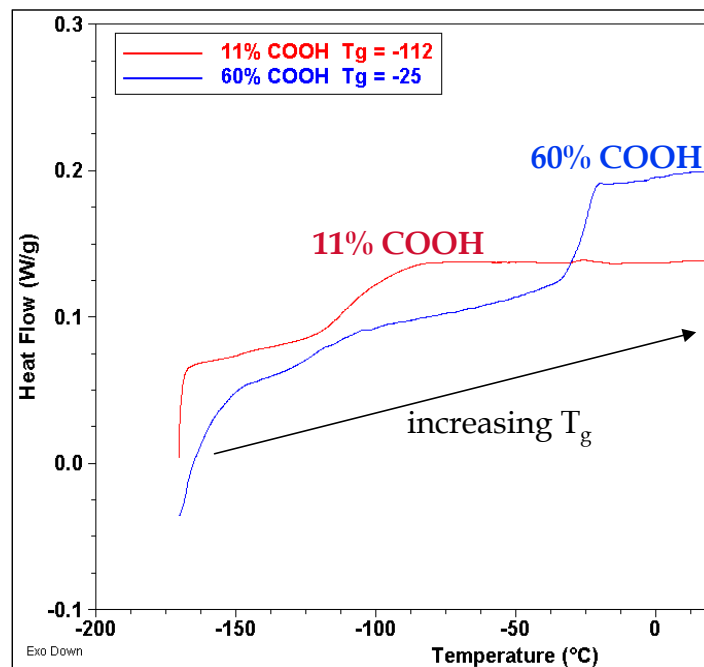


Figure 5.5.  $T_g$ s of Polyorganosiloxanes with Pendent Carboxylic Acid Moieties

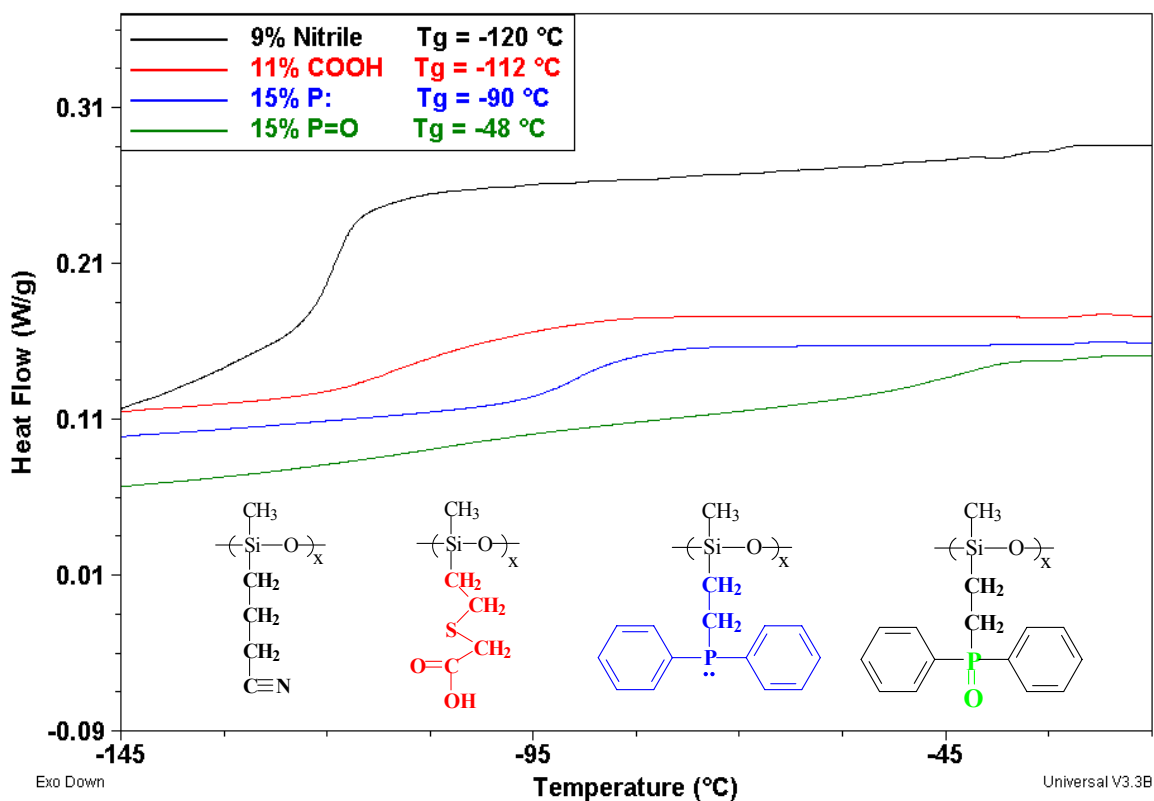


Figure 5.6. Effect of Size and Polarity of Sidechain Chemical Structures on the  $T_g$ s of Polyorganosiloxanes with 10-15 Mol % of Functional Pendent Moieties

$T_g$ s of the networks were increased substantially relative to those of their corresponding oligomers (Table 5.2). The amount of the increase depended on the wt. % of crosslinking reagent used to produce the networks. The  $T_g$  increased by 9 °C to 16 °C as the wt. % crosslinking of reagent increased from 7 to 15%. Moreover, the degree of hydrogen bonding strongly influenced the mobility of the polysiloxane oligomers prior to crosslinking. Therefore, the  $T_g$  increase for networks prepared from strongly hydrogen bonded polysiloxanes was not as great.  $T_g$ s increased by ~ 4 °C for networks with high amounts of polar groups, e.g. 100 % nitrile, or any amount of a very strongly hydrogen bonding group, e.g. 15% phosphine oxide.

### 5.3. 180° Peel Adhesion Strength

Adhesive strengths of the functionalized polyorganosiloxane networks were evaluated using metal to metal 180° peel tests (ASTM D 903) described in Chapter 3. The strong hydrogen bonding properties of random phosphine oxide containing polysiloxanes and the effect of nitrile moiety concentration on polysiloxanes were studied by quantitatively measuring network adhesion strength to Al substrates. It was established that poly(3-cyanopropylmethyl)siloxane (PCPMS) networks exhibited at least double the adhesive strength over nonpolar PDMS networks, independent of molecular weight between crosslinks and oligomer  $M_n$ s (Figure 5.7).<sup>33</sup> The polar PCPMS networks exhibited the desired mode of failure (cohesive), whereas nonpolar PDMS networks failed adhesively. Cohesive strength is the intrinsic strength of the adhesive, and cohesive failure is rupture of an adhesive bond within the adhesive. Adhesive failure is the failure of a bond between the adhesive and adherend (interfacial).<sup>158</sup>

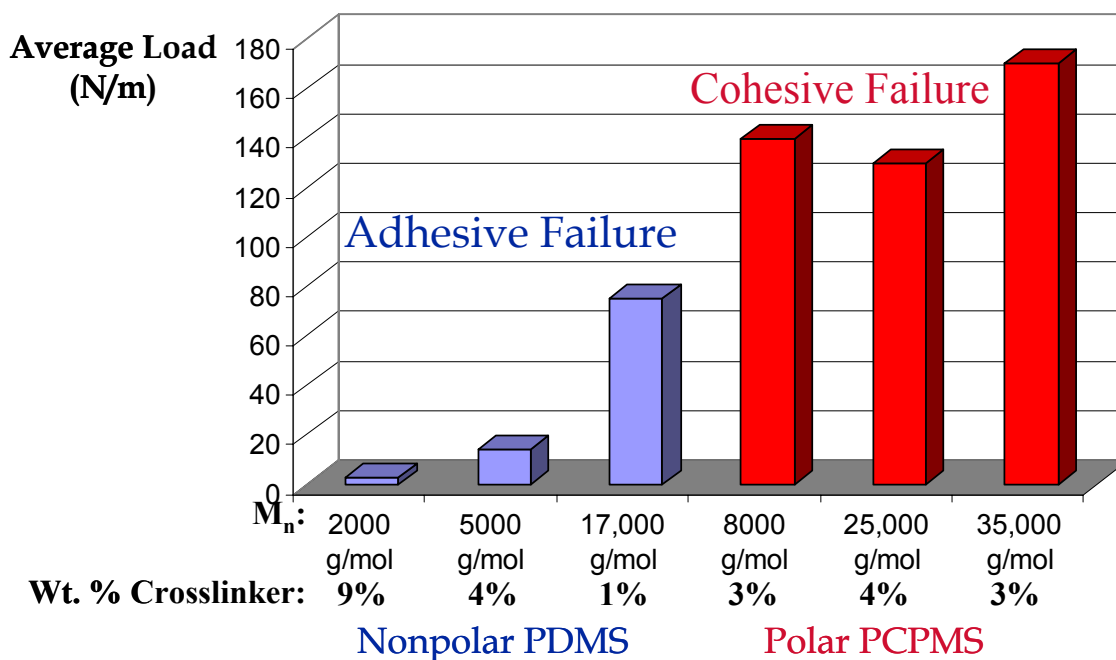


Figure 5.7. 180° Peel Strength to Al Substrates of Nonpolar PDMS Networks Versus Polar Poly(3-cyanopropylmethyl)siloxane Networks

158. H.F. Brinson, "Adhesives and Sealants, Vol. 3" ASM International, 1990.

Adhesion strengths of polyorganosiloxanes containing 9, 27 and 54 mol % of 3-cyanopropyl substituents were measured and compared to strengths for a corresponding sample prepared with a nonpolar PDMS with a similar average number of repeat units ( $n$ ) (Figure 5.8). The adhesion strengths increased (5.5 N/m, 7.9 N/m and 10.0 N/m) with increasing molar fractions of nitrile groups. The 9% nitrile substituted polysiloxane (5.5 N/m) adhesion strength was slightly greater than the adhesion strength of the nonpolar PDMS network (2.5 N/m). An error of 20% was associated with each of the adhesion values and was determined from the average of all of the adhesion values for each of the samples. It should be noted that the adhesion strengths of PCPMS homopolysiloxane with 100 % nitrile substitution to Al substrates (Figure 5.7) were much greater than the lower  $M_n$  oligomers containing 54% and less of the nitrile substituents. Each of the networks failed adhesively. These data suggested that the hydrogen bonding effects were not strong enough below 54% nitrile. The adhesion strength could presumably be increased for these polyorganosiloxanes with lower concentrations of nitrile moieties by preparing networks with higher  $M_n$  oligomers and lower wt. % crosslinking reagents.<sup>33</sup>

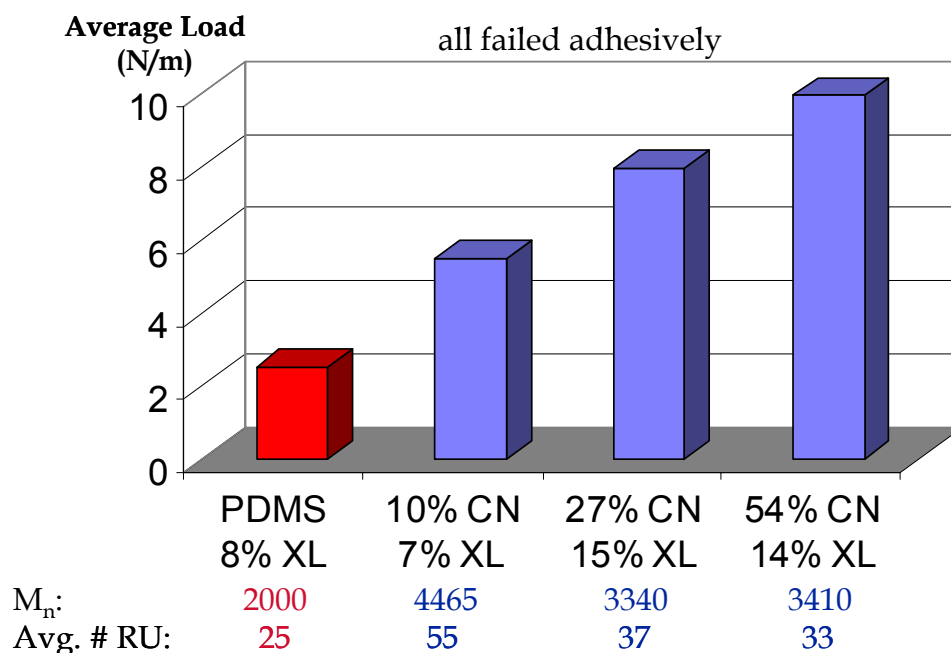


Figure 5.8. Adhesion Strengths for Polyorganosiloxanes with Varied Concentrations of Pendent Nitrile Moieties

The adhesion strength of the phosphine oxide containing polyorganosiloxane network was significantly greater with Al adherends than networks prepared from nonpolar polydimethylsiloxane, polar poly(3-trifluoropropylmethyl)siloxane and nitrile containing polysiloxanes with less than 54 mol % nitrile (Figure 5.9). This phosphine oxide substituted polyorganosiloxane (from an oligomer with 31 average repeat units) exhibited an adhesive strength (46 N/m) 18 times greater than the nonpolar PDMS network (2.5 N/m) (from an oligomer with 25 average repeat units). Interestingly, this network also exhibited an adhesive strength double that of a fluorine containing polysiloxane (PMTFPS) (from an oligomer with 26 average repeat units). This is noteworthy as fluorinated polysiloxanes are a current area of industrial interest for polar polysiloxanes.<sup>159,160</sup>

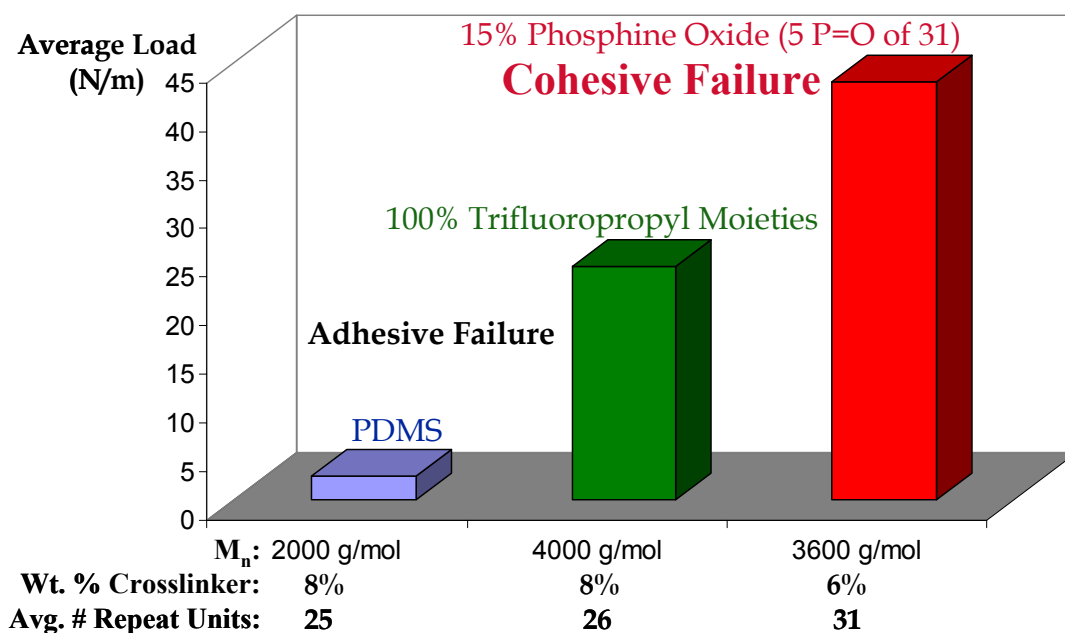


Figure 5.9. A Polyorganosiloxane Network with only 15 Mol % Phosphine Oxide Exhibited an Adhesive Strength Double that of a Poly(trifluoropropylmethyl)siloxane

159. M. D. Beers and J. M. Klosowski, "Silicones", 215, in Adhesives and Sealants, Vol. 3, H. F. Brinson, ASM International, 1990.
160. O. R. Pierce, "Fluorosilicones", in Silicone Technology, ed. P. F. Bruins, John Wiley & Sons, Inc., New York, 1970.

The functional polyorganosiloxane required only 15 mol % phosphine oxide polar moieties to gain a substantial increase in adhesion strength to Al. The significantly larger adhesion strength of the 15 mol % phosphine oxide containing polysiloxanes (46 N/m) over that of the 55 mol % nitrile containing polysiloxane (10 N/m) can be attributed to the hydrogen bonding capability. <sup>1</sup>H NMR hydrogen bonding studies shown earlier revealed that the chloroform proton was much more deshielded by the 15 mol % phosphine oxide containing polysiloxane than by the PCPMS homopolymer. The phosphine oxide containing polysiloxane network failed cohesively, whereas adhesive failure was observed for the nonpolar and fluorinated homopolysiloxanes. Failure for each the samples was determined visually. The important discovery of strong adhesion between phosphine oxide containing polysiloxanes with Al substrates led to the hypothesis that phosphine oxide containing oligomers should also strongly adsorb onto silica-coated AlN thermally conductive microparticles. The following chapter will compare the nitrile and phosphine oxide containing polysiloxanes microcomposites as thermally conductive adhesive materials.

## Chapter 6. Functionalized Polyorganosiloxane Microcomposite Dispersions and Microcomposite Networks as Thermally Conductive Adhesives

### 6.1. Introduction to Functionalized Polyorganosiloxane Microcomposites Networks as Thermally Conductive Adhesives

Efficient thermal management greatly influences the expected lifetime of consumer electronic devices as power sources become increasingly small with higher power densities.<sup>125</sup> Thermally conductive adhesives provide a means for effectively dissipating heat away from delicate microelectronic components.<sup>116</sup> The adhesive binder is typically a polymeric resin filled with high volume fractions of conductive metal or ceramic particles.<sup>161</sup> Adhesives and thermal "greases" have gained recent popularity as attractive alternatives to lead based solders due to economic and safety issues.<sup>1,119,162</sup> Organic polymers are inherently insulating materials with low thermal conductivities ( $k$ ) and require high levels of a conductive filler to achieve maximum heat flow ( $Q$ ).<sup>126</sup> For instance, unfilled polysiloxanes have  $k$  values of  $\approx 0.2 - 0.3$  W/mK.<sup>1</sup> The best conductive adhesives are presently comprised of adhesive binders loaded with Ag, BN and AlN ( $k \sim 150 - 400$  W/mK) to yield materials with  $k$  values of  $\approx 3 - 4$  W/mK.<sup>2</sup>

Specific interactions of three types of functional polyorganosiloxanes with thermally conductive microfillers were investigated. Strong interactions between the resins and fillers are critical in maintaining a stable microcomposite dispersion. Nonpolar polysiloxanes do not form stable suspensions with polar conductive fillers for a reasonable shelf life (filler precipitates in  $< 24$ h). Phosphine substituted polysiloxanes are capable of complexing metals<sup>5</sup>, and should complex acidic metal or ceramic

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161. R. E. Batson, "Industrial Applications for Adhesives", 571, in Adhesives and Sealants, Vol. 3, H. F. Brinson, ASM International, 1990.

162. M. G. Firmstone, P. M. Bartholomew, G. Paterson, R. Dietz and P. Robinson, *Microelectronics International*, **43**, 16-21, May, 1997.

particulates as shown in the model for a filled conductive adhesive (Figure 6.1). The hydrogen bonding capabilities of both nitrile and phosphine oxide substituted polysiloxanes were shown earlier via  $^1\text{H}$  NMR and adhesion strength studies. Each of the materials should hydrogen bond with surface hydroxyls on silica coated AlN or metal oxides (Figures 6.1 and 6.2). These strong interactions yielded microcomposites with higher volume fractions of conductive filler than possible for PDMS resins.

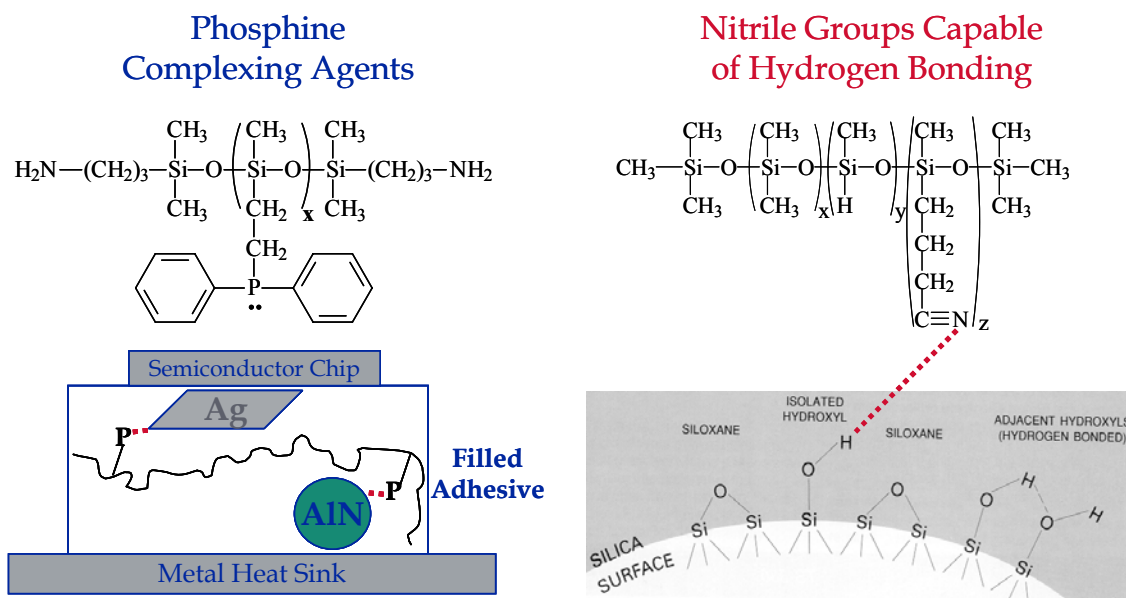


Figure 6.1. Specific Interaction Models Between Phosphine Containing Polysiloxanes with Acidic Metal or Ceramic Particles and Between Nitrile Groups with a Silica Surface

**Silica Coated AlN**  
 0-5% SiO<sub>2</sub>  
 95-100% AlN  
 ρ = 3.3 g/cc

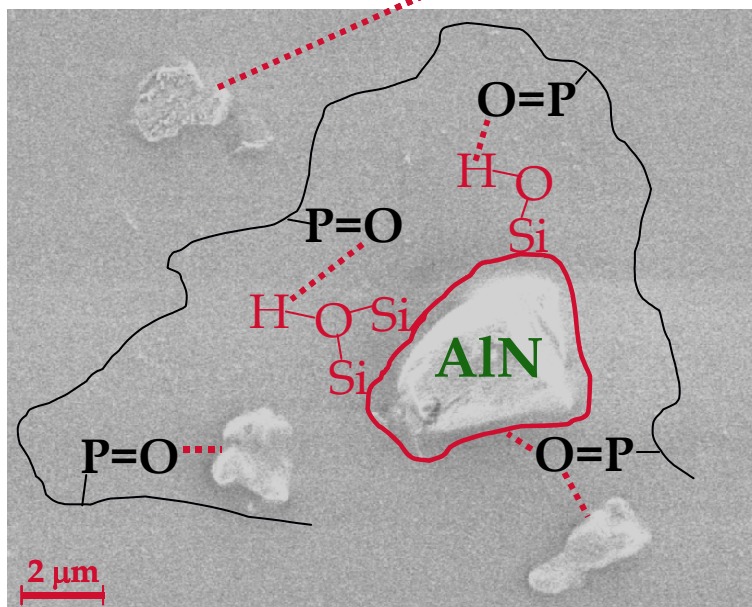
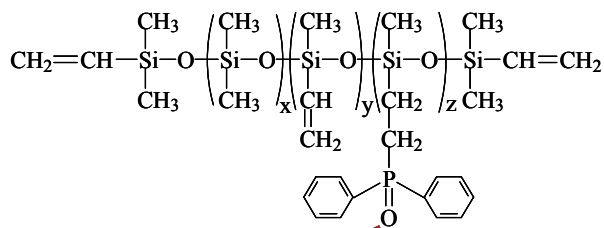
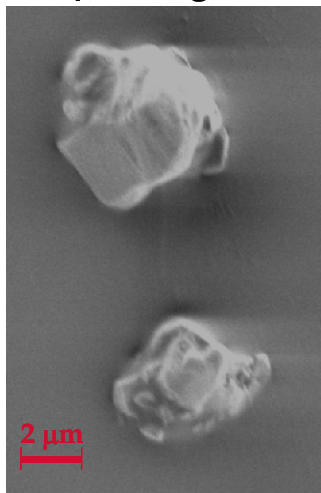


Figure 6.2. A Model of the Specific Interactions Between a Strongly Hydrogen Bonding Phosphine Oxide Moiety with an Actual SEM of Silica-Coated AlN Microparticles

The thermally conductive filler, silica-coated AlN, was kindly provided by IBM and primarily used for investigations of specific interactions with the functional polyorganosiloxanes. A scanning electron microscopy image (SEM) of the particles displayed the irregular shape and size (2 – 10 μm) (Figure 6.2). The particles are coated with 0 – 5 % silica and the bulk core is an AlN ceramic microparticle. A proposed adsorption process was modeled between the pendent phosphine oxide moieties of a polyorganosiloxane with the hydroxy groups of silica-coated AlN microparticles via an actual SEM of the microparticles (Figure 6.2).

## 6.2. Investigation of Specific Interactions Between Functional Polyorganosiloxanes and Silica-Coated AlN via X-Ray Photoelectron Spectroscopy

Secondary interactions between the functional polysiloxanes were investigated using both  $^1\text{H}$  NMR and X-Ray Photoelectron Spectroscopy (XPS). XPS was used to confirm that the silica-coated AlN conductive microparticles were well coated with the functional polyorganosiloxane resins (Figure 6.3). The binding energy of the Si atom of the silica coating on silica-coated AlN microparticles (103.7 eV) was not detected on the uncured functional polysiloxane microcomposite surfaces containing 50 vol.% silica-coated AlN. Only Si 2p photopeaks (102.2 eV) for the Si atom of the polysiloxane backbone of the nitrile and phosphine containing polyorganosiloxanes were identified.

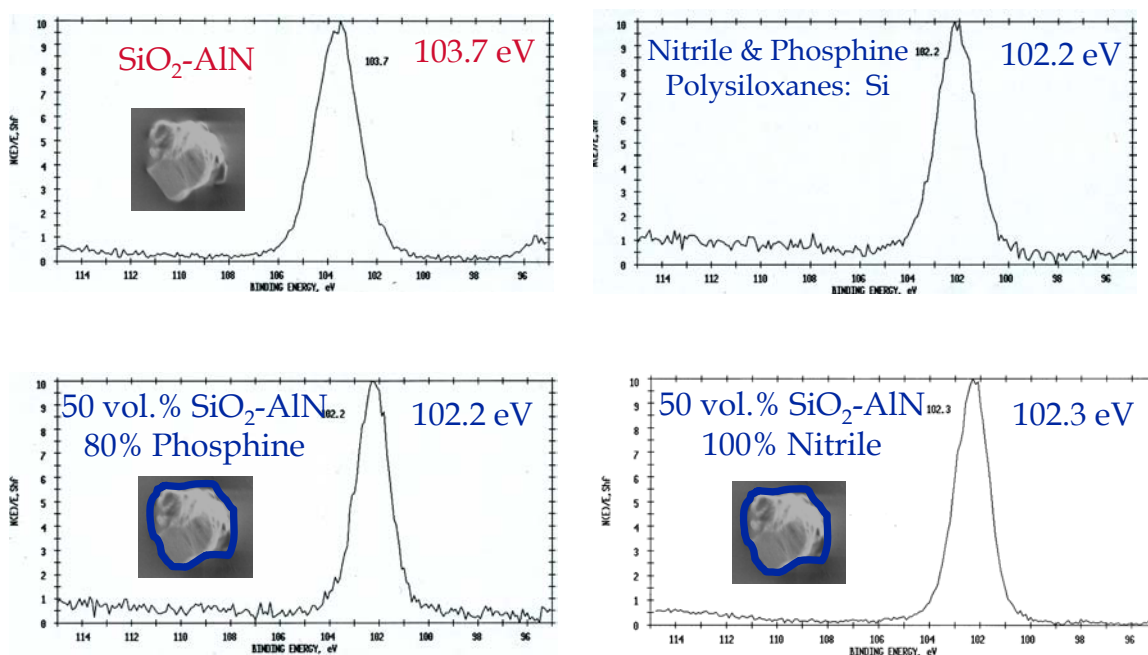


Figure 6.3. Si 2p Photopeaks for Silica Coated AlN, Nitrile and Phosphine Functionalized Polyorganosiloxanes, and Silica Coated AlN/ Nitrile and Phosphine Functionalized Polyorganosiloxane Microcomposites

### ***6.3. Analysis of Dispersion Quality for Functionalized Polyorganosiloxane Microcomposites via Transmission Electron Microscopy***

The dispersion quality and maximum volume fractions of silica-coated AlN in functionalized polyorganosiloxane microcomposites were studied as functions of the type and concentration of pendent polar moieties using transmission electron microscopy (TEM). Neat PCPMS and phosphonyl containing polysiloxane resins were filled with 75 weight % (50 volume %) of the polar thermally conductive silica coated AlN filler to yield stable microcomposite dispersions. TEM samples were prepared by placing a drop of the uncured microcomposites suspended in CH<sub>2</sub>Cl<sub>2</sub> onto copper TEM grids having a 200-300Å thick carbon over-layer. Contrast variations in the TEM images represented differences in thickness or electron density.

TEM verified a dramatic difference in dispersion quality between the polar functionalized polyorganosiloxanes versus nonpolar polydimethylsiloxane. Importantly, an 80 mol % phosphine substituted polyorganosiloxane (light gray) completely enveloped each silica-coated AlN particle (black) (Figure 6.4 A). The nitrile containing homopolysiloxane (PCPMS) (light gray) surrounded the particles, although to a lesser extent (Figure 6.4 B). Adhesion between the silica-coated AlN particles with the nonpolar polydimethylsiloxane (PDMS) resin was poor, and the aggregated particles (black) tore the carbon over-layer (Figure 6.4 C). Each of the TEM images was representative of the observed behavior over the entire TEM grid. It should also be noted that the SEM images (Figure 6.2) of the silica-coated AlN corresponded to the size and shape of the silica-coated AlN observed via TEM.

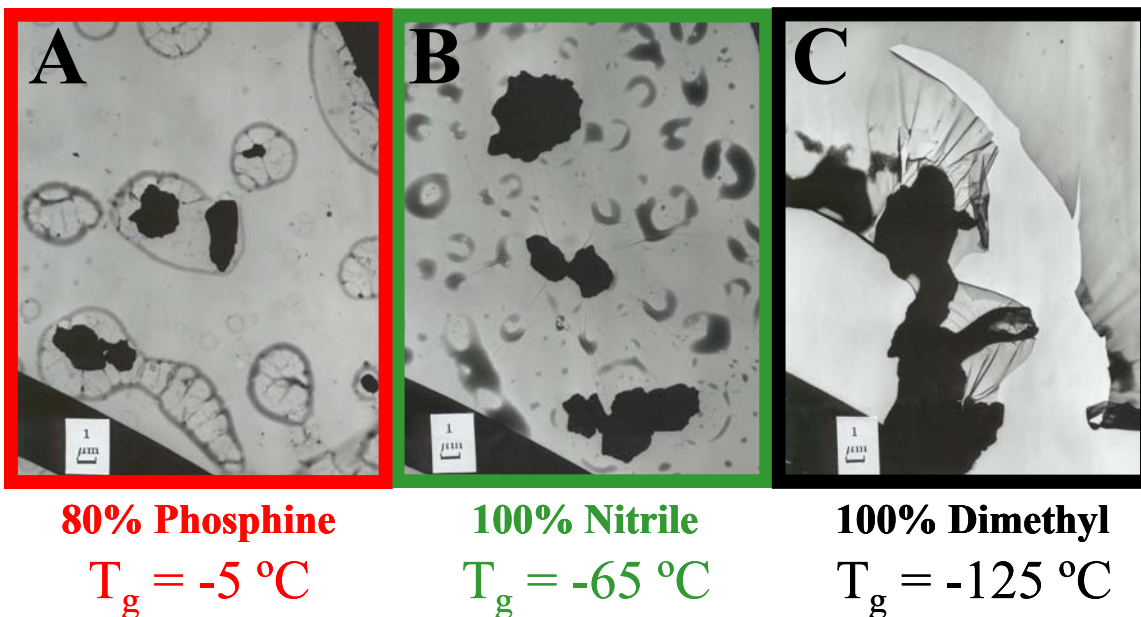


Figure 6.4. Effects of Pendent Moieties on Particle-Resin Adhesion Indicated via TEM Images for Polyorganosiloxane Microcomposites with 20 volume % (45 weight %) Silica-Coated AlN

Interesting images were obtained for the 80% phosphine substituted polyorganosiloxane on the TEM grid (Figure 6.4 A). This particular polyorganosiloxane appeared to dry in "pools". This behavior may be due to different wetting effects associated with the nonpolar carbon grid, or interactions with the solvent,  $\text{CH}_2\text{Cl}_2$ . One future aspect of this work will include a study on the effects of TEM grid and solvent polarity. It appears that the phosphine containing polysiloxane preferred to be in contact with only itself or the polar silica coated AlN filler particles. The strongly hydrogen bonding phosphine substituted polysiloxane presumably dried in "pools" due to poor wetting of the nonpolar carbon over-layer on the copper TEM grid.

Well coated AlN microparticles were also obtained using polyorganosiloxanes with systematically varied concentrations of phosphonyl substituiton. As little as 15 mol % phosphonyl moieties yielded well coated silica-coated AlN microparticles and beneficially lower  $T_g$ s ( $-90\text{ }^\circ\text{C}$ ) (Figure 6.5). Excellent particle-resin adhesion was

maintained even when 50 volume % (75 wt. %) of silica-coated AlN was dispersed throughout each of the phosphonyl substituted polyorganosiloxanes.

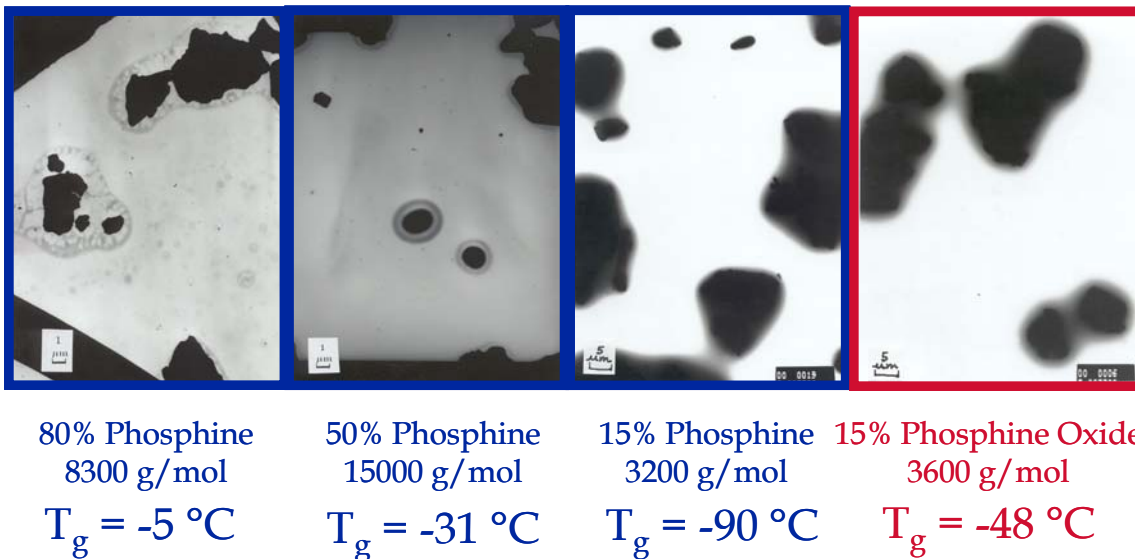


Figure 6.5. Polyorganosiloxanes with Varied Concentrations of Pendent Phosphonyl Moieties Filled with 50 Volume % Yield Well Coated AlN Conductive Microparticles

Preliminary properties of the poly(3-cyanopropylmethyl)siloxane microcomposites filled with 50 vol.% silica-coated AlN were promising. A thermal conductivity of 0.7 W/mK was measured by IBM scientists. This value was expected to improve with the polysiloxane substituted with lower concentrations of phosphonyl and nitrile moieties with lower viscosities. These resins were capable of being filled with higher contents of the conductive filler while remaining processable. IBM's thermal conductivity goal for a polysiloxane microcomposite was 2 W/mK. The best commercial polysiloxane based thermally conductive adhesive material they have found was 1.4 W/mK. Low modulus polysiloxane conductive adhesives are desirable because effects of the CTE mismatch between a metal heat sink and electronic component adherends can thereby be minimized.<sup>1</sup>

Nitrile and phosphine oxide substituted polyorganosiloxanes were further investigated to yield the highest thermal conductivity value possible. Four variables required for maximum thermal conductivity are 1) high volume fraction of the thermally

conductive filler, 2) high k value of the filler, 3) a thin bond line and 4) an air free microcomposite. The nitrile polyorganosiloxane substituted with 9 mol % of 3-cyanopropyl- moieties met the above requirements. This material was filled with 67 volume % (86 weight %) of silica-coated AlN and crosslinked to yield air-free microcomposite networks. This material was also less expensive to prepare relative to phosphonyl substituted polyorganosiloxane resins. The uncured nitrile containing polyorganosiloxane microcomposites were reported by IBM to be stable. The following sections details the effects of nitrile concentration and type of thermally conductive filler on the thermal conductivity for nitrile functionalized polyorganosiloxane microcomposite networks.

#### ***6.4. Investigation of Thermal Conductivity on Functionalized Polyorganosiloxanes Highly Filled with A Variety of Thermally Conductive Microfillers***

Microcomposites comprised of an organic adhesive binder filled with a thermally conductive filler are lightweight nontoxic alternatives to lead based solders.<sup>158</sup> Thermally conductive adhesive microcomposites may be used to dissipate heat away from delicate microelectronic devices (pn-junction based semiconductor discrete and integrated elements), reducing thermally-induced saturation current, extending the onset of thermal runaway and resulting in improved reliability. Aircraft could be improved by using conducting adhesives and nanocomposites which are 80 % lighter than conventional metals and allow simple synthesis and processing routes.<sup>158</sup>

The thermal conductivity of the novel crosslinked thermal transfer media was evaluated by IBM according to a modified ASTM D5470 procedure. The intention was to maximize the heat flow (Q) via a lightweight alternative to lead based solders for microelectronic and aerospace applications. The schematic representation for a thermally conductive adhesive lists the requirements for preparing a highly thermally conductive adhesive microcomposite (Figure 6.6).

## Thermal Conductivity

$$Q = \frac{k A \Delta T}{d}$$

1. **Filler Concentration (k)**
2. **Bond line ideally:  $d = \text{particle size}$**
3. **Particle: size, shape, composition determine microcomposite rheology**
  - high aspect ratio, bimodal size
  - particle surface treatment
  - mixing methods

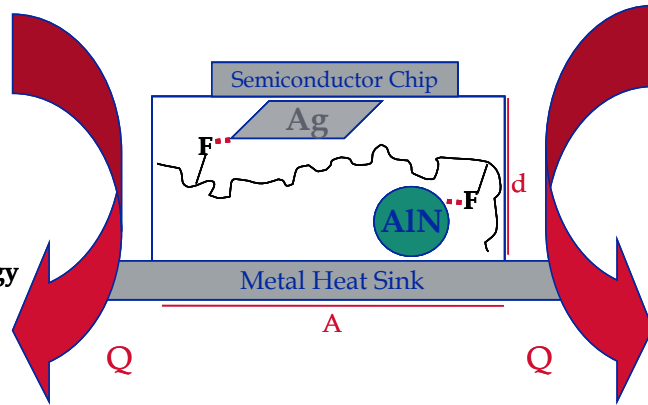


Figure 6.6. Schematic for Maximizing the Heat Flow Away from Delicate Microelectronic Components via Thermally Conductive Adhesive Microcomposites

The most important factors for obtaining a thermally conductive microcomposite are the type, size and shape of the filler particle. The filler must be capable of arranging itself for maximum packing while achieving the thinnest possible layer (ideally the thickness of the thickest particle,  $d$ , in the adhesive layer). The shape and the size distribution govern the packing ability. Flat platelet particles would give a thinner layer, assuming they lie flat. Irregular and spherical particles typically require a bimodal (or multimodal) size distribution to achieve maximum volume %. This explains why the  $k$  value is not necessarily the most important factor when choosing a thermally conductive filler. Polyorganosiloxanes substituted with 9, 27, and 54 mol % nitrile moieties were filled with various thermally conductive microfillers with different:  $k$ -values, densities, average size ranges and shapes (Table 6.1).

Table 6.1. Properties of Thermally Conductive Fillers that were Incorporated into Nitrile Containing Polyorganosiloxanes to Form Thermally Conductive Adhesives

	<u>SiO<sub>2</sub>-AlN</u>	<u>Al spheres</u>	<u>BN powder</u>	<u>Ag flake</u>
k (W/mK)	260	234	250-300	429
ρ (g/cc)	3.3	2.7	2.25	10.5
shape	irregular	spherical	hexagonal	platelike
size	2-10 μm	17-30 μm	8-14 μm	4-8 μm

The thermal conductivity data were obtained by colleagues at IBM (Figure 6.7 and Table 6.2). The polyorganosiloxane substituted with 9 mol % nitrile moieties filled with 67 volume % silica coated AlN was the most effective at conducting heat. The thermal conductivity value for this microcomposite network was greater than 1.4 W/mK, which was at least equal to the best commercial thermally conductive adhesive that IBM has found based on a polysiloxane. The polysiloxanes containing 27 mol % and 54 mol % nitrile moieties could not be filled with 67 volume % of the filler while remaining processable. These oligomers were filled with 65 volume % (85 weight %) and 63 volume % (83 weight %), respectively. This was due to the increasing viscosity of the oligomers as more 3-cyanopropyl- moieties were substituted for methyl- groups.

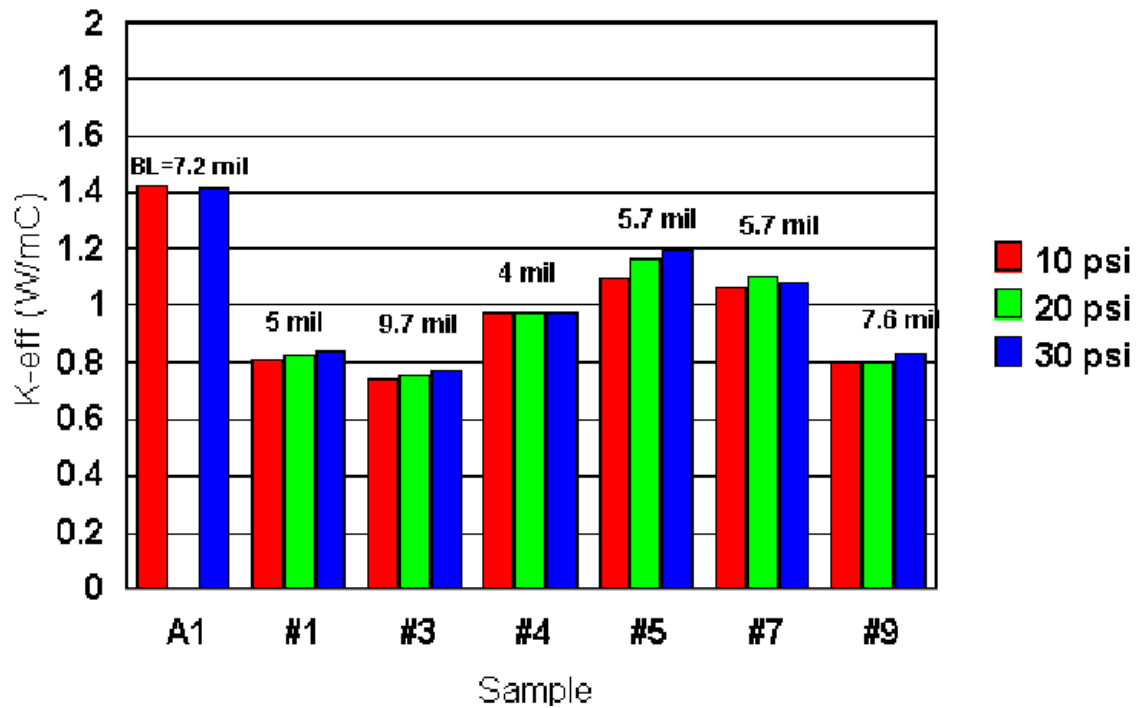


Figure 6.7. Thermal Conductivity Values of Polyorganosiloxane Microcomposite Networks Comprised of Polyorganosiloxanes with Varied Concentrations of Nitrile Moieties and Filled with Various Thermally Conductive Fillers

Table 6.2. Legend to Figure 6.7

Sample	Filler	Volume % Filler	Polysiloxane	k (W/mK)	Bondline
A1	Silica Coated AlN	67%	9 % Nitrile	<b>1.42</b>	7.2 mils
#1	Silica Coated AlN	63%	9 % Nitrile	<b>0.81</b>	5 mils
#3	Boron Nitride	37%	9 % Nitrile	<b>0.75</b>	9.7 mils
#4	Aluminum spheres	66%	9 % Nitrile	<b>0.98</b>	4 mils
#5	Silica Coated AlN	65%	27 % Nitrile	<b>1.18</b>	5.7 mils
#7	Silica Coated AlN	63%	54 % Nitrile	<b>1.08</b>	5.7 mils
#9	Silver flake	30%	9 % Nitrile	<b>0.81</b>	7.6 mils

The bondline thickness did not influence thermal conductivity values as strongly as the volume % of filler. The 9 % nitrile substituted polyorganosiloxane with 67 volume % silica-coated AlN had a thicker bondline of 7.2 mils and higher k value of > 1.4 W/mK relative to the 65 volume % silica-coated AlN filled polyorganosiloxane substituted with

27 % nitrile groups ( $\sim 1.18$  W/mK) having a thinner bondline of 5.7 mils. This was not surprising since thermal conductivity increases exponentially with volume % conductive filler.<sup>2</sup> Moreover, the 27 % nitrile substituted polyorganosiloxane/65 vol % silica-coated AlN microcomposite performed better on average ( $k \sim 1.18$  W/mK) than the 54 % substituted polyorganosiloxane/63 vol % silica coated AlN ( $k = 1.08$  W/mK), where each had identical bondline thicknesses.

The variation of fillers with different  $k$  values, sizes and shapes also did not influence the thermal conductivity values as greatly as did the volume fraction of filler. The BN powder (37 volume %), aluminum sphere (66 volume %) and Ag flake (30 volume %) microcomposites each dispersed in the 9 mol % nitrile polyorganosiloxane yielded microcomposite networks with  $k$  values of less than 1.0 W/mK. Moreover, each of these  $k$  values was higher than observed in an initial study with PCPMS (0.7 W/mK). Resins with lower viscosities,  $T_g$ s and tensile moduli yielded more suitable binders for conductive adhesives, and these properties are addressed in the following sections.

Thermal conductivity increased with volume % of silica coated AlN in nitrile substituted polyorganosiloxanes (Figure 6.8). The first data point represents a PCPMS homopolymer containing 50 volume % silica-coated AlN. The other data points in the graph reveal that higher volume fractions of 63 and 65 % increase the thermal conductivity exponentially. More points will be added to this trendline using the 9 mol % nitrile containing polysiloxane with fillers optimized for the best packing to increase the volume fraction incorporated into the matrix.

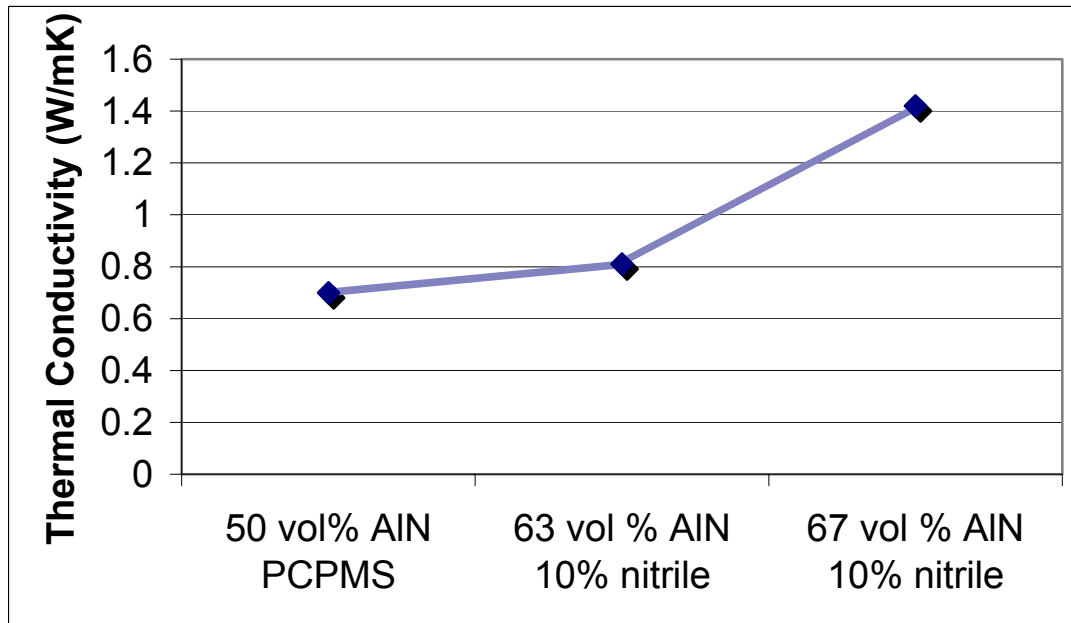


Figure 6.8. Increase in Thermal Conductivity with Increasing Volume % of Silica Coated AlN Thermally Conductive Filler with Nitrile Containing Polysiloxanes

### **6.5. Effect of Thermally Conductive Fillers on the $T_g$ s of Functionalized Polyorganosiloxane Microcomposite Networks**

Each of the functionalized polyorganosiloxane/conductive microcomposite networks was analyzed via DSC to investigate the effect of filler on the  $T_g$  of the network (Table 6.3). The filler had a minimal effect on the  $T_g$  of the network. The  $T_g$ s for the filled microcomposite networks occurred at a lower temperature relative to the unfilled networks. The microcomposite network  $T_g$  values were higher than the oligomers by 2 °C – 12 °C. Each of these polysiloxane microcomposite networks offers low temperature flexibility and would serve as a good potential thermally conductive material over a wide service temperature range.

Table 6.3. T<sub>g</sub> Data for the Thermally Conductive Microcomposite Networks Prepared using Functionalized Polyorganosiloxanes

Polysiloxane	Oligomer Network		Microcomposite	Conductive Filler	Vol % Filler
	T <sub>g</sub> (°C)	T <sub>g</sub> (°C)	T <sub>g</sub> (°C)		
9 % Nitrile	-120	-111	-115	Silica Coated AlN	67%
9 % Nitrile	-120	-111	-118	Silica Coated AlN	63%
9 % Nitrile	-120	-111	-115	Aluminum spheres	66%
27 % Nitrile	-102	-89	-90	Aluminum spheres	66%
54 % Nitrile	-84	-67	-75	Aluminum spheres	65%
15 % P=O	-48	-44	-44	Silica Coated AlN	50%

### **6.6. Effect of Thermally Conductive Fillers on the Weight Loss and Char Yield for Functionalized Polyorganosiloxane Microcomposite Networks**

Thermogravimetric analysis (TGA) was performed on the functionalized polyorganosiloxane microcomposite networks to determine thermal stabilities at high temperatures. Weight % loss and char yield at 900 °C were evaluated for a polyorganosiloxane substituted with 80 mol % phosphine moieties, and a microcomposite filled with 20 volume % (45 wt. %) silica-coated AlN (Figure 6.9). The thermal stabilities of the unfilled and filled phosphine substituted polyorganosiloxanes were quite high, where 5 % weight loss occurred at ~ 400 °C, when heated at a rate of 10 °C/min in air or N<sub>2</sub>. The weight % char yield was increased from ~ 35% to ~ 60 % when 20 volume % of the filler was incorporated. The increase in char yield is beneficial to the flame retardant properties of conductive microcomposites.

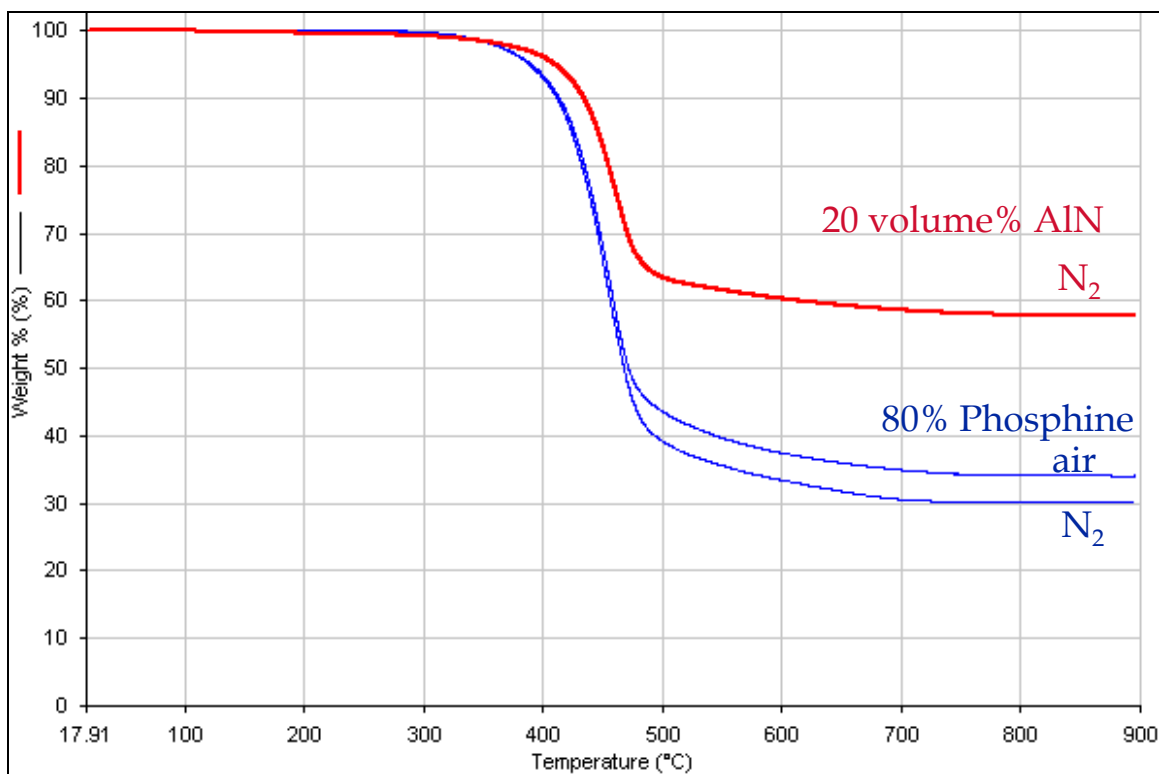


Figure 6.9. TGA Analysis of an 80 Mol % Phosphine Substituted Polyorganosiloxane and the Corresponding Microcomposite Filled with 20 Volume % Silica-Coated AlN

TGA data were compared for the polyorganosiloxane oligomers with 9 mol % nitrile moieties, its unfilled network, and its thermally conductive adhesive microcomposite network when filled with 67 volume % silica-coated AlN (Figure 6.10). Each of the samples was heated at a rate of 10 °C / min in both N<sub>2</sub> (solid lines) and air (dashed lines). The 5% weight loss temperatures and char yields increased dramatically as the oligomer was crosslinked and filled with the silica-coated AlN. The network and microcomposite samples were thermally stable at temperatures greater than 300 °C (at a heating rate of 10 °C / min). The microcomposite had greater than 90% char yield at 900 °C, making it an excellent flame retardant material.

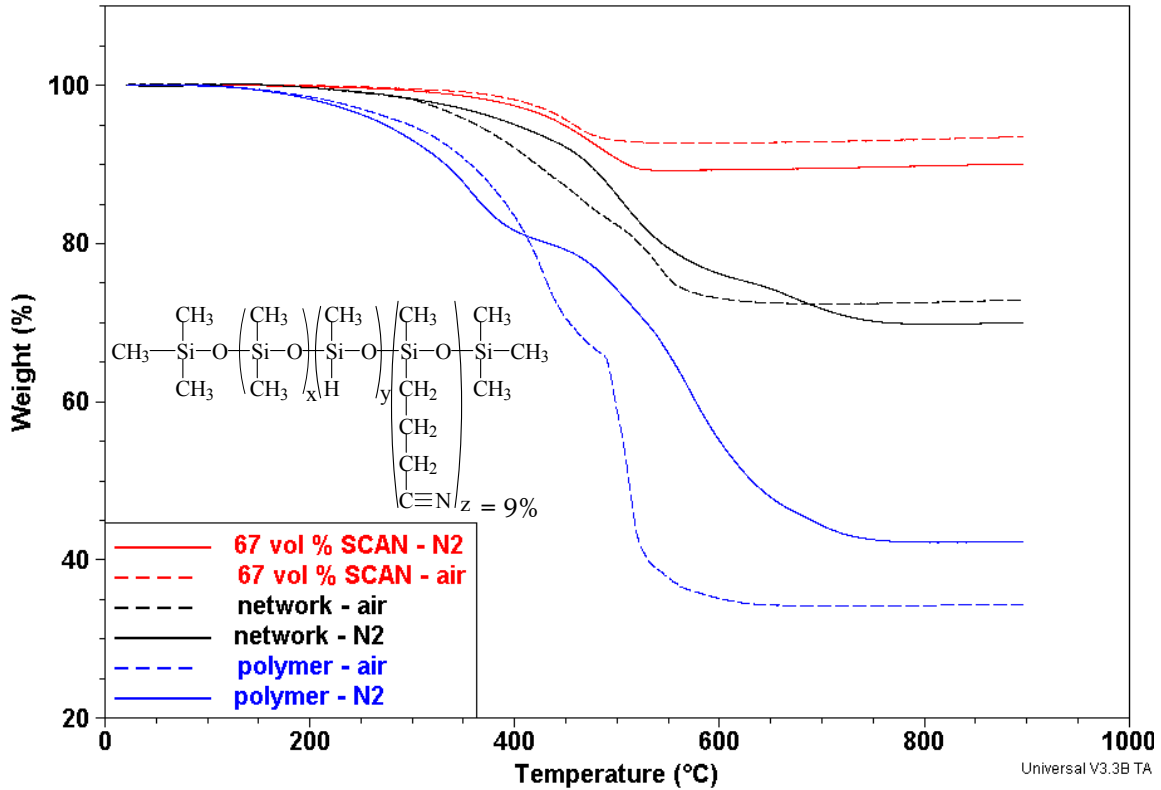


Figure 6.10. TGA Data for a 9 Molar % Nitrile containing Polysiloxane, Network and Microcomposite Filled with 67 Volume % Silica Coated AlN

Very high weight % char yields were observed for the 9 mol % nitrile substituted polyorganosiloxane microcomposites with a variety of conductive fillers (Figure 6.11). The blue curves represent the microcomposite filled with 67 volume % silica-coated AlN. Red curves represent a second type of silica-coated AlN (SCAN 70) (54 vol %) with a different particle size distribution from that used throughout the entirety of this study. Black curves represent the microcomposite prepared with 65 volume % of the Al spheres.

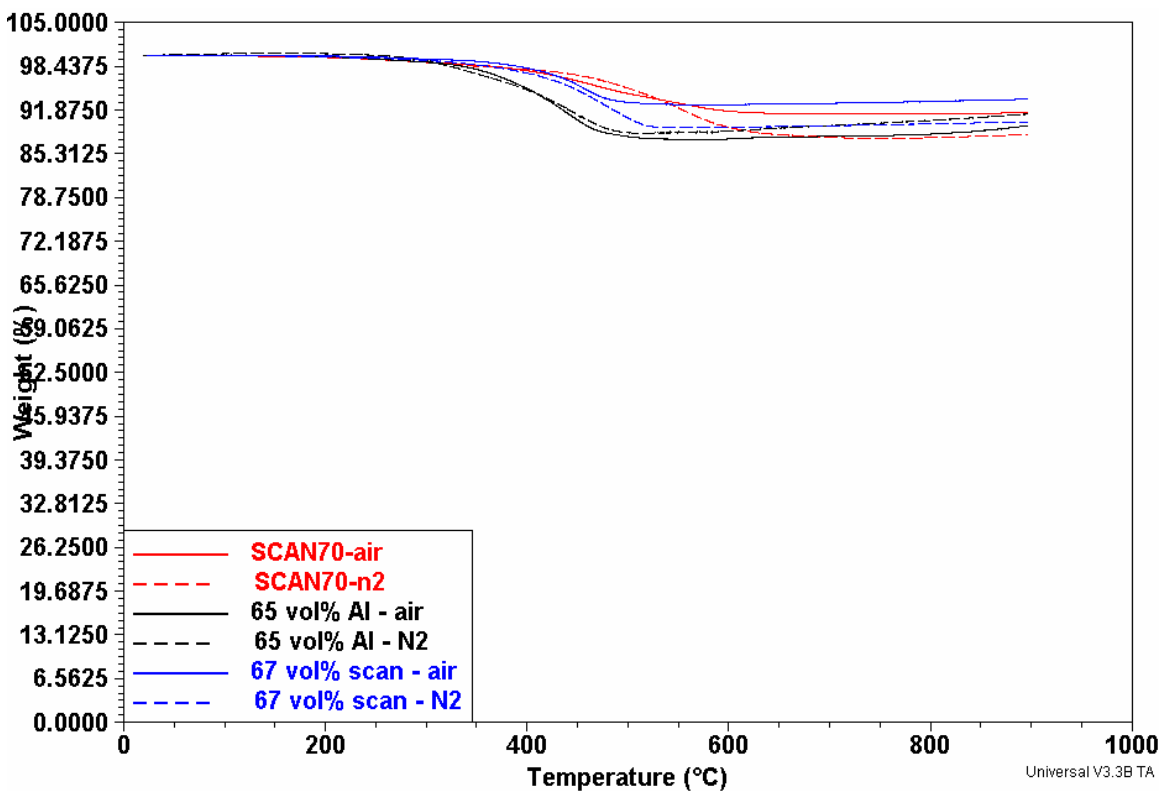


Figure 6.11. Effect of Thermally Conductive Filler on Thermal Stability for Microcomposites Prepared with the 9 Mol % Nitrile Substituted Polyorganosiloxane

## 6.7. Tensile Properties of Functionalized Polyorganosiloxane Microcomposite Networks

The functionalized polyorganosiloxanes prepared in this research are attractive resinous binders as their corresponding thermally conductive microcomposites offer very low temperature flexibility ( $T_g$ s lower than  $-44$  °C). Specifically, the microcomposite filled with 67 volume % silica-coated AlN using the polysiloxane substituted with 9 mol % nitrile exhibited a  $T_g$  of  $-115$  °C. The functionalized polyorganosiloxane microcomposite networks were extremely low tensile moduli materials. This important property aids in minimizing the effects of large CTE mismatches between electronic component adherends and metal lines (heat sink).<sup>126</sup> Tensile properties including Young's modulus (initial stress over strain), tensile strength at break, and % elongation (% strain) were measured.

The tensile tests were based on ASTM D 412 "Standard Test Methods for Vulcanized Rubber and Thermoplastic Rubbers and Thermoplastic Elastomers – Tension". Dogbone specimens were cut from the networks (~ 2 mm thick) using a die with the gauge dimensions of 10 mm x 2.65 mm. Five samples for each type of network and microcomposite were pulled to failure at a rate of 1 mm/min at ambient temperature using a TA.XT2 Texture Analyzer. The error associated with the tensile tests was within  $\pm 10\%$  from the average of 5 samples.

The tensile moduli of unfilled networks based on polyorganosiloxanes with varied concentration of nitrile and of their microcomposites prepared with different thermally conductive fillers were measured (Figure 6.12). Moduli were calculated as the initial ratio of stress to strain. The unfilled nitrile containing polysiloxane networks with different mol fractions of nitrile and wt. % crosslinking reagent (XL) were compared to their filled thermally conductive microcomposite networks. The tensile moduli for the unfilled polyorganosiloxanes increased with increasing wt. % crosslinking reagent. This effect was also observed for the three microcomposites prepared using ~ 66 volume % Al spheres. Tensile moduli of the 9 % nitrile substituted networks filled with Al or silica-coated AlN exhibited at least a 10-fold increase over the unfilled networks. The 22 vol % Ag filled microcomposite yielded the lowest modulus due to the low vol % of filler incorporated into the matrix. All of the tensile values remained well below the upper design limit.<sup>126</sup>

The following figures (Figure 6.12, 6.13 and 6.14) represent the tensile data for the 9%, 27% and 54 mol % nitrile containing polysiloxanes and rounded to 10%, 30% and 55% for clarity. The percentages below the nitrile labels for the unfilled networks correspond to the wt % of crosslinking reagent (XL) required to yield a network. The percentages below the microcomposite samples represent the volume % and type of filler dispersed throughout the resin to yield a conductive adhesive. Fillers studied were silica-coated aluminum nitride (AlN), silver (Ag) and aluminum spheres (Al).

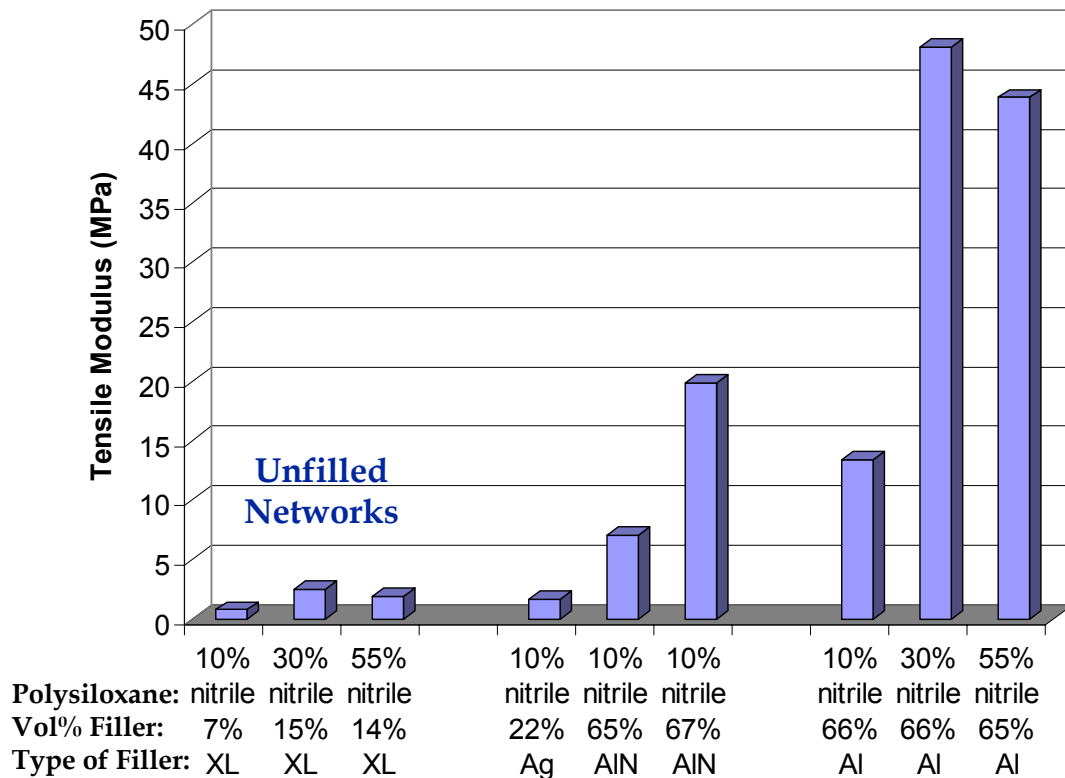


Figure 6.12. Tensile Modulus Data for Polysiloxane Networks with Varied Concentrations of Nitrile and Thermally Conductive Microcomposite Networks

The tensile strength data for the nitrile substituted polyorganosiloxane networks and microcomposites were reported as the stress at failure (Figure 6.13). The tensile strengths increased with increasing wt. % of crosslinking reagent for the unfilled networks.<sup>163</sup> When comparing the 3 microcomposites based on the 9% (10 %) nitrile substituted polyorganosiloxane, the tensile strength increased with increasing volume % of conductive filler, irrespective of the filler. Tensile strengths also increased with increasing concentrations of nitrile moieties for the three microcomposites prepared with ~ 66 volume % of the Al spheres. This was presumably be due to a stronger interaction between the polar aluminum filler with increasing amounts of molar % polar moiety, thereby yielding a stronger microcomposite network.

163. J. E. Mark, Chapter 18 in, "Elastomers and Rubber Elasticity" Editors, J. E. Mark and J. L. Lal, ACS Symposium Series, **193**, Washington D. C., 1982.

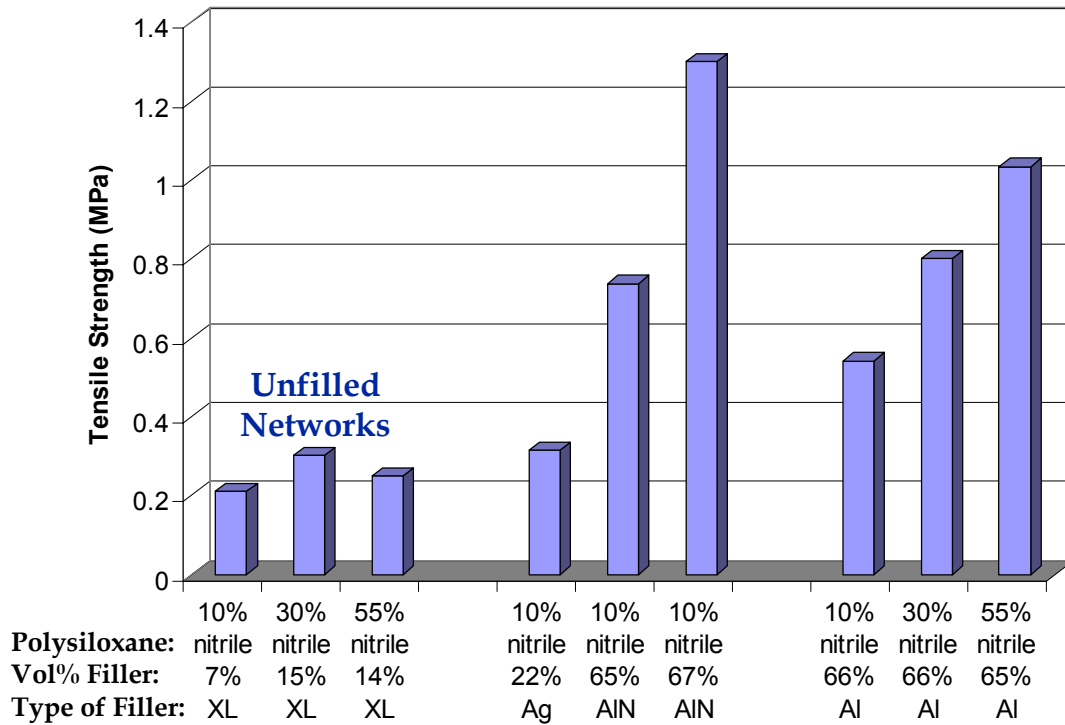


Figure 6.13. Tensile Strength Data for Polyorganosiloxane Networks with Varied Concentrations of Nitrile Moieties and Thermally Conductive Microcomposite Networks

The tensile properties for the PCPMS nitrile homopolymer and phosphine oxide containing polysiloxane microcomposites were also measured and the properties followed expected trends. The tensile moduli of the 15 mol % phosphine oxide substituted polyorganosiloxane and PCPMS networks increased from 0.02 MPa – 0.14 MPa (20 psi) and 0.09 MPa – 0.72 MPa (102 psi), respectively, when filled with 50 volume % of silica-coated AIN. These values were well below the upper design limit for a thermally conductive adhesive of 125,000 psi.<sup>126</sup>

The tensile data for the 9 mol % (10 mol %) nitrile substituted polyorganosiloxane unfilled network and microcomposite with 67 volume % silica coated AIN followed expected trends (Figure 6.14). The microcomposite networks exhibited higher tensile moduli and strengths at break (MPa), accompanied by a lower % elongation. This particular microcomposite network exhibited the highest tensile strength at break (1.3 MPa, 185 psi), the highest thermal conductivity value ( $k = 1.42 \text{ W/mK}$ ) and

lowest  $T_g$  (-115 °C) of all functionalized polyorganosiloxanes synthesized and tested. It would make an excellent candidate for a thermally conductive adhesive binder. The clear network is the unfilled nitrile containing polysiloxane and the dark gray sample is highly filled thermally conductive microcomposite (Figure 6.15).

Figure 6.14. Tensile Data for the 9 Mol % Nitrile Substituted Polyorganosiloxane Unfilled Network and Microcomposite with 67 Volume % Silica-Coated AlN

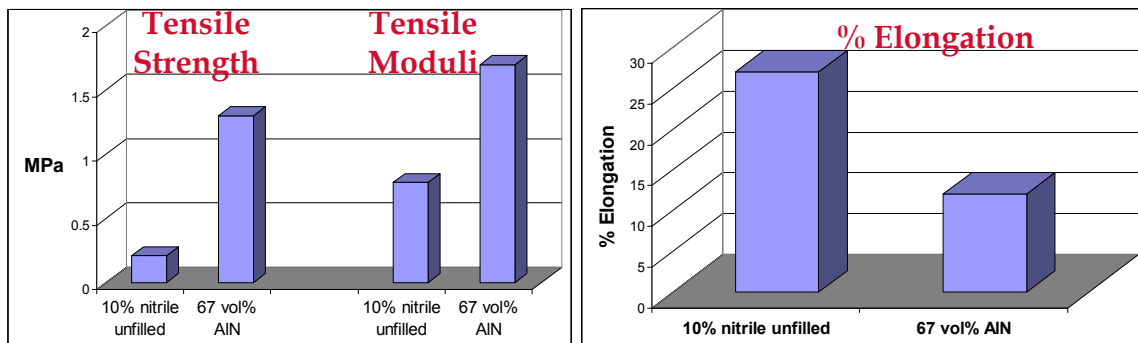


Figure 6.15. Network Tensile Specimens Prepared with a Polyorganosiloxane Substituted with 9 Mol % Nitrile and the Corresponding Thermally Conductive Microcomposite Filled with 67 Volume % Silica-Coated AlN



## Chapter 7. Conclusions

Four families of polyorganosiloxanes with controlled concentrations of pendent nitrile, phosphine, phosphine oxide or carboxylic acid moieties were synthesized using novel methods. Polysiloxane precursors to functionalization and crosslinking reactions with precise molar fractions of methylvinylsiloxy- or methylhydridosiloxy- groups were prepared via respective acid and base catalyzed ring opening co-equilibrations of cyclosiloxane tetramers. Random poly(dimethyl-co-methylhydrido)siloxanes were hydrosilated with allyl cyanide to yield polyorganosiloxanes substituted with systematically varied concentrations of polar 3-cyanopropylmethyl- substituents and reactive hydrido groups. Diphenylphosphine and mercaptoacetic acid were each reacted via free radical processes with the pendent vinyl groups of poly(dimethyl-co-methylvinyl)siloxanes to yield polyorganosiloxanes with controlled concentrations of pendent phosphine or carboxylic acid containing substituents. The free radical reaction conditions were mild enough to leave precise concentrations of vinyl groups intact for further crosslinking reactions. Phosphine oxide containing polysiloxanes, a valuable addition to the family of polysiloxanes, were prepared by oxidizing the phosphines of 2-diphenylphosphineethyl- substituted polyorganosiloxanes.

Specific interactions between functional polyorganosiloxanes and thermally conductive microfillers resulted in stable microcomposite dispersions (that could not be obtained with nonpolar PDMS resins). Polyorganosiloxanes functionalized with nitrile, phosphine or phosphine oxide substituted polyorganosiloxanes yielded stable microcomposite dispersions with at least 50 volume % (75 wt. %) of the polar thermally conductive filler, silica-coated AlN. Dramatic improvements in dispersion quality between silica coated AlN and functionalized polyorganosiloxanes were observed via TEM relative to microcomposites prepared with nonpolar PDMS resins. Hydrogen bonding studies via  $^1\text{H}$  NMR supported this TEM data. A downfield shift for the deshielded proton of chloroform was observed for mixtures containing equivalent ratios of chloroform and nitrile or phosphine oxide substituted polysiloxanes. The magnitude of the proton shift, and consequently the hydrogen bonding of chloroform with the phosphine oxide substituted polyorganosiloxane, was much greater. Specific interactions

were also verified via XPS. XPS studies showed that functionalized polysiloxanes effectively coated silica coated AlN microparticles. Si 2p XPS photopeak was detected only for the Si atoms in the polysiloxane backbones. No Si 2p photopeaks were detected for nitrile and phosphine functional polysiloxane microcomposites with 50 volume % microfiller.

Lightly crosslinked polyorganosiloxane adhesive networks functionalized with systematically varied concentrations of strongly hydrogen bonding nitrile or phosphine oxide moieties were prepared. The residual vinyl or hydrido groups of phosphine oxide or nitrile substituted polysiloxanes were hydrosilated to yield elastomeric networks. Phosphine containing polyorganosiloxanes complexed with the Pt catalyst and prohibited network formation. To date, phosphine oxide containing polysiloxane networks have not reportedly been prepared via Pt catalyzed hydrosilation reactions. Adhesion to Al for a polyorganosiloxane network containing only 15 mol % methyl,2-diphenylphosphine oxideethylsiloxyl- repeat units was twice that of a poly(trifluoropropylmethyl)siloxane (100% trifluoropropyl- units) network and 18 times greater than a PDMS network (each had similar crosslink densities and oligomer  $M_n$ s).

Thermally conductive adhesive microcomposite void free networks were prepared with thin bondlines, ~ 6 mils, containing 50 – 67 volume % silica-coated AlN. A variety of thermally conductive microfillers (Al spheres, BN and Ag flakes) also formed stable microcomposites and networks with the nitrile and phosphine oxide functionalized polysiloxanes. The maximum volume fraction of filler capable of forming a void-free thin microcomposite bondline proved to be the most important factor in yielding a highly thermally conductive adhesive. Although the phosphine oxide containing polysiloxanes exhibited strong specific interactions with polar conductive fillers, only 50 volume % of the silica coated AlN could be dispersed throughout it while remaining processable (properties closer to a viscous liquid rather than the particulates). The viscosity and degree of hydrogen bonding directly influenced the maximum concentration of filler that could be incorporated into the matrices.

Importantly, an extremely low modulus microcomposite network comprised of a functional polyorganosiloxane containing only 9 mol % 3-cyanopropylmethyl-substitution was prepared with 67 volume % (86 wt. %) silica-coated AlN. This

thermally conductive adhesive exhibited a high thermal conductivity value of 1.42 W/mK. The microcomposite had a  $T_g$  of  $-115\text{ }^\circ\text{C}$ , was thermally stable to  $> 400\text{ }^\circ\text{C}$  and had  $> 90\text{ wt } \%$  char yield at  $900\text{ }^\circ\text{C}$  in dynamic TGA measurements. Nitrile functionalized polysiloxanes will be further investigated as potential commercial thermally conductive adhesive binders.

## Recommendations for Future Work

While a promising polyorganosiloxane candidate for thermally conductive adhesives has been developed, the thermal conductivity of the microcomposite has not yet been optimized. The polyorganosiloxane substituted with 9 mol % nitrile moiety was filled with 67 volume % silica-coated AlN to yield a microcomposite network with a thermal conductivity of 1.42 W/mK. The average particle size distribution of the microfiller should be optimized to yield a microcomposite with a volume fraction greater than 67 % that should consequently yield a more thermally conductive adhesive. Since thermal conductivity increases exponentially with volume fraction of filler, the preparation of a thermally conductive polyorganosiloxane microcomposite with a thermal conductivity of 2.0 W/mK or greater is quite reasonable.

The polyorganosiloxanes should be further investigated to evaluate the effects of oligomer  $M_n$  on both network properties and microcomposite dispersion quality. Only low  $M_n$  oligomers were synthesized for this research. Polyorganosiloxanes with  $M_n$ s above the molecular weight for entanglement should still yield materials with low enough tensile moduli, and higher strengths and % elongation to break should be obtained.

The ene-thiol addition of mercaptoacetic acid yielded polyorganosiloxanes with very interesting amphiphilic properties. Future work should involve network formation reactions with these carboxylic acid substituted polyorganosiloxanes. Potential routes include energetically crosslinking the residual vinyl groups pendent to poly(methylvinyl-co-[2-(carboxymethylthio)ethyl]-methyl)-siloxane-*block*-(dimethyl)-siloxanes via UV or electron-beam to yield lightly crosslinked elastomeric networks with controlled polarity. Another objective should be to synthesize polysiloxanes with high contents of carboxylic acid moieties as potential hydrogels.

Molecular weight control is an important parameter in obtaining polysiloxanes with well-defined structures with predictable properties. While molecular weight control was achieved for poly(dimethyl-co-methylvinyl)siloxanes, the percentage of cyclics remaining at equilibrium was not established. Precise control of the methylhydridosiloxy- repeat units was achieved via triflic acid catalyzed equilibrations of  $D_4$  with  $D_4H$ , although the  $M_n$ s were higher than expected. Acid and base catalyzed co-

equilibrations with systematically varied concentrations of  $D_4H$ ,  $D_4Vi$  and  $D_4$  should be monitored via GPC to determine the percentage compositions of the equilibrates and the point at which equilibration reaches a characteristic heterogeneity index of  $\sim 2.0$  for equilibrations.

## VITA

Jennifer K. Hoyt-Lalli, the daughter of Joseph and Rosemary Hoyt, was born in Wilkes-Barre, PA on October 10<sup>th</sup>, 1974. She became the wife of Christopher J. Lalli on May 25<sup>th</sup> 2002 in Virginia Beach, VA. She is the older sister to Joseph Hoyt Jr., and the granddaughter of Elizabeth and Ralph Hoyt, and Ruth and Herman Guillory. She resided in Swoyersville, PA and graduated from Wyoming Valley West High School in 1992. She began her undergraduate career in 1992 at The Pennsylvania State University, State College, PA as a chemistry major. During her junior year, she focused her educational interests in polymer science and began her polymer science career at Avery Dennison, Chemical Div., Mill Hall, PA in 1994 as a co-op student. In 1995, she began a full-time position at Avery Dennison during her educational career at Penn State. She graduated with a Bachelor of Science Degree in Chemistry on August 12<sup>th</sup>, 1996. The following week, August 19<sup>th</sup>, 1996, she entered the graduate program at Virginia Polytechnic Institute and State University under the direction of Dr. Judy Riffle where the emphasis of her career was in the area of nitrile containing siloxanes. She received her Master's degree in Chemistry in 1999 and pursued a Doctor of Philosophy degree under the advisory of Dr. Judy Riffle with a focus on novel organic-inorganic hybrid systems for thermally conductive adhesives. She graduated from Virginia Tech with a Ph.D in organic polymer chemistry on August 5<sup>th</sup>, 2002. She accepted a challenging position as a Research Scientist from Dr. Richard O. Claus with NanoSonic, Inc. in Blacksburg, VA.