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Synthesis, characterization, and evaluation of a heat stabilizing siloxane

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Synthesis, Characterization, and Evaluation of a Heat Stabilizing Siloxane:

A Synthetic Route to an Alkoxy-amino Functional Siloxane

by

Joel Douglas Kennard

Thesis

Submitted to the Department of Chemistry

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MASTER OF SCIENCE

in

Chemistry

Thesis Committee:

Donald Snyder, PhD, Chair

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Gregg Wilmes, PhD

March 15, 2012

Ypsilanti, Michigan

Dedication

Without the wholehearted devotion and support of my partner, Susan, the preparation of this thesis manuscript would be fruitless. As such, this work is dedicated to her indefatigable commitment to me and our family, which is appreciated beyond words.
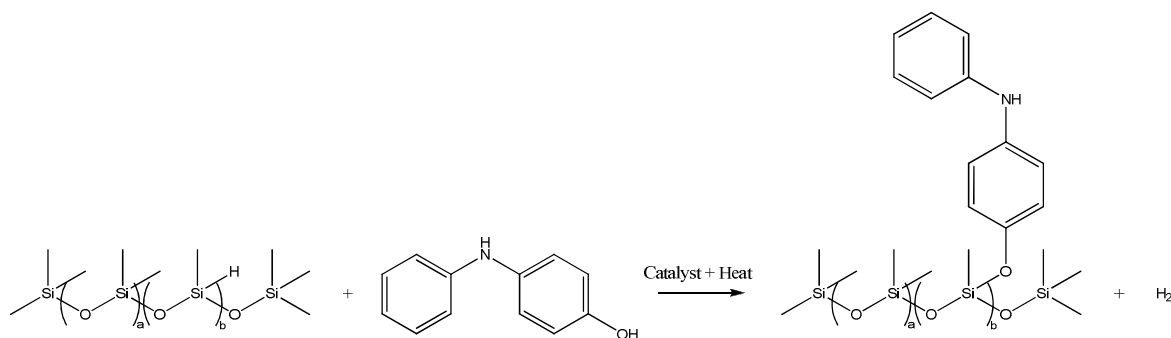
Acknowledgments

While the author alone is responsible for the account detailed, it would be impossible without the persistent dedication, tireless patience, and genuine counsel from the following: Elizabeth Paps and Virginia (Sue) Kelley. Additionally, I am grateful for the support of Wacker Silicones, the corporate sponsor of this thesis.

Abstract

Siloxanes, renowned for their heat resistance and release properties, are prone to oxidize above 200℃. The goal herein is to increase siloxane bath life used in fuser roll applications at temperatures above 200℃, yielding faster production, less waste, and cost savings by keeping the bath viscosity stable through prevention of thermal degradation.

The methods detailed herein react a hydrosiloxane with an amino functional alcohol (4-(phenylamino)-phenol). The alcoholysis (or dehydrogenative coupling) moves forward with the removal of hydrogen and formation of the desired product (Scheme 1). Reactions were conducted on both NMR scale and lab scale.

The results of the synthesis were characterized via NMR spectroscopy and evaluated via heat age studies. The material, confirmed via ^{29}Si NMR, was proven effective through heat age testing in both fluid and elastomer formulations.

Scheme 1: Synthesis of heat stabilizing silicone copolymer

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1. Introduction

Few elements have historical uses dating back as far as silicon, which has been used in the ceramic arts in Japanese, African, and South American pottery dating back to 10,000 BCE. Additionally, recent discoveries of bits of pottery in the Yachanyan Cave in southern China date to 16,000 BCE. Even without the aid of modern instrumentation or production aids, those skilled in the early art were able to make artifacts that have outlasted their civilization. For instance, the Venus of Dolní Věstonice, a ceramic Venus figurine made of loess found in present day Czech Republic, is the oldest known ceramic artifact, dating back to a Paleolithic site between 29,000 and 25,000 BCE. Along with the ceramics, the knowledge of how to process ceramics was passed through generations and combined with the art of metallurgy. With an element seemingly so prevalent to arts and society, it was not fully understood as a formal element until Scheele's work in 1771. Scheele observed a volatile colorless gas (SiF_4) when sulfuric acid and calcium fluoride (i.e. HF) were added to silica.[1-4]

$$2\ CaF_2 + SiO_2 + 2\ H_2SO_4 \rightarrow SiF_4 + 2\ H_2O + CaSO_4$$
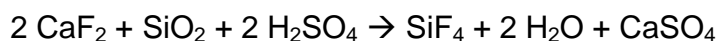
At the time of this work, the framework of silicon as an element was seen in the light of silicates. Silicon in the elemental form was not isolated until 1823 when Berzelius reduced silicon tetrafluoride with metallic potassium, thus obtaining a dark brown powder that was the elemental form of silicon.[5-7] Following this work, Berzelius also isolated a volatile colorless liquid of silicon tetrachloride. Over 30 years later Deville further purified the brown silicon product discovered by Berzelius by melting the brown powder and obtaining grey pellets of elemental silicon.[8,9] Meanwhile, Frie-

drich Woehler introduced the idea that organic compounds could be made from inorganics. Using the silicon halides as a starting point, he propelled the work forward by isolating the first silicon hydrides, analogous to those of carbon. He was the first to isolate the binary hydride of silicon, SiH_4.[10] This discovery led next to the observation that the halides and hydrides of silicon reacted quickly with water or oxygen to revert to SiO_2. In the case of the hydrides, the reversion violently caught fire from the rapid reaction with oxygen. The results of this work established three fundamental conclusions about the properties of silicon: its strong affinity for oxygen, its high activation energy (the need for high temperatures for active reactions), and its decreased stability of hydrides and halides relative to carbon. While the work by Berzelius and Woehler was certainly pioneering, the first work to achieve a carbon substituted derivative of silicon was accomplished by Friedel and Crafts in 1865.[11] Furthermore, along with the feat of a novel silicon compound came an additional fundamental conclusion: carbon-substituted silicon was unreactive in air and water, as opposed to the halide and hydride derivatives. The next major breakthrough came in the hands of Frederic Stanley Kipping, a British chemist trained in Germany. His devotion to the study of silicon, and specifically the earliest development of the silicones, was documented in 57 seminal papers published between 1910 and 1940. All of the works in this volume document the birth of a novel class of materials. Using the novel and emergent Grignard reagents (specifically ethylmagnesium bromide), he isolated many pure silicon monomers based on the controlled stoichiometric reaction with the Grignard and silicon tetrachloride.[12] The only caveat was that methyl substitution on silicon was not feasible because of the pitfalls at the time with using

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methylmagnesium chloride. Not only was methylmagnesium chloride slow to react and difficult to make, but it was insoluble in the ether solvent. The organosilicon chlorides isolated by Kipping were found to react readily with water, replacing the chloride with hydroxyl groups to form "silanols." Depending on the configuration of the organic groups and the relative bulk of the substituents, the monofunctional silanols could be isolated by distillation. However, the silanols were found to be more reactive to what was thought to be (at the time) "ether" formation than the carbon based analogs. Whereas conventional carbon based alcohols required an acid catalyst and a dehydrating agent, the silanols would cleave water and form the "silico-ethers" even more readily. Concurrent with Kipping, Alfred Stock,[13] classically trained in inorganic chemistry, was using micro-prep and milligram scale reactions, carried out predominantly in the gas phase. While the processes were no doubt tedious, the product of many reactions was an oily film sitting on water in the reaction bulb. While not known at the time by the nomenclature used today, the product isolated in this painstaking process was the first observation of methylsilicone. His early work with the silicon hydrides gave rise to the IUPAC nomenclature of organosilicon materials. This fundamental research from Kipping and Stock provided a foundation upon which modern research could be built.

The progression of silicon research henceforth was driven by industry. Many large equipment manufacturers were limited by the lack of thermally stable insulators used in motor production. Even as new technologies were developed like fiberglass with Bakelite coatings, the upper end of insulation still remained around 150°C. Two companies, Corning Glass Works and General Electric, were interested in address-

ing the problem and began research to develop insulators with higher temperature resistance. An organic chemist, James Franklin Hyde, working for Corning Glass Works, developed an ethyl/phenyl polymer that, when coated on fiberglass, gave attractive insulation properties and was thus termed class H insulation (H standing for High Temperature). At the same time, Eugene Rochow, an inorganic chemist from General Electric Research Laboratory, was tasked with improving upon the product Hyde developed at Corning. His work related physical properties to varying methyl/silicon ratios. In either case, the production of siloxanes was an expensive undertaking that required recovery of hazardous materials formed through the course of the Grignard reactions. The next major step came at the hands of two teams at different companies. Since the siloxane production using the Kipping-Grignard route used organomagnesium halide, this meant a nearly three-fold waste in final product (from magnesium chloride, hydrogen chloride, and carbon monoxide by-products). Therefore, the process may have been viable at a lab scale, but the implications at the industrial scale made it impractical. Thus the next progression in siloxane research came in the form of the direct synthesis of methylchlorosilanes. The process was independently developed by Richard Mueller, a professor in Germany, and Eugene Rochow, the aforementioned scientist at General Electric, in the early 1940s and is still the dominant process by which approximately 1.4 million tons of silane are produced and converted into silicones.[21] The direct synthesis is a copper catalyzed reaction between silicon metal (most commonly crushed to a uniform particle size) and methyl chloride (a product of hydrogen chloride and methanol). The development of this process has been the driving force behind the commercial

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feasibility of the silicone industry. To describe the more recent trends in silicones and their properties, it is important to define common nomenclature used both within the field of research and industry.

2. Nomenclature

The building blocks of siloxanes are the monomeric components often referred to as silanes, of which the most simplistic and technically accurate description is silane, depicted in Figure 1.
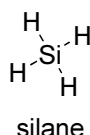
silane

Figure 1: Example of silane

Thus, the structure of silane is analogous to its carbon-based alkane analog, methane. It is therefore not surprising that the hydroxyl-substituted silicon monomer would be called silanol, shown in Figure 2.

silanol
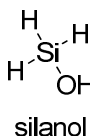
Figure 2: Example of silicon methanol derivative

In the case of organosilicon compounds, by definition at least one hydrogen must be replaced by an organic group (R). The balance of substituents can either be hydrogen or any combination of halogen, alkoxy, amino, or other functional groups (typically represented as X in generalized formulas). Because of the hydrolyzable nature of the X groups when attached to silicon and the low reactivity of the organic substituted silanes by comparison, three general classes of materials can be described, all with respect to functionality. Halosilanes, alkoxysilanes, and aminosilanes are classified exclusively as silicon functional; tetrachlorosilane ($SiCl_4$), methyl triethox-

ysilane ($CH_3Si(OC_2H_5)_3$) and trimethylsilanamine (($CH_3)_3SiNH_2$) are examples of these classes, respectively (Figure 3). An example of solely organofunctional silicon compounds would be vinyl trimethylsilane ($CH_2=CH(CH_3)_3Si$), or chloromethyl trimethylsilane ($ClCH_2(CH_3)_3Si$) (Figure 4). The final group consists of compounds that contain both silicon reactive and organic substituents.

tetrachlorosilane   methyl triethoxysilane   trimethylsilanamine
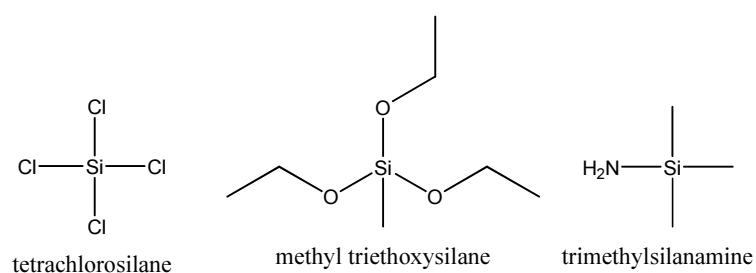
Figure 3: Examples of silicon functional monomers

vinyl trimethylsilane chloromethyl trimethylsilane
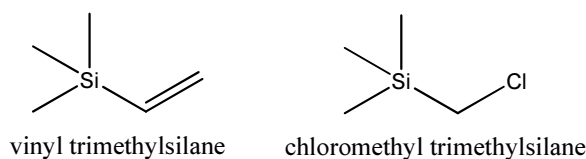
Figure 4: Examples of organofunctional silicon monomers

While this grouping serves classification of silicon compounds well, it also allows for uniformity in naming silicon compounds. In naming, the organofunctional groups are given first, then nonfunctional, then silicon-functional substituents. Finally, within these groups, the hierarchy for naming is organized by alphabetical order and the formula is arranged by increasing carbon number.

  While monomers are easy to identify and name systematically with reference to the singular silicon, higher order silicon compounds are more difficult to assign via such nomenclature standards. Thus any compound with repeating units is referred to as a polymer and given the prefix "poly." The use of "oligo" to represent a class

"in-between" monomers and polymers is rarely used because the delineation is largely arbitrary.

Within the silicon polymers are the "polysilanes," "polysiloxanes," polysilazanes," and "polysilthianes," which are shown below with respect to their characteristic linkages (Figure 5).
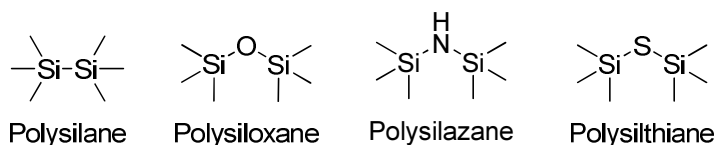
Figure 5: Silicon containing polymers with characteristic linkages

From these classes of silicon containing polymers, the primary focus is on polysiloxanes. The class of polysiloxanes is further classified and named by terminal groups (i.e. OH, Cl, etc.), pendant groups (homopolymers or copolymers), definite number of silicon atoms, or cyclic configuration (i.e. di, tri, tetra, cyclo). A special case exists when hydrogen is bonded to silicon in polysiloxanes where not naming the hydrogen leads to ambiguity, such as the case where polymethylsiloxane could mean either of the two shown in Figure 6.

Figure 6: Example of polymethylsiloxane naming ambiguity

Therefore, the insertion of either an italicized -*H*- or "hydro" is used in the name of the compound. With the application of this, the above silicon hydride compound would be named polymethyl-*H*-siloxane or polymethylhydrosiloxane. Other than the

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case of hydrogen, the naming is straightforward and based on that of the recommendations of Sauer[22] with minor modifications documented by IUPAC.[23]

A convenient shorthand notation used to designate the degree of functionality of the silicon atom in siloxanes is shown in Figure 7; M, D, T, and Q represent the building blocks of polysiloxanes and high molecular weight resin.

$$\begin{matrix} & Me & \\ O_{1/2}- & \!\!Si\!\! & -O_{1/2} \\ & Me & \end{matrix}$$

D (Difunctional)

$$\begin{matrix} & Me & \\ O_{1/2}- & \!\!Si\!\! & -O_{1/2} \\ & O_{1/2} & \end{matrix}$$

T (Trifunctional)

$$\begin{matrix} & Me & \\ Me- & \!\!Si\!\! & -O_{1/2} \\ & Me & \end{matrix}$$

M (Monofunctional)

$$\begin{matrix} & O_{1/2} & \\ O_{1/2}- & \!\!Si\!\! & -O_{1/2} \\ & O_{1/2} & \end{matrix}$$

Q (Quadrifunctional)
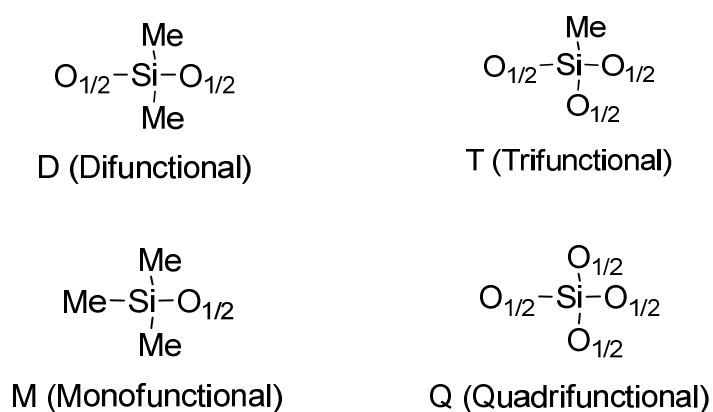
Figure 7: M, D, T, and Q structural units

3. Background

Siloxanes have long been sought after for their combination of desirable physical properties. Originally developed for their thermal stability characteristics, siloxane elastomers are commonly marketed to keep flexibility at temperatures as low as -100℃, while siloxane fluids can retain physical p roperties up to 200℃. Also touted is the low surface tension of the fluids class of siloxanes. This is particularly important when applied to surfaces with variable surface topography. With the combination of heat stability and surface tension, it's not surprising that siloxanes would be of interest in coatings technology. A third characteristic that has served to promote the use of siloxanes in coatings are their release properties. Even the most aggressive adhesives do not adhere well to siloxanes. The combination of these properties has allowed for the development of siloxanes as mold release agents for rubber, plastics, and die-casting, as well as release liners for adhesive face stock.

In addition to release from organic adhesive and casting substrates, siloxanes are used within the non-impact printing industry. The application of siloxane to the process of non-impact printing allows fuser rolls to release from the thermoplastic ink toner. Figure 8 illustrates the general components comprising a fuser roll used in non-impact printing.
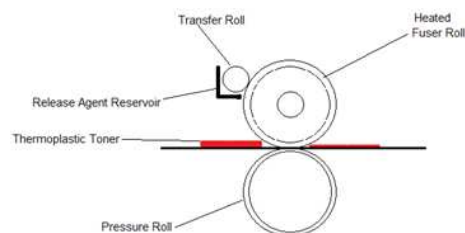
Figure 8: Components of a Fuser Roll in Non-Impact Printing

While the release and thermal stability properties of siloxanes lend themselves to this application, increasing roller speeds and thus temperatures can lead to degradation of siloxane fluids and the subsequent degradation of expensive fuser rolls. At elevated temperatures for sustained periods of time, the viscosity of the oil will increase until the fluid gels, thus becoming incompatible with the roller process. Thermal degradation and viscosity increase is often explained by homolytic bond cleavage (bond dissociation between $Si-CH_3$) yielding radicals available to participate in chain extension and/or crosslinking reactions and thus the viscosity increase. While siloxane polymers and organo-functional silicone co-polymers have been developed for use as fuser oils, the incorporation of heat stabilizers has been limited due to poor compatibility of various agents in the siloxane medium.

The purpose of this work was to develop a synthetic route to produce a siloxane co-polymer that contains a heat stabilizer bonded to the chain, allowing the heat stabilizer to be compatible with the parent siloxane fluid.   The siloxane additive, when mixed with commonly used fuser fluids, contained an aromatic amine as the organo-functional group that functioned as the antioxidant. Prior research has indicated that the ratio of dimethyl units to aromatic amine containing units should be approximately 10 to 1, respectively, with the polymer end units being trimethylsilyl.

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The functionalized polymer was miscible with polydimethylsiloxane and organomodified siloxanes such as amino and mercapto fluids. The additive was characterized via ^{1}H and ^{29}Si NMR as well as FT-IR. Finally, the material was tested to evaluate the efficacy via heat age studies. The synthetic additive was compounded with other siloxane release agents and compared to an iron octoate industry standard stabilizer fluid.

Modern production of siloxanes has relied fundamentally on the direct process discovered by Mueller and Rochow. This process yields a statistical distribution of silanes that are hydrolyzed into linear and branched repeat units of the polymer backbone. These monomers make up the backbone of siloxanes. For example, a silicon functional di-unit or tri-unit (-Cl, -OH, -OR) is reacted with an acid or base catalyst in a step growth polymerization, also yielding the hydrolyzed by-product (HCl, HOH, HOR). Just as the monomer production yields a statistical distribution of silanes, this process gives 80-90% conversion of a particular molecular weight distribution and the balance as low molecular weight silicon containing volatiles, referred to as "lites." The lites are short chain siloxane oligomers of linear and cyclic nature. The viscosity of the final product is tailored by the amount of monofunctional monomer introduced as a reactant. This fundamental reaction can be used to produce a litany of organofuctional siloxanes, such as aminopropyl fluids, mercaptopropyl fluids, vinyl fluids, amyl fluids, and phenyl fluids.

Another key production process in the field of siloxanes is that of the hydrosilation reaction. This reaction is an addition of silicon hydrides to unsaturated compounds (i.e. alkenes and alkynes). The addition is unlike H-X addition to unsatura-

tion in that it occurs in an anti-Markovnikoff fashion. Second only to the direct pro-

cess, it's estimated that 20% of silicone production utilizes this technology. Exam-

ples of products reliant on this technology are silicone elastomers, cure chemistry,

production of organofunctional silanes like amino, mercapto, and epoxy functionali-

ties, and production of silicone polyethers.

  With respect to the goal of this work, the starting point could be with either sil-

icon functional silane starting materials like methyltrichlorosilane, methyltrisilanol, or

methyltrimethoxysilane. Additionally, the final product could be produced from a

parent siloxane, like polymethylhydrogensiloxane. Also, a hydrolysis of a pendant

functional chlorosiloxane, hydroxysiloxane, or alkoxysiloxane would yield the desired

product.

  The route suggested in this work is less common, and the nomenclature is not

commonly mentioned in the literature. The pathway investigated herein is a transi-

tion metal catalyzed metathesis between silicon hydride and an aromatic amino

phenol. In general the reaction scheme detailed in Scheme 2 is most commonly re-

ferred to as a dehydrogenative coupling.
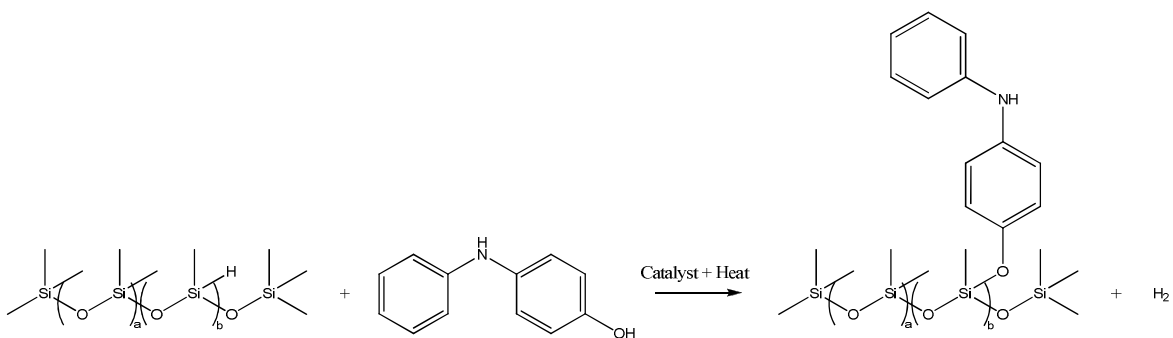
Scheme 2: Dehydrogenative coupling of silicon hydride w/ aromatic amino phenol

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4. Experimental

4.1 NMR Scale Experimental Procedures:

In order to evaluate the potential of various catalysts, initial reactions were carried out on a small scale in NMR tubes, which allowed the reaction progress to be monitored and catalyst efficacy to be determined.

In particular, ^{1}H and ^{29}Si NMR allow the reaction progress to be followed. In the ^{1}H NMR spectra, the silicon-hydride proton decreases as the Si-H is consumed in the dehydrogenative coupling. In the ^{29}Si spectra, the Si-H signal decreases as a Si-O-R signal appears.

For the catalyst study, reagents not available from Wacker were purchased from common vendors such as AlfaAesar or Sigma-Aldrich with reagent grade purity. Reagents were used as provided, either internally or from vendors. J-Young NMR tubes were purchased from Wilmad (528-LPV-7). All ^{1}H and ^{29}Si NMR spectra were recorded at room temperature on a 400 MHz Bruker AVANCE II instrument; chemical shifts are defined in δ (parts per million, ppm) and are reported relative to $CDCl_3$ (^{1}H), TMS (^{29}Si), or Me_2SiO (^{29}Si).

One particular calculation propagated throughout the experimental section is the mole calculation of "D^H." This is an expression of the moles of reactive silicon hydride per mole of hydrogen-containing siloxane. The moles of polymer can be calculated as any other substance, from product of the mass of material divided by the molar mass. In the case of polymers, the molar mass is the average molecular weight (M_n), which is determined theoretically by mass balance or empirically by GPC (Gel Permeation Chromatography), SEC (Size Exclusion Chromatography), or

SFC (Supercritical Fluid Chromatography). From the moles of polymer, the moles of D^H can then be expressed by multiplying the moles of polymer by the number of D^H groups. The number of D^H groups is either determined by mass balance, titration with a strong base, or by spectroscopic means (namely, ^{1}H or ^{29}Si NMR). The calculation of moles D^H allows for a better defined ratio of molar stoichiometry.

4.1.1 Reaction NMR-1
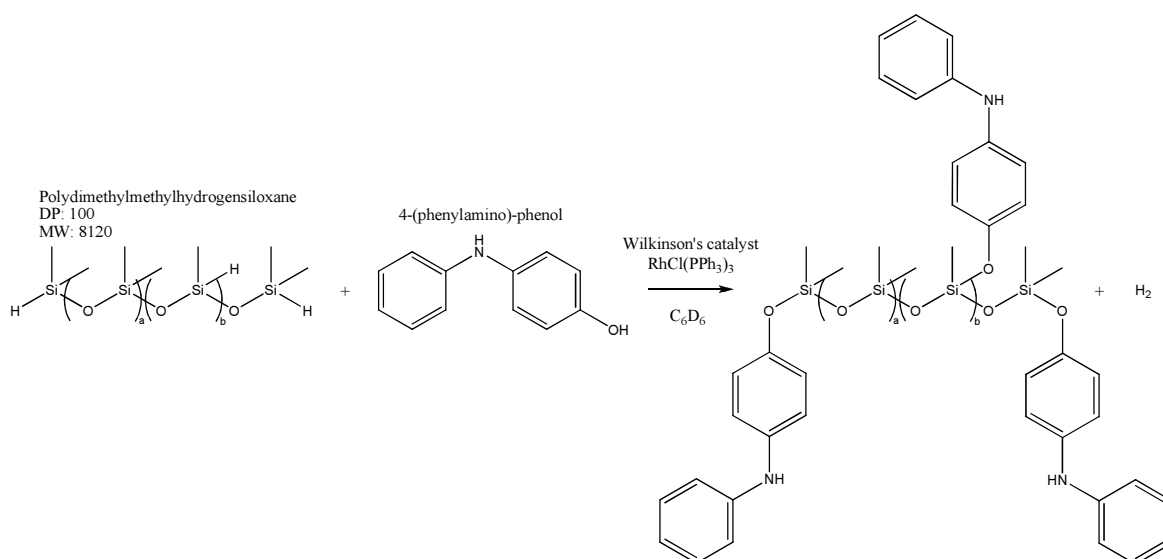
Scheme 3: Reaction NMR-1

In order to test the efficacy of Wilkinson's catalyst (chloro-tris(triphenylphosphine) rhodium(I)) before running a laboratory scale reaction (0.250 kg), a reaction was run in an NMR tube and evaluated via ^{29}Si NMR. Polydimethyl-methylhydrogensiloxane (DP:100-110, MW:8120, 0.5748 g, 0.0708 mmol, 0.7787 mmol D^H) was added to the bottom of a J-Young valved NMR tube. Deuterated benzene (0.3368 g, 4.0024 mmol) was added, and the tube was agitated by a pulse vortex mixer. 4-(Phenylamino)-phenol (0.1562 g, 0.8433 mmol) was added, and the mixture was heated to 70℃ to aid in the dissolutio n of the powder. Temperature control was achieved by using a temperature-controlled recirculating hot oil bath. Finally, Wilkinson's catalyst (0.0154 g, 0.0166 mmol, 1581 ppm Rh, by weight) was added and agitated using a pulse vortex mixer. After vortexing to disperse the pow-dered catalyst, the mixture temperature was ramped to reflux deuterated benzene at 78℃. The reaction progress was evident by the evo lution of gas (H_2) as well as col-

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or change. A ^{29}Si NMR was taken at time intervals to confirm the product and calcu-

late product yields. ^{29}Si NMR confirmed the product with a yield of 66%.

4.1.2 Reaction NMR-2
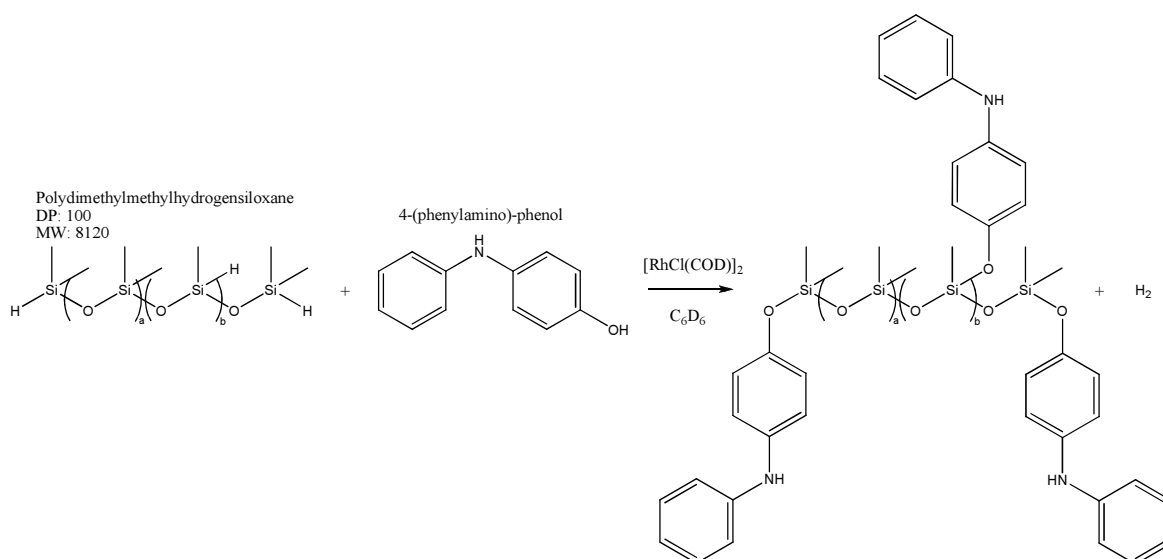
Scheme 4: Reaction NMR-2

In order to test the efficacy of the cyclooctadiene catalyst of rhodium (chloro(1,5- cyclooctadiene)rhodium(I)dimer)rhodium(I)) before running a laboratory scale reaction (0.250 kg), a reaction was run in an NMR tube and evaluated via ^{29}Si NMR. Polydimethylmethylhydrogensiloxane (DP:100-110, MW:8120, 0.6468 g, 0.0797 mmol, 0.8762 mmol D^H) was added to the bottom of a J-Young valved NMR tube. Deuterated benzene (0.3230 g, 3.8384 mmol) was added, and the tube was agitated by a pulse vortex mixer. 4-(Phenylamino)-phenol (0.1578 g, 0.8520 mmol) was then added, and the mixture was heated to 70℃ to aid in the dissolution of the powder. Temperature control was achieved by using a temperature-controlled recirculating hot oil bath. Finally, [RhCl(COD)]$_2$ (0.0097 g, 0.0197 mmol, 3560 ppm Rh, by weight) was added and agitated using a pulse vortex mixer. After vortexing to disperse the powdered catalyst, the mixture temperature was ramped to reflux deuter-

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ated benzene at 78℃. The reaction progress was ev ident by the evolution of gas (H$_2$) as well as color change. The yield via ^{29}Si NMR was 88%.

4.1.3   Reaction NMR-3
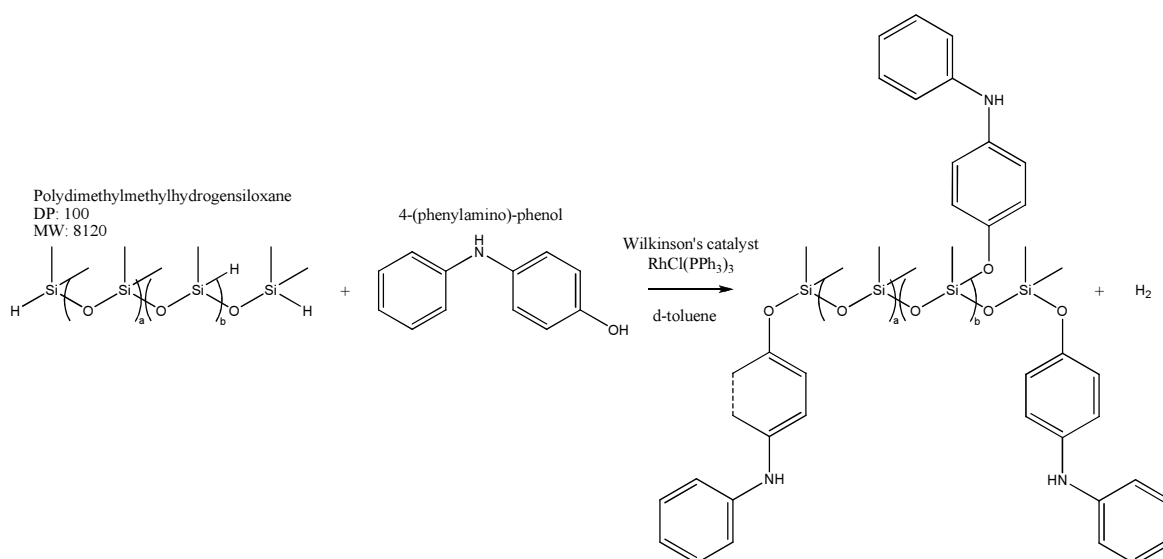
Scheme 5: Reaction NMR-3

A third NMR scale reaction was carried to replicate reaction NMR-1, using toluene-d_8 rather than benzene-d_6 as the solvent. Changing the solvent to d-toluene allowed for higher reaction temperatures. Polydimethylmethylhydrogensiloxane (DP:100-110, MW:8120, 0.6715 g, 0.0827 mmol, 0.9097 mmol D^H) was added to the bottom of a J-Young valved NMR tube. Deuterated toluene (0.3916 g, 4.6536 mmol) was added, and the tube was agitated by a pulse vortex mixer. 4-(Phenylamino)-phenol (0.1695 g, 0.9151 mmol) was added, and the mixture was heated to 70°C to aid in the dissolution of the powder. Temperature control was achieved by using a temperature-controlled recirculating hot oil bath. Finally, Wilkinson's catalyst (0.0162 g, 0.0175 mmol, 1443 ppm Rh) was added and agitated using a pulse vortex mixer. After vortexing to disperse the powdered catalyst, the mixture temperature was ramped to reflux deuterated toluene at 110°C. The reaction progress was

evident by the evolution of gas (H_2) as well as color change. Additionally the ^{29}Si

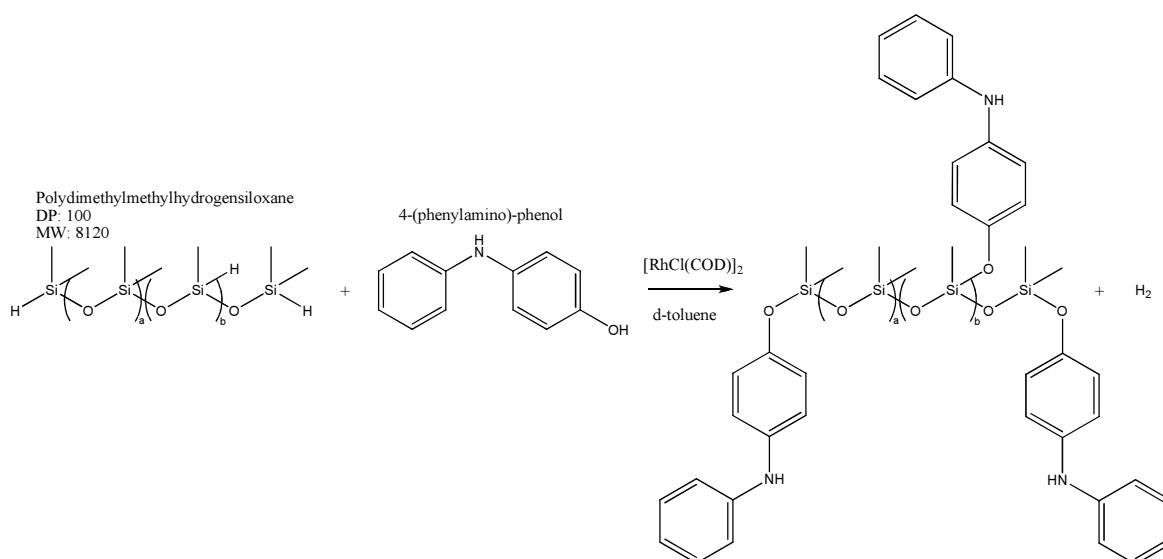spectrum confirmed the yield at 63%.

4.1.4 Reaction NMR-4

Scheme 6: Reaction NMR-4

A fourth NMR scale reaction was carried to replicate reaction NMR-2, using d-toluene rather than d-benzene as the NMR lock solvent. Polydimethylmethylhydrogensiloxane (DP:100-110, MW:8120, 0.6513 g, 0.0802 mmol, 0.8823 mmol D^H) was added to the bottom of a J-Young valved NMR tube. Deuterated toluene (0.3940 g, 4.6821 mmol) was added, and the tube was agitated by a pulse vortex mixer. 4-(Phenylamino)-phenol (0.2113 g, 1.1408 mmol) was added, and the mixture was heated to 70°C to aid in the dissolution of the pow der. Temperature control was achieved by using a temperature-controlled recirculating hot oil bath. Finally, [RhCl(COD)]2 (0.0089 g, 0.0180 mmol, 2935 ppm Rh) was added and agitated using a pulse vortex mixer. After vortexing to disperse the powdered catalyst, the mixture temperature was ramped to reflux deuterated toluene at 110°C. The reaction progress was evident by the evolution of gas (H_2) as well as color change. The ^{29}Si NMR confirmed the yield of reaction NMR-2 with a yield of 97%
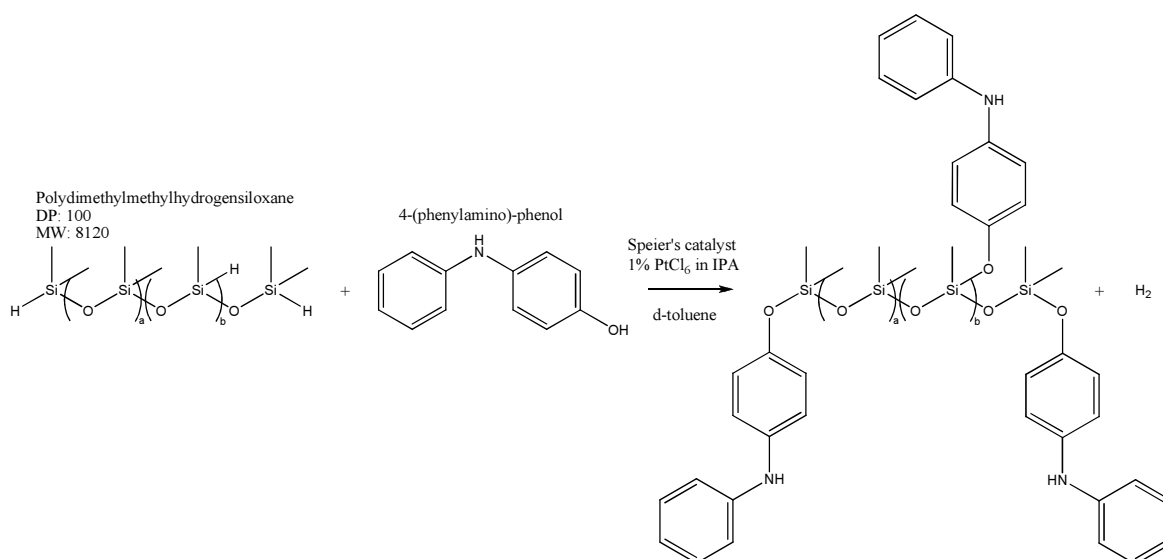
4.1.5   Reaction NMR-5

Scheme 7: Reaction NMR-5

Finally, a fifth NMR scale reaction was conducted using Speier's catalyst (1% chloroplatinic acid hexahydrate in isopropanol). Speier's catalyst was prepared fresh before the addition of ingredients, as it is widely known that this catalyst requires a dwell time to reduce from the hexavalent species to the active catalyst. The catalyst was prepared by dissolving the crystals of $PtCl_6$ in isopropyl alcohol (0.0012 g $PtCl_6$ in 0.1200 g IPA). Polydimethylmethylhydrogensiloxane (DP:100-110, MW:8120, 0.6015 g, 0.0741 mmol, 0.8148 mmol D^H) was added to a J-Young valved NMR tube. Deuterated toluene (0.3604 g, 4.2828 mmol) was added, and the tube was agitated by a pulse vortex mixer. 4-(Phenylamino)-phenol (0.1485 g, 0.8017 mmol) was added, and the mixture was heated to 70° C to aid in the dissolution of the powder. Temperature control was achieved by using a temperature-controlled recirculating hot oil bath. Finally, Speier's catalyst (0.1212 g, 0.2340 mmol, 371 ppm Pt) was added and agitated using a pulse vortex mixer. After vortexing to dis-

perse the powdered catalyst, the mixture temperature was ramped to reflux deuterated toluene at 110°C. The reaction progress was e vident by the evolution of gas (H_2) as well as color change. The ^{29}Si reaction yield was calculated at 82%.

4.2 Lab Scale Experimental Procedures:

Although the NMR scale reactions proved to be successful, preparation of the polymer on a larger scale was necessary for proof of concept. The synthesis on a larger scale would also allow for better agitation, temperature control, and monitoring of bulk volume effects.

For the lab scale experiments, reagents not available from Wacker were purchased from common vendors such as AlfaAesar or Sigma-Aldrich with reagent grade purity. Reagents were used as provided, either internally or from vendors. NMR tubes were purchased from Wilmad (528-PP-7). All ^{1}H and ^{29}Si NMR spectra were recorded at room temperature on a 400 MHz Bruker AVANCE II instrument; chemical shifts are defined in δ (parts per million, ppm) and are reported relative to $CDCl_3$ (^{1}H), TMS (^{29}Si), or Me_2SiO (^{29}Si).

Reactions were carried out in a 250 mL three-neck round-bottom flask. Temperature control was achieved via a thermocouple reading the flask temperature controlled by the thermo-controller providing resistive heating to the heating mantle. The middle neck of each flask was dedicated to a stir shaft with a crescent stir blade, which was connected to a variable speed motor for control over agitation. Finally a cold water condenser and receiving flask was connected to a neck to collect any volatile low molecular weight components. Each reaction was carried out under a blanket of nitrogen, and thus quantitative measurement of the hydrogen gas evolved was not feasible.

Product isolation for non-crosslinked fluids was carried out by cooling to room temperature and filtering to remove any un-reacted particulate solids.

4.2.1 Reaction LS-6
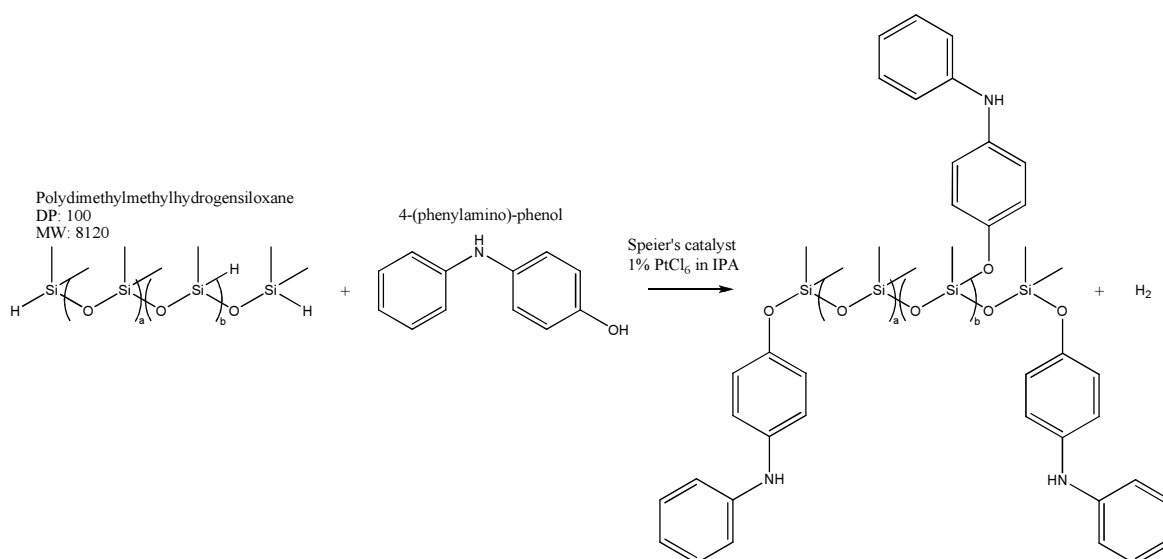
Scheme 8: Reaction LS-6

The first lab scale reaction was initiated by preparing a solution of Speier's catalyst (0.0367 g chloroplatinic acid hexahydrate in 3.67 g isopropanol) in a 20-dram vial. After preparing the catalyst, 4-(phenylamino)-phenol (26.30g, 141.99 mmol) was added to a round-bottom flask and heated to 80°C until the solid transitioned into a liquid. Next, polydimethylmethylhydrogensiloxane (DP:100-110, MW:8120, 97.30 g, 11.98 mmol, 131.81 mmol D^H) was added to the round bottom flask with agitation provided by the cresent stir blade. Upon addition of the polydimethylmethylhydrogensiloxane, the temperature was increased to 145°C. Once the temperature was stable at 145°C, the Speier's catal yst solution (3.67 g, 7.08 mmol, 109 ppm Pt) was added drop-wise with agitation, and the reaction was monitored visually.

The reaction proceeded with release of hydrogen gas. As the reaction progressed, the material grew in viscosity, until an elastomeric network was formed. As

the elastomer grew in viscosity, the material moved up the stirring shaft, eventually precluding the motor from driving the stirring shaft.

The workup procedure of vacuum stripping to remove low molecular weight volatiles with filtration to remove solid particulates was precluded by the elastomeric form of the material. Thus the material was harvested from the flask and tested for crosslink density by attempted dissolution in toluene; however, the material did not dissolve. As such the material gelled elastomer was removed using physical means, by pulling the gel out of the three-necked flask. Moreover, the yield calculation was precluded due to the final product form, making this reaction unsuccessful.

4.2.2   Reaction LS-7

Polydimethylmethylhydrogensiloxane
DP: 100
MW: 8120

4-(phenylamino)-phenol

Speier's catalyst
1% PtCl$_6$ in IPA

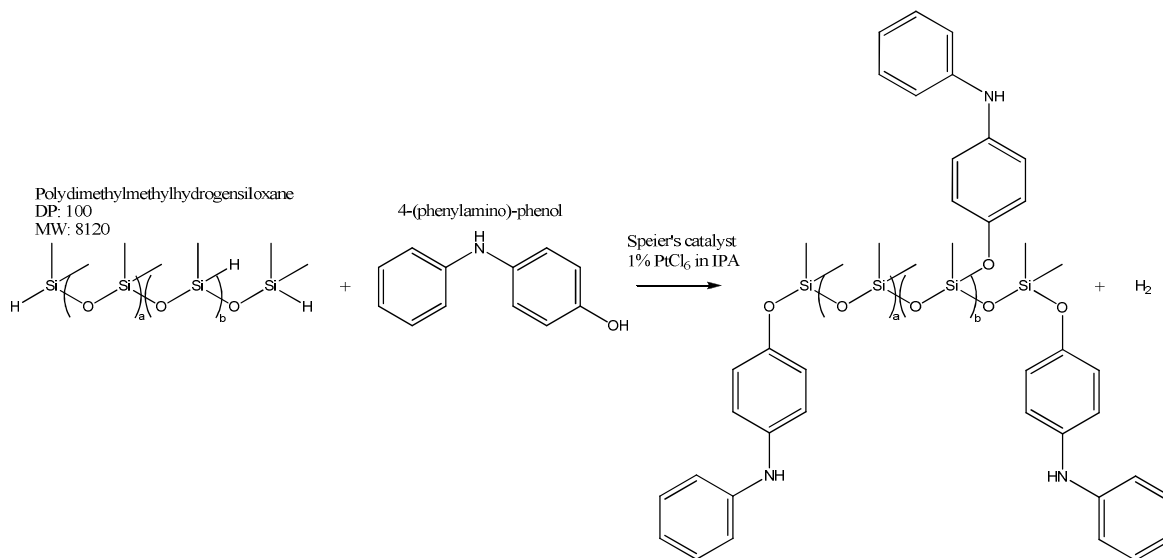**Scheme 9: Reaction LS-7**

The second lab scale reaction was carried out, repeating the first lab scale attempt. A solution of Speier's catalyst (0.0367 g chloroplatinic acid hexahydrate in 3.67 g isopropanol) was prepared in a 20-dram vial. After preparing the catalyst, 4-(phenylamino)-phenol (26.30.g, 141.99 mmol) was added to a round bottom flask and heated to 80℃ until the solid melted. Upon mel ting, polydimethylmethylhydro-gensiloxane (DP:100-110, MW:8120, 97.30 g, 11.98 mmol, 131.81 mmol D^H) was added to the round bottom flask with agitation provided by the cresent stir blade. Upon addition of the polydimethylmethylhydrogensiloxane, the temperature was in-creased to 145℃. Once the temperature was stable at 145℃, the Speier's catalyst solution (3.67 g, 7.08 mmol, 109 ppm Pt) was added drop-wise with agitation, and the reaction was monitored visually. The temperature was maintained at 145℃ for

one hour, at which point a sample was taken to measure the volatile content (2.75% by weight) and ^{1}H NMR. A sample was also taken at 3 hours for ^{1}H NMR.

The reaction developed with release of hydrogen gas. As was noted in reaction LS-6, the material grew in viscosity, eventually crosslinking to a solid in the vessel.

The workup procedure of vacuum stripping to remove low molecular weight volatiles and filtration to remove solid particulates was precluded by the elastomeric form of the material.

4.2.3   Reaction LS-8
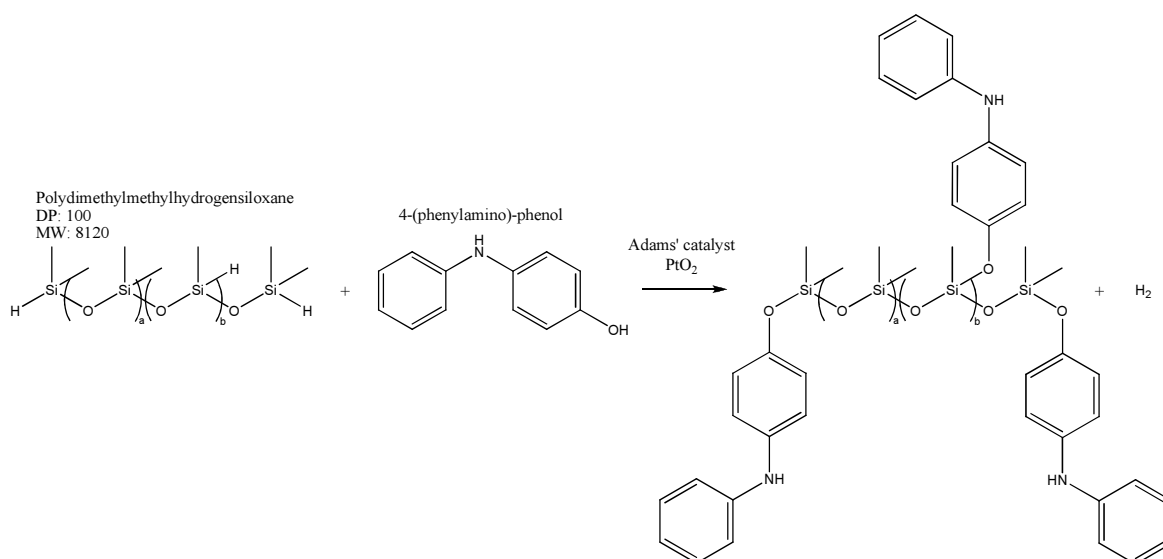
Scheme 10: Reaction LS-8

The next lab scale reaction was carried out akin to the aforementioned exper-iment. However, rather than using Speier's catalyst, Adams' catalyst (platinum diox-ide (neat)) was used. The dry powder of 4-(phenylamino)-phenol (25.00.g, 134.97 mmol) was added to a round bottom flask and heated to 80°C to melt the solid. Then polydimethylmethylhydrogensiloxane (DP:100-110, MW:8120, 99.98 g, 12.31 mmol, 135.44 mmol D^H) was added to the round bottom flask with agitation provided by the cresent stir blade. Upon addition of the polydimethylmethylhydrogensiloxane, the temperature was increased to 120°C. Once the t emperature was stable at 120°C, platinum dioxide catalyst (0.01 g, 0.0639 mm ol, 100 ppm Pt) was added with agitation, and the reaction was monitored visually. The reaction was sampled at 14 hours to evaluate the degree of reaction; however, no gas evolution had occurred for visual evidence of reaction and work-up was not done. Upon cooling, the siloxane

(fluid) and the 4-(phenylamino)-phenol (solid) began to phase separate, and further

evidence of no reaction was the recovered solid in the reaction flask.

4.2.4 Reaction LS-9
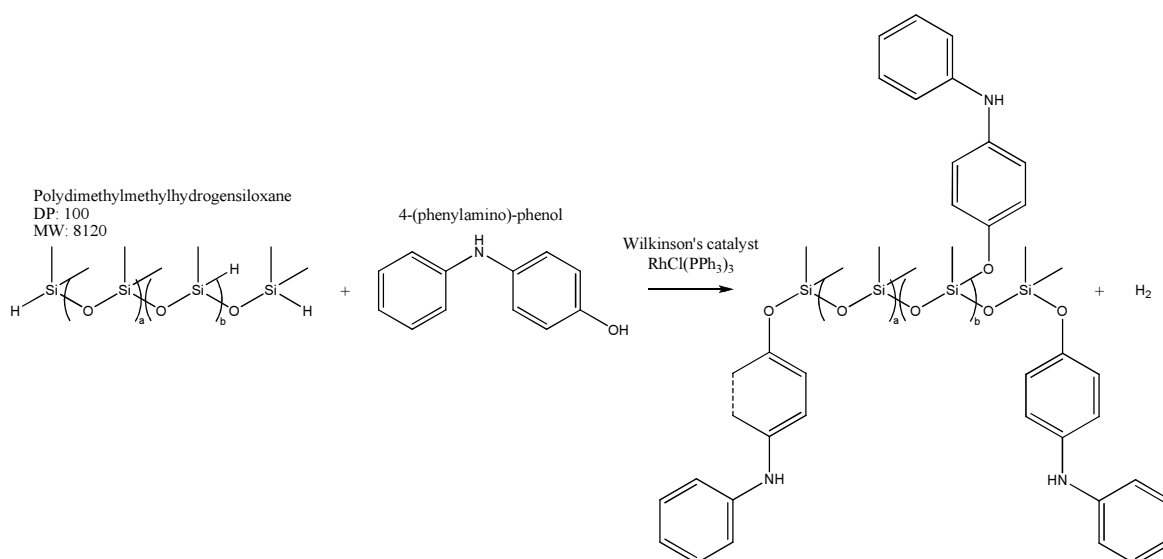
Scheme 11: Reaction LS-9

Another preparation of the antioxidant siloxane was attempted on the lab scale using Wilkinson's catalyst. The dry powder of 4-(phenylamino)-phenol (24.78 g, 133.78 mmol) was added to a round bottom flask and heated to 80℃ until the solid melted. After the powder melted, polydimethylmethylhydrogensiloxane (DP:100-110, MW:8120, 99.09 g, 12.20 mmol, 134.44) was added to the round bottom flask with agitation provided by the cresent stir blade. Upon addition of the polydimethylmethylhydrogensiloxane, the temperature was increased to 120℃. Once the temperature was stable at 120℃, Wilkinson's catalyst (1.12 g, 1.21 mmol, 997 ppm Rh) was added with agitation, and the reaction was monitored visually. The reaction was sampled at 24, 32, and 41 hours to monitor the reaction via NMR. After 53 hours of reaction, the viscosity began to climb and the material started to climb the stirring shaft. As before, the gelled elastomer was not subjected to the workup of vacuum stripping and filtration.

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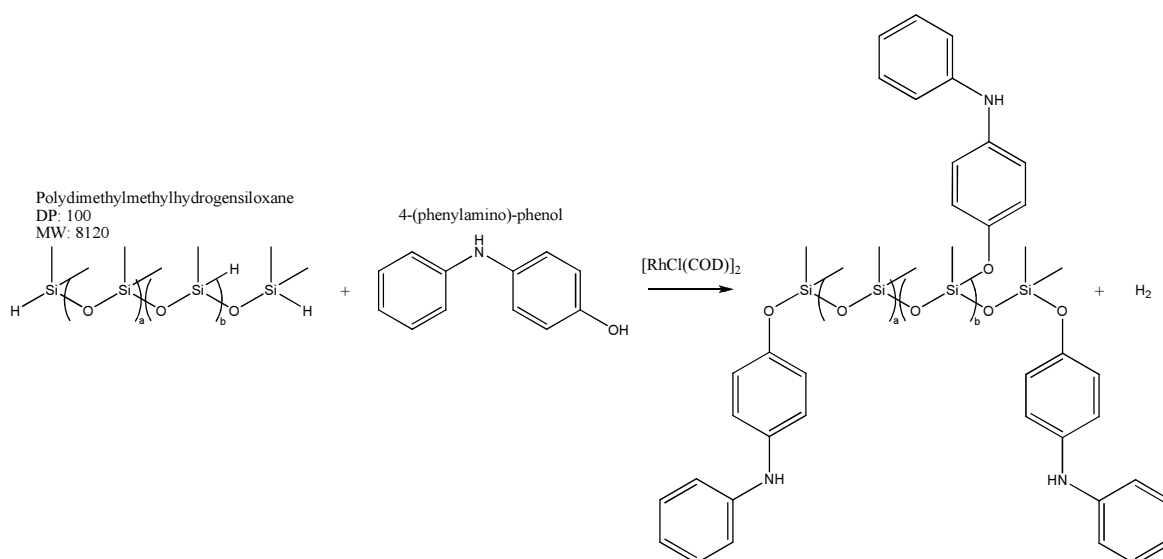
4.2.5   Reaction LS-10

Scheme 12: Reaction LS-10

A preparation to replicate reaction NMR-4 was carried out on a lab scale. The dry powder of 4-(phenylamino)-phenol (24.94 g, 134.65 mmol) was added to a round bottom flask and heated to 80℃ until the solid mel ted. Then polydimethylmethylhydrogensiloxane (DP:100-110, MW:8120, 99.75 g, 12.28 mmol, 135.12 mmol D^H) was added to the round bottom flask with agitation provided by the cresent stir blade. Upon addition of the polydimethylmethylhydrogensiloxane, the temperature was increased to 120℃. Once the temperature was stable at 120℃,[RhCl(COD)]2 (0.30 g, 0.60 mmol, 1001 ppm Rh) was added with agitation and the reaction monitored visually. After 19 hours, the material had solidified to a gel, and the typical work-up of vacuum stripping and filtration was not feasible.

4.2.6   Reaction LS-11
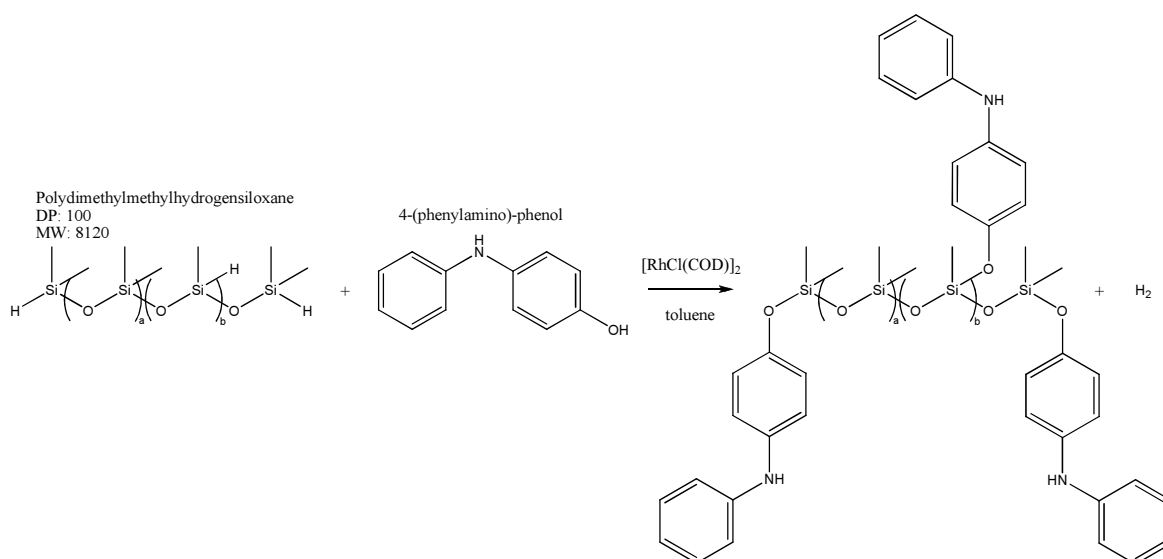
Scheme 13: Reaction LS-11

A preparation to replicate reaction NMR-4 and LS-10 was carried out with a lower temperature. The dry powder of 4-(phenylamino)-phenol (24.94 g, 134.65 mmol) was added to a round bottom flask and heated to 80℃ until the solid melted. Upon melting, polydimethylmethylhydrogensiloxane (DP:100-110, MW:8120, 99.75 g, 12.28 mmol, 135.12 mmol D^H) was added to the round bottom flask with agitation provided by the cresent stir blade. Upon addition of the polydimethylmethylhydro-gensiloxane, the temperature was increased to 90℃. Once the temperature was stable at 90℃, [RhCl(COD)]2 (0.30 g, 0.60 mmol, 1 001 ppm Rh) was added with agitation, and the reaction was monitored visually. To mitigate the previously ob-served crosslinking and gelling, 100 mL of toluene was added after 20 hours of heat-ing at 90℃. The reaction was allowed to progress and was monitored visually for 53 hours. Each time the reaction flask ingredients were allowed to cool, the unreacted 4-(phenylamino)-phenol would solidify at the bottom of the flask. Thus the toluene

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dissolved the mixture of siloxane reactant and product in the top phase. The bi-phase material was not suited for vacuum stripping but was worked up by vacuum filtration. At this point, no mass balance was noted, but a sample of the filtered product was measured by NMR for reaction conversion.

4.2.7 Reaction LS-12
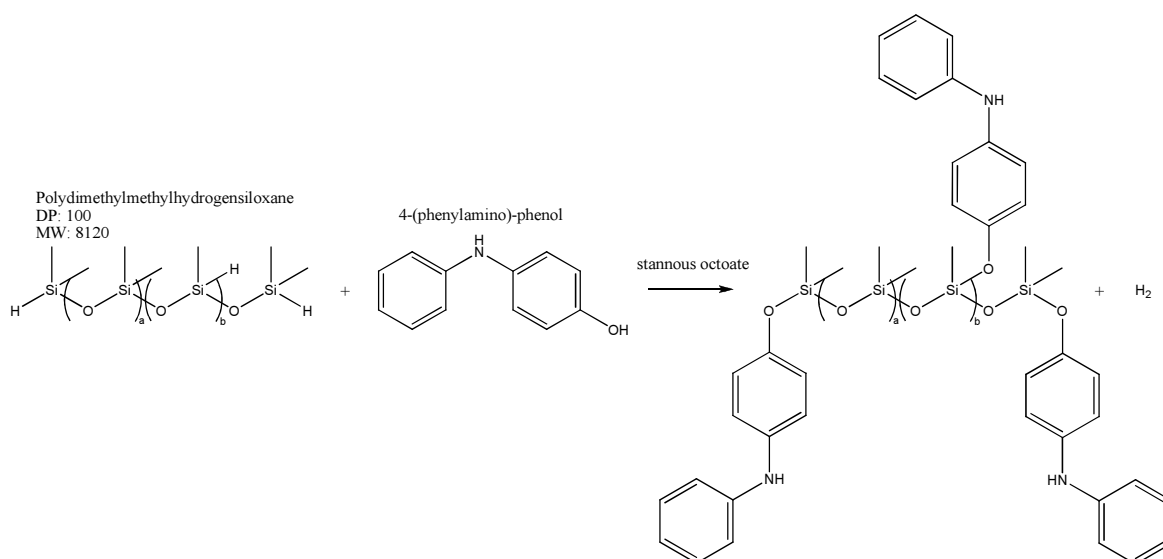
Scheme 14: Reaction LS-12

Another preparation of the target siloxane was attempted on the lab scale using stannous octanoate as a catalyst. The dry powder of 4-(phenylamino)-phenol (24.92 g, 134.54 mmol) was added to a round bottom flask and heated to 80°C until the solid melted. Then polydimethylmethylhydrogensiloxane (DP:100-110, MW:8120, 99.65 g, 12.27 mmol, 134.99 mmol D^H) was added to the round bottom flask with agitation provided by the cresent stir blade. Upon addition of the polydimethylmethylhydrogensiloxane, the temperature was increased to 90℃. Once the temperature was stable at 90℃, stannous octanoate (0.43 g, 1.05 mmol, 1004 ppm Sn) was added with agitation, and the reaction was monitored visually. The reaction was allowed to progress for 5 hours; however, it quickly progressed to a crosslinked elastomer, and the run was terminated without workup.
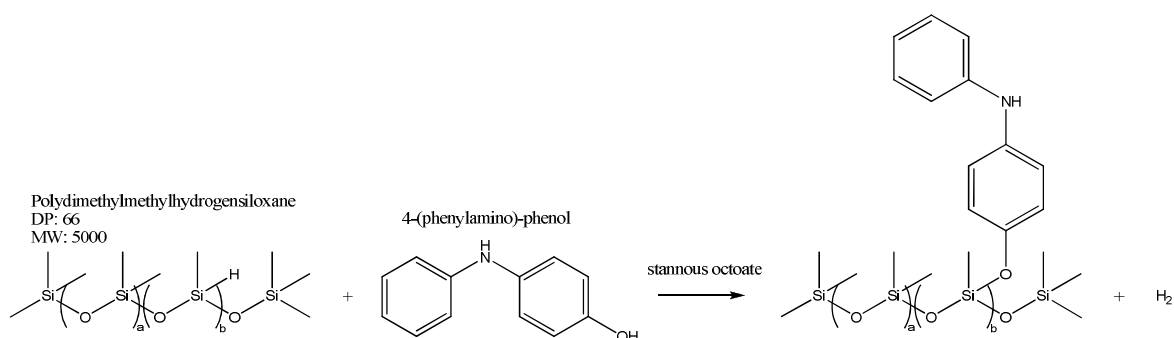
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4.2.8   Reaction LS-13

Scheme 15: Reaction LS-13

Another preparation of the antioxidant siloxane was attempted on the lab scale using stannous octanoate to catalyze the reaction. Additionally, the polydimethylmethylhydrogensiloxane was changed to mitigate the chance of producing a crosslinked elastomer. The dry powder of 4-(phenylamino)-phenol (12.45 g, 67.21 mmol) was added to a round bottom flask and heated to 80°C until the solid melted. Once the solid melted, polydimethylmethylhydrogensiloxane (DP:66, MW:5048, 112.12 g, 22.21 mmol, 55.52 mmol D^H) was added to the round bottom flask with agitation provided by the cresent stir blade. Upon addition of the polydimethylme-thylhydrogensiloxane, the temperature was increased to 90°C. Once the temperature was stable at 90°C, stannous octanoate (0.43 g , 1.05 mmol, 1000 ppm Sn) was added with agitation, and the reaction was monitored visually. After 65 hours of reaction, the material was cooled to prepare for workup. The material was passed under vacuum through filters of 6, 1, and 0.45 um size. The material was clear with a hint of tan (straw) color. The reaction yield (12.5%) was evaluated via NMR spectroscopy.

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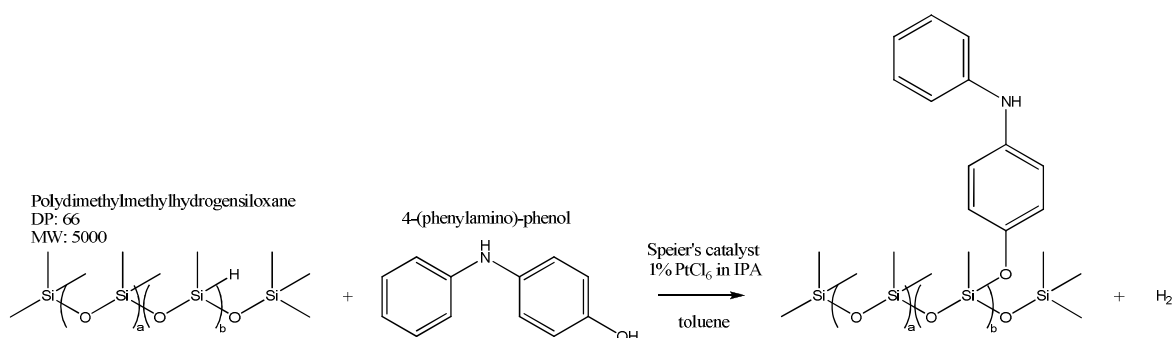
4.2.9   Reaction LS-14

Scheme 16: Reaction LS-14

A preparation of the heat stabilizing siloxane was attempted on the lab scale using Speier's catalyst to catalyze the reaction. Reaction LS-14 was also carried out in a 500 mL round bottom flask to accommodate the incorporation of solvent. Because the reaction uses Speier's catalyst, a 1% solution was made (0.0332 g chloroplatinic acid hexahydrate in 3.29 g isopropanol) before addition of ingredients to the vessel. After preparation of the 1% solution of Speier's catalyst, toluene (232.15 g, 2519.53 mmol) was added to an empty 500 mL round bottom flask. Following the addition of toluene, the dry powder of 4-(phenylamino)-phenol (13.82 g, 74.61 mmol) was added and dissolved into the toluene. Once the addition of 4-(phenylamino)-phenol was made, the temperature was increased to 100°C. Polydimethylmethylhydrogensiloxane (DP:66, MW:5048, 107.85 g, 21.36 mmol, 53.41 mmol D^H) was added to the round bottom flask with agitation provided by the cresent stir blade. Upon addition of the polydimethylmethylhydrogensiloxane, the matrix was stirred for 10 minutes. After stirring, the Speier's solution was added dropwise to the flask (3.32 g, 6.41 mmol, 100 ppm Pt) with agitation, and the reaction was monitored visually. As the reaction progressed, the material changed color from a light brown tea color to a dark brown color. After 35 hours of reaction, the temperature was in-

creased to 110°C and toluene was refluxed for an additional 28 hours. With a total reaction time of 64 hours, the material was cooled and vacuum filtered through #6 paper, where the unreacted 4-(phenylamino)-phenol was collected on the filter paper (4.34g). The weight of the dried 4-(phenylamino)-phenol gave a 31.40% recovery of the reactant. After filtration, nitrogen was bubbled through the material to aid in evaporating the toluene. The reaction conversion of silicon hydride was evaluated via NMR spectroscopy to be 69.36%.

4.2.10 Reaction LS-15
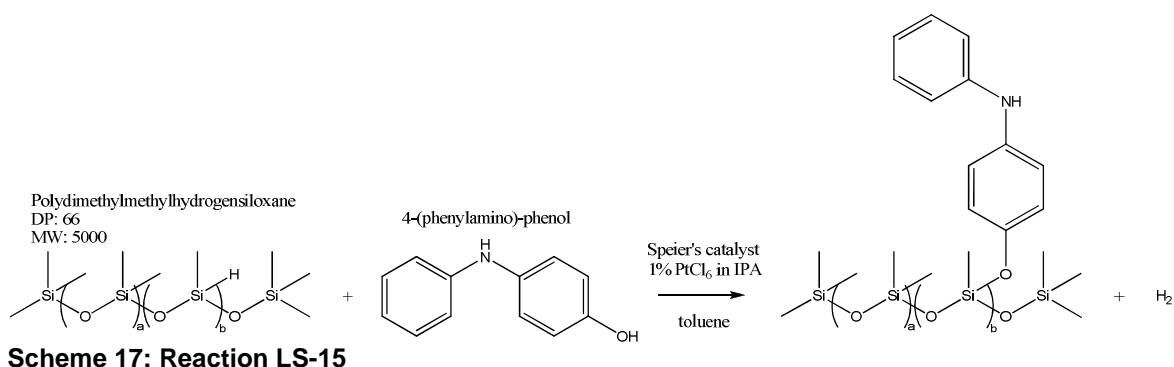
Scheme 17: Reaction LS-15

A final preparation of the antioxidant siloxane was attempted in order to re-peat reaction LS-14. The conditions were identical to reaction LS-14; however, the batch size was doubled. After monitoring the reaction for 34 hours at 110°C, the material was cooled and filtered through #6 paper, where the unreacted 4-(phenylamino)-phenol was collected on the filter paper (16.03g or 30% recovery). After filtration, the toluene was evaporated by sparging the material with nitrogen. The isolated reaction product, minus the toluene, weighed 233.75 g. The reaction extent was evaluated via NMR spectroscopy as well as by mass balance. Based on the mass balance, 11.61 grams and thus 62.68 mmol of 4-(phenylamino)-phenol were incorporated into the reaction product. Given that 215.7 grams of the starting siloxane had 106.82 mmol of silicone hydride groups to participate in the reaction, the reaction conversion of silicon hydride as calculated by mass balance is 58.68%. This is in good agreement with the calculated value from ^{29}Si NMR, which estimates the reaction conversion of silicon hydride at 59.93%.

5. **Characterization**

The primary route of characterization for the series of experiments was silicon-29 NMR. The technique is useful for silicone polymer characterization due to the wide range of chemical shifts for siloxane building blocks. In the case of the above detailed experiments, the reaction progress could be monitored and quantified by the decrease in the methylhydrogen signal at -36 ppm and the introduction of the alkoxy-functionalized repeat unit at -67 ppm. The integration of these signals also can give quantitative information regarding the degree of reaction progress.

In addition to the ^{29}Si NMR, ^{1}H NMR was useful for monitoring the reaction progress. The quantitative decrease in the silicon hydride signal at 4.7 ppm can also be used to monitor the degree of reaction progress. Also theoretically possible is the ability to use the aryl signal from the aromatic phenol. However, as the aryl groups are added to the polymer, the lines broaden due to the increasing microstates of substitution and make the comparison of integrals more imprecise.

6. Evaluation

While the primary goal of this research was to synthesize and characterize the target functional polymer, ultimately the evaluation of the polymer was necessary to test the efficacy in the final application. To that end, lab scale evaluation studies against industry standard benchmarks were conducted to evaluate the efficacy of the target molecule.   A heat age study was conducted to compare the antioxidant siloxane added to silicone fluids typically used in the fuser application in relation to several control fluids, as well as industrially common iron octoate additives. In order to assess the antioxidant in other applications, the additives were added to commonly used room temperature cure (RTV) formulations, as well as liquid silicone rubber formulations, and a separate heat age study was conducted.

6.1 Fluid Evaluation Experimental

The fluid evaluation consisted of four control polymers. The control polymers were neat polydimethylsiloxane, mercaptofunctional dimethysiloxane, and two aminofunctional dimethylsiloxanes (same structure but made with different catalysts). For comparison, samples of commercial iron octanoate and the aromatic aminosiloxane test polymer were added to the control polydimethylsiloxane and the most stable aminofunctional siloxane.

Samples were prepared by mixing the heat stabilizer into the parent fluid until the materials were homogenous under light agitation. Each sample was made to a batch size of 200 g in glass jars. The jars were placed in an oven set at 230℃. Each sample was monitored weekly for changes in viscosity. Viscosity was meas-

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ured using a Paar Physica rheometer. The viscosity chart (Figure 15) over time was

plotted to indicate the efficacy in the final application.

6.2 Elastomer Evaluation Experimental

The elastomer evaluation consisted of two types of base elastomer, RTV (room temperature vulcanization) and LSR (liquid silicone rubber). The control formulation for the RTV consisted of the base rubber and catalyst, mixed, vacuum de-gassed, placed in a slab mold, and cured in a press at room temperature. The experimental RTV consisted of the base rubber, to which the aromatic aminosiloxane stabilizer was added and mixed, vacuum de-gassed, then cured into test slabs at room temperature using the same technique.

The LSR control formulation consisted of equal parts A side and B side, which when mixed was composed of polydimethylmethylvinyl siloxane, silica, polymethylhydrogen siloxane, proprietary platinum-complex catalyst, and a proprietary catalyst inhibitor. This formulation was mixed on a Hobart mixer for 15 minutes. While the materials were mixing, the mixer sides were scraped every 5 minutes. The compounded A and B sides were then vacuum de-gassed. Then the material was placed in a mold and cured for 5 minutes at 165℃. The experimental LSR formulation was compounded as above, but after 5 minutes of mixing, the aromatic aminosiloxane stabilizer was added and mixed for 15 minutes, scraping the mixer sides 3 times therein. The material was vacuum de-gassed, then placed in a mold to be cured at 165℃ for 5 minutes.

Once the sample slabs were prepared, they were placed in an oven at 204℃ for 7 days. After the heat age, physical properties of tensile (ASTM D-412), elonga-

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tion (ASTM D-412), durometer (ASTM D-2240) and tear (ASTM D-624.B) were test-ed to evaluate the efficacy of the additive in the elastomer.

Tensile strength and elongation were measured to determine the response of the rubber to axial force. In the case of tensile strength, the axial force was carried out until the material broke. In the case of elongation, a yield point is measured. The yield point is the maximum axial stress the material can withstand without de-formation.

Durometer is a measurement of hardness, or the resistance to permanent indentation. The device for measuring durometer works by measuring the indenta-tion depth left by a standard size probe with a standard force.

Tear strength is a measurement of the shear strength of a material. This test is similar to the tensile strength test. However, the material is compromised with a slit tear cut with a die to a standard dimension. With the tear (or cut) in place, the force to complete the tear is measured on a load cell.

7. Results and Discussion

The objective of the work herein was to develop a synthetic pathway to a siloxane copolymer containing a siloxy linkage to a diphenyl amine group. Feasible routes were evaluated in both NMR and lab scale reactions and characterized by NMR spectroscopy. Finally, the siloxane copolymer was tested to evaluate the efficacy with regard to inhibition of thermal degradation.

7.1 Discussion of Synthesis

Many synthetic routes could yield a similar copolymer; however, this work aimed to utilize commercially available materials in the design of the synthesis. For example, a common approach en route to the desired product would be through condensation/equilibration of an alkoxy silane into a polydimethylsiloxane using a basic catalyst such as potassium hydroxide. While this route, in general, is widely used in industry to fashion siloxane copolymers of limited molecular weight, it requires that the starting alkoxy silane be readily available and highly pure. In the specific case of this work, the dimethoxy-or diethoxy-aromatic aminophenoxysilane monomer could be prepared, but the purification would be excessively complex and direct polycondensation difficult to control. Since common industrial starting materials were to be used in the synthesis, the route of catalytic dehydrogenation between the phenolic amine and a silicon hydride of the methylhydrogen siloxane, detailed in the background discussion, was pursued. To that end, catalysts thought to be effective in the dehydrogenative coupling were chosen and evaluated. The primary method of evaluating catalyst efficacy was monitoring reaction progress over time using NMR spectroscopy.

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Table 1: NMR scale reaction overview

ID	Methyhydrogen Fluid	4-(phenylamino)-phenol (mmol)	Catalyst	Solvent	Reaction Conversion (%)
NMR-1	$M^HD_aD^H{}_bM^H$ MW: 8120	0.8433	$RhCl(PPh_3)_3$	d-benzene	63.44
NMR-2	$M^HD_aD^H{}_bM^H$ MW:8120	0.8520	$[RhCl(COD)]_2$	d-benzene	88.72
NMR-3	$M^HD_aD^H{}_bM^H$ MW:8120	0.9151	$RhCl(PPh_3)_3$	d-toluene	63.54
NMR-4	$M^HD_aD^H{}_bM^H$ MW:8120	1.1408	$[RhCl(COD)]_2$	d-toluene	97.65
NMR-5	$M^HD_aD^H{}_bM^H$ MW:8120	0.8017	$PtCl_6$	d-toluene	82.65

The NMR reaction series provided a valuable comparison for catalyst efficacy. From the results of the study summarized in Table 1, the lab scale reaction could be carried out with the knowledge that a particular catalyst could work. Additionally, it allowed for product yields to be predicted and for the final material to be characterized without the workup typically needed in lab scale reactions. Figure 9 shows an example of the ^{29}Si NMR obtained from the NMR tube reactions. The annotated peaks in Figure 11 were used to track conversion.

However, what the NMR scale reactions were unable to predict was the final state of the reaction product. The lab scale reactions gave insight to the effect of backbone structure on the final makeup of the material.

Reactions LS-6 and LS-7 were the first reactions carried out on a lab scale. Additionally, they were the first reactions to yield an elastomeric product, which precluded the workup of the material. The transition of the siloxane from a fluid to an elastomer made it evident that a reaction was taking place. Furthermore, a failed

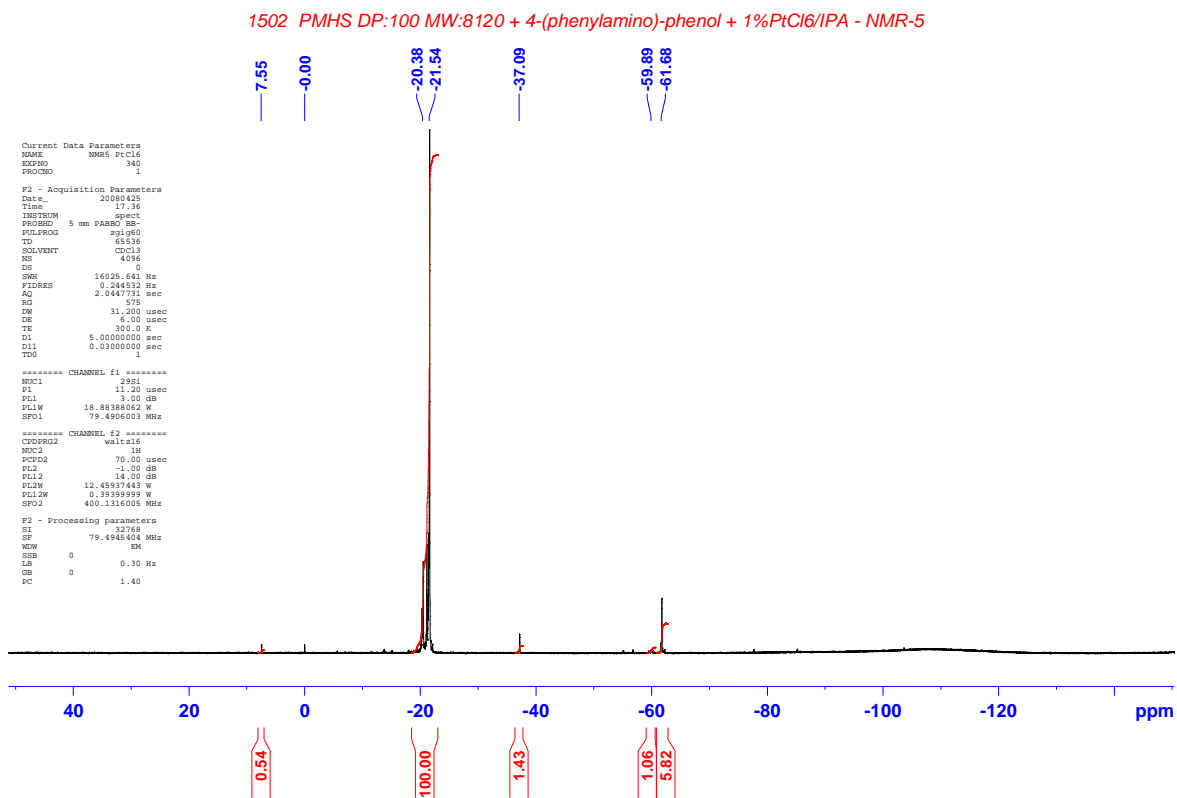attempt to dissolve the material in toluene gave evidence for the highly crosslinked nature of the material.

Figure 9: ^{29}Si NMR of NMR-5

The next lab reaction, LS-8, was carried out with a platinum dioxide catalyst, with the aim that a less effective catalyst would prevent the material from quickly forming a crosslinked elastomer. However, platinum dioxide proved an inefficient catalyst, and after 14 hours of reaction time, no reaction was noted via NMR. Platinum dioxide is the only catalyst without ligand support to keep the catalyst homogenous in the reaction matrix. It is likely that this structural difference is what made platinum dioxide an ineffective catalyst in this process.

The next three reactions, LS-9 through LS-11, attempted to utilize rhodium complexes to accelerate the dehydrogenative coupling reaction. Reaction LS-9, in

particular, used the triphenylphosphine-supported rhodium to catalyze the coupling. However, akin to LS-6 and LS-7, while the rhodium catalyst proved to be efficient at catalysis, it also led to a crosslinked elastomer.

Rhodium was also used in reactions LS-10 and LS-11 to catalyze the dehydrogenative coupling. Specifically, the cyclooctadiene ligand complex was used with positive results. However, like the previous reactions, the material transitioned from a fluid to elastomer quickly, due to excessive crosslinking.

A final catalyst evaluation on the lab scale was carried out using stannous octoate (reaction LS-12). It was expected that tin would be a less efficient catalyst than rhodium or platinum. However, the tin octoate catalyst quickly converted the material to an elastomer, thus precluding workup and evaluation.

Since each catalyst proved to be efficient at converting the dehydrogenative coupling (with the exception of platinum dioxide), the base methylhydrogen siloxane was hypothesized to be the cause of the material converting to a crosslinked elastomer across the reaction coordinate. Therefore, a new methylhydrogensiloxane copolymer was selected for use in the reaction. Rather than selecting a fluid with end-group silicon hydrides, a trimethylsilyl end-group co-polymer was selected. Additionally, the choice was made to use a lower molecular weight starting siloxane with a modified ratio of dimethyl to methylhydrogen units. Thus, keeping the chain from becoming extended and lessening the statistical likelihood of pendant crosslinking would decrease the probability of crosslinking to the solid elastomer. This was a critical consideration since in order to characterize the structure and evaluate the efficacy of the heat stabilizing siloxane by formulation, a liquid material was required.

With regard to pendant crosslinking, a number of adducts, albeit less favorable both sterically and kinetically, give rise to the potential for crosslinking. In the presence of catalyst and heat, water can form a tri-functional, pendant silanol which then can react with another in-the-chain silicon hydride, forming a link between two polymer chains. In addition to this, the aromatic amino phenol can couple two chains by reaction between the phenol hydroxyl group and the secondary amine. This relies on a slower bond formation between silicon and nitrogen and is sterically unfavorable, but it is a potential side reaction that can lead to the crosslinking observed.

In light of the necessity of the material to be fluid, reaction LS-13 was carried out using a methylhydrogensiloxane copolymer with a lower molecular weight, un-functionalized endgroups, and lower silicon hydride content. The structural change in the starting siloxane yielded a change in the final state of the reaction product. The reaction (similar to the preceding LS-12) yielded a straw (tan) colored fluid. This fluid could be characterized and incorporated into a heat age (stability) study.

The product of LS-13 confirmed the efficacy of the modified methylhydro-gensiloxane by yielding a fluid rather than an elastomer. Thus the reaction sequence was repeated using chloroplatinic acid as a reaction catalyst for reactions LS-14 and LS-15. These two reactions were nearly identical, but LS-15 repeated LS-14 at twice the scale. Both reactions yielded a fluid product, which were characterized, before being used in the heat age evaluation study. The mass balance of LS-15, calculated according to the equation in Figure 10, was in good agreement with the calculated value from the ^{29}Si NMR, as noted in Table 2.

$$Reaction\ Conversion\ of\ Silicon\ Hydride\ \%$$

$$Reaction\ Conversion\ of\ Silicon\ Hydride(\%) = \frac{Moles\ of\ reacted\ phenol}{Moles\ of\ silicon\ hydride} \times 100$$

Figure 10: Calculation of Reaction Conversion from Mass Ballance

Table 2: Lab scale reaction overview

ID	Methyhydrogen Fluid	4-(phenylamino)-phenol (mmol)	Catalyst	Solvent	Reaction Conversion (%) via ^{29}Si NMR	Reaction Conversion (%) via Mass Balance
LS-6	$M^HD_aD^H{}_bM^H$ MW: 8120	141.99	PtCl$_6$	–	–	–
LS-7	$M^HD_aD^H{}_bM^H$ MW:8120	141.99	PtCl$_6$	–	–	–
LS-8	$M^HD_aD^H{}_bM^H$ MW:8120	134.97	PtO2	–	–	–
LS-9	$M^HD_aD^H{}_bM^H$ MW:8120	133.78	RhCl(PPh$_3$)$_3$	–	–	–
LS-10	$M^HD_aD^H{}_bM^H$ MW:8120	134.65	[RhCl(COD)]$_2$	–	–	–
LS-11	$M^HD_aD^H{}_bM^H$ MW:8120	134.65	[RhCl(COD)]$_2$	–	–	–
LS-12	$M^HD_aD^H{}_bM^H$ MW:8120	134.54	Sn(C$_8$H$_{15}$O$_2$)$_4$	–	–	–
LS-13	MD_aD_bM MW:5048	67.21	Sn(C$_8$H$_{15}$O$_2$)$_4$	Toluene	12.52	–
LS-14	MD_aD_bM MW:5048	74.61	PtCl$_6$	Toluene	69.36	–
LS-15	MD_aD_bM MW:5048	74.66	PtCl$_6$	Toluene	59.93	58.68

7.2 Discussion of Spectral Data

Ultimately the synthetic route using a transition metal catalyzed dehydrogenative reaction between the anti-oxidant alcohol and a parent hydrosiloxane was readily characterized by ^{29}Si NMR. This characterization is best evaluated by comparing the reaction product spectrum to that of the starting materials. To that end, the ^{29}Si spectrum of the parent hydrosiloxane (Figure 11) contains the structural information needed to characterize the polymer. Thus with signals at δ7.5 (M, or trimethylsilyl end unit), δ-21.7 (D or dimethylsiloxy unit), and δ-37.3 (D^H, or the pendant functional hydrosiloxy unit) the starting material is readily characterized. In addition, the integral values correspond well to the expected ratio of end groups to repeat units.
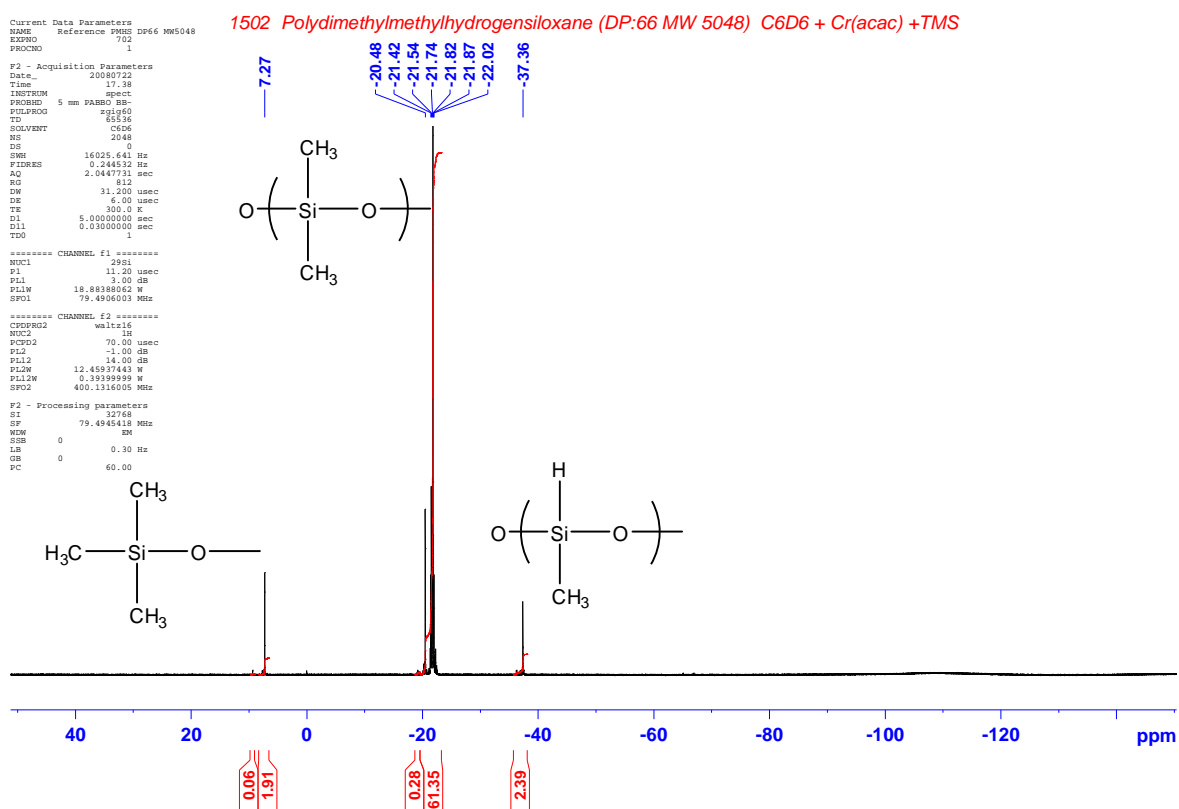

Figure 11: ^{29}Si NMR of polydimethylmethylhydrogensiloxane starting material

Using the spectral information from the parent hydrosiloxane, characterization of the reaction product is clearly defined by the decrease in signal intensity of the signal at δ-37.3 and the appearance of a new signal at δ-61.7 (Figure 12). The signal at δ-61.7 is formed from the change in bond character from a silicon hydride to a siloxy or silicon alkoxy bond. This change in the electron density around the silicon nucleus is the primary cause behind the change in chemical shift of that repeat unit.
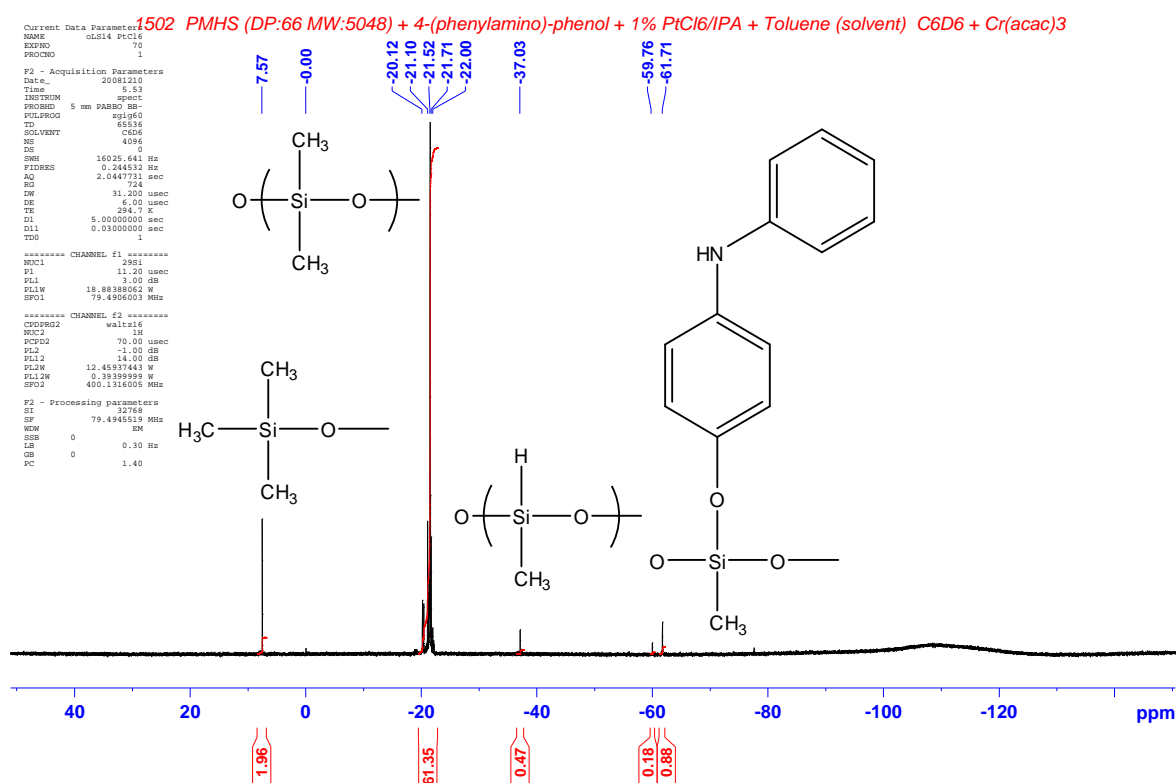

Figure 12: ^{29}Si NMR of LS-14 reaction product

Not only does the [29]Si spectrum give qualitative structural details relative to the polymer building blocks, but it can serve as a tool in evaluating the reaction extent (as noted in the first several NMR tube reactions). Thus the reaction conversion of silicon hydride can be evaluated. Tables 1 and 2 detail these conversions based

on the integral values from the NMR signals as calculated by the equation in Figure 13.

$$Reaction\ Conversion\ of\ Silicon\ Hydride(\%) = \frac{\sum I_P}{\sum I_P + \sum I_R} \times 100$$

Figure 13: Calculation of Reaction Conversion from NMR Integrals

Since the NMR signal is directly proportional to the number of nuclei, it can be used to represent mole content by normalizing for the number of nuclei represented in a signal. In most cases with regard to ^{29}Si NMR, the number of nuclei responsible for a signal is unity. Therefore, to calculate the reaction yield from the NMR, the sum of the reaction product signals is divided by the sum of the reactant and product signals, multiplied by 100. This value gives the percentage of reaction conversion, or product yield.

Another spectral technique, FTIR, was used to make measurements over the course of the reaction. However, no observable changes in the spectra were noted, other than decrease of the signal at 2100 cm^{-1} caused by decreasing Si-H. Nevertheless, this spectral change is an efficient way to monitor the reaction progress. It was, however, unfortunate that a band arising from the Si-O-C(aryl) was not observed. This is most likely due to overlap with other Si-O-C bands from the dimethyl repeat units. Figure 14 shows an example FTIR of the reaction, run neat on CLEARTRAN (ZnS) transmission windows.
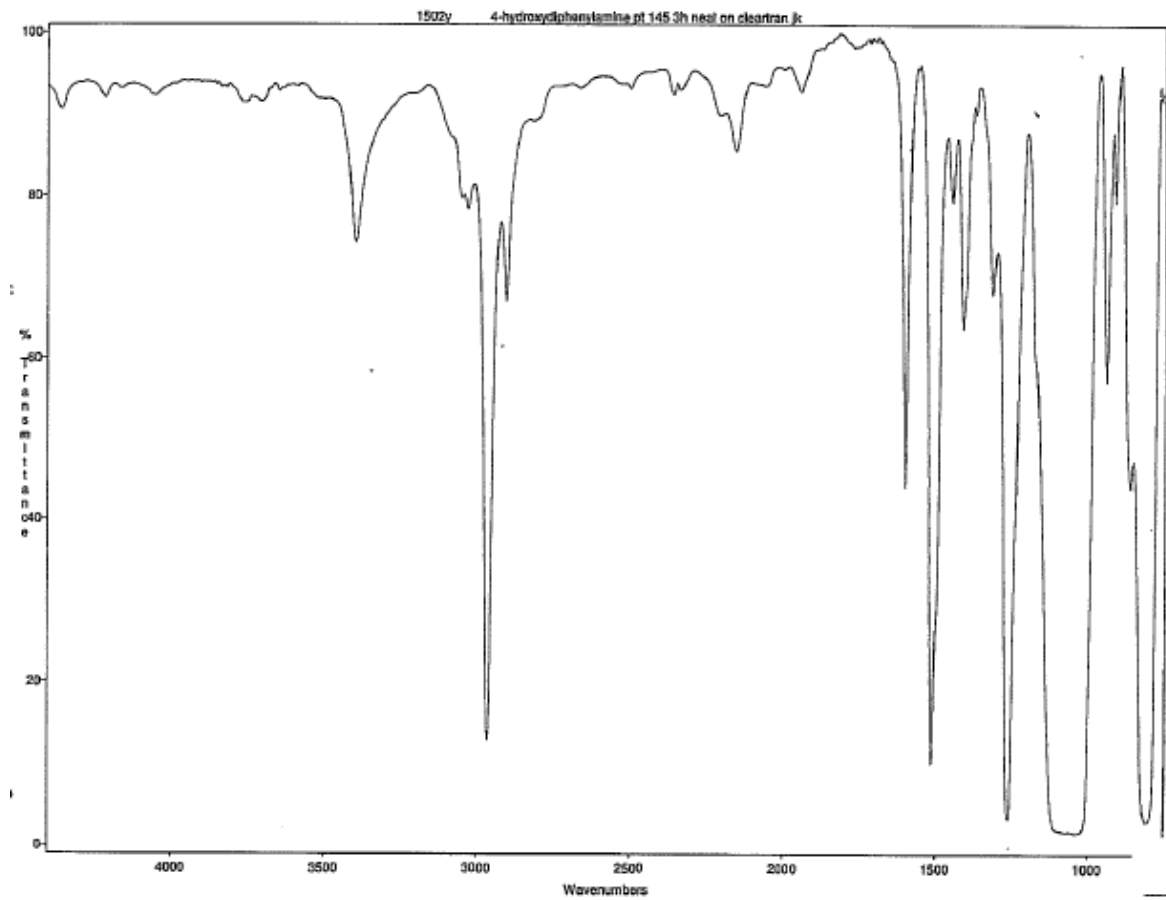
Figure 14: FTIR of LS14 reaction product

7.3 Discussion of Heat Age Evaluation

Finally, evaluation of the product through heat age stability studies shows both efficacy in delaying gelation in fluids, as well as increasing resistance to degradation in physical properties such as tensile, elongation, tear, and durometer when heat aged with respect to LSR formulations.

Figure 15 clearly illustrates the efficacy of the siloxane additive when formulated into polydimethylsiloxane and polydimethylmethylaminosiloxane. In each case, the viscosity stability is increased by 5 weeks. This result is particularly noteworthy, since the heat age study was deliberately designed to give an accelerated failure response.
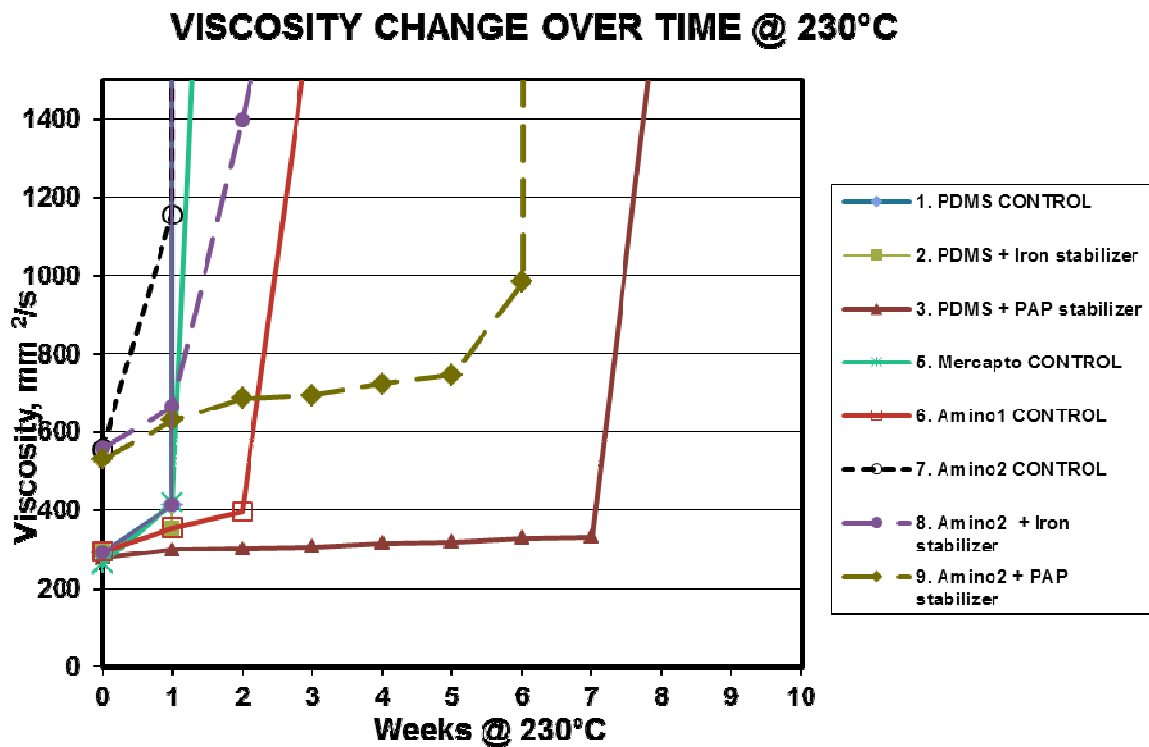

Figure 15: Fluid formulation heat age results

Additionally, the siloxane additive shows promise when formulated into elastomers, such as RTV and LSR. While viscosity is a salient characteristic to the fluid formulation, other physical tests are used to provide similar information on the solids. These tests are tensile strength, elongation, tear, and durometer. With regard to LSR, Figure 17 clearly shows the increased thermal stability provided by the siloxane additive. The additive gives enhanced resistance to tear and tensile strength decrease, as well as retention of elongation with respect to the LSR. Additionally, with respect to the RTV, the properties of tensile strength and elongation are particularly improved with the formulation of the heat stabilizer, as shown in Figure 16.
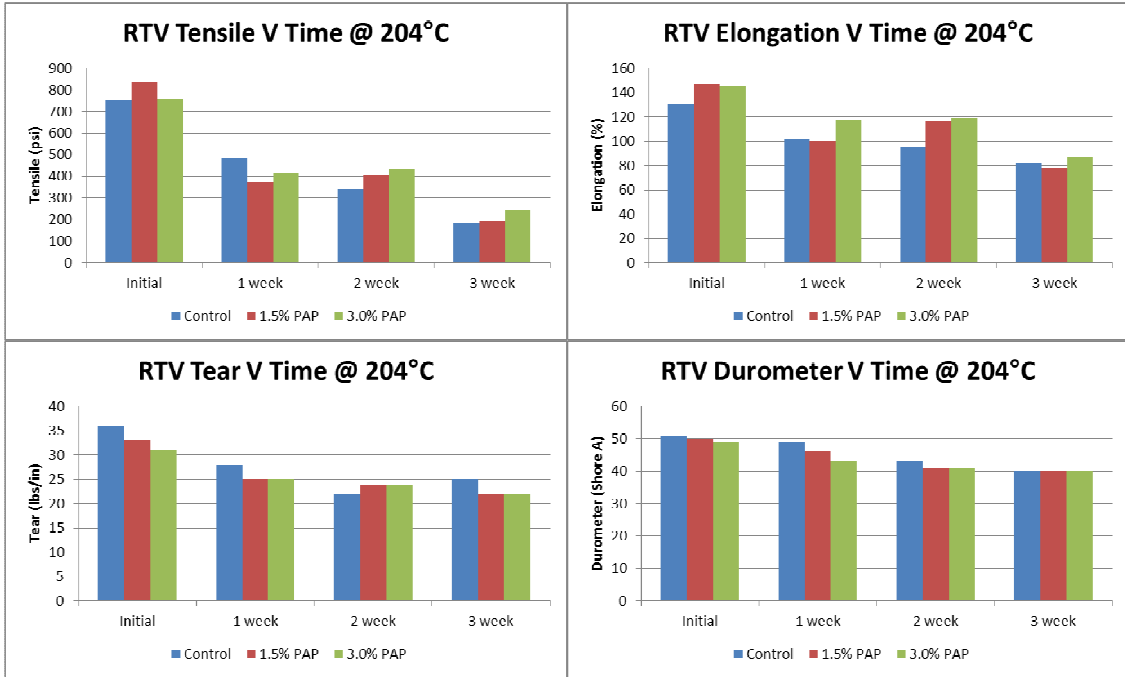
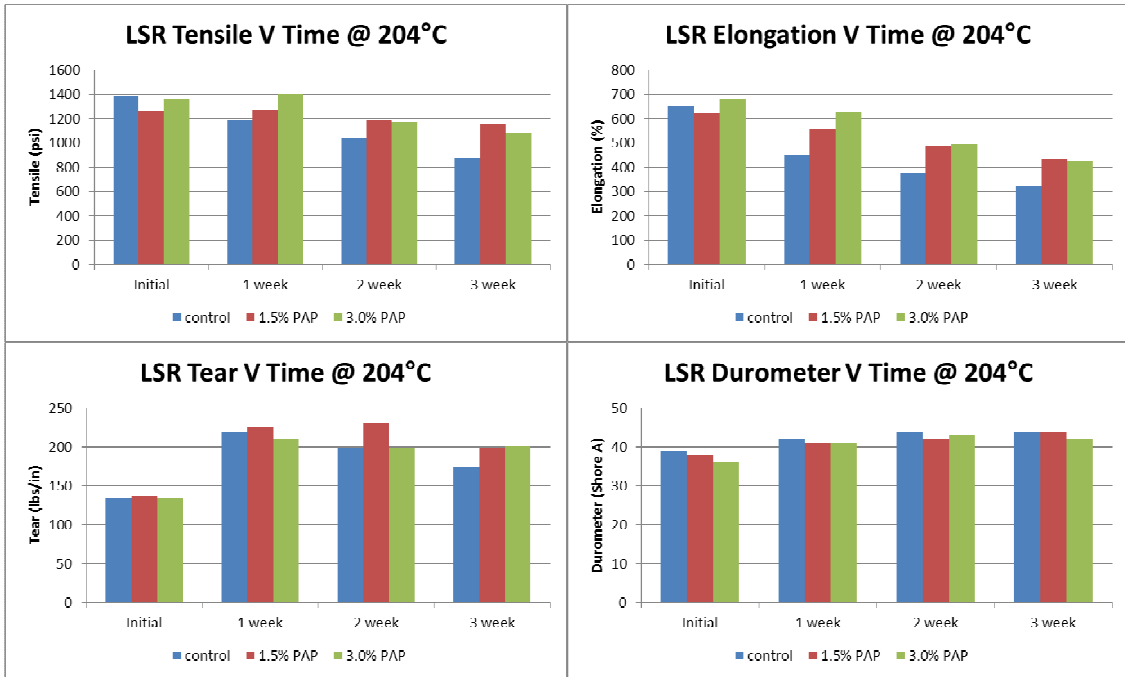**Figure 16: RTV formulation heat age results**

Figure 17: LSR formulation heat age results

Conclusion

The reaction detailed in LS-14 gave the best results, as measured by reaction conversion calculated by ^{29}Si NMR, for preparation of the target siloxane. Additionally, reaction LS-15 confirmed the results of LS-14 both spectrally and by mass balance. This is particularly important, because the agreement of the spectral evidence with the mass balance gives indication that any phenol not recovered via filtration was indeed reacted onto the polymer silicon hydride groups.

Further, from study of the reactions that failed to give a fluid product, it was learned that for each reaction that formed an elastomer the catalyst did function as expected, but the starting hydrosiloxane substrate was too readily crosslinked to yield the required fluid state. The yields in these cases were not evaluated; however, the change in the materials state (from fluid to elastomer) was an evident sign that the chain extension and crosslinking was taking place due to the action of the catalyst. To eliminate the aforementioned chain extension and crosslinking, a hydrosiloxane with no end group functional silicon hydride and with a lower mole percentage pendant silicon hydride allowed for a reaction product that was easily isolated as a fluid.

The physical state of the product was a key parameter to function in the final application, as the product was required to be miscible with a continuous phase of siloxane fluid of a viscosity range between 100-1000 cps. Furthermore, it was confirmed that the alkoxy-amino functionalized polysiloxane, when formulated into common grades of fuser fluids, gave improved heat stability. Additionally, the heat

stabilizer showed promise in elastomer formulations inasmuch as it improved physical testing results after heat age conditioning.

Future work in regard to this project might be well suited to evaluate alternative synthetic routes to the reaction product, either through functionalization of silanes and subsequent condensation/equilibration or through controlled hydrolysis of pendant silanol or chlorosiloxanes. Additionally, work could be focused at the interface of formulation of the product into more applications where heat stability is critical and measurement of the parameters from which the extended life might benefit.

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