Synthesizing Self-Healing and Recyclable Silicones

Using the Diels-Alder Reaction as a Cross-Linker:

Investigation of Various Dienes and Dienophile Systems

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Equipped with his five senses, man explores the universe around him and calls the adventure Science. - Edwin Powell Hubble

One, remember to look up at the stars and not down at your feet. Two, never give up work. Work gives you meaning and purpose and life is empty without it. Three, if you are lucky enough to find love, remember it is there and don't throw it away. — Stephen Hawking
To my family
Abstract

This thesis focuses on the synthesis of recyclable and self-healing polysiloxane elastomer networks. These features were achieved through the use of thermally reversible Diels-Alder (DA) and retro-Diels-Alder (rDA) reactions. In this work, for the model system, two different dienes (3 and 8) and six dienophile were explored, of which five of the dienophiles are commercially available and one of them was synthesized in the lab (13) to produce a series of model DA adduct. Model systems consisting of diene-functionalized trisiloxanes and bismaleimides as dienophiles were utilized to develop a fundamental understanding of how the electronic differences in the coupling systems would influence the efficiency of the overall reaction. Then for the elastomers, three different methylhydrosiloxane-dimethylsiloxane copolymer, trimethylsiloxane terminated (PDMS) with different molecular weights and Si-H group mole percentages [32 a = 3-4% Si-H and 13000 g/mol; 32 b = 7-9% Si-H and 5500-6500 g/mol; 32 c = 25-30% Si-H and 2000-2600 g/mol] were used and functionalized with two different dienes (3 and 8) to produce six polymeric diene systems (33 a, 33 b, 33 c, 34 a, 34 b and 34 c). After analyzing the model systems, the optimal temperature for adduct formation was determined to be between 60 °C – 70 °C, while the rDA reactions occur were found to occur between 90 °C and 110 °C, depending on the system. The tensile strengths of the elastomer systems correlated well with the cross-link densities of individual elastomers (elastomers were elongated between 0.3 cm and 2.54 cm). Furthermore, the hardness of the elastomers also correlated with the cross-link density of the elastomer (Shore 00 values ranged from 32 to 8). However, all of the elastomers displayed a decrease in their Shore 00 values after being damaged and healed. Of particular note in this study are elastomers 35 b and 35 c. Not only were these the only examples of
translucent and colourless materials, the elastomers fully cured at room temperature in only 5 h. After mechanical damage the elastomers were heated to 80 °C to induce mobility in the polymer chains, complete healing of the mechanical damage was observed to occur in approximately 3 min and upon cooling to room temperature it cured and got solid again.
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Chapter 1: Introduction

1.1 Silicon Chemistry

1.1.1 Silicon Atom

Silicon (Si) is found in Group 14 \((3s^2\ 3p^2)\) of the Periodic Table and is classified as a metalloid and semiconductor. Silicon is the second most abundant element in the Earth’s crust (28%) after oxygen and is commonly found as silicon dioxide (SiO\(_2\)). Given that silicon is located in the same group as carbon it is often anticipated that silicon will display a similar chemical behaviour to carbon. However, the two elements have two distinct chemical differences that lead to different relevant reactivities under the same conditions (Figure 1-1)\(^1\). Firstly, the silicon atom’s van der Waals radius is 50% larger than that of carbon, which results in longer bond lengths between silicon and other elements compared to similar bonds for carbon (Table 1-1). Consequently, the rotational barrier for silicon is lower than for carbon, which ultimately results in less stable \(\pi\) bonds to silicon. Secondly, the weaker electronegativity of silicon when compared to carbon, has a significant effect on bond polarity that results in some unique bond strengths and enables reactions that are not possible with carbon-based chemistry (Table 1-1). For instance, the Si-F bond is one of the strongest single bonds between atoms in the Periodic Table whereas the C-F bond is a relatively weak bond. In addition, the Si-H bond is quite weak while the C-H bond is extraordinarily strong.\(^3\) Except when it is bonded to electropositive elements such as alkali metals, silicon is typically the electropositive atom in the bonds that it forms. As a result, nucleophilic attack occurs at \(\text{Si}^{\delta^+}\) in a Si-H molecule whereas with a C-H bond the nucleophilic attack takes place at \(\text{H}^{\delta^+}\) (Scheme 1-1).\(^4\)
Although both atoms (Si and C) are found in Group 14, silicon does not always react in a similar manner when compared to carbon (Scheme 1-1). For instance, silicon has only recently been shown to be capable of forming stable double and triple bonds.\textsuperscript{5-9} On the other hand, silicon’s capacity to form hypervalent species, makes silicon special in terms of nucleophilic substitution reactions with lower activation energies.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Electronegativity</th>
<th>σ-Bond Strength</th>
<th>Average Bond Lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>1.7</td>
<td>C-C: 83</td>
<td>1.54</td>
</tr>
<tr>
<td>H</td>
<td>2.1</td>
<td>C-Si: 76</td>
<td>C-Si: 1.87</td>
</tr>
<tr>
<td>C</td>
<td>2.5</td>
<td>Si-Si: 53</td>
<td>C-O: 1.43</td>
</tr>
<tr>
<td>Cl</td>
<td>3</td>
<td>C-H: 83</td>
<td>Si-O: 1.66</td>
</tr>
<tr>
<td>N</td>
<td>3</td>
<td>Si-H: 76</td>
<td>Si-N: 1.21</td>
</tr>
<tr>
<td>O</td>
<td>3.5</td>
<td>C-O: 86</td>
<td>C-F: 1.16</td>
</tr>
<tr>
<td>F</td>
<td>4</td>
<td>Si-O: 108</td>
<td>Si-F: 1.25</td>
</tr>
</tbody>
</table>

\[ \text{Scheme 1-1 nucleophilic attack on carbon and silicon atoms (Adopted from reference \textit{with permission})} \]
1.2 Fundamentals of Polymer Chemistry

Polymer is being defined as a large molecule chain (macromolecules) consisting of smaller units (monomers) that are connected to each other through a covalent bond. These units can be connected in various methods and produce different kinds of polymer structures such as linear, branched, star-shaped, comb-shaped, ladder, semi-ladder and network structures (Figure 1-2).\(^10\)

![Figure 1-2](image)

Figure 1-2 Different kinds of polymer structures. a) linear, b) branched, c) star-shaped, d) comb-shaped, e) ladder, f) semi-ladder and g) network\(^{10}\) (Adopted from the reference with permission)

The molecular weight of each polymer depends on the number of repeating units which is called the degree of polymerization (\(DP\)) and is showing with a number or letter. For instance, the molecular weight of polystyrene with \(DP\) of 100 would be 100x104. If there is only one kind of monomer repeating along the polymer chain, the polymer will be called “homopolymer” while having more than one kind of monomer make a copolymer. If there
is orderliness for these repeating units they are called alternating copolymers, otherwise they will be called random copolymers.\textsuperscript{11}

Carothers (1929)\textsuperscript{12} was the first one who represented a classification for polymers according to their repeating units (addition or condensation polymers). This classification depends on the similarity of atoms in repeating units compared to starting monomer. Thus, addition polymer is the one in which the same atoms in monomer is repeating along the polymer chain, while condensation polymers contain less atoms due to the side reactions occurring during the polymerization. Yet, this classification failed to include all kinds of polymers. As a result, Flory\textsuperscript{13} introduced the polymerization mechanism to be used to categorize polymers which can be either step-growth or chain growth polymerization. Step-growth polymerization takes place modestly. Said otherwise, the monomers unite step by step to produce polymer chain slowly over time. However, in the chain-growth polymerization, chain propagation occurs rapidly from the active sides of the monomers and the process may take only few seconds. In other words, the molecular weight increases consecutively by the linkage of the monomers (Figure 1-3).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1-3.png}
\caption{Figure 1-3 a) Step-growth and b) chain-growth polymerization over time in various temperatures (T)\textsuperscript{14}(Adopted from the reference with permission)}
\end{figure}
The schematic of step-growth and chain-growth polymerization have been illustrated in Figure 1-4 and Figure 1-5 respectively.\textsuperscript{14}

Figure 1-4 Step-growth polymerization: a) unreacted monomer, b) 50\% reacted, c) 75\% reacted, d) 100\% reacted (Adopted from the reference with permission)

Figure 1-5 Chain-growth polymerization: a) unreacted monomer, b) 50\% reacted, c) 75\% reacted, d) 100\% reacted (Adopted from the reference with permission)

In addition to these classifications, polymers can be categorized based on their response to temperature. As it was mentioned before, one type of polymers is network
structure that can be formed when linear or branched polymers adding together. The process of producing these networks through covalent bonds is called cross-linking. Cross-linked polymers, experience a fast acceleration in molecular weight that cannot flow or melt easily. These kinds of polymers are classified as thermosets and the ones that are not cross-linked (linear or branched) and can flow or melt are in the group of thermoplastic polymers.

1.2.1.1 Thermoplastic and Thermoset Polymers

Thermoplastics and thermoset polymers are the two main general class of polymers. Distinguishing these two classes of polymers is possible by examining the effect that temperature has on the elastic modulus of the polymers. Polymers that can be repeatedly softened and hardened by variations in temperature are classed as thermoplastics and typically the individual polymer strands can move independently of each other. On the other hand, thermoset polymers possess individual chains that are covalently bonded to each other (highly cross-linked). As a result, once these types of polymers are formed into solids they cannot return to a liquid state.\textsuperscript{15} Thermoset polymers are typically tougher and more brittle than thermoplastics and cannot flow as a viscous liquid and do not display a $T_m$. Elastomers are examples of thermoset polymers that are lightly cross-linked and typically have a $T_g$ value lower than room temperature; the polymer chains can be reversibly stretched without being degraded and/or deformed.\textsuperscript{16,17} Phenolic and urea formaldehyde resins, unsaturated polyesters, and epoxy resins are some examples of thermosetting polymers. And some examples of thermoplastics are polyethylene, polypropylene, polystyrene, and poly(vinyl chloride) (Figure 1-6 and Figure 1-7).\textsuperscript{15}
Some thermosetting polymers: (1) phenolic’s high modulus & excellent heat and creep resistance under pressure; (2) urea-formaldehyde resins such as laminates \(^{18}\)

Cross-linking is typically an irreversible process in polymer chemistry that is used to improve the mechanical properties of polymers such as strength, elongation, tensile modulus (Young’s modulus), toughness, and viscoelasticity. However, highly cross-linked materials are more fragile and are prone to cracking.\(^{19}\) In order to make the cross-linked polymers more efficient and reusable, reversible cross-linking have been introduced as kind of a self-healing process.\(^{20,21}\) Typically, the reversible cross-links require an external
stimulus such as heat or chemical activation to occur.\textsuperscript{22,23} The Diels-Alder/retro Diels-Alder (Section 1.6) is one example of a reversible cross-link employed in polymer chemistry.

### 1.2.2.1 Polymer Strength

The strength of a polymer is represented by the stress required to break a polymer sample. The applied stress can take on a number of different forms such as tensile (stretching of the polymer), compressional (compressing the polymer), flexural (bending of the polymer), torsional (twisting of the polymer), and impact stressors (hammering on the polymer).\textsuperscript{24} As a result, highly cross-linked polymers are stronger due to the greater networking and restricted motions of the polymer chains. However, tougher polymers are more brittle and are more prone to cracking. The features effecting the poly strength are molecular weight (Figure 1-8), cross-linking and crystallinity. Thus, the polymers strength can be ordered as linear $<$ branched $<$ cross-linked $<$ network.

![Figure 1-8 Dependence of the poly strength to molecular weight](image)

Figure 1-8 Dependence of the poly strength to molecular weight
1.2.2.3 Ultimate Elongation of a Polymer

The percentage of elongation of a polymer is the ratio between the polymer’s increased length and initial length after breakage at a controlled temperature (Figure 1-9). In other words, elongation can be calculated by the relative increase in length. \( \varepsilon = \frac{\Delta L}{L} \times 100 \). Thermoplastics have the highest elongation percentage (>100%) compared to other materials.\textsuperscript{25,26}

![Elongation Graph](image)

**Figure 1-9** Elongation to break of the polymer

1.2.2.4 Young’s Modulus

The elastic modulus, or Young’s modulus, is a measure of the stiffness of solid materials that can be measured by the ratio of stress to the strain in a linearly elastic region of the material (Figure 1-10). For polymers, the mechanical properties are dependent on temperature since the polymers would be in different physical phases at different temperatures. At lower temperatures polymers are typically more brittle and tougher due to lower internal energies (glassy). The glass transition state (\( T_g \)) can be defined as a temperature where a polymer in a crystalline phase converts to a flexible and pliable polymer that can be shaped (amorphous phase). Furthermore, the melting temperature (\( T_m \))
of a polymer is the temperature at which polymer chains can flow freely such as in a viscous liquid (Figure 1-11).²⁷

Figure 1-10 Ratio of stress to the strain (Young’s modulus)

Figure 1-11 Possible physical states of polymers
1.3 Silicone Chemistry

Silicones, or polysiloxanes (RR’SiO)n, are polymers that consist of an inorganic backbone chain of Si-O bonds and organic side groups typically consisting of methyl groups. Silicone polymers have found a variety of applications in fields such as the pharmaceutical industry, the electronics industry, and the automotive industry (Figure 1-12).28-29 Silicones can be formulated into different forms such as solids, liquids, semi-viscous pastes, greases, oils, and rubbers. In these various forms silicones exhibit thermal stability, electrical resistance, hydrophobicity, low thermal conductivity (insulator), low chemical reactivity, and low toxicity. These properties have led to silicones
being utilized for the production of insulator coatings, anti-foaming agents, water repellent coatings, mold-release agents, and as a component of agricultural products.

Siloxanes are thermally stable and typically exhibit consistent behaviour over a wide range of temperatures (-100 °C to 350 °C).\textsuperscript{29} The thermal stability of silicones can be examined via the polymers’ degradation rate, maximum degradation temperature, residue yield, and the temperature at which degradation commences.\textsuperscript{30,31} The relative permittivity of silicone compounds is very low and is independent of molecular weight of the polymer and temperature.\textsuperscript{32,33} For instance, the relative permittivity of oligomers (lower molecular weight compounds, < 100 repeat units) and higher molecular weight compounds is almost the same (~2.75). As a comparison, water and acetone have relative permittivity values of 20.7 and 78.5 respectively. Even if the silicone undergoes thermal decomposition, the polymer will decompose to silica, which is in and of itself still an excellent insulator. This has led to silicone polymers being used in industrial coatings and insulators.\textsuperscript{34}
One of the other advantages of silicone polymers is their surface hydrophobicity, which is mostly the result of hydrophobic methyl side groups and the flexibility of the polymer backbone that reduces wettability of the coated surface. The chain flexibility is the result of the relatively large angle of the Si-O-Si bonds (145°) and the low bending force constant of the chain. Moreover, the longer Si-O bond (1.64 Å) versus C-C bond (1.53 Å) decreases steric hindrance and intramolecular blocking. As a result, silicone polymers can be used for the prevention of adhesion in automobile tire moulds.

Functionalizing silicone polymers can be used to manipulate their physical and structural properties, such as their capacity to form cross-links.
1.3.1 The Hydrosilylation Reaction

There are so many methods to produce cross-linked polymers such as using free radicals, radiation, and click chemistry.\textsuperscript{36-38} One of the most common methods used to functionalize silicone polymers to obtain a new C-Si bond from carbon-carbon multiple bond is the hydrosilylation reaction. For this reaction an Si-H group on the polymer chain adds to an unsaturated bond.\textsuperscript{39,40} The hydrosilylation reaction is usually catalyzed by transition-metal (precious or non-precious) complexes that can include, but are not limited to, platinum, rhodium, iridium, iron, nickel, aluminum, boron, alkaline-earth metals, copper, and titanium. Of these catalysts platinum and rhodium tend to be the most reactive producing higher yields even when utilized at room temperature.\textsuperscript{41} The first hydrosilylation reaction was performed by Sommer et al. in 1947 using peroxide as a catalyst (Scheme 1-2).\textsuperscript{42}

\[
\text{R-CH=CH}_2 + \text{SiHCl}_3 \xrightarrow{\text{diacetylperoxide}} \text{RCH}_2\text{CH}_2\text{SiCl}_3
\]

Scheme 1-2 Hydrosilylation reaction using peroxide as catalyst

Two metal-based catalysts, Speier’s catalyst (late 1950s)\textsuperscript{43} and Karstedt’s catalyst (early 1970s)\textsuperscript{44}, typically are the most commonly used of the hydrosilylation catalysts. Speier’s catalyst is a homogeneous transition metal catalyst obtaining from the organic solution of hexachloroplatinic acid H\textsubscript{2}PtCl\textsubscript{6}.6H\textsubscript{2}O in isopropyl alcohol (1-10\%).\textsuperscript{41} Karstedt’s catalyst (Figure 1-13) Pt\textsubscript{2}(CH\textsubscript{2} = CHSiMe\textsubscript{2})\textsubscript{2}, given its relatively high solubility in polysiloxane compounds and high selectivity and reactivity, has become known as the catalyst of choice for hydrosilylation reactions involving Polydimethylsiloxane (PDMS) compounds.\textsuperscript{45,46}
However, the use of Karstedt’s catalyst in hydrosilylation reactions is not without its shortcomings; a number side reactions are possible (Scheme 1-3). Some of the possible side reactions include dehydrogenative silylation, hydrogenation of olefins, isomerization of olefins, olefin oligomerization, and redistribution of hydrosilanes. However, given the platinum stability of these particular platinum compounds towards heat, moisture, and oxygen, Karstedt’s catalyst is still the primary for both academic and industrial scale reactions.
The hydrosilylation catalytic cycle using Karstedt’s catalyst is illustrated in Figure 1-14.\textsuperscript{50} This mechanism consists of four steps. In the first step the silane compound is coordinated with the platinum complex. Then, the olefin coordinates with the metal complex followed by the production of the new Pt-C single bond in the Chalk-Harrod mechanism, while in the modified mechanism a new silicon-carbon bond is produced. In the last step for the both mechanisms hydrosilylation is been completed and the catalyst is been regenerated.\textsuperscript{51,52}

Figure 1-14 Chalk-Harrod and modified Chalk-Harrod mechanism for the hydrosilylation of alkenes\textsuperscript{50,51} (Adopted from the reference with permission)

1.4 Esterification Reactions

In general terms esterification is the conversion of a carboxylic acid and/or one of its derivatives to an ester via a reaction with an alcohol. The reaction between alcohols and carboxylic acids in the presence of an acid catalyst (Fischer esterification)\textsuperscript{53,54} or base can lead to ester production (Scheme 1-4)\textsuperscript{55}, although reactions under basic conditions are not
optimal. Carboxylic acids are weak acids (pKa $\sim$ 5) while alcohols are even weaker still (pKa $\sim$ 16). Comparing the acidity of these two functional groups carboxylic acids are $1 \times 10^{11}$ times stronger acids than alcohols. As a result, a base would deprotonate the carboxyl acid, which would lead to the formation of a carboxylate conjugate base that would decreases the electrophilic nature of the carbonyl carbon as a result of resonance stabilization of the negative charge on oxygen.$^{55}$

![Scheme 1-4 Mechanism for a Fischer esterification](Adopted from the reference with permission)

Acid-catalyzed esterification reactions are an equilibrium process. As a result, obtaining high yield requires shifting the reaction equilibrium toward the products. To achieve this either excess amounts of starting materials should be used, or the products should be removed from the reaction flask in order to force the reaction to compensate and generate more of the product. One strategy for employing Le Chatelier’s Principle in these reactions is through the use of dehydrating agents such as molecular sieves in the reaction flask, or by actively removing the product water using a Dean-Stark apparatus, which ensures the continuous removal of water from the reaction flask.$^{56}$
1.4.1 Enzyme-Mediated Esterification Reactions

Recently, the use of enzymes as catalysts for various kinds of organic reactions such as hydrolysis, C-C bond formation, and redox reactions has gained popularity. Enzymatic catalysts are being used in both industry and academia as a replacement for catalytic metals and organocatalysis. Generally, the three dimensional structure of enzymes makes them a perfect catalyst due to their high chemoselectivity and stereoselectivity (regio-, diastereo- and enantioselectivity). The ribbon structure of a most common catalytic enzyme, lipase B from the yeast Candida antarctica is shown in Figure 1-15. 57,58

![Figure 1-15 Three dimensional structure of Candida antarctica enzyme](Adopted from the reference with permission)

Novozyme-435 (N435) is a commercially available immobilized lipase B from C. antarctica (CalB) that has been used as a catalyst for esterification reactions. Kazlauskas’ rule explains that (R)-enantiomers of bulky substituents are more favourable for this enzyme compared to (S)-enantiomers. Furthermore, as the difference in the size increases, so does the selectivity between the two enantiomers. 59-61 Consequently, esterification, transesterification, and polymerization reactions using N435 as a catalyst (Scheme 1-5) are more stereo- and enantio-selective than traditional acid-catalyzed reactions.
The lipase’s active site consists of histidine, serine, and aspartate amino acids as basic, nucleophilic, and basic units respectively (Figure 1-16). The enzymes’ high stereoselectivity for secondary alcohols is the result of the active site binding pocket consisting of Thr42, Ser47, and Trp104. One of the benefits of N435 is that it can be recovered, recycled, and be used repeatedly. As can be seen in Scheme 1-5, the reaction between the enzyme and a carboxylic acid leads to a tetrahedral intermediate transition state that is stabilized by three hydrogen bond donors. The removal of water produces an acyl enzyme intermediate that can be attacked by an alcohol to produce the ester-like intermediate. Finally, the ester product is ejected and the catalyst is regenerated.
1.5 Self-Healing Materials

Methods such as gluing, fusing and mending are often used to repair damaged surfaces caused by degradation and material failure. Given the global reliance on polymer-based materials highly durable materials with extended life times are in high demand as the result of a desire to lower repair and maintenance costs. The concept of self-healing polymeric materials comes from the natural healing of cuts and wounds in human beings and other species.

Two general types of healing mechanisms exist: healing resulting from a chemical reaction or from sort of physical interaction. Self-healing materials ideally have the capacity to repair or heal themselves (automatically and autonomously) without any external stimulus. However, most synthetic materials are not capable of performing spontaneous repairs. Currently there is two types of self-healing processes: (1) autonomic, which occurs without any external stimulus; and (2) nonautonomic, which requires some...
form of external activation.\textsuperscript{66,67} The self-healing of materials (e.g., polymers, coatings, concrete, \textit{etc.}) can be categorized into two distinct processes as follows\textsuperscript{68}:

1. Healing through the release of a healing agent or agents

2. Healing via reversible cross-links

For the first strategy an active healing agent is incorporated into the polymeric product during its production. These active agents are typically liquids that are contained in microcapsules, channels, or fibers. After mechanical damage to the polymeric material the reactive liquids pour from their encapsulating structure into the crack and start the self-repairing process typically employing catalysts or hardeners to congeal and fix the crack. In other words, the fracture of the liquid-containing capsules is the driving force for the release of the active agents and commencement of the healing process (Figure 1-17). Unfortunately, this method of healing, which is categorized as autonomic self-healing because no external energy is involved in the healing process and crack closure, can typically only be utilized once per region of material; once the healing compounds are consumed no further healing is possible.\textsuperscript{69,70}
1.5.1 Physical Principles of Self-Healing

Generally, self-healing is a process by which a material suffers some form of damage but which is subsequently repaired via the reconnection of broken polymer chains either through a chemical or physical interactions.\textsuperscript{71,72} The physical interactions usually occur from the interdiffusion and intermolecular interactions, which are highly dependent on the chemical nature of the polymer and the length of the polymer backbone. However, there are conflicting reports in the literature when it comes to this phenomenon; some reports claim that shorter polymeric chain lengths provide the higher chance of interdiffusion,
while others claim that longer chains produce a stronger entanglement of the polymer chains. An excellent summary for these phenomena is the Wool and O’Connor theory that consist of a five-step process (Figure 1-18) that occurs at, or above, the glass transition temperature of the polymer. At its $T_g$ a polymers is softened and flexible, facilitating the physical self-healing process.

Figure 1-18. The Wool and O’Connor model for the physical self-healing of polymers (Adopted from the reference with permission)

With this theory, since it is a physical process, efficient movement of the different polymeric compartments is the principal consideration in designing a proficient self-healing system. After damage occurred on the polymer’s surface (Figure 1-18), surface rearrangement, surface approach, wetting, diffusion, and randomization are the events that must occur in order lead to a cured surface with roughly the same mechanical and physical properties (sometimes the quality lowers over time) as the virgin material. The first two
steps (surface rearrangement and surface approach) are both crucial steps that initiate self-healing process. In order to prevent contact failure of the two collapsed sides, a wetting step must occur in the polymer to provide sufficient mobility on the both sides of the injured area. The wetting process can be gained by either increasing the temperature (i.e., heating the polymer) or by adding solvent to the system.\textsuperscript{18,76} As long as the wetting step is done appropriately, diffusion should occur easily given the increased chain mobility of the polymer ultimately leading to increased contact between two parts of the damaged polymer. Lastly, a randomization step completes the self-healing process and fills the damaged area.

1.5.2 Chemical Principles of Self-Healing

Chemical self-healing is divided into two categories: one is established through covalent bonds that can be both reversible and irreversible processes, and the other is achieved through supramolecular network formation, which is a reversible process (Figure 1-19).\textsuperscript{77}
1.5.2.1 Covalent Bond Network Formation

1.5.2.1.1 Irreversible Networks

In the irreversible healing process, one of the common methods involved in healing is encapsulation of active agents within the polymer matrix or the activation of catalysts \textit{in situ} that leads to crack filling and ultimately healing. With this method once damage takes place, the encapsulated active agent releases and reacts with the catalyst at the damage site to produce new covalent bonds. Since this is a one-time process after one damage event occurs all of the active agents will be consumed. This network curing method is referred to as \textit{irreversible covalent bond formation}. The examples of these
kinds of reactions include, but are not limited to ring-opening methathesis polymerization (ROMP), nucleophile addition to epoxides, and click reactions (Figure 1-20).

1.5.2.1.2 Reversible Networks

Various kinds of reactions produce new covalent bonds that can be applied to the field of self-healing polymer chemistry including: thiol/disulfide linkages, radical-based methods, polycondensation reactions, and Diels-Alder/retro-Diels-Alder (DA/retro-DA) cycloaddition reactions (Figure 1-20). The most widely used reversible covalent bond
system in self-healing studies has been the Diels-Alder reaction, which has the capacity to producing new C-C bond in high yields and with controlled stereochemistry (Section 1.6).65

1.5.2.2 Supramolecular Network Formation

Supramolecular polymers are group of monomers connecting to each other through reversible and directional secondary interactions such as hydrogen bonding, ionomers, metal bonding, and π-π stacking interactions (Figure 1-21).78

The first supramolecular network based on hydrogen bonds was developed in 1997 by Meijer et al.79 using 2-ureido-4[1H]-pyrimidinone (UPy) units capable of forming four

Figure 1-21 Reversible interactions to produce supramolecular polymer networks 65(Adopted from the reference with permission)
hydrogen bonds. The stability of these bonds and their associated lifetime is something to be considered in order to develop strong polymeric networks. In the specific case involving UPy, the hydrogen bonds are so strong that even after exposing the system to water, despite the competition between water molecules and monomer units to form hydrogen bonds, the connections between the polymer chains remained intact (Figure 1-22).

Figure 1-22 Hydrogen bonds between UPy units leading to polymeric networks ⁷⁸ (Adopted from the reference with permission)

1.6 The Diels-Alder Reaction

Cycloaddition reactions are one group of chemical transformations that can be used for the self-healing and recycling of polymers. Cycloaddition reactions involve the formation of a new cyclic compound from two or more unsaturated starting materials and formation of a new C-C bond. These reactions usually take place under thermal or photochemical conditions with high stereoselectivity (Scheme 1-6). ⁸⁰,⁸¹
The focus of this section is the reversible [4+2] cycloaddition known as the Diels-Alder (DA) reaction\textsuperscript{83} that occurs between a 4-electron nucleophilic conjugated diene and a 2-electron electrophilic dienophile. The history of the DA reaction goes back to 1928 when Otto Diels and his student Kurt Alder reported the reaction of cyclopentadiene and quinone, ultimately leading to the development of a class of reactions that earned them the Noble Prize in Chemistry in 1950 (Scheme 1-7).\textsuperscript{84}

Scheme 1-6. Examples of different cycloaddition reactions and their mechanisms \textsuperscript{82}

Scheme 1-7. The first reported DA reaction by Diels and Alder in 1928 \textsuperscript{84}
1.6.1 Diels-Alder Reaction and Mechanism

The Diels-Alder reaction typically takes place between a diene and an alkene or alkyne (referred to as the dienophile) that not only produces two new $\sigma$ bonds from a $\pi$ bond, but that can also result in the creation of up to four new stereo-centers. Cycloaddition reactions can be described using frontier molecular orbital (FMO) theory, which was first introduced by Kenichi Fukui in 1952 and then extended by the Woodward-Hoffman rules in 1965. According to FMO theory, if the molecular orbitals (MO) symmetry of the reactant is the same as the MOs of product in the ground state, the reaction is feasible thermally, but if reactant MO is the same as the MO of the first excited state of the product, then the reaction is photochemically allowed. And if the MO symmetry of the reactant and product are different, the cycloaddition reaction will not occur in a concerted manner. As a result, the highest occupied molecular orbital (HOMO) of one component and the lowest unoccupied molecular orbital (LUMO) of the other component, should be examined to consider the symmetry and feasibility of the cycloaddition reaction (Figure 1-23).

![Figure 1-23. Frontier molecular orbitals of the reactants in a Diels-Alder Reaction](image)

The $[\pi 4+ \pi 2]$ cycloaddition occurs via a disrotatory mechanism in order to produce two new $\sigma$ bonds from two $\pi$ bonds in a concerted fashion (Figure 1-24).
Conrotatory (both sets of orbitals rotate clockwise or both rotate counter clockwise) and disrotatory (one set of orbitals rotates clockwise and the other rotates counter clockwise) processes consist of rotation of frontier molecular orbitals in order to achieve optimal overlap of orbital lobes.

The formation of new $\sigma$ bond occurs only if the $p$ orbitals of the terminal carbons of the two reactants can overlap with each other properly. This can take place through two mechanisms: (1) suprafacial or (2) antarafacial attack. With a suprafacial interaction the same faces of the $p$ orbitals of the $\pi$ system overlap and in an antarafacial, attack occurs from opposite side (180° twist) of the $p$ orbitals of the $\pi$ system (Figure 1-25).
Cycloaddition reactions yielding four to six membered rings should go through suprafacial-suprafacial transition state due to the ring strain.\(^{56}\)

### 1.6.2 Classification of Diels-Alder Reactions

The Diels-Alder reaction can be categorized in two different ways: (i) according to the reactants - they can be classified into two groups either as (a) homo-Diels-Alder reaction in which the reactants consist of only hydrocarbon moieties, and (b) hetero-Diels-Alder reactions in which the reactants, either diene or dienophile, possess one or more heteroatoms to produce heterocycles;\(^{94}\) (ii) considering the presence of electron withdrawing and electron donating groups on the reactants and their influence on the reaction rate in agreement with Woodward-Hoffman rules. This second category can be divided into three distinct classes:\(^{95}\)

1. The normal demand Diels-Alder reaction
2. The inverse demand Diels-Alder reaction
3. The neutral Diels-Alder reaction

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Figure 1-25. Suprafacial and antrafacial interactions of \(\sigma\) orbitals to form new \(\sigma\) bond in the Diels-Alder reaction \(^{89}\) (Adopted from the reference with permission)
The reaction rate for the Diels-Alder reaction is related to the energy gap between the HOMO and LUMO orbitals of the diene and dienophile. The lower the gap, the more efficient the orbital overlap and the higher reaction rate. In the normal demand DA reaction, electron donating groups on the diene will increase the energy of the HOMO orbitals and electron withdrawing groups on the dienophile will decrease the energy of LUMO orbitals of dienophile, ultimately resulting in a lower energy gap (HOMO\text{diene}–LUMO\text{dienophile}) and acceleration of the reaction rate. On the other hand, a similar observation is made for the inverse demand DA reaction (LUMO\text{diene}–HOMO\text{dienophile}) that also leads to reduction of the energy gap and higher reaction rates. For the neutral DA reaction, the difference between the energy gap of HOMO\text{diene}–LUMO\text{dienophile} and LUMO\text{diene}–HOMO\text{dienophile} is not considerable. Therefore, both electron withdrawing and electron demanding groups can be presented on the diene and dienophile.\textsuperscript{96–98} The normal demand DA reaction (A and B adducts) and the inverse demand DA reaction (C and D adducts) have been illustrated in Scheme 1.\textsuperscript{99}
For all of the different DA reactions, the symmetry of the molecular orbitals of the reactant and product should be the same. This phenomenon is known as the conservation of orbital symmetry and leads to a more stable transition state resulting in a concerted cycloaddition reaction (i.e., in accordance with the Woodward-Hoffmann rule). Molecular orbitals and the bonding interactions of the simplest DA reaction between butadiene and ethylene are shown in Figure 1-26, followed by an illustration of the frontier orbital interactions for different electronic demands in Figure 1-27.
Figure 1-26 Molecular orbital and bonding interactions between butadiene and ethylene in the DA cycloaddition reaction \(^{35}\) (Adopted from the reference with permission)

![Molecular orbital interactions for different categories of DA reactions](image)

Figure 1-27. Frontier molecular orbital interactions for different categories of DA reactions
Dienes in Diels-Alder Reactions

Dienes in the Diels-Alder reaction can be both cyclic and acyclic with various kinds of substitutions. Conjugated dienes can exist in two conformations: \( s\text{-cis} \) or \( s\text{-trans} \). As a result of the steric hindrance imparted by the hydrogen atoms on terminal carbons the \( s\text{-cis} \) conformation is less stable. Thus, it is capable of participation in the DA reaction. However, a rotation about the C-C single bond can activate \( s\text{-trans} \) conformer for this reaction (Scheme 1-9).\(^{56,101}\)

![Scheme 1-9. The \( s\text{-cis} \) and \( s\text{-trans} \) conformation of conjugated dienes.](image)

The electronic properties of substituents on the diene and dienophile influence the rate of the DA reaction (Table 1-2). Generally, cyclic dienes are more reactive than open-chain ones.\(^{102}\)

<table>
<thead>
<tr>
<th>Open-Chain</th>
<th>Outer Ring</th>
<th>Inner-Outer</th>
<th>Across Ring</th>
<th>Inner Ring</th>
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Table 1-2. Different types of dienes\(^{102}\)
For the locked \textit{s-trans} conformers that cannot undergo a C-C rotation, such as those involving cyclic system, participating as diene in a DA reaction is not possible (Scheme \textit{1-10}).\textsuperscript{55}

\textbf{Scheme 1-10. Locked s-trans conformations}

\textbf{1.6.3 Dienophiles in Diels-Alder Reactions}

Dienophiles are compounds containing double or triple bonds. Since dienes behave like nucleophiles (electron-rich compounds) and dienophiles as electrophiles (electron-deficient compounds) in DA reactions, electron-withdrawing groups on dienophiles can make them better electrophiles by removing electron density from C-C double/triple bond, which leads to more reactive compounds (Table \textit{1-3}).\textsuperscript{56,103}

In the DA reaction the stereochemistry of the dienophile is preserved. In other words, a \textit{cis} cyclic adduct will be obtained from a \textit{cis} dienophile and a \textit{trans} dienophile produces a \textit{trans} cyclic adduct.
1.6.4 Stereochemistry of the Diels-Alder Reaction

The Diels-Alder cycloaddition reaction is capable of producing up to four chiral centers. These chiral centers can be predicted by the suprafacial *endo* and *exo* interactions of the reaction components. For the *endo* transition state, the reactants interact with each other from the most sterically congested position (Alder rule) to produce adducts (Scheme 1-11).

![Scheme 1-11](image)

Scheme 1-11. The endo and exo orientations possible in a Diels-Alder reaction.\(^{106}\)
The endo adduct is the major product as the transition state involves an interaction between the diene and dienophile in such a way that the unsaturated substituent on the dienophile overlaps with the $\pi$ system of the diene.\textsuperscript{107-108}

1.6.5 The Diels-Alder Reaction and Polymer Chemistry

In the past few years, the use of DA reaction in the field of polymer chemistry for self-healing and cross-linking purposes has been increased due to the reaction’s thermal and mechanical reversibility and high yields. This thermal reversibility can be used to produce reactive sites \textit{in situ}.\textsuperscript{109} Various numbers of these mendable polymeric materials using diene-dienophile systems especially furan-maleimide moieties have been used that are capable of retro DA reaction.\textsuperscript{110}

Among different DA reactants (dienes & dienophiles) furan and maleimide units have garnered attention in polymer chemistry with organic backbone as result of their capacity to reaction at relatively low temperatures (25-70 °C), and the retro DA reaction temperature for these reactants is around 90-110 °C. Thus, the accessible thermally reversible nature of these particular units makes their DA adducts attractive for use in smart, responsive materials under mild condition.\textsuperscript{111,112} Moreover, flexibility of the polymer chains is one of the features that has always been sought for in elastomers to improve the self-healing process. In 2002, Gandini \textit{et. al.}\textsuperscript{113} produced low-$T_g$ elastomers using polymeric dienes cross-linked with bismaleimides (Scheme 1-12).
Lehn group in 2009,\textsuperscript{115} produced dynamers with organic backbone using reversible DA reaction that can be done at room temperature. These synthesized long and highly flexible chains from bis(diene) and bis(dienophile) are capable of self-healing in few minutes at room temperature and produce thin film elastomers that have $T_g$ lower than room temperature that will prevent crystallization of the polymer (Scheme 1-13).
Research reported by Picchioni et al. in 2015 involved the production of a reversible rubber system. In this report commercially available ethylene-propylene rubber was modified with maleic anhydride and then reacted with furfurylamine to form a polymer possessing furan moieties that was subsequently cross-linked with a bismaleimide (dienophile moiety) to produce reversible rubbers (Scheme 1-14). In this research, DA reaction occurs at 50 °C - 70 °C, whereas rDA is occurring at more than 150 °C.
1.7 Silicones and the Diels-Alder Reaction

One of the earliest examples the DA reaction being applied to silicone chemistry by Gandini et al. in 2002 involved the use of polymeric dienophiles (synthesized from siloxane copolymers containing pendant propylamine chains) cross-linked to bisfurans (Scheme 1-15) to produce reversible rubbers, especially for tire manufactures to reduce the number of damaged tires. It has been indicated in this study that copolymers with lower maleimide units are completely soluble and failed to produce a healable network due to the lack of intermolecular coupling. However, using copolymers with richer reactive moieties were good enough to produce anticipated gel (network).
Recently, Kickelbick et al.\textsuperscript{117} in 2015 studied different polysiloxane chains of various molecular weights that were modified with furan and maleimide moieties to increase the flexibility of the resultant elastomers and were able to improve the self-healing properties of these elastomer (Figure 1-28).\textsuperscript{117} The strength of this study is comparing the flexibility of the synthesized networks (using furan and maleimide) from cross-linking of the nanoparticles with (a) poly(butylmethacrylates) and (b) polysiloxanes. The study shows that rigid thermoplasts (a) undergo less cross-linking reactions compared to modified polysiloxanes (b) that are thermally reversible cross-linked. Thus, polysiloxanes extend the mobility and flexibility of the polymer backbone.
Figure 1-28. (a) Poly(butylmethacrylates) and (b) Polysiloxanes modified with furan and maleimide moieties synthesized by Kickelbick et. al. 117 (Adapted from the reference with permission)

In 2016, Xia et al. 113 reported research on polydimethylsiloxane chains including maleimide fragments cross-linked by bisfuran compounds to form healable PDMS elastomers that have potential applications in the biomedical field as artificial skin and tissue engineering scaffolds (Scheme 1-16). In this specific DA reaction the N-H groups
on the furan chain provided hydrogen bonding with the C=O group on the maleimide, which led to better reconnection (healability) after damage occurred.

Most recently in Zelisko’s lab (2017), temperature-controlled self-healing elastomers have been synthesized using siloxane chain grafted with maleimide moiety and polyhedral oligomeric silsesquioxane (POSS) modified with furan active groups. The thermally reversible DA reaction between these two diene and dienophile polymeric systems led to cross-linking networks capable of recyclability.
To conclude, according to previous studies that some of them were mentioned in this section, changing the diene and dienophile structures attached to the different PDMS with variable average molecular weight can lead to production of elastomers with different mechanical properties. Moreover, using various diene and dienophile systems can be effective on cross-linking density and self-healing temperature to afford higher quality elastomers.

1.8 Polymers and the Environment

In the beginning of 19th century, production of rubber and then plastic materials expanded rapidly. The waste disposal of these kinds of modern polymeric materials with the ancient methods were impossible since the plastics are non-biodegradable.\textsuperscript{119} The marine conservation society in 2008 found that over 50% of the litter is plastic, consisting of 7393 plastic bags, 7025 pieces of plastic trays and cups and 16243 plastic drinks bottles which is 77% more than plastic waste in 1994. Burning the plastics in the open air leads to spreading the poisonous chemicals and harmful greenhouse gases such as CO\textsubscript{2} and methane that causes global warming and effects on livings health as well. As a result, discovering the recycling and recovery methods have become an interesting and necessary topic to be achieved. The use of plastics in the twentieth century rose dramatically especially in the
packaging (30% of all synthetic polymers) due to the plastics light weight, transparency, flexibility and low cost. In regards with the applications of plastics and their properties, environmentalists’ priority is to recycle and reuse these materials after their service life which is both economically and environmentally advantageous because it takes two-thirds less energy to use recycled plastics at the first step of material production other than using the virgin plastics. Because of the high usage and applications of polymers in different aspects of modern human lifestyle, it cannot be expected to decrease or eliminate the usage of these materials. Yet, it is required to recycle these building blocks to prevent the misusage of these polymeric compounds.

1.9 Hypothesis and Thesis Objectives

Pollution by polymers is a growing concern, especially because of the disposable nature of many polymers; this issue could be addressed by developing methodologies for prolonging lifetimes of polymers, especially for ones as ubiquitous as silicones. Although there have been reports of self-healing silicone systems based on the Diels-Alder reaction, the systems are rather limited, especially as it pertains to low temperature (>50°C) self-healing phenomena. Given the existing data involving self-healing polymers and the Diels-Alder reaction, it is hypothesized that it is possible to synthesize a silicone elastomeric system that has the capacity to self-heal at room temperature, and ultimately to be recycled. The combination of various siloxane-based maleimide and furan systems in the synthesis of silicone elastomers will be explored to confirm or refute this hypothesis.
Chapter 2: Results and Discussion

In this section the cross-linking, self-healing, and recyclability of silicone elastomers will be examined and discussed. The characterization and analysis of model compounds was then extended to polymeric systems in the form of elastomers.

2.1 The Model Systems

In order to synthesize a library of model compounds, two different dienes and six different dienophiles were used to investigate Diels-Alder (DA) and retro Diels-Alder (rDA) reactions involving these compounds. The studies involving the model compounds were designed to establish the optimal temperatures for DA/rDA reactions to afford the highest adduct yield, so that these conditions could then be extend to polymeric siloxane systems. The procedures contained in this section are thoroughly outlined in Chapter 1.

Both of the diene systems were synthesized through a two-step reaction that is illustrated in Scheme 2-1\textsuperscript{122} and Scheme 2-2\textsuperscript{117}. All of the bisdienophiles (Figure 2-1) used in these studies (14, 15, 16, 17, 18), were commercially available except for 13, which was obtained from a two-step reaction (Scheme 2-3)\textsuperscript{123}.

![Different bismaleimides](image)

Figure 2-1 Different bismaleimides
Synthesizing one of the model diene systems (5) as was mentioned before, was done in a two-step reaction. In the first step, chemoenzymatic esterification was done to produce compound 3 with 75% yield followed by a hydrosilylation reaction in the presence of Karstedt’s catalyst to obtain compound 5 in 81% yield.

Scheme 2-2 Synthesis of the model furan-modified trisiloxane (diene) 9.

Compound 6 was treated with n-butyllithium to yield a furanyl-2-lithium. The furanyl-2-lithium subsequently performed a nucleophilic substitution on 7 to afford 8 in an 85% yield.
Overall 12 different model DA reactions were investigated in this study. For every Diels-Alder reaction, equimolar amounts of the diene and dienophile were reacted in the absence of solvent at temperatures ranging from 40 °C to 80 °C to optimize maleimide conversion (Table 2-1, Table 2-2, Table 2-3). Since the chemical transformation in all of these reactions is the same, the discussion will focus on the reaction between 5 and 13 (Scheme 2-4), but can easily be extrapolated to the other Diels-Alder reactions involving the model compounds.

The disappearance of bismaleimide alkene resonance at 5.2 ppm in the $^1$H NMR (Figure 2-2) confirmed the consumption of the maleimide ring. Moreover, the two doublets corresponding to the alkene protons of the newly synthesized cyclohexene ring (Scheme 2-4, Figure 2-2) were observed at 6.41 and 6.44 ppm indicating the successful formation of the Diels-Alder adduct. The bridgehead proton of the adduct was assigned to the resonance at 5.35 ppm. The most shielded protons (0.41-0.46 ppm) were used as reference protons to calculate the exo and endo adducts ratios (Figure 2-2). Furthermore, a
gCOSY NMR spectrum (Figure 2-3) was acquired to confirm that the resonances at 3.02-3.04 and 3.40-3.71 ppm corresponded to the exo and endo adducts, respectively. Owing to ~90° dihedral angle between proton d and the exo proton e (Scheme 2-4), the correlation between these two protons are not observable in the gCOSY NMR spectrum. As a result, the protons were assigned as follows: 3.02 (e-exo), 3.04 (f-exo), 3.41 (e-endo), 3.69 (f-endo) (Figure 2-2).

Scheme 2-4 The model Diels-Alder reaction between compounds 5 and 13

All of the model adducts that were synthesized, and the corresponding starting materials are summarized in Table 2-2. Reactions number 1-6 occurred between model ester furan 5 and six unique bismaleimide compounds while reactions 7-12 involved an aliphatic furan and the same bismaleimides compounds used for reactions 1-6. So, from now on bismaleimides will be named as number 13 to 18 for the ease of labeling.
Figure 2-2 $^1H$ NMR spectrum of model Diels-Alder adduct 23
Figure 2.3 COSY NMR spectrum illustrating the correlation between the endo protons and the bridgehead proton. Note that the exo proton is not correlated with the bridgehead proton.
Table 2-1. Model Diels-Alder reactions of furanyl-2-methyl-11-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)undecanoate with 6 different dienophiles

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<td><img src="image13.png" alt="Diene 5" /></td>
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</table>
In order to optimize the conversion of the bismaleimide compounds to the corresponding Diels-Alder adduct, a range of temperatures from 40 °C to 80 °C was applied to all of the model systems and the maleimide consumption, amount of exo adduct formation, and overall yield of the reactions was determined using $^1$H NMR (Table 2-3). Based on these data it was determined that, for the model compounds, the optimal temperature for the reactions was between 65 °C and 75 °C over a period of 24 h.
Table 2-3. Optimized reaction condition for the all of the model systems. The red numbers denote the reaction conditions that resulted in the highest overall yield.

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<td>2</td>
</tr>
<tr>
<td>12</td>
<td>40 °C</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>50 °C</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>60 °C</td>
<td>10</td>
<td>9</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>70 °C</td>
<td>19</td>
<td>15</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>80 °C</td>
<td>19</td>
<td>16</td>
<td>3</td>
</tr>
</tbody>
</table>

* Reaction numbers correspond to those listed in Table 2-1 and Table 2-2
Of all the model reactions, two presented some rather unique results. Comparing the yields of the reactions 4 and 10 with the others, it becomes apparent that these two systems resulted in relatively high conversion of the maleimide compound at 40 °C while the other reactions required higher temperatures (>50 °C) to achieve similar levels of maleimide conversion. These results encouraged me to attempt the DA reaction using the novel tetramethyldisiloxane-bismaleimide 13 at room temperature and over a shorter timeframe. Quite unexpectedly the reaction produced 80% conversion of the maleimide in 5 h at room temperature; to the best of our knowledge this represents the first reported instance of a siloxane-based Diels-Alder reaction taking place at room temperature. Under these conditions the endo isomer was the major product but the concentration of the exo isomer could be increased by increasing the reaction temperature and the reaction time. Given that the purpose of the Diels-Alder reaction in this thesis is to form covalent bonds between silicone polymers, the formation of a Diels-Alder adduct between polymer chains was of paramount concern, and not whether the adduct was the result of a predominantly endo or exo cycloaddition. These results were obtained only for the newly synthesized bismaleimide 13; none of the commercially available bismaleimide compounds underwent the Diels-Alder reaction at room temperature.

To better understand the nature of the DA/rDA process, the reaction between 5 and 13 was monitored using variable temperature (VT) 1H NMR experiments (Figure 2-4). Examination of the NMR spectra revealed that the resonance at 5.2 ppm (●) corresponding to the maleimide alkene protons disappeared as the temperature increased, signifying that the DA reaction was taking place, and then reappeared once the temperature reached 85 °C indicating that the rDA reaction was now the dominant reaction. The formation of the new
endocyclic double bond formation (■) and endo/exo protons (*/▲) and their subsequent disappearance over the experimental temperature range can be clearly observed. The retro DA reaction for both reactions 4 and 10 begins at 70 °C and 60 °C degrees, respectively, and continues to completion at 85 °C (Figure 2-4, Table 2-3). These data suggest that 85 °C which would be the ideal temperature at which all of the Diels-Alder linkages in the elastomers could be reversed and the material could be recycled. The variable 1H NMR data for each model experiment have been shown in Figure 2-5 to Figure 2-15.

The VT NMR of the reaction number 6 (Figure 2-6), the progress of the reaction (maleimide consumption and bridgehead proton appearance) is really slow owing to the lower yield of adduct compared to the others. Moreover, no endo adduct is observed in this reaction. The same thing can be observed for reaction number 3 in Figure 2-7.
Figure 2-5 VT $^1$H NMR spectra of the reaction #1 (40 °C, 50 °C, 60 °C, 70 °C, 80 °C) illustrating maleimide consumption (●) and the formation of the new endocyclic double bond (■), the bridgehead proton (♦), and the exo (▲) and endo (♦) adduct products.

Figure 2-6 VT $^1$H NMR spectra of the reaction #2 (40 °C, 50 °C, 60 °C, 70 °C, 80 °C) illustrating maleimide consumption (●) and the formation of the new endocyclic double bond (■), the bridgehead proton (♦), and the endo (♦) adduct products.
Figure 2-7 VT $^1$H NMR spectra of the reaction #3 (40 °C, 50 °C, 60 °C, 70 °C, 80 °C) illustrating maleimide consumption (●) and the formation of the new endocyclic double bond (■), the bridgehead proton (♦), and the endo (*) adduct products.

Figure 2-8 VT $^1$H NMR spectra of the reaction #5 (40 °C, 50 °C, 60 °C, 70 °C, 80 °C) illustrating maleimide consumption (●) and the formation of the new endocyclic double bond (■), the bridgehead proton (♦), and the exo (▲) and endo (*) adduct products.
Figure 2-9 VT $^1$H NMR spectra of the reaction #6 (40 °C, 50 °C, 60 °C, 70 °C, 80 °C) illustrating maleimide consumption (●) and the formation of the new endocyclic double bond (■), the bridgehead proton (♦), and the exo (▲) and endo (♦) adduct products.

Figure 2-10 VT $^1$H NMR spectra of the reaction #7 (40 °C, 50 °C, 60 °C, 70 °C, 80 °C) illustrating maleimide consumption (●) and the formation of the new endocyclic double bond (■), the bridgehead proton (♦), and the endo (♦) adduct products.
Figure 2-11 VT $^1$H NMR spectra of the reaction #8 (40 °C, 50 °C, 60 °C, 70 °C, 80 °C) illustrating maleimide consumption (●) and the formation of the new endocyclic double bond (■), the bridgehead proton (♦), and the endo (*) adduct products.

Figure 2-12 VT $^1$H NMR spectra of the reaction #9 (40 °C, 50 °C, 60 °C, 70 °C, 80 °C) illustrating maleimide consumption (●) and the formation of the new endocyclic double bond (■), the bridgehead proton (♦), and the endo (*) adduct products.
Figure 2-13 VT $^1$H NMR spectra of the reaction #10 (40 °C, 50 °C, 60 °C, 70 °C, 80 °C) illustrating maleimide consumption (●) and the formation of the new endocyclic double bond (■), the bridgehead proton (♦), and the exo (▲) and endo (♦) adduct products.

Figure 2-14 VT $^1$H NMR spectra of the reaction #11 (40 °C, 50 °C, 60 °C, 70 °C, 80 °C) illustrating maleimide consumption (●) and the formation of the new endocyclic double bond (■), the bridgehead proton (♦), and the endo (♦) adduct products.
Figure 2-15 VT $^1$H NMR spectra of the reaction #12 (40 °C, 50 °C, 60 °C, 70 °C, 80 °C) illustrating maleimide consumption (●) and the formation of the new endocyclic double bond (■), the bridgehead proton (♦), and the exo (▲) and endo (♦) adduct products.

Among three ortho 14, para 15, and meta 16 phenylenebismaleimides, the reactivity of the meta compound 16 in the model DA reactions was the highest. The relatively low reactivity of ortho compound 14 was attributed to the steric hindrance of the two maleimide rings, which inhibit addition of a furan ring attached to a bulky siloxane chain. It was anticipated that the para compound 15 would be more reactive in the model DA reactions than the meta analogue 16 owing to the planarity of 15 and the maximal distance between the two maleimide rings. The arrangement of the maleimide rings in 15 diminishes steric hindrance and should, in theory increase the yield of the cycloaddition reaction. However, this was not the case. As the steric considerations appeared to favour successful adduct formation, some basic calculations were performed by Dr. Travis Dudding (Brock University,
Department of Chemistry) to try and elucidate an electronic explanation for the lack of reactivity associated with 15 (Figure 2-16).

![Figure 2-16. Computationaly-derived electronic charges on (a) N,N’-(1,3-phenylene)bismaleimide and (b) N,N’-(1,4-phenylene)bismaleimide atoms.]

As can be seen in Figure 2-16, the *meta* 16 and *para* 15 compounds are virtually identical from an electronic standpoint, suggesting that electronic charge distribution is not the key factor responsible for the difference in reactivities between these two species.

DSC (Differential Scanning Calorimetry) and TGA (Thermogravimetric Analysis) analyses were performed for each model reaction to study the DA/rDA equilibrium and the reversibility of the system. The samples prepared from 1:1 mixture, by mass, of the diene:dienophile of interest mixed in a flask and stirred in the absence of solvent at 80 °C
for 24 h to yield the DA adduct in approximately 85% (not for all of the model systems). Then, three cycles of heating and cooling were applied to each sample from 30 °C to 120 °C with a ± 4 °C heating/cooling rate. The DSC and TGA thermographs for the reaction between 5 and 13 (Figure 2-17) is discussed here as a representative sample of all the model reactions. The thermal experiments subjected the sample to 7 heating/cooling cycles seven times at a ± 4 °C heating/cooling rate with the hold time of 20, 30 and 40 min in order to examine the system’s stability, repeatability, and reversibility. The DSC trace for the reaction between 5 and 13 (Figure 2-17a) shows that for the the model system the DA and retro DA reactions occur at around 55 °C and 105 °C, respectively; the DA reaction occurs again in the cooling cycle at roughly 50 °C. The stability of the heating and cooling process over the course of 7 cycles confirmed the recyclability and repeatability of DA/rDA reaction. The remaining 11 thermographs for the other model reactions can be found in the Appendix; these systems displayed similar thermal behaviours to the model reaction between 5 and 13.
Moreover, the TGA trace (Figure 2-17b) indicated that the compounds do not demonstrate appreciable degradation as evidenced by weight loss after being subjected to 7 heating and cooling) cycles. This is evidenced by the minimal weight loss (from 1.75 mg to 1.63 mg observed for the reaction mixture indicating that the reaction mixtures are capable of undergoing multiple DA/rDA reactions.

2.2 Synthesis of Diels-Alder Cross-Linked Siloxane Elastomers

In an effort to better understand the target elastomeric systems, 12 different model DA adducts were synthesized over varying timeframes and temperatures. This data was then extended to the synthesis of elastomeric silicone materials cross-linked using the Diels-Alder reaction. Using three different siloxane polymers (32 a, 32 b and 32 c) with varying concentrations of the furan diene, with two different furan moieties (3 and 8) generated six different diene systems (Scheme 2-5 and Scheme 2-6) that could be reacted with six different dienophiles to yield 36 different elastomers. All of the elastomers were synthesized with a 1:1 mole ratio of diene:dienophile (Scheme 2-7, Scheme 2-8).
Synthesizing cross-linked siloxane elastomers using the Diels-Alder reaction required that the number of diene units along the polymer backbone be calculated. In this study, three different concentrations of Si-H moieties along the PDMS backbone were examined. The first one possessed 3-4 mol% of methylhydrosiloxane units over a PDMS polymer with an average molecular weight (M_n) of 13,000 g/mol. From the \(^1\)H NMR spectrum of the product it was determined that 33 a and 34 a possessed approximately 1 furan moiety for every 32 dimethylsiloxane units, which means half of this number represents the amount of bismaleimides 13-18 required for the reaction since the cross-linker possesses two dienophile units. The second system (33 b and 34 b), was 7-9 mol% methylhydrosiloxane units a molecular weight of 5,500-6,500 g/mol, leaving approximately 1 furan unit for every 13 dimethyl siloxane units in the polymer backbone. For (33 c and 34 c), which was 25-30 mol% methylhydrosiloxane with a molecular weight
range of 2,000-2,600 g/mol, the polymer contained 1 furan unit for every 3 dimethyl siloxane groups. The solvent-free Diels-Alder reaction (Scheme 2-7, Scheme 2-8, Scheme 2-9) was performed in a polytetrafluoroethylene (PTFE, Teflon™) mould (37.6 mm L x 13.8 mm W x 3 mm D) with three cavities. Once the components of the reaction were placed in the mould the entire system was placed in an oven and the elastomers were permitted to cure. Among all of these 36 elastomers, 15 of them worked perfectly and produced solid elastomers with different colours ranging from clear and colourless, light yellow to brownish. Furthermore, each of the elastomers indicate various mechanical properties (elongation and hardness) that will be discuss later. Moreover, 5 of the elastomers didn’t cure completely (liquid on the top) mostly because of the low cross-link density. 12 of all didn’t cure at all and it was expectable according to the model systems. Eventually, 4 of the DA reactions in the mould were not attempted in spite of the data from the model reactions because the cost of the bismaleimide was prohibitive.

In the following sections, the reasons of why some of the elastomers worked perfectly, some of them cured incomplete and some of them did not cure at all, will be discussed in more details.
Scheme 2-7 DA reactions in the mould with diene 33a, 33b, 33c and dienophile 13-18
Scheme 2-8 DA reactions in the mould with diene 34 a, 34 b, 34 c and dienophile 13-18
All of the elastomers utilizing the commercially available dienophiles (14-18) were synthesized at temperatures ranging from 60 °C to 70 °C in an oven over the course of 24 to 48 h. These results were consistent with earlier work in the Zelisko lab involving elastomer formation utilizing diene- and dienophile-modified siloxane polymers. However, silicone elastomers utilizing bismaleimide 13 as the dienophile were fully formed at room temperature in only 5 h. Since the temperature for the both model and polymeric DA reaction for this specific bismaleimide 13 were lower compared to the other systems (models and elastomers), the retro DA also occurred at 80 °C (Figure 2-4), compared to the other systems that typically displayed the onset of the rDA reaction at approximately 100 °C. To the best of my knowledge this is the first, and only, reported case of a self-healing silicone elastomer based on the Diels-Alder reaction where healing occurs at room temperature.

2.3 Solid-State NMR

Solid-state $^1$H NMR analysis of the cross-linked PDMS elastomer confirmed the appearance of adduct peak on the spectra at around 3 ppm as it was observed previously.
on the model adduct $^1$H NMR. Solid-state NMR were taken from two of the elastomers (35 b and 41 c) and have been shown in Figure 2-18 and Figure 2-19 respectively. So, the results extended to the other synthesized elastomers.

Figure 2-18 Solid-state $^1$H NMR of compound 35 b. The peaks at 3.02, 3.40 and 3.68 ppm confirm existence of exo and endo adduct protons
2.4 Imaging the Elastomers

In addition to using solid state $^1$H NMR to confirm the self-healing and reversible nature of the DA reactions in the silicone elastomers, optical and scanning electron microscopy (SEM) were used to observe the surface of virgin and healed elastomer surfaces for an elastomer (36 b) made by reacting 33 b and bismaleimide 14 (Figure 2-20), chosen at random from all synthesized elastomers involving the commercially available bismaleimides. Once can observe a faint scratch on the surface of the elastomers after self-healing. Even though a scar is visible on the surface of the elastomer, the silicone material was completely healed (i.e., one solid elastomer rather than two individual pieces). The elastomer was imaged at
various magnifications to truly understand the implications of the healing process on the surface of the elastomeric material.

Figure 2-20. Optical microscopy images of (top) and scanning electron microscopy (SEM) images (bottom) of 36 b virgin elastomer (a) & (d), bisected elastomer (b), and the “scar” of a healed elastomer (c), (e), & (f) obtained by heating the sample to 120 °C and then permitting it to cool and heal.
The elastomers made using the commercially available dienophiles (14-18) were all yellow to light brown in colour. However, elastomers formulated using 13 as the dienophile were are all clear and colourless (Figure 2-21 (a), (b), and (c)). SEM imaging of the elastomer 35 b revealed an extremely well healed elastomer – the scar was nearly imperceptible. These data suggest that silicone elastomers employing 13 as the cross-linker are more efficient not only in terms of their initial synthesis, but also with respect to their self-healing, which was observed to occur in 2-3 min after heating the sample to 80 °C to increase chain mobility within the elastomer.

In addition to developing a self-healing silicone elastomer in an effort to extend the useful lifetimes of such materials, it was also of interest to look at the capacity of these elastomers to be recycled; specifically it was of interest to examine the efficiency with which the elastomers could be remoulded into different forms and subsequently reused, a feat that is not trivial with traditional silicone elastomers. To explore the capacity of the elastomers to be recycled, specifically through remoulding, a sample of the elastomer made from 35 b was heated to 80 °C in a small vial. The solid sample underwent the retro-Diels-Alder reaction and became fluid. After cooling and being left at the room temperature for a few hours the sample underwent the Diels-Alder reaction to form a solid elastomer once again, this time in the cylindrical shape of the vial (Figure 2-22).
Figure 2-21 Photographs and SEM images for the elastomer made from 35 b: (a), (b), (c) photographs of virgin, bisected, and healed elastomer respectively; (d), (e) SEM images of a virgin and healed elastomer at 200 x magnification; (f), (g) the same virgin and healed elastomer imaged at 2.5k x magnification; (h) the healed elastomer imaged at 500 x magnification. The cuts/scars are highlighted in (b), (c), (e), (g), and (h).
2.5 Tensile Strength Measurements

The tensile strength of the polysiloxane elastomers was examined for virgin elastomers and for elastomers that had been healed (Figure 2-23). 36 a required the application of a greater force (12 N) that the other elastomers in this series, but it broke after only being elongated by roughly 1.27 cm. Elastomer 35 b was elongated by 3.3 cm but suffered catastrophic failure after the application of only 1 N of force.
Figure 2-23 Comparing the tensile strength of the 35 b, 36 b, 38 b, 39 b and 40 b

Figure 2-24 Comparing the tensile strength of the 41 b, 42 b and 46 b
The elastomers using \textbf{34} \textbf{c} as diene and compounds \textbf{13-18} as dienophiles proved to be too brittle and broke upon attempts to remove them from the moulds. As a result it was not possible to obtain accurate tensile strength measurements for these elastomers.

It was also of interest to compare the tensile strength of the elastomers both before and after healing, with a specific focus on the \textbf{35} \textbf{b} and \textbf{35} \textbf{c} (Figure 2-26). When compared to the virgin elastomer, the healed elastomer \textbf{35} \textbf{b} elongated more after being healed, although a smaller overall force was required before catastrophic failure was observed. Interestingly, with the healed elastomer catastrophic failure did not occur at the scar; failure was always observed within the virgin portion of the elastomer suggesting that the healed portion of the elastomer is in fact more robust than the undamaged areas.
Given the higher degree of cross-linking found in the PDMS-(iii)-A-4 elastomer, the virgin elastomer possessed a fairly high tensile strength whereas the healed became brittle and lost its elasticity (Figure 2-27).

Figure 2-26 Comparing the tensile strength of elastomer 35 b before and after healing

Figure 2-27 Comparing the tensile strength of elastomer 35 c and after healing
2.6 Differential Scanning Calorimetry (DSC) Analysis of Cross-Linked Elastomers

DSC analysis was performed on model reactions to confirm the temperatures at which DA and rDA reactions were occurring as well as the reproducibility of the reactions. DSC analysis was also performed on the elastomers to ensure that the polymeric networks remained stable, especially for elastomer PDMS-(ii)-A-4 with its low reaction temperature. Seven cycles of heating and cooling were performed from 30 °C to 120 °C with a heating/cooling rate of ±4 °C and a holding time of 30 min after each step in temperature (Figure 2-28). As was observed with the model reactions, the DA reaction for the elastomer occurred at room temperature. However, since the instrument that was used for this analysis start the heating from 35 °C the DA reaction is observable at approximately 45 °C which is the completion of the reaction not the start point, while the retro DA reaction took place at 100 °C (Figure 2-28). No significant thermal decomposition was observed for the elastomer.
2.7 Hardness Measurements

The durometer is an instrument used to commonly measure the hardness of polymers, elastomers, and rubbers. Different scales are applied to different kinds of materials. Silicone polymers typically are subjected to Shore 00 measurements as these materials are typically more resistant to compression stress and indentation. To put the hardness values of the Shore 00 scale into context chewing gum has Shore 00 value of 20 and polyurethane rubbers can have a hardness value between 30 and 70. In this study, the hardness of the elastomers was measured both before damage and after healing (Table 2-4).

<table>
<thead>
<tr>
<th>Elastomer</th>
<th>Virgin</th>
<th>Healed</th>
<th>Change in Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>35 b</td>
<td>66</td>
<td>60.2</td>
<td>-5.8</td>
</tr>
<tr>
<td>36 b</td>
<td>62.4</td>
<td>58.7</td>
<td>-3.7</td>
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<tr>
<td>38 b</td>
<td>45.8</td>
<td>36</td>
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<td>39 b</td>
<td>39.1</td>
<td>31.3</td>
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<tr>
<td>40 b</td>
<td>54.8</td>
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<td>-7.4</td>
</tr>
<tr>
<td>41 b</td>
<td>34</td>
<td>29.1</td>
<td>-4.9</td>
</tr>
<tr>
<td>42 b</td>
<td>32</td>
<td>28</td>
<td>-4</td>
</tr>
<tr>
<td>46 b</td>
<td>40</td>
<td>36.7</td>
<td>-3.3</td>
</tr>
<tr>
<td>35 c</td>
<td>68.3</td>
<td>56.7</td>
<td>-11.6</td>
</tr>
<tr>
<td>36 c</td>
<td>82.4</td>
<td>77.2</td>
<td>-5.2</td>
</tr>
<tr>
<td>38 c</td>
<td>76.2</td>
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<tr>
<td>40 c</td>
<td>64.4</td>
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</tr>
<tr>
<td>46 c</td>
<td>66.9</td>
<td>60.2</td>
<td>-6.7</td>
</tr>
</tbody>
</table>

Comparing the hardness of these synthesized elastomers, it can be determined that the elastomers made from higher Si-H percentage (25-30% Si-H) are harder as a result of their higher cross-link density. However, the elastomers made from 7-9% Si-H polymers
are softer and more flexible. The changes in hardness after elastomers being healed varies and no trend can be observed for them.

A summary of the silicone elastomer networks were synthesized is shown in Table 2-5 (the synthesized elastomers’ numbers have been written in the coloured boxes). The red boxes represent elastomers that did not cure in the oven after 72 h at 70 °C. The yellow boxes represent elastomers that cured, but did not do so completely; these elastomers were sticky on top or very fragile and could not be removed from the moulds. Green boxes represent perfectly formed elastomers and the black boxes represent elastomers that were not attempted, in spite of the model system results, simply because the cost of the bismaleimide was prohibitive.

The elastomers synthesized from 3-4% Si-H mol% polymer (33 a and 34 a) because of the lower mole percentage of active sites (3-4%) and relatively higher molecular weight (Mn = 13000 g/mol) are difficult to be cured and make the elastomers. It seems to be difficult for the dienophiles to find enough diene moieties to do sufficient cross-linking density to get perfect elastomers. So, most of them remained liquid during the 72 h reaction period. Except for the elastomers 35 a and 36 a that were using compounds 13 and 14 respectively as the dienophile which produced not perfect elastomers but solid at the bottom and liquid on the top which wasn’t solid enough to take out from the mould and do the analysis. Moreover, as it was anticipated none of the DA reactions that were used compound 15 as dienophile went to completion. Because, none of the model DA reactions with this specific dienophile (15) yielded DA adducts. Overall, according to the model reactions, the results illustrated in the Table 2-5 were almost predictable.
Table 2-5 Summary of Diels-Alder cross-linked silicone elastomers.a

<table>
<thead>
<tr>
<th>Elastomers</th>
<th>Diene</th>
<th>Dienophile</th>
</tr>
</thead>
<tbody>
<tr>
<td>33 a</td>
<td>13</td>
<td>35 a</td>
</tr>
<tr>
<td>33 b</td>
<td>14</td>
<td>36 a</td>
</tr>
<tr>
<td>33 c</td>
<td>15</td>
<td>37 a</td>
</tr>
<tr>
<td>34 a</td>
<td>16</td>
<td>38 a</td>
</tr>
<tr>
<td>34 b</td>
<td>17</td>
<td>39 a</td>
</tr>
<tr>
<td>34 c</td>
<td>18</td>
<td>40 a</td>
</tr>
</tbody>
</table>

Red = systems that did not cure; yellow = elastomers that did not cure completely; green = elastomers that cured completely and could be analyzed further; black = elastomers that were not attempted in spite of the data from the model reactions because the cost of the bismaleimide was prohibitive.

## 2.8 Conclusions & Future Outlook

The DA reaction was studied in this thesis as a cross-linker for the production of various siloxane elastomer networks. To achieve this goal, furan-modified polysiloxanes with different average molecular weights and different furan concentrations were reacted with a library of bismaleimide compounds. The results illustrated that the novel compound tetramethybis[(N-maleimidomethyl)oxy]disiloxane 13 had the highest maleimide conversion overall, and more importantly the reaction occurred at room temperature and in only 5 h. SEM analysis of these elastomers was used to confirm the self-healing capacity of the elastomers and revealed that, especially with elastomers made with 13, healing was quite efficient. To the best of my knowledge this is the first, and only, reported case of a self-healing silicone elastomer based on the Diels-Alder reaction where healing occurs at room temperature after the elastomer being heated at around 70 °C – 80 °C for rDA reaction to occur. Which can be a tremendously important property in industry from the view point of using less energy to recycle the elastomers. Moreover, specifically for the
aforementioned elastomer (35 b), the double cross-linking in the damaged area made that area stronger than what it was before which can be a really useful property in industry. This was confirmed with the tensile strength measurement of the healed elastomer. As it was illustrated before, the elongation of the healed elastomer compared with the virgin one increased and the breakage of the elastomer did not occur on the same damaged area. Hardness measurements indicated that all of the elastomers after being damaged and healed get softer which can be the result of the smaller amount of cross-link density in the network compared to the virgin elastomers.

The goal of this research was to extend the life-time of the elastomers by making them recyclable and reduce the amount of plastic wastes which leads to less plastic pollution that is a global concern for today’s modern lifestyle. The use of bismaleimide molecules as cross-linkers for furan-modified silicone polymers led to the development of recyclable polysiloxane networks whose synthesis, and subsequent healing and recycling, can be temperature controlled because of the DA/rDA reaction and the specific bismaleimide moiety being employed as a cross-linker. Time and temperature are the most important factors in industry of self-healing that was improved in this research by producing clear and colourless elastomers at room temperature in 5 h. For the future studies, the flexibility of the networks can be increased by using silicone polymers modified with both diene and dienophile moieties instead of using molecule bismaleimides.
Chapter 3: Experimental

3.1 Instrumentation

Nuclear Magnetic Resonance (NMR) Spectroscopy. $^1$H, $^{13}$C, $^{29}$Si, variable temperature (VT) and solid-state NMR were carried out using a Brucker AV-300 digital NMR spectrometer with a 7.05 Tesla Ultrashield magnet equipped with a BBFO Z-gradient ATMA probe head.

Infrared Spectroscopy (IR). Attenuated Total Reflectance Fourier Transform IR (ATR-FT-IR) spectra were acquired on a Bruker Alpha Optic GmbH 2012. All spectra were an average of 24 scans at 2 cm$^{-1}$ resolution using neat samples on a diamond window.

Mass Spectrometry (MS). Electron Impact (EI) and Fast Atom Bombardment (FAB) mass spectrometry was performed using a Thermo DFS high-resolution mass spectrometer in positive ion mode.

Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC). The thermal analyses were conducted using a Perkin-Elmer STA 8000 instrument which has a temperature range from 30 °C to 1600 °C. Octadecane was used for calibration (27.95 °C melting point) while aluminium was used as the standard.

Scanning Electron Microscopy (SEM). The samples were mounted onto SEM stubs with double-sided carbon tape and then placed into the chamber of a Polaron Model E5100 sputter coater (Polaron Equipment Ltd., Watford, Hertfordshire) and approximately 15 nm of gold was deposited onto the stubs. The samples were viewed in a Tescan Vega II LSU scanning electron microscope (Tescan USA, PA) operating at 10kV.
**Tensile Strength.** A MARK-10 single-column force tensiometer consisting of: a M5-200 force gauge, ESM303 compression test stand, G1101 vise-action grip was used to analyze the tensile strength of the elastomer samples.

**Durometer.** A digital durometer (Check-Line OS-1E) was used to measure Shore 00 according to ASTM D-2240.

### 3.2 Materials

Toluene, tetrahydrofuran (THF), diethyl ether, n-butyl lithium, furan, 11-bromoundec-1-ene, N,N'-(1,3-phenylene)dimaleimide, silica gel (230-400 mesh), molecular sieves (4Å beads, 8-12 mesh), 10-undecenoic acid, furfuryl alcohol, Pt(0)-1,3-divinyl-1,1,3,3-tetramethyl-disiloxane complex (Karstedt’s catalyst, Pt(dvs)) in xylene, lipase B from *C. antarctica* immobilized on Lewatit VPOC1600 cross-linked divinylbenzene resin (Novozym-435, N435), trimethylsilyl terminated-poly(dimethylsiloxane-co-methylhydrosiloxane) (3-4% methylhydrosiloxane) with an average Mn of 13,000 g/mol (32a), trimethylsilyl terminated-poly(dimethylsiloxane-co-methylhydrosiloxane) (7-9% methylhydrosiloxane) with an approximate molecular weight of 5,500-6,500 g/mol (32b) and trimethylsilyl terminated-poly(dimethylsiloxane-co-methylhydrosiloxane) (25-30% methylhydrosiloxane) with an approximate molecular weight of 2,000-2,600 g/mol (32c) were obtained from Sigma–Aldrich (Oakville, Ontario, Canada). Heptamethyltrisiloxane was obtained from Gelest (Morristown, PA, USA). All compounds were used as received unless otherwise stated.
3.3 Synthesis of the Model Compounds

All the reactions were performed under nitrogen atmosphere. Molecular sieves were kept in the oven at least five days prior to being used.

3.3.1 Synthesis of the Diene

Two different diene systems were synthesized in order to make a library of elastomers and to compare their properties.

3.3.1.1 Synthesis of furan-2-ylmethyl undec-10-enoate (3)

\[
\begin{align*}
\text{Furfuryl alcohol (1.96 g, 20 mmol) was added to a solution of 10-undecenoic acid (1.85 g, 10 mmol) in toluene (15 mL). Afterwards, the enzymatic catalyst N435 (4% w/w, 0.15 g) was introduced to the flask followed by the addition of molecular sieves (about 1 g). The reaction mixture heated to 110 °C and stirred for 48 h. The reaction mixture filtered through a medium porosity fritted Büchner funnel containing a 2 cm Celite® pad and the solvent was removed using a rotary evaporator. The crude product was dissolved in diethyl ether and washed with distilled water and then extracted with a saturated solution of sodium bicarbonate and brine (x3 each). The organic layer was dried over anhydrous sodium sulfate and the light yellow oil was purified using silica gel column chromatography using 9:1 hexane:ethyl acetate as the elution solvent to yield 3 as a colourless liquid (28.7 g, 0.11 mol, 83 %). Spectral analyses were consistent with published data.} \\
\text{^1H NMR (300 MHz, CDCl$_3$) $\delta$ 7.42 (dd, $J = 0.63$, 0.57 Hz, 1H), $\delta$ 6.35-6.40 (m, 2H), $\delta$ 5.74-5.90 (m, 1H), $\delta$ 5.74 (s, 2H), $\delta$ 4.90-5.02 (m, 2H), $\delta$ 2.32 (t, $J = 7.4$ Hz, 2H), $\delta$ 2.03 (q, $J = 6.8$ Hz, 2H),}
\end{align*}
\]
\( \delta 1.60-1.64 \) (m, 2H), \( \delta 1.27 \) (s, 10H). \(^{13}\)C \({}^1\)H NMR (101 MHz, CDCl\(_3\)) \( \delta 173.45, 149.66, 143.18, 139.18, 114.13, 110.52, 110.45, 57.86, 34.14, 29.25, 29.03, 28.90, 24.85 \) ppm.

### 3.3.1.2 Synthesis of furanyl-2-methyl-11-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)undecanoate (5)

![Diagram of the compound](image)

After dissolving 3 (2.64 g, 10 mmol) in toluene (10 mL) and heating the reaction to 85 °C in a 100 mL round bottom flask equipped with a condenser, 1,1,1,3,5,5,5-heptamethyltrisiloxane (2.50 g, 11.2 mmol) was introduced to the flask and stirred for 10 min followed by the addition of Karstedt’s catalyst (25 \( \mu \)L). The reaction mixture stirred over night until \(^1\)H NMR confirmed that there was no longer a Si-H resonance in the spectrum. After the completion of the reaction, activated carbon was added to the mixture at room temperature and stirred for 2 h. The reaction was then vacuum filtered through a pad of Celite\(^\circledR\) using a Büchner funnel to yield 5 \(^{125}\) (4.13 g, 9.1 mmol, 81\%) as a light yellow oil. Spectral analyses were consistent with published data\(^{125}\). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta 7.42 \) (s, 1H), \( \delta 6.35-6.39 \) (m, 2H), \( \delta 5.05 \) (s, 2H), \( \delta 2.32 \) (t, \( J = 7.5 \) Hz, 2H), \( \delta 1.61 \) (t, \( J = 7.2 \) Hz, 2H), \( \delta 1.26 \) (s, 14H), \( \delta 0.44 \) (t, \( J = 7.5 \) Hz, 2H), \( \delta 0.08 \) (s, 18H), \( \delta -0.01 \) (s, 3H). \(^{13}\)C \({}^1\)H NMR (101 MHz, CDCl\(_3\)) \( \delta 173.47, 143.17, 110.52, 110.44, 57.84, 34.16, 33.22, 29.49, 29.46, 29.33, 29.23, 29.09, 24.88, 23.06, 17.62, 1.85, -0.27 \) ppm. \(^{29}\)Si \({}^1\)H NMR (60 MHz, CDCl\(_3\)) \( \delta 6.76 \) ppm.
3.3.1.3 Synthesis of 2-(undec-10-en-1-yl)furan (8)

The THF was dried over molecular sieves 5 days before being used. Furan was distilled over KOH and under nitrogen immediately before use. THF (80 mL) was cooled in an ice bath prior the addition of n-buthyllithium (20 mL, 48 mmol, 2.5 M solution in pentane). The freshly distilled furan (3.4 mL, 50 mmol) was added drop-wise to the reaction flask and allowed to stir for 30 min at 0 °C. 11-Bromoundec-1-ene (9.32 g, 40 mmol) was introduced to the reaction mixture slowly at room temperature and the reaction was allowed to stir over night. The reaction mixture was quenched with a saturated aqueous solution of NH₄Cl (40 mL) and then extracted with ethyl acetate (3 x 40 mL). After drying the organic phase with MgSO₄ and removing the solvent using a rotary evaporator, compound 8 was obtained from column chromatography using n-hexane (7.5 g, 34.1 mmol, 85%)¹²⁶ as the elution solvent as a clear and colourless liquid. Spectral analyses were consistent with published data¹²⁶. 

\(^1\)H NMR (300 MHz, CDCl₃) δ 7.29 (d, \(J = 1.2\) Hz, 1H), δ 6.27 (dd, \(J = 2.0, 1.9\) Hz, 1H), δ 5.98 (t, \(J = 2.8\) Hz, 1H), δ 5.75-5.90 (m, 1H), δ 4.91-5.03 (m, 2H), δ 2.62 (t, \(J = 7.5\) Hz, 2H), δ 2.05 (q, \(J = 6.7\) Hz, 2H), δ 1.60-1.69 (m, 2H), δ 1.30 (s, 12H).

\(^{13}\)C \(^\{^1\}\)H NMR (101 MHz, CDCl₃) δ 156.63, 140.60, 139.24, 114.09, 110.01, 104.49, 33.81, 29.48, 29.45, 29.33, 29.17, 29.12, 28.93, 28.03, 27.98 ppm.
3.3.1.4 Synthesis of 3-(11-(furan-2-yl)undecyl)-1,1,3,5,5,5-heptamethyltrisiloxane (9)

After dissolving 8 (2.64 g, 10 mmol) in toluene (10 mL) and heating the solution to 85 °C in a 100 mL round bottom flask equipped with a condenser, 1,1,1,3,5,5,5-heptamethyltrisiloxane (2.5 g, 11.2 mmol) was added to the solution and stirred for 10 min prior to the addition of Karstedt’s catalyst (25 µL). The reaction mixture stirred over night until $^1$H NMR confirmed that there is no Si-H resonances remained in the spectrum. After the hydrosilylation was complete, activated carbon was added to the mixture at room temperature and stirred for 2 h and the mixture was subsequently vacuum filtered through a pad of Celite® using a Büchner funnel to compound 9 (4.25 g, 9.6 mmol, 80%) as a light yellow liquid. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.28 (d, $J = 1.2$ Hz, 1H), δ 6.35-6.39 (dd, 2H), δ 5.05 (s, 2H), δ 2.32 (t, $J = 7.5$ Hz, 2H), δ 1.61 (t, $J = 7.2$ Hz, 2H), δ 1.26 (s, 14H), δ 0.44 (t, $J = 7.5$ Hz, 2H), δ 0.08 (s, 18H), δ -0.01 (s, 3H). $^{13}$C {$^1$H} NMR (101 MHz, CDCl$_3$) δ 156.65, 140.59, 110.00, 104.48, 33.23, 29.65, 29.58, 29.37, 29.19, 29.04, 27.98, 23.06, 17.62, 1.85, -0.27 ppm. $^{29}$Si {$^1$H} NMR (60 MHz, CDCl$_3$) δ 6.76 ppm.

3.3.1.5 Synthesis of N-hydroxymethylmaleimide (11)

After dissolving 8 (2.64 g, 10 mmol) in toluene (10 mL) and heating the solution to 85 °C in a 100 mL round bottom flask equipped with a condenser, 1,1,1,3,5,5,5-heptamethyltrisiloxane (2.5 g, 11.2 mmol) was added to the solution and stirred for 10 min prior to the addition of Karstedt’s catalyst (25 µL). The reaction mixture stirred over night until $^1$H NMR confirmed that there is no Si-H resonances remained in the spectrum. After the hydrosilylation was complete, activated carbon was added to the mixture at room temperature and stirred for 2 h and the mixture was subsequently vacuum filtered through a pad of Celite® using a Büchner funnel to compound 9 (4.25 g, 9.6 mmol, 80%) as a light yellow liquid. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.28 (d, $J = 1.2$ Hz, 1H), δ 6.35-6.39 (dd, 2H), δ 5.05 (s, 2H), δ 2.32 (t, $J = 7.5$ Hz, 2H), δ 1.61 (t, $J = 7.2$ Hz, 2H), δ 1.26 (s, 14H), δ 0.44 (t, $J = 7.5$ Hz, 2H), δ 0.08 (s, 18H), δ -0.01 (s, 3H). $^{13}$C {$^1$H} NMR (101 MHz, CDCl$_3$) δ 156.65, 140.59, 110.00, 104.48, 33.23, 29.65, 29.58, 29.37, 29.19, 29.04, 27.98, 23.06, 17.62, 1.85, -0.27 ppm. $^{29}$Si {$^1$H} NMR (60 MHz, CDCl$_3$) δ 6.76 ppm.
Compound 11 was synthesized from a suspension of maleimide (24.5 g, 0.25 mol) in 37% formalin (20.3 ml, 0.72 mol) to which 0.75 mL of a 5% sodium hydroxide solution was added over 10 min at 30 °C. The reaction was allowed to stir for 3 h at 30 °C. After filtration, the crude product was recrystallized from ethyl acetate to obtain 11 (24 g, 0.19 mol, 76%). Spectral analyses were consistent with published data. $^1$H NMR (300 MHz, CDCl$_3$) δ 6.77 (s, 2H), δ 5.08 (d, $J$ = 7.8, 2H), δ 2.95 (t, $J$ = 7.9 Hz, 1H). $^{13}$C {$^1$H} NMR (101 MHz, CDCl$_3$) δ 170.07, 134.63, 61.13 ppm.

3.3.1.6 Synthesis of tetramethybis[(N-maleimidomethyl)oxy]disiloxane (13)

Compound 11 (25.5 g, 0.2 mol) was dissolved in dry THF (50 mL), followed by the addition of triethylamine (27.9 mL, 0.2 mol) and 1,3-dichloro-1,1,3,3-tetramethyldisiloxane (20.3 g, 0.1 mol). The reaction mixture stirred at room temperature for 4 h under a nitrogen atmosphere. The crude mixture was filtered through a sintered glass Büchner funnel and the filtered inorganic salts were washed with diethylether. After removing the solvent, diethylether (40 mL) was added to the reaction mixture and it was washed with distilled water (3x20 mL), dried over sodium sulfate, filtered, and concentrated using a rotary evaporator to yield compound 13 as a white, shiny powder (29 g, 0.075 mol, 76.3%). $^1$H NMR (300 MHz, CDCl$_3$) δ 6.75 (s, 4H), δ 5.14 (s, 4H), δ 0.16 (s, 12H). $^{13}$C {$^1$H} NMR (101 MHz, CDCl$_3$) δ 169.82, 134.56, 60.01, -1.11 ppm. $^{29}$Si {$^1$H} NMR (60 MHz, CDCl$_3$) δ -10.08 ppm. High-Res MS-FAB+ [C$_{14}$H$_{20}$N$_2$O$_7$Si$_2$ + NH$_4$]$^+$ : 402
amu, \([C_{14}H_{20}N_2O_7Si_2 + Na]^+ : 407\) amu, \([C_{14}H_{20}N_2O_7Si_2 + K]^+ : 423\) amu. Elemental Analysis (%): Calculated: C: 43.73, H: 5.24, Found: C: 43.59, H: 5.16.

3.3.1.7 Model Diels-Alder Reactions

All of the 12 model Diels-Alder reactions were set up at one of the following temperatures, five various temperatures 40 °C, 50 °C, 60 °C, 70 °C and 80 °C, in an effort to optimize the reaction temperature and maleimide conversion. The reactions were performed neat in 2 dram vials with a 1:1 mole ratio of diene:dienophile. The reactions were stirred 24 h to yield the DA adduct. The \(^1H\) NMR spectra for these reactions can be found in the appendix.

3.4 Synthesis of the Elastomers

3.4.1 Synthesis of furan-2-ylmethylundecanoatesiloxane-dimethylsiloxane copolymers (33 a, 33 b, 33 c)

Trimethylsilyl-terminated poly(dimethylsiloxane-co-methylhydrosiloxane) (32 a, 32 b, 32 c) was dissolved separately in toluene (80 mL) before the addition of Karstedt’s catalyst (180 µL). After 10 min of stirring, compound added to the flask under reflux and stirred overnight. Activated charcoal was added to the reaction after it was cooled to the room temperature and stirring continued for an additional 5 h. The reaction was filtered through a pad of Celite\(^\circledR\) using Büchner funnel to yield polymer after removal of the solvent (Table 3-1). \(^1H\) NMR (33 a) (300 MHz, CDCl\(_3\)) \(\delta = 7.40\) (d, 1.9 Hz, 1H), 6.38-6.34 (m,
(s, 2H), 2.33-2.28 (m, 2H), 1.63-1.58 (m, 2H), 1.24 (m, 14H), 0.50-0.45 (m, 2H), 0.06 (s, 167H).\(^{13}\)C \{\(^{1}\)H\} NMR (101 MHz, CDCl\(_3\)) \(\delta = 173.38, 149.69, 143.15, 110.51, 110.43, 57.83, 34.15, 33.34, 29.49, 29.39, 29.26, 29.10, 24.88, 22.97, 17.49, 1.77, 1.51, 0.52, -0.50. \(^{29}\)Si \{\(^{1}\)H\} NMR (60 MHz, CDCl\(_3\)) \(\delta = -21.95\). IR: \(\nu = 1743\) cm\(^{-1}\) (C=O), 1258 cm\(^{-1}\) (C-O).

\(^{1}\)H NMR (33 b) (300 MHz, CDCl\(_3\)) \(\delta = 7.40 (d, 1.9\) Hz, 1H), 6.39-6.35 (m, 2H), 5.05 (s, 2H), 2.33-2.28 (m, 2H), 1.63-1.58 (m, 2H), 1.24 (m, 14H), 0.51-0.46 (m, 2H), 0.06 (s, 77H).\(^{13}\)C \{\(^{1}\)H\} NMR (101 MHz, CDCl\(_3\)) \(\delta = 173.38, 149.69, 143.13, 110.50, 110.41, 57.81, 34.13, 33.32, 29.49, 29.38, 29.25, 29.09, 24.88, 22.96, 17.49, 1.75, 1.51, 0.52, -0.50. \(^{29}\)Si \{\(^{1}\)H\} NMR (60 MHz, CDCl\(_3\)) \(\delta = 7.20, -21.97\). IR: \(\nu = 1742\) cm\(^{-1}\) (C=O), 1258 cm\(^{-1}\) (C-O).

\(^{1}\)H NMR (33 c) (300 MHz, CDCl\(_3\)) \(\delta = 7.41 (s, 1H), 6.39-6.35 (m, 2H), 5.05 (s, 2H), 2.34-2.29 (t, \(J = 7.5\) Hz, 2H), 1.64-1.59 (t, \(J = 7.0\) Hz, 2H), 1.25 (m, 14H), 0.52-0.47 (m, 2H), 0.07 (s, 19H).\(^{13}\)C \{\(^{1}\)H\} NMR (101 MHz, CDCl\(_3\)) \(\delta = 173.36, 149.73, 143.13, 110.50, 110.41, 57.82, 34.11, 33.32, 29.49, 29.38, 29.25, 29.11, 24.88, 22.96, 17.49, 1.51, 0.52, -0.50. \(^{29}\)Si \{\(^{1}\)H\} NMR (60 MHz, CDCl\(_3\)) \(\delta = -21.94\). IR: \(\nu = 1742\) cm\(^{-1}\) (C=O), 1258 cm\(^{-1}\) (C-O).

Table 3-1 Moles and masses used for synthesizing compounds 33 a, 33 b and 33 c and their yields

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Mole required/Mass used</th>
</tr>
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<tr>
<td></td>
<td>32 a</td>
</tr>
<tr>
<td>Compound 3</td>
<td>10 mmol/25 g</td>
</tr>
<tr>
<td>Product (Yield)</td>
<td>33 a (20 g, 80 %)</td>
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</table>
3.4.2 Synthesis of furan-2-ylmethylundecanoatesiloxane-dimethylsiloxane copolymers (34 a, 34 b, 34 c)

Trimethylsilyl-terminated poly(dimethylsiloxane-co-methylhydrosiloxane (32 a, 32 b, 32 c) was separately dissolved in toluene (80 mL) before the addition of Karstedt’s catalyst (180 µL). After 10 min of stirring, compound 8 was added to the reaction flask. The reaction was heated to reflux and stirred overnight. Activated charcoal was added to the mixture after it had cooled to room temperature and the mixture continued to stir for an additional 5 h. The reaction was then filtered through a pad of Celite® using Büchner funnel to yield polymer after rotary evaporation (Table 3-2). $^1$H NMR (34 a) (300 MHz, CDCl$_3$) δ= 7.30 (s, 1H), 6.27 (s, 1H), 5.96 (d, J = 2.5 Hz, 1H), 2.63-2.58 (t, J = 7.5 Hz, 2H), 1.66-1.61 (t, J = 7.2 Hz, 2H), 1.28 (m, 16H), 0.53-0.48 (m, 2H), 0.08 (s, 88H). $^{13}$C { $^1$H} NMR (101 MHz, CDCl$_3$) δ= 140.55, 110.00, 104.47, 33.33, 29.68, 29.56, 29.40, 29.22, 28.04, 27.98, 22.96, 17.50, 1.77, 1.51, 1.03, 0.53, -0.47. $^{29}$Si { $^1$H} NMR (60 MHz, CDCl$_3$) δ= -21.95. IR: ν = 1257 cm$^{-1}$ (C-O).

$^1$H NMR (34 b) (300 MHz, CDCl$_3$) δ= 7.29 (s, 1H), 6.27 (s, 1H), 5.96 (d, J = 2.5 Hz, 1H), 2.64-2.59 (t, J = 7.5 Hz, 2H), 1.66-1.61 (t, J = 7.2 Hz, 2H), 1.27 (m, 16H), 0.53-0.48 (m, 2H), 0.08 (s, 88H). $^{13}$C { $^1$H} NMR (101 MHz, CDCl$_3$) δ= 140.58, 109.99, 104.47, 33.35, 29.68, 29.57, 29.40, 29.20, 28.05, 27.98, 22.96, 17.50, 1.77, 1.51, 1.03, 0.53, -0.48. $^{29}$Si { $^1$H} NMR (60 MHz, CDCl$_3$) δ= -21.95. IR: ν = 1257 cm$^{-1}$ (C-O).
$^1$H NMR (34 c) (300 MHz, CDCl$_3$) $\delta$= 7.29 (s, 1H), 6.27 (s, 1H), 5.96 (d, $J$ = 2.5 Hz, 1H), 2.64-2.59 (t, $J$ = 7.5 Hz, 2H), 1.66-1.61 (t, $J$ = 7.2 Hz, 2H), 1.27 (m, 16H), 0.53-0.48 (m, 2H), 0.08 (s, 20H). $^{13}$C ($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$= 140.58, 109.99, 104.47, 33.35, 29.68, 29.57, 29.40, 29.20, 28.05, 27.98, 22.96, 17.50, 1.77, 1.51, 1.03, 0.53, -0.48. $^{29}$Si ($^1$H) NMR (60 MHz, CDCl$_3$) $\delta$= -21.95. IR: $\nu$ = 1258 cm$^{-1}$ (C=O).

Table 3-2 Moles and masses used for synthesizing compounds 34 a, 34 b and 34 c and their yields

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Mole required/Mass used</th>
<th>Mole required/Mass used</th>
<th>Mole required/Mass used</th>
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</thead>
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<tr>
<td></td>
<td>32 a</td>
<td>32 b</td>
<td>32 c</td>
</tr>
<tr>
<td>Compound 8</td>
<td>10 mmol/25 g</td>
<td>23 mmol/25 g</td>
<td>35 mmol/10 g</td>
</tr>
<tr>
<td>Product (Yield)</td>
<td>34 a (22 g, 88 %)</td>
<td>34 b (23.5 g, 94 %)</td>
<td>34 c (6.8 g, 68 %)</td>
</tr>
</tbody>
</table>

3.4.3 DA Synthesis in the Mould (Elastomers)

To synthesize the silicone elastomers in the mould, the diene and dienophile compounds were dissolved in chloroform and ultrasonicated for 30 min at 35 °C, to produce a homogeneous mixture. After mixing the solvent was removed in vacuo at room temperature and the reaction mixture was added to the mould and put into the oven for 24 h at 60 °C-70 °C in order to form the cross-linked elastomers. This method was applied to the synthesis of all of the elastomers except for the ones involving the tetramethybis[(N-maleimidomethyl)oxy]disiloxane 13 as the dienophile as these elastomers were formed at room temperature over 5 h.
3.4.3.1.1 Appendix

- Synthesized Molecules Characterization

Appendix Figure 1 $^1$H NMR of compound 3
Appendix Figure 2 $^{13}$C NMR of compound 3
Appendix Figure 3 $^1$H NMR of compound 8
Appendix Figure 4 $^{13}$C NMR of compound 8
Appendix Figure 5 $^1$H NMR of compound 5
Appendix Figure 6 $^{13}$C NMR of compound 5
Appendix Figure 7 $^{29}\text{Si}$ NMR of compound 5
Appendix Figure 8. $^1$H NMR of compound 9
Appendix Figure 9. $^{13}$C NMR of compound 9
Appendix Figure 10. $^{29}$Si NMR of compound 9
Appendix Figure 11. $^1$H NMR of compound 13
Appendix Figure 12. $^{13}$C NMR of compound 13
Appendix Figure 13. $^29$Si NMR of compound 13
Appendix Figure 14. $^1H$ NMR of compound 11
Appendix Figure 15. $^{13}$C NMR of compound 11
➤ Model Diels-Alder Adducts $^1$H NMR*

1. Reaction #1

Appendix Figure 16. DA adduct $^1$H NMR of reaction number 1

* Reaction numbers correspond to Table 2-1 and 2-2
Reaction #2

Appendix Figure 17. DA adduct $^1$H NMR of reaction number 2
2. Reaction #3

Appendix Figure 18. DA adduct $^1$H NMR of reaction number 3
3. Reaction #4

Appendix Figure 19. DA adduct $^1$H NMR of reaction number 4
4. Reaction #5

Appendix Figure 20. DA adduct $^1$H NMR of reaction number 5
5. Reaction #6

Appendix Figure 21. DA adduct $^1$H NMR of reaction number 6
6. Reaction #7

Appendix Figure 22. DA adduct $^1$H NMR of reaction number 7
7. Reaction #8

Appendix Figure 23. DA adduct $^{1}$H NMR of reaction number 8
Reaction #9

Appendix Figure 24. DA adduct $^1$H NMR of reaction number 9
8. Reaction #10

Appendix Figure 25. DA adduct $^1$H NMR of reaction number 10
Appendix Figure 26. DA adduct $^1$H NMR of reaction number 11
9. Reaction #12

Appendix Figure 27. DA adduct $^1$H NMR of reaction number 12
DSC Analysis of Model Reactions

1. Reaction #1

Appendix Figure 28. DSC analysis of model reaction number 1

2. Reaction #2

Appendix Figure 29. DSC analysis of model reaction number 2

* The reaction numbers correspond to Table 2-1 and Table 2-2
3. Reaction #3

Appendix Figure 30. DSC analysis of model reaction number 3

4. Reaction #4

Appendix Figure 31. DSC analysis of model reaction number 4
Reaction #5

Appendix Figure 32. DSC analysis of model reaction number 5

5. Reaction #6

Appendix Figure 33. DSC analysis of model reaction number 6
6. Reaction #7

Appendix Figure 34. DSC analysis of model reaction number 7

7. Reaction #8

Appendix Figure 35. DSC analysis of model reaction number 8
8. Reaction #9

Appendix Figure 36. DSC analysis of model reaction number 9

9. Reaction #10

Appendix Figure 37. DSC analysis of model reaction number 10
10. Reaction #11

Appendix Figure 38. DSC analysis of model reaction number 11

11. Reaction #12

Appendix Figure 39. DSC analysis of model reaction number 12
Synthesized Diene polymeric systems Characterization

33 a

Appendix Figure 40°H NMR of compound 33 a
Appendix Figure 41 $^{13}$C NMR of compound 33 a
Appendix Figure 42 $^{29}$Si NMR of compound 33 a
Appendix Figure 43: $^1$H NMR of compound 33 b
Appendix Figure 44 $^{13}$C NMR of compound 33b
Appendix Figure 45 $^{29}\text{Si}$ NMR of compound 33 b
Appendix Figure 46 $^1$H NMR of compound 33c
Appendix Figure 47 $^{13}$C NMR of compound 33c
Appendix Figure 48 $^{29}\text{Si}$ NMR of compound 33c
Appendix Figure 49 $^1$H NMR of compound 34a
Appendix Figure 50 $^{13}$C NMR of compound 34 a
Appendix Figure 51 $^{29}$Si NMR of compound 34a
Appendix Figure 52 $^1$H NMR of compound 34 b
Appendix Figure 53\textsuperscript{13}C NMR of compound 34 b
Appendix Figure 54 $^{29}$Si NMR of compound 34 b
Appendix Figure 55 $^1$H NMR of compound 34 c
Appendix Figure 56 $^{13}$C NMR of compound 34c
Appendix Figure 57 $^{29}$Si NMR of compound 34c
3.4.3.1.2 Vita

Paria Azadi Namin was born in Tehran, Iran on June 29, 1991. Her high school education was completed at Iran high school in Tehran (capital city of Iran) and got her diploma in mathematics in 2008. Later, she obtained her B.Sc. in applied chemistry from one of the prestigious Universities of Iran, Kharazmi University of Tehran in 2015. Afterwards, she applied for M.Sc. in organic chemistry and worked on her thesis under supervision of Prof. Mohammad Saeed Abae at Chemistry and Chemical Engineering Research Center of Iran and completed her M.Sc. in 2017. She began her second M.Sc. in organic chemistry in 2018 under supervision of Dr. Paul Zelisko.
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