

**SILANE BASED RADICAL POLYMERIZATION: FUNCTIONALIZED  
HOMOPOLYMERS AND COPOLYMERS**

**SILANE BASED RADICAL POLYMERIZATION: FUNCTIONALIZED  
HOMOPOLYMERS AND COPOLYMERS**

**By**

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## ABSTRACT

This thesis presents a study on silane based polymerization in two parts.

In Part A, diphenylvinylsilane (**1**) underwent oligomerization with initiation by azo(*bisisobutyronitrile*) (AIBN) or benzoyl peroxide (BPO). The vinyl groups were preferentially consumed under either set of conditions. Several products were isolated; these included oligomers **3**, an AIBN adduct **4**, a dimer **5**, and a trimer **6**. The residual SiH moieties could be subsequently coupled hydrosilylatively with alkynes or vinylsilicones. The efficiency of the radical reactions was very low. 15% starting material was recovered even with 200 mol% of initiating radicals added to the reaction mixture. The relative radical reactivities of the two functional groups is discussed.

In Part B, **1** was radically copolymerized with styrene and methyl methacrylate (MMA). From the results of infrared and <sup>1</sup>H NMR it was determined that **1** participated in copolymerization via a vinyl type polymerization and not in the form of a hydrogen-transfer type polymerization. Residual SiH groups along the backbone of the polymer remained reactive. A vinylsilicone and 9-vinylanthracene were grafted onto the copolymer from MMA and **1** by hydrosilylation and radical methods, respectively.

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## **GENERAL INTRODUCTION**

Hydrosilanes and vinylsilanes are both important silylfunctional materials which are radically active. In this work, we decided to explore the possibility of exploiting the radical reactivity of both types of functional groups when contained on the same molecule.

In the first part of this thesis (Part A), the radical homopolymerization of a hydrovinylsilane is described while in the second part (Part B), the radical copolymerization of a hydrovinylsilane with vinyl hydrocarbon monomers is investigated. In each of these sections a separate introduction, results, discussion, and conclusion will be presented.

## **Part A**

## CHAPTER 1: INTRODUCTION

### 1.1 Radical Chemistry

The beginnings of radical chemistry can be traced back to the early twentieth century with the discovery of the persistent triphenylmethyl radical by Gomberg.<sup>1</sup> Since then there has been a steady increase of interest in this field of chemistry. In the 1920's, the existence of less stabilized alkyl radicals was discovered by Paneth.<sup>2</sup> The origins of organic synthesis via radical reactions began in 1937 with the description of a radical reaction involving the phenylation of aromatic compounds by benzoyl peroxide.<sup>3</sup> In that same year, Kharasch<sup>4</sup> discovered that the anti-Markovnikov addition of hydrogen bromide to alkenes occurs through a chain process involving radicals. The results of these earlier studies were collected by Waters<sup>5</sup> and Walling<sup>6</sup> into two texts of radical chemistry.

Insight into radical chemistry continued into the 1950's and the 1960's and was also compiled into a two volume collection edited by Kochi.<sup>7</sup> The 1970's saw the development of new synthetic methods involving radicals, namely substitution reactions of aromatic compounds.<sup>8</sup> More recently, alkyl radicals have been used in the formation of aliphatic carbon-carbon bonds and also in the synthesis of natural products and other target molecules.<sup>9</sup>

Although somewhat obscured by the shadow of carbon and its overwhelming array of transformations, the chemistry of silicon has become an area of ever-increasing

importance. Two reactions, the direct synthesis of halosilanes<sup>10</sup> and the transition-metal-complex catalyzed hydrosilylation process<sup>11</sup> opened the door to organosilicon chemistry. The direct synthesis made silicones<sup>12</sup> commercially available. Hydrosilylation made thousands of new organosilanes available which, in turn, has led to their further exploitation. From such an abundance of information available,<sup>13</sup> the radical reactivity of silanes is rather a small fraction of the total wealth residing in organosilicon chemistry but nonetheless is an important area of study.<sup>7,14</sup> The other Group IV elements also have significant radical chemistries. Tin, in particular, has been used extensively as a reducing agent.<sup>7,15</sup>

The work to be described in this thesis focuses on the radical behaviour of silicon and carbon. As knowledge of the chemistry of carbon-centered radicals is quite broad, as evidenced by many reviews,<sup>5,6,7</sup> special emphasis in this work will be placed on silicon centered radicals and their chemistry. The chemistry of carbon radicals will also be outlined, but primarily for the subset of carbon-centered radicals that are affected by the presence of a proximal silyl group. These areas will be discussed in turn.

## 1.2 The Nature of Silicon

Silicon is located directly below carbon in group IV of the periodic table. Its ground state configuration is  $1s^2 2s^2 2p^6 3s^2 3d^0$ . Carbon does not possess vacant d-orbitals and this is an important distinction between carbon and silicon. The vacant 3d-orbitals of silicon can be involved in its chemistry and also makes possible the higher coordination states, penta- and hexa-coordination of silicon.

The properties of organosilanes usually depend upon the relative bond strengths and the electronegativity of silicon with respect to the elements to which it is bound and the extent to which the valence p- and empty d-orbitals are involved. Comparisons of the Si and C bond strengths<sup>16</sup> and electronegativities<sup>17</sup> are listed in Table 1-1 and Table 1-2, respectively.

**Table 1-1: Approximate Bond Dissociation Energies**

Si-H (Me <sub>3</sub> Si-H)	339 kJ	C-H	420 kJ
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**Table 1-2: Pauling Scale of Electronegativities**

Si:	1.8	H:	2.1	C:	2.5
-----	-----	----	-----	----	-----

The data in the tables shows that Si-H is weaker than C-H and that silicon is more electropositive than carbon. As a consequence of the relative electronegativity, the polarizations of the two bonds are in opposite directions, Si<sup>δ+</sup>-H<sup>δ-</sup> versus C<sup>δ-</sup>-H<sup>δ+</sup>. These features play an important role in radical reactions of an organosilane, as will be apparent in the ongoing material.

### 1.3 Silicon Centered Radicals

A comparison of the properties of  $\cdot\text{CH}_3$  and  $\cdot\text{SiH}_3$  is given in Table 1-3.<sup>18,19</sup> Unlike the methyl radical, the silyl radical is pyramidal rather than planar (Figure 1-1). The H-Si-H angle is  $111^\circ$  in  $\cdot\text{SiH}_3$  and the unpaired electron possesses 21% s character. An  $\text{sp}^3$  orbital would possess 25% s character. The substitution of H by silyl groups on silyl-centered radicals leads to a change in the structure of these radicals. The methylsilyl radical is similar to a normal silyl radical, however disilyl-substituted silyl radicals are more planar with trisilyl radicals reaching true planarity. The trend toward planarity in disilyl and trisilyl radicals is due to the conjugative interaction between the unpaired electrons and the d-orbitals of silicon or due to the electropositiveness of the neighbouring silicon atoms. Electronegative substituents have the opposite effect. Electron density is reduced at the radical center and the unpaired electron is drawn closer to that center. The end results are an increase in s-character for the orbital and a pyramidal shape for the radical. It is for this reason that the trichlorosilyl radical is nearly tetrahedral.

**Table 1-3: Properties of Carbon and Silicon Radicals**

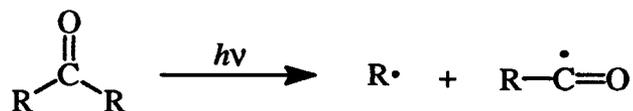
Radical	% s-Character of Unpaired Electron	Bond Angle	Structure
$\cdot\text{CH}_3$	0	$120^\circ$	planar
$\cdot\text{SiH}_3$	21	$111^\circ$	pyramidal



One of the best direct routes to silyl radicals is with silylmercurials,  $(R_3Si)_2Hg$ , but it is a route that would rather be avoided because of the toxicity of mercury compounds. Irradiation of these compounds,  $\lambda_{max} \sim 400$  nm, with ultraviolet or visible light results in decomposition to radicals. Like silylmercurials, azosilanes,  $R_3SiN=N-SiR_3$  can also form silyl radicals upon photolysis.

A direct source of carbon radicals is through the photolytic decomposition of ketones (Scheme 1-2). Similar work on acylsilanes ( $\alpha$ -silyl ketones,  $R_3Si(C=O)Me$ ), was longer in coming because they were difficult to synthesize (only since 1960). Nonetheless, irradiation does lead to silyl radicals.

**Scheme 1-2**

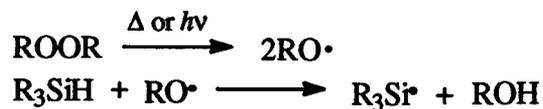


Direct photolysis of alkylhydrosilanes,  $R_3SiH$ , leads to silylenes rather than silyl radicals<sup>20</sup> although hydrosilanes which possess a suitable chromophore such as a phenyl may give silyl radicals.<sup>21</sup> However photodecomposition in the presence of sensitizers such as acetone and benzophenone does lead to silyl radicals.

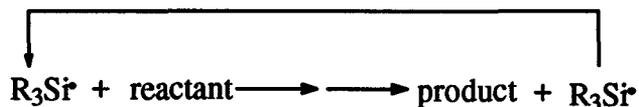
The most common and convenient route to silicon centered radicals is  $H^\bullet$  abstraction from hydrosilanes,  $R_3SiH$ . This method involves an initiator, such as  $ROOR$ , which upon

thermolysis or photolysis yields radicals,  $\text{RO}^\bullet$  abstracts  $\text{H}^\bullet$  to form  $\text{Si}^\bullet$  (Scheme 1-3). The silyl radicals can then take part in a chain process (Scheme 1-4).

### Scheme 1-3

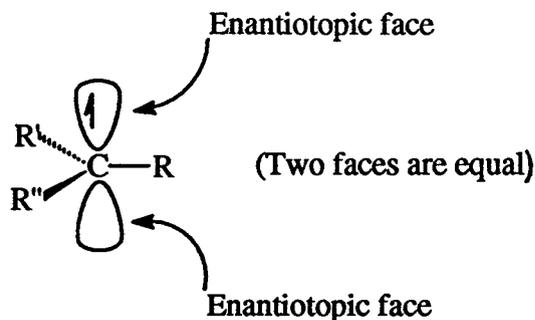


### Scheme 1-4



## 1.5 Stereochemistry

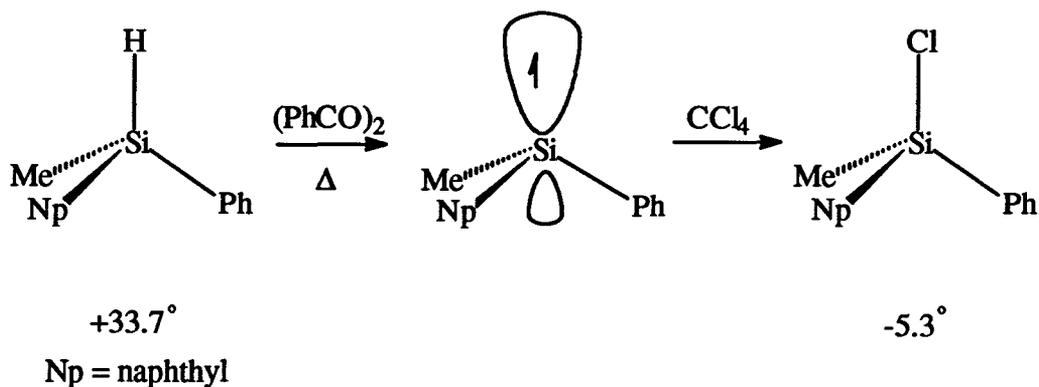
In general, when free radicals are generated at an asymmetric carbon atom, the optical activity of the parent compound is lost and racemic products are formed. The loss of optical activity is due to the planar configuration of carbon radicals (Figure 1-2). As indicated in the drawing, the carbon centered radical is planar and not optically active. Attack from either side is equally likely, leading to racemic (optically inactive) products.



**Figure 1-2**

The question of conformational stability for silyl radicals arises due to their variable geometry; from tetrahedral to pyramidal to near planar. Sakurai and coworkers<sup>22</sup> demonstrated that unlike carbon centered radicals, chiral silyl radicals produced from optically active hydrosilanes undergo chlorine abstraction reactions mostly with retention of configuration. For example, when an optically active hydrosilane such as (+)-methyl(1-naphthyl)phenylsilane was heated in carbon tetrachloride in the absence of any benzoyl peroxide, no reaction took place. However, with the addition of benzoyl peroxide the corresponding chlorosilane, (-)-chloromethyl(1-naphthyl)phenylsilane was formed with substantial (>90%) retention of stereochemistry (Scheme 1-5). Since no reaction occurred without benzoyl peroxide, this is indicative of a chain process involving naphthylphenylmethylsilyl radicals.

Scheme 1-5

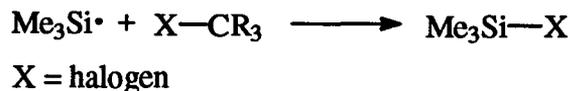


## 1.6 Hydrosilanes

Hydrosilanes ( $R_3Si-H$ ) are remarkably versatile compounds which serve as convenient starting materials for the introduction of silicon-based groups into organic molecules. The relatively weak  $Si-H^{23, 24}$  bond is susceptible to cleavage under ionic, transition metal, or radical conditions.<sup>25</sup> In the latter case, the silyl radicals generated may participate in a variety of chain reactions with olefins, acetylenes and with chlorinated hydrocarbons as described above.

Halogen abstraction<sup>26</sup> by silyl radicals forms silicon-halogen bonds ( $Si-X$ ) that are stronger than carbon - halogen bonds ( $C-X$ ) (Scheme 1-6). This process is exothermic, to the extent of  $\sim 18-25$  kcal/mol.

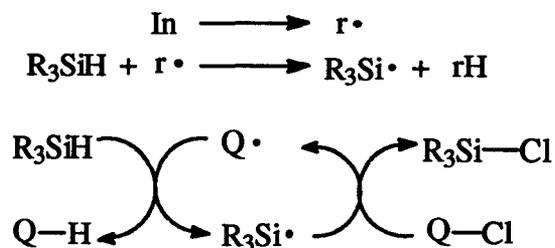
## Scheme 1-6



The origin of this strengthening has been attributed either to  $p_\pi-d_\pi$  back bonding or an increased ionic contribution to bonding. It may be that the increased size of silicon simply facilitates better bonding orbital overlap by reducing lone-pair and bond pair repulsion.

The reduction of halide Q-Cl to Q-H by means of a hydrosilane,  $\text{R}_3\text{SiH}$ , is shown in Scheme 1-7. Silyl radicals in the chain processes are first formed from initiator-derived (In) radicals ( $r^\cdot$ ) by hydrogen abstraction. The chain nature of halogen abstraction proceeds via the chain carriers  $\text{Q}^\cdot$  and  $\text{R}_3\text{Si}^\cdot$ .

## Scheme 1-7



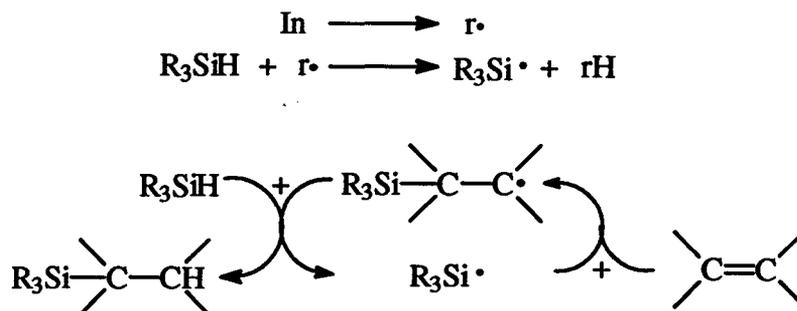
Initiators which are commonly employed include benzoyl peroxide, di-*tert*-butyl peroxide, and azo compounds such as azo(*bis*isobutyronitrile) (AIBN). The stability of the carbon radical plays a decisive role, with the alkyl chlorides being increasingly reactive in the

order tertiary > secondary > primary > CH<sub>3</sub> in the chlorine abstraction step, which is believed to be the rate limiting step. This result is consistent with the general trend that hyperconjugation or resonance stabilization plays an important role, and thus the carbon radicals with increasing stability are formed with increasing ease.

The more synthetically interesting application of radical chain reactions is the hydrosilylation reaction of hydrosilanes with olefins.<sup>27</sup> The term hydrosilylation refers to the addition of a hydrosilane to an olefin. There are two synthetically useful methods for carrying out this reaction; one of these is a silyl radical process. This involves a radical chain process promoted by peroxides, ultraviolet light, high energy radiation or heat. The other method is a transition metal complex-catalyzed process, for example Pt(0) complexes, which involve ligand transfer reactions.

In the former case, the chain nature of the radical hydrosilylation reaction between a hydrosilane and an olefin proceeding through chain carriers  $\cdot\text{CH}_2\text{R}-\text{CH}_2\text{SiR}_3$  and  $\cdot\text{SiR}_3$  is shown in Scheme 1-8.

Scheme 1-8

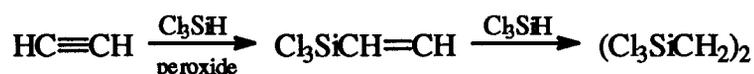


As hydrosilanes are efficient chain-transfer agents, telomerization or polymerization only occurs if the olefin is extremely reactive as with acrylonitrile, methyl methacrylate, and styrene.<sup>7</sup>

Since olefins are normally nucleophilic (electron-rich) in nature, reactions with electrophilic (electron-poor) species are favored. The presence of electron-withdrawing groups on silyl radicals, such as chlorine, increases their electrophilic character. The implication is that halohydrosilanes are more reactive than alkylhydrosilanes which has been shown experimentally: the reactivity of hydrosilanes for peroxide promoted hydrosilylation was found to follow the order  $\text{Cl}_3\text{SiH} > \text{MeCl}_2\text{SiH} > \text{EtSiH}_2 > \text{Et}_3\text{SiH}$ . Phenylhydrosilanes such as  $\text{Ph}_3\text{SiH}$ ,  $\text{Ph}_2\text{SiH}_2$ , and  $\text{PhSiH}_3$  were also found to be quite effective while trialkoxyhydrosilanes was less useful. It should be noted that by varying reaction conditions, hydrosilylation with alkylhydrosilanes can proceed efficiently.<sup>28</sup>

Radical hydrosilylation of silyl radicals to acetylenes is closely related to that observed for olefins. In fact, the same initiators and chain processes are involved. Also, hydrosilane addition can occur once or twice (Scheme 1-9).

### Scheme 1-9



### 1.7 $\alpha$ - and $\beta$ - Silyl Carbon Radicals

Silyl radicals play an integral role as chain carriers in a number of radical processes, as has been described. In addition to silyl radicals, the presence of a silyl group can affect the stability of carbon-centered radicals.  $\alpha$ -,  $\beta$ -, and  $\gamma$ -silyl substituted carbon radicals have a silicon atom in the  $\alpha$ ,  $\beta$ , and  $\gamma$  position from the carbon radical center, respectively (Figure 1-3).

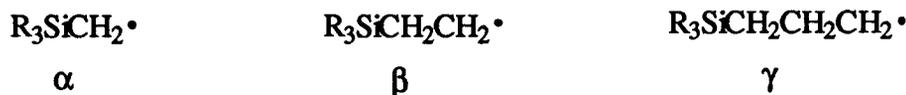
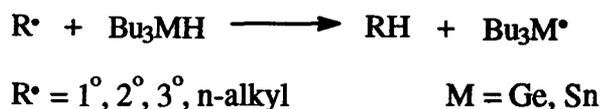


Figure 1-3

Wilt<sup>29,30</sup> has demonstrated that  $\alpha$ - and  $\beta$ - radicals are stabilized by silicon to some extent. In these experiments, the rate of radical H<sup>•</sup> abstraction by silyl stabilized radicals and the rate of formation of silyl stabilized radicals were both examined.

The rates of H<sup>•</sup> abstraction from R<sub>3</sub>GeH and R<sub>3</sub>SnH were determined for Me<sub>3</sub>SiCH<sub>2</sub><sup>•</sup>, Me<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub><sup>•</sup>, and Me<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub><sup>•</sup> (Scheme 1-10). The radical reactivity for hydrogen abstraction was Me<sub>3</sub>SiCH<sub>2</sub><sup>•</sup> > n-alkyl > Me<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub><sup>•</sup> > Me<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub><sup>•</sup>. This order can be explained by examination of the transition state. The  $\alpha$ -radical is most reactive because silicon is able to stabilize the developing negative charge in the transition state, (the  $\alpha$ -effect, Scheme 1-11). An analogy of the  $\alpha$ -effect can be drawn to ionic organosilicon chemistry, where silicon can stabilize the  $\alpha$ -carbanion by negative hyperconjugation of the low lying  $\sigma^*$  orbitals with adjacent full p-orbitals (Figure 1-4).<sup>31</sup> The  $\alpha$ -radical is more reactive than the alkyl radical due to the stabilization of the transition state in the  $\alpha$  case. However, the overall difference is not very large because of the compensatory effects provided by different C-H bond strengths. The C-H bond in SiMe<sub>4</sub> is weaker than the C-H bond in an alkane.

#### Scheme 1-10



## Scheme 1-11

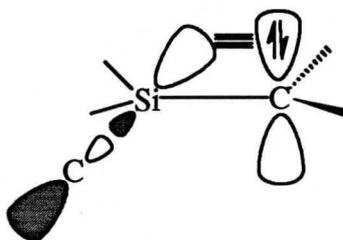
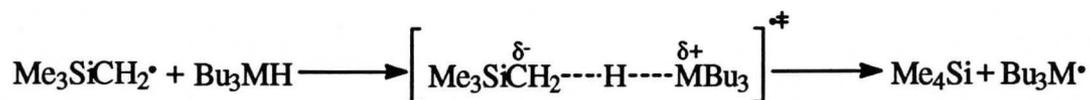
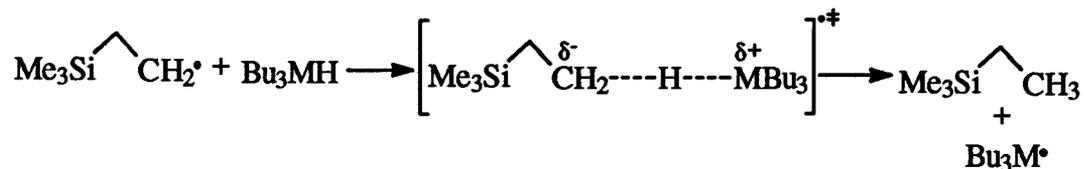


Figure 1-4

The  $\beta$ -radical is less reactive than the  $\alpha$ - or the unsubstituted carbon radical due to two factors. First, the silicon destabilizes the developing negative charge in the transition state (Scheme 1-12) because just as in ionic organosilicon chemistry, the  $\beta$ -effect (Figure 1-5),<sup>31</sup> silicon would favor the development of a positive charge at the radical rather than a negative charge. Consequently, this would tend to inhibit stabilization with the charge dispersed as shown in Scheme 1-12.

## Scheme 1-12



In ionic organosilicon chemistry, the  $\beta$ -effect is the ability of silicon to stabilize and promote the generation of a cation in the  $\beta$ -position due to  $(\sigma\text{-p})\pi$  overlap between the bonding  $\sigma$ - level of the C-Si with the adjacent empty p-orbitals of the carbon (Figure 1-5). Second, the C-H bond formed  $\beta$ - to the silicon atom is weaker than the C-H bond formed in an alkane.

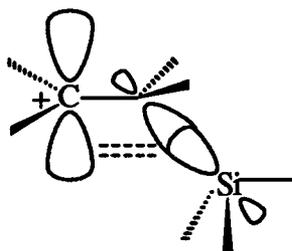


Figure 1-5

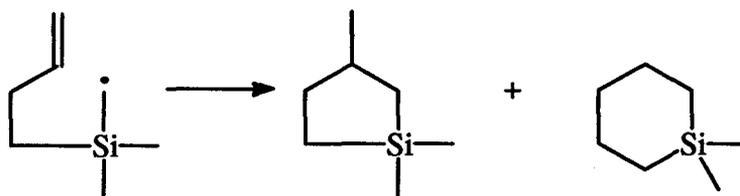
The  $\gamma$ -silyl radical has a reactivity that lies between *n*-alkyl and  $\beta$ . The remoteness of the silicon atom from the radical center suggests no polar or thermochemical effects. Any differences can be attributed to the steric effects from the bulky trimethylsilyl group.

The rate of formation of silyl stabilized radicals were determined by the reaction of  $\text{Me}_3\text{SiCH}_2\text{-Br}$ ,  $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{-Br}$ ,  $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{-Br}$ , and *n*-alkyl with  $\text{Bu}_3\text{Ge}^\bullet$  (Scheme 1-13).<sup>29,30</sup> In the investigation of the rates of formation of the radicals, it is important to consider the (thermodynamic) bond strengths of the C-Br in the starting materials. The  $\alpha$ -radical was the most stable. The  $\beta$ -radical is less stabilized but the C-Br bond strength is reduced. The  $\gamma$ -radical is similar to the alkyl because the silicon is too far to participate in any stabilization ( $\text{Me}_3\text{SiCH}_2\text{-Br} > \text{Me}_3\text{SiCH}_2\text{CH}_2\text{-Br} > \text{Me}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{-Br} \sim n\text{-alkyl}$ ).

### Scheme 1-13



As has been outlined, above  $\alpha$ -silyl radicals can abstract  $\text{H}^\bullet$  atoms. Of more importance to this work is the ability of these radicals to add to vinyl groups (Scheme 1-14).<sup>32,33</sup>

**Scheme 1-14****1.8 Vinylsilanes**

The  $\alpha$ -silyl radical is also involved in the radical polymerization of vinylsilanes. Vinylsilanes ( $R_3Si-CH=CH_2$ ), like hydrosilanes, are important silyl functional materials. These compounds are able to undergo homopolymerization under radical initiation which involves the  $\alpha$ -silyl radical as the propagating intermediate. Bailey and coworkers,<sup>34</sup> examined the reactivity of vinyltrichlorosilane and vinylalkoxysilanes. Vinyltrichlorosilane was found to polymerize through the vinyl group at moderate pressures at 290° C with over 90% conversion. The polymers were of low molecular weight, approximately 645, which consisted mainly of linear tetramers. Lower temperatures led to lower conversions while higher temperatures led to decomposition. High pressures resulted in slightly higher molecular weights, 800-1000. The homopolymerization of vinyltrichlorosilane with peroxide initiators at 50° to 90° C has also been described in patent literature.<sup>35</sup>

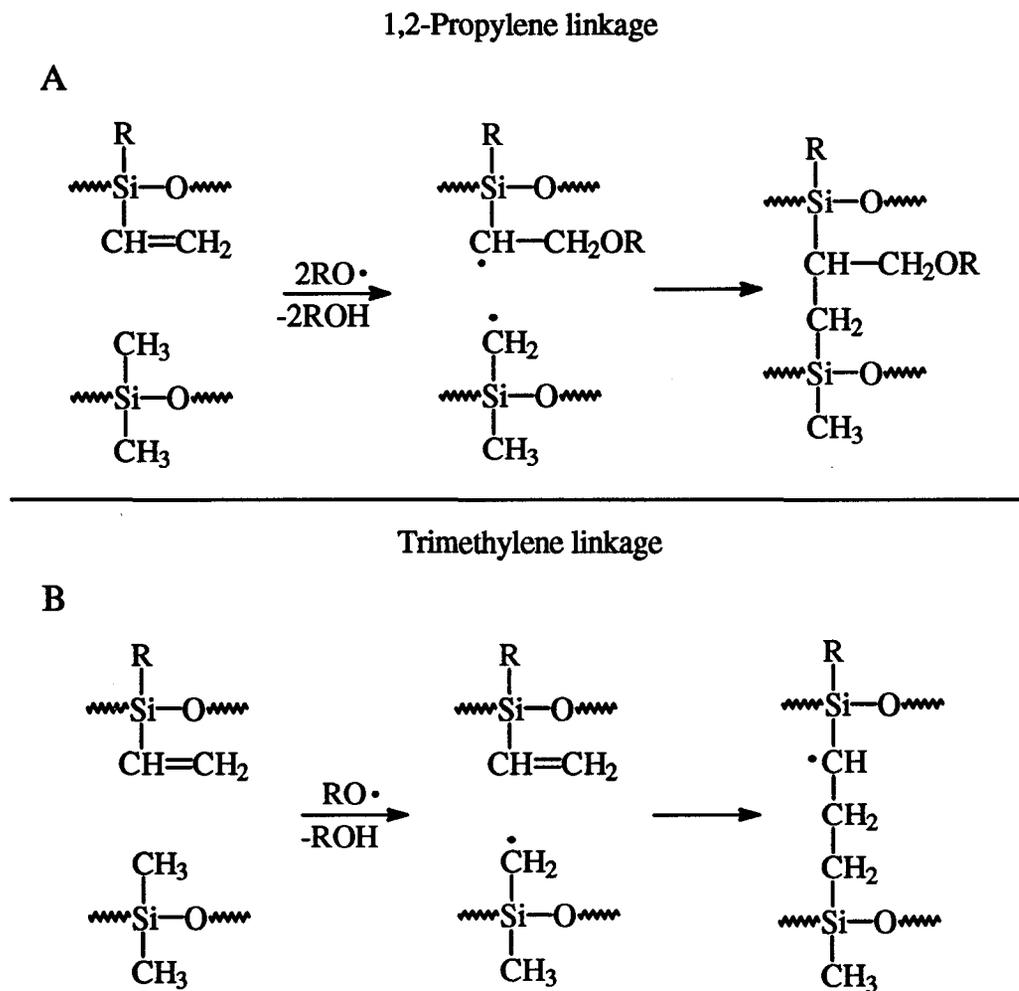
Vinylalkoxysilanes were also found to undergo radical homopolymerizations. These compounds readily polymerize through the vinyl group using peroxide initiators at 130° C

to viscous liquid polymers. Vinyltriethoxysilane polymerizes to give materials with a molecular weight of 5000 to 8000.

Korshak and coworkers<sup>36</sup> investigated the polymerization of a number of vinylalkylsilanes with a radical initiator, di-*tert*-butyl peroxide. Under high pressures, (6000 atm.) at a temperature of 130° C and with up to 3% initiator, only polymers of low molecular weight (1000-3000) were obtained. Even with the most active olefin of those tested, vinyltriethylsilane, the degree of polymerization did not exceed 18.

The radical crosslinking of vinylsilicones is an important technology for forming silicone rubbers.<sup>34a, 37</sup> The mechanism involved may be a vinyl to methyl crosslinking. A peroxide initiator such as di-*tert*-butyl peroxide, may either generate  $\alpha$ -silyl and methylene radicals leading to a 1,2-propylene linkage (Scheme 1-15A) or a methyl radical which adds to the vinyl group forming a trimethylene linkage (Scheme 1-15B).

Scheme 1-15

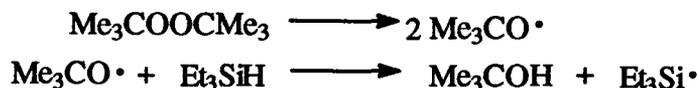


### 1.9 Hydrovinyldisilanes

We are interested in examining the radical reactivity of silane moieties that bear both Si-H and Si-CH=CH<sub>2</sub> functional groups. Previously, the reactivity of hydrovinyldisilanes has primarily been exploited under transition metal catalysis.<sup>38</sup> Thus, Asanuma and

coworkers<sup>39</sup> and Corriu and coworkers<sup>40</sup> have examined the sequential reactivity of hydrovinylnsilanes. The vinyl group was first reacted using Ziegler-Natta copolymerization or hydrosilylation. Subsequent crosslinking through Si-H groups and residual vinyl groups can be induced using hydrosilylation,<sup>39b, 41</sup>  $\gamma$ -radiation<sup>42</sup> or UV radiation<sup>43</sup> or pyrolysis.<sup>40, 44</sup> In these cases, it is difficult to gauge the relative reactivity of the two functional groups in which we are interested, SiH and Si-CH=CH<sub>2</sub>.

The relative reactivity of vinyl- and hydrosilanes under radical conditions can be compared using reaction rates. However, the availability of absolute rate constants for the formation of silyl radicals as well as their reactivity were, for a long time, extremely limited. This, however, changed in the early 1980's with the work of Ingold and coworkers.<sup>45</sup> They initiated a series of kinetic studies using laser flash photolysis techniques on the formation of the triethylsilyl radical by reaction of *tert*-butoxy radicals with triethylsilane. They also examined the decay of the silyl radical by its reaction through halogen abstraction of organic halides,<sup>46</sup> and through additions to ketones<sup>47</sup> and unsaturated compounds.<sup>48</sup> In these experiments, laser light generates the *tert*-butoxy radicals that react with triethylsilane (Scheme 1-16) leading to silyl radicals which in turn can react with other substrates. Similar experiments lead to the absolute constants for the formation of a variety of other silyl radicals, R<sub>3</sub>Si<sup>•</sup> where R can vary among alkyl, alkoxy, Cl, Ph, or H.<sup>49, 50</sup>

**Scheme 1-16**

Ingold and coworkers, through laser flash photolysis, made available some absolute rate constants for radical abstraction of H<sup>•</sup> from SiH and for radical addition to vinyl compounds. This data has been compiled in Landolt-Börnstein edited by Fischer.<sup>51</sup>

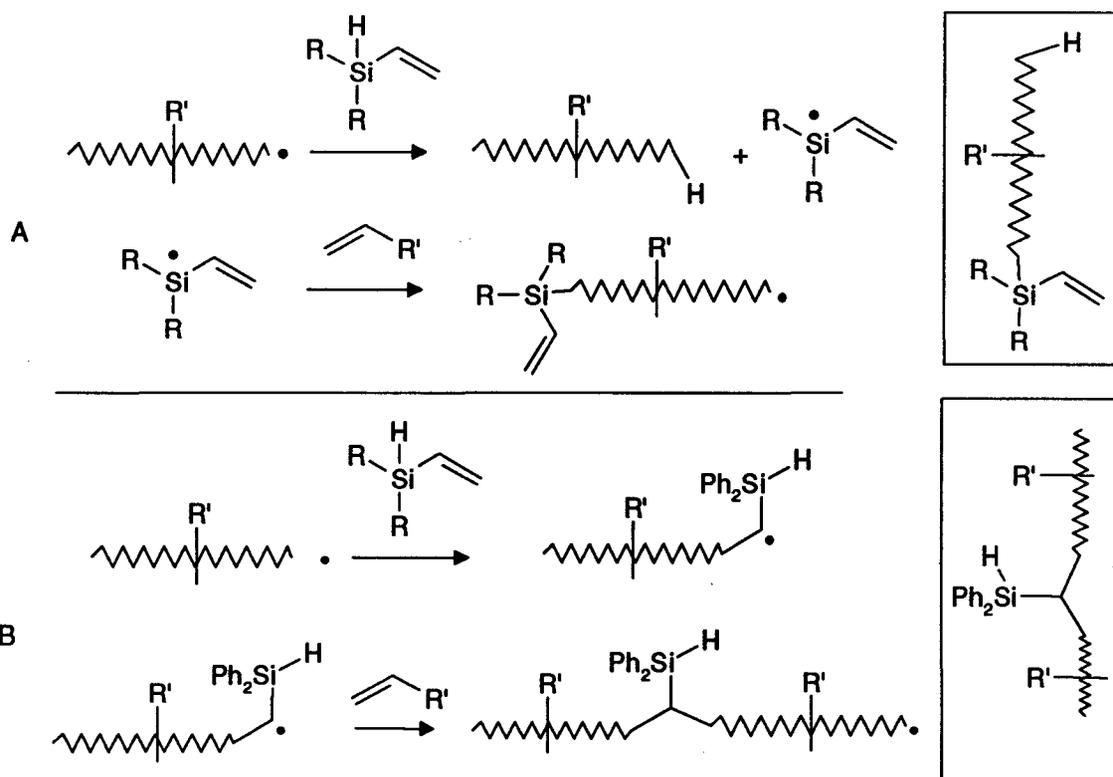
The vinyl group generally reacts more rapidly than the Si-H group under similar conditions. The results of two studies of the radical reactivity of vinylhydrosilanes are consistent with this observation. The  $\gamma$ -ray crosslinking of diethylvinylsilane has been examined by Hayakawa *et al.*<sup>52</sup> and the AIBN catalyzed polymerization of ethylvinylhydrosilane by the group of Iwakura.<sup>53</sup> In both cases, the Si-H group was found to be less reactive than the vinyl group but the structures of the materials were in neither case described in the literature, nor were the products further utilized.

**1.10 Objectives**

If the reactivity of the Si-H and Si-CH=CH<sub>2</sub> groups when on the same nucleus is sufficiently different under radical conditions, it may be possible to use the groups independently in sequential radical reactions. For instance, in a copolymerization one could expect end functionalized polymers if  $k_{\text{Si-H}} \gg k_{\text{Si-CH=CH}_2}$  (Scheme 1-17A), whereas if the relative rates are reversed, a backbone functionalized polymer would result (Scheme 1-

17B). These relative rates may, in turn, be dependent on the nature of the spectator groups on silicon. Our exploration of the relative reactivity of these two functional groups under radical conditions and our exploitation of the resulting products is described below.

Scheme 1-17



## CHAPTER 2: RESULTS

### 2.1 Preparation of Hydrovinylsilane 1

$\text{Ph}_2\text{SiHCH}=\text{CH}_2$  **1** was utilized in this study because of the convenience in following its reactions and the opportunity to modify the electronic demands of the phenyl groups by standard chemistry. Thus, **1** was prepared from  $\text{Ph}_2\text{SiClH}$  in high yield using vinylmagnesium bromide in THF.

### 2.2 Polymerization of 1 using a Platinum Catalyst

As a benchmark for the radical reactivity described below, **1** was hydrosilylatively polymerized using Speier's catalyst ( $\text{H}_2\text{PtCl}_6$ ) in benzene.<sup>54</sup> The resultant white polymer **2** [ $(\text{Ph}_2\text{SiCH}_2\text{CH}_2)_n$ ] had a low molecular weight of  $M_w = 2000$  and a polydispersity of 1.4. Residual SiH groups and  $\text{SiCH}=\text{CH}_2$  groups in a 1:1 ratio could be seen in the  $^1\text{H}$  NMR and  $^{29}\text{Si}$  NMR.

### 2.3 Radical Reactivity of 1

A benzene solution (0.6 M) of **1**, added to a benzene solution of benzoyl peroxide (BPO, 1 mol%), was heated to reflux. Under these conditions, no products could be isolated; >95% of the starting material was recovered.<sup>28</sup> Therefore, much larger initiator loads were used.

The reaction of **1** with 10 mol% AIBN led to 50% product and 50% recovered starting material. Of particular importance for the discussion below is the relative reactivity of the two functional groups (Scheme 2-1, Table 2-1); in the product mix **3**, the ratio of SiH / SiCH=CH<sub>2</sub> groups was 4:1. The low molecular weight species identified in the product mixture are shown in Figure 2-1 and include the interesting AIBN adduct **4**,<sup>55</sup> other incompletely characterized AIBN adducts, hydrosilylative dimers **5**, trimers **6** and higher oligomers. It is important to note that the product was clearly not (Ph<sub>2</sub>SiCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub> based on the spectroscopic, particularly NMR, data.

From the reports in the literature, the rates of abstraction of SiH and addition to SiCH=CH<sub>2</sub> should both be accelerated when oxy rather than carbon based radicals are used. To determine if the relative reactivity of SiH versus SiCH=CH<sub>2</sub> was also affected, the use of a peroxide initiator was attempted. With BPO as the initiator, the molecular weight of the product was the same as for that initiated with AIBN. The product distribution and SiH / SiCH=CH<sub>2</sub> ratio (Scheme 2-1, Table 2-1) were also the same.

Scheme 2-1

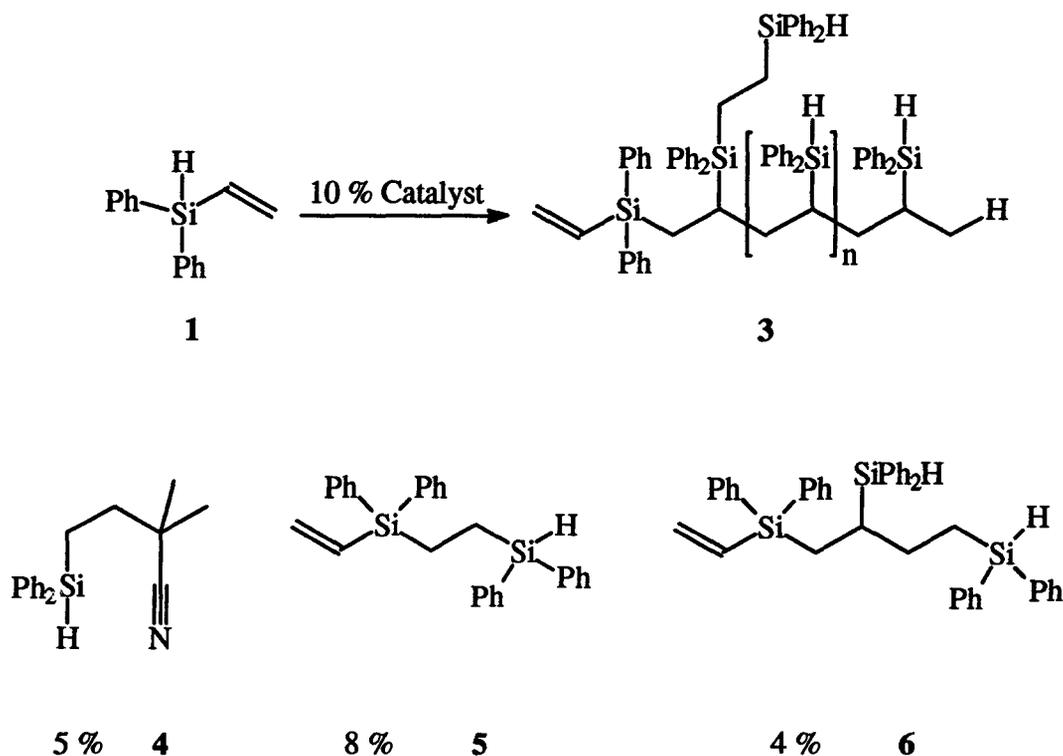


Figure 2-1

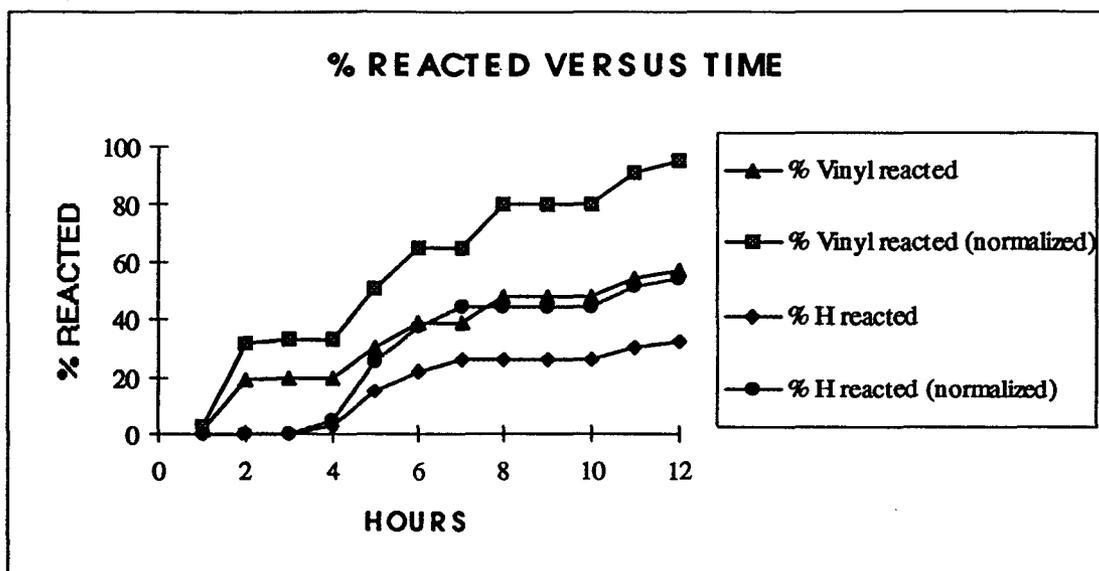
Performing the reaction neat with 10 mol% AIBN, in the hope of increasing the radical chain lengths and, simultaneously, the molecular weight of the product, still led to 20% unreacted starting materials (Table 2-1). The  $M_w$  of the polymeric species was found to be 940, not significantly different from the reaction run at lower concentration. The ratio of residual SiH / SiCH=CH<sub>2</sub> groups was found to be 3.5:1 (49% SiH remained).

### 2.3.1 100% AIBN reaction

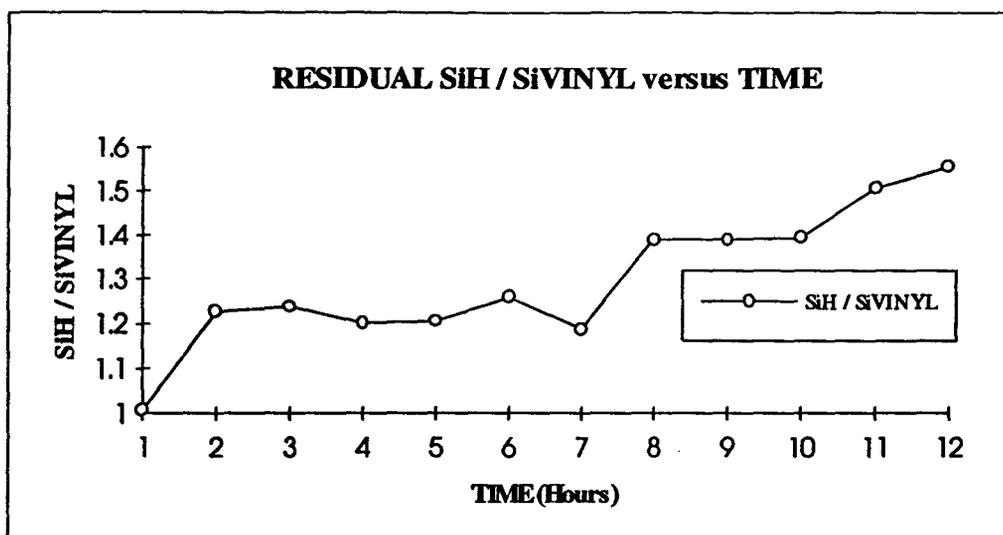
In an attempt to force the reaction to completion, the reaction (0.6 M in benzene) was attempted with 100 mol% AIBN as the initiator. Recovered **1** still accounted for 15% of the product mixture. The ratio of residual SiH / SiCH=CH<sub>2</sub> groups was found to be 3.2:1 (Table 2-1).

### 2.3.2 Slow Introduction of Radical Initiator to **1**

In a further attempt to clarify the relative reactivity of the SiH vs. SiCH=CH<sub>2</sub> groups, the reaction was run with the very slow addition of initiator utilizing a syringe pump. It was hoped that this would minimize termination reactions and facilitate maximum radical chain lengths. A syringe pump was used to add a solution of AIBN (20 mol%) to **1** (0.6 M) over a period of 12 hours. Aliquots were taken each hour. The relative conversion of SiH and SiCH=CH<sub>2</sub> is given in Figure 2-2 and Figure 2-3 (see also Table 2-1). The preferential consumption of SiCH=CH<sub>2</sub> under these conditions as well is clearly demonstrated.



**Figure 2-2:** Plot of the relative reactivity (consumption) of SiH and SiCH=CH<sub>2</sub> groups in the radical reaction of 1 initiated by the slow addition of AIBN with time; raw data  $\diamond$  and  $\Delta$ , respectively, and normalized for recovered starting material,  $\circ$  and  $\square$ , respectively



**Figure 2-3:** Relative reactivity of SiH versus SiCH=CH<sub>2</sub>: Functional Group (SiH/SiVinyl) ratio with time

**Table 2-1:** Effect of Reaction Conditions on the Relative Consumption of SiH and SiVinyl Groups

Initiator	mol%	[1]	SiH unreacted (mol%)	SiVinyl unreacted (mol%)	Ratio unreacted SiH/SiVinyl	Recovered [1] (mol%)
BPO	1	0.6 M	-	-	-	95
AIBN	10	0.6 M	28	7	4:1	50
BPO	10	0.6 M	28	7	4:1	50
AIBN	10	neat	49	14	3.5:1	20
AIBN	100	0.6 M	54	17	3.2:1	15
AIBN <sup>a</sup>	20	0.6 M	31	9	3.4:1	50

<sup>a</sup>added over 12 hours

## 2.4 Laser Flash Photolysis Experiments

Laser flash photolysis experiments<sup>56</sup> were also carried out to obtain information on the reactivity of the SiH and SiVinyl groups. **7** and **8** (Figure 2-4) are models of compound **1** and were synthesized to separately determine the rate of H<sup>•</sup> abstraction by tert-butoxy radicals and the rate of silyl radical addition to vinylsilanes. **7** was prepared from Ph<sub>2</sub>SiClH in good yield using ethylmagnesium bromide in ether and **8** was prepared from Ph<sub>2</sub>SiClMe using vinylmagnesium bromide, also in good yield. In contrast to **1**, **7** has a ethyl group in place of a vinyl group and **8** has a methyl group in place of a hydrogen.

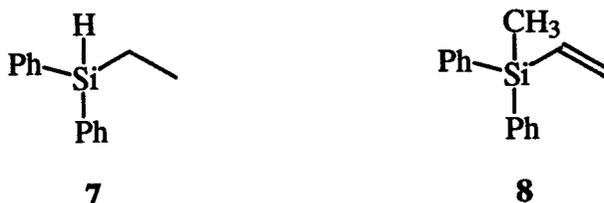
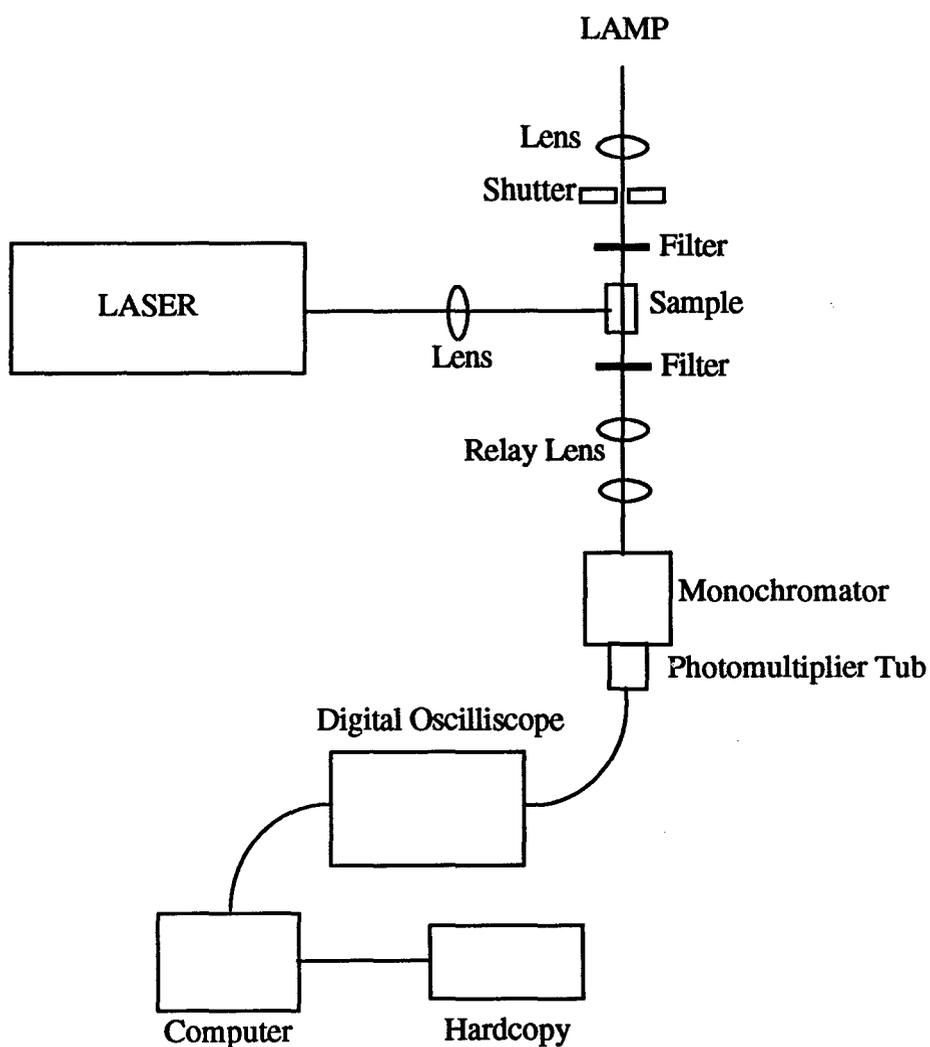


Figure 2-4

### 2.4.1 Laser Flash Photolysis System

The development of laser flash photolysis dates back to the late 1960's. This technique involves the generation of a transient species using an intense laser pulse and the monitoring of this species by absorption or emission. The transient in this work is the silyl radical. Characterization of the short-lived intermediate can be accomplished by examination of its growth and decay traces.

A typical laser flash photolysis system consists of a sample cell, monitoring source, excitation source, lenses and filters, detector, and analysis/output devices (Figure 2-5). The sample cell is made from optical quality quartz which is free from surface defects which could cause interference with optical transmission and clean transient detection. The typical monitoring source is a xenon arc lamp used in conjunction with shutters to prevent undue photolysis of the sample. A window or orifice (1 to 2mm) is used to concentrate the monitoring beam into the sample. The laser serves to excite the sample. Filters decrease the laser dose while lens and mirrors concentrate but do not focus the probe and photolysis beams into the sample. A relay lens and additional filters image the photolysis cross-section onto the detector. Typically the detector consists of a monochromator/photomultiplier tube combination. The monochromator can cover a range of 230-800 nm. The photomultiplier tube which is located at the exit slit of the monochromator converts the light intensity into the corresponding electrical signal. Output from the photomultiplier is then converted to digital form and transferred to a computer for processing. Computer control not only allows for data acquisition and processing but also for greater speed and reproducibility of experiments.



**Figure 2-5**

### 2.4.2 Decay Kinetics of Transient

A representative decay trace of a transient from a laser experiment is shown in Figure 2-6. This plot shows the change in optical density ( $A$ ) which is a function of the transient concentration at a monitoring wavelength versus the time. As is shown in equations 1-4,

the amount of time that it requires the transient to decay to  $1/e$  of the original concentration is the lifetime of the transient. The decay which is usually of first order can be analyzed using linear least squares procedures.

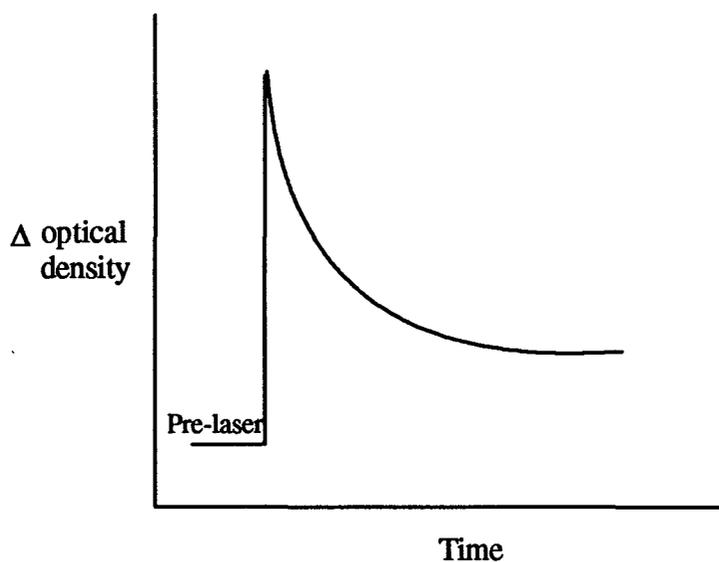
$$A_t = A_o e^{-kt} \quad (1)$$

$$A_t/A_o = e^{-kt} \quad (2)$$

$$\ln A_t/A_o = -kt \quad \text{if } A_t = (1/e)A_o \quad (3)$$

$$1 = k\tau \text{ or } \tau = 1/k \quad (4)$$

The mathematical definition of a transient lifetime in a first order reaction is given by this kinetic scheme. This simplification provides a transient lifetime ( $\tau$ ) in seconds from the inverse of the rate constant.



**Figure 2-6**

### 2.4.3 Growth Kinetics of Transient

The possibility exists that the primary photolysis product does not possess a conveniently measurable absorbance but that one of its reaction products does. In such a case, the growth kinetics as shown in Figure 2-7 of the signal producing transient could be monitored to give kinetic information about its formation and decay of the precursor. As an example, take the hypothetical organic moiety shown in Scheme 2-2 where C does not have a measurable absorbance but D does.

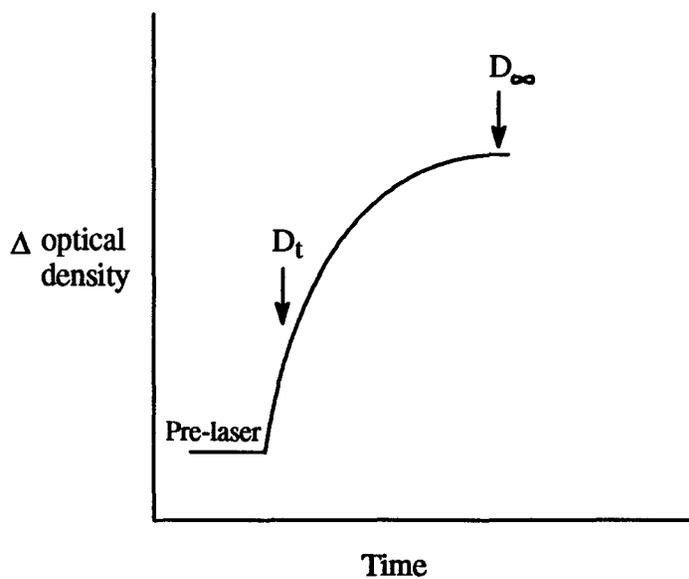


Figure 2-7

## Scheme 2-2



$$k_{\text{expt}} = k_0 + k_x(X) \quad (7)$$

A small increase in the concentration of D can be expressed as a small decrease in the concentration of C multiplied by the fraction of events leading to signal formation.

$$dD = \frac{-k_x(X)}{k_{\text{expt}}} dC \quad (8)$$

Integration gives (9).

$$D - D_0 = \frac{-k_x(X)}{k_{\text{expt}}} (C - C_0) \quad (9)$$

After application of the boundary conditions  $D_0=0$ ,  $C_\infty=0$ , and  $D_\infty=k_x(X)C_0/k_{\text{expt}}$ , the expression of C in terms of first order kinetics  $C=C_0\exp(-k_{\text{expt}}t)$  and rearrangement leads to equation (10).

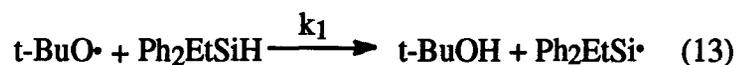
$$\ln \frac{D_\infty - D_t}{D_\infty} = -k_{\text{expt}}t \quad (10)$$

This equation gives the composite rate for the formation of the signal due to D as well as all the modes of decay of C.

#### 2.4.4 Determination of Absolute Rate Constants using Laser Flash Photolysis

In this work, a kinetic study of the growth of ethyldiphenylsilyl radicals by reaction of *tert*-butoxy radicals and decay of ethyldiphenylsilyl radicals by reaction with vinylsilanes was performed using flash photolysis techniques. All the flash photolysis experiments were carried out at 22° C under oxygen free conditions using an excitation wavelength of 308 nm (HCl/Xe/H<sub>2</sub>/He, 15 ns, *ca.* 40 mJ) supplied by an excimer laser. The laser acted to generate *tert*-butoxy radicals by the photodecomposition of di-*tert*-butyl peroxide (Scheme 2-3). This reaction is an instantaneous process. The *tert*-butoxy radicals in turn abstract H• from **7** to generate the silyl radical. The rate constant for the abstraction of H• from **7** by *tert*-butoxy radicals was determined first. The transient absorption due to the peroxide radicals are too weak to be used for kinetic studies. However, the product silyl radicals could be monitored at a single wavelength, λ = 325 nm, because they show a strong absorbance.

#### Scheme 2-3



A representative growth trace of the silyl radical is shown in Figure 2-8. The trace is a plot of the change in optical density *versus* time at a monitoring wavelength of 325 nm.

The kinetic analysis of the growth of the silyl radical leading to the absolute rate constant for the H<sup>•</sup> abstraction by *tert*-butoxy radicals from ethyldiphenylsilane is as shown earlier.

$$-d[t\text{-BuO}^\bullet] = (k_0 + k_1[\text{Ph}_2\text{EtSiH}])[t\text{-BuO}^\bullet] \quad (14)$$

$$d[\text{Ph}_2\text{EtSi}^\bullet]/dt = k_1[\text{Ph}_2\text{EtSiH}][t\text{-BuO}^\bullet] \quad (15)$$

$$d[\text{Ph}_2\text{EtSi}^\bullet] = \frac{k_1[\text{Ph}_2\text{EtSiH}]}{k_0 + k_1[\text{Ph}_2\text{EtSiH}]} d[t\text{-BuO}^\bullet] \quad (16)$$

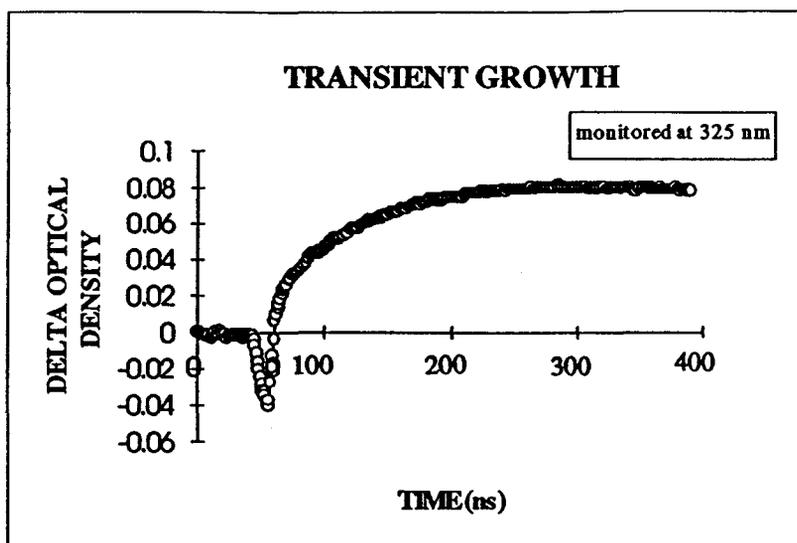
$$\ln \frac{[\text{Ph}_2\text{EtSi}^\bullet]_\infty}{[\text{Ph}_2\text{EtSi}^\bullet]_t} = (k_0 + k_1[\text{Ph}_2\text{EtSiH}])t \quad (17)$$

Since optical density (A) is a function of the transient concentration, substitution gives

(18).

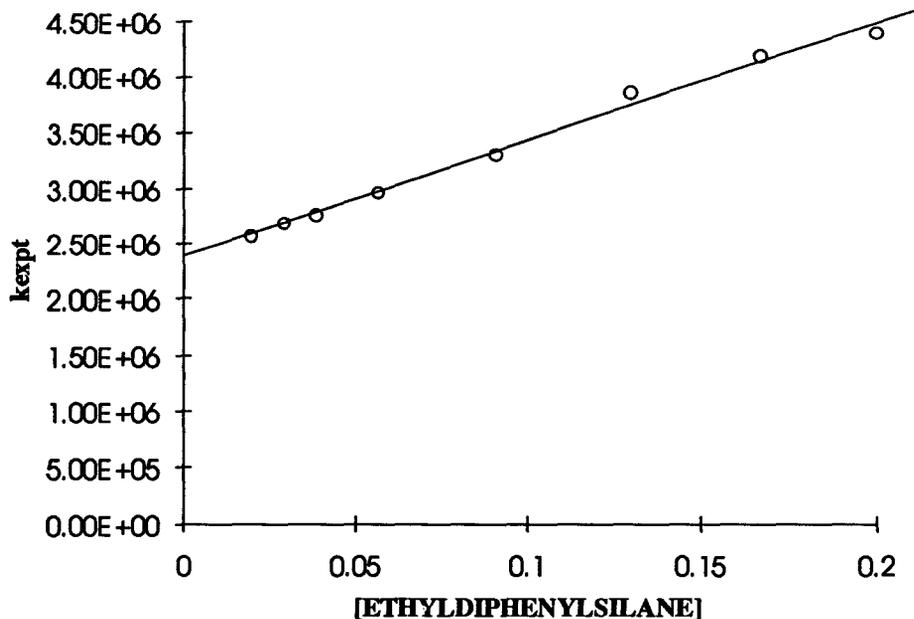
$$\ln \frac{[A]_\infty}{[A]_\infty - [A]_t} = (k_0 + k_1[\text{Ph}_2\text{EtSiH}])t \quad (18)$$

$$k_{\text{expt}} = k_0 + k_1[\text{Ph}_2\text{EtSiH}] \quad (19)$$



**Figure 2-8: Growth Trace of Ethyldiphenylsilyl Radicals**

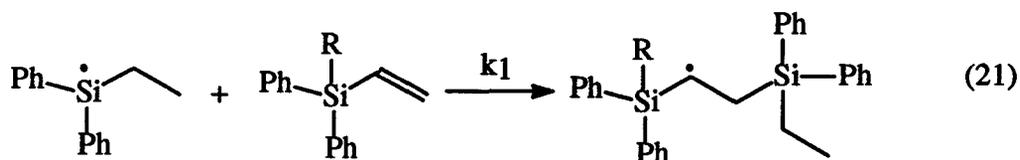
In this analysis  $k_{\text{expt}}$  is an experimental pseudo first order rate constant,  $k_0$  is the rate of *tert*-butoxyl decay in the solvent and  $k_1$  is the absolute rate constant for the reaction of *tert*-butoxyl with ethyldiphenylsilane. Monitoring the time profile of the growth of the silyl radical at different concentrations of the parent molecule,  $\text{Ph}_2\text{EtSiH}$ , led to values for  $k_{\text{expt}}$ . A plot  $k_{\text{expt}}$  versus  $[\text{Ph}_2\text{EtSiH}]$  as shown in Figure 2-9 gives  $k_1$  as the slope and  $k_0$  as the y-intercept. The absolute rate constant for the reaction of *tert*-butoxy radicals with 7 was found to be  $(1.1 \pm 0.1) \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ .



**Figure 2-9:** Evaluation of  $k_1$  for  $H^\bullet$  abstraction from **7** by *tert*-butoxy radicals

In the second part of the kinetic study, the absolute rate constants for the reaction of silyl radicals with **1** and **8** were determined (Scheme 2-4). The silyl radicals were again obtained from **7** by  $H^\bullet$  abstraction from *tert*-butoxy radicals generated from the photodecomposition of di-*tert*-butyl peroxide, but this time the concentration of **7** was high so that the silyl radical would be formed instantaneously.

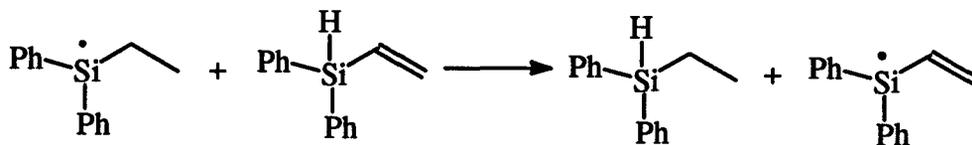
## Scheme 2-4



R = H or Me

In the case where R = H, the reaction of the radical generated from 7 can result in H<sup>•</sup> abstraction to form a second silyl radical from 1 (Scheme 2-5). This reaction can be viewed as a transparent process and thus the absolute rate constant obtained would be due only to the addition of the silyl radical to the vinyl group.

## Scheme 2-5



1

The kinetics of the decay of the silyl radicals were monitored at a wavelength of 325 nm for a series of samples with a variable concentrations of vinylsilane. A representative decay trace is shown in Figure 2-10.

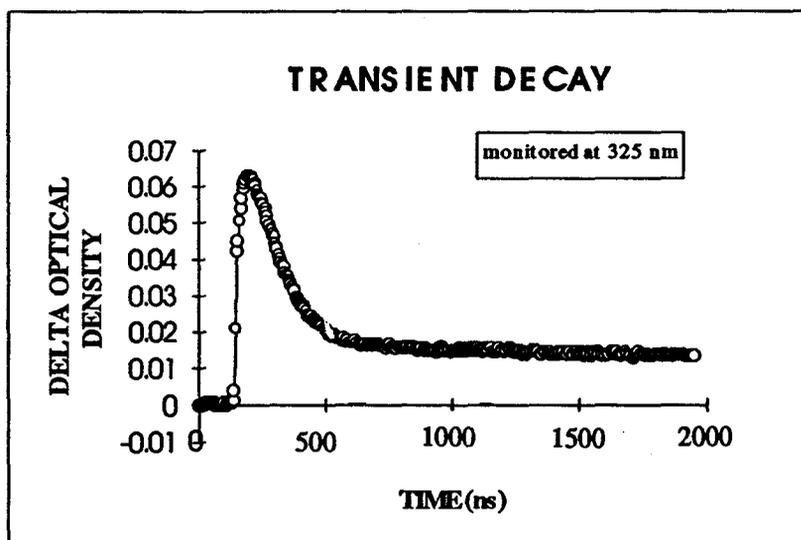


Figure 2-10: Decay Trace of Ethyldiphenylsilyl Radicals

Monitoring the decay of the silyl radical at variable concentrations of vinylsilane led to values for the experimental rate constant,  $k_{\text{expt}}$ . This rate was related to the elementary steps of the reaction according to equation (22).

$$k_{\text{expt}} = k_0 + k_1(X) \quad X=1 \text{ or } 8 \quad (22)$$

The values of  $k_1$  and  $k_0$  were obtained from the slope and y-intercept respectively from a plot of  $k_{\text{expt}}$  versus [vinylsilane]. The value of  $k_1$  was the absolute rate for the additions of

the silyl radicals generated from **7** with the vinylsilanes and the value of  $k_0$  was the rate of decay of silyl radicals. Rate constants for the reactions are summarized in Table 2-2.

**Table 2-2:** Absolute Rate Constants for Addition of Ethyldiphenylsilyl Radicals to Vinylsilanes

substrate	$k_1, M^{-1}s^{-1}$
<b>1</b>	$(4.4 \pm 0.3) \times 10^7$
<b>8</b>	$(3.1 \pm 0.3) \times 10^7$

### 2.4.5 Transient UV Absorption Spectra

Transient species, that is radicals, which contain a suitable chromophore can absorb ultraviolet light just as a reactant or product would and this has only recently been exploited to follow reactions involving reactive intermediates. The lack of previous studies is due to the fact that reactive intermediates are extremely short-lived, which makes them difficult if not impossible to monitor using conventional methods.

Nanosecond time resolved electronics and fast excitation sources allow these experiments to be carried out.

In laser flash photolysis experiments, the principle remains the same as for the absorption of a molecule in that the absorption of light by a chromophore is monitored. The difference here is that before using the UV light the sample is subjected to a very fast laser pulse that produces a transient. This is then exposed to a UV flash lamp where the change in optical density is monitored.

The transient absorption spectra of  $\text{Ph}_2\text{EtSi}^\bullet$  are shown in Figure 2-11. These spectra were obtained by plotting the top optical density from a series of decay traces which were recorded at different monitoring wavelengths against the wavelength at which the decay was measured. The spectra in Figure 2-11 are time resolved, that is, the spectra were taken at different times after the excitation pulse, with time increasing from 1 to 4.

Characteristic absorptions are found for transient species.

Triphenylsilyl radicals,  $\text{Ph}_3\text{Si}^\bullet$ , show a strong absorption band,  $\lambda_{\text{max}}$ , at around 325 nm and a weaker band at a longer  $\lambda$ .  $\text{Ph}_2\text{EtSi}^\bullet$  would be expected to show a similar transient absorption. The spectra in Figure 2-11 show similar absorptions; each possess a  $\lambda_{\text{max}}$  at around 325 nm and a weaker band at a longer  $\lambda$ . It is evident from these spectra that the transient detected is consistent with the phenylsilyl radical. Also, the fact that these spectra have the same appearance at distinct times after the laser pulse indicates that the absorption is due to only one transient, the silyl radical.

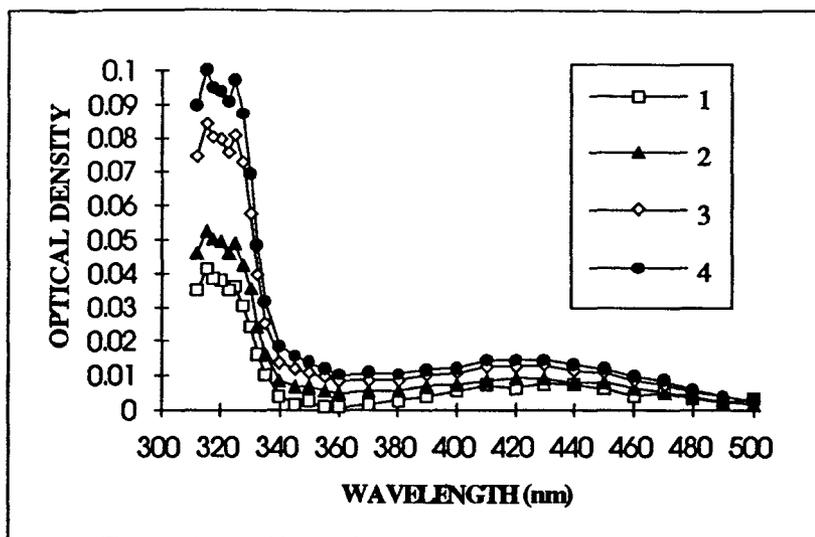
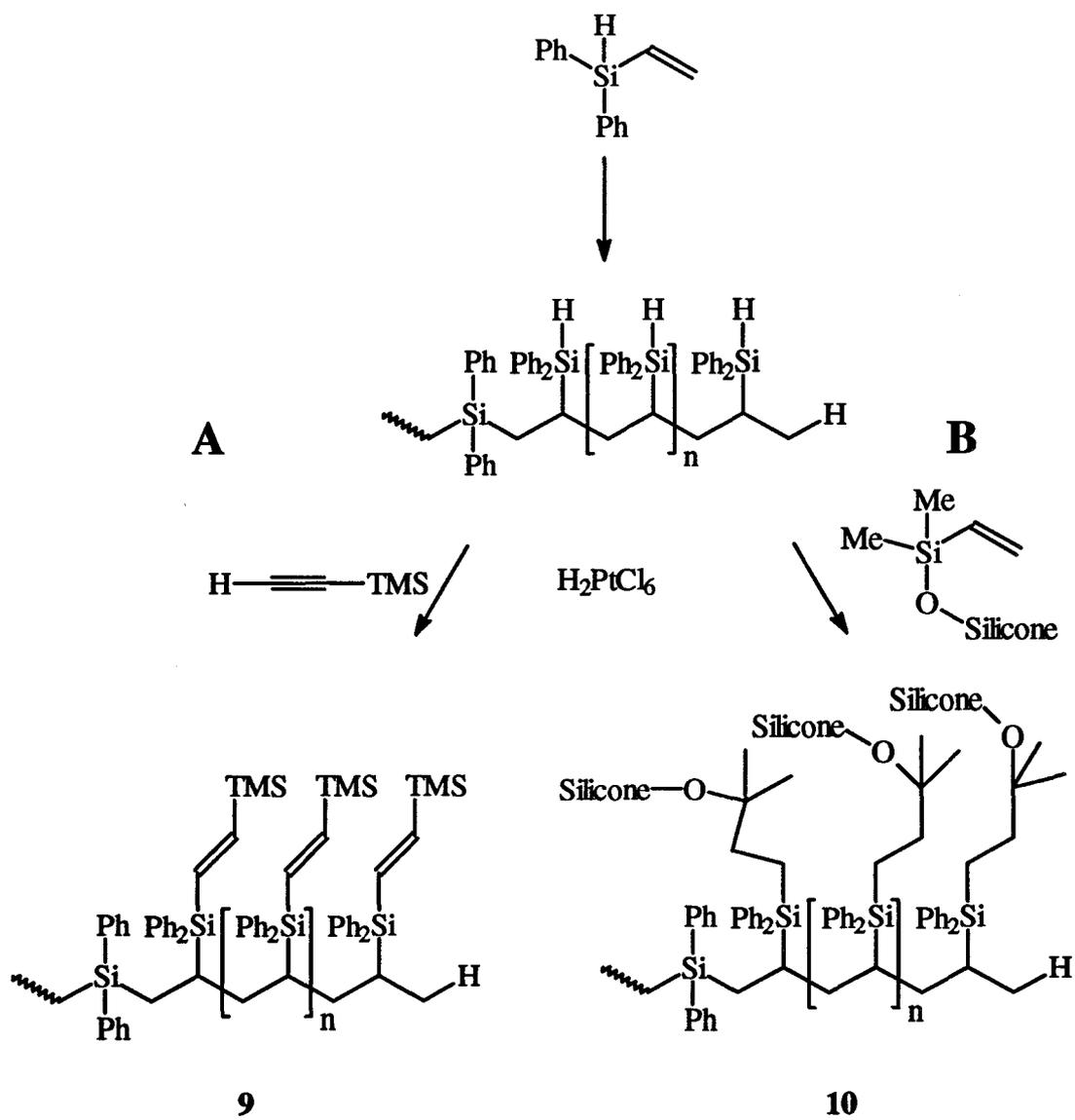


Figure 2-11: Transient Absorption Spectra of  $\text{Ph}_2\text{EtSi}^\bullet$

## 2.5 Hydrosilylation by Si-H Groups

The possibility exists that the preferential consumption of the  $\text{SiCH}=\text{CH}_2$  groups could have arisen because the SiH groups are in some way protected during the reaction. To ascertain that the SiH groups remaining after the radical reaction retain their reactivity, the hydrosilylation of these groups was performed. The  $\text{H}_2\text{PtCl}_6$  catalyzed reaction of **3** with  $\text{HC}\equiv\text{CSiMe}_3$  led to complete conversion of the SiH groups to an oligomeric vinylsilane species **9** (Scheme 2-6A); similarly, hydrogen-terminated silicones reacted quantitatively to form comb type silicone oligomers **10** (Scheme 2-6B), demonstrating that the SiH groups remain available for reaction throughout the radical process.

Scheme 2-6



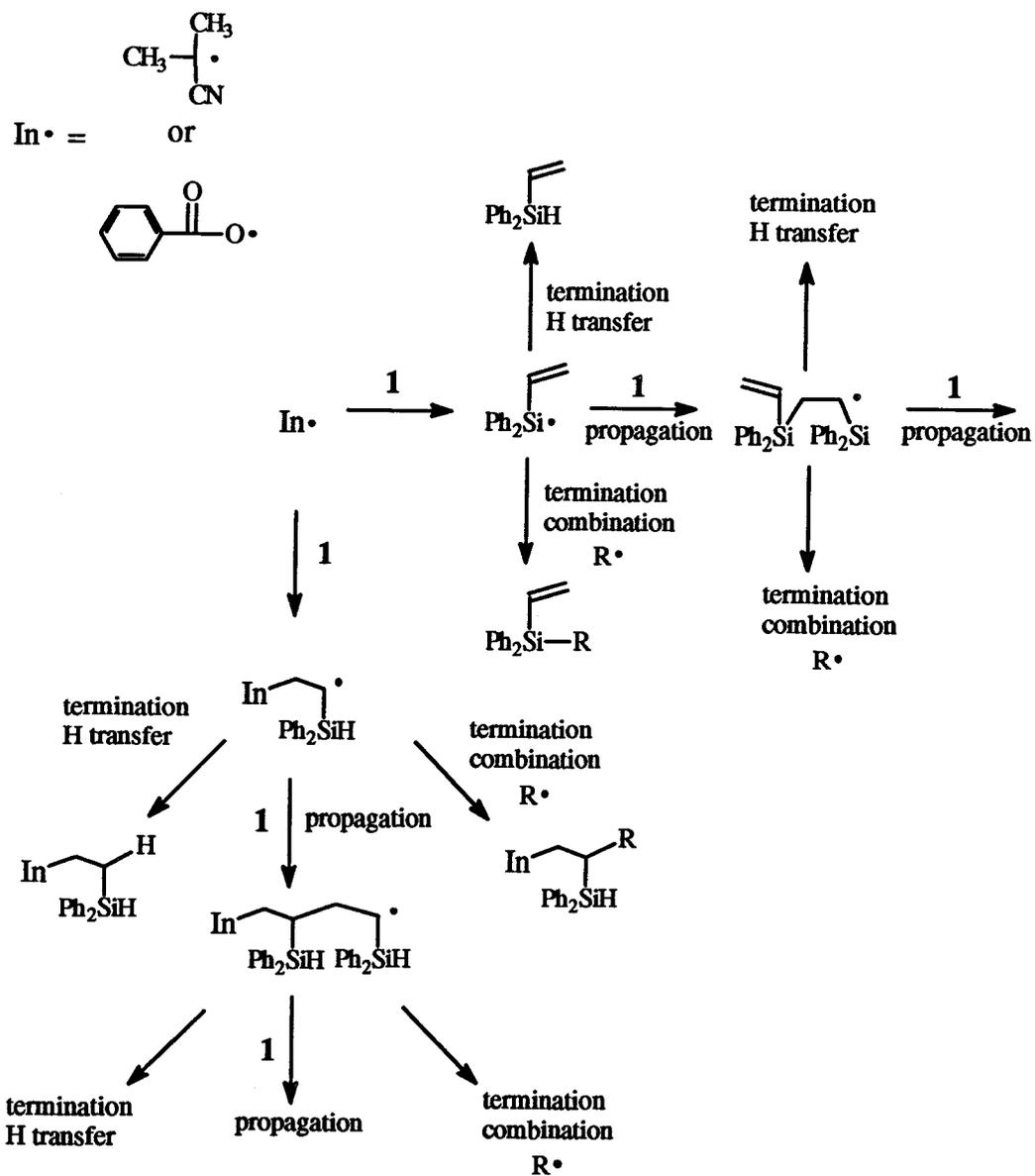
## CHAPTER 3: DISCUSSION

### 3.1 Relative Reactivity of Radicals

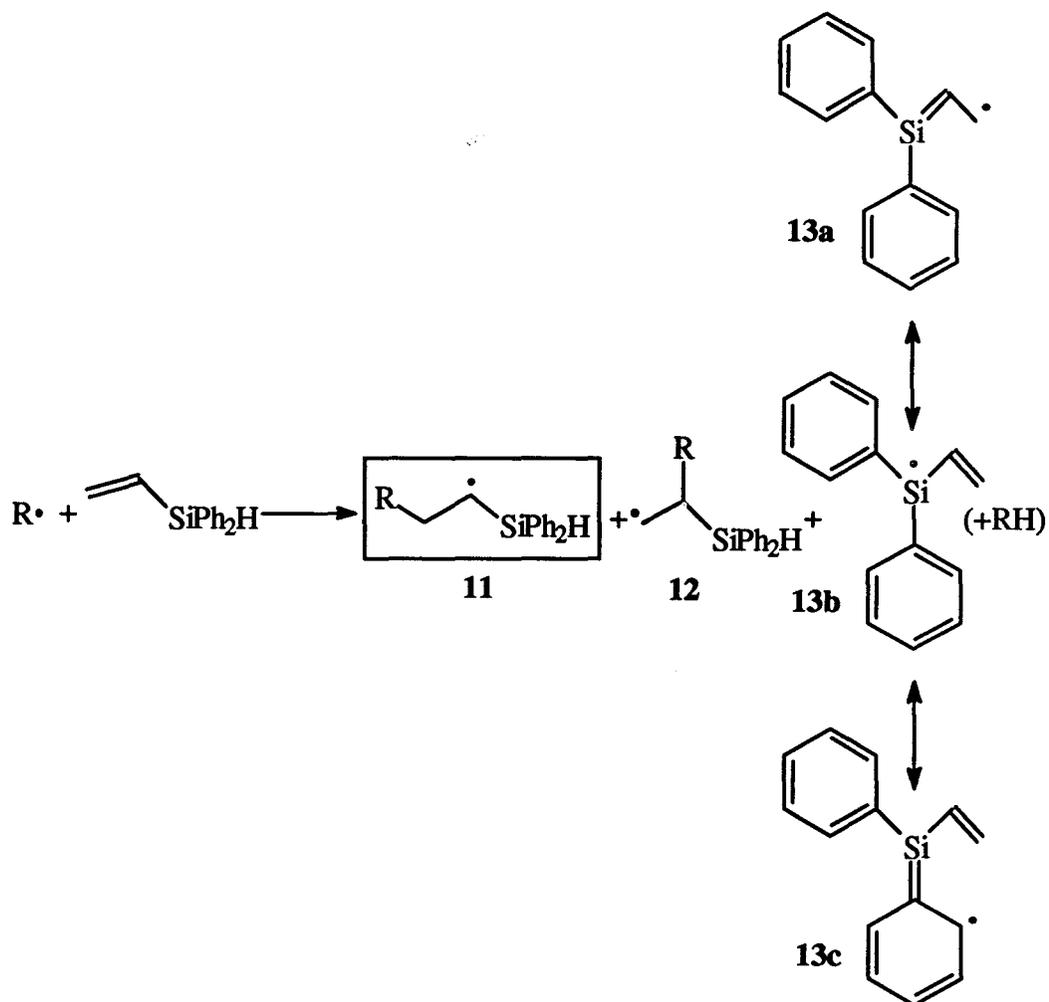
In the radical activation of **1** with AIBN or BPO, a variety of radical entities as shown in Scheme 3-1 are possible. Each radical entity has the possibility of propagating or terminating through H transfer or radical combination. The radicals (Scheme 3-2) may be divided into two classes, carbon- **11**, **12** or silicon-based **13**. The relative reactivity of these will be discussed in turn.

Wilt has demonstrated that  $\alpha$ - and  $\beta$ -silyl carbon-based radicals are stabilized with respect to the all carbon systems, whereas the  $\gamma$ -radical is of comparable reactivity.<sup>29, 30</sup> In the reaction of **1** with an initiating or propagating radical, addition to the  $\beta$ -silyl position of the olefin leading to an  $\alpha$ -silyl carbon radical was preferred (Scheme 3-2) as shown by the formation of **4** and the other products. In addition to the electronic effect of the silyl group, this regiochemical preference results from the greater relative stability of 2° versus 1° radicals and the ease of addition to the  $\beta$ -silyl position on steric grounds (*vide infra*). The tendency for radical addition to the  $\beta$ -position has previously been noted.<sup>55</sup>

Scheme 3-1



Scheme 3-2



The silicon based radical **13** produced by abstraction of  $\text{H}^\bullet$  from  $\text{R}_3\text{SiH}$  will, in contrast, not be particularly stabilized; the resonance structures which contribute to the stability of the analogous carbon system require invoking the comparatively unstable silenes **13 a-c** (Scheme 3-2).<sup>27a, 50</sup>

These reactivity trends are apparent from the reaction rates of H<sup>•</sup> abstraction from Et<sub>3</sub>SiH when compared to the radical addition to vinylsilanes. A primary carbon radical abstracts H<sup>•</sup> from Et<sub>3</sub>SiH with a rate constant of  $7 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$  whereas *t*-butyl radical addition to vinyltrimethylsilane is only slightly faster at  $k = 9.6 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ .<sup>57</sup>

Corresponding reactions between peroxy radicals and hydrosilanes are somewhat faster.

The abstraction from Et<sub>3</sub>SiH by *t*-BuO<sup>•</sup> occurs with a rate constant of  $k = 5.4 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ .

<sup>1,4</sup> Laser studies in this work showed that H<sup>•</sup> abstraction from **7** by *tert*-butoxy radicals occurred at a faster rate than for carbon centered radicals, but was slower than the rate of silyl radical addition to the vinyl group in **1** and **8**. The faster rate of radical addition to **1** as compared to **8** can be attributed to the greater steric congestion provided by the methyl group.

### 3.2 Reactivity of SiH versus SiVinyl

The experimental evidence outlined above clearly indicates the enhanced reactivity (consumption) of the vinylsilane with respect to the hydrosilane functionality. However, these results clearly indicate that the radical chains of both the silyl based radical formed from abstraction of SiH and the carbon based radical formed from the radical addition to a vinylsilane are extremely short. At 0.6 M of **1**, with 20 mol% of initiating radicals, 50% of the starting material was recovered. This was not a result of the rapid termination of chains due to high radical concentrations. Adding the initiator over 12 hours did not

increase the conversion. Even in the case of 100 mol% AIBN addition, 15% starting material was recovered.

Given these relative rates, the results of Iwakura are somewhat surprising.<sup>53</sup> His group has examined the radical reactivity of some vinylsilanes. They observed that  $\text{PhSiH}_2\text{CH}=\text{CH}_2$  underwent oligomerization with AIBN or  $\text{H}_2\text{PtCl}_6$  catalysis; the former gave an oil, the latter a soluble polymer. Otherwise, no characterization of the materials was reported. Copolymerization of this and related species with styrene apparently occurred strictly through the vinyl group; residual  $\text{SiH}_2$  groups could be observed spectroscopically and chemically cleaved from the copolymer.

The isolation of small molecules in this work also points to the vinyl group being more reactive. There were several interesting products from the reaction of **1** with AIBN and BPO. In particular, the presence of **4** is extremely interesting. It results from the addition of  $\text{Me}_2\text{C}^\bullet\text{CN}$ , obtained from the thermal decomposition AIBN, to **1** followed by the intermolecular abstraction of  $\text{H}^\bullet$  from an  $\text{SiH}$  group (Figure 3-1). The yield of this product is 5%. However, based on the 10 mol% AIBN (20 mol% radicals) added, this constitutes a 25% yield. We are currently trying to optimize this yield. In addition, hydrosilylation products with and without telomerization are observed. Thus, the dimer **5** and the trimer **6** were isolated in 8% and 4% yields, respectively. The remaining products were oligomeric, from the  $^1\text{H}$  NMR spectral data they are predominantly oligomers of the vinyl group with possible branching through silicon **3**. Radical hydrosilylation would lead to 1:1 consumption of the hydrosilane and vinylsilane functionalities while vinyl

oligomerization would exclusively lead to vinyl consumption. Although radical hydrosilylation had undoubtedly occurred, spectral evidence shows greater vinyl consumption, an indication that vinyl oligomerization had preferentially taken place. The lower reactivity of the SiH group as compared to the SiVinyl was probably due to electronic rather than steric effects (Scheme 3-2).

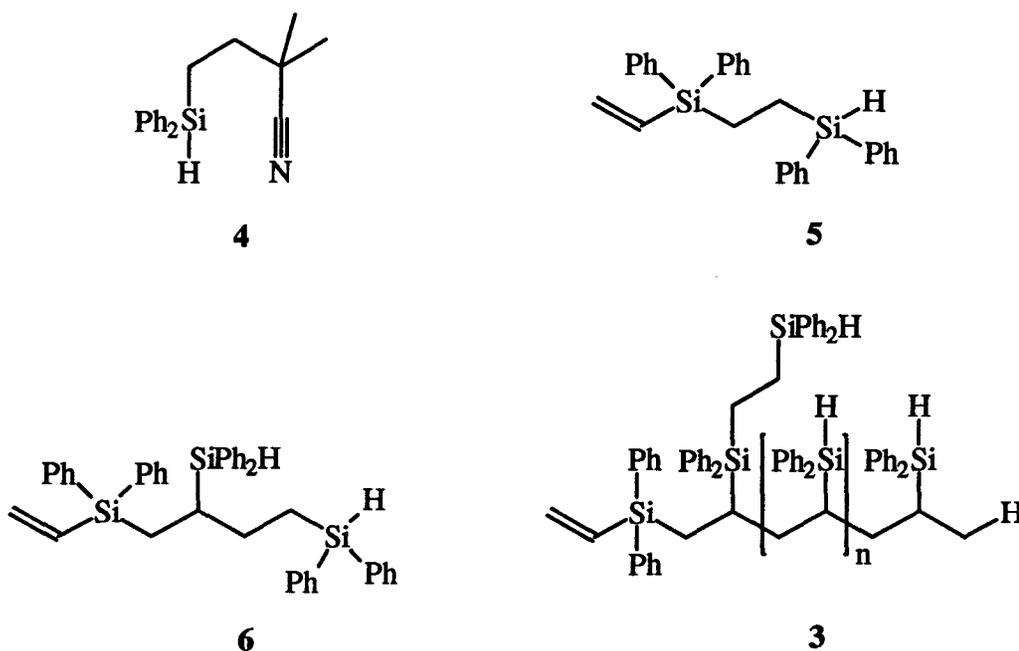


Figure 3-1

### 3.3 Persistence of Carbon Radicals in Polymerizations

Generally vinylsilanes do not polymerize easily under radical conditions, as judged by the relatively harsh conditions necessary to get only reasonably high molecular weight

materials and the necessity, furthermore, of having electron-withdrawing groups on silicon ( $R_3SiCH=CH_2$ ,  $R = Cl, OMe$ ); vinyltrialkylsilanes react only sluggishly under radical conditions.<sup>34, 35, 36</sup>

This was the case in our study; the hydrovinylsilane **1** did not polymerize very well. In the vinylsilanes, the major problem is radical persistence. The carbon centered radical is not persistent enough to maintain propagation as in styrene, methyl methacrylate, etc. The  $\alpha$ -silyl group cannot sufficiently stabilize the propagating radical. As a result, termination predominates. Termination most likely occurs through combination as opposed to H transfer because combination is a faster process. Combination is a diffusion controlled process whereas H transfer to silicon or carbon centered radicals is not. Increasing the persistence of the propagating radical could make the polymerization of vinylsilanes more efficient. The radical could be made more persistent by placing a stabilizing group, such as a phenyl,  $\alpha$  to the silicon which would provide resonance stabilization in the propagating chain (Figure 3-2).

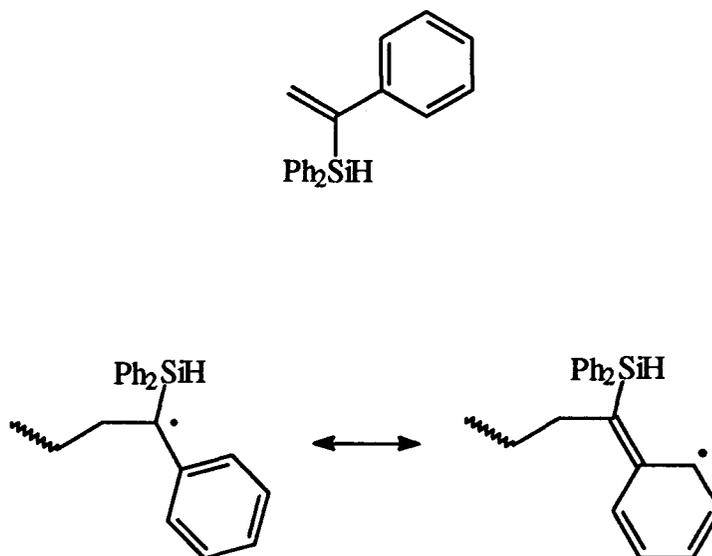


Figure 3-2

### 3.4 Hydrosilylation by SiH Groups

The consumption of the  $\text{SiCH}=\text{CH}_2$  groups in the radical reactions of **1** resulted in oligomers with SiH groups along the backbone. These residual SiH moieties could subsequently be hydrosilylatively coupled with an alkyne or a vinyl terminated silicone giving **9** and **10**, respectively. Since the SiH groups retained their reactivity, this is an indication that the preferential consumption of the  $\text{SiCH}=\text{CH}_2$  groups under radical activation could not have arisen because the SiH groups were some way protected during the reaction.

### 3.5 Concluding Remarks

Under radical activation, the reactivity of the SiH is lower than that of the SiCH=CH<sub>2</sub> group in hydrovinylnsilanes. In these radical reactions several interesting species were isolated; these included the AIBN adduct **4**, the dimer **5**, the trimer **6** and oligomers **3**. Moreover, the SiH groups in the oligomers retained their reactivity. The platinum catalyzed reactions of **3** with HC≡CSiMe<sub>3</sub> and vinyl terminated silicones led to complete conversion of the SiH groups to oligomeric vinyl silane species **9** and comb type silicone oligomers **10**.

**Part B**

## CHAPTER 4: INTRODUCTION

### 4.1 Silicon in Polymers

The introduction of silicon into polymers can lend unique characteristics to the materials produced, which lends credibility to the suggestion that silicon is not merely “carbon with a higher atomic number.” The past decade has witnessed rapid growth in the number of structural types of silicon based polymers available and the understanding of the special role that silicon plays in these materials.<sup>58</sup> Silicon containing polymers can include linear siloxane polymers  $(-\text{SiRR}'\text{O}-)_n$  with various alkyl and aryl side groups, sesquisiloxane polymers having a ladder structure, siloxane-silarylene polymers  $[-\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2(\text{C}_6\text{H}_4)_m-]_n$ , in which phenylenes are either *meta*- or *para*-substituted, silalkylene polymers  $[-\text{Si}(\text{CH}_3)_2(\text{CH}_2)_m-]_n$ , polysilanes  $[-\text{SiRR}']_n$ , polysilazanes  $[-\text{SiRR}'\text{NR}''-]_n$  and so on.

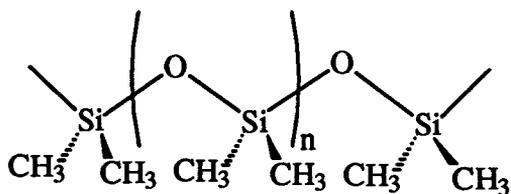
The presence of silicon in the structure of these polymers has an effect on the properties of the materials; including flexibility (poly(dimethylsiloxane) (Figure 4-1) has one of the lowest glass transition temperatures ( $T_g$ ) known for any polymer<sup>†</sup>), glass transition temperature, thermal stability and permeability to gases such as oxygen. These properties have led to variety of applications for silicon containing polymers which include

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<sup>†</sup> The  $T_g$  is the temperature at which amorphous or crystalline thermoplastics, that are glassy at low temperatures, change to a rubbery elastomer or flexible plastic.

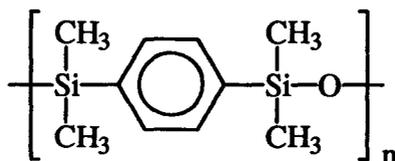
high performance fluids, elastomers, coatings, surface modifiers, separation membranes, photoresists, soft contact lenses, body implants and ceramics to name a few.

To a large degree, the different properties of polymers and their end use depends on their  $T_g$ . The low  $T_g$  for poly(dimethylsiloxane) (Figure 4-1) is the result of extraordinary chain flexibility. This flexibility may be attributed to three factors. First, the Si-O bond (1.64 Å) is significantly longer than the C-C bond (1.54 Å); steric congestion is diminished as a result. This circumstance is generally true for inorganic and semi-inorganic polymers. Almost any single bond involving inorganic atoms (Si-Si, Si-C, Si-N, P-N) is longer than the C-C bond. Second, the Si-O-Si bond angle is much more open than the usual tetrahedral bond of approximately  $110^\circ$ ; angles from  $120^\circ$ - $180^\circ$  have been observed. Finally, the oxygen atoms are not sterically encumbered by side groups. Siloxane polymers have a higher permeability to gases than most other elastomeric materials and as a result have been of interest for use as gas separation membranes.



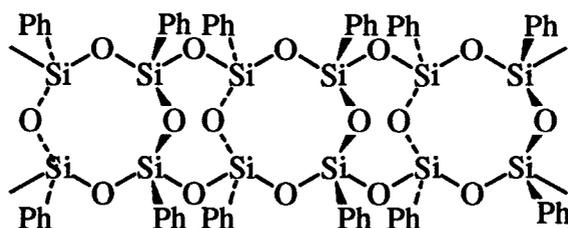
**Figure 4-1**

The introduction of arylene rings, the siloxane-arylene polymers (Figure 4-2), increases the rigidity of the backbone leading to an increase in the  $T_g$  and/or giving rise to crystallinity and thermal stability.



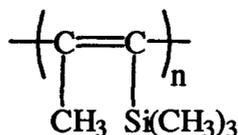
**Figure 4-2**

One incentive to develop polymers with inorganic backbones was the belief that they would display thermal stability at high temperatures as compared to organic polymers.<sup>59</sup> Polyorganosiloxanes resist oxidation at temperatures up to 200°- 250° C. Also, silicone ladder polymers (Figure 4-3), in which the silicon atom is able to form bonds in a ladder like structure which restricts the motion of the Si-O bonds in the backbone, lead to materials which are thermally stable up to 300° C.



**Figure 4-3**

The incorporation of silyl groups into organic polymers also affects their properties. For instance the presence of a trimethylsilyl group,  $\text{Si}(\text{CH}_3)_3$  as a side chain in an acetylene repeat unit in silalkylene polymers such as poly(1-trimethylsilyl-1-propyne) (Figure 4-4) leads to high gas permeability.<sup>60</sup>



**Figure 4-4**

Considering the properties silicon can impart to carbon-based homopolymers, it would be desirable to incorporate silicon-containing monomers in copolymerizations.

Copolymerizations with silicon monomers could introduce sufficient chain irregularity to make the polymer inherently noncrystallizable or add functional groups such as vinyl or hydrogen to the polymer backbone which would allow for further elaboration of the

polymer structure.<sup>58</sup> Studies have shown that radical copolymerizations of vinyl silanes with organic vinyl monomers lead to copolymers that are thermally stable,<sup>61, 62</sup> have enhanced elasticity,<sup>37b, c</sup> and can be used as lubricant additives<sup>62</sup> or insulators.<sup>63</sup>

#### 4.2 Copolymerization of Vinylsilanes with Various Organic Vinyl Monomers

The radical copolymerization of vinyl derivatives of silicon such as vinylsilicones, vinylhalosilanes, vinylalkoxysilanes, vinylsiloxanes, vinylalkylsilanes as well as vinylhydrosilanes have been studied. Hurd and coworkers as well as other groups examined the reactivity of vinylsilicones.<sup>62, 63, 64</sup> The starting silicones were prepared by the hydrolysis of vinylchlorosilanes. For example, methylvinylpolysiloxane (Figure 4-5), obtained from the hydrolysis of methylvinylchlorosilane, was copolymerized with a variety of monomers. These monomers included methyl methacrylate, styrene, dichlorostyrene, acrylonitrile, and butyl methacrylate. The polymerizations were carried out using benzoyl peroxide or butyl perbenzoate initiators. The structures of the copolymers were not described but generally all the copolymers were colorless, hard, and tough.

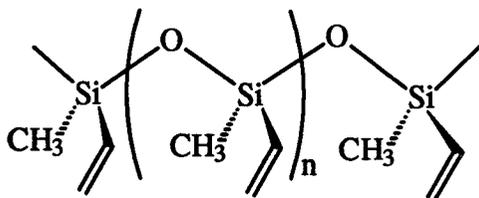


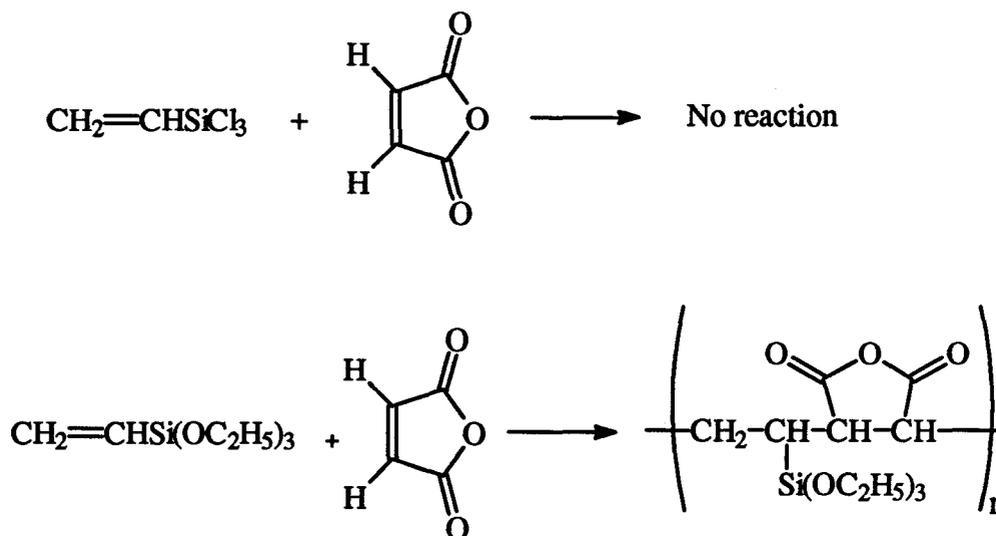
Figure 4-5

Studies were also performed on vinyltrichlorosilane and vinyltriethoxysilane.<sup>65, 66</sup>

Vinyltrichlorosilane was found to copolymerize to some extent with other vinyl monomers such as vinyl acetate, methyl methacrylate, and acrylonitrile using peroxide catalysts, but in most cases the copolymers contained only small percentages, approximately 2%, of vinyltrichlorosilane monomer.

Vinyltriethoxysilane differed markedly from vinyltrichlorosilane in copolymerization reactions with ethyl maleate and maleic anhydride (Scheme 4-1). Whereas vinyltrichlorosilane did not react with these compounds using peroxide initiators, vinyltriethoxysilane reacted extensively. The vinyltriethoxysilane-maleic anhydride copolymers were hard and brittle with molecular weights up to 3000.

**Scheme 4-1**



Thompson<sup>67</sup> investigated the copolymerization of six alkoxy silanes with chlorostyrene, vinyl chloride, and acrylonitrile using diacetyl peroxide. The monomers as shown in Figure 4-6 included vinyltrimethoxy-, vinyltriethoxy-, vinyltriisopropoxy-, vinylmethyldiethoxy-, vinelethyldiethoxy-, and vinylphenyldiethoxysilanes. No copolymerizations took place with chlorostyrene. In all cases the polymerization rates decreased rapidly as the concentration of the alkoxy silane increased, an indication of a very low rate constant for self-propagation of the alkoxy silane.

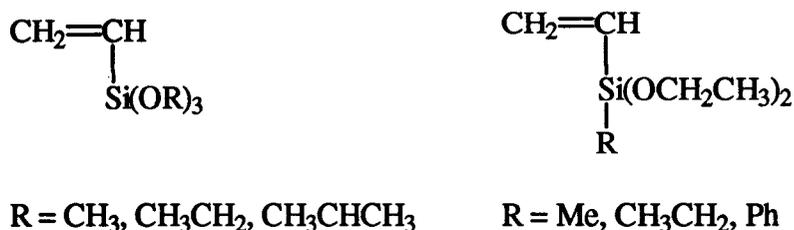


Figure 4-6

Bailey<sup>68</sup> copolymerized a series of simple vinylsiloxanes (Figure 4-7), tris(trimethylsiloxy)vinylsilane, bis(trimethylsiloxy)methylvinylsilane, and dimethyl(trimethylsiloxy)vinylsilane with various organic vinyl monomers including acrylonitrile, styrene, vinyl acetate, vinyl chloride, perfluorovinyl chloride, and *N*-vinylpyrrolidone. As a rule, in the copolymerization reactions the total polymerization rate and the molecular weight of the copolymers were markedly affected by the amount of vinylsiloxanes in the monomer mixture. An increase in the percentage of the vinylsiloxane

in the monomer mixture resulted in a decrease in the polymerization rate as well as a decrease in the molecular weight of the copolymers.

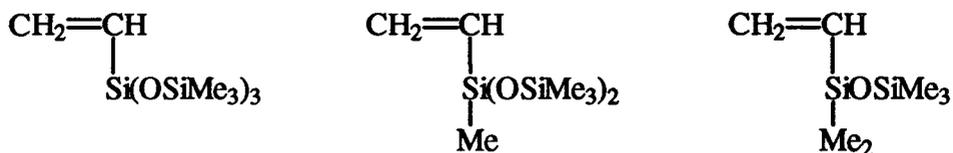


Figure 4-7

The same trend was observed by Nametkin *et al.*<sup>(69)</sup> They radically copolymerized trimethylvinylsilane and dimethylphenylvinylsilane (Figure 4-8) with styrene and methyl methacrylate using benzoyl peroxide as the catalyst at 80° C. The copolymers that were formed consisted mainly of the hydrocarbon monomer irrespective of the initial ratio of silane to hydrocarbon monomer. Any increase in the vinylsilane content in the initial monomer mixture led to decrease in the copolymer yield as well as a decrease in the overall polymerization rate and molecular weight of the copolymer formed. These results were attributed to a low activity of the polymer radical which has a vinylsilane molecule at its terminus.

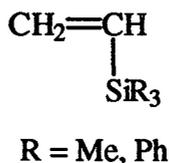


Figure 4-8

### 4.3 Copolymerization of Hydrovinylsilanes

The previous work that has been reported on radical copolymerizations involving hydrovinylsilanes is of importance to this thesis. Iwakura and coworkers<sup>53</sup> investigated the radical copolymerizations of hydrovinylsilanes with styrene. They used silane molecules which possessed a single vinyl or allyl group and two Si-H groups. The monomers that were used are shown in Figure 4-9.

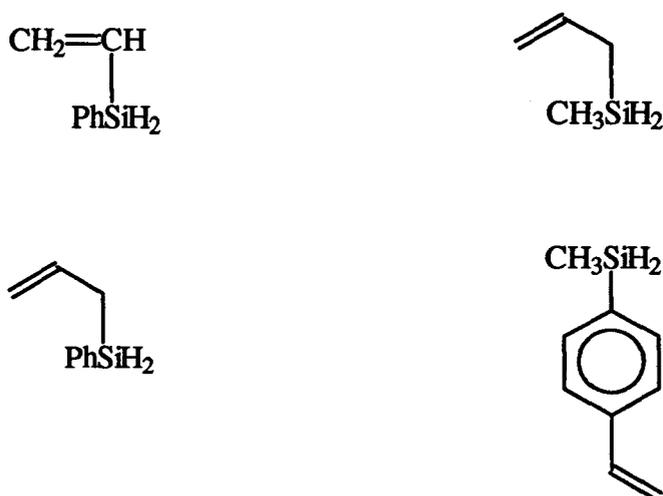


Figure 4-9

<sup>1</sup>H NMR and infrared spectroscopic analysis of the copolymers suggested that the copolymerization of the silanes proceeded through vinyl type polymerization, and there was no evidence that silicon-hydrogen added to an unsaturated bond (hydrosilylation).

However, no information was available of the effect on molecular weight with differing initial ratios of the two monomers.

#### **4.4 Objectives of Our Study**

As described above, the introduction of silicon into polymer systems may result in novel physical properties which serves as an incentive to search for new silicon containing polymers. The previous part of this work (Chapter 1) dealt with the homopolymerization of a hydrovinylnsilane, **1**, under radical conditions. Under these conditions, the reactivity of Si-H was found to be lower than that of the Si-CH=CH<sub>2</sub> group when both groups are present on the same silicon atom. As an extension of the previous study and in keeping with the theme of radical activation, the possibility of copolymerizing a hydrovinylnsilane monomer with hydrocarbon monomers was examined. We decided to explore the possibility of synthesizing a functionalized copolymer by copolymerizing **1** with vinyl hydrocarbon monomers such as styrene and methyl methacrylate. Under radical activation the silane should be incorporated into the polymer backbone through vinyl consumption. In addition to examining the effect of having a phenyl substituent on silicon, our goal was to determine the molecular weight distributions of the products. Moreover, we proposed to determine the reactivity of the residual Si-H functional groups towards grafting reactions by hydrosilylation or radical methods. The results of our experiments are presented in the following section.

## CHAPTER 5: RESULTS AND DISCUSSION

### 5.1 Copolymers of 1 with Styrene and Methyl methacrylate

The results of the radical copolymerization of 1 with styrene and methyl methacrylate (MMA) are shown in Table 5-1 and Table 5-2 respectively.

**Table 5-1:** Copolymerization of 1 with Styrene

Molarity of styrene Styrene:1 ratio	Mol. Fraction of 1 in monomer mixture	Copolymer yield, %	Silicon content of copolymer, %	Mol. fraction 1 in copolymer	Molecular Weight, $M_w$	Poly-dispersity
0.6 M 5:1	0.17	34	0.65	0.025	9700	1.8
0.6 M 2:1	0.33	22	1.03	0.040	8500	1.8
0.6 M 1:1	0.50	13	1.28	0.050	4500	1.8

Polymerization of 0.6 M Styrene in the absence of 1:  $M_w = 10000$  and polydispersity was 1.9.

2

**Table 5-2: Copolymerization of 1 with MMA**

Molarity of MMA MMA:1 ratio	Mol. Fraction of 1 in monomer mixture	Copolymer yield, %	Silicon content of copolymer, %	Mol. fraction 1 in copolymer	Molecular weight	Polydispersity
2 M 2:1	0.33	66	2.00	0.77	6000	3.0
0.6 M 5:1	0.17	75	1.33	0.050	10000	2.3
0.6 M 2:1	0.33	65	1.74	0.067	6900	2.2
0.6 M 1:1	0.50	54	2.31	0.091	4500	2.0

Polymerization of 2.0 M MMA in the absence of 1:  $M_w = 21000$  and polydispersity was 3.0.

Polymerization of 0.6 M MMA in the absence of 1:  $M_w = 17750$  and polydispersity was 2.3.

The data in Table 5-1 and Table 5-2 show that the activity of 1 in the radical copolymerization with styrene and methyl methacrylate is low. The copolymers consisted mainly of the hydrocarbon monomer irrespective of the initial ratio of silicon monomer to hydrocarbon monomer. As the amount of 1 was increased in the initial monomer mixture, the copolymer yield decreased. In addition, a decrease resulted in the molecular weight of the copolymers formed (Figure 5-1). An increase in the concentration of the original monomer mixture, 0.6 M to 2.0 M for methyl methacrylate:1 (2:1 ratio), did not significantly increase the % content of silicon in the copolymers, 1.74 to 2.00. The

decrease in the overall rate of polymerization for styrene and methyl methacrylate can be attributed to the low activity of the polymer radical which terminated with the silane 1.

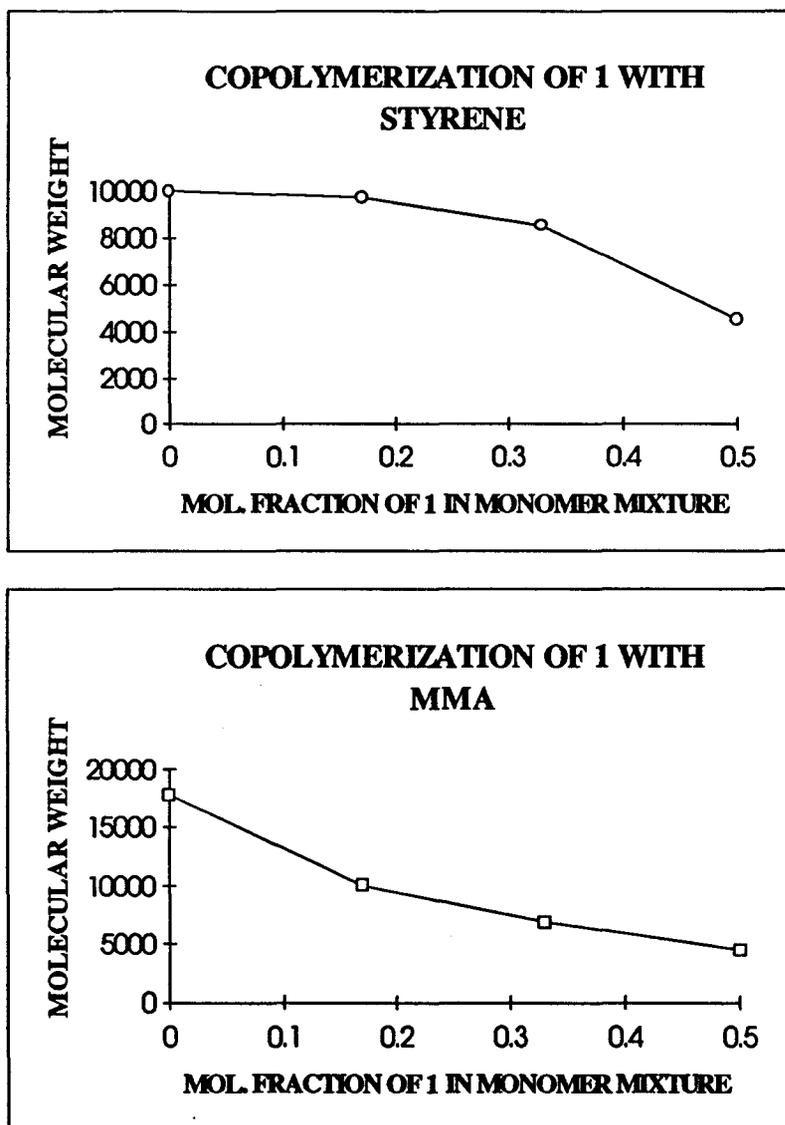


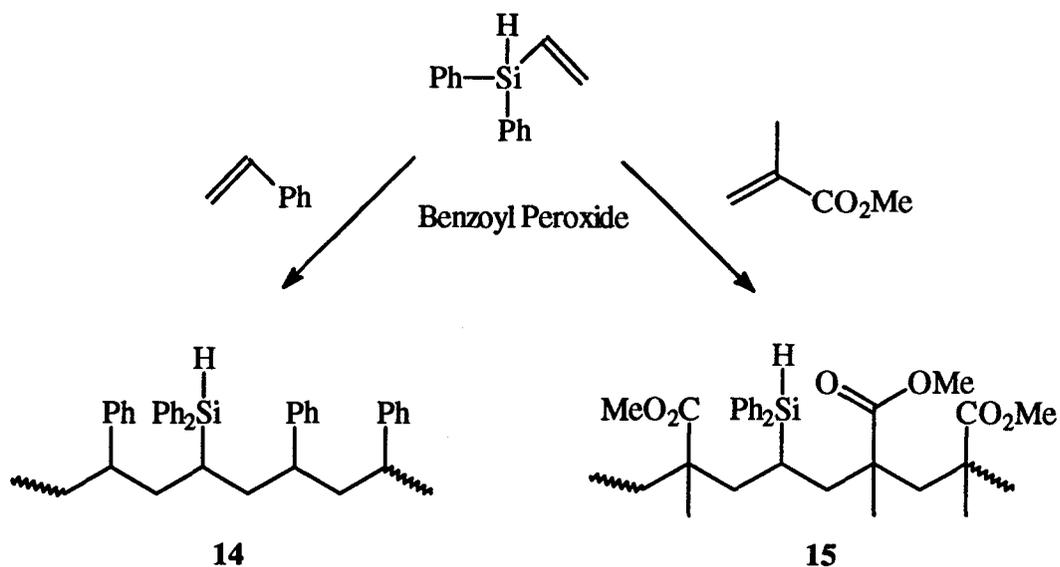
Figure 5-1

In the copolymerization reactions, since the SiH bond might be able to add to a double bond, there was the possibility that chain-transfer via transfer of the H from the SiH group could occur. However,  $^1\text{H}$  NMR and infrared spectroscopic analyses revealed the contrary; the copolymerizations underwent vinyl consumption. The copolymers of styrene and **1** had a typical (for SiH) infrared absorption at  $2115\text{ cm}^{-1}$  and a proton signal at 4.00 - 5.00 ppm ( $^1\text{H}$  NMR) for the SiH group while the copolymers of methyl methacrylate and **1** had a typical infrared absorption at  $2135\text{ cm}^{-1}$  and proton signal at 4.50 - 5.00 ppm, respectively. In both set of copolymers, the intensity of the SiH band in the infrared spectra increased as the content of **1** increased in the original monomer mixture.

## 5.2 Grafting Reactions

The copolymers **14** and **15** obtained in this work as shown in Scheme 5-1 consisted mainly of the hydrocarbon monomer. Incorporation of **1** into the polymer through the vinyl group left residual SiH functional groups along the backbone of the copolymer. To determine whether these groups were reactive, grafting reactions by hydrosilylation and radicals methods were attempted with **15**.

Scheme 5-1

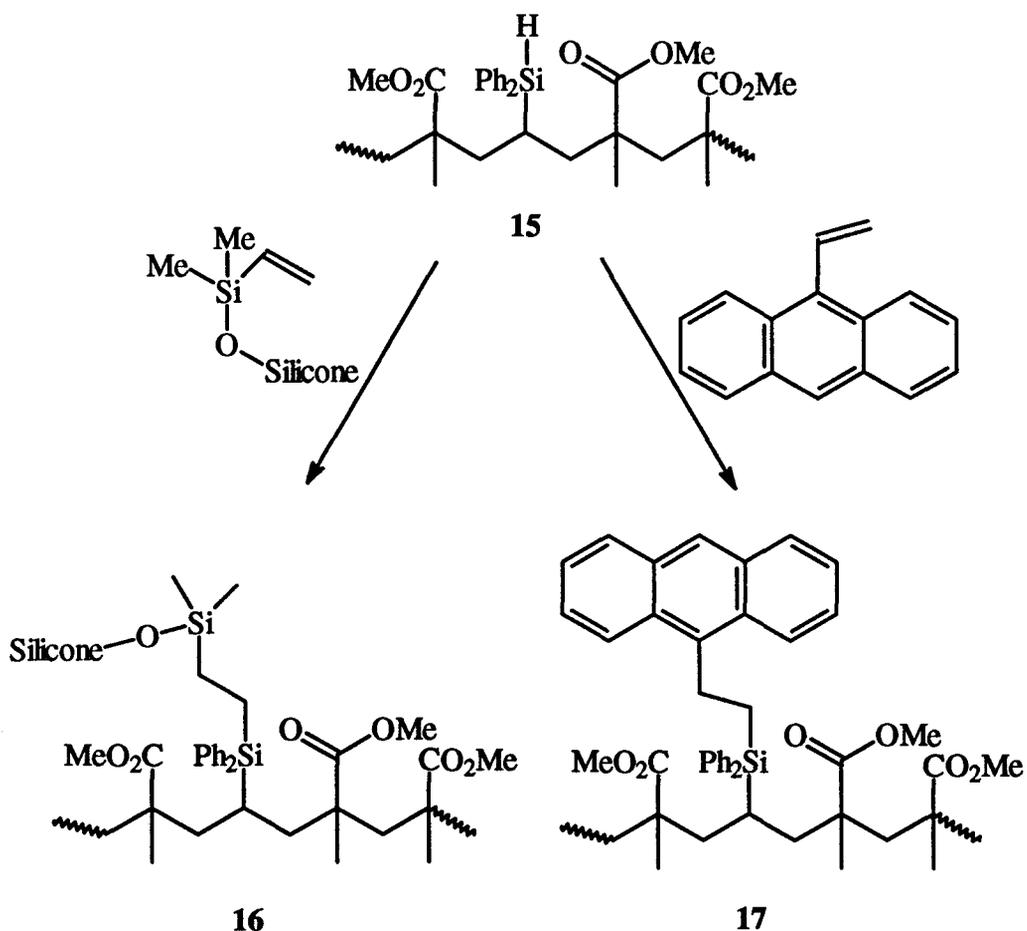


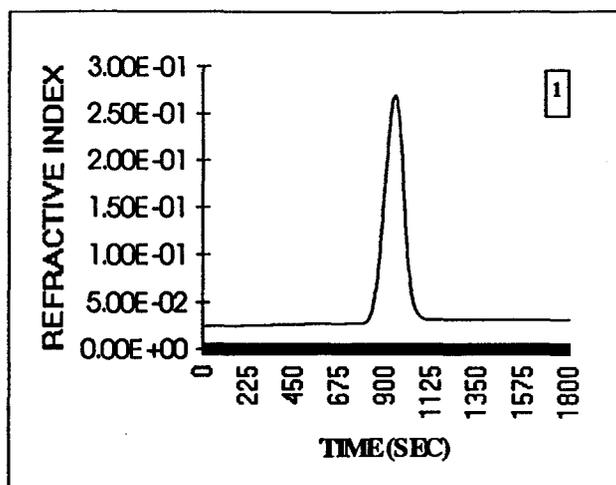
The hydrosilylation and radical grafting reactions are shown in Scheme 5-2. The  $[(\text{PPh}_3)_3\text{Rh}]\text{Cl}$  catalyzed hydrosilylation of **15** with a divinyl terminated silicone was performed in benzene at  $50^\circ\text{C}$  and proceeded with complete conversion of SiH groups to **16**.

9-Vinylanthracene was chosen for the radical reaction to be grafted onto **15** because the reaction could be monitored easily using UV light. This reaction was carried out in a sealed ampoule at  $140^\circ\text{C}$  using dicumyl peroxide as the radical catalyst in benzene. Evidence did suggest that 9-vinylanthracene had been grafted onto **15** to give **17**. The gel permeation chromatographs (Figure 5-2, Figure 5-3) of the polymer product **17**, in 1 monitored by the reactive index (Figure 5-2) and in 2 monitored by UV (Figure 5-3) at  $\lambda$

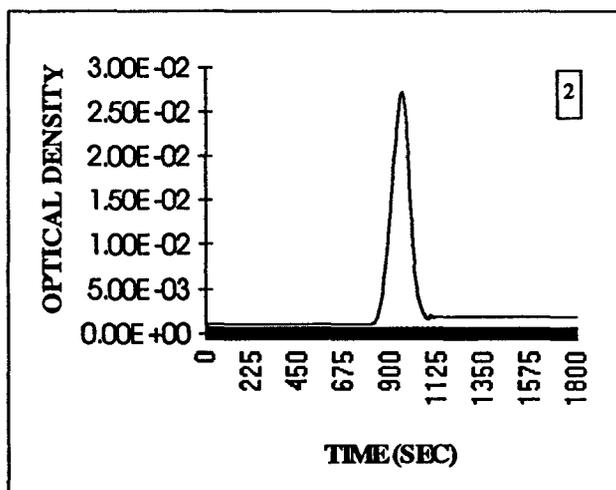
370 nm had the same retention times. This is an indication that the grafting reaction had taken place although it was not entirely clear whether the grafting occurred exclusively at the SiH group and/or also somewhere else along the backbone of the polymer **15**; small absorption bands for SiH were still present in the infrared spectrum.

Scheme 5-2





**Figure 5-2:** Gel Permeation Chromatograph (Refractive Index Detection) of 17



**Figure 5-3:** Gel Permeation Chromatograph (UV Detection) of 17

### 5.3 Concluding Remarks

The radical copolymerization of **1** with styrene and methyl methacrylate occurred through vinyl group of **1**. The low incorporation of **1** into the copolymers can be attributed to the low activity of the polymer radical which terminated with the silane unit. Residual SiH groups along the backbone of copolymer **15** allowed grafting reactions by hydrosilylation and radical methods.

## CHAPTER 6: EXPERIMENTAL

### 6.1 General Experimental Procedures

All reactions were carried out in dry apparatus under a nitrogen atmosphere with the use of septa and syringes for the transfer of reagents.

### 6.2 Instrumentation and Analytical Procedures

Fourier transform  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on a Bruker AC-200 (200 MHz, 50.3 MHz for carbon) and Bruker AC-300 (300 MHz, 75.5 MHz for carbon) spectrometers.  $^{29}\text{Si}$  NMR was performed on a Bruker AC-300 (at 59.6 MHz for silicon). Chemical shifts are reported with respect to tetramethylsilane as a standard, set to 0 ppm. Coupling constants ( $J$ ) are recorded in hertz (Hz). The abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = doublet of doublets of doublets, m = multiplet are used in reporting the spectra.

Electron impact (EI) mass spectra were recorded at 70 eV with a source temperature *ca.* 200° C on a VG analytical ZAB-E mass spectrometer equipped with a VG 11-250 data system. Fourier infrared spectra were obtained on a BIO RAD FTS-40 spectrometer. Samples were run as either neat films with NaCl windows or as a KBr pellet.

The molecular weight distributions of the oligomers were analyzed using a Waters Gel Permeation Chromatograph equipped with a Waters 410 Differential Refractometer

and a Waters 490 Programmable Multiwavelength Detector. Two Jordi Mixed bed columns in series were utilized with 1,1,1-trichloroethane as solvent flowing at 1.5 mL/min. Narrow molecular weight polystyrene standards from Polymer Laboratories were used for calibration of the chromatographic system. Chromatograms were analyzed using Maxima 820 Software, version 3.0 running on a Fujikama 386-20SX.

Rate constant measurements were obtained at 22° C by nanosecond laser flash photolysis experiments which employed the pulses from a Lumonics TE-861M excimer laser filled with Xe/HCl/H<sub>2</sub>/He (308 nm, 15 ns, *ca.* 40 mJ) mixtures and a microcomputer-controlled detection system.<sup>70</sup>

UV-VIS spectra were measured in 1 cm quartz cuvettes on a Perkin-Elmer Lambda 9 UV/VIS/NIR Spectrometer. Contact angle measurements were performed on a NRL C.A. Goniometer, Rané-hart Inc.

### 6.3 Materials

Methanol (Caledon, reagent grade), hexanes (Caledon, reagent grade), chloroform (BDH, reagent grade), chlorodiphenylsilane (United Chemicals, 95%), chloromethyldiphenylsilane (Lancaster, 97%), vinylmagnesium bromide (Aldrich, 1.0 M solution in tetrahydrofuran), bromoethane (BDH), magnesium turnings (BDH), benzoyl peroxide (Aldrich), di-cumyl peroxide (Aldrich), (trimethylsilyl)acetylene (Aldrich, 98%), vinylmethyl-terminated poly(dimethylsiloxane) (United Chemicals, viscosity = 4-6 Cs), 9-vinylanthracene (Aldrich, 97%), and tris(triphenylphosphine)-rhodium (I) chloride (Aldrich) were used as received. Di-*tert*-butyl peroxide (Aldrich, 98%) was passed

through alumina (Fisher Scientific) which was activated by heating at 500° C for 24 h. *iso*-Octane (Caledon, reagent grade) was refluxed for two days and then distilled from calcium hydride (Aldrich). A 0.1 M solution of Speier's catalyst (hydrogen hexachloroplatinate (IV) hydrate, H<sub>2</sub>PtCl<sub>6</sub>) was prepared with anhydrous isopropyl alcohol (Caledon, reagent grade). Anhydrous isopropyl alcohol was obtained by distillation under nitrogen after it was dried with sodium (BDH) over night. Azo(*bis*isobutyronitrile) (Kodak) was recrystallized from methanol prior to use. Diethyl ether (BDH, reagent grade) was distilled from sodium/benzophenone (Aldrich) under a nitrogen atmosphere. Benzene (BDH, reagent grade) was washed with sulfuric acid (Fisher Scientific) and distilled from sodium under a nitrogen atmosphere. Styrene (Aldrich, 99%) and methyl methacrylate (Aldrich, 99%) were purified by vacuum distillation and stored under a nitrogen atmosphere. 1,1,1-Trichloroethane (Caledon, reagent grade) was filtered using a Type HA 0.45 μm Millipore filter.

#### **6.4 General Experimental Procedures for Grignard Reactions**

A chlorosilane was added dropwise to a stirred solution of vinylmagnesium bromide (1.1 eq.) in THF (1.0 M) at 0° C. Once addition was complete, the mixture was slowly warmed to room temperature and stirred for an additional 2 h. The reaction mixture was then slowly poured into an ice-water bath and extracted with diethyl ether. The ether layer was subsequently washed with a saturated brine solution and then dried over

anhydrous sodium sulfate. Once the sodium sulfate was removed by filtration, the solvent was evaporated in vacuo. Distillation gave the silane as a colorless liquid.

#### 6.4.1 Diphenylvinylsilane (1)

Chlorodiphenylsilane (10 g, 45.9 mmol), vinylmagnesium bromide (1.0 M in Et<sub>2</sub>O, 50.5 mL, 50.5 mmol). b.p.: 108° C/1 mm Hg. Yield: 90% (8.7 g, 41.4 mmol). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): δ 5.11 (d, 1H, J = 3.0 Hz), 5.89 (dd, 1H, J = 19.4, 4.4 Hz), 6.24 (dd, 1H, J = 14.5, 4.4 Hz), 6.45 (ddd, 1H, J = 19.4, 14.5, 3.0 Hz), 7.30-7.60, 7.50-7.70 (m, 10H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 200 MHz): δ 128.00, 129.71, 132.62, 133.25, 135.43, 136.99. <sup>29</sup>Si NMR (CDCl<sub>3</sub>, 300 MHz): δ -21.60. IR (neat): ν 3051, 3003, 2971, 2124, 1590, 1485, 1428, 1404, 1304, 1115, 1007, 960, 816, 796 cm<sup>-1</sup>. MS (m/z): 210 (29, M<sup>+</sup>), 181 (47), 155 (8), 132 (100), 105 (72), 91 (7), 79 (14), 53 (24).

#### 6.4.2 Ethyldiphenylsilane (7)

Bromoethane (5 g, 45.9 mmol) was added to magnesium turnings (1.7 g, 70.8 mmol) in diethyl ether (25 mL) under nitrogen. The mixture was stirred for 1 h. and then cooled to 0° C. The addition of chlorosilane (9 g, 41.1 mmol) and subsequent work up was as above. b.p.: 110° C/1 mm Hg. Yield: 70% (6.1 g, 28.8 mmol). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): δ 1.08-1.18 (m, 3H), 4.86 (t, 1H), 7.20-7.50, 7.48-7.70 (m, 10H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 200 MHz): δ 4.14, 8.11, 127.93, 129.48, 134.42, 135.13. <sup>29</sup>Si NMR (CDCl<sub>3</sub>, 300 MHz): δ -11.52. IR (neat): ν 3068, 3018, 2957, 2874, 2116, 1428, 1114, 1013, 966, 807, 734, 700 cm<sup>-1</sup>. MS (m/z): 212 (24, M<sup>+</sup>), 183 (100), 134 (34), 105 (45), 79 (9).

### 6.4.3 Methyldiphenylvinylsilane (8)

Chloromethyldiphenylsilane (10 g, 43.0 mmol), vinylmagnesium bromide (1.0 M in Et<sub>2</sub>O, 47.3 mL, 47.3 mmol). b.p.: 124° C/2 mm Hg. Yield: 69% (6.7 g, 29.7 mmol). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): δ 0.61 (s, 3H), 5.77 (dd, 1H, J = 20.0, 3.9 Hz), 6.17 (dd, 1H, J = 14.6, 3.9), 6.48 (dd, 1H, J = 20.0, 14.6), 7.20-7.60, 7.50-7.70 (m, 10H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 200 MHz): δ -4.11, 127.85, 127.97, 129.30, 129.51, 134.83, 134.89, 135.84, 136.25. <sup>29</sup>Si NMR (CDCl<sub>3</sub>, 300 MHz): δ -14.31. IR (neat): ν 3050, 3010, 2961, 1591, 1427, 1251, 1113, 1008, 958, 792, 730 cm<sup>-1</sup>. MS (m/z): 224 (77, M<sup>+</sup>), 209 (100), 197 (54), 183 (53), 165 (8), 146 (52), 120 (45), 105 (48), 93 (8), 79 (7).

### 6.5 Measurement of Absolute Rate Constants

Silane solutions (1.0 M) in *iso*-octane and di-*tert*-butyl peroxide:*iso*-octane (1:4, v/v) solutions were prepared. Samples were contained in 3 x 7 mm cells constructed from rectangular Suprasil quartz and fitted with rubber septa. In all cases the samples were deoxygenated. Quenchers were added directly to the cells by a microliter syringe as aliquots from standard solutions. Laser flash photolysis was used to generate di-*tert*-butyoxyl radicals. The absolute rate constant for the growth of the ethyldiphenylsilyl radicals was determined in di-*tert*-butyl peroxide:*iso*-octane as the solvent. The absolute rate constants for the addition reactions of ethyldiphenylsilyl radicals were determined in di-*tert*-butyl peroxide:*iso*-octane and ethyldiphenylsilane as the solvent. The ethyldiphenylsilyl radicals were generated by the laser flash photolysis of di-*tert*-butyl

peroxide in the presence of ethyldiphenylsilane. Absolute rate constants were calculated by linear least squares fits of growth or decay rate *versus* quencher concentration data using Inplot 4.0 (Graphpad, Inc.)

## 6.6 General Procedure for Hydrosilylation

A benzene solution of the monomer or oligomer (0.6 M) and 5 drops Speier's catalyst was stirred at 50° C for 12 h. The solvent was removed in vacuo and the crude product was purified by precipitation. Precipitation involved dissolving the polymer in chloroform, precipitating the polymer with the addition of methanol, and then decanting the liquid. This process was repeated several times.

### 6.6.1 Preparation of Polymer 2

**1** (1 g, 4.8 mmol), Speier's catalyst, benzene (7 mL), 12 h, 50° C. Yield: 50% (0.5017 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): δ 0-0.30, 0.20-1.65 (m, 3H), 4.42-5.10 (m, 0.05H), 5.20-6.48 (m, 0.15H), 6.60-8.00 (m, 10H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 200 MHz): δ 1.03, 3.65, 7.41, 127.73, 129.11, 134.33, 134.95, 135.64, 135.86. <sup>29</sup>Si (CDCl<sub>3</sub>, 300 MHz): δ -9.55, -7.71, -3.86, 6.19, 8.746. IR: ν 3067, 3044, 2910, 2879, 1589, 1485, 1427, 1261, 1110, 716 cm<sup>-1</sup>. M<sub>w</sub> = 1800 and polydispersity 1.4.

## 6.7 General Procedure for Radical Polymerization

Nitrogen was bubbled through the benzene for 1 h before beginning the reactions. A benzene solution of the monomer and a radical initiator, azo(*bisisobutyronitrile*) (AIBN)

or benzoyl peroxide was heated at 80° C for 12 h. The solvent was removed in vacuo and the crude products were purified by radial chromatography using a hexane/ether (99:1) mixed solvent system.

### 6.7.1 Radical Polymerization of (0.6 M) Diphenylvinylsilane (1) with 10% AIBN

1 (0.6 M, 1.0 g, 4.8 mmol), AIBN (0.1 eq, 78.1 mg, 0.48 mmol), benzene (7 mL), 12 h, 80° C.

#### 6.7.1a Crude Material

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz, integration based on the 10 aromatic protons of SiPh<sub>2</sub>): δ 0.20-2.80 (m, 2.66H), 4.66-4.95, 5.16-5.17 (m, 0.77H), 5.65-6.55 (m, 1.72H), 7.00-7.60, 7.30-7.80 (m, 10H). 50% (0.50 g) of 1 recovered. From <sup>1</sup>H NMR of crude material: 43% vinyl reacted and 23% SiH reacted.

#### 6.7.1b Oligomeric Material 3

Yield 50% (0.50 g). <sup>1</sup>H (CDCl<sub>3</sub>, 200 MHz): δ 0.10-0.14, 0.10-2.3 (m, 4H), 4.20-4.87 (m, 0.5H), 5.65-6.57 (m), 6.60-8.00 (m, 10H). <sup>13</sup>C (CDCl<sub>3</sub>, 200 MHz): δ 4.25, 4.66, 4.84, 5.38, 5.75, 6.03, 12.16, 22.12, 23.43, 26.08, 36.09, 127.77, 127.91, 128.17, 129.30, 129.36, 129.50, 129.71, 129.89, 132.68, 133.31, 133.72, 134.27, 135.13, 135.45, 136.98. <sup>29</sup>Si (CDCl<sub>3</sub>, 300 MHz): -13.52, -12.50, -10.94, -3.46. IR (neat): ν 3089, 3048, 3014, 2914, 2116, 1589, 1485, 1427, 1108, 802, 725 cm<sup>-1</sup>. M<sub>w</sub> = 770 and polydispersity 1.4.

### 6.7.1c AIBN Adduct 4

Yield: 5% (0.05 g).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.24-1.65 (m, 10H), 4.87 (t, 1H), 7.30-7.60, 7.50-7.70 (m, 10H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.78 ( $\text{CH}_3$ ), 26.06 ( $-\text{SiCH}_2\text{CH}_2-$ ), 34.25 ( $-\text{SiCH}_2\text{CH}_2-$ ), 36.06 ( $-\text{CMe}_2\text{CN}$ ), 124.90 ( $-\text{CN}$ ), 128.15 (meta C), 129.86 (para C), 133.27 (ortho C), 135.04 ( $\text{C}-\text{SiCH}_2-$ ). IR (KBr):  $\nu$  3086, 2977, 2932, 2233, 2119, 1589, 1485, 1428, 1191, 1113, 906, 874, 807, 700  $\text{cm}^{-1}$ . MS (m/z): 278 (7,  $\text{M}^+$  - 1), 201 (25), 183 (100), 146 (11), 105 (45), 83 (31).

### 6.7.1d Dimer 5

Yield: 8% (0.08 g).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  1.11-1.42 (m, 4H), 4.83 (t, 1H), 5.74 (dd, 1H,  $J = 20.0, 4.0$ ), 6.21 (dd, 1H,  $J = 14.7, 4.0$ ), 6.48 (dd, 1H,  $J = 20.0, 14.7$ ), 7.19- 7.60, 7.40-7.62 (m, 20H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  4.59, 6.00, 126.73, 126.84, 126.93, 128.19, 128.30, 128.39, 128.49, 128.59, 128.84, 128.95, 129.05, 130.41, 130.50, 130.61, 134.10, 136.11, 136.20, 136.29, 136.38, 137.95. IR (KBr):  $\nu$  3085, 3067, 3049, 3011, 2914, 2119, 1589, 1486, 1428, 1405, 1112, 1053, 1009, 808, 758, 700  $\text{cm}^{-1}$ . MS (m/z): 420 (8,  $\text{M}^+$ ), 393 (10), 342 (20), 314 (18), 259 (40), 238 (10), 209 (74), 183 (100), 131 (9), 105 (43), 53 (8).

### 6.7.1e Trimer 6

Yield: 4% (0.04 g).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  0.14, 0.78-2.33 (m, 7H), 4.55-4.82 (m, 2H), 5.71 (dd, 1H,  $J = 20.2, 3.8$ ), 6.20 (dd, 1H,  $J = 14.7, 3.8$ ), 6.46 (dd, 1H,  $J = 20.2, 14.7$ ), 7.15-7.61, 7.40-7.70 (m, 30H).  $^{13}\text{C}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  4.60, 6.00, 8.20,

22.70, 34.90, 127.74, 127.91, 128.96, 129.08, 129.14, 129.45, 133.73, 134.28, 134.68, 134.85, 135.02, 135.08, 135.19, 135.26, 135.31, 135.38, 135.47, 135.51, 135.66, 135.72. IR(KBr):  $\nu$  3067, 2999, 2904, 2848, 2111, 1588, 1485, 1427, 1303, 1262, 1109, 1066, 998, 846, 800, 726  $\text{cm}^{-1}$ . MS (m/z): 630 (2,  $\text{M}^+$ ), 553 (4), 447 (4), 393 (8), 369 (4), 341 (4), 259 (46), 209 (9), 183 (100), 159 (12), 105 (34).

### 6.7.2 Radical Polymerization of (0.6M) Diphenylvinylsilane (1) with 10% BPO

1 (0.6 M, 1 g, 4.8 mmol), benzoyl peroxide (0.1 eq., 115.1 mg, 0.48 mmol), benzene (7 mL), 12 h, 80° C.

#### 6.7.2a Crude Material

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz, integration based on the 10 aromatic protons of  $\text{SiPh}_2$ ):  $\delta$  0.2-2.80 (m, 1.47H), 4.63-4.95, 5.14-5.15 (m, 0.77H), 5.64-6.57 (m, 1.78H), 7.00-7.59, 7.50-7.80 (m, 10H). 50% (0.50g) of 1 recovered. From  $^1\text{H}$  NMR of crude material: 43% vinyl reacted and 23% vinyl reacted.

#### 6.7.2b Oligomeric Material 3

Yield 50% (0.50 g).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  0.1-0.14, 0.1-2.8 (m, 3H), 4.42-5.01 (m, 0.50H), 5.68-6.57 (m), 6.60-8.00 (m, 10H).  $^{13}\text{C}$  ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  4.14, 4.67, 6.03, 14.20, 24.64, 29.70, 30.44, 127.81, 128.00, 129.33, 129.53, 129.69, 130.16, 132.64, 133.20, 135.10, 135.22, 135.43, 136.93.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ , 300 MHz):

-12.87, -12.04, -11.30, -9.16, -7.98, -3.85. IR(neat):  $\nu$  3067, 2910, 2112, 1589, 1483, 1427, 1262, 1110, 806, 728.  $M_w = 770$  and polydispersity 1.4.

### 6.7.2c Dimer 5

Yield: 9% (0.09 g).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  1.10-1.47 (m, 4H), 4.84 (t, 1H), 5.74 (dd, 1H,  $J = 20.0, 4.0$ ), 6.21 (dd, 1H,  $J = 14.7, 4.0$ ), 6.48 (dd, 1H,  $J = 20.0, 14.7$ ), 7.20-7.55, 7.40-7.65 (m, 20H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  4.60, 6.04, 126.90, 127.24, 127.33, 128.50, 128.59, 128.70, 129.25, 130.83, 130.97, 131.01, 134.57, 136.75, 136.80, 136.69, 136.88, 138.01. IR (KBr):  $\nu$  3067, 2905, 2111, 1587, 1485, 1427, 1261, 1110, 805, 729  $\text{cm}^{-1}$ . MS (m/z): 420 (9,  $M^+$ ), 393 (8), 342 (17), 314 (19), 259 (35), 238 (8), 209 (79), 183 (100), 131 (11) 105 (50), 53 (5).

### 6.7.2d Trimer 6

Yield: 4% (0.04 g).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200MHz):  $\delta$  0.14, 0.70-2.00 (m, 7H), 4.58-4.90 (m, 2H), 5.77 (dd, 1H,  $J = 4.0, 20.0$ ), 6.24 (dd, 1H,  $J = 14.7, 4.1$ ), 6.50 (dd,  $^1\text{H}$ ,  $J = 20.0, 14.7$ ), 7.15-7.60, 7.40-7.70 (m, 30H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  4.64, 6.01, 8.20, 22.67, 127.50, 127.84, 129.01, 129.30, 133.60, 134.10, 134.20, 134.10, 135.09, 135.37, 135.65, 135.70, 135.91, 136.01. IR (KBr):  $\nu$  3067, 2910, 2112, 1589, 1484, 1427, 1262, 1110, 806, 729  $\text{cm}^{-1}$ . MS (m/z): 630 (2,  $M^+$ ), 553 (3), 447 (5), 393 (10), 369 (10), 341 (3), 259 (40), 209 (15), 183 (100), 159 (8), 105 (35).

### 6.7.3 Radical Polymerization of Diphenylvinylsilane (1) with 10% AIBN Neat

1 (1 g, 4.8 mmol), AIBN (0.1 eq., 78.1 mg, 0.48 mmol), 12 h, 80° C.

Crude: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz, integration based on the 10 aromatic protons of SiPh<sub>2</sub>): δ 0.20-2.80 (m, 3H), 4.60-5.00, 5.16-5.17 (m, 0.69H), 5.65-6.56 (m, 1.09H), 7.00-7.42, 7.30-7.80 (m, 10H). 23% (0.23 g) of 1 recovered. From <sup>1</sup>H NMR of crude material: 64% of vinyl reacted and 31% of SiH reacted. M<sub>w</sub> = 940 and polydispersity 1.4.

### 6.7.4 Radical Polymerization of (0.6 M) Diphenylvinylsilane (1) with 100% AIBN

1 (0.6 M, 0.5 g, 2.4 mmol), AIBN (1 eq., 390.3 mg, 2.4 mmol), benzene (3.5 mL), 12 h, 80° C.

Crude: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz, integration based on the 10 aromatic protons of SiPh<sub>2</sub>): δ 0.30-2.80 (m, 11H), 4.60-5.00, 5.12-5.13 (m, 0.65H), 5.67-6.56 (m, 1.06), 7.00-7.50, 7.45-7.80 (m, 10H). 15% (0.075g) of 1 recovered. From <sup>1</sup>H NMR of crude material: 65% vinyl reacted and 35% SiH reacted. M<sub>w</sub> = 690 and polydispersity 1.5.

### 6.7.5 Syringe Addition of AIBN to Diphenylvinylsilane (1)

1 (2 g, 9.5 mmol), benzene (10 mL). AIBN (0.2 eq., 312.3 mg, 1.9 mmol) in benzene (4.8 mL) was added dropwise at a rate of 0.4 mL/h for a duration of 12 h using a Harvard Apparatus Syringe Infusion Pump 22. An aliquot (0.5 mL) was removed from the reaction mixture every hour, the solvent evaporated in vacuo, and a <sup>1</sup>H NMR taken. The data in Table 6-1 is the integration of the SiH and SiVinyl regions based on 10 aromatic

protons of SiPh<sub>2</sub> for each fraction. After reaction was stopped: M<sub>w</sub> = 770 and polydispersity 1.4.

**Table 6-1: Conversion of SiH and SiVinyl Functional Groups in 1 with Time**

Hours	Unreacted SiH	Unreacted SiVinyl
0	1.000	3.000
1	1.000	2.982
2	1.000	2.448
3	1.000	2.424
4	0.970	2.424
5	0.847	2.109
6	0.776	1.852
7	0.733	1.852
8	0.733	1.582
9	0.733	1.582
10	0.733	1.579
11	0.692	1.379
12	0.675	1.303

## 6.8 Hydrosilylation of Oligomer 3

### 6.8.1 Oligomeric Vinylsilane 9

**3** (0.3222 g), (trimethylsilyl)acetylene (1 mL, 0.695 g, 7.08 mmol), Speier's catalyst, benzene (10 mL), 12h, 50° C. Yield: 0.1305g. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): δ -0.20-0.00, -0.10-0.20 (m, 9H), 0.10-2.30 (m, 3H), 6.54 (d,1H), 6.71 (d,1H), 6.50-8.00 (m, 10H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 200 MHz): δ -1.56, -1.06, -.21, -13, 4.08, 4.79, 8.52, 22.60, 23.25, 25.70, 25.97, 29.67, 34.19, 35.58, 127.68, 127.82, 127.99, 128.24, 129.16, 129.27, 129.39, 129.54, 134.12, 134.38, 134.48, 134.59, 134.81, 134.93, 134.98, 135.13, 135.25, 135.45, 135.54, 135.66, 135.87, 136.05, 136.34, 143.56, 144.04, 145.96, 157.43.

$^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  -15.32, -13.88, -10.48, -7.28, -6.91, -2.70. IR (KBr):  $\nu$  3068, 2954, 2899, 1589, 1427, 1404, 1248, 1173, 1107, 1014, 837  $\text{cm}^{-1}$ .  $M_w = 1000$  and polydispersity 1.5.

### 6.8.2 Comb Type Silicone Oligomer 10

**3** (0.3534g), vinyl dimethyl-terminated poly(dimethylsiloxane) (1 mL, 0.93 g), Speier's catalyst, benzene (5 mL), 12h, 50° C. Yield: 0.1718g.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  -0.20-0.60, (m, 32H), 0.10-2.00 (m, 9H), 6.60-8.00 (m, 20H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  -0.478, 0.268, 1.04, 1.55, 9.94, 15.29, 127.72, 129.04, 135.00, 135.65.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  -22.44, -20.79, -9.80, -9.50, -3.39, -3.100, 8.01. IR (KBr): 3070, 2963, 2909, 1595, 1428, 1408, 1261, 1100, 1024, 801  $\text{cm}^{-1}$ .  $M_w = 6700$  and polydispersity 2.9.

### 6.9 General Method for Copolymerization

Nitrogen was bubbled through the benzene for 1 h before beginning reactions.

A benzene solution of styrene or methyl methacrylate (MMA), **1** and a radical initiator (1 mol % based on styrene or methyl methacrylate), benzoyl peroxide was heated at 80° C for 12 h. The solvent was removed in vacuo and the crude product was purified by precipitation. Precipitation involved dissolving the polymer in chloroform, precipitating the polymer with the addition of hexanes, and then decanting the liquid. This process was repeated exhaustively.

### 6.9.1 Styrene:Diphenylvinylsilane (1) - Copolymer 14

#### 6.9.1a (0.6 M) Styrene:Diphenylvinylsilane (1) - 1:1

Styrene (0.6 M, 2.0 g, 20 mmol), **1** (1 eq., 4.0 g, 20 mmol), benzoyl peroxide (0.0465 g, 0.20 mmol), benzene (27 mL). Yield: 13% (0.2780 g).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.28-1.78, 1.60-2.80 (m, 3H), 4.00-5.00 (m, 0.11H), 6.20-6.90, 6.88-7.64 (m, 5H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  9.92, 17.09, 17.39, 18.80, 40.38, 42.31, 43.46, 44.18, 46.54, 47.31, 125.48, 125.63, 126.40, 126.63, 127.29, 127.41, 127.64, 127.95, 129.03, 129.31, 129.45, 129.71, 130.26, 132.63, 132.75, 133.06, 133.26, 133.50, 134.68, 135.03, 135.08, 135.28, 135.44, 135.53, 145.09, 145.20, 145.30, 145.67, 146.02.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  -16.72, -12.63, -7.52, -2.70. IR (KBr):  $\nu$  3026, 2922, 2849, 2115, 1601, 1493, 1451, 1111, 908, 806, 757, 734  $\text{cm}^{-1}$ .  $M_w = 4500$  and polydispersity 1.8.

#### 6.9.1b (0.6 M) Styrene:Diphenylvinylsilane (1) - 2:1

Styrene (0.6 M, 2.0 g, 20 mmol), **1** (0.5 eq., 2.0 g, 10 mmol), benzoyl peroxide (0.0465 g, 0.20 mmol), benzene (27.8 mL). Yield: 22% (0.4782 g).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  1.20-1.80, 1.60-2.80 (m, 3H), 4.00-5.00 (m, 0.05H), 6.20-7.00, 6.88-7.70 (m, 5H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  16.45, 18.78, 40.38, 42.31, 43.46, 44.18, 46.54, 47.31, 125.63, 127.62, 127.94, 129.00, 129.42, 129.68, 130.22, 132.70, 133.17, 133.50, 135.06, 135.23, 135.51, 145.04, 145.15, 145.25, 145.60, 145.97.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  -16.72, -12.63, -7.52, -2.70. IR (KBr):  $\nu$  3082, 3060, 3026, 2922, 2849, 2115, 1601, 1493, 1451, 1429, 1272, 1028, 908, 757  $\text{cm}^{-1}$ .  $M_w = 8500$  and 1.8.

### 6.9.1c (0.6 M) Styrene:Diphenylvinylsilane (1) - 5:1

Styrene (0.6 M, 2.0 g, 20 mmol), **1** (0.2 eq., 0.81 g, 4 mmol), benzoyl peroxide (0.0465 g, 0.20 mmol), benzene (29 mL). Yield: 34% (0.7226 g).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  1.05-1.78, 1.60-2.80 (m, 3H), 4.00-4.50 (m, 0.03H), 6.20-6.90, 6.85-7.70 (m, 5H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  16.45, 18.78, 40.36, 42.31, 43.46, 44.18, 46.54, 47.31, 125.60, 127.62, 127.92, 128.99, 129.41, 130.21, 132.71, 135.49, 145.25, 145.61.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  -16.72, -12.63, -7.52, -2.70. IR (KBr):  $\nu$  3082, 3060, 3026, 2923, 2849, 2119, 1601, 1583, 1493, 1451, 1271, 1069, 1028, 908, 757  $\text{cm}^{-1}$ .  $M_w$  = 9700 and polydispersity 1.8.

Poly(styrene) obtained from the same conditions as above but in the absence of diphenylvinylsilane was found to have  $M_w$  = 10000 and polydispersity of 1.9, respectively.

### 6.9.2 Methyl methacrylate:Diphenylvinylsilane (1) - Copolymer 15

#### 6.9.2a (2.0 M) Methyl methacrylate:Diphenylvinylsilane (1) - 2:1

Methyl methacrylate (2.0 M, 4.0 g, 40 mmol), **1** (0.5 eq., 4.2 g, 20 mmol), benzoyl peroxide (0.0967 g, 0.40 mmol), benzene (20 mL). Yield: 66% (3.7370 g).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz, integration based on the 10 aromatic protons of  $\text{SiPh}_2$ ):  $\delta$  0.60-1.00, 0.85-1.20, 1.10-1.60, 1.55-1.95, 1.75-2.20 (m, 60H), 3.30-3.90 (m, 36H), 4.51-4.66, 4.61-4.73, 4.70-4.90, 4.90-5.06 (m), 5.55-5.67(m), 6.17-6.26 (m), 6.36-6.63 (m), 7.20-7.60, 7.40-7.80 (m, 10H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 200 MHz): 16.35, 18.64, 44.48, 44.83, 51.70, 54.37, 127.69, 129.29, 129.45, 134.73, 135.27, 135.35, 176.83, 177.74, 178.01.

$^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ , 300 MHz): -17.76, -13.58. IR (KBr):  $\nu$  2996, 2951, 2131, 1722, 1435, 1387, 1148, 989, 842, 809, 753  $\text{cm}^{-1}$ .  $M_w = 6000$  and polydispersity 3.0.

Poly(methyl methacrylate) obtained from the same conditions as above but in the absence of diphenylvinylsilane was found to have  $M_w = 21000$  and polydispersity of 3.0, respectively.

#### **6.9.2b (0.6 M) Methyl methacrylate:Diphenylvinylsilane (1) - 1:1**

Methyl methacrylate (0.6 M, 2.0 g, 20 mmol), **1** (1 eq., 4.2 g, 20 mmol), benzoyl peroxide (0.0484 g, 0.20 mmol), benzene (27 ml). Yield: 54% (1.2947 g).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz, integration based on the 10 aromatic protons of  $\text{SiPh}_2$ ):  $\delta$  0.60-1.00, 0.80-1.20, 1.10-1.60, 1.50-1.90, 1.80-2.20 (m, 50H), 3.30-3.90 (m, 30H), 4.51-4.66, 4.61-4.73, 4.70-4.90, 4.90-5.06 (m), 5.55-5.67 (m), 6.17-6.26 (m), 6.36-6.63 (m), 7.20-7.60, 7.50-7.75 (m, 10H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  16.24, 18.08, 18.85, 20.38, 29.46, 34.99, 37.69, 44.34, 44.70, 51.59, 53.08, 54.62, 127.87, 129.62, 130.00, 134.23, 135.77, 136.54, 176.92, 177.62.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  -17.47, -13.60. IR (KBr):  $\nu$  2996, 2951, 2130, 1731, 1453, 1387, 1241, 1193, 1149, 989, 754  $\text{cm}^{-1}$ .  $M_w = 4500$  and polydispersity 1.8.

#### **6.9.2c (0.6 M) Methyl methacrylate:Diphenylvinylsilane (1) - 2:1**

Methyl methacrylate (0.6 M, 2.0 g, 20 mmol), **1** (0.5 eq., 2.1 g, 10 mmol), benzoyl peroxide (0.0484 g, 0.20 mmol), benzene (27.8 mL). Yield: 65% (1.5859 g).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz, integration based on the 10 aromatic protons of  $\text{SiPh}_2$ ):  $\delta$  0.60-1.00,

0.80-1.20, 1.10-1.60, 1.50-1.90, 1.80-2.20 (m, 70H), 3.30-3.90 (m, 42H), 4.51-4.66, 4.61-4.73, 4.70-4.90, 4.90-5.06 (m), 5.55-5.67 (m), 6.17-6.26 (m), 6.36-6.63 (m), 7.20-7.60, 7.50-7.75 (m, 10H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  16.39, 18.69, 44.49, 44.84, 51.71, 53.23, 54.77, 127.99, 129.74, 130.12, 134.35, 134.99, 135.89, 136.66, 177.03, 177.73, 178.57.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  -7.23, -16.96. IR (KBr):  $\nu$  2997, 2951, 2135, 1731, 1484, 1436, 1388, 1242, 1193, 1149, 989, 754  $\text{cm}^{-1}$ .  $M_w = 6900$  and polydispersity 2.2.

#### **6.9.2d (0.6 M) Methyl methacrylate:Diphenylvinylsilane (1) - 5:1**

Methyl methacrylate (0.6 M, 2.0 g, 20 mmol), **1** (0.2 eq., 0.84 g, 4 mmol), benzoyl peroxide (0.0484 g, 0.20 mmol), benzene (29 mL). Yield: 75% (1.6698 g).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz, integration based on the 10 aromatic protons of  $\text{SiPh}_2$ ):  $\delta$  0.60-1.00, 0.80-1.20, 1.10-1.60, 1.50-1.95, 1.80-2.20 (m, 95H), 3.30-3.90 (m, 57H), 4.51-4.66, 4.61-4.73, 4.70-4.90, 4.90-5.06 (m), 5.55-5.67 (m), 6.17-6.26 (m), 6.36-6.63 (m), 7.20-7.60, 7.50-7.75 (m, 10H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  16.26, 18.27, 44.38, 44.73, 51.60, 52.97, 54.51, 127.76, 129.50, 129.88, 134.11, 134.75, 135.65, 136.75, 176.81, 177.62, 178.35.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  -17.44, -13.57. IR (KBr) 2996, 2952, 2137, 1722, 1588, 1485, 1388, 1272, 1146, 1146, 989, 842, 753  $\text{cm}^{-1}$ .  $M_w$  10000 and polydispersity 2.3.

Poly(methyl methacrylate) obtained from the same conditions as above but in the absence of diphenylvinylsilane was found to have  $M_w = 17750$  and polydispersity of 2.3, respectively.

## 6.10 Grafting of Copolymer 15

### 6.10.1 Grafted Copolymer 16

Benzene was added to polymer **15** (0.8 g), vinyldimethyl-terminated poly(dimethylsiloxane) (2 mL, 1.86 g), and tris(triphenylphosphine)-rhodium (I) chloride (0.05 g, 0.054 mmol) to just give a homogenous solution. The reaction mixture was stirred at 50° C for 12 h. The solvent was removed under vacuo and the crude product was purified by precipitation as described earlier. Yield: 0.4114 g.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz, integration based on the 10 aromatic protons of  $\text{SiPh}_2$ ):  $\delta$  -0.10-0.20, 0.10-0.30 (m), 0.60-1.00, 0.80-1.20, 1.10-1.60, 1.55-1.95, 1.80-2.20 (m, 60H), 3.30-3.90 (m, 36), 5.55-6.61 (m), 7.20-7.60, 7.50-7.75 (m, 10H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  -0.71, 0.06, 0.83, 16.24, 18.53, 20.88, 44.33, 44.68, 45.32, 51.55, 52.54, 53.22, 127.59, 129.03, 129.18, 129.36, 129.92, 134.63, 135.10, 135.25, 135.25, 135.75, 136.10.  $^{29}\text{Si}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  -21.93, -20.82, -19.52, -16.98, -13.44, -6.19, -5.82, -4.20, -3.84. IR (KBr):  $\nu$  2998, 2952, 2843, 1731, 1485, 1450, 1388, 1273, 1243, 1194, 1149, 989, 966, 843, 753  $\text{cm}^{-1}$ .  $M_w = 12000$  and polydispersity 1.9. Contact angle of a water droplet on a film of the polymer cast from  $\text{CHCl}_3$  on a glass microscope slide: 65° (angle of uncoated glass slide 14°).

### 6.10.2 Grafted Copolymer 17

Polymer 15 (0.8 g), 9-vinylanthracene (2.0 g, 1.0 mmol), di-cumyl peroxide (0.2 g, 20.0 mmol), and benzene (10 mL) were introduced into a Pyrex ampoule of 20 mL capacity, degassed three times and vacuum sealed. The ampoule was then heated in a thermostated oil-bath at 140° C at 15 h. The reaction mixture was purified by precipitation as described above. Yield: 0.4004 g. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): δ 0.60-1.00, 0.85-1.20, 1.10-1.60, 1.55-1.95, 1.75-2.20 (m, 60H), 3.30-3.90 (m, 36H), 5.55-6.61 (m), 7.20-7.60, 7.40-7.80 (m, 10H). <sup>13</sup>C (CDCl<sub>3</sub>, 200 MHz): δ 16.27, 18.57, 20.77, 44.32, 44.67, 45.32, 51.55, 52.55, 54.25, 127.58, 127.82, 129.18, 129.51, 134.81, 135.22, 135.51, 135.75, 176.68, 177.56, 177.85, 178.13. IR (KBr): 2998, 2952, 2843, 2135, 1725, 1486, 1435, 1389, 1272, 1144, 989, 914, 843, 753, 702 cm<sup>-1</sup>. UV-VIS (1,1,1-trichloroethane): λ 392, 371, 353 nm. M<sub>w</sub> = 10000 and polydispersity 1.9.

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