Technische Universität München
Fakultät für Chemie
Fachgebiet Molekulare Katalyse

Functionalized Hybrid Silicones – Catalysis, Synthesis and Application

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Vollständiger Abdruck der von der Fakultät für Chemie der Technischen Universität München zur Erlangung des akademischen Grades eines

Doktors der Naturwissenschaften
(Dr. rer. nat.)

genehmigten Dissertation.

Vorsitzender: Univ.-Prof. Dr. M. Schuster
Prüfer der Dissertation: 1. Univ.-Prof. Dr. F. E. Kühn
2. Univ.-Prof. Dr. O.Nuyken (i.R.)

Die Dissertation wurde am 16.02.2012 bei der Technischen Universität München eingereicht und durch die Fakultät für Chemie am 08.03.2012 angenommen.

The following dissertation was prepared between April 2009 and March 2012 at the Chair of Inorganic Chemistry, Department of Molecular Catalysis of the Technische Universität München.

I would like to express my deep gratitude to my academic supervisor

Prof. Dr. Fritz E. Kühn

for his support and confidence and the freedom of scientific research.

This work was supported by a research grant from the BASF Construction Chemicals GmbH, Trostberg, Germany.

Acknowledgement

I would like to express my sincere gratitude to Prof. Dr. Oskar Nuyken and Dr. Eckhart Louis for their ongoing support and their undamped enthusiasm for my research topic. They supported this work with many inspiring discussions, new ideas and critical questions.

I thank the BASF Construction Chemicals GmbH, Trostberg, for giving me the opportunity to work on an industrial cooperation project. Especially, I would like to thank Dr. Simone Klapdohr and Dr. Burkhard Walther, who accompanied this project from the industrial perspectice, for their support and the nice time I had in Trostberg during the application technological tests.

I am very grateful to Prof. Dr. James Crivello for his support with the photopolymerization experiments and the very nice and fruitful time at the Rensselaer Polytechnic Institute.

I would like to thank all the colleagues at the Technische Universität München for the nice working atmosphere. Especially, I thank my lab mate Simone Hauser for the very comfortable lab climate, for her friendly and polite nature, for various inspiring conversations, also besides chemistry, and for solving small computer problems.

I also thank the lab neighbors from the east-west corridor, Jenny Ziriakus, Christina Müller, Philipp Altmann and Stefan Huber, for the nice time we spent together, especially during the coffee breaks, and for their generosity concerning chemicals.

Many thanks also to the colleagues from the Si-Institute, Dr. Peter Gigler, Dr. Stefanie Riederer and Dr. Daniel Canella for many inspiring discussions concerning silicon chemistry and to Dr. Manuel Högerl and Dr. Magnus Buchner for the maintainance of the NMR spectrometer.

All technicians at the TUM, especially Georgeta Krutsch for NMR experiments and Thomas Schröferl for GC-MS, are gratefully acknowledged. Furthermore, I am grateful to Dr. Marianne Hanzlik for performing several TEM measurements.

I also thank the technicians at the BASF in Trostberg, especially Andrea Schneider and Andreas Brey for their support during the application technological tests.

Many thanks go to Prof. Dr. Peter Härter, Tobias Kubo and Peter Richter who made the supervision of the practical courses in Weihenstephan almost a pleasure.

Furthermore, I am very grateful to the secretaries of the Chair of Inorganic Chemistry for their excellent support with respect to all bureaucratic issues. Additionally, I thank the TUM graduate school for unbureaucratic financial support.

My bachelor students Simone Keller and Hannah Weinzierl are gratefully achnowledged for their enthusiastic and energetic contribution to my research.

Finally and most of all, I would like to thank my mother and my boyfriend for their perpetual support, patience and trust!

Contents

Abbreviations and Trade Names

Å	Ångstroem
AAS	atomic absorption spectroscopy
Ac	acetate
Aerosil® 812S	fumed silica
AGE	allyl glycidyl ether
Ancamine® K54	2,4,6-*tris*-dimethylaminomethylphenol
Anti-terra® U80	wetting and dispersing additive
Ar	Aryl
Araldite® 2047-1	cold curing two-part methacrylate adhesive
Barytmehl N	barite flour
BDDVE	1,4-butandiol divinyl ether
BHT	butylated hydroxytoluene (2,6-di-*tert*-butyl-*p*-cresol)
BNT-CAT® 440	dibutyltin diketonate
br	broad
Bu	butyl
t-bu	tertiary butyl
Byk® 057	defoamer
Byk® 354	leveling additive with air-releasing effect
Bz	benzyl
C	celsius
cHex	cyclohexyl
COD	cyclooctadiene
COSY	correlation spectroscopy
d	day(s)
DAMO-T	*N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane
DBTL	dibutyltin dilaurate
DBU	1,8-diazabycyclo-undec-7-ene
DETA	diethylentriamine
DIPB	1,3-diisopropenylbenzene
DN 1146	3-(*N*-methylamino)propyltrimethoxysilane
DN AMMO	3-aminopropyltrimethoxysilane
DPI-TFPB	diphenyliodonium tetrakis(pentafluorophenyl)borate
EDA	ethylendiamine
eq.	equivalents
Et	ethyl
g	gramm
GC	gas chromatography
glycidyl-BPA	*bis*-glycidyl-poly(bisphenol-A-*co*-epichlorohydrin)
GPC	gel permeation chromatography
h	hour(s)
HexMTS	1,1,3,3,5,5-hexamethyltrisiloxane
HMQC	heteronuclear multiple quantum coherence
HMTS	1,1,1,3,5,5,5-heptamethyltrisiloxane
IOC-8	(4-*n*-octyloxyphenyl)phenyliodonium hexafluoridoantimonate
IPDA	isophoronediamine
IR	infrared

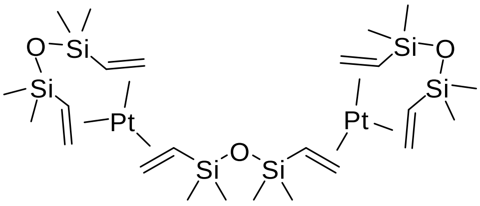
IV	iodine value
K	Kelvin
L	liter or ligand
M	metal
mbar	millibar
Me	methyl
Mes	mesithyl
mg	milligramm
MHz	megahertz
mmol	millimol
M_n	molecular weight (number average)
MS	mass spectrometry
MSA	methanesulfonic acid
MTBE	methyl *t*-butyl ether
m/z	mass-to-charge ratio
nbn	norbornene
NHC	*N*-heterocyclic carbene
nm	nanometer
NMR	nuclear magnetic resonance
Novolak-glycidyl ether	poly(phenylglycidyl ether)-*co*-formaldehyde
Omyalite 95T	treated ultrafine calcium carbonate
Palatinol® N	low viscosity plasticizer on phthalic ester basis
PDMS	polydimethylsiloxane
PDMS-H_2	α,ω-dihydropolydimethylsiloxane
Ph	phenyl
PMDS	1,1,1,3,3-pentamethyldisiloxane
ppm	parts per million
Proglyde^{TM}-DMM	dipropylene glycol dimethyl ether
q	quaternary
R	residue
SIKRON® SF 600	untreated silica flour
TEG-DVE	triethylene glycol divinyl ether
TEM	transmission electron microscope
TFA	trifluoro acetic acid
THF	tetrahydrofuran
TIB 208	dioctyltin di-(2-ethylhexanoate)
TIB 223	dioctyltin diketonoate
TMDS	1,1,3,3-tetramethyldisiloxane
TOF	turn over frequency
VCO	vinylcyclohexen oxide
UV	ultraviolet
UV 9380C	*bis*(dodecylphenyl)iodonium hexafluoridoantimonate
X	hetero-substituent

1. Introduction

1.1 Hydrosilylation

The Pt-catalyzed hydrosilylation of olefins is one of the most important laboratory and industrial instruments for the preparation of functionalized organosilicon compounds or silicone polymers.[1],[2] Silicones bearing organic, chemically active side groups are of major industrial importance and silane-functionalized olefins, dienes or polymers have gained substantial industrial interest as elastomers, sealants, adhesives or release coatings.[3],[4],[5] γ-Substituted propylsilanes and -siloxanes are important intermediates in the functionalization of silicones and play important roles as adhesion-promoting or cross linking agents.[6],[7]

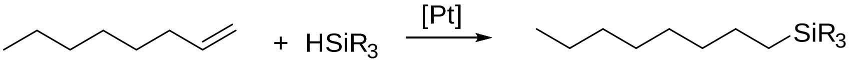
Among a variety of catalysts, which enable the addition of hydrosilanes to carbon-carbon multiple bonds, [Pt_2(*sym*-tetramethyldivinyldisiloxane)$_3$] ('*Karstedt*'s catalyst', **I**)[8] and hexachloroplatinic acid (H_2PtCl_6 • 6 H_2O in isopropanol, '*Speier's* catalyst', **II**)[9] are still by far the two most commonly used catalysts for this reaction (figure 1.1).



I

Figure 1.1. *Karstedt*'s catalyst (**I**).

The platinum catalyzed hydrosilylation of olefins occurs almost exclusively in an *anti-Markovnikov* way leading to the terminal (β) hydrosilylation product, as shown in scheme 1.1.[10]



Scheme 1.1. Platinum catalyzed hydrosilylation of *n*-octene leading to the terminal hydrosilylation product.

In some cases, side reactions such as the formation of the *Markovnikov* (α) product or the isomerization or reduction of the olefin cannot be completely suppressed.

Extensive reviews on the catalyzed hydrosilylation of unsaturated carbon-carbon multiple bonds, focusing on different aspects and applications of the reaction were provided by *Ojima et al.* [11], *Voronkov et al.* [12], *Brook* [13], *Reichl* and *Berry* [14], *Roy* [15] *Marciniec* [4], our group [5] and *Troegel* and *Stohrer* [7]. Many new strategies have been developed to improve reaction conditions and reaction efficiency. Thus, completely new ligand classes have been developed for homogeneous catalysts, asymmetric hydrosilylation has become an important tool in chiral synthesis, and new materials accessible *via* hydrosilylation ranging from block copolymers to dendrimers and functionalized silicones have been developed.[4],[5],[7],[16],[17]

1.2 Polysilalkylene Siloxanes as Hybrid Silicones

The organo-functionalization of silicones and the development of new functional polymers combining the chemical properties of silicones and organic compounds are important strategies for the development of new materials. Polysilalkylene or -arylene siloxanes (figure 1.2), so called hybrid silicones, have been developed to avoid the drawback of the depolymerization of classical polysiloxanes and to obtain elastomers with enhanced thermal stability and unique surface properties.[5],[18]

In contrast to *n*-paraffins, linear polydimethylsiloxanes (PDMS) exhibit extremely low inter- and intramolecular interaction and remain liquid down to -50°C even at chain lengths of 1000 repeating units or more.[1] Both, paraffins and PDMS show advantages and disadvantages in rheology, surface activity, chemical resistance, and ecological behavior. Therefore, industrial and academic research groups have looked for potential synergistic effects from chemically combining (poly)siloxane and (poly)alkylene or -arylene building blocks in one molecular copolymer backbone.[18],[19] Thus, polycarbosiloxanes, as shown in figure 1.2, became an important class of functional materials with desirable physicochemical properties. They consist of alternating siloxane and organic linker units and exhibit unique physical properties such as high thermal stability, solubility, surface behavior and, chemical resistance.[5],[18]

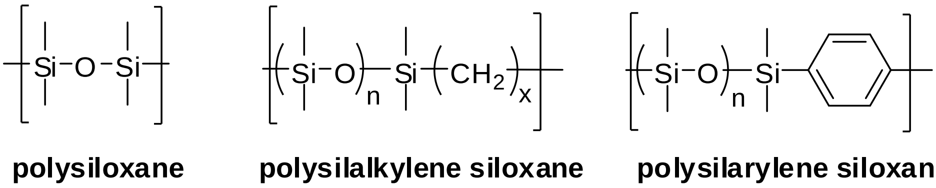
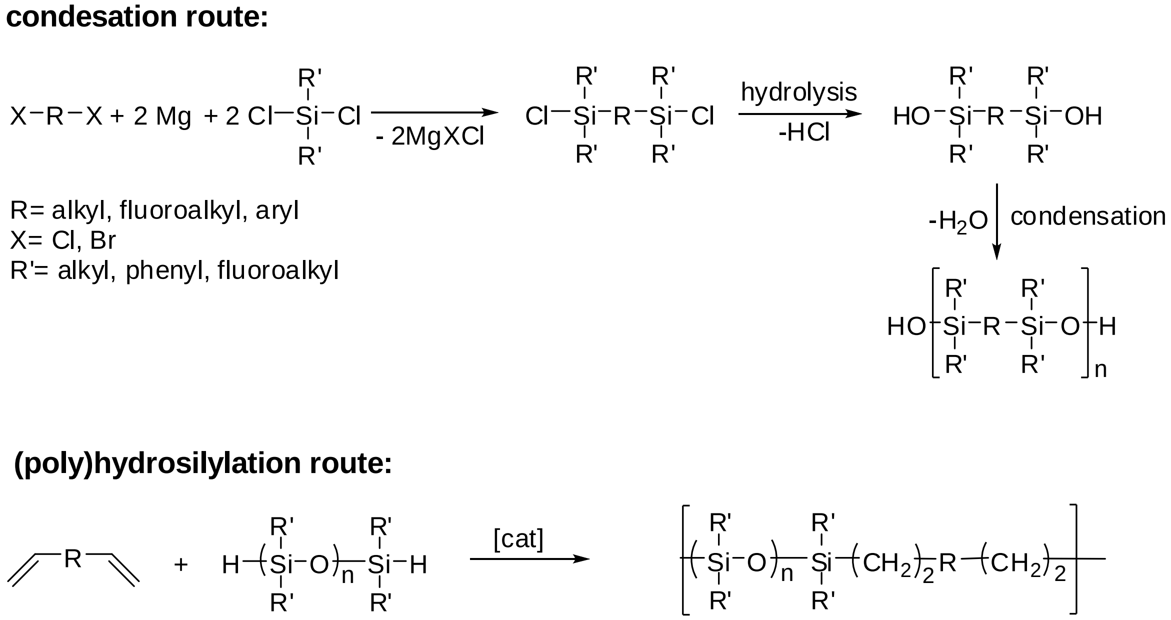


Figure 1.2. Nomenclature of poly(carbo)siloxanes.

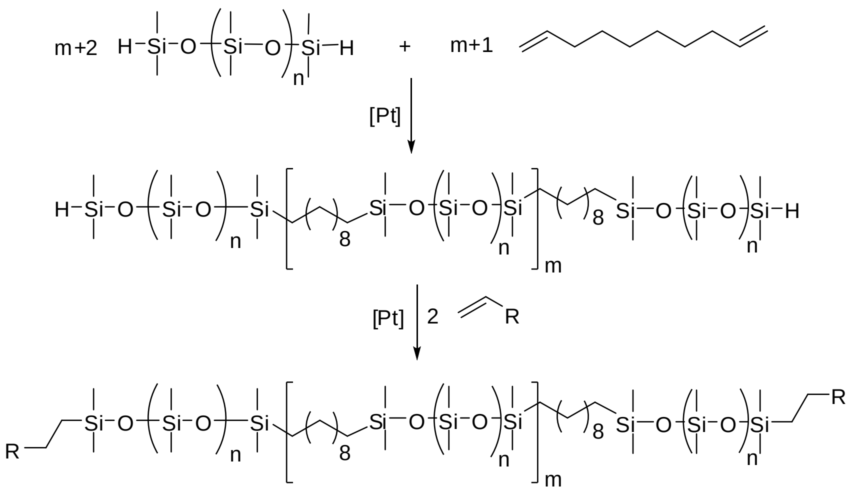
Two synthetic strategies can be applied for the preparation of these hybrid materials: the condensation of (α,ω-*bis*)silanol compounds or the (poly)hydrosilylation α,ω-dienes with α,ω-dihydrodi- or oligosiloxanes, according to scheme 1.2.[5],[19]



Scheme 1.2. Synthesis of polysilalkylene siloxanes (hybrid silicones) *via* condensation and hydrosilylation.

As the formation of HCl in the preparation of the *bis*-silanol compounds significantly reduces the tolerance of functional groups within the condensation type reaction, hydrosilylation has established as the most important route for the preparation of organo-modified silicones.

The molecular weight of the resulting hybrid polymers can be predetermined by the stoichiometry of the two building blocks, while their properties can be tuned by variation of the building blocks. If the siloxane component is used in excess, an α,ω-Si-H terminated polymer is obtained, which can be further functionalized *via* hydrosilylation with an olefin bearing a functional group. Thus, functional polysilakylene siloxanes with telechelic epoxy, hydroxy, amino or alkoxysilyl groups can be prepared *via* hydrosilylation of the Si-H-telechelic prepolymers with the corresponding olefin. The synthetic approach is shown in scheme 1.3.



R= CH_2-Si(OMe)$_3$, CH_2-NH_2, CH_2-glycidyl,...

Scheme 1.3. Synthesis and functionalization of a polysilalkylene siloxane.

The combination of organic building blocks and siloxane units within one molecule leads to copolymers with outstanding properties. *Louis et al.* described the synthesis of low to medium molecular weight Si-H-terminated and alkyl-Si-telechelic co-polyadducts of 1,9-decadiene and 1,1,3,3-tetramethyldisiloxane with unique properties[18]:

- Colorless or slightly yellow liquids
- High thermal and chemical stability
- Liquid below 0°C
- low dependence of kinematic viscosity from temperature
- Low surface tension
- Enhanced spreading capability.

These findings indicate that extremely interesting product properties can be associated with these novel hybrid silicones which seem worth to be investigated in more detail. Especially in release coatings, flooring and roofing applications or adhesives, these outstanding properties can be of great value.

1.3 Objectives of this Work

During this project novel functionalized polysilalkylene, -arylene or -oxylene siloxanes shall be developed and characterized with respect to their polymer properties such as molecular weight distribution, viscosity, surface activity, wetting ability or capillary deactivation. It is to be investigated if the polysilalkylene siloxane backbone of these new hybrid materials can be synthesized *via* a hydrosilylation-type step growth polyaddition reaction of suitable α,ω-Si-H- and α,ω-$H_2C=CH$-carriers, followed by the functionalization of the Si-H-terminated prepolymers with different functional groups such as epoxides, amines or alkoxysilanes to be able to cure them for coating applications.

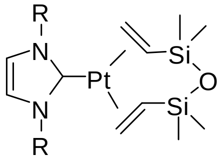
Initially, the activity and selectivity of several different common hydrosilylation catalysts shall be tested and compared, as there is a high demand on an active, versatile and efficient hydrosilylation catalyst which allows the cost-efficient large-scale preparation of organo-modified silicones. Special attention is to be be given to the tolerance towards functional groups and to the chemo- and regioselectivity of the catalyst.
In a second step, different α,ω-dienes are to be tested in model hydrosilylation reactions to deepen the understanding of their reaction behavior and to determine their suitability as building blocks in the straight-forward synthesis of hybrid silicone backbones. Furthermore, several monoolefins bearing different functional groups, such as epoxides, amines, alcohols, acrylates or cyclic fragments shall be tested as reagents for efficient end-capping. In all hydrosilylation reactions special attention must be given to chemo- and stereoselectivity as well as to minimum byproduct formation to avoid contaminations and to obtain ideal polymer properties.

With the results of these preliminary tests concerning the tolerance of functional groups and possible side reactions, a targeted synthesis of different novel functional hybrid silicones shall be developed. Several hybrid silicones with different organic linkers, different siloxane units and end groups shall be prepared and tested with respect to their potential applicability in construction chemical applications. Due to their expected unique interfacial properties potential fields of application are release coatings, paint and ink, wetting agents or roofing and flooring.

2. Catalysis

2.1 Platinum Catalysts and Reaction Mechanism

Although a wide range of potent catalysts is known for the hydrosilylation reaction of C=C double bonds, *Karstedt's* catalyst [Pt_2(*sym*-tetramethyldivinyldisiloxane)$_3$] (**I**, figure 1.1) and *Speier's* catalyst ($H_2PtCl_6 \cdot 6\ H_2O$ in isopropyl alcohol, **II**) are still by far the most common hydrosilylation catalysts. Other Pt-complexes such as [$Pt(PPh_3)_4$], [$PtCl_2(NH_3)_2$], [$Pt_2Cl_4L_2$] (L=PPh_3, nitrile, alkene,…) have also been used in hydrosilylation reactions.[4],[5] Many derivatives of *Karstedt's* catalyst with various carbenes or phosphines, (silylated) unsaturated alcohols, diynes and quinones have been synthesized to improve the selectivity and efficiency of the catalytic system.[4],[5] Strategies for optimizing the hydrosilylation reaction by the use of promoters, switchable catalysts or low-cost transition metal catalysts were recently reported in a review.[7] N-heterocyclic carbene (NHC) ligated platinum(0) complexes (**III**, figure 2.1) were reported by *Markó et al.* and show high chemo- and regioselectivity in the hydrosilylation of several alkenes. Furthermore, many functional groups are tolerated and the isomerisation rate of the double bond is reported to be much lower compared to *Karstedt's* catalyst.[20]

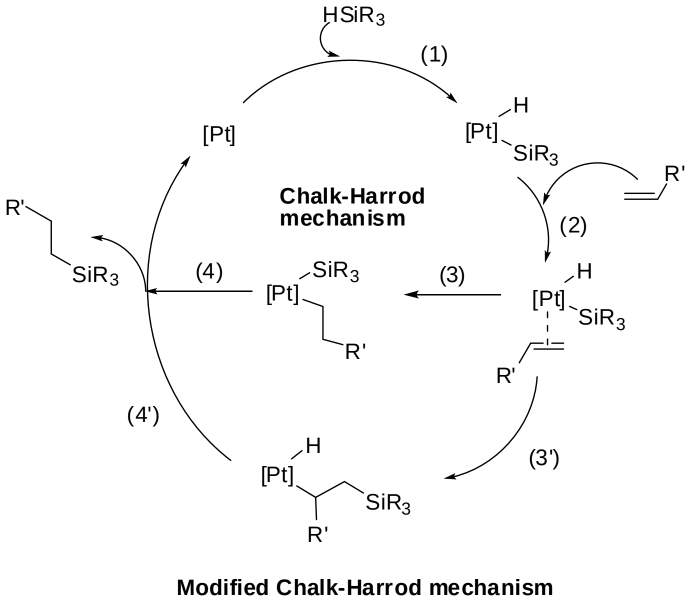


R= Me, Cy, tBu

III

Figure 2.1. NHC-Pt(0) complex (**III**) as reported by *Markó et al.*

In 1965, *Chalk* and *Harrod* proposed a mechanism for the platinum-catalyzed hydrosilylation, as shown in scheme 2.1, with four important key steps: 1) oxidative addition of Si-H to the metal center, 2) coordination of the alkene to the metal, 3) insertion of the alkene into the M-H bond and 4) reductive elimination of the Si-C product.[21] The modified Chalk-Harrod mechanism describes the migratory olefin insertion into the metal-silyl bond rather than into the metal-hydride bond (3') followed by reductive elimination of the Si-C product (4').[22]

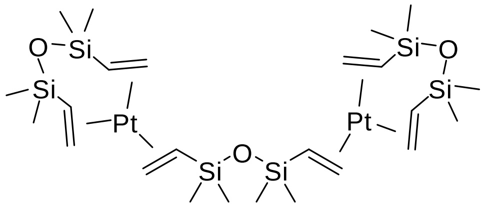


Scheme 2.1. *Chalk-Harrod* and modified *Chalk-Harrod* mechanism of the Pt-catalyzed alkene hydrosilylation.

This simple model is still widely accepted, although it lacks information on the formation of side products such as vinylsilanes or isomerized alkenes as well as on the occurance of an induction period observed in some cases.[22] Furthermore, it is still discussed whether the catalysis proceeds in homogeneous phase or on the surface of colloidal platinum formed *in situ*.[23] To explain the inconsistency of the catalytic cycle, the mechanism has been modified and expanded several times.[24] In general, it appears, that at least for Pt, two redox paths (0 ↔ II and II ↔ IV) are capable to sustain the catalytic cycle.

2.2 Test and Comparison of Different Hydrosilylation Catalysts

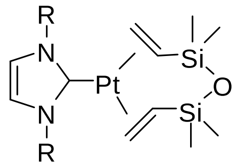
First of all, the catalytic activity of several well-established platinum-based hydrosilylation catalysts was examined and compared. The six different catalysts are given in figure 2.2.



I

H_2PtCl_6 x 6 H_2O

II



R= Mes

III

$Pt(PPh_3)_3$

IV

$Pt(PPh_3)_4$

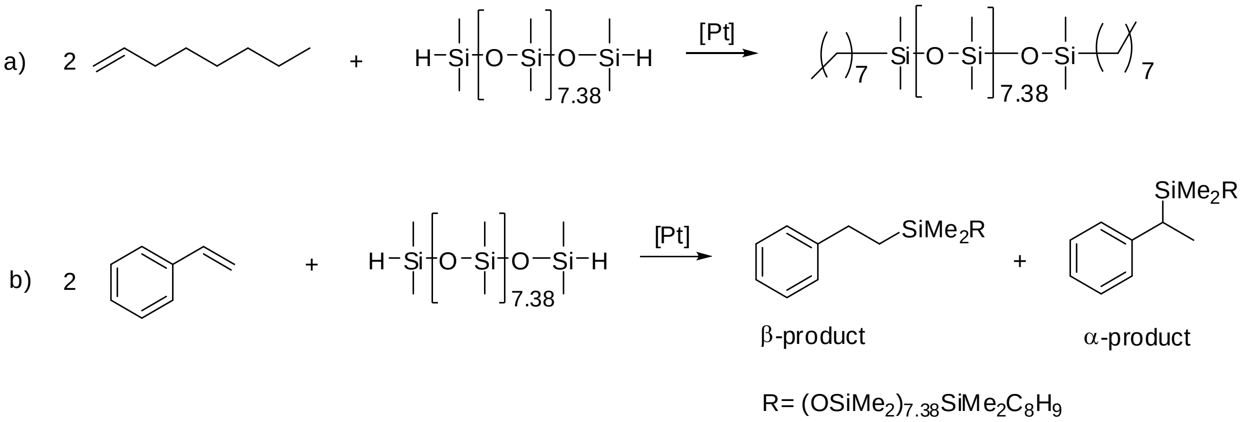
V

$PtCl_2(NH_3)_2$

VI

Figure 2.2. Different platinum-based hydrosilylation catalysts.

The hydrosilylation of *n*-octene and styrene, respectively, with α,ω-dihydropolydimethylsiloxane (PDMS-H_2, M= 680g/mol) were chosen as standard test reactions (scheme 2.2).



Scheme 2.2. Test reactions for different hydrosilylation catalysts.

These reactions can be regarded as models for the synthesis of hybrid silicone backbones containing aliphatic or aromatic organic building blocks.

All reactions were carried out in an atmosphere of argon, using two equivalents of the olefin. The substrates were mixed in a 50mL Schlenk flask at 40°C and the catalyst was added. In general, 10 ppm Pt corresponding to the total amount of substrates were used. For the insoluble solid catalyst **VI**, 100 ppm Pt were used. A thermo sensor was used to monitor the increase in temperature after addition of the catalyst. The activation temperature is defined as the temperature above which the exothermic reaction starts and a strong increase in temperature is observed. After that period, all reactions were stirred at the given reaction temperature for 2h.

The results for the catalytic performance of the six catalysts **I–VI** in the hydrosilylation of *n*-octene with PDMS are given in table 2.1.

Table 2.1. Catalytic performance of **I–VI** in the hydrosilylation of *n*-octene with PDMS-H_2.

Catalyst	**I**	**I**	**II**	**III**	**IV**	**V**	**VI**
Pt concentration [ppm]	10	2	10	10	10	10	100
Activation temperature [°C]	40	40	50	80	70	95	85
Reaction temperature [°C]	75	75	75	100	85	115	115
Reaction time [h]	2	2	2	2	2	2	2
Residual Si-H [%][a]	13	10	7	17	10	8	54
Residual Si-H [%][b]	12	9	4	12	7	6	54
Conversion of Si-H[a] [%]	87	90	93	83	90	92	46
Isomerisation of olefin[c] [%]	3.2	3.1	4.3	2.4	3.1	3.1	-
Color	yellow	none	yellow	none	none	none	none

a: Determined by ^{1}H-NMR; b: Determined with Na-butylate;
c: Determined by ^{1}H-NMR from the signal intensity at 5.4 ppm.

All catalysts were active in the hydrosilylation of *n*-octene with PDMS-H_2. In all cases the terminal (β) addition product, as shown in scheme 2.2a, was formed exclusively. Catalysts **I**, **II**, **IV** and **V** displayed very similar performances, leading to Si-H conversions above 90%. Because of the high reaction temperatures and the stoichiometric use of *n*-octene, all reactions were incomplete with respect to Si-H. The lowest activation temperature was observed for catalysts **I** and **II**. Both catalysts were already active at moderate temperatures and led to very exothermic reactions. Furthermore, with these catalysts a color change to slightly yellow could be observed during the reaction. For **I**, only 2 ppm of Pt were required to maintain the complete catalytic activity. Least conversion was observed with catalyst **VI** (46%) and also the NHC-complex **III** gave somewhat lower conversion rates (83%).

For **VI**, the low activity is possibly due to the poor solubility of the solid catalyst in the reaction mixture. In contrast to **I–V**, it was used as a solid and only suspended in the reaction mixture. In all cases, an isomerization of the terminal $H_2C=CH-CH_2$- double bond of *n*-octene to its internal isomer $CH_3-CH=CH$- could be observed.[25] The degree of isomerization was in the range of 3%. Also for **III**, which has been reported to be more selective than *Karstedt's* catalyst [20], an isomerization of > 2% was observed.

Because of the low over all conversion, no isomerization could be observed in the presence of catalyst **VI**. Because of its poor catalytic activity, **VI** is not further investigated.

The results of the catalytic performance of **I–V** in the hydrosilylation of styrene with PDMS are given in table 2.2.

Table 2.2. Catalytic performance of **I–V** in the hydrosilylation of styrene with $PDMS-H_2$.

Catalyst	**I**	**II**	**III**	**IV**	**V**
Pt concentration [ppm]	10	10	10	10	10
Activation temperature [°C]	40	50	95	82	80
Reaction temperature [°C]	75	75	120	95	95
Reaction time [h]	2	2	2	2	2
Residual Si-H [%]^a	0	0	2.7	0	0
Residual Si-H [%]^b	0	0	1.5	0	0
Conversion of Si-H^a [%]	100	100	97.3	100	100
α-Product	24.5	25.6	24.7	25.3	24.9
β-Product	75.5	74.4	75.3	74.7	75.1
Color	yellow	yellow	none	yellow	none

a: Determined by ^{1}H-NMR; b: Determined with Na-butylate.

In all cases the formation of an α-product, as shown in scheme 2.2b, was observed. This can be explained by the +M-effect of the aromatic ring, which leads to a negative polarization of the α-carbon atom and thus facilitates the formation of the α-product.

For all catalysts **I–V** the α to β ratio was about 1:3. All catalysts exhibited very high conversions, only **III** was slightly less active. In general, this reaction was faster and more exothermic than the hydrosilylation of *n*-octene. Again, the lowest activation temperatures were observed for **I** and **II**.

In conclusion, all tested common platinum based hydrosilylation catalysts were active in the hydrosilylation of *n*-octene and styrene with PDMS-H_2 and could therefore be used in the synthesis of polysilalkylene siloxanes. The best results were obtained with catalyst **I** and **II**, which led to almost quantitative Si-H conversion at low activation temperatures. Catalysts **III**, **IV** and **V** were slightly less active and reqired higher activation temperatures. These features will render them less favorable for large-scale applications. With $PtCl_2(NH_3)_2$ (**VI**) only moderate yields of the hydrosilylation product were obtained.

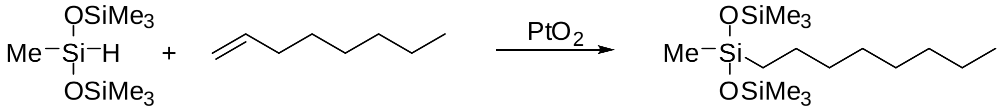
As a result of these performance tests, *Karstedt's* catalyst (**I**) was mainly used for the preparation and functionalization of hybrid silicones.

2.3 PtO_2 as Heterogeneous Hydrosilylation Catalyst

Compared to homogeneous catalysts, heterogeneous catalysts are rarely used in hydrosilylation reactions. Although they can be easily removed by filtration and reused in several cycles their large-scale application is quite limited. Many systems suffer from significant leaching or lose their activity after only a few runs. However, especially for the very expensive and biological hazardous Pt-catalysts their separation from the reaction mixture and recycling would be highly desirable.

Accordingly, the catalytic activity and recyclability of PtO_2 (**VII**) is examined. This compound was described as potent hydrosilylation catalyst, especially for the hydrosilylation of aminated alkenes by *Mioskowski et al.* in 2002 [26] and is since then occasionally used for this purpose [27],[28],[29].

As a test reaction to explore the potential of PtO_2 (**VII**) as a catalyst for the hydrosilylation of olefins, the hydrosilylation of *n*-octene with 1,1,1,3,5,5,5-heptamethyltrisiloxane (HMTS) was chosen (scheme 2.3).



Scheme 2.3. Hydrosilylation of *n*-octene with HMTS.

HMTS can be regarded as a model for poly(dimethyl-*co*-hydromethyl)siloxanes, which are important intermediates in the functionalization of silicones.[30]

First of all, the catalytic activity of PtO_2 (**VII**) was compared with that of the well established homogeneous systems, Karstedt's catalyst (**I**), H_2PtCl_6 (**II**) and $Pt(PPh_3)_4$ (**V**). All catalysts were examined under standard hydrosilylation conditions, i.e. the siloxane and a slight excess of *n*-octene (1.1 eq) were stirred at room temperature under argon, the catalyst was added and the reaction mixture was moved to a 80°C preheated oil bath. For the homogeneous catalysts 10 ppm of platinum (with respect to the total weight of the reaction mixture (0.002 mol-%)) were used. In the case of PtO_2, 100 ppm of platinum were applied because smaller amounts were difficult to be weighed accurately. With the homogeneous catalysts, the reaction was spontaneous and strongly exothermic and the product solution turned yellow due to the formation of colloidal platinum.[23] With PtO_2 the hydrosilylation reaction proceeded without a significant increase in temperature and the product solution remained colorless. In all cases only the desired terminal addition product (scheme 2.3) was formed. Except for traces of 2-octene – as a result of isomerization – no byproducts were formed.

To follow the reaction progress by ^{1}H-NMR spectroscopy samples were taken every 15 min. Yields were calculated based on the ratio of the Si-H signal of the silane at 4.7 ppm and the Si-CH_2 signal of the product at 0.5 ppm. The corresponding conversion plots at 80°C are shown in figure 2.3.

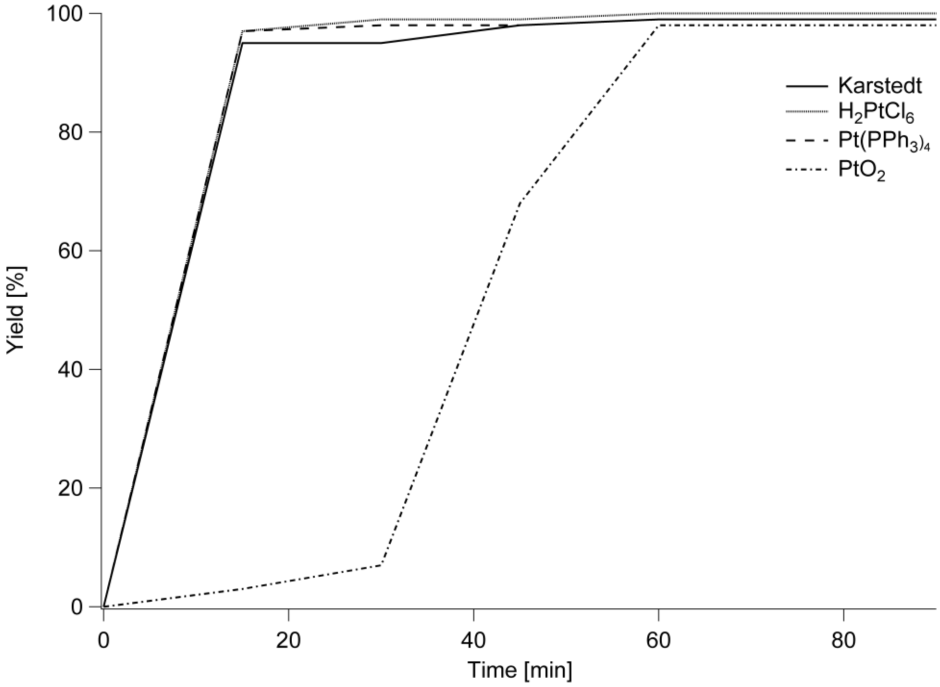


Figure 2.3. Comparison of homogeneous hydrosilylation catalysts and PtO_2 at 80°C.

With all three homogeneous catalysts **I**, **II** and **IV**, the reaction was complete within 15 min. With PtO_2 an induction period of approx. 30 min was observed, followed by a fast and complete reaction. 100% conversion was reached after 60 min.

As the next step, the catalytic performance of four different PtO_2 species (**VIIa**–**VIId**) was compared. Product characteristics of **VIIa**–**VIId** are summarized in table 2.3.

Table 2.3. Characteristics of the different PtO_2 species **VIIa**–**VIId**.

Catalyst	**VIIa**	**VIIb**	**VIIc**	**VIId**
Composition	PtO_2[a]	$PtO_2 \cdot H_2O$[a]	$PtO_2 \cdot H_2O$, cryst.[a]	$PtO_2 \cdot H_2O$[b]
Pt content [%]	81-83	77-81	>80	≈79
Surface [m^2/g]	>60	-	-	-

a: Commercial; b: Prepared from $H_2PtCl_6 \cdot 6\ H_2O$ and $NaNO_3$ at 600°C according to [31].

Transmission-electron-microscopical (TEM) images (figure 2.4) of the four PtO_2-catalysts show major differences in their morphology.

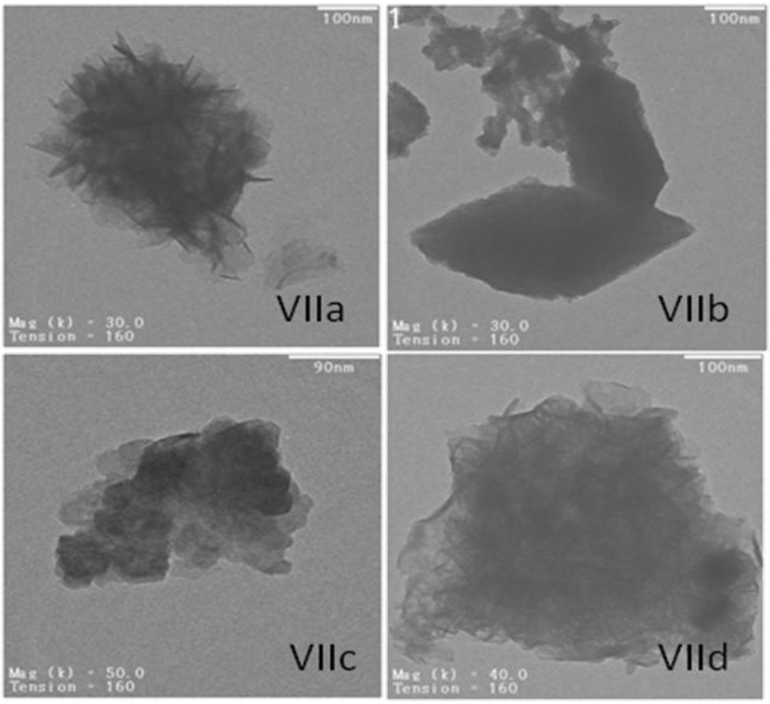


Figure 2.4. Electron-microscopical images of **VIIa**–**VIId**.

The catalytic performance of **VIIa**–**VIId** in the hydrosilylation of *n*-octene with HMTS at 100°C is shown in figure 2.5.

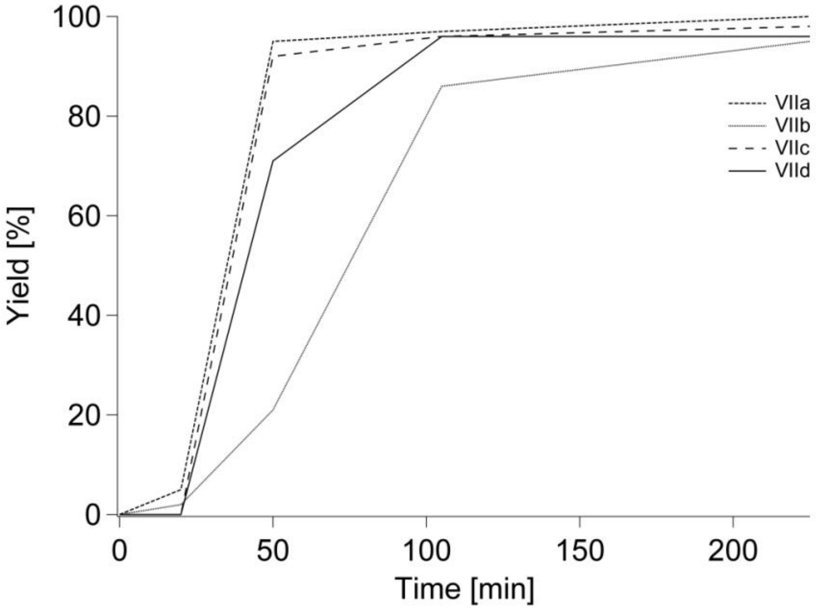


Figure 2.5. Catalytic performance of different PtO_2 species **VIIa**–**VIId**.

Best results were obtained with catalyst **VIIa**; **VIIc** was slightly less active followed by catalyst **VIId**, which was prepared according to [31]. Only with catalyst **VIIb** the reaction was still incomplete after 100 min at 100°C. In general, the differences in the catalytic activity of the four different PtO_2 species are not substantial. Because of its best performance, **VIIa** was chosen as catalyst for the following experiments.

To study the reaction kinetics in more detail, the amount of PtO_2 (**VIIa**) was varied. Figure 2.6 shows the corresponding conversion-time plots at 60°C for 1000 ppm Pt (0.2 mol-%), 100 ppm Pt (0.02 mol-%) and approx. 10 ppm Pt (0.002 mol-%). Samples were taken every 15 min and the reaction progress was followed by ^{1}H-NMR spectroscopy as described above.

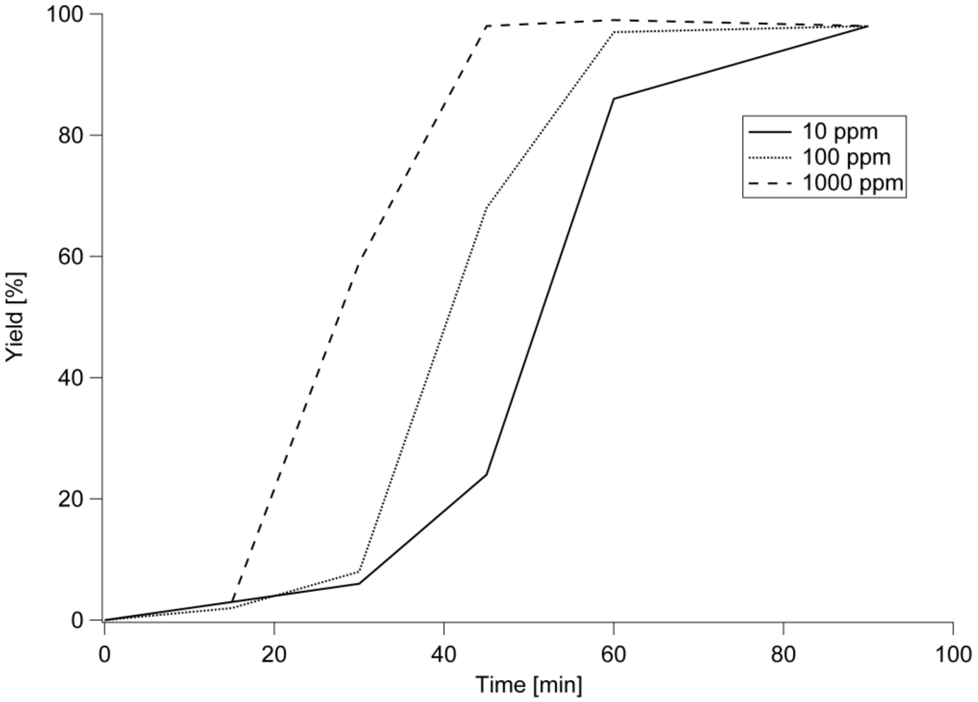


Figure 2.6. Variation of the amount of PtO_2 at 60°C.

Obviously the reaction is completed faster when increasing the concentration of the catalyst. For a catalyst loading of 1000 ppm Pt as PtO_2 the reaction was complete within 40 min. However, even with a very low catalyst loading of only 10 ppm Pt (0.002 mol-%) the reaction proceeded within 90 min. Again, in all cases an induction period was observed, ranging from 15 min (1000 ppm Pt) to 45 min (10 ppm Pt). After that, the reaction proceeded smoothly, indicating that obviously, a certain minimum concentration of a catalytically active species has to be formed *in situ* before the reaction can take place. Interestingly, even when only 10 ppm Pt were used, it appeared that the solid catalyst did not dissolve completely. Obviously, only a minor portion of the PtO_2 is consumed to initiate the hydrosilylation reaction. Unfortunately, it was not possible to determine the amount of the dissolved platinum species by classical quantitative analysis such as atomic absorption spectroscopy (AAS) because of a strong interference with the silicone matrix.

Anyway, PtO_2 has to be regarded as catalyst precursor, which is reduced *in situ* to transfer the Pt to a lower oxidation state (II or 0) which is required for oxidative addition of the silane.[21] A certain minimum amount of the active species has to be generated first and to dissociate into the the substrate before the reaction can occur. As expected, this minimum concentration of the active species is reached more rapidly with higher PtO_2 loadings than for lower ones – probably with larger PtO_2 amounts available, the particles more easily to dissolve are more abundant.

As described previously, the morphology of commercially available PtO_2 varies and a detailed picture concerning which particles release the active species preferably could not be obtained.

As figure 2.6 shows, the slope of the conversion-time curves at the times of maximal turnover, i.e. after the induction period, remains nearly the same in all cases. Thus, it is to assume that always about the same, small amount of Pt is dissolving. From this experiment also the turn-over-frequencies (TOFs) of PtO_2 were determined (table 2.4). The turnover frequency (TOF) is defined as (mol product)/[(mol platinum)•(reaction time in h)]. The highest obtained number indicates a "lower estimate" of the real activity of the active species.

Table 2.4. Turn-over-frequencies for different amounts of PtO_2.

Amount of PtO_2 [ppm]	TOF [h^{-1}]
1000	1200
100	12000
10	95000

For the calculation, the steepest slope of every curve, corresponding to approx. 60% conversion in 15 min was used. With a TOF of (likely >>) 95000/h, PtO_2 is a highly active and efficient hydrosilylation catalyst. As stated above, depending on the amount of PtO_2 that is actually converted to the active species, the corresponding TOF is most likely considerably higher, for it is assumed in these calculations that all PtO_2 dissolves to obtain at least a lower limit for the TOF.

After these more fundamental studies, the reusability of the remaining PtO_2 was examined with *in situ* IR spectroscopy at 85°C. After each cycle the reaction mixture was allowed to stand until the PtO_2 had completely precipitated, whereafter the clear and colorless product solution was carefully removed with a syringe and fresh substrates were added to the solid catalyst. It cannot be excluded that very small amounts of the fine catalyst were also removed during this procedure. Accordingly, 300 ppm of Pt were used to minimize the effects of such a Pt-loss. The reaction behavior of the first seven cycles is shown in figure 2.7. The reaction progress was determined by monitoring the decrease of the Si-H absorption band at 2100 cm^{-1} *via in situ* IR spectroscopy. No significant changes in appearance and quantity of the remaining PtO_2 catalyst were noticeable to the naked eye throughout the recycling experiments.

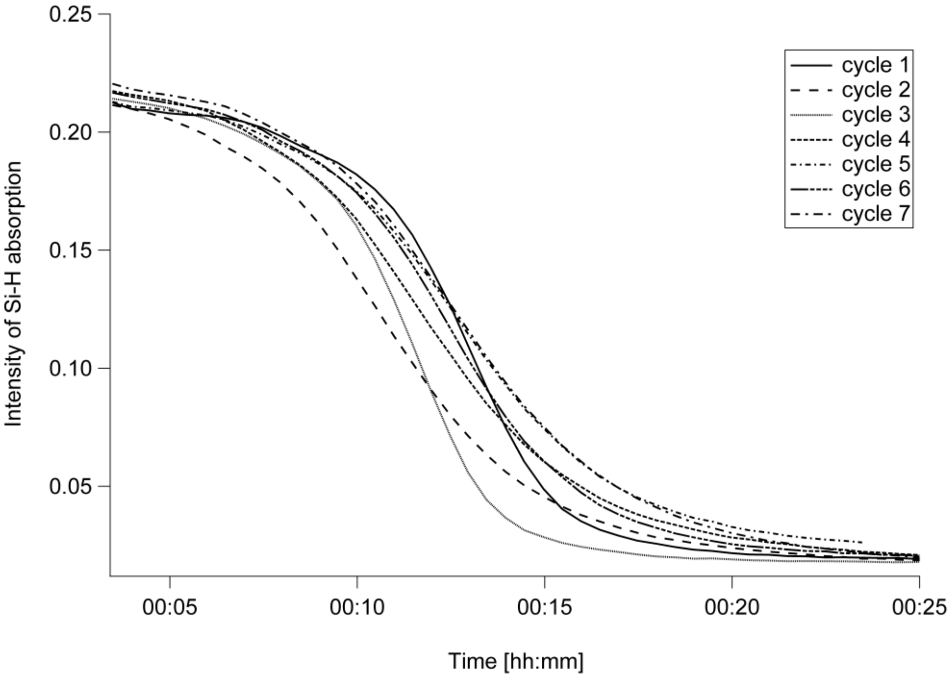


Figure 2.7. First seven cycles of the recycling of PtO_2 at 85°C.

The remaining catalyst can be used for at least six recycling steps without significant loss of activity. In all cases the reaction is complete within 25 min and an induction period of approx. 8 min can be observed. Because about the same induction period is observed in every catalytic cycle, it is assumed that the catalytically active species has to be formed anew at the beginning of each cycle to initiate the hydrosilylation reaction. The easiest way to explain such a reaction behavior is that only a small portion of the PtO_2 is dissolved to form the active species and is removed with the product solution after the reaction. In every following cycle the active species has to be formed again to maintain the catalytic performance.

To further prove this assumption, the reaction behavior of the supernatant solutions towards fresh substrates was examined. For this purpose, the supernatants of the first four recycling cycles were filtered through a 0.45 µm syringe filter to remove all traces of the heterogeneous catalyst and subsequently mixed with fresh substrates. The reaction progress was followed by *in situ* IR spectroscopy as shown in figure 2.8.

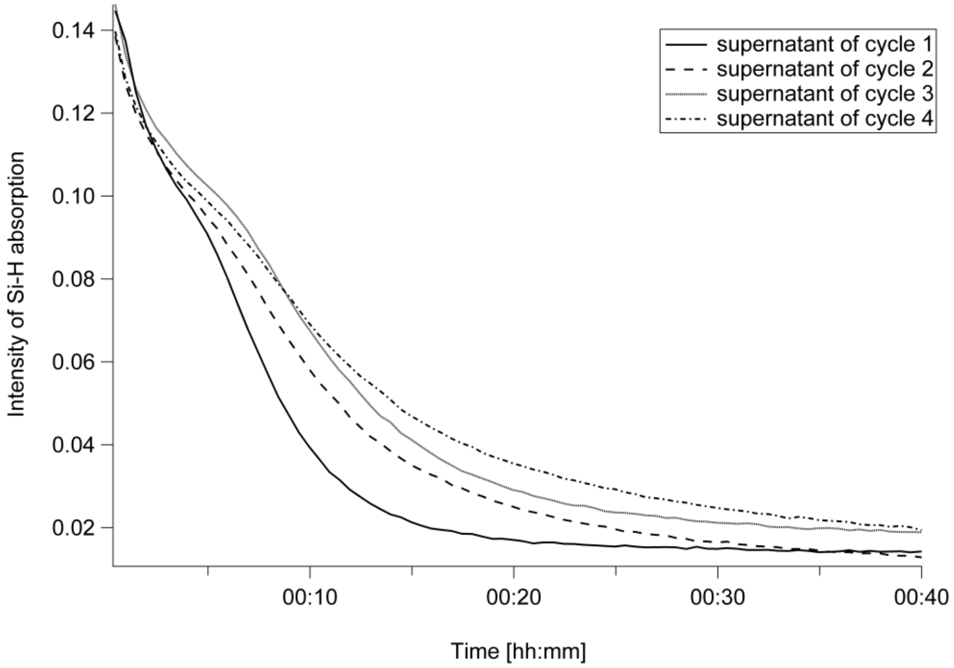


Figure 2.8. Catalytic behavior of the supernatant of the first four recycling cycles.

The supernatants show high catalytic activity without a significant initiation period. In all cases the reaction proceeds with almost 100% conversion after 40 min. The very similar reaction velocity in each cycle suggests that always an equal amount of active species is present at each run. The doubling of the reaction time - compared to the original run - can be explained by a dilution effect. After full conversion the reaction can be restarted repeatedly by adding fresh substrates to the product solution. This is shown in figure 2.9 for the supernatant of cycle 1.

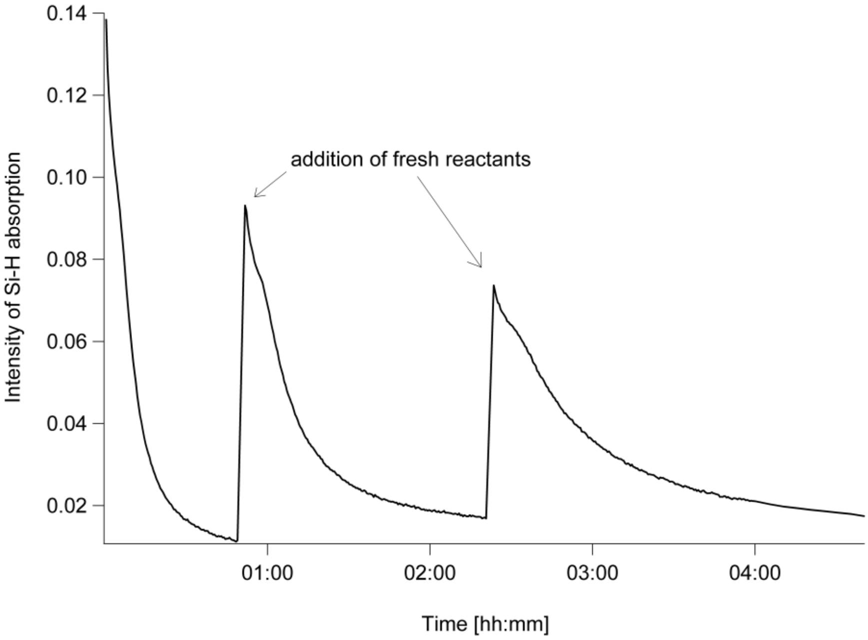


Figure 2.9. Repeated addition of fresh substrates to the supernatant of cycle 1.

Based on these experiments, it is evident that the active species is formed *in situ* and is soluble in the reaction mixture. It is highly catalytically active and can be “reused” by addition of fresh substrates to the supernatant.

To better understand the activation raction, which generates the active species from the PtO_2 precursor, the solid catalyst was independently pre-treated with both, the Si-H compound and the olefin for 2h at 85°C. After that, the solid catalyst-precursor was quantitatively filtered off and the filtrates were mixed with a stoichiometric amount of the respective other compound. The pre-treated HMTS phase showed immediate high reactivity when removed from the solid catalyst-precursor and mixed with *n*-octene. No induction period was observed. On the other hand, when *n*-octene was stirred with PtO_2 under the same conditions, after removal of PtO_2 and addition of HMTS, nearly no reaction took place. Therefore it can be concluded that the active species is formed from PtO_2 in presence of the silane, probably by reduction of Pt(IV) to Pt(II) or Pt(0). With *n*-octene instead, this species is not formed. Figure 2.10 shows these results in comparison with the normal catalysis with solid PtO_2.

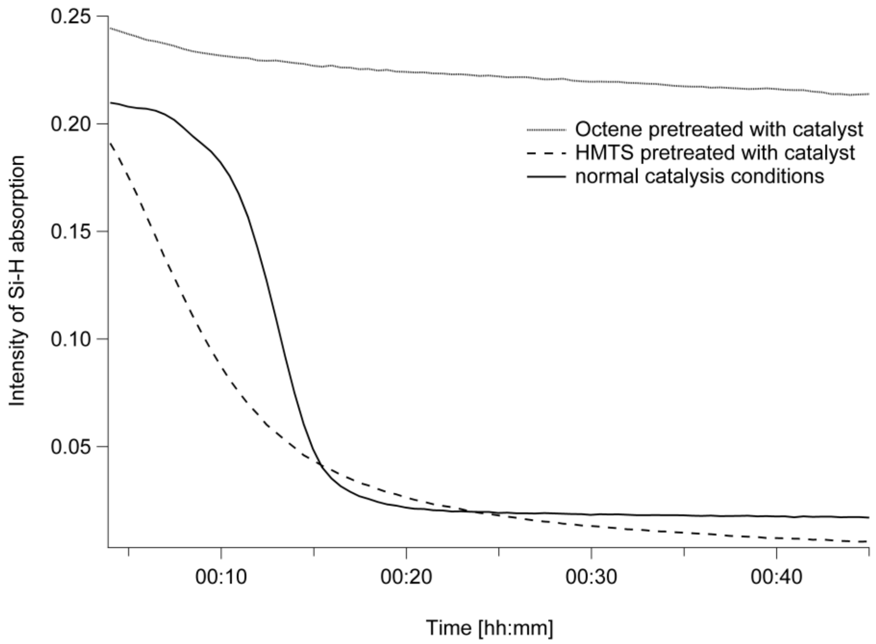
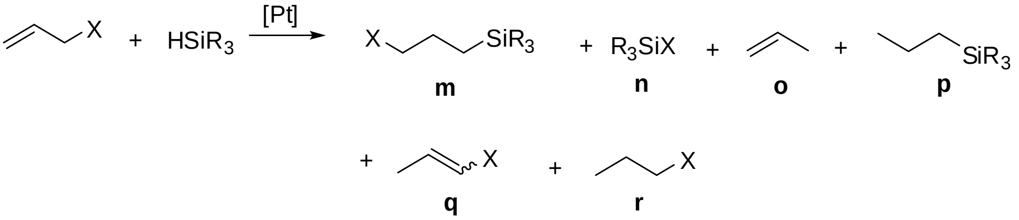


Figure 2.10. Effect of pretreatment.

In conclusion, it can be stated that PtO_2 is a highly active and regioselective hydrosilylation catalyst precursor. In the reaction of HMTS with *n*-octene TOFs of at least 95000/h were obtained. After complete conversion the remaining, unused PtO_2 can be removed from the reaction mixture by simple decantation or filtration and can be utilized for many (>>7) runs. The presence of an induction period in every cycle indicates that the active species has to be formed from unused PtO_2 *in situ* before the reaction can take place. The active species is soluble in the reaction mixture and is removed with the product after each cycle where it is immediately active upon addition of fresh substrates. In presence of the Si-H compound, the active species is generated from PtO_2, probably by reduction of Pt(IV) to Pt(II) or Pt(0). Due to the very small amount of PtO_2 reacting even with large excesses of HMTS, the identification of the true nature of the active species might be difficult to achieve, at least with the currently available spectroscopic means. The notion of a largely “self dosing” catalyst is probably attractive for (industrial) applicants.

2.4 Hydrosilylation of Isopropenyl Compounds

The hydrosilylation of allylic compounds is of outstanding importance for the industrial production of γ-substituted propylsilanes and -siloxanes and silicone polyethers. γ-Substituted propylsilanes and -siloxanes are important intermediates in the functionalization of silicones and play important roles as adhesion-promoting or cross linking agents.[6],[7],[32] Unfortunately, the direct platinum catalyzed hydrosilylation of allylic compounds is often very unselective.[7],[9],[20],[33] Besides the desired hydrosilylation product **m**, a C-X bond cleavage is often observed leading to the formation of R_3SiX (**n**) and propene (**o**). The formed propene can be further hydrosilylated to give propylsilane (**p**). Further byproducts can be isomerized olefins (**q**) or reduction products (**r**), as shown in scheme 2.4.



Scheme 2.4. Possible byproducts in the platinum catalyzed hydrosilylation of allylic compounds.

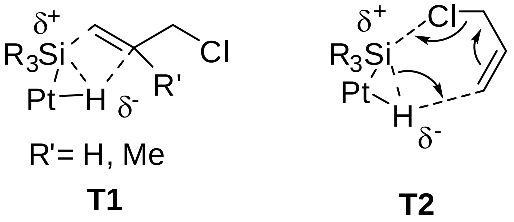
In contrast to allylic systems, the hydrosilylation of isopropenyl compounds, their isomers, is almost completely unexplored. Interestingly, the only products formed in the hydrosilylation of, for example, isopropenyl acetate with 1,1,1,3,3-pentamethyldisiloxane are acetoxypentamethyldisiloxane and *n*-propylpentamethyldisiloxane, just the main byproducts in the hydrosilylation of allyl acetate. This surprising result calls for basic studies of the isopropenyl system.

As background information and for easier understanding of the reaction mechanisms that are proposed as result of the following studies, an overview on the existing mechanistic models for allylic systems is given in the next paragraph.

2.4.1 Mechanistic Models for the Hydrosilylation of Allyl Compounds

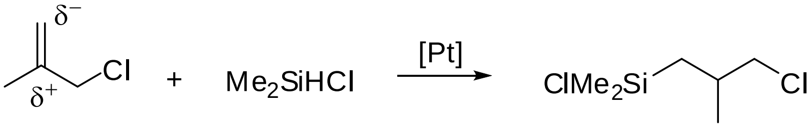
In the hydrosilylation of allylic systems, the formation of the hydrosilylation product **m** (scheme 2.4) can be explained by the *Chalk-Harrod* mechanism.[21]

For the byproduct formation only few mechanistic models exist:
It was first mentioned by *Wagner* in 1953, who proposed two vague reaction sequences.[34] In 1960 *Speier et al.* proposed an allylic substitution mechanism for the byproduct formation in the platinum catalyzed hydrosilylation of allyl chloride with different chloro silanes.[35] Two different transition states **T1** and **T2**, as shown in scheme 2.5, lead either to product formation (**T1**) or to the formation of the cleavage products R_3SiCl and propene *via* **T2**.



Scheme 2.5. Suggested transition states for product formation *via* **T1** and byproduct formation *via* **T2** in the hydrosilylation of methallyl chloride (R'= Me) or allyl chloride (R'= H).

Thus, the hydrosilylation of 2-methylallylchloride leads to the hydrosilylation product only (scheme 2.6). This is explained by the different polarity of the C-C double bond in 2-methylallylchloride which therefore prefers the **T1**-type transition state.

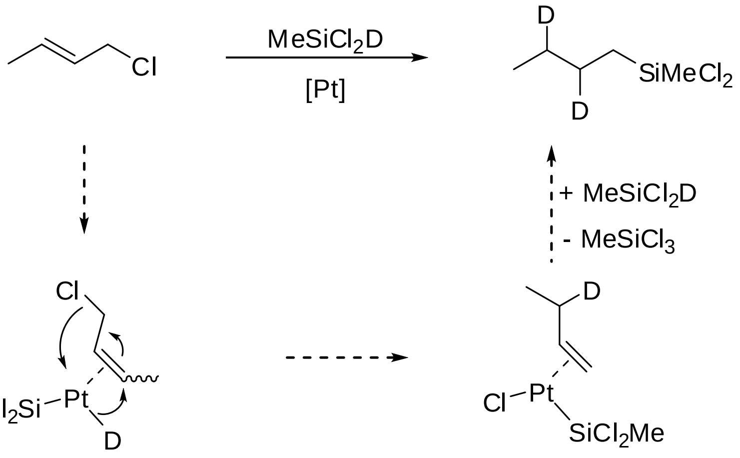


Scheme 2.6. Hydrosilylation of 2-methylallylchloride with dimethylchlorosilane.

This consecutive-competitive reaction mechanism was later on confirmed by *Marciniec et al.* who investigated the kinetics of the hydrosilylation of allyl chloride with trichlorosilane on Pt/C particles.[33]

An allylic substitution mechanism was also suggested by *Roy et al.* in 2008.[15] He explored the platinum catalyzed hydrosilylation of crotylchloride with deuterodichloromethylsilane and analyzed the deuterium distribution in the formed butylsilane.

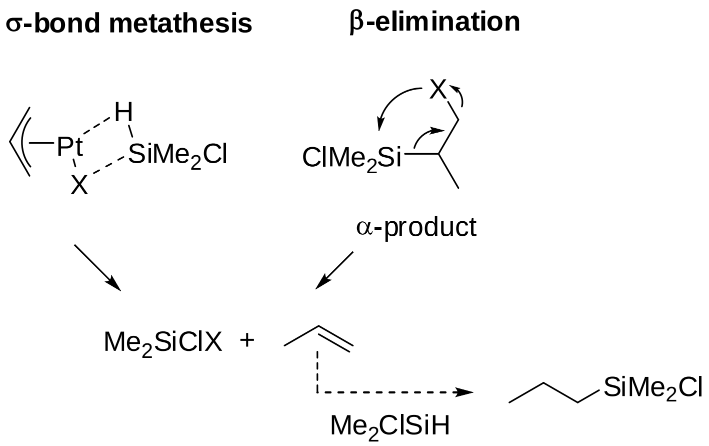
A nucleophilic attack of the deuteride at the allylic position leads after reductive elimination to the formation of 3-deutero-butene and methyltrichlorosilane (scheme 2.7). The 3-deutero-butene is further hydrosilylated to give 2,3-dideuterobutylsilane as only product.



Scheme 2.7. Proposed mechanism for the hydrosilylation of crotylchloride with deuterodichloromethylsilane.

Recently, *Gigler* suggested two further mechanistic approaches for the platinum catalyzed hydrosilylation of allyl chloride with dimethylchlorosilane.[36] The first one is based on the σ-bond metathesis between the silane and the allylic compound as shown on the left in scheme 2.8. The initial step is the oxidative addition of the olefin to the platinum center. The corresponding allyl complex performs the H-X exchange and Me_2SiCl_2 and propene are formed.

In the second model, as shown on the right in scheme 2.8, the formation of an unstable α-product as an intermediate is suggested which undergoes β-elimination in an Peterson-olefination-type-like manner and thus leads to the formation of Me_2SiCl_2 and propene. In both cases the formed propene is further hydrosilylated with another equivalent of silane to form propylsilane.



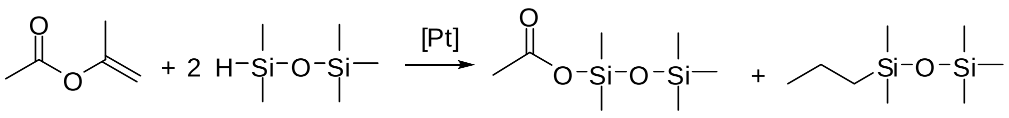
Scheme 2.8. *Gigler's* proposed mechanisms for the byproduct formation in the hydrosilylation of allyl chloride.

The hydrosilylation of allyl chloride with several different di- and trisiloxanes was examined by *Gulinski et al.*[37]

2.4.2 General Observations

During our investigation of the Pt-catalyzed hydrosilylation of several isopropenyl and allyl compounds with 1,1,1,3,3-pentamethyldisiloxane (PMDS), we observed in many cases C-O bond cleavage, leading to the simultaneous formation of two cleavage products.

Thus, the *Karstedt*-catalyzed hydrosilylation of isopropenyl acetate with PMDS leads to the formation of acetoxypentamethyldisiloxane (**P1**) and pentamethyl-*n*-propyldisiloxane (**P2**) as shown in scheme 2.9. The formation of **P2** is evidence of the intermediate existence of free propene in line with similar findings from reaction studies on allylchloride.[35],[36]



P1 **P2**

Scheme 2.9. *Karstedt*-catalyzed hydrosilylation of isopropenyl acetate with pentamethyldisiloxane.

With a platinum concentration of 100 ppm, the reaction was complete within 180 min and a product ratio **P1**:**P2** of 1:0.9 could be observed. The ^{1}H- and ^{29}Si-NMR spectra clearly indicate the formation of the two products (figure 2.11).

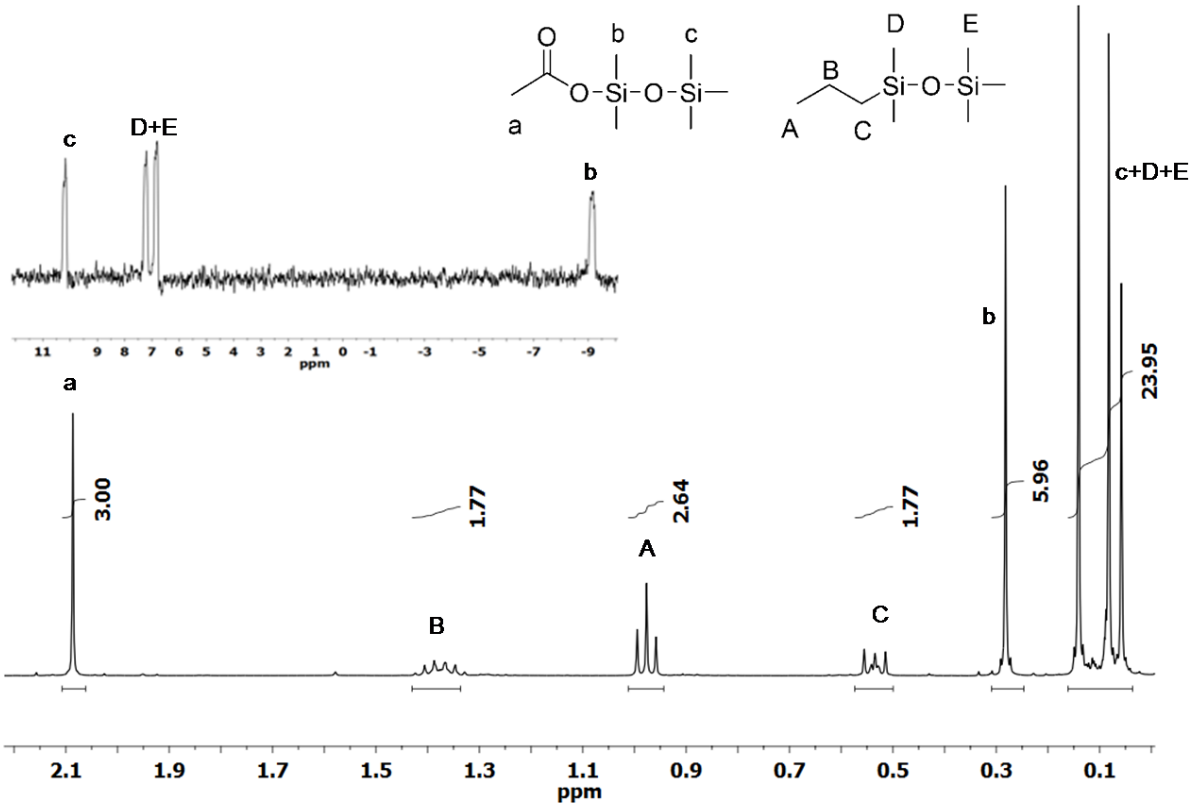


Figure 2.11. ^{1}H- and ^{29}Si-NMR (left corner) spectra of the hydrosilylation of isopropenyl acetate with PMDS.

2.4.3 Kinetic Considerations

To study the kinetics in of the reaction, the amount of catalyst was varied between 20 and 300 ppm Pt. The reaction progress was followed by ^{1}H-NMR spectroscopy where samples were taken every 30 min. Yields were calculated from the intensity ratio of the educt-Si-H signal at 4.7 ppm versus the Si-CH_3 signal of product **P1** at 0.3 ppm and the Si-CH_2 signal of product **P2** at 0.5 ppm, respectively. The corresponding time-yield plot for the formation of **P1** at 70°C is shown in figure 2.12.

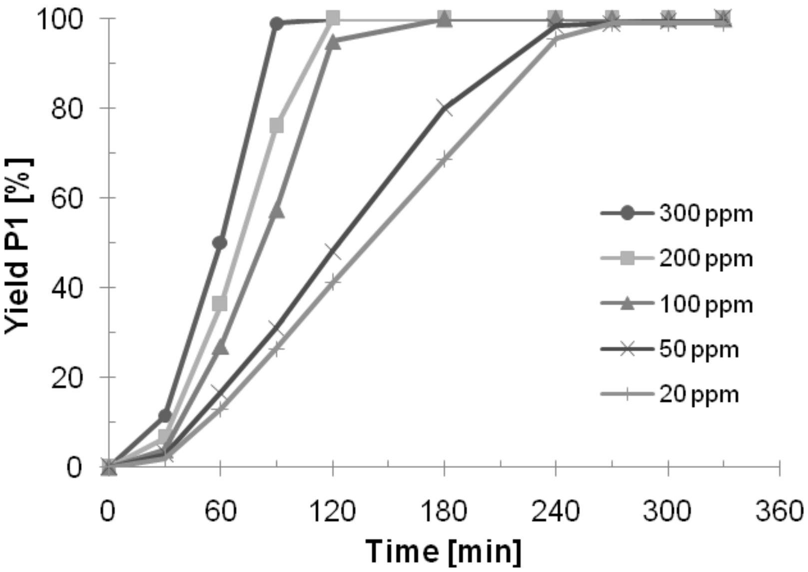


Figure 2.12. Time-yield plot for the formation of acetoxypentamethyldisiloxane **P1** in the hydrosilylation of isopropenyl acetate with pentamethyldisiloxane at 70°C with different catalyst concentrations.

The reaction velocity increases with catalyst concentration. For a catalyst loading of 300 ppm Pt (0.06 mol%) the reaction completes within 90 min whereas with a catalyst loading of only 20 ppm Pt (0.005 mol%) it needs 300 min to complete.

From these experiments the turn over frequencies (TOF) for the formation of acetoxypentamethyldisiloxane (**P1**) could be determined and are given in table 2.5. The turnover frequency (TOF) is defined as (mol product **P1**)/[(mol platinum)•(reaction time in h)]. After complete conversion, the concentration of **P1** is equal to the olefin concentration ([olefin] = [product **P1**]= 3.37 mmol).

Table 2.5. Turn-over-frequencies (TOFs) for the formation of **P1** at 70°C using *Karstedt's* catalyst.

Pt concentration [ppm]	**Amount of Pt** [mg]	**Amount of Pt** [mmol]	**Reaction time** [h]	**TOF** [h^{-1}]
20	0.02674	0.000137	5	4920
50	0.06685	0.000343	4.5	2180
100	0.1337	0.000685	3	1640
200	0.2674	0.001371	2	1230
300	0.4011	0.002056	1.5	1090

The formation of propylpentamethyldisiloxane **P2** behaves similar, the reaction rate increases with higher catalyst concentration (figure 2.13).

Also another effect is obvious: the total amount of **P2** decreases with decreasing catalyst concentration. With 300 ppm Pt the **P1**:**P2** ratio is about 1:0.7 while it is only 1:0.4 when 20 ppm Pt are used.

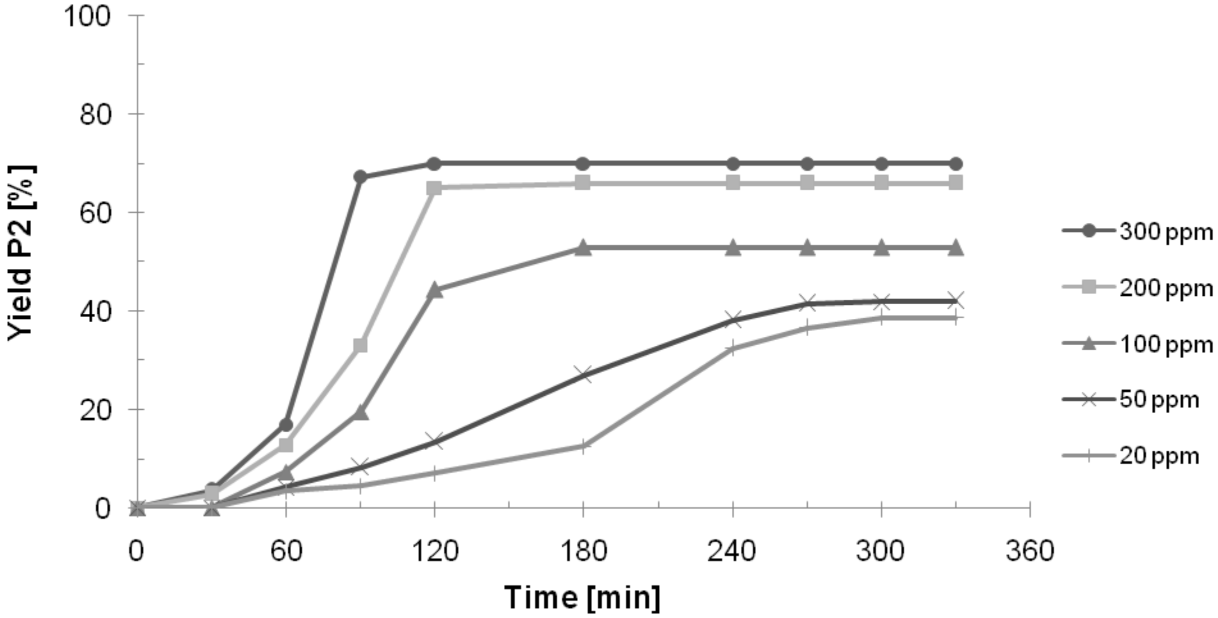
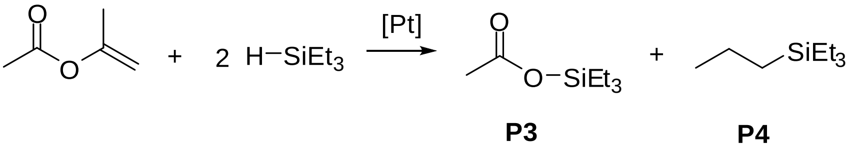


Figure 2.13. Time-yield plot for the formation of propylpentamethyldisiloxane **P2** in the hydrosilylation of isopropenyl acetate with pentamethyldisiloxane at 70°C with different catalyst concentrations.

The formation of **P2** proceeds *via* two steps. In the first reaction step **P1** and propene are formed from the substrate. In a second step, the free propene is hydrosilylated with another equivalent of pentamethyldisiloxane to give **P2**. If the catalyst concentration is reduced, the reaction velocity decreases and a higher amount of the volatile propene is able to escape from the reaction mixture (especially when the reaction vessel was opened for sampling).

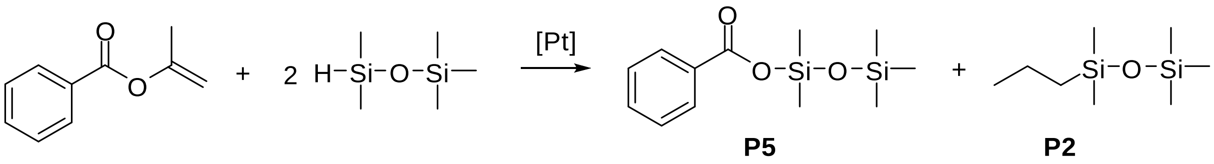
2.4.4 Scope and Limits of the Reaction

To investigate the scope of this type of reaction, the substituent of the isopropenyl compound as well as the silane were varied. When triethylsilane was used instead of PMDS the C-O bond cleavage in isopropenyl acetate also took place, leading to the formation of acetoxytriethylsilane (**P3**) and triethylpropylsilane (**P4**), as shown in scheme 2.10. The reaction was, however, much slower than with PMDS and needed 2d, instead of 2h, to complete at the same conditions (70°C, 100 ppm Pt). Because of the lower reaction velocity, resulting in higher propene losses, also the total yield of triethylpropylsilane was lower leading to a **P3**:**P4** ratio of only 1:0.4.



Scheme 2.10. Reaction of isopropenyl acetate with Et_3SiH.

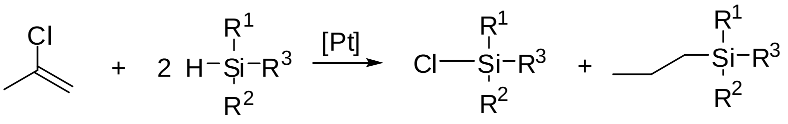
When isopropenyl benzoate was used instead of the acetate, the C-O bond cleavage likewise took place and the two cleavage products benzoyloxypentamethyldisiloxane (**P5**) and *n*-propylpentamethyldisiloxane (**P2**) were formed as depicted in scheme 2.11.



Scheme 2.11. Reaction of isopropenyl benzoate with PMDS.

With a platinum concentration of 100 ppm, at 70°C the reaction proceeded smoothly within 4h. The ratio of the two cleavage product was about 1:0.6. Possibly, in comparison to isopropenyl acetate, the poorer solubility of propene in the reaction mixture and the longer reaction times lead to higher propene losses.

Also 2-chloropropene reacts with PMDS or Et_3SiH to the corresponding products chloropentamethyldisiloxane (**P6**) and propylpentamethyldisiloxane (**P2**), as well as chlorotriethylsilane (**P7**) and triethylpropylsilane (**P4**) according to scheme 2.12.



P6: $R^1 = R^2 = Me$, $R^3 = OSiMe_3$
P7: $R^1 = R^2 = R^3 = Et$

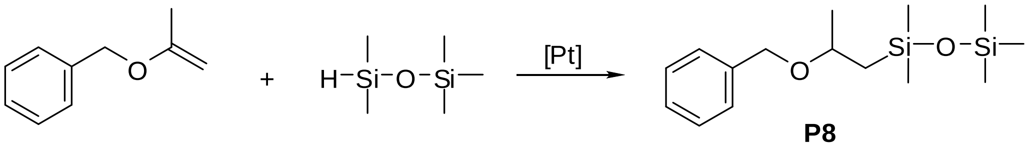
Scheme 2.12. Reaction of 2-chloropropene with PMDS or Et_3SiH.

For PMDS the reaction proceeded within 48h with a platinum concentration of 100 ppm at 70°C. The ratio of **P6**:**P2** was about 1:1 due to the use of an impermeable pressure tube. With Et_3SiH, however, even after 72h and a platinum concentration of 1000 ppm the reaction was still incomplete. The **P7**:**P4** ratio was only about 1:0.3.

These results indicate that an easy and versatile route for the preparation of different chloro- and acetoxysilanes and -siloxanes was found. As there is a significant demand especially for unsymmetrically substituted disiloxanes such as chloropentamethyldisiloxane in industry and a simple versatile synthesis is still missing, our findings might be of significant industrial interest. The separation of the two simultaneously formed products of type **n** and type **p** (see Scheme 2.4) might be a challenge due to the similarity of their boiling points and the formation of azeotrops.

Moreover, our findings clearly indicate that the C-O bond cleavage always takes place if the substituent at the isopropenyl group is a good leaving group such as acetate, benzoate or chloride.

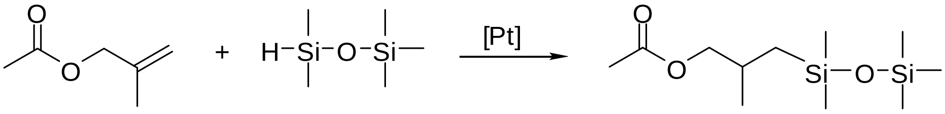
In contrast to that, isopropenyl ether does not undergo C-O bond cleavage and hence its *Karstedt*-catalyzed hydrosilylation with PMDS leads to the formation of the terminal hydrosilylation product **P8** only (scheme 2.13).



P8

Scheme 2.13. Hydrosilylation of isopropenyl benzyl ether with PMDS.

Also with 2-methyl-2-propenyl acetate (methallyl acetate) the terminal hydrosilylation product **P9** is the only product formed, as shown in scheme 2.14.



P9

Scheme 2.14. Hydrosilylation of 2-methyl-2-propenyl acetate (methallyl acetate) with PMDS.

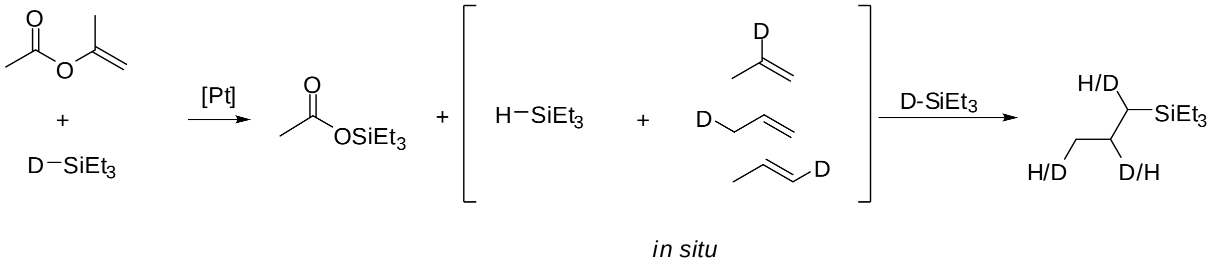
This difference in reactivity can be explained by electronic reasons. In isopropenyl ether the ether group is a bad leaving group. In methallyl acetate the saturated CH_2 group prevents C-O bond cleavage and, additionally the +I effect of the methyl group leads to a strong polarization of the double bond.[35]

The same reactivity pattern applies to allylic systems, where the hydrosilylation of allyl acetate leads to the formation of acetoxysilane (**n**) and propylsilane (**p**), whereas the hydrosilylation of allyl ethers only leads to the hydrosilylation product (**m**) and some isomerized byproducts (**q**) (scheme 2.4).

2.4.5 Deuteration Experiments and Mechanistic Proposal

To further investigate the reactivity of isopropenyl acetate and to strengthen the understanding of the mechanism of the C-O bond cleavage, a deuteration experiment with triethyl(silane-d) (Et_3SiD) was performed. In this case, the two cleavage products, acetoxytriethylsilane (**P3**) and a dideuterated triethylpropylsilane (triethyl(propyl-d^2)silane, $Et_3SiPr\text{-}d^2$, **P4-d^2**) were formed. The reaction needed 48h to complete (70°C, 100 ppm Pt) and the **P3**:**P4-d^2** ratio was about 1:0.3.

To our surprise, during the reaction a H/D-scrambling over the whole propene molecule was observed which resulted in a deuterium distribution in the triethylpropylsilane molecule as depicted in scheme 2.15.



Scheme 2.15. Deuterium distribution in the reaction of triethyl(silane-d) with isopropenyl acetate.

After 24h, it was possible to obtain a deuterium spectrum where deuterated propene as well as triethyl(propyl-d^2)silane ($Et_3SiPr\text{-}d^2$) were visible. The signals of the deuterated propene appeared at 5.6 (CD), 4.7 (CDH) and 1.4 ppm (CH_2D). The signals at 1.2 (CHD), 0.9 (CH_2D) and 0.4 ppm (CHD-Si) can be assigned to triethyl(propyl-d^2)silane (figure 2.14).

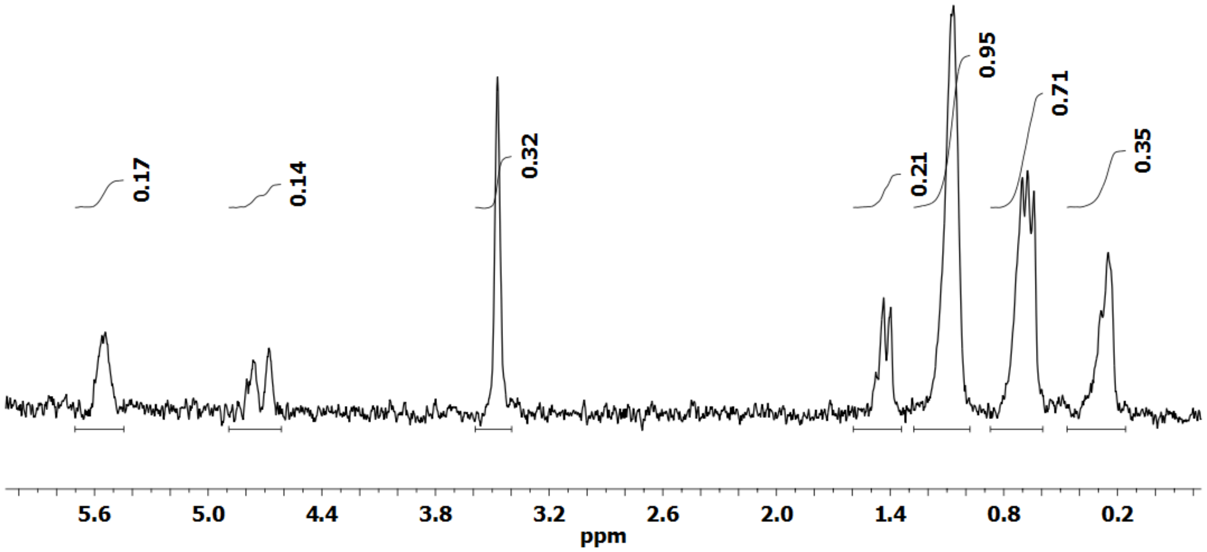
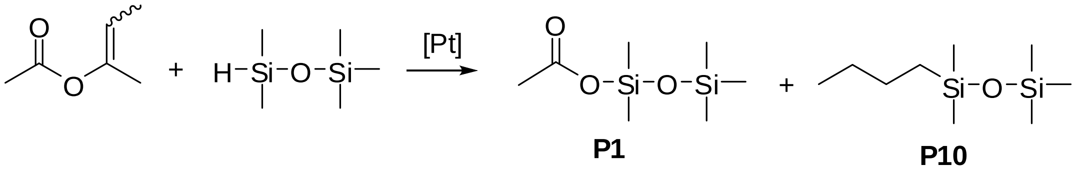


Figure 2.14. ^{2}H-NMR spectrum during the reaction of triethyl(silane-d) with isopropenyl acetate.

In the propene molecule, the ratio of deuteration is about 1:1:2 for the CD to CHD to CH_2D position, as can be estimated from the integrals of the corresponding signals in the ^{2}H-NMR spectrum. The same pattern can also be found in the dideuterated triethylpropylsilane where the deuteration at the CHD-Si and CDH_2 position of the propyl group is about 1:2. Due to the reaction with a second equivalent of Et_3SiD the highest degree of deuteration is found in the CHD-position of triethylpropylsilane. Mass spectrometry clearly indicates that only double deuterated species of triethylpropylsilane are formed. During the reaction a signal of H-triethylsilane can be observed at 3.6 ppm in the ^{1}H-NMR spectrum.

A similar behavior was found by *Ryan* and *Speier* in the hydrosilylation of 3-methyl-1-butene with trichloro(silane-d). They observed a H/D exchange between Si-D and C-H leading to a deuterium distribution of 2.5 D’s per molecule. The olefin was thought to engage in a series of reversible reactions in which it adds the catalyst and eliminates it, by which process it becomes isomerized and deuterated.[38]

To further examine this isomerization, 2-acetoxy-2-butene was used in the hydrosilylation with PMDS and again the products of the C-O bond cleavage, in this case acetoxypentamethyldisiloxane (**P1**) and *n*-butylpentamethyldisiloxane (**P10**), as shown in scheme 2.16, were obtained.



Scheme 2.16. Reaction of 2-acetoxy-2-butene with PMDS.

With a platinum concentration of 100 ppm the reaction needed 2d at 70°C to complete. The ^{1}H-NMR spectrum clearly indicates the formation of these two products only (figure 2.15).

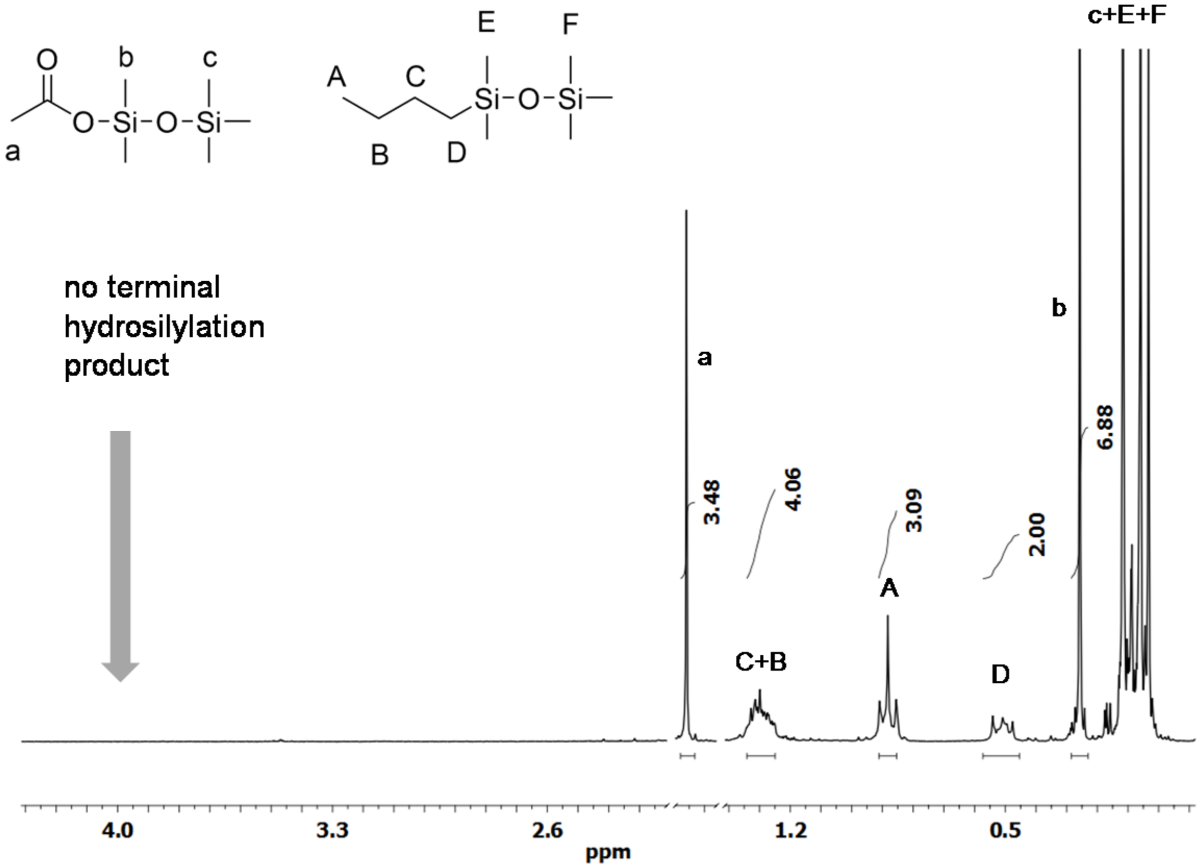


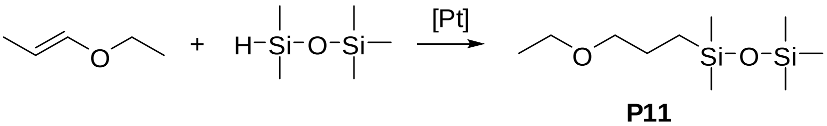
Figure 2.15. ^{1}H-NMR spectrum of the hydrosilylation of 2-acetoxy-2-butene with PMDS. (For clarity, signals of residual 2-butene-2-ol acetate are cut out.)

The same reaction behavior was found when 2-chloro-2-butene was used instead, leading to the formation of chloropentamethyldisiloxane (**P6**) and *n*-butylpentamethyldisiloxane (**P10**). In both cases, with triethylsilane no reaction was observed after 3d even at very high catalyst concentrations.

This means, that again in both cases, isomerization takes place generating *n*-butene from 2-butene. The absence of a signal in the region of 4 ppm proves that no uncleaved hydrosilylation product is formed. Therefore it is likely, that the isomerization takes place in the free olefin after C-O or C-Cl bond cleavage.

If Et_3SiD was reacted with propene using *Karstedt's* catalyst, also an H/D-scampling over the whole propene molecule was observed, resulting in the formation of triethyl(propyl-d)silane (**P4-d**) and indicating an isomerization of the free olefin.

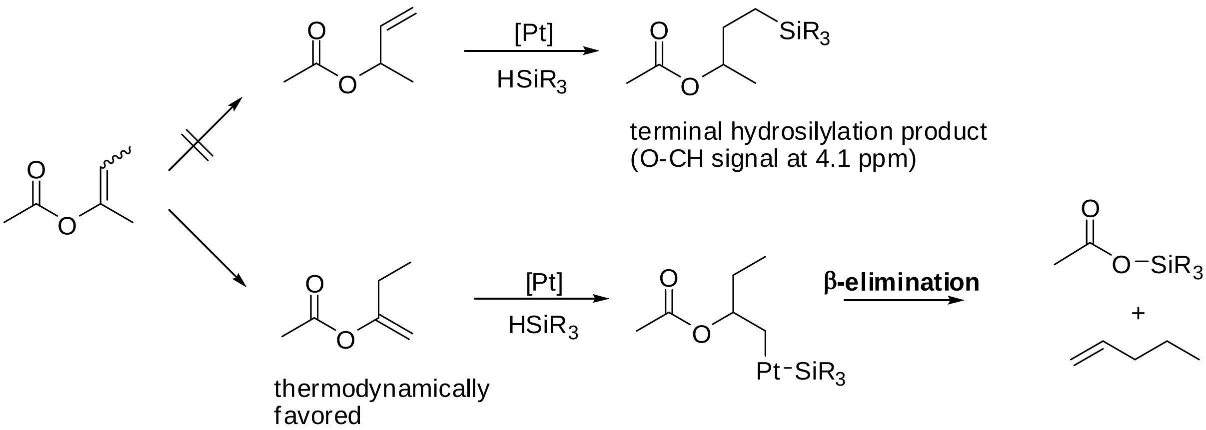
In contrast to the type of reactions described before, the reaction of ethyl-1-propenyl ether with PMDS leads to the formation of the terminal hydrosilylation products **P11** only, as shown in scheme 2.17.



P11

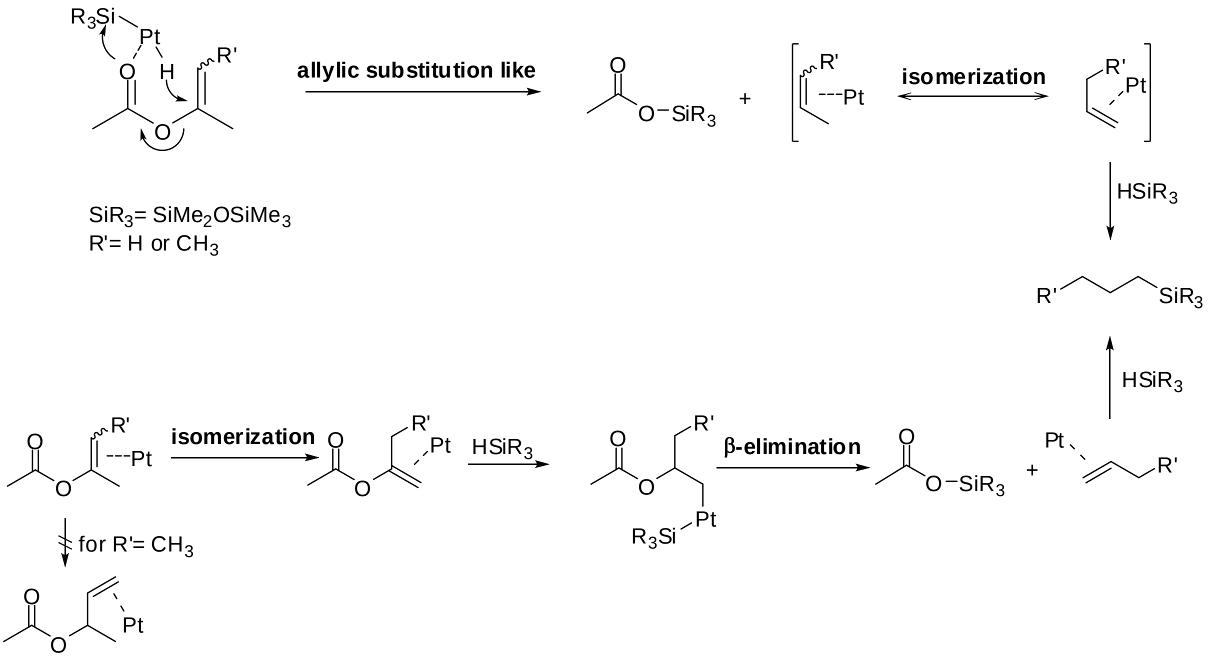
Scheme 2.17. Reaction of ethyl-1-propenyl ether with PMDS.

Even after 70h at high platinum concentrations and 75°C the reaction was incomplete. With Et_3SiH even no reaction took place. The fact, that the hydrosilylation product **P11** is formed, suggests, that in this ether structure isomerization can also happen without or prior to a C-O bond cleavage. However, for 2-acetoxy-2-butene, the absence of an uncleaved hydrosilylation product indicates that only the higher substituted isomer which is thermodynamically favored can be formed because only this isomer would then be able to undergo β-elimination to form the two products (scheme 2.18).



Scheme 2.18. Isomerization and possible product formation in the hydrosilylation of 2-acetoxy-2-butene with PMDS.

With all these observations and results two mechanistic approaches can be postulated. The first one, as shown on top of scheme 2.19, is based on the allylic substitution like mechanism where the negatively polarized hydride attacks the quarternary carbon atom, leading to the C-O bond cleavage. Attack of the second oxygen atom on the positively polarized silicon center results in the formation of acetoxysilane/ -siloxane and free olefin. The free olefin is then isomerized and subsequently hydrosilylated by another H-Si equivalent to form the terminal hydrosilylation product.



Scheme 2.19. Proposed mechanisms.

The second mechanism is based on the assumption that after oxidative addition an unstable intermediate (isomer of the α-product in allylic systems) is formed which undergoes β-elimination and after reductive elimination leads to the formation of the known products. In this approach, the isomerization of the olefin happens prior to C-O bond cleavage and only leads to the higher substituted isomer which is thermodynamically favored. This isomer is then able to undergo β-elimination to form the acetoxysilane and the free terminal olefin which is then further hydrosilylated (scheme 2.19).

In conclusion, the hydrosilylation of isopropenyl acetate with 1,1,1,3,3-pentamethyldisiloxane or triethylsilane leads to the exclusive formation of acetoxysiloxane/ -silane) and propylsiloxane/ -silane. The same reaction pattern can be observed for all other isopropenyl compounds bearing good leaving groups such as isopropenyl benzoate or chloride. In contrast to that, if a bad leaving group such as an ether functionality is present, only the hydrosilylation product is generated and the reaction is run *via* the classical *Chalk-Harrod* mechanism.

Kinetic measurements prove that the reaction velocity increases with catalyst concentration. Also the total yield of propylsiloxane rises with an increase of catalyst concentration. This can be explained by the fact that the formation of the hydrosilylation product proceeds *via* two steps. In the first reaction step acetoxysiloxane and propene are formed from the isopropenyl acetate.

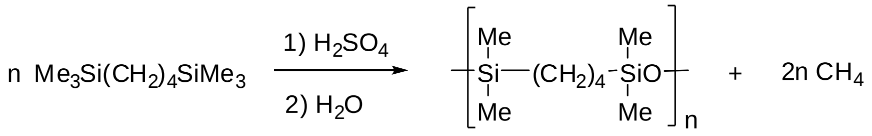
In a second step, the free propene is hydrosilylated with another equivalent of pentamethyldisiloxane to give propylsiloxane. When the catalyst concentration is reduced, the reaction velocity decreases and a higher amount of the volatile propene is able to escape from the reaction mixture unless impermeable pressure tube reactors are used.

Deuteration experiments and the use of internal olefins such as 2-acetoxy-2-butene and ethyl-1-propenyl ether suggest, that an isomerization of the double bond takes place during the reaction. Two mechanistic approaches which include the cleavage of the C-O bond either by an allylic substitution-like mechanism or *via* oxidative addition and β-elimination, the isomerization of the double bond and the hydrosilylation of the free olefin, can be proposed.

3. Synthesis and Functionalization of Hybrid Silicones

3.1 State of the Art

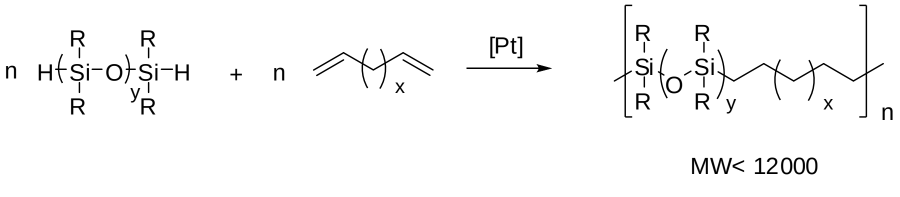
The first example of a hybrid silicone was published in 1955 by *Sommer* and *Ansul*, who reported the synthesis of ‘paraffin-siloxanes’ containing the 1,6-disilahexane group (scheme 3.1).[39]



Scheme 3.1. First synthesis of hybrid silicones.

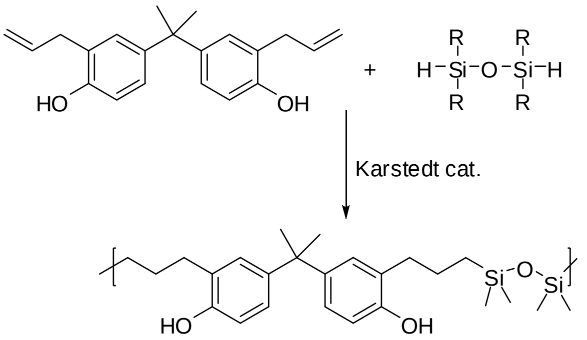
Since then, the hydrosilylation-type step growth polyaddition between suitable α,ω-SiH- and α,ω-H_2C=CH-carriers, as illustrated in scheme 3.2, has been extensively studied as synthetic route for the preparation of these versatile materials.

The reaction of simple terminal dienes like 1,5-hexadiene, 1,7-octadiene or 1,9-decadiene with 1,1,3,3-tetramethyldisiloxane (TMDS) in the presence of Karstedt’s catalyst has been object to profound studies.[18],[40] As with other step growth polymerization reactions stoichiometric balance is extremely important and only low to moderate molecular weights could be obtained ($M_w < 12000$). An end group analysis of these copolymers performed by *Sargent* and *Weber* revealed, that the limitation of the molecular weight is due to an isomerization of terminal double bonds into internal ones, leading to an inhibition of the addition reaction.[41]



Scheme 3.2. Hydrosilylation polymerization of α,ω-Si-H- and α,ω-H_2C=CH-carriers.

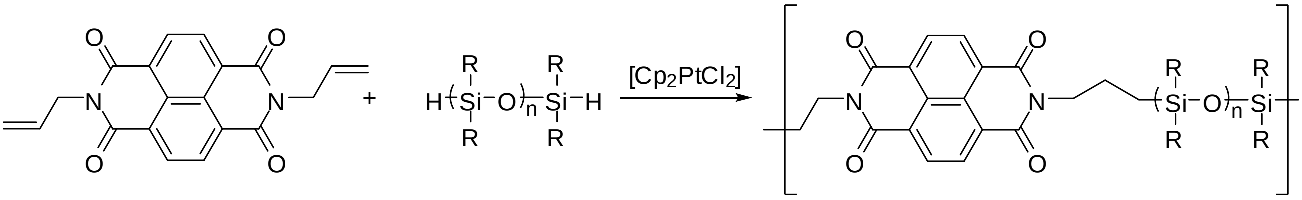
The addition of 1,1,3,3-tetramethyldisiloxane (TMDS) to diallyl bisphenol A was reported by *Lewis* and *Mathias* in 1993 (scheme 3.3).[42]



Scheme 3.3. Hydrosilylation polymerization of diallyl bisphenol A.

The hydrosilylation polymerization of fluorinated derivatives of bisphenol A diallyl ether as well as the reaction with hydride terminated polydimethylsiloxanes (PDMS-H_2) has also been performed successfully.[43],[44] Different siloxane spacers were applied and it turned out, that T_g decreases with increasing siloxane segment lengths. However, again, the isomerization of the allyl group to internal double bonds prevents the formation of high molecular weight copolymers.

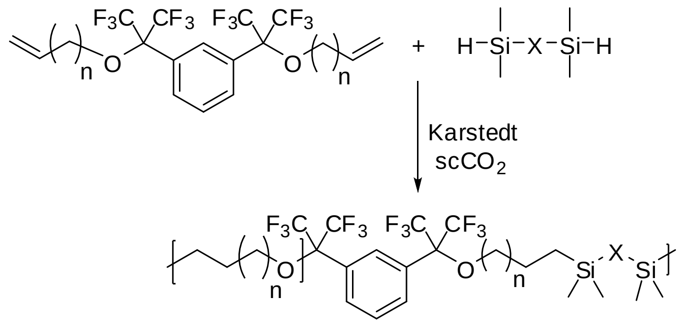
Well-defined polymers containing silylethylene siloxy or silanamine units have been prepared by *Boileau et al.*[45] Poly(imidesiloxane)s were patented by *Kreuzer et al.*[46] High conversion rates and short reaction times were achieved when reacting N,N'-dialkenyldiimine with a dihydro-organosilicon compound in the presence of [Cp_2PtCl_2], as shown in scheme 3.4.



Scheme 3.4. Synthesis of poly(imidesiloxane)s.

Alternating polyimide-poly(hybridsiloxane) copolymers have also been prepared by *Boutevin et al.* from allyl-terminated oligoimides and hydrosilane telechelic poly(hybridsiloxane)s as thermoplastic elastomers.[47] Further poly(silarylene-siloxane)polyimides have been prepared from different allyl-terminated oligoimides and hydride-functional silarylene siloxanes by *Homrighausen et al.*[48]

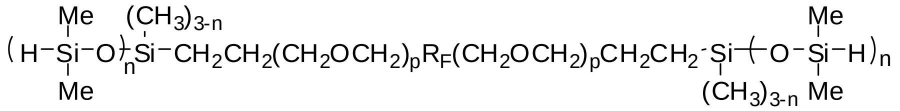
Poly(styrene-*b*-siloxane) multi-block copolymers have been prepared by polyhydrosilylation of α,ω-dihydro polydimethylsiloxanes (PDMS-H_2) with α,ω-diallyl- or divinyl polystyrene.[49] *Cassidy et al.* prepared fluorine containing polysilalkylene siloxanes in supercritical carbon dioxide ($scCO_2$), which yielded higher molecular weights in shorter reaction times than in other solvents such as benzene (scheme 3.5).[50]



x= CH_2CH_2, O, $SiMe_2OSiMe_2$, 1,4-C_6H_4
n= 3,10

Scheme 3.5. Synthesis of fluorine containing polysilalkylenes in supercritical CO_2.

A particular hybrid-silicone from Shin-Etsu, SIFEL®, is also worth mentioning (figure 3.1). It consists of a perfluoroether backbone combined with an addition-curing silicone crosslinker and is prepared *via* hydrosilylation of the vinyl silicone capped perfluoroether with a crosslinker containing several Si-H end groups.[51] It is described as liquid perfluoroelastomer and successfully used in O-rings, diaphragms and in aerospace industry.



$$(H-\underset{Me}{\overset{Me}{Si}}-O)_n\overset{(CH_3)_{3-n}}{Si}-CH_2CH_2(CH_2OCH_2)_pR_F(CH_2OCH_2)_pCH_2CH_2-\underset{(CH_3)_{3-n}}{Si}(-O-\underset{Me}{\overset{Me}{Si}}-H)_n$$

R_F= perfluoropolyether or perfluoroalkylene group
n= 1, 2, 3
p= 0 or 1

Figure 3.1. General formula for SIFEL®.

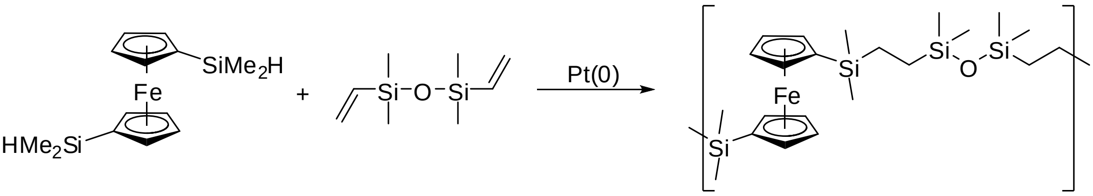
Very recently, the synthesis of different silicone organic elastomer gels by hydrosilylation of α,ω-unsaturated polyoxyalkylenes with organohydrogensiloxanes was reported in a patent.[52]

The synthesis of a novel oligomeric divinyl-terminated aromatic ether containing resin and its polymerization with silane containing compounds such as TMDS, leading to transparent, clear polymers exhibiting high thermal and oxidative stability has also been reported.[53]

Siloxane-containing polycarbonates have been prepared from allyl-terminated polycarbonates in the presence of *Wilkinson's* catalyst.[54]

The kinetics of the $PtCl_2$-catalyzed hydrosilylation of technical divinylbenzene with 1,1,3,3-tetramethyldisiloxane were examined by *Buchmeiser et al.*[55]

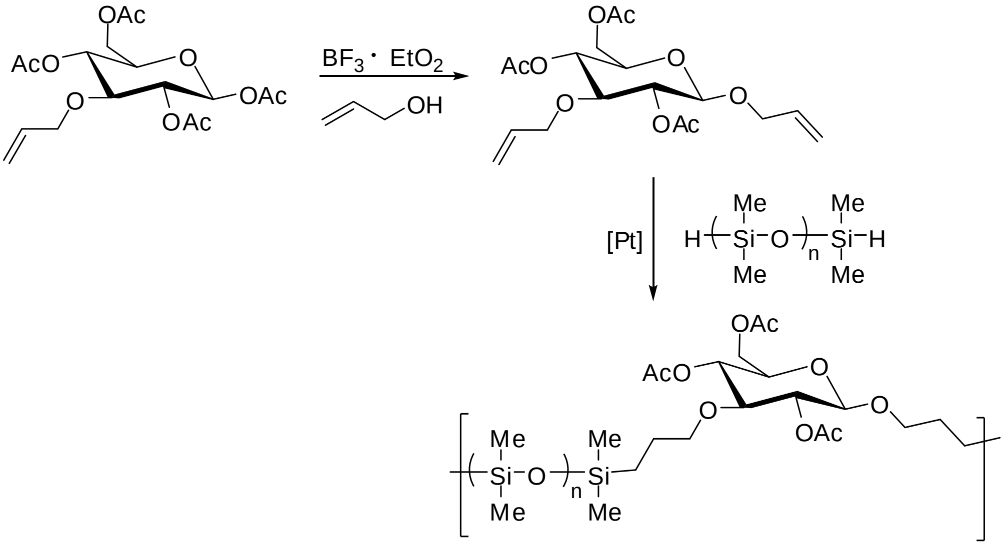
Recently, dimethylsilyl-substituted ferrocenes $FC(SiMe_2H)_2$ [$FC = (\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4)$] have been used to produce a series of new iron-containing organometallic polymers *via* hydrosilylation with dialkenyl-substituted ferrocenes $FC(SiMe_2(CH_2)_xCH{=}CH_2)_2$ (x = 0 or 1) or with divinyltetramethyldisiloxane in the presence of a Pt(0) catalyst (scheme 3.6).[56]



Scheme 3.6. Hydrosilylation polymerization of dimethylsilyl-substituted ferrocenes.

The polyhydrosilylation of terminal unsaturated fatty acid esters with several polyfunctional hydrosilylating agents has also been reported, leading to organic-inorganic hybrid materials with high transparency and good thermal stability.[57]

Carbohydrate-segmented polysiloxanes, as illustrated in scheme 3.7, can be synthesized by hydrosilylation of bisallyl-substituted carbohydrate derivatives with Si-H terminated siloxanes ($PDMS\text{-}H_2$).[58]



Scheme 3.7. Synthesis of β-allyl glucopyranoside and its polyhydrosilylation with PDMS-H_2.

Alternating copolymers containing alternating trehalose and siloxane units were synthesized by the hydrosilylation reaction of a trehalose-based diallyl compound with telechelic SiH-containing siloxanes in the presence of Karstedt's catalyst.[59] The synthesis of poly(poly(L-lactide)-*block*-polydimethylsiloxane] copolymers by polyhydrosilylation was reported by *Sauvet et al*. [60]. Siloxane-containing copolymers prepared from α,ω-diallyl-polyethylene oxide [61] or α,ω-diallyl-polysulfone [62] have also been reported some time ago. The synthesis of silicon-containing polyesters *via* hydrosilylation of undecylenic acid esters was reported recently.[63]

Polysilalkylene siloxanes combine the properties of classical silicones with those of classical organic polymers depending on the building blocks used. Thus, a variety of unique copolymers with tailor-made properties can be designed.

Their molecular weight and telechelic functionalization (Si-H or C=C) can be determined by the stoichiometry of the two building blocks. *Carother's* equation relates the number-average degree of polymerization X_n to the extent of reaction p and average functionality f_{avg} in a step growth reaction:

$$X_n = 2 / (2 - pf_{avg})$$

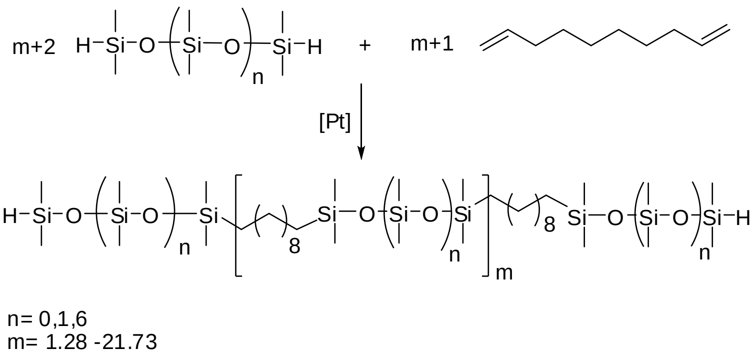
For a generic polymer made from a difunctional monomer AA, such as a diene, with N_A functional groups and an excess of difunctional monomer BB, such as PDMS-H_2, with N_B functional groups (f_{avg}= 2), the stoichiometric imbalance r is defined as $r = N_A/N_B$ ($N_B > N_A$). With p=1, this leads to

$$X_n = 1 + r / (1 - r).$$

Thus, the number-average molecular weight of the resulting copolymer can be controlled by offsetting the stoichiometry of the two difunctional monomers and the polymer will have the same endgroup functionality as the monomer used in excess.[64]

3.2 Synthesis of Si-H-terminated Hybrid Silicones

Several hybrid silicones have been prepared *via* the *Karstedt*-catalyzed polyhydrosilylation of 1,9-decadiene with different α,ω-Si-H carriers as depicted in scheme 3.8.



Scheme 3.8. Synthesis of Si-H terminated hybrid silicones containing 1,9-decadiene as organic building block.

Three different siloxane building blocks with different chain lengths were used: 1,1,3,3-tetramethyldisiloxane (TMDS, n= 0), 1,1,3,3,5,5-hexamethyltrisiloxane (HexMTS, n= 1) and an α,ω-dihydropolydimethylsiloxane (PDMS-H_2) with on average 8 silicon atoms per molecule (n= 6, M_n= 580 g/mol). In all cases, only the terminal (*anti-Markovnikov*) hydrosilylation product was observed. By variation of the stoichiometry several hybrid polymers with different chain lengths were obtained.

The degree of polymerization m gives the number of repeating units within the polymer and was varied from 1.3 to 21.7. In all cases, an excess of the siloxane component was used to build up α,ω-Si-H terminated copolymers.

These were obtained as colorless to yellowish oils in almost quantitative yield. With increasing m and thus increasing molecular weight, an increase in viscosity was observed.

The polyhydrosilylation reaction was performed by slowly adding the diene, containing 10 ppm of platinum in form of *Karstedt's* catalyst (**I**), to the siloxane compound at slightly elevated temperature (40°C). The reaction was highly exothermic and a thermo sensor was employed to monitor the increase in temperature and an ice bath was used to keep temperature below 85°C. After complete addition, the reaction mixture was stirred at 75°C for 1h to allow complete reaction. After cooling to ambient temperature, the molecular weight was determined by ^{1}H-NMR spectroscopy: the integrals of the areas of peaks due to several groups within the molecule are a function of the degree of polymerization m when the integral of the Si-H moiety at 4.7 ppm is set to 2.

The average degree of polymerization m was used for the calculation of the molecular weight using the following equation:

$$M = 2 \times M\ (siloxane) + M\ (diene) + m\ [M\ (siloxane) + M\ (diene)]$$

All hybrid silicones prepared *via* the polyhydrosilylation of 1,9-decadiene with the three different siloxanes are summarized in table 3.1.

Table 3.1. Composition and molecular weight of Si-H-terminated hybrid silicones **1a-SiH–3b-SiH** containing 1,9-decadiene linkers .

compound	**siloxane**	**diene**	**m^a**	**M^a (g/mol)**
1a-SiH	TMDS	1,9-decadiene	4.02	1500
1b-SiH	TMDS	1,9-decadiene	15.40	4600
2a-SiH	HexMTS	1,9-decadiene	1.42	1050
2b-SiH	HexMTS	1,9-decadiene	15.48	5920
3a-SiH	PDMS-H_2	1,9-decadiene	1.28	2220
3b-SiH	PDMS-H_2	1,9-decadiene	21.73	16900

a: Determined by ^{1}H-NMR spectroscopy, error: ± 5%.

Figure 3.2 shows the ^{1}H-NMR spectrum of **2a-SiH** with a degree of polymerization of m= 1.42. The assignment of the signals and the determination of the chain length are given in table 3.2.

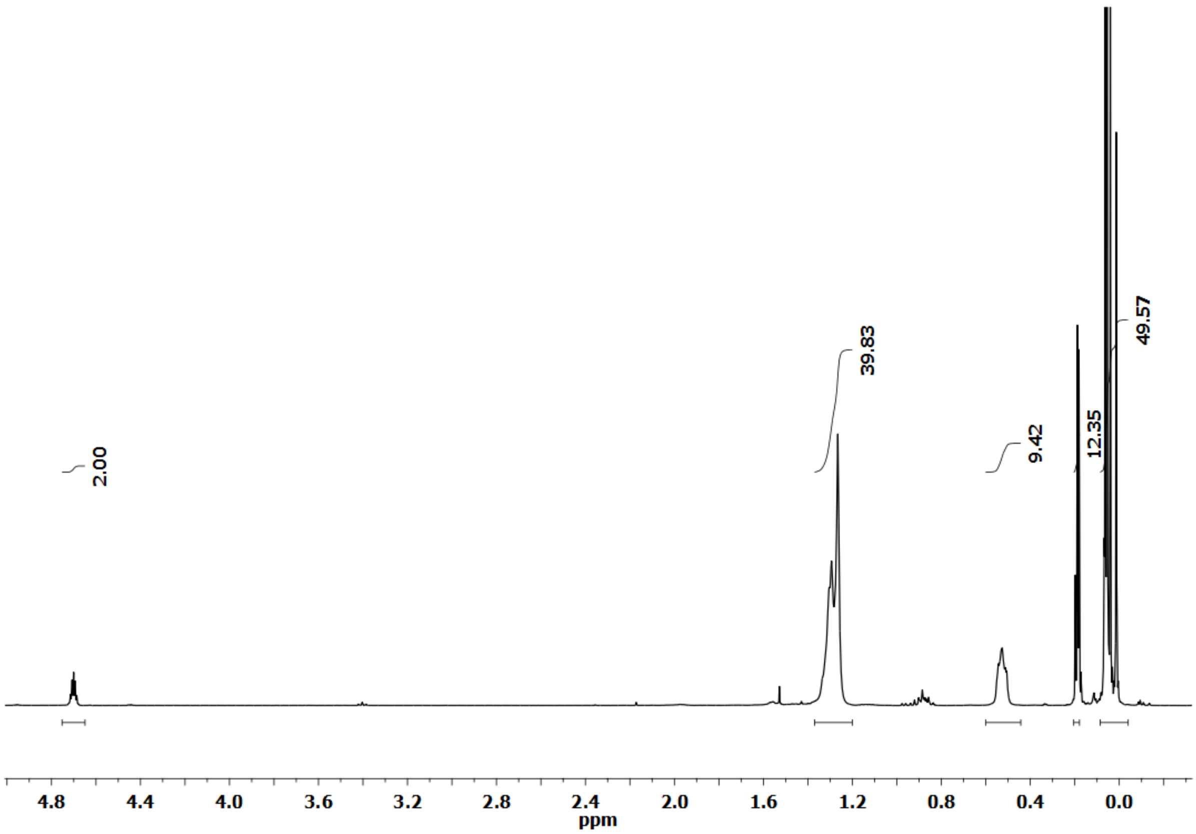


Figure 3.2. ^{1}H-NMR spectrum of **2a-SiH**.

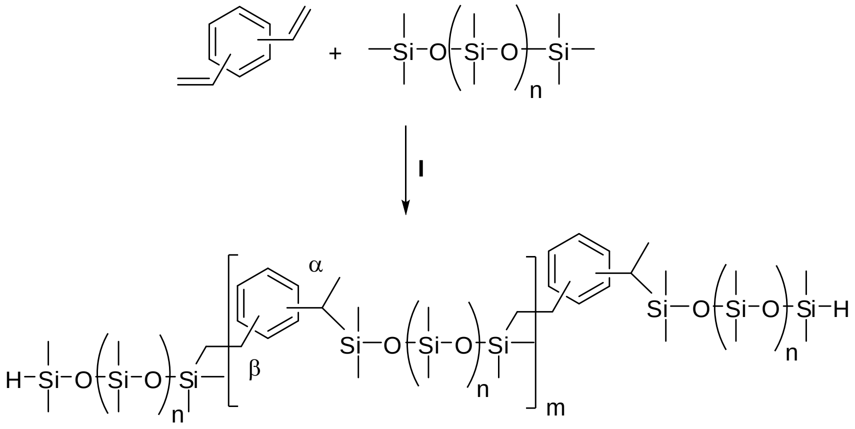
Table 3.2. Assignment of ^{1}H-NMR signals and determination of the chain lengths for **2a-SiH**.

group	signal (ppm)	integral	degree of polymerization m
Si-CH_3	0.03	49.57 =18m + 24	1.42
H-Si(CH_3)	0.19	12.35	-
CH_2-Si	0.50	9.42 = 4m + 4	1.36
CH_2	1.27	39.83 = 16m + 16	1.49
Si-H	4.70	2.00	-

In all cases, an isomerization of the terminal double bonds into their internal isomers was observed as a side reaction. Internal double bonds could be identified in the ^{1}H-NMR spectrum by the signal at 5.4 ppm. With an increasing amount of diene, an increase in olefin isomerization was observed. As described before (section 2.2), the rate of isomerization is about 3% of the total amount of C=C double bonds.

This olefin isomerization and also the comparatively high costs of 1,9-decadiene lower the commercial interest in this type of building block. Thus, more selective low-cost alternatives need to be found to enable the cost-efficient synthesis of hybrid silicones.

Divinylbenzene is such an interesting building block for the preparation of polysilarylene siloxanes. Due to its chemical structure it can hardly undergo any isomerization reactions and furthermore, it is conveniently commercially available in technical grade (80%) as a mixture of isomers. In general, its *Karstedt* catalyzed hydrosilylation is faster and more exothermic than the hydrosilylation of 1,9-decadiene. In contrast to the hydrosilylation of linear, non-aromatic dienes, also an α-addition is observed, leading to the formation of the *Markovnikov*-product. This behavior is similar to that observed in the hydrosilylation of styrene as described in section 2.2. The ratio of α- to β-addition is approx. 3 : 7. Thus, the resulting copolymers contain different contact points with different connectivity between the two building blocks (scheme 3.9).



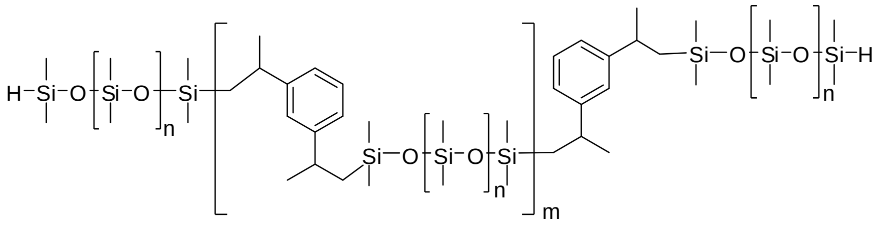
4a-SiH: n= 7.38, m= 3.5, M_n= 4330 g/mol

Scheme 3.9. Polyhydrosilylation of divinylbenzene with PDMS-H_2 (M_n= 680 g/mol).

The degree of polymerization m can be determined from the integrals of the Si-CH_3 groups and the aromatic ring, as they are independent from the type of connection. Technical divinylbenzene (80%) consists, besides of *o*-, *m*- and *p*-isomers also of a significant amount (12%) of the corresponding ethylstyrenes. The terminal ethyl groups cannot be hydrosilylated and lead to a premature termination of the polymer chain. A complete end group analysis was performed by *Buchmeiser et al.* [55]. Thus, when technical divinylbenzene is used as a building block for the preparation of polysilarylene siloxanes, very undefined polymers with undefined end groups are obtained which makes an industrial application very difficult.

Better results could be obtained if pure divinylbenzene would be used, but the high costs of purification make also this approach commercially uninteresting.

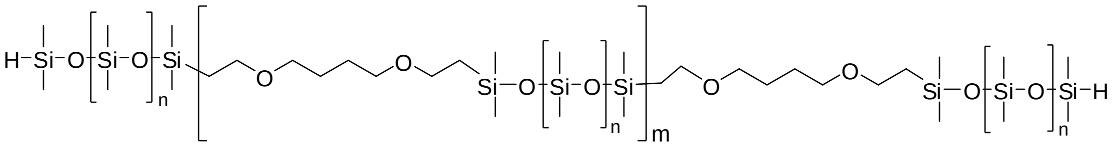
In order to avoid the complications observed with divinylbenzene, 1,3-diisopropenyllbenzene (DIPB) was tested as a building block for the preparation of polysilarylene siloxanes. Like divinylbenzene, it can hardly undergo isomerization reactions and because of the presence of the methyl group in the α-position, only the terminal (*anti-Markovnikov*) product can form. Therefore very well-defined copolymers can be prepared in quantitative yield. Again, two different siloxanes, HexMTS and PDMS-H_2 (M_n= 680 g/mol), were used. Compared to divinylbenzene, the reaction is less exothermic and needs a higher activation temperature (> 60°C). Structure, degree of polymerization m and molecular weight of the obtained hybrid silicones **5a-SiH** and **5b-SiH** are shown in figure 3.3.



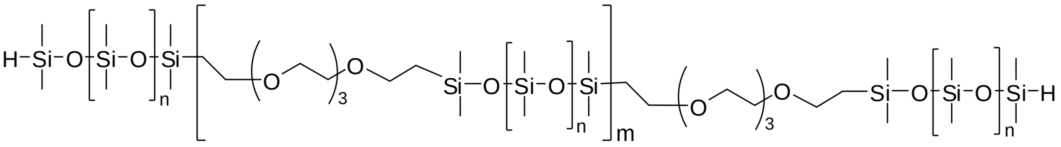
5a-SiH: n= 1.00, m= 6.06, M_n= 2800 g/mol
5b-SiH: n= 7.38, m= 1.80, M_n= 3030 g/mol

Figure 3.3. Structure, degree of polymerization m and molecular weight of the hybrid silicones prepared from 1,3-diisopropenylbenzene with HexMTS and PDMS-H_2.

Also divinyl ethers, such as butanediol divinylether (BDDVE) or triethylene glycol divinyl ether (TEG-DVE) can be used as building blocks for the preparation of hybrid silicones. Again, these monomers cannot undergo isomerization and only the terminal addition products are formed. Neither a reduction of the double bond nor an elimination of ethylene is observed and very well-defined copolymers are formed. Their *Karstedt*-catalyzed polyhydrosilylation reaction is less exothermic than with aliphatic or aromatic dienes and higher activation energies (> 60°C) are necessary. Some examples of hybrid silicones obtained *via* the *Karstedt*-catalyzed hydrosilylation of BDDVE or TEG-DVE with HexMTS or PDMS-H_2 (M= 680 g/mol) are shown in figure 3.4.



6a-SiH n= 1.00, m= 5.65, M_n= 2520 g/mol
6b-SiH n= 7.38, m= 1.68, M_n= 2880 g/mol



7a-SiH n= 1.00, m= 4.10, M_n= 2300 g/mol
7b-SiH n= 7.38, m= 1.53, M_n= 2910 g/mol

Figure 3.4. Structure, degree of polymerization m and molecular weight of the hybrid silicones prepared from BDDVE and TEG-DVE with HexMTS and PDMS-H_2.

As an example, the ^{1}H-NMR spectrum of **6a-SiH** with the assigned signals is given in figure 3.5. Again, m can be determined from the integrals of certain specific groups within the molecule related to the signal of the Si-H group at 4.7 ppm.

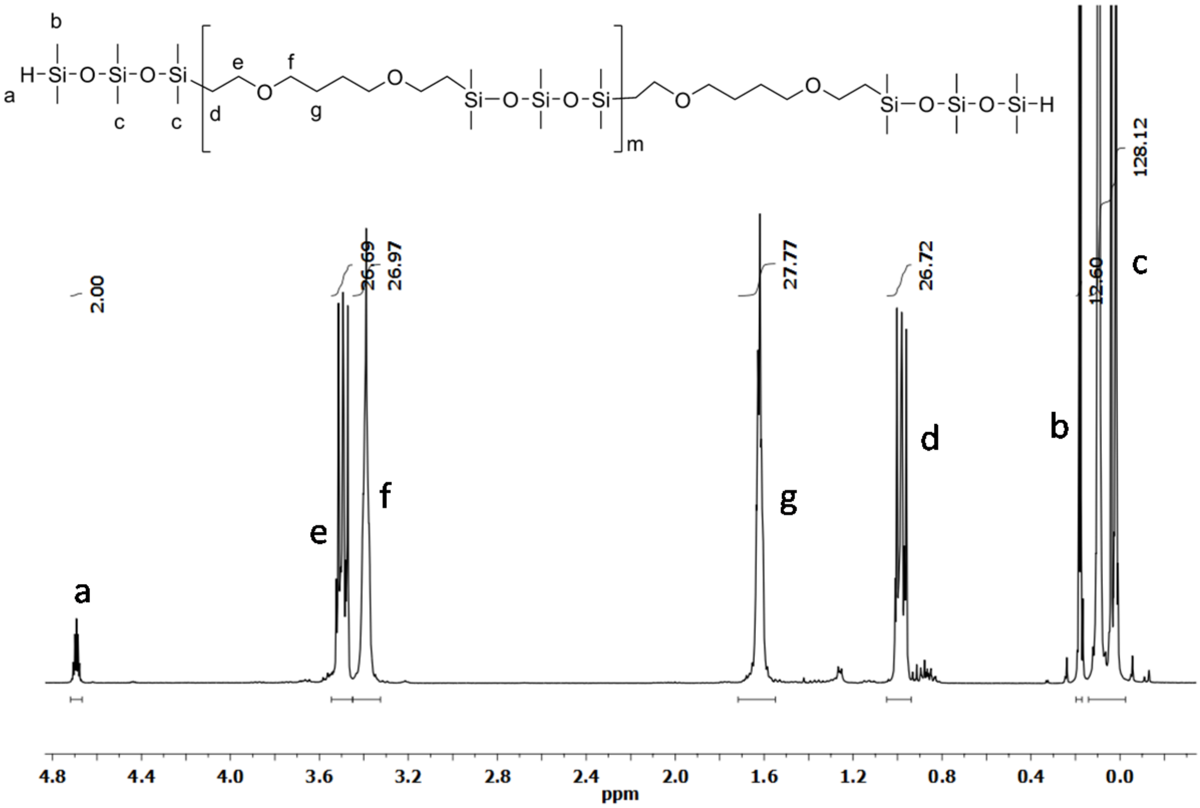
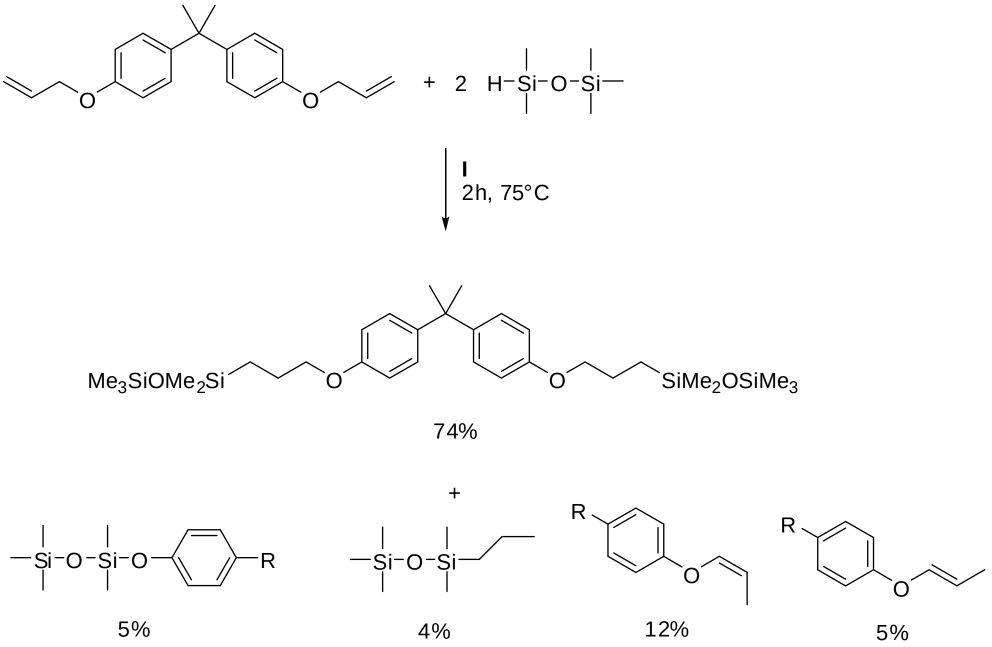


Figure 3.5. ^{1}H-NMR spectrum of **6a-SiH**.

Bisphenol A diallyl ether is a further interesting building block in the preparation of hybrid silicones. It is well known in the literature, that the hydrosilylation of allylic systems is accompanied by an isomerization of the terminal double bond. Levels of isomerization can be as high as 30%.[65] Thus, the reactivity of bisphenol A diallyl ether was first examined using 1,1,3,3,3-pentamethyldisiloxane (PMDS) as a model component for α,ω-dihydropolydimethylsiloxanes, according to scheme 3.10.



Scheme 3.10. Hydrosilylation of bisphenol A diallyl ether with PDMS using **I**.

Additionally to olefin isomerization, which leads to the formation of a *cis*- (12%) and a *trans*-isomer (5%) also a C-O bond cleavage is observed leading to the formation of *n*-propylpentamethyldisiloxane (4%) and an Si-O-adduct (5%). This type of reaction is similar to the findings described in section 2.4 and similar results are obtained in the hydrosilylation of allyl phenyl ether (section 3.3.8). Despite of the presence of the aromatic ring, the ether group is still a bad leaving group and therefore, only small amounts of the cleavage products are formed. Both side reactions lead to end groups which cannot be further hydrosilylated. In a copolymer, this would lead to an undefined polymer structure and a premature termination of the polymer chain. The terminal hydrosilylation product could only be obtained in 74% yield which makes a large-scale application of bisphenol A diallyl ether in the preparation of hybrid silicones difficult and uneconomical. Also the fact that bisphenol A and some of its derivatives are suspected to be endocrine disruptors, complicates its industrial application.

In general, the use of allylic systems can be problematic in the preparation of hybrid silicones, due to their tendency towards isomerization (and cleavage) reactions and thus the formation of undefined end groups. Furthermore, the accumulation of isomerized, unreacted diene in the process may cause problems with product purification and quality. In order to avoid such an isomerization reaction, 2-methyl-3-(2-methylallyloxy)prop-1-en (bismethallyl ether, BME) and 2-methyl-4-(2-methyl-allyloxy)but-1-ene (isoprenyl methallyl ether, IME) were synthesized according to [66] and tested as building blocks in the preparation of polysilalkylene siloxanes (figure 3.6).

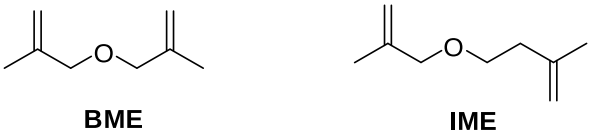


Figure 3.6. Structure of 2-methyl-3-(2-methylallyloxy)prop-1-en (BME) and 2-methyl-4-(2-methyl-allyloxy)but-1-ene (IME).

Both compounds bear methyl groups in the α-position and can hardly undergo isomerization. Thus, BME reacts smoothly with TMDS to form well-defined copolymers in quantitative yield. No side-reactions were observed. With 10 ppm Pt in form of *Karstedt's* catalyst, the reaction was exothermic with an activation temperature of approx. 60°C and proceeded smoothly within 12h. Figure 3.7 shows the ^{1}H-NMR spectrum of the resulting copolymer **8a-SiH** with a degree of polymerization of m= 7.68.

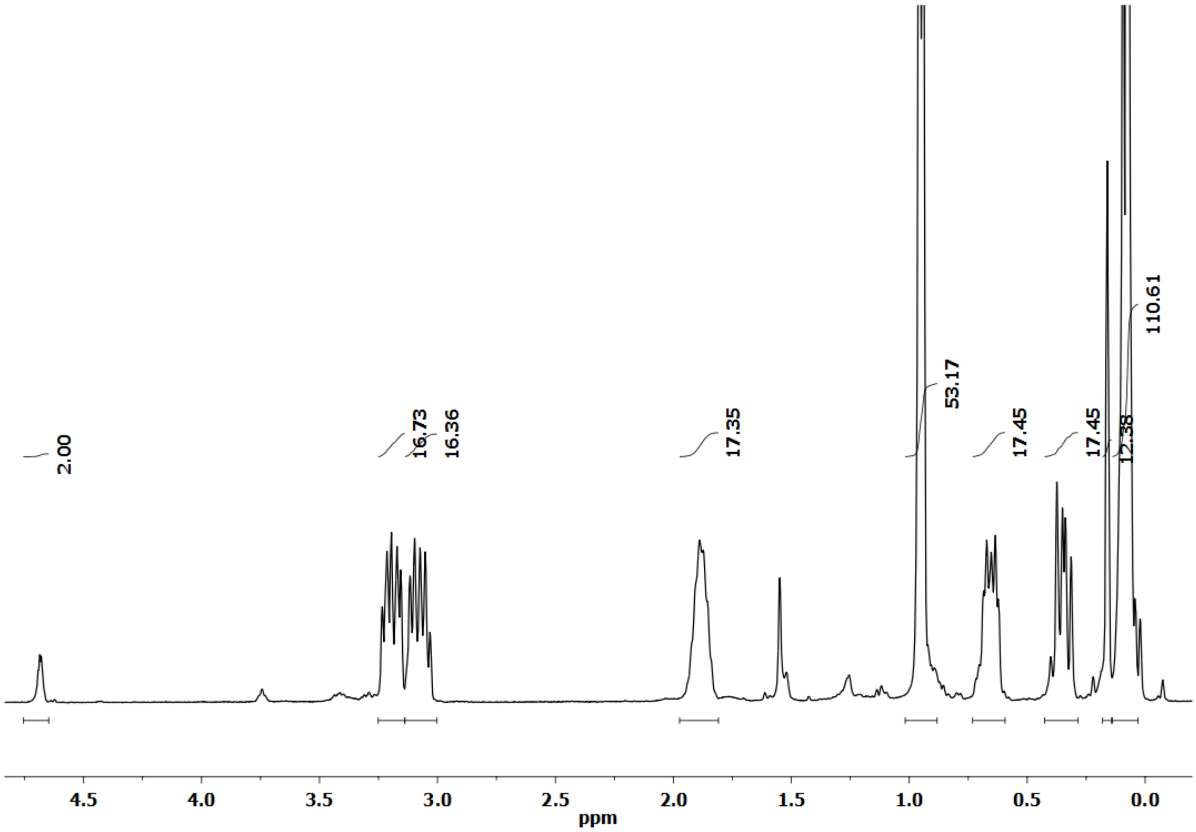


Figure 3.7. ^{1}H-NMR spectrum of a copolymer **8a-SiH** built up from BME and TMDS.

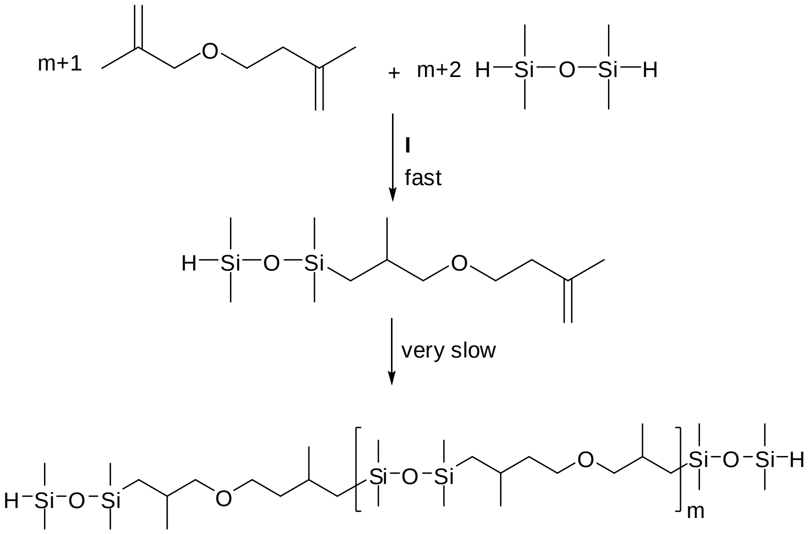
The assignment of the signals and the determination of m is given in table 3.3.

Table 3.3. Assignment of ^{1}H-NMR signals and determination of m for copolymer **8a-SiH**.

Group	**Signal (ppm)**	**Integral**	**Degree of Polymerization m**
Si-CH_3	0.07	110.61= 12m + 12	8.22
H-Si(CH_3)	0.16	12.38	-
CH_2-Si	0.36/ 0.65	17.45/ 17.45 = 2m + 2	7.73/ 7.73
CH_3	0.94	53.17 = 6m + 6	7.86
CH	1.89	17.35 = 2m + 2	7.68
CH_2-O	3.07/ 3.20	16.36/ 16.73= 2m + 2	7.18/ 7.37
Si-H	4.69	2	-

Thus, 2-methyl-3-(2-methylallyloxy)prop-1-en (BME) can be regarded a good building block for the straight-forward synthesis of hybrid silicones.

In contrast, the polyhydrosilylation of 2-methyl-4-(2-methyl-allyloxy)but-1-ene (IME) with TMDS is very slow. With an excess of TMDS, even after 9d at 100°C, still traces of unreacted methylbutenyl groups are visible in the ^{1}H-NMR spectrum of the resulting polymer **9a-SiH**. Obviously, the methallyl group is much more reactive than the methylbutenyl group, which leads to the formation of a monosubstituted intermediate which is fairly inert towards further hydrosilylation (scheme 3.11).



9a-SiH, m= 7.04

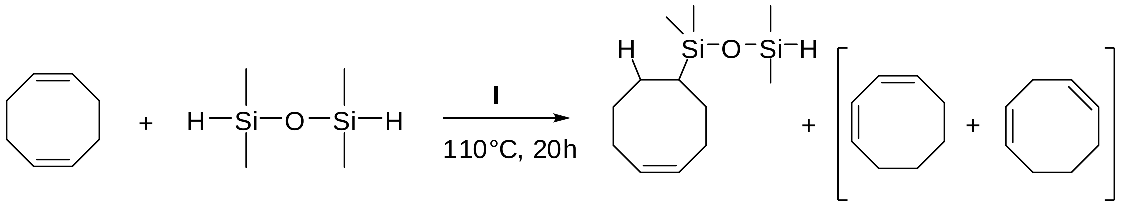
Scheme 3.11. Hydrosilylation polymerization of IME with TMDS.

With these findings, 2-methyl-4-(2-methyl-allyloxy)but-1-ene (IME) seems to be rather unsuitable for the preparation of polysilalkylene siloxanes. Nonetheless, the different reactivity of the two double bonds could be an advantage in the specific synthesis of methylbutenyl-terminated polymers which could then be further functionalized *via* the C=C double bond.

Also some further dienes are potential candidates for the targeted construction of hybrid silicones. Conjugated dienes, such as butadiene or isoprene, would be interesting as easily available, simple and short aliphatic spacers. Also cyclic dienes such as 1,5-cyclooctadiene (1,5-COD) would be of great interest because they are conveniently commercial available and would lead to the formation of novel hybrid silicones with cycloaliphatic spacers in the polymer chain. Unfortunately, their application in the preparation of hybrid silicones is very difficult.

The hydrosilylation of isoprene with an excess of PDMS-H_2 in the presence of *Karstedt's* catalyst (**I**) leads to the formation of several isomerized, reduced or monohydrosilylated species. This unselectivity was already reported in the literature, also for metal catalysts other than platinum.[67]

The *Karstedt*-catalyzed hydrosilylation of 1,5-COD with TMDS or PDMS-H_2 was slow and incomplete. Usually, internal double bonds are completely inert towards hydrosilylation when **I** is used.[8] In this case, the high reactivity of the Si-H group in TMDS or PDMS-H_2 and the ring-strain of COD facilitate the addition reaction and provide, that a mono-addition product, as shown in scheme 3.12, was formed.



Scheme 3.12. Hydrosilylation of 1,5-COD with TMDS, leading to the mono-addition product only.

Even at elevated temperatures of 120°C, no further reaction could be induced. Only some intramolecular rearrangements to 1,3- or 1,4-cyclooctadiene were observed as side-reactions. Thus, 1,5-COD cannot be used for the preparation of polysilalkylene siloxanes. Nevertheless, it might be interesting for their terminal functionalization.

Also when dicyclopentadiene was used instead of COD, only the mono-addition product was formed. In this case, only the norbornene-like C=C double bond seems to be reactive enough to undergo hydrosilylation. With cyclopentadiene no reaction was observed even after 24h at 85°C in the presence of PMDS-H_2 and *Karstedt's* catalyst. Additionally the use of this monomer is plagued by its easy dimerization which was observed as a side-reaction.

In conclusion, several dienes can be used in the straight-forward synthesis of hybrid silicones with average molecular weights well above 1000 g/mol. Very unpolar hybrids are obtained when 1,9-decadiene or 1,3-diisopropenylbenzene are used. More amphiphilic polymers are obtained with butandiol divinyl ether, triethylene glycol divinyl ether or bismethallyl ether (BMI). Allylic systems are less useful for linear high molecular weight hybrid silicones because of their high tendency towards isomerization reactions. Because of their poor and uncontrolled reactivity conjugated and cyclic dienes are not suitable for the preparation of hybrid silicones.

3.3 Functionalization of Hybrid Silicones

The Si-H terminated hybrid silicones can be further functionalized by reacting them with monoolefins carrying various functional groups. Thus, a number of α,ω-functionalized hybrid polymers can be prepared and studied as components in the preparation of curable systems. For example epoxy-functional hybrid silicones can be crosslinked similar to purely organic epoxy resins in the presence of amine hardeners or photochemically. Amino-terminated hybrid silicones can be used as binders in epoxy or polyurea applications and alcohol-functional polymers may find application in the preparation of polyurethanes or polyesters. Alkoxysilyl-terminated hybrid polymers crosslink rapidly with moisture in the presence of a tin catalyst to give release coatings. Isocyanate end-groups are interesting for the preparation of polyurethanes and polyureas whereas (meth)acrylfunctional hybrid silicones can be used as monomers in the preparation of poly(meth)acrylates.[68]

The functionalization of the hybrid polymers can be achieved by simple addition of the corresponding functional olefin to the Si-H-telechelic hybrid silicones. Usually, no additional catalyst is needed as 10 ppm of Pt are already present in the prepolymer.
In order to get an overview, which functional groups are tolerated during the hydrosilylation reaction and which olefins can be used for efficient functionalization of hybrid silicones, several different olefins were tested in standardized test reactions using 1,1,3,3,3-pentamethylsiloxane (PMDS) or PMDS-H_2 as models for Si-H terminated hybrid silicones.

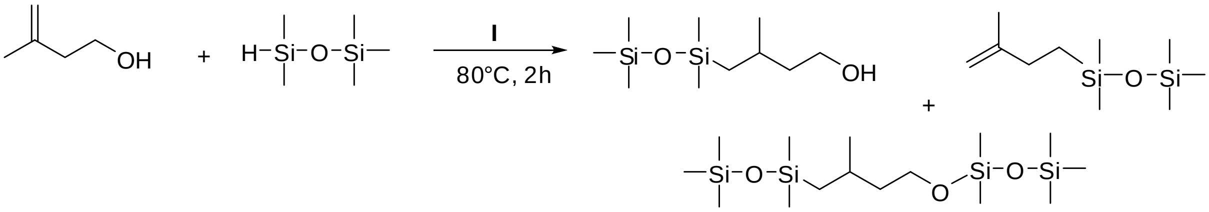
3.3.1 Functionalization with Alcohols

The hydrosilylation reaction between unsaturated alcohols and α,ω-dihydropolysilalkylene siloxanes leads to the formation of hydroxy-terminated hybrid silicones. This strategy is known in the preparation of hydroxyalkyl-terminated polysiloxanes, which can for example be prepared from allyl or propargyl alcohols or 5-hexene-1-ol and PDMS-H_2 or α,ω-*bis*(trimethylsiloxy)-methylhydridesiloxane using *Karstedt's* or *Speier's* catalyst. In the case of α,ω-*bis*(trimethylsiloxy)-methylhydridesiloxane, the resulting hydroxy-functionalized comb-type polymers can be used for the synthesis of poly(siloxanes-urethane)[69]. *Zhan et al.* recently reported several α-{3-[(2,3-dihydroxy)propoxy]propyl}-ω-butyl-polydimethylsiloxanes with different siloxane chain lengths.[70]

Phosphated organopolysiloxane derivatives, gained from hydroxyalkyl-terminated polysiloxanes *via* phosphatation have been used for improving the water-resistance of leather and textiles [71] while alcohol-functional silicone-polymers found an application in the preparation of polyurethanes or polyesters.[72]

In order to obtain a hydroxy functionalization, several different olefins bearing hydroxy groups were tested in the *Karstedt*-catalyzed hydrosilylation with PMDS.

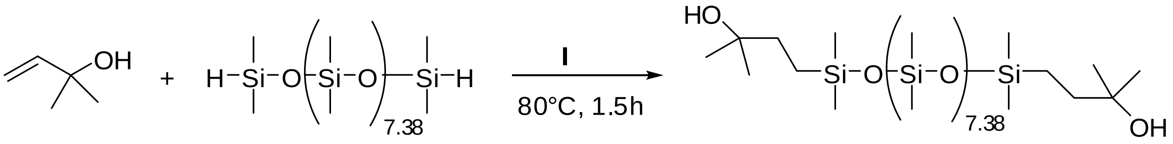
Isoprenol, an inexpensive and easily available olefin would be an interesting candidate for the functionalization of hybrid silicones. Its hydroxy moiety can be further transferred into (poly)esters or -ethers. In the presence of *Karstedt's* catalyst (**I**) or PtO_2 (**VII**), isoprenol reacts with PMDS, HexMTS or PDMS-H_2 completely with respect to SiH. Elevated temperatures of >75°C are necessary to start the reaction, which then proceeds within 2h (catalyst **I**) to 24h (catalyst **VII**). In all cases, the proton balance in the ^{1}H-NMR spectra does not fit with the exclusive formation of the Si-C addition product. GC-MS analysis reveals the formation of a product mixture with the desired Si-C adduct being the main product (81%). Yet, another Si-C adduct, possibly hydrosilylated isoprene (15%) and a Si-O addition product (4%) could be identified as byproducts (scheme 3.13).



Scheme 3.13. Hydrosilylation of isoprenol with PMDS.

When the reaction is performed with HexMTS in a pressure tube, much higher amounts of byproducts are formed because volatile intermediates such as isoprene cannot escape from the reaction mixture. With these findings, isoprenol is not a preferred candidate for the functionalization of hybrid silicones *via* platinum-catalyzed hydrosilylation.

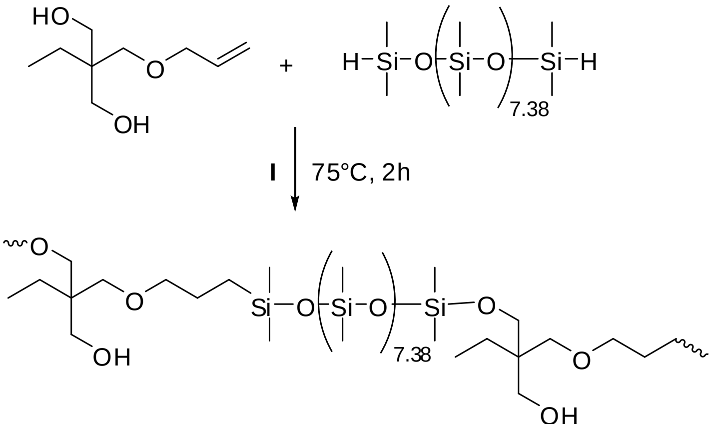
In contrast to that, the *Karstedt*-catalyzed hydrosilylation of 2-methyl-3-buten-2-ol, an isomer of isoprenol, with PDMS-H_2 proceeds smoothly within 1.5h at 80°C (scheme 3.14). No byproduct formation is observed.



Scheme 3.14. Hydrosilylation of 2-methyl-3-buten-2-ol with PDMS-H_2.

Hydroxybutylvinylether was also examined as potential candidate for the hydroxy-functionalization of hybrid silicones. Unfortunately, its *Karstedt*-catalyzed hydrosilylation with PMDS or PDMS-H_2 is also not completely selective towards Si-C addition. A large excess of PMDS is necessary to obtain full olefin conversion. Small amounts of a Si-O addition product could be detected by ^{29}Si-NMR spectroscopy.

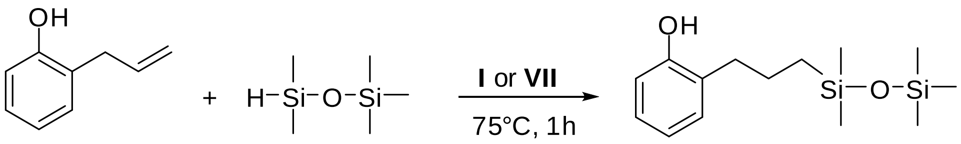
Also trimethylolpropane monoallyl ether (TMPME) is an interesting compound for the preparation of hydroxy-telechelic hybrid silicones. When it is hydrosilylated with PDMS-H_2 in the presence of *Karstedt*'s catalyst, large amounts of Si-O addition products can be observed, leading to the formation of a partially crosslinked, highly viscous product, as shown in scheme 3.15.



Scheme 3.15. Hydrosilylation of TMPME with PDMS-H_2.

Also traces of trimethylolpropane mono-2-propenyl ether can be observed as a product of olefin isomerization. Thus, the preparation of TMPME-terminated hybrid silicones is not accomplished *via* hydrosilylation of TMPME.

Hydroxy-functional hybrid silicones with pendant aromatic groups can be obtained by hydrosilylation of 2-allylphenol. Its platinum catalyzed hydrosilylation with PDMS-H_2 or PMDS using **I** or **VII**, mainly led to the formation of the terminal hydrosilylation product, as shown in scheme 3.16.



Scheme 3.16. Hydrosilylation of 2-allylphenol with PMDS.

Some 2-propenyl phenol (8%) was obtained as a result of isomerization. When *Karstedt's* catalyst was used, the reaction was very exothermic and proceeded within 1h at 75°C. With **VII**, slightly longer reaction times (2h) and higher temperatures (120°C) were necessary.

Hydroxy-terminated allylpolyether are further interesting compounds for the (hydroxy-) functionalization of polysilalkylene siloxanes. The results of the hydrosilylation of two different hydroxy-terminated allylpolyethers with PDMS-H_2 are given in 3.3.8.

3.3.2 Functionalization with Epoxides

Epoxy-functionalized siloxanes (and silanes) have first been prepared by *Crivello et al.* by stepwise hydrosilylation of short-chain siloxanes with allyl glycidylether or 4-vinylepoxycyclohexane using *Wilkinson's* catalyst.[73] The epoxy-functional siloxanes could be polymerized photochemically, thermally or using Pt catalysts. The synthesis and thermal or photochemical curing of epoxy telechelic cycloaliphatic substituted siloxanes was reported by *Soucek et al.* [74],[75]

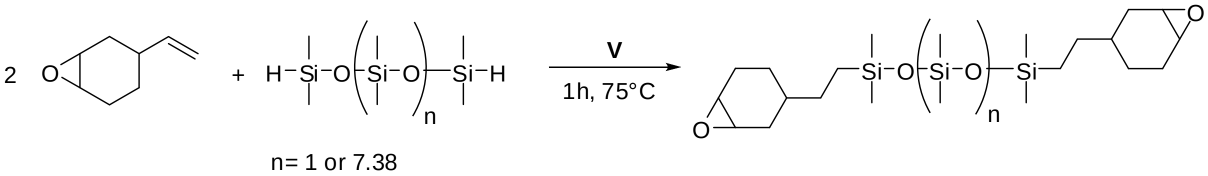
The fact that epoxy-telechelic systems can be easily cured thermally or photochemically and the excellent properties of the resulting films, such as thermal, mechanical, and chemical resistance, low shrinkage, and good adhesion characteristics makes the preparation of epoxy-functionalized hybrid silicones highly desirable.

Two different epoxides, vinylcyclohexene oxide (4-vinylepoxycyclohexane, VCO) and allyl glycidylether (AGE) were tested in the platinum-catalyzed hydrosilylation with PDMS-H_2 or HexMTS.

Using *Karstedt's* catalyst (**I**), the hydrosilylation of PDMS-H_2 or HexMTS with VCO leads to the formation of an unsoluble gel. This gelation was described as a result of a platinum catalyzed epoxide ring-opening polymerization and could be inhibited by addition of trace amounts of a base, such as PPh_3 to the reaction mixture.[76]

It was reported that the active species for this side reaction is colloidal platinum formed *in situ* by the reduction of the catalyst by Si-H containing organosilanes.[77]

If $Pt(PPh_3)_4$ (**V**) was used as hydrosilylation catalyst no such gelation was observed and the terminal addition product was formed exclusively, as shown in scheme 3.17.



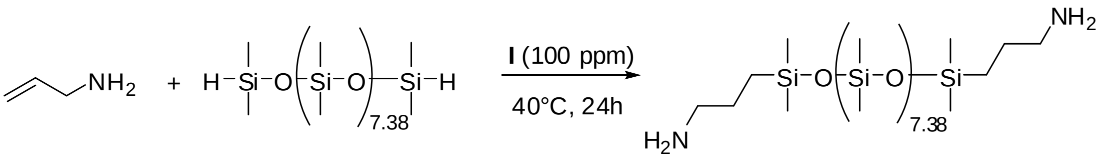
Scheme 3.17. Hydrosilylation of VCO with PDMS-H_2 (n= 7.38) or HexMTS (n= 1).

Also allyl glycidyl ether (AGE) is a potential candidate for the preparation of epoxy-telechelic hybrid silicones. Its hydrosilylation with PDMS-H_2 or HexMTS can be catalyzed by *Karstedt's* catalyst and leads to the formation of the terminal hydrosilylation product. In contrast to VCO, no gelation was observed but, as already described for other allylic compounds, isomerization of the terminal double bond occured as a side reaction. Thus, a 10%-excess of AGE was necessary to obtain complete Si-H conversion. After the reaction, isomerized AGE could be removed *in vacuo*. Another disadvantage of AGE in its large-scale application as functionalizing agent of polysilalkylene siloxanes might be its toxicity.

3.3.3 Functionalization with Amines

Amino-terminated carbosiloxanes have been synthesized by *Chakraborty et al. via* hydrosilylation of α,ω-dihydrosiloxanes bearing cycloaliphatic side groups with *t*-BOC protected allyl amine using *Karstedt's* catalyst. After deprotection, the amino-functionalized polymers could be cured with epoxy-telechelic carbosiloxanes.[74] Amino- or ammonium terminated carbosilanes have also been obtained *via* the direct hydrosilylation of allylamine in the presence of *Karstedt's* or *Speier's* catalyst or PtO_2.[29],[78]-[80]

The hydrosilylation of allylamine with PMDS or PDMS-H_2 in the presence of *Karstedt's* catalyst requires high catalyst concentrations (> 100 ppm Pt), possibly due to catalyst poisoning by the primary amino group. It can be performed at 40°C and leads within 24h to the formation of the *anti-Markovnikov* product (scheme 3.18). Small amounts of byproducts, possibly as a results of Si-N addition could also be observed as well as minimal hydrogen evolution. No allylic rearrangement took place. An excess of allyl amine was used to ensure complete SiH conversion.



Scheme 3.18. Hydrosilylation allyl amine with PDMS-H_2.

Also *N*-BOC-allylamine was tested for the amino-functionalization of siloxane compounds. Its *Karstedt*-catalyzed hydrosilylation with HexMTS proceeded smoothly within 20h at 60°C when THF was used as a solvent for the solid allyl compound. In this step, no byproduct formation was observed. In a second step, the protecting group could be removed by addition of trifluoro acetic acid (TFA). Interestingly, the NMR spectra of the obtained deprotected amino-terminated compound differ from those of the direct hydrosilylation product of allyl amine. Especially the different chemical shift of the NH_2-group in the ^{1}H-NMR spectrum (5.67 ppm if N-BOC allyl amine was used and deprotected vs. 1.20 ppm for the direct hydrosilylation of allyl amine), make the formation of a amino-terminated product *via* this method questionable. Furthermore, in contrast to the direct hydrosilylation of allyl amine, this two-step procedure is costly and complex and does not bring any reasonable advantage.

1,4-Vinylaniline can be used for the preparation of amino-functional hybrid silicones with pendant aromatic groups, as its *Karstedt*-catalyzed hydrosilylation with PMDS leads within 6h at 75°C to the formation of the terminal hydrosilylation product. Trace amounts of an Si-N addition product can also be observed. Besides that, the major drawback for the industrial use of 1,4-vinylaniline in the amino-functionalization of hybrid silicones are its high costs.

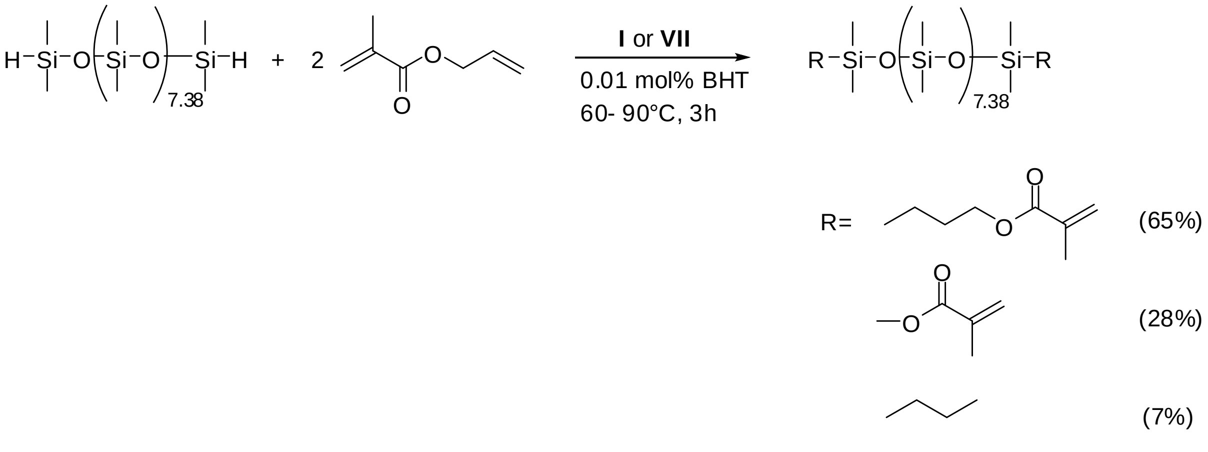
Costs may also limit the industrial use of 3-butene-1-amine in the functionalization of hybrid silicones, though its hydrosilylation with PMDS using **I** proceeds smoothly within 12h at 75°C. Again, the relatively long reaction times indicate that some catalyst poisoning occurs.

In contrast, oleylamine, as inexpensive and easily available amino compound with internal double bonds, is completely inert towards hydrosilylation. This again shows the high selectivity of *Karstedt's* catalyst towards terminal double bonds.

3.3.4 Functionalization with (Meth)acrylates

The direct hydrosilylation of (meth)acrylate esters with different methyl-hydrogen siloxanes, leading to the formation of α-, β- and 1,4-addition products has been reported [81],[82] as well as different indirect routes to acrylate-functionalized siloxanes.[83] Water-repellent organically-modified siloxanes have been prepared by reacting Si-H-polysiloxanes with *i*-butyl methacrylate, 1-hexadecene, and vinyltriethoxysilane.[84] Hydrosilylation of methacrylate-based hindered amine light stabilizers (HALS) led to the formation of products with two or three HALS groups in one molecule.[85] The platinum catalyzed hydrosilylation of allyl (meth)acrylate and its byproduct formation is subject of a patent as well as of some scientific articles.[86]

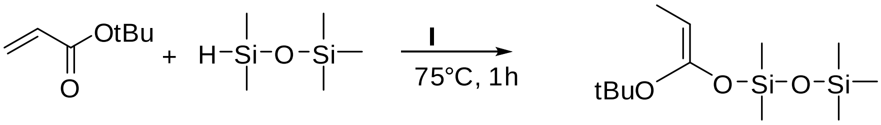
The hydrosilylation of allyl methacrylate needs to be performed in the presence of an inhibitor such as BHT (butylated hydroxytoluene) or phenothiazine to avoid polymerization of the methacryl group. With 0.01 mol% BHT, the *Karstedt*- or PtO_2-catalyzed hydrosilylation of allyl methacrylate with PDMS-H_2 occurs exclusively on the allylic position while the methacrylic double bond remains intact. The hydrosilylation reaction is accompanied by a C-O bond cleavage, leading to the formation of *n*-propyl-PDMS and an Si-O addition product, as described in section 2.4 for isopropenyl acetate. The resulting product distribution is shown in scheme 3.19.



Scheme 3.19. Hydrosilylation of allyl methacrylate with PDMS-H_2.

The direct hydrosilylation of *t*-butyl methacrylate with PMDS-H_2 using *Karstedt’s* catalyst, mainly results in the formation of the β-addition product. Thus, the methacrylic double bond is able to undergo hydrosilylation if no other double bond is present in the molecule.

In contrast, the *Karstedt*-catalyzed hydrosilylation of *t*-butyl acrylate with PMDS occurs almost exclusively *via* an 1,4-addition pathway and leads to the formation of a ketene acetale as depicted in scheme 3.20.



Scheme 3.20. Formation of a ketene acetale in the hydrosilylation of *t*-butyl acrylate with PMDS.

When 3-methyl-3-butenyl methacrylate, prepared according to [66], is hydrosilylated with PMDS, all three addition types can be observed and a complex mixture is obtained. Thus, the use of (meth)acrylates as functionalizing agents for hybrid silicones is quite limited.

3.3.5 Functionalization with Anhydrides

Anhydride functionalized (carbo)siloxanes can be used in the preparation of high temperature vulcanizing (HTV) epoxies.

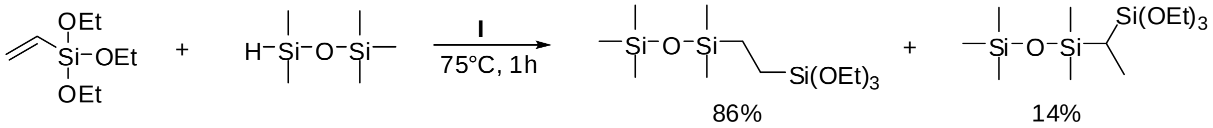
The hydrosilylation of nadic anhydride (methylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride) with 1,1,3,3-tetramethyldisiloxane was been reported by Buese [87] and Lin [88]. The latter article describes the use of the dianhydride-functional siloxane in the synthesis and curing of siloxane- and imide-modified epoxy compounds. The synthesis and properties of poly(imide-siloxane) polymers and copolymers based on 5,5′-bis(1,1,3,3-tetramethyl-1,3-disiloxanediyl) norbornane dicarboxylic anhydride and their employment in the preparation of high-molecular-weight thermoplastics and elastoplastics was reported by *Hallgren et al.*[89] In all cases, the purification of the silicon-containing dianhydride was very difficult. A new strategy for a two-step synthesis of telechelic α,ω-bisanhydride oligosiloxanes was reported by *Guida-Pietrasanta et al.* in 2001 to avoid the problems of purification and incomplete hydrosilylation addition.[90]

In accordance with the problems described in literature, synthesis and purification of *bis*-anhydride-functional siloxanes were very difficult to achieve and no pure products could be obtained *via* direct hydrosilylation of TMDS or PDMS-H_2 with nadic anhydride or methyl nadic anhydride.

3.3.6 Functionalization with Trialkoxysilanes

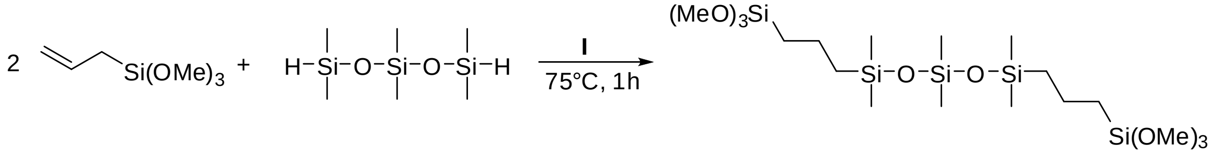
Trialkoxysilyl groups are important functional groups for the preparation of silicone rubbers, hard coatings, gels or membranes.[68],[91]-[97] When reacting with water, they hydrolyze and condensate, accompanied by a release of the corresponding alcohol, to form three-dimensional networks. The condensation reaction can be catalyzed by tin catalysts.[68],[96],[97]

Trialkoxy vinyl silanes are well-known reagents for the functionalization of siloxane chains with trialkoxysilyl groups.[91]-[94] To test the applicability of triethoxy vinyl silane in the functionalization of hybrid silicones it was reacted with PMDS in the presence of *Karstedt's* catalyst (**I**). The highly exothermic reaction proceeded within 1h at 75°C and resulted in the formation of an α-and a β-addition product, as depicted in scheme 3.21.



Scheme 3.21. Hydrosilylation of triethoxy vinyl silane with PMDS.

Also allyl trimethoxy silane is a common reagent for the preparation of trimethoxysilylpropyl-functionalized siloxanes. Because of steric effects, the hydrolysis of its methoxy groups is faster than the hydrolysis of the above mentioned triethoxy groups.[95] Furthermore, during its *Karstedt*-catalyzed hydrosilylation with HexMTS or PDMS-H_2, neither α-addition nor olefin isomerization or any other byproduct formation was observed (scheme 3.22).



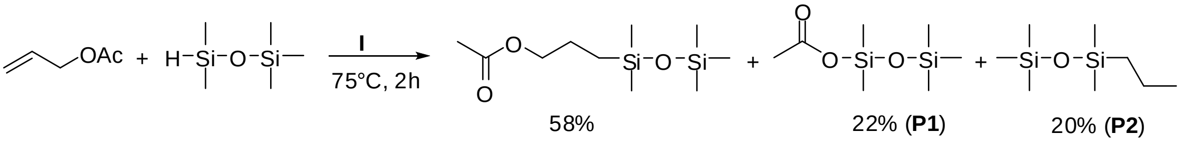
Scheme 3.22. Hydrosilylation of allyl trimethoxy silane with HexMTS.

These observations make allyl trimethoxy a very interesting functionalizing agent for hybrid silicones.

3.3.7 Functionalization with Acetates

Acetate-functional (hybrid) silicones can be prepared by reacting alkenes bearing acetate groups with α,ω-SiH carriers.

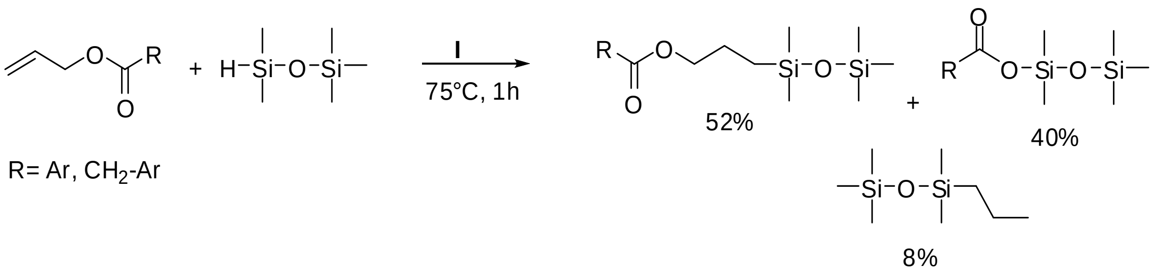
As already described in section 2.4, the platinum catalyzed hydrosilylation of γ-substituted allylic compounds, such as allyl acetate is very unselective.[36],[37] Thus, the *Karstedt*-catalyzed hydrosilylation of allyl acetate with PMDS leads to the formation of a product mixture, consisting of the terminal hydrosilylation product (acetoxypropylpentamethyldisiloxane) and two C-O-bond cleavage products, acetoxypentamethyldisiloxane (**P1**) and *n*-propylpentamethyldisiloxane (**P2**) as depicted in scheme 3.23.



Scheme 3.23. Hydrosilylation of allyl acetate with PMDS.

A comprehensive study of this reaction pathway was given in section 2.4. For better comparability with the results of the hydrosilylation of isopropenyl compounds (section 2.4), for the hydrosilylation of allyl acetate compounds also 100 ppm Pt were used. The molar ratio of acetoxypropylpentamethyldisiloxane: acetoxypentamethyldisiloxane: *n*-propylpentamethyldisiloxane in the reaction product is about 2.6: 1.0: 0.9. The formation of slightly less *n*-propylpentamethyldisiloxane than acetoxypentamethyldisiloxane indicates, that again some (10%) of the volatile propene has escaped from the reaction mixture. The same reactivity was observed when PDMS-H_2 was used instead of PMDS, and also the use of PtO_2 instead of *Karstedt's* catalyst led to the same product distribution.

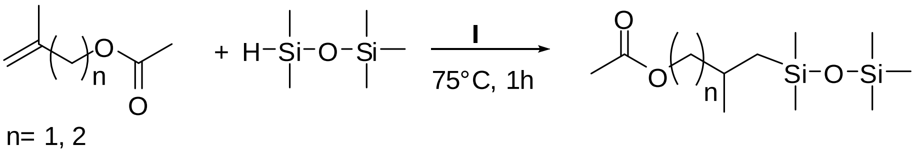
Allyl benzoate or allyl phenyl acetate react in the same manner. Their *Karstedt*-catalyzed hydrosilylation with PMDS also led to the formation of the respective terminal hydrosilylation products, benzoyloxypropylpentamethyldisiloxane and phenyl acetoxypropylpentamethyldisiloxane, and two byproducts resulting from C-O bond cleavage, as shown in scheme 3.24.



Scheme 3.24. Hydrosilylation of allyl benzoate (R= Ar) or allyl phenyl acetate (R= CH_2-Ar) with PMDS.

In both cases, the ratio was about 1.3: 1: 0.2 for the terminal hydrosilylation product versus the Si-O addition product and *n*-propylsiloxane. The reaction was very exothermic and could hardly be controlled. This led to an abrupt propene evolution and thus only small amounts of *n*-propyl-siloxane were formed.

In contrast to that, the *Karstedt*-catalyzed hydrosilylation of 3-methyl-3-butenyl acetate and 2-methyl-2-propenyl acetate with PMDS proceeded without C-O bond cleavage and led to the formation of the terminal hydrosilylation product only (scheme 3.25). The difference in reactivity can be explained by electronic reasons (section 2.4).



Scheme 3.25. Hydrosilylation of 2-methyl-2-propenyl acetate (n= 1) or 3-methyl-3-butenyl acetate (n= 2) with PMDS.

Vinyl acetate and vinyl propionate are completely inert towards platinum-catalyzed hydrosilylation. Even with very high catalyst concentrations (>1000 ppm) at elevated temperatures (85°C), no addition reaction took place.

3.3.8 Functionalization with Ether Groups

Allylpolyethers are interesting and versatile compounds for the functionalization of poly(carbo)siloxanes. The chain-end-functionalization of a non-polar (hybrid) silicone chain with a long polar polyether chain leads to completely new polymer properties. This strategy is well known in the functionalization of silicones. Thus, allyl-functionalized polyethylene oxide (PEO) or polypropylene oxide (PPO) blocks have been efficiently added to siloxanes *via* hydrosilylation.[98] The resulting polyether-functionalized silicones show a reduction of surface tension, the ability to form emulsions in aqueous systems, foam improving properties, and can be used in the production of polyurethane foams.[98],[99] Chinese scientists recently patented polyether-modified siloxane betain phosphate as leather treatment [100] as well as epoxypropoxypropyl-terminated polyether and phenyl co-modified polysiloxanes.[101] In 2008, *Ferenz et al.* patented polyether-modified siloxane copolymers as hydrophilic softeners for natural and synthetic fibers.[102] Comb-like polysiloxanes with pendant oligo(oxyethylene) side chains and trimethoxysilyl groups have been reported for the preparation of electrolyte membranes.[92],[103]

Two different hydroxy-terminated allylpolyethers (EO/PO-*block*-copolymers) with different chain lengths (IV=13.7 or 16.7) were tested in the *Karstedt*-catalyzed hydrosilylation of PDMS-H_2. In both cases a significant amount of internal double bonds as a product of allyl-isomerization was observed. A 30%-excess of the allylpolyether was necessary, to obtain complete Si-H consumption. Also when PtO_2 (**VII**) or an NHC-Pt(0) complex (**III**) were used as hydrosilylation catalysts, this side-reaction could not be suppressed.

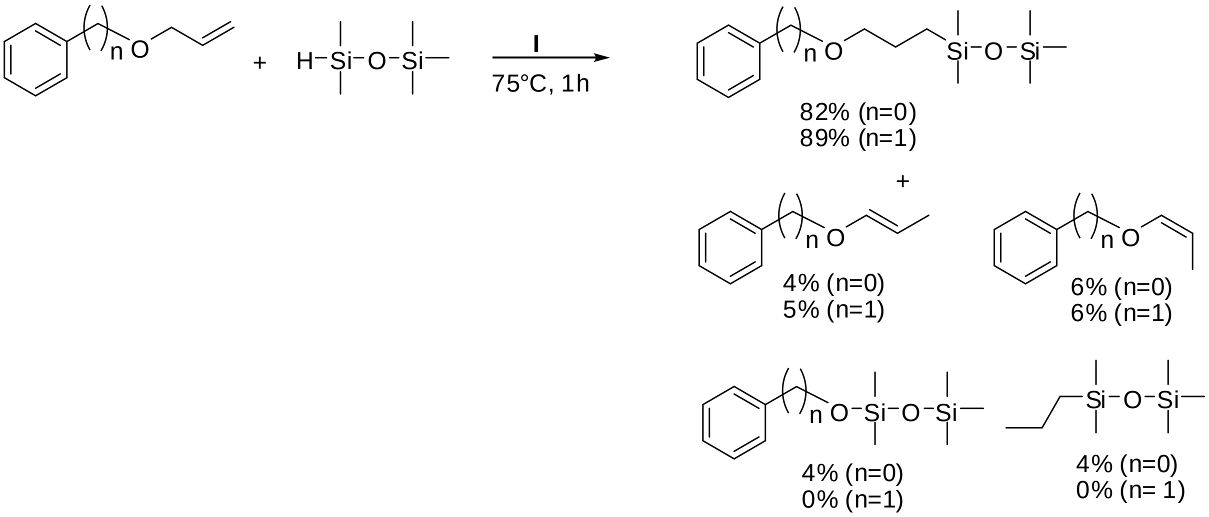
The use of vinyl or isoprenyl polyethers instead of allyl polyethers is complicated by the fact that these compounds are usually base-stabilized. The presence of the base leads to a condensation of the siloxane chains and makes their functionalization impossible. Because neutralization is complicated and cost-intensive, the use of stabilized vinyl polyethers in the functionalization of silicones is quite limited.

Non-stabilized vinyl or divinyl ethers, such as butanediol divinylether (BDDVE) or triethylene glycol divinyl ether (TEG-DVE) can be used instead without complications in the preparation or functionalization of hybrid silicones. As already described in section 3.2, they do not undergo isomerization and neither α-addition nor ethylene-elimination is observed.

Isobutyl vinyl ether can be regarded as model for vinyl or divinyl ethers. Its *Karstedt*-catalyzed hydrosilylation with PMDS or PDMS-H_2 proceeds smoothly within 1.5h at 75°C. The PMDS-adduct can be destilled *in vacuo* (30°C, $1 \cdot 10^{-3}$ mbar) without β-elimination of ethylene.

Also the hydrosilylation of 4-benzyloxy-2-methyl-1-butene (benzyl isoprenyl ether), which was prepared according to [104], with PMDS runs in 4h at 80°C without any byproduct formation. Due to the presence of the methyl group at the C=C double bond, no exothermy is observed and slightly longer reaction times are necessary to obtain full olefin conversion. Benzyl isoprenyl ether can be regarded as a model for isoprenol-started polyethers or for isopropenyl ether compounds such as isoprenyl methallyl ether (IME) as described in section 3.2.

Allyl phenyl and allyl benzyl ether can be regarded as models for allylpolyethers or bisphenol A diallyl ether, which has already been examined as a building block for the preparation of hybrid silicones (section 3.2). As described before, the platinum- catalyzed hydrosilylation of allyl ethers is accompanied by significant amounts of allyl-isomerization. The composition of the reaction mixture of the *Karstedt*-catalyzed hydrosilylation of allyl phenyl and allyl benzyl ether with PMDS is given in scheme 3.26.



Scheme 3.26. Hydrosilylation of allyl phenyl (n= 0) and allyl benzyl ether (n= 1) with PMDS.

Both hydrosilylations are very exothermic and proceed within 1h at 75°C in the presence of 10 ppm Pt in form of *Karstedt's* catalyst. In both cases, an olefin isomerization, which leads to the formation of a *cis*- (6%) and a *trans*-isomer (4-5%) occured.

For allyl phenyl ether also a C-O bond cleavage was observed, leading to the formation of *n*-propylpentamethyldisiloxane (4%) and an Si-O-adduct (4%). A similar product distribution was observed in the hydrosilylation of bisphenol A diallyl ether as described in section 3.2.

The use of benzyl isopropenyl ether in the hydrosilylation with PMDS was already described previously (section 2.4.4).

Due to the above mentioned side-reactions, the use of allylic ethers is problematic in the preparation and functionalization of hybrid silicones. In contrast, vinyl, isopropenyl or isoprenyl ethers can be hydrosilylated without difficulty and thus, be used as building blocks or terminal functionalizing agents for hybrid silicones.

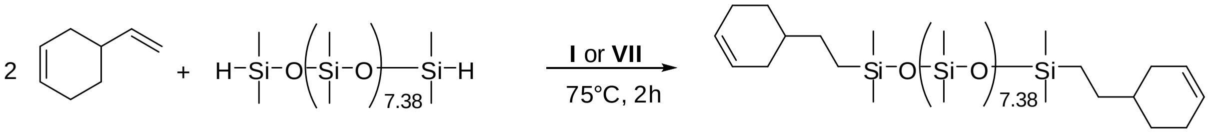
3.3.9 Functionalization with Aliphatic, Cycloaliphatic or Aromatic Groups

Although alkyl groups can hardly be regarded as functional groups, the physicochemical properties of silicones can be significantly modified when longer alkyl chains are introduced. Alkyl silicones show biological inertness, excellent oiliness, spreading, moisturizing and softening effects and are therefore used in cosmetic applications, as surfactants for paints or varnishes, lubricants, coatings, foam inhibitors, or moisture protectives.[105]
Poly(carbo)siloxanes can also be modified with aromatic functionalities. Styrene, α-methylstyrene, allylmethoxy benzene and allyl dimethoxy benzene can be added on Si-H-functional polysil(ox)anes in the presence of *Karstedt's* catalyst.[106] 4-vinylcyclohexene has been used to prepare polysiloxanes with pendant unsaturated cyclic fragments.[107] Also tricyclodecadiene can be added in 1,2- or 9,10-position to Si-H containing polysiloxanes in the presence of H_2PtCl_6 .[108]

The platinum-catalyzed hydrosilylation of *n*-octene and styrene with PDMS-H_2 has been investigated previously (section 2.2). For reasons of completeness, the hydrosilylation of *n*-octene was also performed with PMDS in the presence of *Karstedt's* catalyst. The terminal addition product could be separated from small amounts of isomerized octene, which were formed as byproducts, by vacuum distillation.

Also α-methylstyrene has been tested in the *Karstedt*-catalyzed hydrosilylation with PMDS. In contrast to styrene, no α-addition took place and the reaction was less exothermic, due to the presence of the methyl group in α-position.

4-vinylcyclohexene can be used for the synthesis of (hybrid) silicones with pendant unsaturated cyclic fragments. In the presence of *Karstedt's* catalyst (**I**) or PtO_2 (**VII**), the addition of PDMS-H_2 occurs mainly on the vinylic double bond, while the internal double bond stays almost intact (scheme 3.27), only small a amount (approx. 5%) of the internal double bond also undergoes hydrosilylation.



Scheme 3.27. Hydrosilylation of 4-vinylcyclohexene with PDMS-H_2.

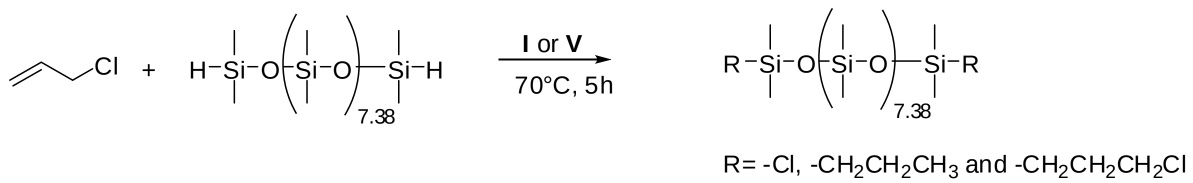
In systems with higher ring strain, such as norbornene or cyclopentene, the internal double bonds can be completely hydrosilylated with PDMS-H_2 in the presence of *Karstedt's* catalyst. In these cases, both reactions reached full Si-H conversion after 2-4h at 75°C and polysiloxanes with pendant cycloaliphatic end groups were obtained.

In contrast to that, the hydrosilylation of 1,1-diphenylethene with PDMS-H_2 proceeds very slowly (> 24h, 80°C). Obviously, the strong steric hindrance, caused by the two aromatic rings, decreases the reaction velocity.

3.3.10 Further Functionalizations

3.3.10.1 Hydrosilylation of Allyl Chloride

Chloroalkyl-functionalized silicones are important intermediates in the preparation of high-value materials and play important roles as adhesion-promoting or cross linking agents.[6],[7],[32] Unfortunately, as already described in section 2.4, the platinum catalyzed hydrosilylation of substituted allylic compounds is usually very unselective.[36],[37] Thus, the *Karstedt*-catalyzed hydrosilylation of allyl chloride with PDMS-H_2 leads to the formation of the terminal hydrosilylation product (α,ω-chloropropyl-polydimethylsiloxane) and α,ω-chloro- and *n*-propyl-PDMS and mixtures thereof as depicted in scheme 3.28.



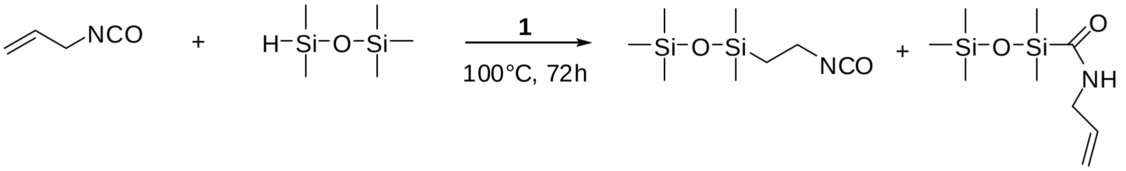
Scheme 3.28. Hydrosilylation of allyl chloride with PDMS-H_2.

The ratio of the three types of addition products Si-C: Si-Cl: Si-*n*-Pr is about 1:2:1. Again, the *n*-propyl-PDMS is formed in substoichiometric amount because of a propene loss during the reaction.

3.3.10.2 Hydrosilylation of Allyl Isocyanate

Isocyanate-functional siloxanes are important intermediates in the preparation of silicone-containing polyurethanes or polyureas. *Smid et al.* reported the successful hydrosilylation of *m*-isopropenyl-α,α-dimethylbenzylisocyanate (*m*-TMI) with different Si-H carriers and the conversion of the isocyanate-functionalized siloxanes into polyurethanes and polyureas.[109] The hydrosilylation of allyl isocyanate with Si-H containing polysiloxanes has been reported in a patent but neither yields nor product analysis were provided.[110]

The direct platinum-catalyzed hydrosilylation of allyl isocyanate is very difficult and large amounts of byproducts are formed resulting from reaction with the isocyanate group. Thus, its *Karstedt*-catalyzed hydrosilylation with PMDS led to the formation of a complex mixture (scheme 3.29) and no defined product could be obtained. Furthermore, catalyst-poisoning led to very long reaction times.



Scheme 3.29. Hydrosilylation of allyl isocyanate with PMDS.

3.3.10.3 Hydrosilylation of Acrolein Diethylacetal

The hydrosilylation of alkenal derivatives especially that of acrolein acetal is reported in a German patent [111] for the preparation of acid-cleavable surfactants. Acetal-functional siloxanes have also been used as intermediates in the synthesis of carbohydrate-functional siloxanes.[112]

The *Karstedt*-catalyzed hydrosilylation of acrolein diethylacetal with PDMS-H_2 proceeded smoothly within 2h at 75°C. In contrast, the hydrosilylation of acrolein with PDMS-H_2 led to the formation of a complex product mixture, which could not be fully analyzed. Additionally, the industrial applicability of acrolein diethylacetal in the functionalization of hybrid silicones is limited by the comparable high costs of the functional olefin.

4. Stability of Differently-Substituted Silicon-Containing Model Compounds

As potential impregnating agents polysilalkylene siloxanes have to resist extreme environmental conditions. Especially heat, humidity, high acid or base concentrations have to be tolerated.

To examine the stability of differently-substituted Si-C-adducts under extreme conditions, six model compounds with different functional groups (**A–F**, figure 4.1) were synthesized as described previously (section 3.3), purified by distillation and examined with respect to their tolerance towards heat, water, sulfuric acid, methanesulfonic acid (MSA), sodium hydroxide and 1,8-diazabicycloundec-7-ene (DBU).

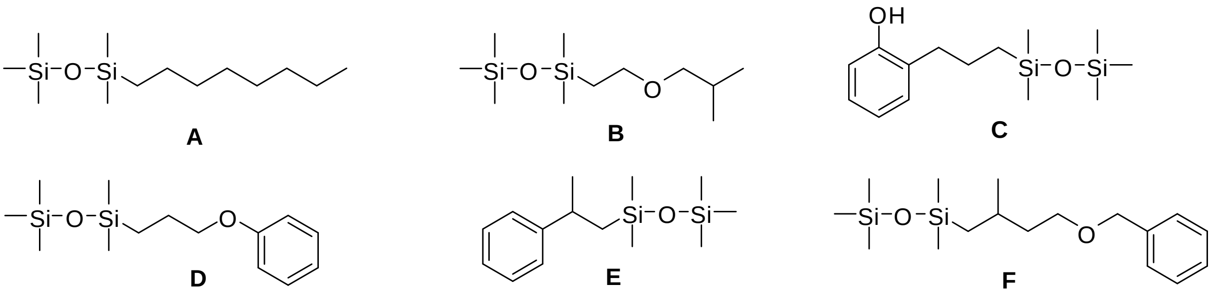


Figure 4.1. Model compounds **A–F** for the determination of the stability of differently-substituted hybrid silicones.

For this purpose, 1.5 mL aliquots of each substance were taken and 0.5 mL H_2O (dest.), 0.5 mL sulfuric acid (0.1 M) or 0.5 mL sodium hydroxide (0.1 M) were added, respectively and the resulting emulsions were heated to 70°C for 14d and shaken regularly. Additionally, 0.95 mL aliquots of each substance were mixed with 0.05 mL DBU or 0.05 mL MSA, respectively and also heated to 70°C for 14d. Samples were taken after 1, 2, 5, 7 and 14 days and analyzed by ^{1}H-NMR spectroscopy and GC-MS. The obtained results are summarized in table 4.1.

Table 4.1. Stability of differently-substituted model compounds **A**–**F**.

Compound	Conditions	1d	2d	5d	7d	14d	Remarks
A	**neutral**	-	-	-	-	-	white precipitate
	basic	-	-	-	-	-	white precipitate
	acidic	-	-	-	-	-	
	DBU	-	-	-	-	-	yellow, oily
	MSA	#	#	#	#	#	
B	**neutral**	-	-	-	-	-	
	basic	-	-	-	-	-	turbid
	acidic	-	-	-	-	-	
	DBU	-	-	-	-	#	yellow
	MSA	x	x	x	x	x	gas evolution
C	**neutral**	-	-	-	-	-	yellow
	basic	#	#	#	#	#	orange, turbid
	acidic	-	-	#	#	#	
	DBU	x	x	x	x	x	black, viscous
	MSA	x	x	x	x	x	pink
D	**neutral**	-	-	-	-	-	yellow precipitate
	basic	-	-	-	-	-	
	acidic	-	-	-	-	-	
	DBU	-	-	-	-	#	dark yellow
	MSA	#	#	#	#	#	pink to orange
E	**neutral**	-	-	-	-	-	
	basic	-	-	-	-	-	turbid
	acidic	-	-	-	-	-	-
	DBU	-	-	-	-		yellowish
	MSA	#	#	#	#	#	pink
F	**neutral**	-	-	-	-	-	
	basic	-	-	-	-	-	turbid
	acidic	-	-	-	-	-	
	DBU	-	-	-	-		yellow
	MSA	#	#	#	x	x	brown, viscous

neutral: in the presence of H_2O; basic: in the presence of NaOH; acidic: in the presence of H_2SO_4; DBU: in the presence of DBU; MSA: in the presence of methanesulfonic acid.
-: no changes;
#: significant changes but product in parts still intact (decomposition < 50%);
x: complete decomposition.

In the presence of water, diluted sulfuric acid or diluted sodium hydroxide, no decomposition was observed for the samples **A**, **B**, **D**, **E** and **F**. During 14 days, in some cases a slight turbidity and trace amounts of a white to yellow precipitate were observed. Sample **C**, which contains a hydroxy-functionality, turned yellow and more and more changes were visible in the ^{1}H-NMR spectrum as a result of decomposition. The resulting signals could not be completely assigned to a special decomposition product but the degree of decomposition of less than 10% could determined. Thus, slightly basic or acidic conditions at elevated temperatures are tolerated by all model compounds with the exception of **C**.

In the presence of DBU, all samples turned turbid and yellowish. Sample **C** became highly viscous and turned black during the first day. Complete decomposition, as a result of deprotonation of the hydroxyl group, was observed in the ^{1}H-NMR spectrum. The black color of the decomposition product might indicate the formation of a chinhydrone- or polyphenylene-like structure. All other samples (**A**, **B**, **D**, **E**, **F**) stayed almost intact as no changes could be detected in their ^{1}H-NMR spectra. After 14 days, additional signals were visible in the GC of compounds **B**, **D** and **F**, indicating the formation of small amounts of byproducts, resulting from ether cleavage and siloxane equilibration. The best stability was provided by compounds **A** and **E**, which do not contain any functional group.

However, all systems decomposed, at least in parts, in the presence of methanesulfonic acid (MSA). Complete decomposition was observed with model compounds **B**, **C** and **F**. In the case of **B**, the addition of methanesulfonic acid led to a strong gas evolution, possibly ethylene as a result of β-elimination, and the immediate decomposition of the compound. After one day, only Si-CH_3 groups could be detected by ^{1}H-NMR spectroscopy. Also compound **C** decomposed completely within the first day in the presence of MSA. After seven days, also compound **F** could not be detected any more and a strong increase in viscosity as well as a color change to dark-brown was observed. In the ^{1}H-NMR and GC-MS spectra of samples **A**, **D** and **E**, changes were detected, indicating a partly decomposition of these substances. After 14 days, also compound **D** was completely decomposed.

In conclusion, all model compounds, with the exception of **C** widely resist the harsh conditions and may be used as outdoor impregnating agents. In the case of **C**, the presence of a hydroxyl moiety significantly lowers the tolerance towards acids and bases. The presence of oxyethylene units, as in **B**, can be problematic in strong acidic environments due to β-elimination of ethylene. Best results were obtained with **A** and **E**, which do not contain any functional groups.

5. Synthesis and Application of Functionalized Hybrid Silicones

For the straight forward synthesis of functionalized hybrid silicones, especially for cost-sensitive construction chemical applications, it is required that all hydrosilylation reactions for the synthesis of the polymers as well as for their functionalization, proceed smoothly at reasonable temperatures, within a short period of time and as little byproduct formation as possible. Side reactions and the formation of byproducts represent significant issues in industrial processes because they cause additional efforts for purification and separation of the desired products and increase the costs of the production process. Well defined functional polymers with a high degree of functionalization (>99%) are necessary to obtain good film properties of the cured systems. In two-part systems (2K-systems) the exact determination of molecular weight and functionality is extremely important to set the balance between resin and hardener and to obtain uniform films. Furthermore, building blocks and functionalizing agents should be easily available and cheap enough to allow large-scale production.

With the results obtained from the test reactions (section 3.2 and 3.3) and the stability test (section 4), several dienes and functional olefins seem suitable for the synthesis and functionalization of novel hybrid silicones. 1,9-decadiene, butandiol divinyl ether, triethylene glycol divinyl ether and 1,3-diisopropenyl benzene could be identified as reasonable building blocks in the synthesis of hybrid silicone backbones. Their hydrosilylation proceeds smoothly without byproduct formation, they are easily available and with the exception of 1,9-decadiene relatively inexpensive and the resulting polymers exhibit good stability towards heat, acidic and basic media.

Several olefins with various functional groups can be used as functionalizing agents for the Si-H-terminated prepolymers. These functionalizing agents should also be cheap, non-toxic and easily available. Furthermore, complete and selective hydrosilylation is important to obtain complete functionalization. During testing, the most promising results were obtained with vinylcyclohexene oxide (4-vinylepoxycyclohexane, VCO), allyl glycidyl ether (AGE), allyl amine and allyl trimethoxysilane.

5.1 Epoxy-functional Hybrid Silicones

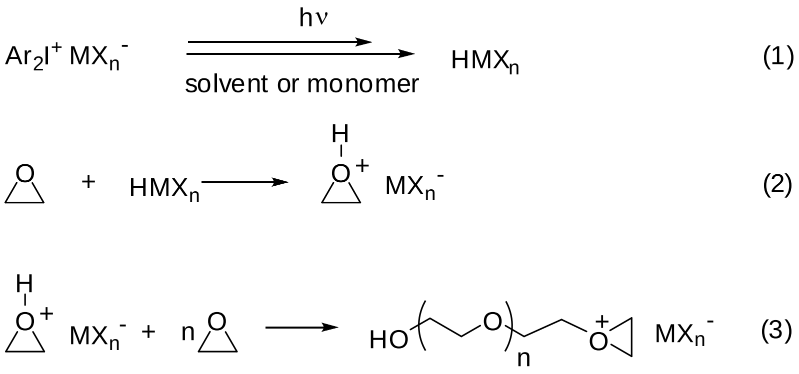
Epoxy-functional hybrid silicones can be prepared by hydrosilylation of Si-H-terminated prepolymers with vinylcyclohexene oxide (VCO) or allyl glycidyl ether (AGE). The industrial use of AGE is limited by toxicity concerns and by the fact that significant amounts of isomerization products were observed as byproducts during the hydrosilylation reaction.

The resulting epoxy-functional hybrid silicones can be properly cured either photochemically or thermically.

5.1.1 Photochemical Curing of Epoxy-functional Hybrid Silicones

The preparation of epoxy-functional siloxane monomers and oligomers and their reactivities in photoinitiated cationic polymerization were first examined by *Crivello* and *Lee* in 1990.[73] Monomers and oligomers bearing terminal cycloaliphatic epoxy groups were found to be especially reactive in cationic ring-opening polymerization and these materials were suggested as attractive candidates for use in photocurable coatings, printing inks, adhesives, and elastomers. Since then, interest and research activity in photoinitiated cationic crosslinking polymerizations of multifunctional epoxide monomers and oligomers has increased rapidly as this technology has found broad use in many industrial applications.

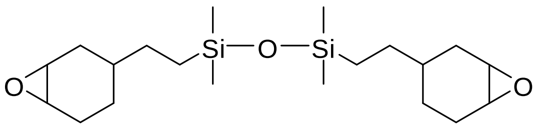
Depicted in scheme 5.1 is a generalized mechanism for the photoinitiated cationic ring-opening polymerization of epoxide monomers using a diaryliodonium salt cationic photoinitiator.[113] Irradiation of the photoinitiator with wavelengths in the range of 250-360 nm generates a number of reactive species that subsequently react with the solvent or monomer to give the strong protonic acid, HMX_n (1). Ring-opening polymerization takes place by protonation of the monomer (2) followed by the repetitive addition of monomer molecules to the growing oxonium ion polymer chain end (3).[114]



Scheme 5.1. Generalized mechanism for the photoinitiated cationic ring-opening polymerization of epoxide monomers.

There are several major motivating factors driving the adoption of this technology. First, the ability to conduct these crosslinking polymerizations very rapidly, with low energy and without the use of an inert atmosphere, provides important economic incentives. Second, because solvents are not necessary, there are no emissions and the environmental consequences of these polymerizations are minimal. Lastly, the thermal, mechanical, and chemical resistance, low shrinkage, and adhesion characteristics of the network polymers that are formed are excellent. The industrial impact of photoinitiated polymerizations in general and photoinitiated cationic polymerizations in particular is predicted to markedly increase in the future as this technology undergoes further maturation.[115],[116]

It is well known that monomers such as **TMDS-VCO** (figure 5.1) undergo efficient cationic ring opening photopolymerization to give crosslinked materials with excellent thermal and chemical resistance.[117]



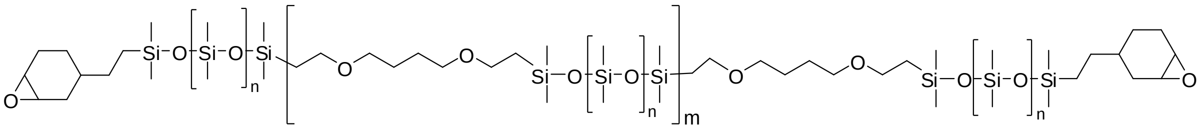
TMDS-VCO

Figure 5.1. Structure of epoxy-functional siloxane **TMDS-VCO**.

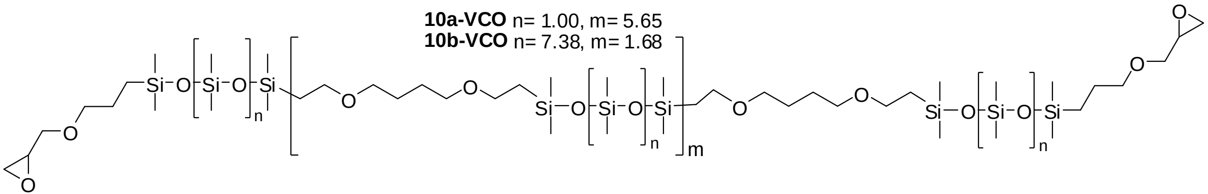
Unfortunately, such low molar mass difunctional monomers produce hard, brittle, glasslike materials with little elongation and minimal flexibility.[114]

It seemed, therefore, reasonable to attempt to expand the range of mechanical properties obtained in this class of monomers by the preparation of epoxy–silicone systems with a variety of different flexible backbone structures between the two crosslinkable epoxide groups.

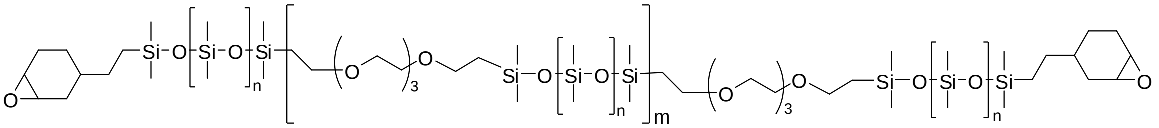
Therefore, twelve different hybrid silicones were prepared *via* the platinum-catalyzed polyhydrosilylation reaction. In order to obtain a set of different hybrid materials, the silicone character of the polymers was varied as well as the organic building block. For a broad variation of the properties of the polymers with respect to polarity and structure 1,4-butanediol divinyl ether, triethylene glycol divinyl ether, 1,3-diisopropenylbenzene and 1,9-decadiene were choosen as organic building blocks. The silicone content was varied through the use of two different types of siloxane building blocks, 1,1,3,3,5,5-hexamethyltrisiloxane (HexMTS) and α,ω-dihydropoly(dimethylsiloxane) (PDMS-H_2, M_n= 580 or 680 g/mol) with different chain lengths. Figure 5.2 shows the structures and designation of the hybrid silicones used in this study and table 5.1 gives an overview of their composition and molecular weight.



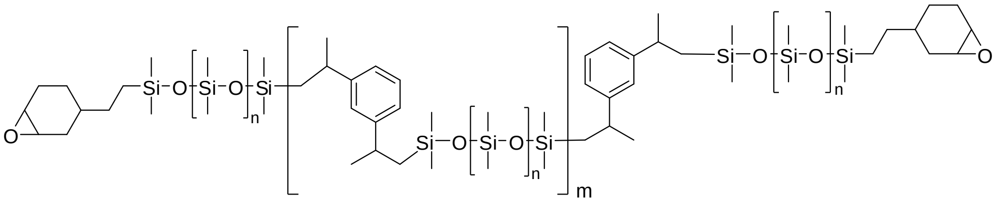
10a-VCO n= 1.00, m= 5.65
10b-VCO n= 7.38, m= 1.68



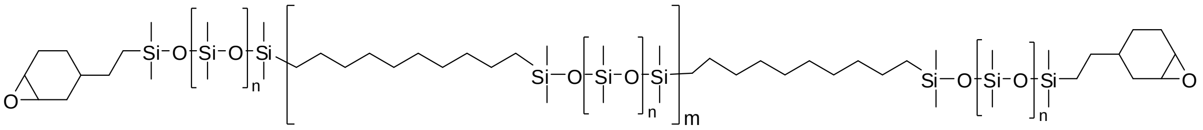
10c-AGE n= 1.00, m= 6.44



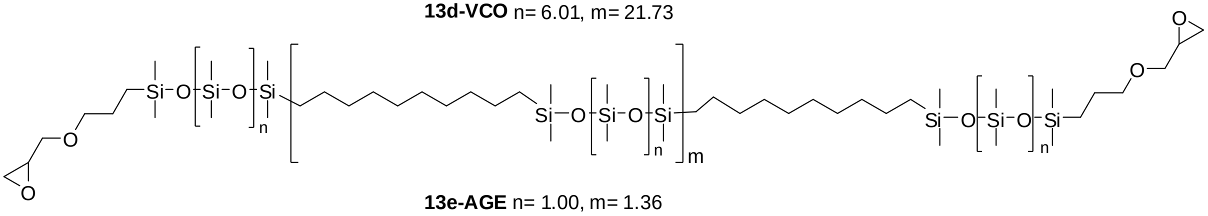
11a-VCO n= 1.00, m= 4.10
11b-VCO n= 7.38, m= 1.53



12a-VCO n= 1.00, m= 6.06
12b-VCO n= 7.38, m= 1.80



13a-VCO n= 1.00, m= 1.31
13b-VCO n= 6.01, m= 1.28
13c-VCO n= 1.00, m= 15.48
13d-VCO n= 6.01, m= 21.73



13e-AGE n= 1.00, m= 1.36

Figure 5.2. Structures of epoxy-functional hybrid silicones used in this study.

Table 5.1. Composition and molecular weight of epoxy-functional hybrid silicones **10a-VCO–13e-AGE**.

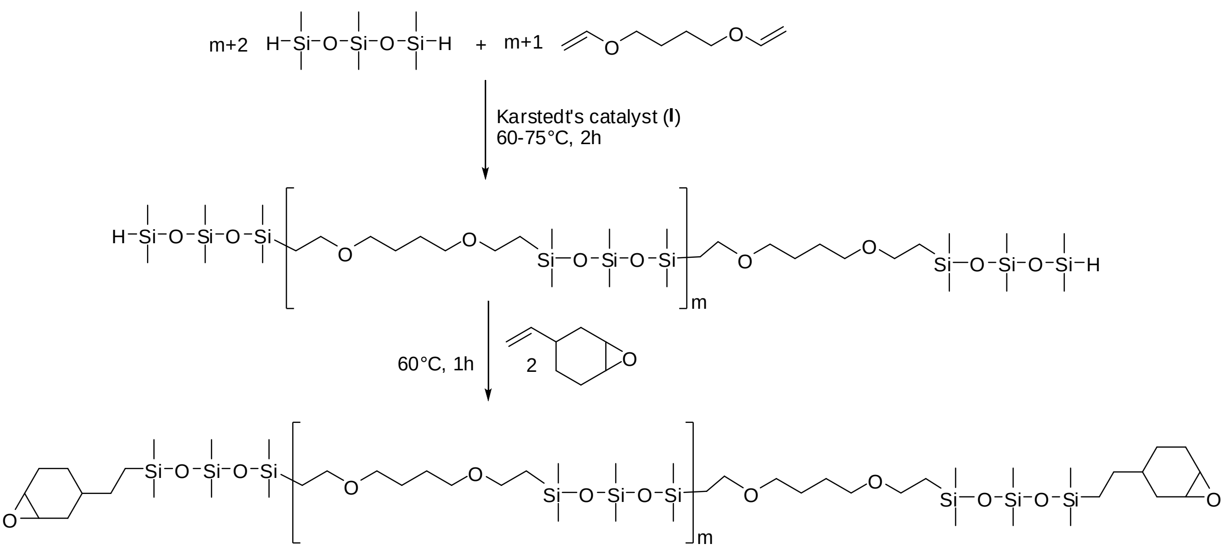
Compound	Siloxane	Diene	Epoxide	m^a	M^a (g/mol)	M_n^b (g/mol)
10a-VCO	HexMTS	1,4-butandiol divinyl ether	VCO	5.65	2770	3190
10b-VCO	PDMS	1,4-butandiol divinyl ether	VCO	1.68	3130	2950
10c-AGE	HexMTS	1,4-butandiol divinyl ether	AGE	6.44	3050	3770
11a-VCO	HexMTS	triethylene glycol divinyl ether	VCO	4.10	2550	2670
11b-VCO	PDMS	triethylene glycol divinyl ether	VCO	1.53	3160	2980
12a-VCO	HexMTS	1,3-diisopropenyl benzene	VCO	6.06	3050	2950
12b-VCO	PDMS	1,3-diisopropenyl benzene	VCO	1.80	3280	3280
13a-VCO	HexMTS	1,9-decadiene	VCO	1.31	1260	1780
13b-VCO	PDMS	1,9-decadiene	VCO	1.28	2470	3320
13c-VCO	HexMTS	1,9-decadiene	VCO	15.48	6170	6210
13d-VCO	PDMS	1,9-decadiene	VCO	21.73	17150	19400
13e-AGE	HexMTS	1,9-decadiene	AGE	1.36	1260	1710

a: Determined by ^{1}H-NMR spectroscopy, error: ± 5%; b: Determined by GPC.

In the first step of the synthesis, α,ω-Si-H-terminated prepolymers were synthesized by the platinum catalyzed polyhydrosilylation reaction of HexMTS or PDMS-H_2 with the above mentioned α,ω-dienes using *Karstedt's* catalyst or $Pt(PPh_3)_4$, as described in section 3.2. *Karstedt's* catalyst was used for the synthesis of the copolymers **10a-VCO–12b-VCO** and **13e-AGE**, while $Pt(PPh_3)_4$ was used for the synthesis of **13a-VCO–13d-VCO**.

In a second hydrosilylation reaction using the same catalyst, the α,ω-Si-H terminated prepolymers were functionalized with epoxy groups by reacting them with 4-vinyl-epoxycyclohexane (VCO) or allyl glycidyl ether (AGE).

As an example, scheme 5.2 shows the synthesis of **10a-VCO** from HexMTS and 1,4-butandiol divinyl ether and its functionalization with VCO.



Scheme 5.2. Synthesis of epoxy-functionalized hybrid silicone **10a-VCO**.

As already described in 3.3.2, in the presence of *Karstedt's* catalyst, a platinum catalyzed epoxide ring-opening polymerization can occur as a side reaction, leading to the spontaneous gelation of the epoxy-terminated copolymer.[76] In the case of 1,4-butanediol divinyl ether, triethylene glycol divinylether and 1,3-diisopropenylbenzene *Karstedt's* catalyst could be used for the polyhydrosilylation reaction as well as for all subsequent functionalizations. It appears, that the presence of oxygen atoms or aromatic groups in the polymer backbones inhibits the formation of colloidal platinum and, therefore, gelation. Less reactive glycidyl ether systems do generally not undergo this platinum catalyzed ring-opening epoxide polymerization. Therefore copolymers **10a-VCO–12b-VCO** and **13e-AGE** were prepared using *Karstedt's* catalyst.

In case of 1,9-decadiene, no functional group is present in the polymer that could prevent the formation of colloidal platinum. Therefore, *Karstedt's* catalyst could not be used in the synthesis of **13a-VCO–13d-VCO** because spontaneous gelation was observed in every case. Thus, $Pt(PPh_3)_4$ was chosen for these reactions which is also known as active and selective hydrosilylation catalyst and contains the gelation inhibiting base PPh_3.

The chain length and also the molecular weight of the copolymers was determined by ^1H-NMR-spectroscopy and was verified independently by GPC. Figure 5.3 shows the ^1H-NMR spectrum of **10a-VCO**. The assignment of the signals and the determination of the chain length are given in table 5.2.

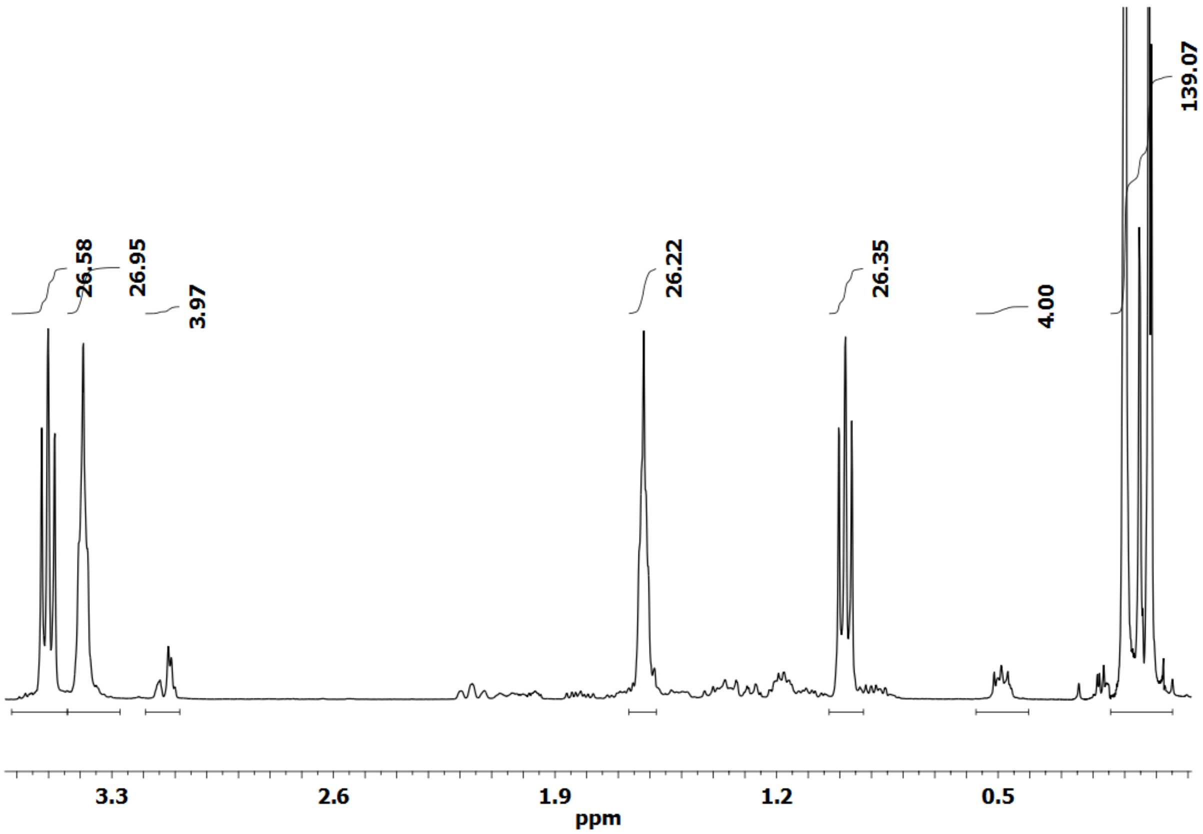


Figure 5.3. ^{1}H-NMR spectrum of **10a-VCO**.

Table 5.2. Assignment of ^{1}H-NMR signals and determination of the chain lengths for **10a-VCO**.

Group	**Signal (ppm)**	**Integral**	**Degree of Polymerization m**
Si-CH_3	0.05	139.07 =18m + 36	5.73
epoxy-CH_2-Si	0.5	4.00	-
CH_2-Si	0.99	26.35 = 4m + 4	5.59
CH_2	1.62	26.22 = 4m + 4	5.55
epoxy-CH	3.12	3.97	-
CH_2-O	3.39	26.95 = 4m + 4	5.74
CH_2-O	3.50	26.58 = 4m + 4	5.65

The molecular weight was determined using the following equation:

$$M = 2 \times M\ (siloxane) + M\ (diene) + m\ [M\ (siloxane) + M\ (diene)]$$
$$+ 2 \times M\ (epoxy\ component),$$

which results in

$$M = 2 \times 208.48\ g/mol + 142.20\ g/mol + 5.65 \times 350.68\ g/mol + 2 \times 124.18\ g/mol$$
$$= 2770\ g/mol$$

for copolymer **10a-VCO**.

Figure 5.4 shows the inverse gated ^{29}Si-spectrum of this copolymer.

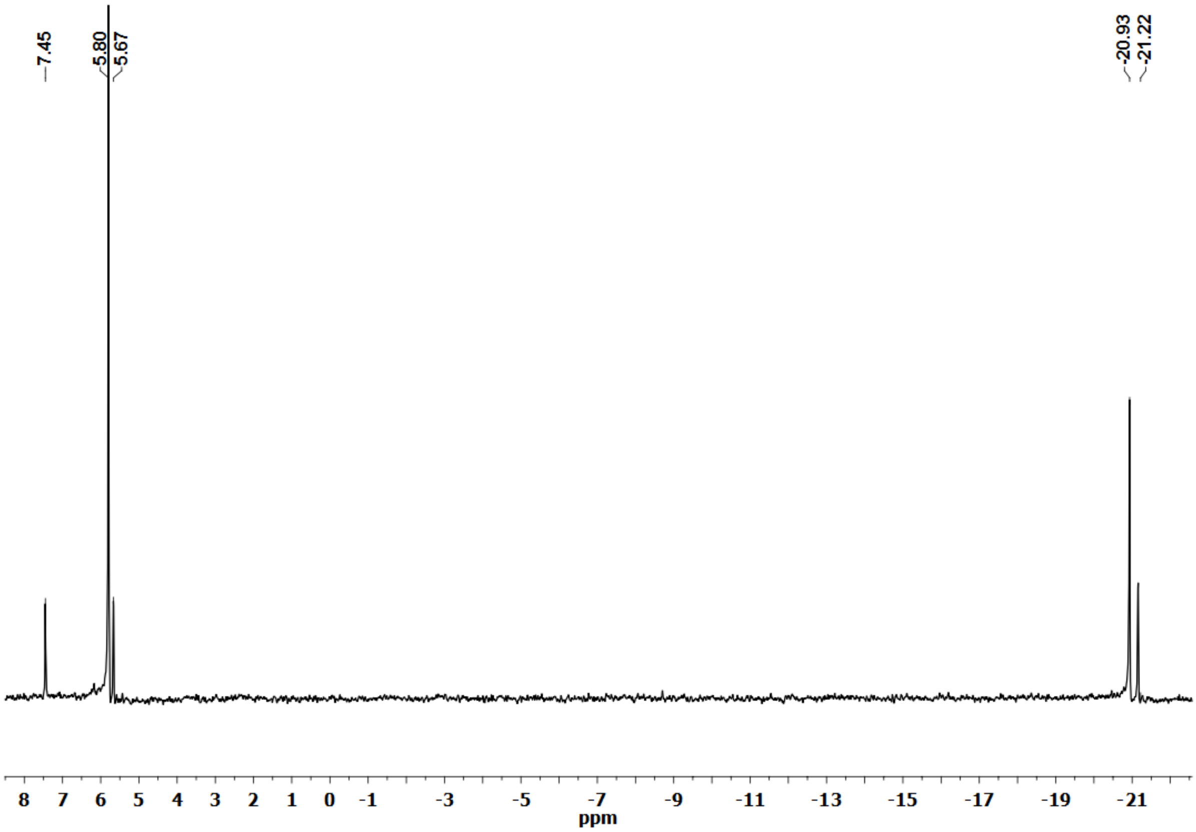


Figure 5.4. Inverse gated ^{29}Si-NMR spectrum of **10a-VCO**.

The strong signal at 5.80 ppm was assigned to the Si atoms directly bonded to carbon atoms in the oxyalkylene spacer group. The strong signal at -20.9 ppm is produced by the Si atoms located between two other silicon atoms in the polymer chain. The signal at 7.4 ppm is assigned to the Si atoms at the very ends of the copolymer, linked to the group containing the epoxy moiety (epoxy-<u>Si</u>-O-Si-). The low intensity signals at -21.2 and 5.67 ppm can be assigned to the silicon atoms in immediate vicinity to the very last silicon atoms (epoxy-Si-O-<u>Si</u>-O-Si- and epoxy-Si-O-Si-O-<u>Si</u>-).

Figure 5.5 shows the ^{1}H-NMR spectrum of copolymer **10c-AGE**.

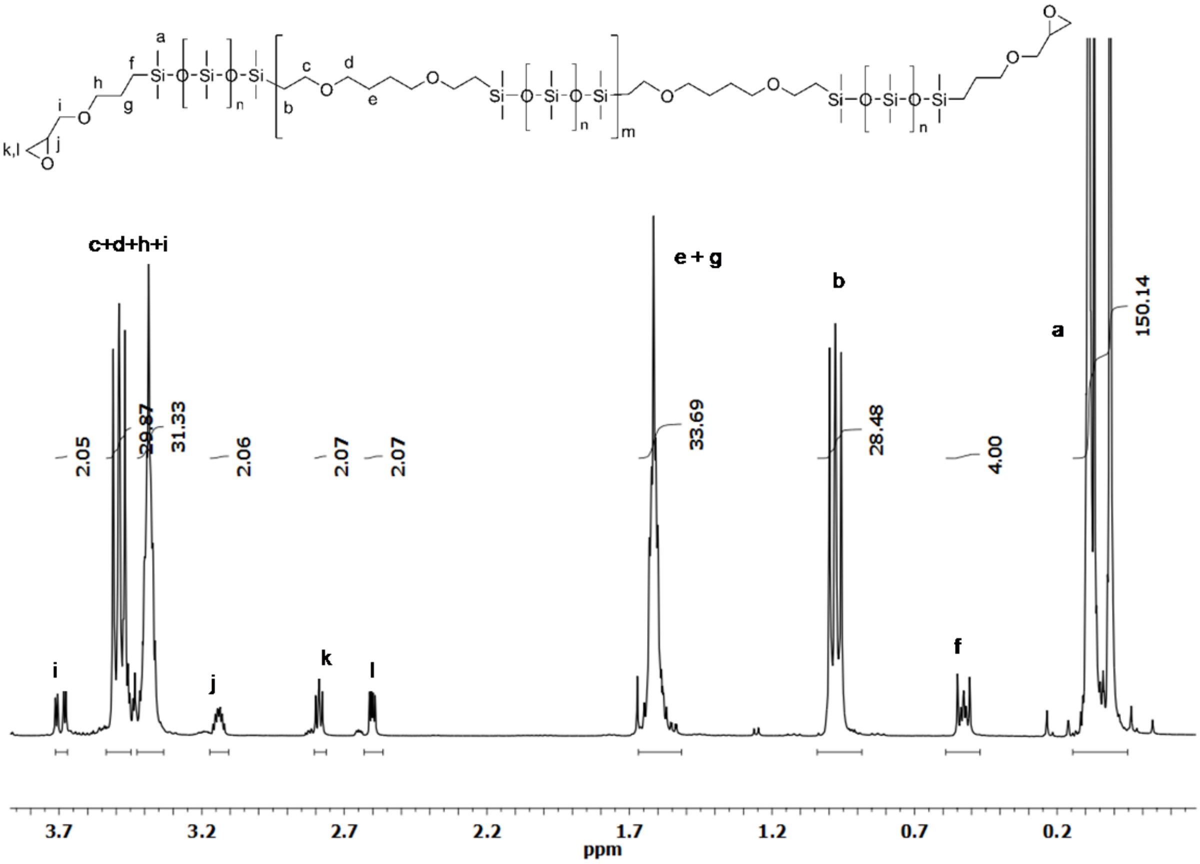
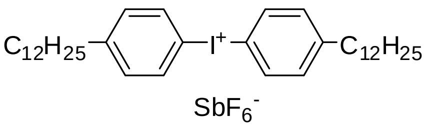


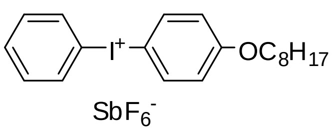
Figure 5.5. ^{1}H-NMR spectrum of **10c-AGE**.

As noted at the outset of this section, there is considerable interest in epoxy-functional monomers and oligomers that undergo rapid photoinduced cationic polymerization and also give good mechanical and thermooxidative properties. It was, therefore, particularly interesting to evaluate the rates of the photopolymerizations of several representative epoxy-functionalized telomers prepared during the course of this investigation and to determine whether a relationship between their structures and their reactivity can be established. In this investigation, the rates of polymerization were measured by optical pyrometry. This method involves following the course of the temperature of a monomer or oligomer sample during a photopolymerization in real time with an infrared camera (optical pyrometer). The greater the rate of increase in the temperature of a sample, the more reactive the monomer or oligomer.

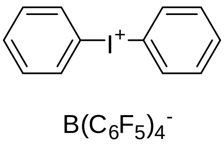
As a first step in this study, three different photoinitiators were tested in the photopolymerization of **10a-VCO**. Figure 5.6 shows the structure and short hand designations of these photoinitiators. **UV 9380C** was used as 50% solution in propylene carbonate.



UV 9380C



IOC-8



DPI-TFPB

Figure 5.6. Structure and trade names for the photoinitiators used in this study.

Figure 5.7 shows a study of the course of the polymerization of telomer **10a-VCO** with 2 wt% of the three different photoinitiators as determined by optical pyrometry.

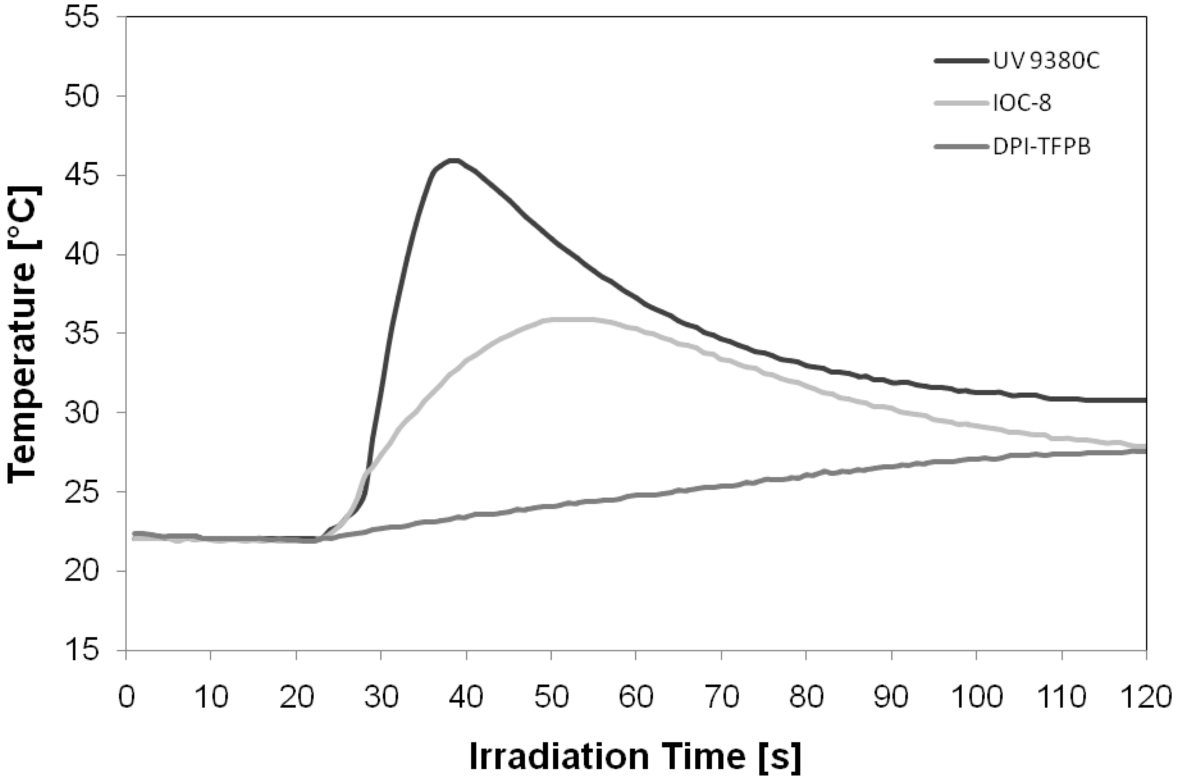


Figure 5.7. Progress of photopolymerization of **10a-VCO** with different photoinitiators at a light intensity of 2340 mJ/cm^2 min.

The best results were obtained with **UV 9380C** which is a very lipophilic photoinitiator having good solubility in the hybrid silicone **10a-VCO**. **IOC-8** is a more polar photoinitiator and less soluble in **10a-VCO**. The borate initiator **DPI-TFPB** is even less soluble and as a result, exhibits very poor photoinitiation activity. With **UV 9380C** and **IOC-8** soft, elastic and transparent rubber-like films were obtained.

When using the borate initiator, red inclusions of undissolved photoinitiator could be observed within the polymer film. Due to the overall better performance of **UV 9380C**, this photoinitiator was used in all subsequent photopolymerization reactions.

Figure 5.8 shows a study of the effect of the variation in the amount of photoinitiator **UV 9380C** used in the UV curing of **10a-VCO**.

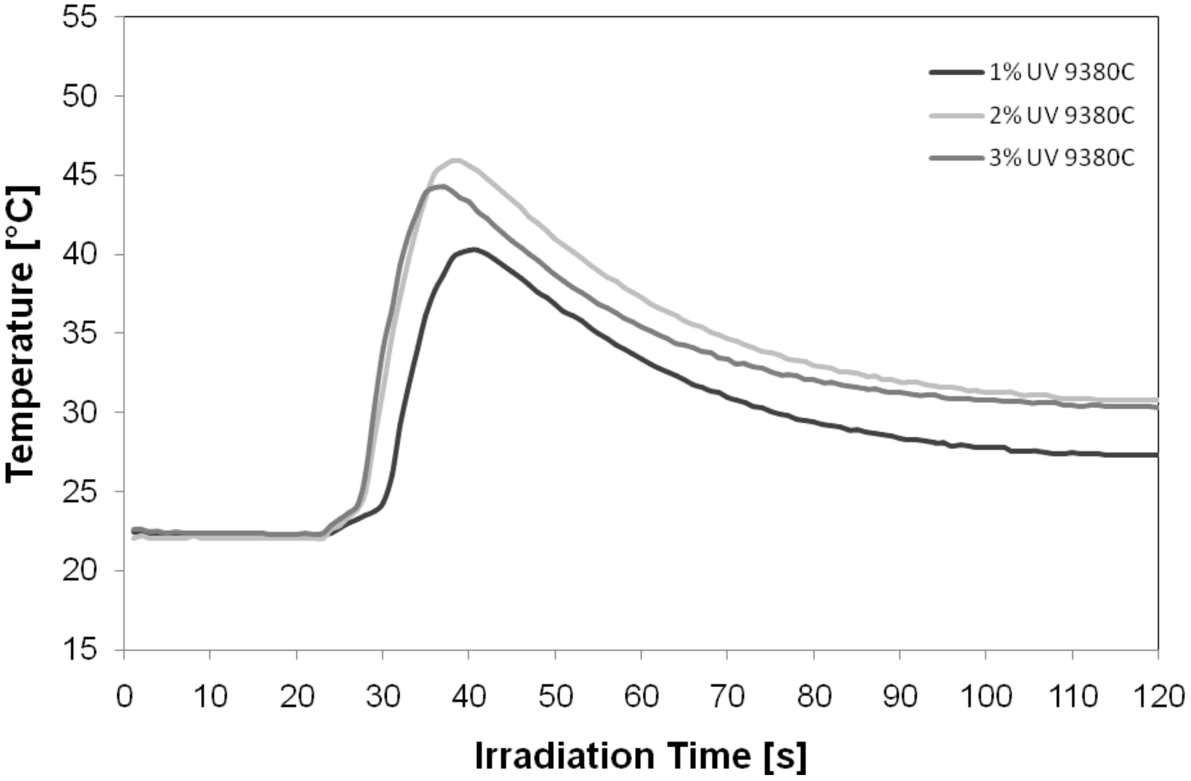


Figure 5.8. Variation of the amount of photoinitiator used in the photopolymerization of **10a-VCO** (all concentrations are given as weight percent).

Since there was very little difference in photopolymerization rates using 3 wt% and 2 wt% **UV 9380C** photoinitiator and because 1% gives somewhat slower photopolymerization rates, 2 wt% photoinitiator **UV 9380C** were used for all following experiments.

Figure 5.9 shows a study of the reactivities of the six telomers **10a-VCO**–**12b-VCO** bearing epoxycyclohexane terminal groups with different siloxane spacer lengths and different organic building blocks.

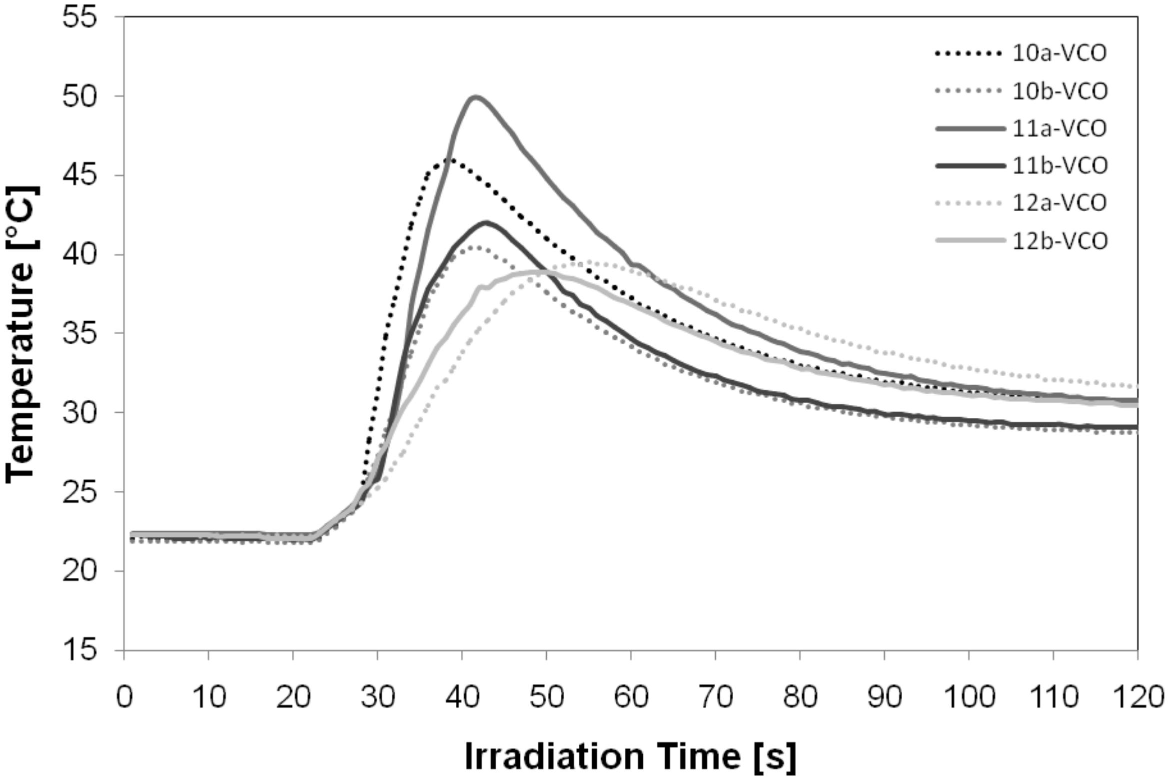


Figure 5.9. Comparison of cationic photopolymerizations of the six difunctional epoxycyclohexane hybrid silicones **10a-VCO–12b-VCO** with different siloxane spacer lengths and different organic building blocks.

The most rapid rate of temperature increase along with the highest ultimate sample temperature was observed with the copolymer containing HexMTS as a short siloxane block and triethylene glycol as the organic spacer (**11a-VCO**). It is likely that the polarity of the triethylene glycol building block leads to a better solubility of the ionic photoinitiator and consequently fast polymerization was observed. When 1,4-butandiol divinyl ether was used as an organic linker in combination with HexMTS as the siloxane unit (**10a-VCO**), polymerization was somewhat slower due to the decrease in polarity and resulting poorer photoinitiator solubility. When a longer siloxane chain (PDMS) was employed, the photopolymerization was also slowed down due to a further decrease in polarity of the polymer and thus poorer solubility of **UV 9380C**. Thus, **11b-VCO** which contains both triethylene glycol and PMDS units was less reactive than its HexMTS analogue **11a-VCO**, but faster than the very non-polar **12b-VCO** which contains an aromatic ring as a linker in the polymer chain. As already observed for the short siloxane containing systems **11a-VCO** and **10a-VCO**, the polymerization rate decreased when butandiol divinyl ether (**10b-VCO**) was used instead of triethylene glycol divinylether (**11b-VCO**).

The very non-polar systems containing 1,3-diisopropyl benzene units in combination with HexMTs (**12a-VCO**) and PDMS (**12b-VCO**) displayed the lowest reactivity.

In summary, the rate of polymerization increases with increasing polarity of the copolymer. The polarity decreases in the order: **11a-VCO** > **10a-VCO** > **11b-VCO** > **10b-VCO** > **12a-VCO** > **12b-VCO**.

In all cases, a short induction period was observed. This might be due to the presence of small amounts of basic impurities that inhibit the cationic ring-opening polymerization. The induction period is the longest for those polymers with the poorest reactivity. In the hybrid silicones **12a-VCO** und **12b-VCO** a competing light absorption due to the aromatic rings present in the polymer backbone could also contribute to the observed low rates of polymerization.

In Figure 5.10, the reactivity of the epoxycyclohexyl- (**10a-VCO**) and glycidyl ether terminated (**10c-AGE**) telomers derived from HexMTS and 1,4-butandiol divinyl ether are compared.

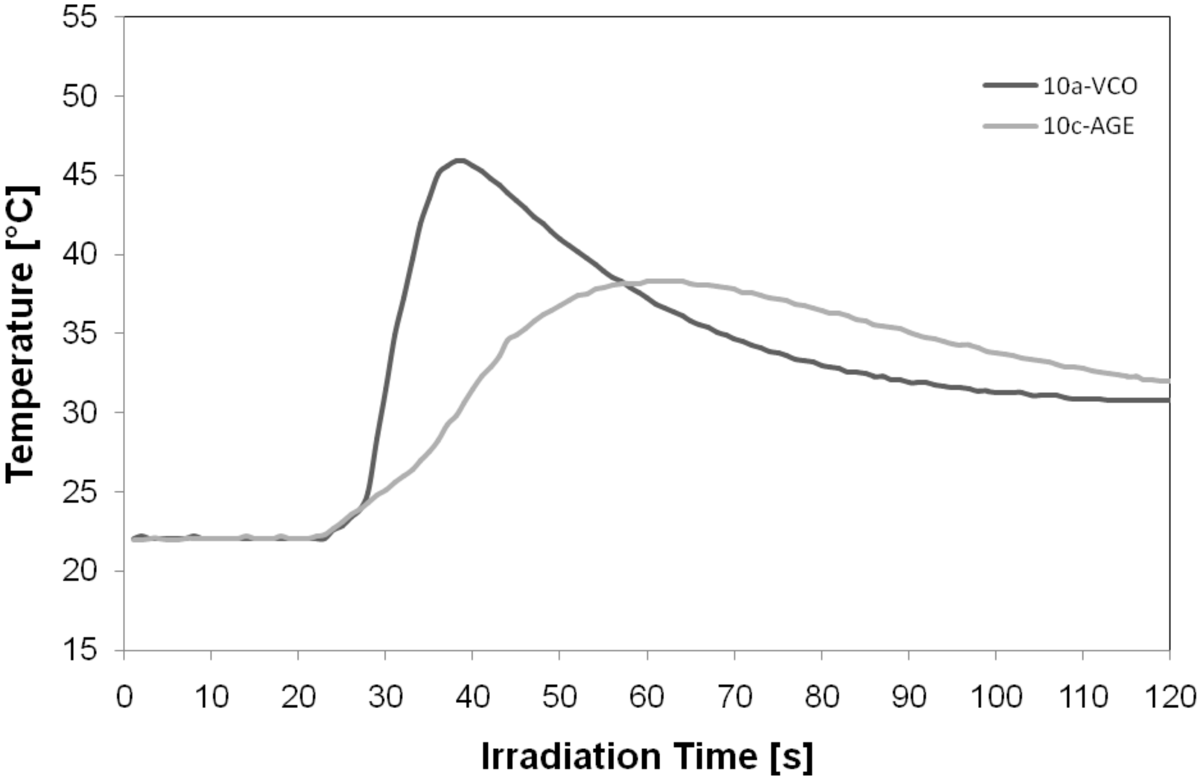


Figure 5.10. Comparison of epoxycyclohexyl- and glycidyl ether terminated HexMTS-butandiol divinyl ether copolymer **10a-VCO** and **10c-AGE**.

In accordance with the literature, the epoxycyclohexyl terminated telomer **10a-VCO** is much more reactive than its glycidyl ether terminated analogue **10c-AGE**. The rather poor reactivity of this and other glycidyl ethers in photoinduced and thermally induced cationic polymerizations can be attributed to two factors. First, the ring strain of the glycidyl ether is lower than in the epoxycyclohexyl functional system. Second, the presence of the two oxygen atoms of the glycidyl ether moiety provides a means for the stabilization of the protonated species through simultaneous coordination to both oxygen atoms *via* the formation of a pseudo five-membered ring.[113]

The rates of polymerization $R\mathrm{p}/[\mathrm{M}_0]$ for the six epoxycyclohexyl-terminated telomers **10a-VCO–12b-VCO** and the glycidyl terminated telomer **10c-AGE** are given in table 5.3. They were determined from the linear portions of the slopes of the irradiation time/temperature curves depicted in Figure 5.9. The order of the rates is as expected, with the highest polymerization rate for the most polar copolymer and the lowest rate for the least polar one.

Table 5.3. Rates of polymerization ($R\mathrm{p}/[\mathrm{M}_0]$) for the six epoxycyclohexyl-terminated hybrid silicones **10a-VCO–12b-VCO** and the glycidyl ether terminated telomer **10c-AGE**.

Copolymer	Rate of Polymerization $\mathrm{Rp}/[\mathrm{M}_0]$ (°C/s)
10a-VCO	2.83
10b-VCO	1.56
11a-VCO	3.00
11b-VCO	1.98
12a-VCO	1.05
12b-VCO	0.97
10c-AGE	0.73

Figure 5.11 shows a comparison of the reactivity of **TMDS-VCO** with five difunctional hybrid silicone telomers **13a-VCO–13e-AGE** having 1,9-decadiene as organic spacer, different siloxane spacer lengths and either epoxycyclohexyl or glycidyl ether functional groups.

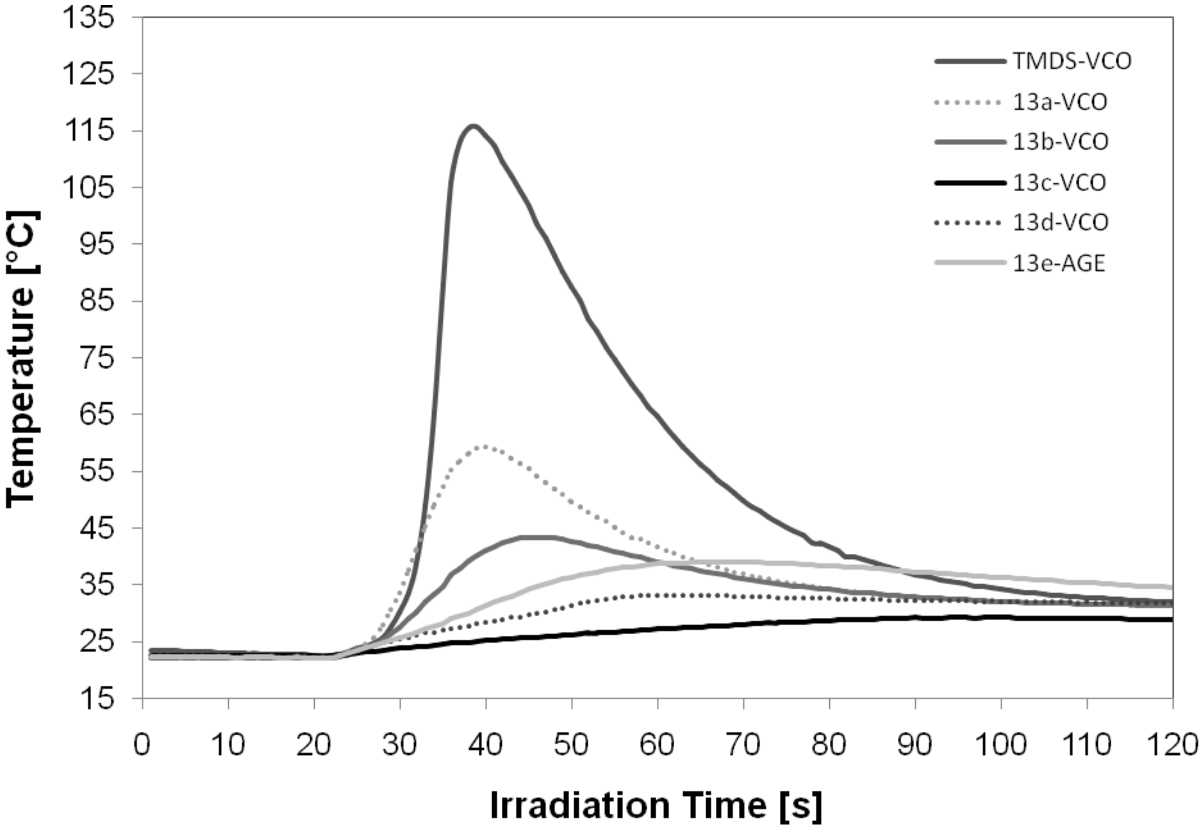


Figure 5.11. Comparison of the reactivity of monomeric **TMDS-VCO** with various difunctional hybrid silicone telomers having different siloxane spacer lengths and different molecular weights using 1,9-decadiene as organic building block.

The most rapid rate of temperature increase along with the highest ultimate temperature was observed with **TMDS-VCO**, a very short monomeric difunctional siloxane with epoxycyclohexyl end groups. The most reactive hybrid silicone was **13a-VCO** with a molecular weight of approx. 1500 g/mol and with epoxycyclohexyl end groups. Increasing the silicone character of the system by using a longer siloxane unit decreased the rate of the photopolymerization, (**13b-VCO**). This is also due to an increase in the epoxy equivalent weight. The same telomer containing glycidyl ether end groups (**13e-AGE**) displayed a further reduction in the polymerization rate. When the chain lengths, and thus the molecular weight, were further increased, very low rates of polymerization along with a very low over all temperature increase were observed because of the very low concentration of epoxy groups present in the copolymers (**13c-VCO** and **13d-VCO**).

The rates of polymerization *R*p/[M_0] for **TMDS-VCO** and the five hybrid silicone telomers **13a-VCO**–**13e-AGE** are given in Table 5.4. They were determined from the linear portions of the slopes of the irradiation time versus temperature curves depicted in Figure 5.11.

Table 5.4. Rates of polymerization (*R*p/[M_0]) for **TMDS-VCO** and **13a-VCO**–**13e-AGE**.

Copolymer	**Rate of Polymerization Rp/[M_0] (°C/s)**
TMDS-VCO	18.97
13a-VCO	3.68
13b-VCO	1.45
13c-VCO	0.25
13d-VCO	0.43
13e-AGE	0.54

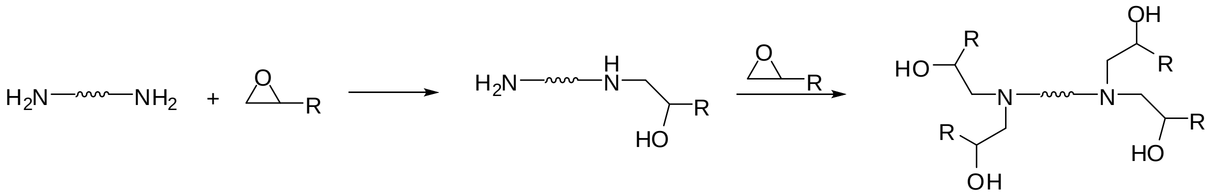
The order of the rates is as expected, with the highest polymerization rate observed for the copolymer with the shortest polymer chain and very low rates for the longer polymer chains. This is reasonable because the density of the epoxy-functional groups decreases in the same order (**TMDS-VCO**>>**13a-VCO**>**13b-VCO**>**13c-VCO**). It is noteworthy that the very long hybrid silicone **13d-VCO**, containing PDMS as siloxane building block was slightly more reactive than its HexMTS analogue **13c-VCO**, probably due to solubility effects. Despite its lower molecular weight, the glycidyl ether terminated system **13e-AGE**, containing 1,9-decadiene was slightly less reactive than its 1,4-butandiol divinyl ether analogue **10c-AGE**. This can be explained by the better solubility of the photoinitiator in the ether containing copolymer **10c-AGE**.

In contrast to the cured hybrid silicones, the cured films of **TMDS-VCO** are brittle and hard. The films of **13a-VCO**, **13b-VCO** and **13e-AGE** are soft, elastic, rubber-like transparent materials. In the case of **13d-VCO**, a translucent, very soft but completely crosslinked film was obtained. For **13c-VCO** incomplete crosslinking was observed, leading to a sticky gel.

In conclusion, photochemical curing of epoxy-functional hybrid silicones with different silicone characters and different organic building blocks can be easily achieved in the presence of a lipophilic photoinitiator to give stabile, soft, elastomeric and transparent films. The rate of polymerization increases with increasing polarity of the copolymer backbone, possibly because of better solubility of the ionic photoinitiator. When the molecular weight of the telomers was varied, the highest polymerization rate was observed for the shortest polymer chain. Furthermore, when identical hybrid silicone copolymers were compared having either epoxycyclohexyl or glycidyl ether functional end groups, it was observed that the rate of polymerization of those telomers bearing glycidyl ether end groups was substantially lower than that of their counterparts bearing epoxycyclohexyl groups.

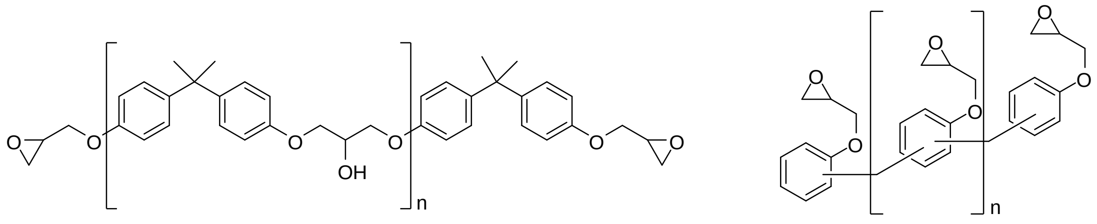
5.1.2 Thermal Curing of Epoxy-functional Hybrid Silicones

Epoxy-functional hybrid silicones can also be cured thermically with multifunctional amines as curing agents. In these two-component systems (2K-systems) the multifunctional amine hardener acts as a *N*-nucleophile and thus, crosslinker between the epoxy moieties. In order to obtain a crosslinked polymer from a difunctional epoxy polysilalkylene siloxane, the amine curing agent must have at least three active hydrogen atoms (i. e. NH functionalities), as depicted in scheme 5.3.



Scheme 5.3. Thermal curing of epoxy-functional compounds with amines.

A stoichiometric balance of epoxy groups and active hydrogen atoms is necessary to obtain complete crosslinking and good film properties. The curing speed depends on the type and loading of the amine and the type of epoxy resin. The most commonly used glycidyl ether type resins easily cure at room temperature while inner epoxides such as cyclohexyl epoxide or epoxidized polybutadiene can hardly be cured. In general, primary aliphatic amines, such as diethylenetriamine (DETA) or isophoronediamine (IPDA) lead to faster curing than secondary or aromatic ones. Tertiary amines do not directly undergo a reaction with epoxy resins but act as catalysts for their anionic ring-opening polymerization. Therefore, tertiary amines are often added to epoxy systems to achieve complete curing by polymerizing excessive epoxy groups.[68],[118] Two of the most common conventional epoxy resins are diglycidyl ether of poly(bisphenol-A-*co*-epichlorohydrin) (glycidyl-BPA) or poly(phenylglycidyl ether)-*co*-formaldehyde (Novolak-glycidyl ether), both shown in figure 5.12.



glycidyl-BPA

Novolak-glycidyl ether

Figure 5.12. Two of the most common conventional epoxy resins.

For the formulation of high-value adhesives with good impact resistance and good low temperature properties, the addition of elastifying epoxy resins is often recommended. Thus, epoxy-functional (hybrid) silicones, which combine the benefits of silicone and epoxy resins, can be used as elastifying components in mixtures with the classical systems.[75] It has been reported in literature, that higher adhesive strengths and increased thermal stability and flexibility were obtained with low molecular weight epoxy resins when siloxanes were incorporated in the backbone.[119] Silicones can also be used for toughening of epoxides. The phase separation of the siloxane component from the epoxide matrix results in a rubber toughening mechanism that effectively retards the fracture and thus improves fracture toughness.[120]-[122] However, the phase incompatibility of siloxanes and glycidyl-BPA often leads to problems when compounding.[123]

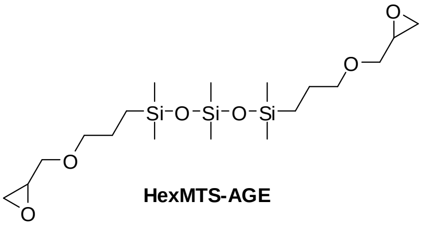
Epoxy-functional silicones can also be cured directly to give more elastic and flexible films than conventional epoxy resins. Mechanical and thermal properties of polydimethylsiloxane epoxides have been investigated extensively.[119]-[125]

Thus, attempts were made to cure the epoxycyclohexyl- and glycidyl-functional hybrid silicones **10a-VCO–12b-VCO** and **10c-AGE** either directly or as mixtures with conventional epoxy resins. Both curing approaches were performed with the most common amine hardeners, diethylenetriamine (DETA), ethylenediamine (EDA) or isophorone diamine (IPDA) with a stoichiometric balance of epoxy groups and active hydrogen atoms (NH:epoxy= 1:1).

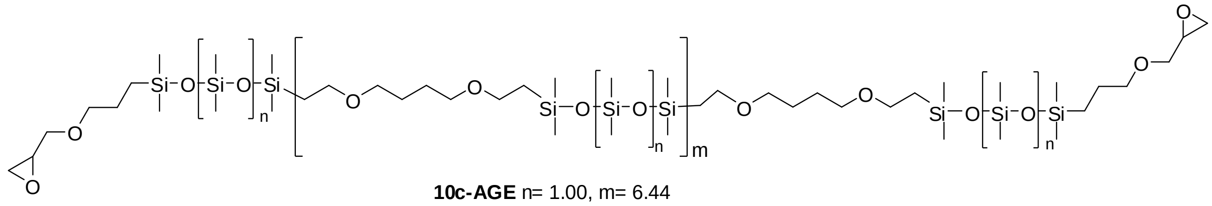
3 wt% of 2,4,6-*tris*-(dimethylaminomethyl)phenol (Ancamine® K54) were employed as a catalyst for the crosslinking of potentially excessive epoxy groups and 10 wt% of benzylalcohol were used as reaction accelerator and solvent. Byk-additives such as Byk® 354 (leveling additive with air-releasing effect) or Byk® 57 (defoamer) were employed to improve miscibility and film properties.

First of all, the epoxycyclohexyl-functional hybrid silicones **10a-VCO–12b-VCO** were tested with respect to their ability to undergo crosslinking with DETA as the amine curing agent. In all cases, no curing occurred and no epoxy-ring opening could be observed, neither at ambient nor at elevated temperatures (100°C).
In 50/50 mixtures with glycidyl-BPA (*bis*-glycidyl-poly(bisphenol-A-*co*-epichlorohydrin) or Novolak-glycidyl ether (poly(phenylglycidyl ether)-*co*-formaldehyde), only the conventional epoxide cured, leading to the formation of very inhomogeneous films with brittle islands within the liquid carbosiloxane. Obviously, inner epoxides such as cyclohexyl epoxide can hardly be cured with amines. Steric hindrance through the presence of the siloxane chain possibly additionally complicates the nucleophilic attack by the amine. Also tertiary amines as catalysts for anionic epoxide polymerization are obviously inactive for inner epoxides. The formation of homogeneous films is additionally complicated by the very poor miscibility of epoxy-functional hybrid silicones, conventional epoxy resins and amine hardener.

In contrast, glycidyl-functional hybrid silicones can be cured in the presence of amine hardeners. Thermal curing of **10c-AGE** and **HexMTS-AGE** (figure 5.13) with DETA, ETA or IPDA in the presence of Ancamine® K54 (3 wt%) and benzylalcohol (10 wt%) was achieved within 4 (DETA) to 24h (IPDA) at 100°C. No curing was observed at room temperature.



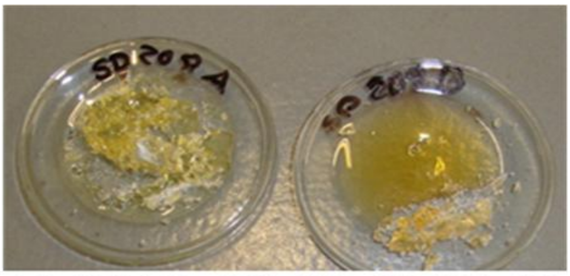
HexMTS-AGE



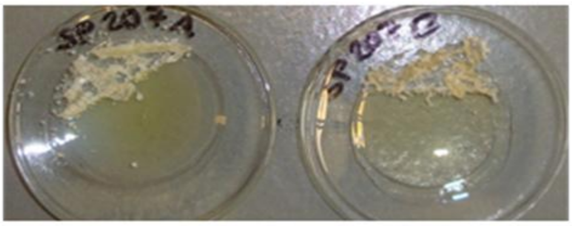
10c-AGE n= 1.00, m= 6.44

Figure 5.13. Glycidyl-functional (hybrid) silicones for thermal curing with amines.

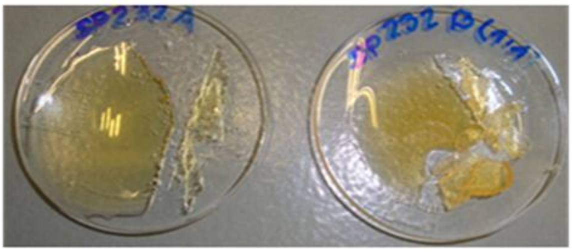
In all cases, slightly yellow, elastic and soft but partly brittle and sticky networks were obtained. In general, the cured products of **HexMTS-AGE** were harder and less flexible than their **10c-AGE** analogues. The reaction mixtures were initially turbid due to the poor miscibility of carbosiloxane and amine but cleared during curing. The crosslinked products obtained from **HexMTS-AGE** and **10c-AGE** with DETA, ETA and IPDA are shown in figure 5.14.



a) HexMTS-AGE + DETA **b) HexMTS-AGE** + EDA



c) 10c-AGE + DETA **d) 10c-AGE** + EDA



e) HexMTS-AGE + IPDA **f) 10c-AGE** + IPDA

Figure 5.14. Cured products of glycidyl-telechelic hybrid siloxanes with different amines.

Brittle films were obtained as a result of incomplete crosslinking. For DETA, this is possibly due to an inactivity of the secondary amino group and thus only 80% crosslinking of the epoxy moieties. For ETA, it is likely, that the low boiling point of the amine is responsible for incomplete curing. The best results were obtained with IPDA, also because of the better miscibility with the hybrid silicone epoxy resin.

Figure 5.15 shows the IR-spectrum of **HexMTS-AGE** prior and after reaction with DETA. The disappearance of the epoxy absorption signal at 909 cm^{-1} in the cured product (blue) is clearly visible. Additionally, though stoichiometric amounts of amine and epoxide were used, excessive amino groups are still visible in the IR spectrum (3425 cm^{-1}), indicating incomplete curing.

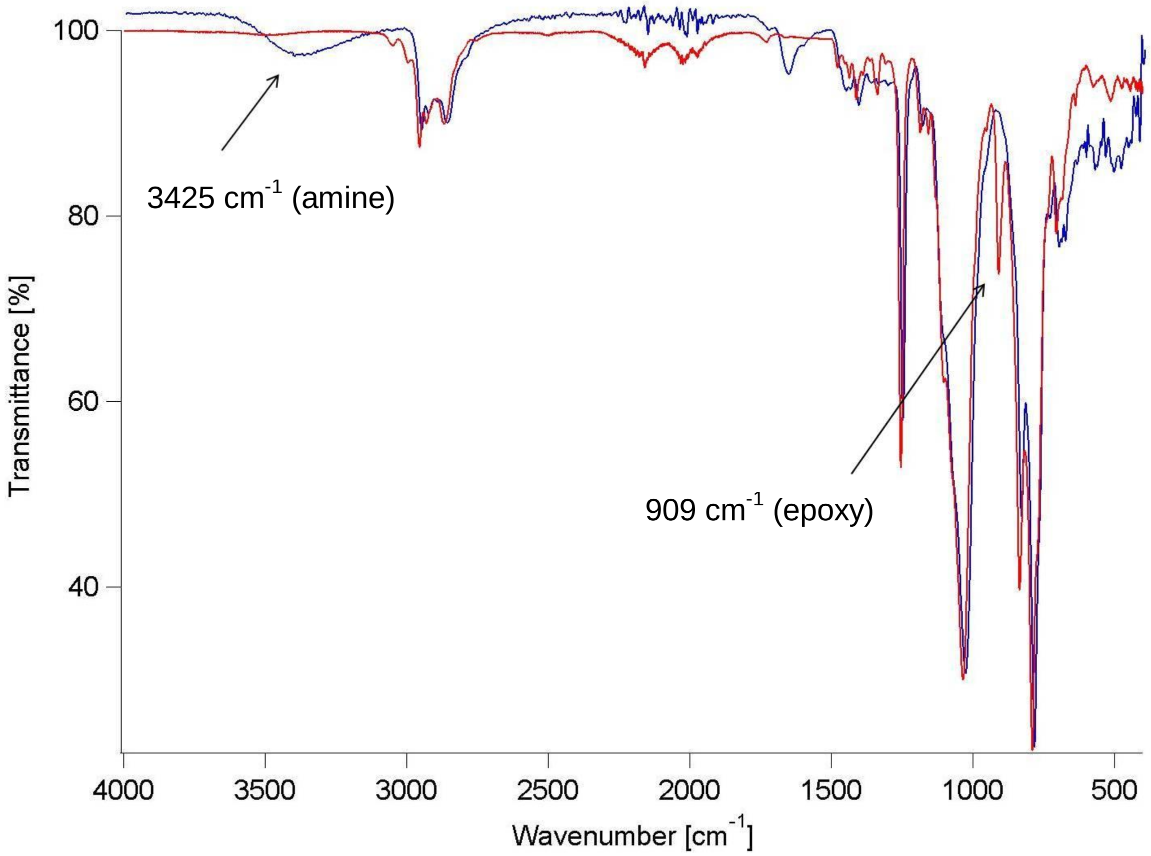


Figure 5.15. IR-spectrum of **HexMTS-AGE** prior (red) and after (blue) reaction with DETA.

A 50/50 mixture of glycidyl-BPA and **HexMTS-AGE** could be cured with DETA at ambient temperature within 3d. Sufficient miscibility of the components was achieved in the presence of 10 wt% benzylalcohol. Again, the reaction mixture was initially turbid and cleared during curing to give a hard film with low elasticity and promising mechanical properties. In the cured film, a partial phase separation of the components was still visible (figure 5.16).

An optimized formulation would surely further improve the curing behavior the mechanical properties of the resulting film. Thus, glycidyl-functional hybrid silicones have potential either as elastic, highly flexible epoxy coatings or as modifiers for conventional epoxy resins.

Figure 5.16. 50/50 mixture of **HexMTS-AGE** and glycidyl-BPA cured with DETA at ambient temperature.

5.2 Preparation and Thermal Curing of Amino-functional Hybrid Silicones

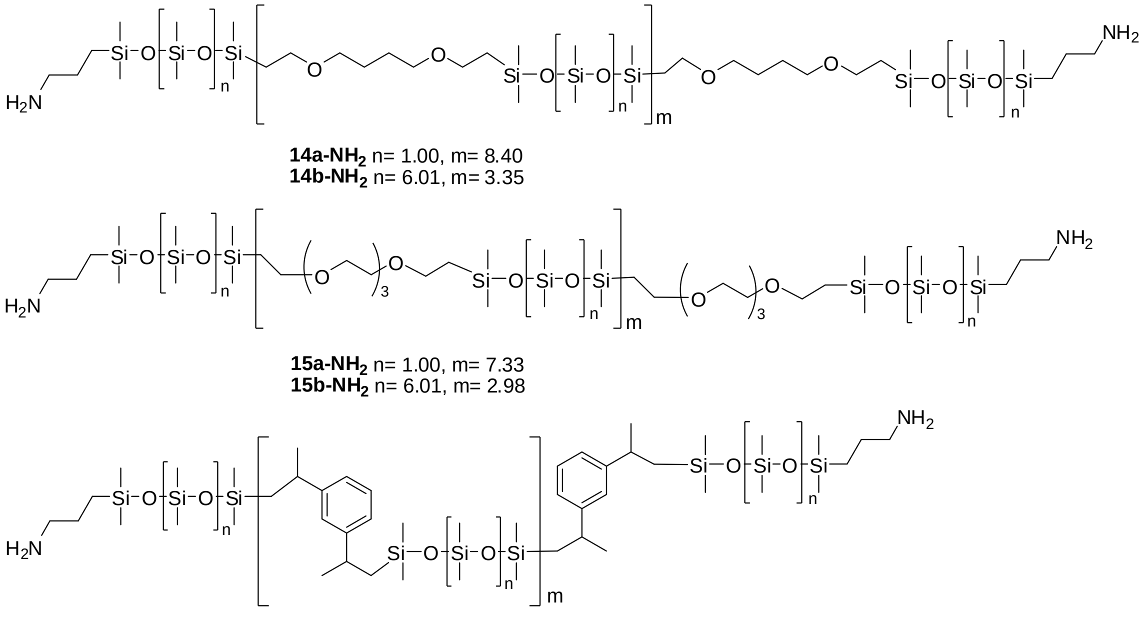
Hybrid silicone containing epoxy film coatings can also be prepared by curing conventional epoxides such as glycidyl-BPA (*bis*-glycidyl-poly(bisphenol-A-*co*-epichlorohydrin) or Novolak-glycidyl ether (poly(phenylglycidyl ether)-*co*-formaldehyde), with amino-telechelic polysilalkylene siloxanes. Again, the phase incompatibility of siloxanes and conventional epoxy resins may result in inhomogeneous films but is usually less problematic due to the presence of polar amino-groups in the silicone component.[126]

The better miscibility enhances compatibility, ensures homogeneous particle distribution, and thus leads to effective toughening.[126],[127] Interpenetrating networks with good electrical, thermal, and mechanical properties have also been obtained from siloxane hybrids.[128],[129] Best results could be obtained when epoxy- and amino-telechelic siloxanes were cured together. Amino-terminated siloxanes have been extensively studied as components of a large number of segmented materials.[130]-[133] The thermal curing of telechelic glycidyl epoxide siloxanes and amino-telechelic siloxanes, both bearing pendant methyl, cyclopentyl or cyclohexyl groups was reported by *Soucek et al*.[75] *Weber et al.* prepared minimal adhesive polymer surfaces from epoxy- and amino-telechelic siloxanes as foul-release coatings.[131]

Only cost issues argue against the combined curing of epoxy- and amino-telechelic siloxanes. Amino-telechelic siloxanes can also be used for the preparation of silicone-containing polyureas.[132],[133]

Amino-telechelic hybrid silicones can be prepared *via* the direct hydrosilylation of Si-H-terminated prepolymers with allyl amine (section 3.3.3). In the test reactions high catalyst concentrations and an excess of allylamine were employed to obtain complete conversion, but as the reaction conditions are not yet optimized, these findings should not hinder an efficient industrial application of this procedure.

Six different hybrid silicones with different silicone content and different organic building blocks were prepared *via* the *Karstedt*-catalyzed polyhydrosilylation reaction and subsequently functionalized with allyl amine. The silicone character was varied by using 1,1,3,3,5,5-hexamethyltrisiloxane (HexMTS) and α,ω-dihydropolydimethylsiloxane (PDMS-H_2, M_n= 580 g/mol) as siloxane spacers, while 1,4-butanediol divinyl ether, triethylene glycol divinyl ether and 1,3-diisopropenylbenzene were employed as organic linkers. The obtained amino-functional copolymers are shown in figure 5.17, their composition and molecular weight are given in table 5.5.



14a-NH_2 n= 1.00, m= 8.40
14b-NH_2 n= 6.01, m= 3.35

15a-NH_2 n= 1.00, m= 7.33
15b-NH_2 n= 6.01, m= 2.98

16a-NH_2 n= 1.00, m= 6.40
16b-NH_2 n= 6.01, m= 2.72

Figure 5.17. Amino-telechelic hybrid silicones **14a-NH_2–16b-NH_2**.

Table 5.5. Composition and molecular weight of amino-telechelic hybrid silicones **14a-NH_2–16b-NH_2**.

Compound	**Siloxane**	**Diene**	**m[a]**	**M[a] (g/mol)**
14a-NH_2	HexMTS	1,4-butandiol divinyl ether	8.40	3620
14b-NH_2	PDMS-H_2	1,4-butandiol divinyl ether	3.35	3840
15a-NH_2	HexMTS	triethylene glycol divinyl ether	7.33	3740
15b-NH_2	PDMS-H_2	triethylene glycol divinyl ether	2.98	3810
16a-NH_2	HexMTS	1,3-diisopropenyl benzene	6.40	3040
16b-NH_2	PDMS-H_2	1,3-diisopropenyl benzene	2.72	3440

a: Determined by ^{1}H-NMR spectroscopy, error: ± 5%.

The amino-terminated hybrids were used as hardeners for the curing of glycidyl-BPA or Novolak-glycidyl ether. Again, 2,4,6-*tris*-(dimethylaminomethyl)phenol (Ancamine® K54) was employed as a catalyst for the crosslinking of potentually excessive epoxy groups and benzylalcohol or isopropanol were used as reaction accelerators and solvents. Like in the case of the epoxy-telechelic hybrid silicones, the miscibility of the conventional epoxy resins and the silicone-containing amines was limited. The attempt of curing Novolak-glycidyl ether with **14a-NH$_2$** led to a complete phase separation of the two components and no cured products could be obtained. The miscibility of **14a-NH$_2$** and glycidyl-BPA in the presence of benzylalcohol was slightly better but even after three weeks at ambient temperature, only a sticky and turbid inhomogeneous gel was formed. To improve the miscibility with glycidyl-BPA and thus the resulting film properties, different formulations were tested using the hybrid silicones **14a-NH$_2$**, **14b-NH$_2$** and **15a-NH$_2$**. As the molecular weight of the amino-telechelic hybrid silicones can only be calculated by ^{1}H-NMR spectroscopy with an error of approx. 5%, this uncertainty may result in a stoichiometric imbalance of amino and epoxy groups. Therefore, the molecular ratio of epoxy resin to amino-polymer was varied from 0.8: 1 to 1: 0.8. Furthermore, the effect of isopropanol as a solvent and Byk® 354 as an additive was investigated. The different formulations and the results obtained after 7d at ambient temperature are summarized in table 5.6. In all cases, 3% Ancamine® K 54 were used as a catalyst.

Table 5.6. Curing of amino-telechelic hybrid silicones **14a-NH$_2$**, **14b-NH$_2$** and **15a-NH$_2$** with glycidyl-BPA.

Polymer	**mmol (Polymer): mmol (Glycidyl-BPA)**	**Solvent** [10%]	**Additive** [0.1%]	**Film properties after 7d**
14a-NH$_2$	1 : 2	isopropanol	-	not mixible, not cured
14a-NH$_2$	1 : 2	isopropanol	Byk 354	not mixible, not cured
14a-NH$_2$	1 : 2	benzylalcohol	-	not mixible, not cured
14a-NH$_2$	1 : 2	benzylalcohol	Byk 354	not mixible, not cured
14b-NH$_2$	1 : 2	isopropanol	-	not mixible, not cured
14b-NH$_2$	1 : 2	isopropanol	Byk 354	not mixible, not cured
14b-NH$_2$	1 : 2	benzylalcohol	-	not mixible, not cured
14b-NH$_2$	1 : 2	benzylalcohol	Byk 354	not mixible, not cured
15a-NH$_2$	1 : 1	benzylalcohol	-	turbid yellow, not cured
15a-NH$_2$	0.9 : 1	benzylalcohol	-	turbid yellow, sticky gel
15a-NH$_2$	0.8 : 1	benzylalcohol	-	turbid yellow, sticky gel
15a-NH$_2$	1 : 0.9	benzylalcohol	-	turbid yellow, sticky gel
15a-NH$_2$	1 : 0.8	benzylalcohol	-	turbid yellow, sticky gel

With **14a-NH$_2$**, which contains HexMTS and 1,4-butanediol divinyl ether, the miscibility was too low to achieve complete, homogeneous curing. The miscibility could neither be improved by addition of benzylalcohol or isopropanol nor with Byk® 354. Also with **14b-NH$_2$**, which ontains a longer siloxane chain, the miscibility was not sufficient to achieve homogeneous curing and also with **15a-NH$_2$**, only a turbid, yellow, sticky gel was obtained.

Because of the poor miscibility of the amino-terminated hybrid silicones with conventional epoxy resins, **HexMTS-AGE** (figure 5.13) was used as epoxy component instead. With this α,ω-epoxy-siloxane much better miscibility of the two components was achieved and homogeneously cured films could be obtained during one week at ambient temperature. Several different formulations containing **HexMTS-AGE** and **14a-NH$_2$**, **14b-NH$_2$** or **15a-NH$_2$** were prepared to compare the curing behavior and the resulting film properties.

3% of Ancamine® K54 were used as a catalyst and 10% of either benzylalcohol, MTBE (methyl *tert*-butyl ether) or isopropanol were employed as solvents. Also the influence of two different additives, Byk® 354 (leveling additive with air-releasing effect) and Byk® 57 (defoamer), was investigated. The different formulations and the results obtained after 7d at ambient temperature are summarized in table 5.7.

Table 5.7. Curing of amino-telechelic hybrid silicones **14a-NH$_2$**, **14b-NH$_2$** and **15a-NH$_2$** with **HexMTS-AGE**.

Entry	**Polymer**	**mmol (Polymer): mmol (HexMTS-AGE)**	**Solvent** [10%]	**Additive** [0.1%]	**Film properties after 7d**
1	**14a-NH$_2$**	1 : 2	benzylalcohol	-	cured, clear, sticky
2	**14a-NH$_2$**	1 : 2	benzylalcohol	Byk 354	cured, beige
3	**14a-NH$_2$**	1 : 2	benzylalcohol	Byk 57	cured, beige, very sticky
4	**14a-NH$_2$**	1: 2	isopropanol	-	cured, beige, sticky
5	**14a-NH$_2$**	1 : 2	MTBE	-	not cured, beige, sticky
6	**14a-NH$_2$**	1 : 0.5	benzylalcohol	-	not cured, liquid
7	**14b-NH$_2$**	1 : 2	benzylalcohol	-	cured, slightly turbid
8	**14b-NH$_2$**	1 : 2	benzylalcohol	Byk 354	cured, slightly turbid
9	**14b-NH$_2$**	1 : 2	benzylalcohol	Byk 57	cured, slightly turbid, sticky
10	**14b-NH$_2$**	1: 2	isopropanol	-	cured, slightly turbid, sticky
11	**14b-NH$_2$**	1: 2	MTBE	-	cured, sticky
12	**15a-NH$_2$**	1 : 2	benzylalcohol	-	clearly cured, yellowish
13	**15a-NH$_2$**	1 : 2	benzylalcohol	Byk 354	cured, turbid
14	**15a-NH$_2$**	1 : 1.9	benzylalcohol	Byk 354	cured, turbid
15	**15a-NH$_2$**	0.9 : 2	benzylalcohol	Byk 354	cured, turbid

In almost all cases, cured films were obtained. No major differences could be observed with respect to the hybrid silicones used. With **14a-NH$_2$** and **15a-NH$_2$**, which contain a short siloxane spacer, completely cured and almost tack-free films were obtained. Slightly poorer curing was observed for **14b-NH$_2$**, leading to sticky and turbid films. Only when a large excess of amine was present in the mixture or in the presence of MTBE, no curing took place (table 5.7, entry 5 and 6). In contrast, no large differences were observed when the epoxy to amine ratio was slightly varied (table 5.7, entry 13, 14, 15). The addition of 0.1% Byk® 354 enhanced the dehesive character of the films. However, when 0.1% Byk® 57 was added, sticky films very obtained (table 5.7, entry 3 and 9). Also the use of different solvents such as benzylalcohol, isopropanol and MTBE, led to differences in the cured products. Best, tack-free results were obtained with benzylalcohol while formulations containing isopropanol or MTBE remained sticky or did not cure at all.

Best overall results were obtained with **15a-NH$_2$** in the presence of 10% benzylalcohol and 0.1% Byk® 354.

Therefore, 10% benzylalcohol and 0.1% Byk® 354 were also used in the preparation of filled film systems. Filler materials such as quartz or barite powder can be used to reduce the costs of the adhesive or sealant and the shrinkage during the curing process. Additionally, fillers often reduce the cohesion and thus simulate better adhesion. Usually, not more than 80 wt% of the filler are added to the binder, to allow easy and complete incorporation and a processible viscosity of the resulting mixture.[68]

The different compositions and the resulting film properties after 2d at ambient temperature are summarized in table 5.8.

Table 5.8. Filled films of amino-telechelic hybrid silicones **14a-NH$_2$**, **14b-NH$_2$** and **15a-NH$_2$** with **HexMTS-AGE**.

Entry	**Polymer**	**Polymer: HexMTS-AGE**	**Filler**	**Film properties after 2d**
1	**14a-NH$_2$**	1 : 2	-	sticky, film can be removed from PE-foil
2	**14a-NH$_2$**	1 : 2	10 wt% Aerosil 812S	cured, clear, sticky
3	**14a-NH$_2$**	1 : 2	33% Barytmehl N	cured, inhomogeneous, very sticky
4	**14a-NH$_2$**	1 : 2	50% Barytmehl N	cured, inhomogeneous, very sticky
5	**14a-NH$_2$**	1 : 2	50% Omyalite 95T	cured, sticky, very flexible
6	**14a-NH$_2$**	1 : 2	15 wt% Aerosil 812S	cured, clear
7	**14b-NH$_2$**	1 : 2	15 wt% Aerosil 812S	cured, turbid
8	**14b-NH$_2$**	1 : 2	10wt% Aerosil 812S	cured, inhomogeneous, sticky
9	**14b-NH$_2$**	1 : 2	50% Omyalite 95T	cured, sticky, very flexible
10	**14b-NH$_2$**	1 : 2	50% SIKRON SF 600+ 0.5% Anti-terra® U80	cured, very flexible
11	**15a-NH$_2$**	1 : 2	10 wt% Aerosil 812S	cured, clear, very sticky
12	**15a-NH$_2$**	1 : 2	50% Omyalite 95T	not cured
13	**15a-NH$_2$**	1 : 2	15 wt% Aerosil 812S	cured, clear
14	**15a-NH$_2$**	1 : 2	50% SIKRON SF 600+ 0.5% Anti-terra U80	cured, flexible, tack-free

With all three amino-terminated copolymers, curing can be achieved in the presence of different fillers such as barite flour (Barytmehl N), fumed silica (Aerosil® 812S), treated ultrafine calcium carbonate (Omyalite 95T) or untreated silica flour (SIKRON® SF 600). With 10-15 wt% of Aerosil® 812S, clear and transparent elastic films were obtained and even with filler contents of up to 50% (in total), homogeneous incorporation and complete curing was observed. With Omyalite 95T and Barytmehl N, the resulting films were very sticky.

Best results were obtained with 50% SIKRON® SF 600 (untreated silica flour) and 0.5% Anti-terra® U 80 (wetting and dispersing additive) where completely cured and almost tack-free films were obtained (table 5.8, entry 10 and 14). Therefore, this composition, as summarized in table 5.9, was used as standard formulation to investigate and compare the performance of all six different hybrid silicones **14a-NH_2–16a-NH_2** with respect to their curing with **HexMTS-AGE** and the resulting general coating properties.

Table 5.9. Formulation for the preparation of epoxies containing hybrid silicones **14a-NH_2–16a-NH_2**.

Component	Proportion
Binder	13.5 mmol (1 eq.)
HexMTS-AGE	27.0 mmol (2 eq.)
Benzylalcohol	10 wt%
Ancamine® K54	3 wt%
SIKRON® SF 600 (untreated silica flour)	50 % (in total), added in two portions
Anti-terra® U 80	0.5 % (to total weight)
Byk® 354	0.1 % (to total weight)

As potential applications of the cured products are in the field of floor and roof covering or concrete coatings, several application-technological tests were performed to determine hardness, tensile strengths, elongation-to-break, penetration depth and pull off adhesion on concrete. The application-technological tests were performed on the basis of DIN EN 1542 (measurement of bond strength by pull-off) and DIN EN ISO 527-1 (general principles for the determination of tensile properties). All samples were prepared using the standard formulation summarized in table 5.9 and stored at standard laboratory climate (23°C, 50% rel. humidity) for 7d.

Tensile-strength (F_{MAX}) and elongation-to-break (ε-F_{MAX}) were determined using a tensile testing maschine Zwicki 1120 type Z2.5/TN1P with a prestress of 0.2 N and a position-controlled testing speed of 1.0 mm/min. For each hybrid silicone binder **14a-NH_2–16a-NH_2**, three dumb-bell shaped test specimen were prepared according to DIN EN ISO 527-2 (specimen 5A) and the average is reported. These multipurpose test specimen are 75 mm long, with the center section being 4 mm wide, 1.5 - 2.2 mm thick and 20 mm long (gauche lengths). These test specimen were also used to determine the Shore-A-hardness according to DIN EN ISO 868 (determination of indentation hardness by means of a durometer (Shore hardness)) using a Zwick 3130 durometer.

Here, the average of six measurements is reported. The resulting values for tensile strengths (F_{MAX}), elongation-to-break (ε-F_{MAX}) and Shore-A-hardness for **14a-NH$_2$–16a-NH$_2$** are summarized in table 5.10.

Table 5.10. Tensile strengths (F_{MAX}), elongation-to-break (ε-F_{Max}) and Shore-A-hardness for **14a-NH$_2$–16a-NH$_2$**.

Binder	**Composition**	**M^a [g/mol]**	**Properties after 7d**	**Shore-A-hardness**	**F_{Max} [N/mm^2]**	**ε-F_{max} [%]**
14a-NH$_2$	HexMTS+ BDDVE+	3620	not cured, very sticky	45^b	0.45^b	53.0^b
14b-NH$_2$	PDMS+ BDDVE	3840	cured, sticky	35	0.14	28.3
15a-NH$_2$	HexMTS+ TEG-DVE	3740	not cured, very sticky	50^b	0.25^b	20.9^b
15b-NH$_2$	PDMS+ TEG-DVE	3810	cured, sticky	37	0.23	37.2
16a-NH$_2$	HexMTS+ DIPB	3040	not cured, very sticky	49^b	0.43^b	41.2^b
16b-NH$_2$	PDMS+ DIPB	3440	cured, slightly sticky	42	0.19	24.4

a: Determined by ^{1}H-NMR spectroscopy, error: ± 5%.
b: Determined after 14d: 7d at standard climate, 7d at 80°C.

With **14a-NH$_2$**, **15a-NH$_2$** and **16a-NH$_2$**, which contain HexMTS as short siloxane spacer, no complete curing could be achieved after 7d at standard laboratory climate (23°C, 50% rel. humidity). To perform the application-technological tests on completely cured and tack-free coatings, these samples were stored at 80°C for additional 7d. Then, the general coating properties could be determined. Thus, with this formulation, only those binders, which contain a long siloxane spacer units, such as **14b-NH$_2$**, **15b-NH$_2$** and **16b-NH$_2$** can be cured at ambient temperature. Obviously, the longer siloxane chain leads to a more unpolar copolymers which can easier be cured with **HexMTS-AGE**, possibly due to better miscibility.

For all binders the Shore-A-hardness values are in the range of 35–50. Thus, the resulting coatings can be regarded as soft to medium soft elastomers.

Slightly smaller values were determined for **14b-NH$_2$**, **15b-NH$_2$** and **16b-NH$_2$**, possibly because these systems were only cured at room temperauture and thus did not achieve absolute curing.

Also the tensile strength (F_{MAX}) is slightly lower for the systems cured at ambient temperature (**14b-NH$_2$**, **15b-NH$_2$**, **16b-NH$_2$**) than for those cured at 80°C (**14a-NH$_2$**, **15a-NH$_2$** and **16a-NH$_2$**). For all systems, the resulting F_{Max} values are below 0.5 N/mm^2 and thus very small. For a reasonable large-scale application as roof covering or concrete coating, at least 1.5 N/mm^2 should be achieved. But for the very first experiments using a not yet optimized formulation, these results are quite promising.

The elongation-to-break (ε-F_{MAX}) is in the region of 21 (**15a-NH$_2$**) to 53% (**14a-NH$_2$**). Conventional epoxies only show an elongation-to-break of approx. 3%, but to achieve effective crack bridging in concrete, higher values (>100%) are desirable.

If curing was performed at elevated temperatures (80°C), the best results were obtained with **14a-NH$_2$** and **16a-NH$_2$** bearing a short siloxane spacer and 1,4-butanediol divinyl ether or 1,3-diisopropenylbenzene as organic building block. When the more polar triethylene glycol divinyl ether was used as organic spacer (**15a-NH$_2$**), lower values were obtained, possibly because of a poorer miscibility of the components.

The pull off adhesion on concrete was determined according to DIN EN 1542. Six grit-blasted concrete slabs (20 x 25 cm test surface) were coated with the six different binders **14a-NH$_2$–16b-NH$_2$** using the standard formulation described above. The amount per plate is given in table 5.11. All plates were conditioned at standard climate for 28d and at 80°C for additional 7d to achieve complete curing. Five circular steel dollies (Ø = 50 mm) per plate were used and adhered to the surface using a cold curing two-part methacrylate adhesive (Araldite® 2047-1). The adhesive was allowed to dry for 2h, whereafter 5 mm deep drill holes were drilled around each dolly. The pull-off adhesion was determined using a BPS Wenningsen's F15D Easy M200 pull-off equipment with a testing force of 100 N/s. The results of the pull off adhesion test (f_h: adhesive tensile strength) and the observed types of failure are summarized in table 5.11.

Table 5.11. Results of the pull-off adhesion test and corresponding types of failure.

Binder	**Amount per plate [g]**	***f_h* [N/mm^2], type of failure [%]**	***f_h* [N/mm^2], type of failure [%]**	***f_h* [N/mm^2], type of failure [%]**	***f_h* [N/mm^2], type of failure [%]**	***f_h* [N/mm^2], type of failure [%]**
14a-NH$_2$	115	0.880	0.758	0.872	0.869	0.804
		A/B : B : B/C	A/B : B : B/C	A/B : B : B/C	A/B : B : B/C	A/B : B : B/C
		25 : 5 : 70	25 : 5 : 70	30 : 20 : 50	30 : 10 : 60	20 : 5 : 75
14b-NH$_2$	120	0.696	0.393	0.668	0.460	0.589
		B/C	B/C	A/B : B/C	B/C	B : B/C
		100	100	2 : 98	100	5 : 95
15a-NH$_2$	120	0.904	0.457	0.923	0.589	0.830
		B : B/C	B : B/C	B : B/C	B : B/C	A/B : B : B/C
		5 : 95	10 : 90	25 : 75	30 : 70	20 : 20 : 60
15b-NH$_2$	100 (liquid)	0.512	0.517	0.442	0.544	0.484
		A/B : B/C	B/C	B/C	B/C	B/C
		5 : 95	100	100	100	100
16a-NH$_2$	110	0.598	0.662	0.644	0.595	0.730
		A/B : B/C	B/C	B/C	B/C	B/C
		5 : 95	100	100	100	100
16b-NH$_2$	100	0.595	0.623	0.450	0.349	0.707
		B/C	B/C	B/C	B/C	B/C
		100	100	100	100	100

f_h: adhesive tensile strength
A/B: adhesion fracture adhesive/coating;
B: cohesion fracture coating;
B/C: adhesion fracture coating/substrate (concrete);
C: cohesion fracture substrate (concrete).

For all hybrid silicones **14a-NH$_2$–16b-NH$_2$**, complete wetting of the concrete substrate was observed leading to the formation of homogeneous elastomeric surface coatings. Neither bubbles, cracks or significant shrinkage was observed. Again, the systems containing HexMTS as siloxane spacer did not cure at ambient temperature, while the systems with the longer siloxane spacer (**14b-NH$_2$**, **15b-NH$_2$**, **16b-NH$_2$**) formed almost tack-free coatings within one week at ambient temperature. An image of the coated surfaces obtained with **15b-NH$_2$** (left) and **16b-NH$_2$** (right) after 7d at standard climate is shown in figure 5.18.

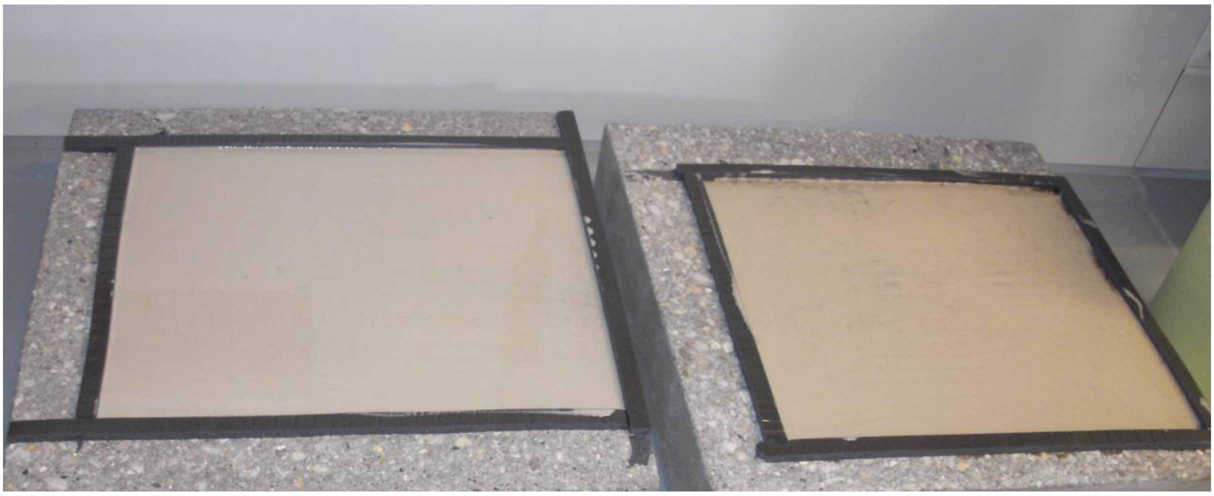


Figure 5.18. Coated surfaces using **15b-NH$_2$** (left) and **16b-NH$_2$** (right).

For all binder systems, the pull-off adhesion strength was in the range of 0.5–0.9 N/mm^2. The most common type of fraction was a failure of adhesion between coating and concrete (B/C). In some cases also a break of adhesion between coating and adhesive (A/B) and a cohesion fracture (B) in the coating was observed. No cohesion failure in the substrate (concrete) was observed (C).

The highest pull-off adhesion values and thus, the best test results were obtained with **14a-NH$_2$**, followed by **15a-NH$_2$** and **16a-NH$_2$**. These findings agree with those of the tensile strength and elongation-to-break determination experiments. Obviously, the general coating properties improve when only a short siloxane chain is present in the hybrid silicone backbone. Unfortunately, these systems do not cure at ambient temperature.

In conclusion, all amino-terminated hybrid silicone resins **14a-NH$_2$–16b-NH$_2$** could be cured with **HexMTS-AGE** to form homogeneous, soft and elastic coatings on concrete. Those systems containing a short siloxane chain (**14a-NH$_2$**, **15a-NH$_2$**, **16a-NH$_2$**) required elevated temperatures to achieve complete and tack-free curing. If this was provided, the best results were obtained with **14a-NH$_2$**, which contains a short siloxane chain and 1,4-butandiol divinyl ether as organic spacer. For all systems, the obtained values for tensile strength, pull-off adhesion as well as elongation-to-break are quite low but for the very first experiments using a not yet optimized formulation, the results are very promising.

One of the major general advantages of hybrid silicones is their distinct spreading capability and good penetration depth into concrete. Therefore, these properties were also investigated for the cured systems of **14a-NH_2–16b-NH_2**. For this purpose, small plates (5x 5 cm) of grit-blasted concrete were coated using the standard formulation as described above and, after complete curing (7d standard climate, 7d 80°C) cut into pieces with an angle grinder. Figures 5.19 shows a cross section of the coated plate of **15b-NH_2**.

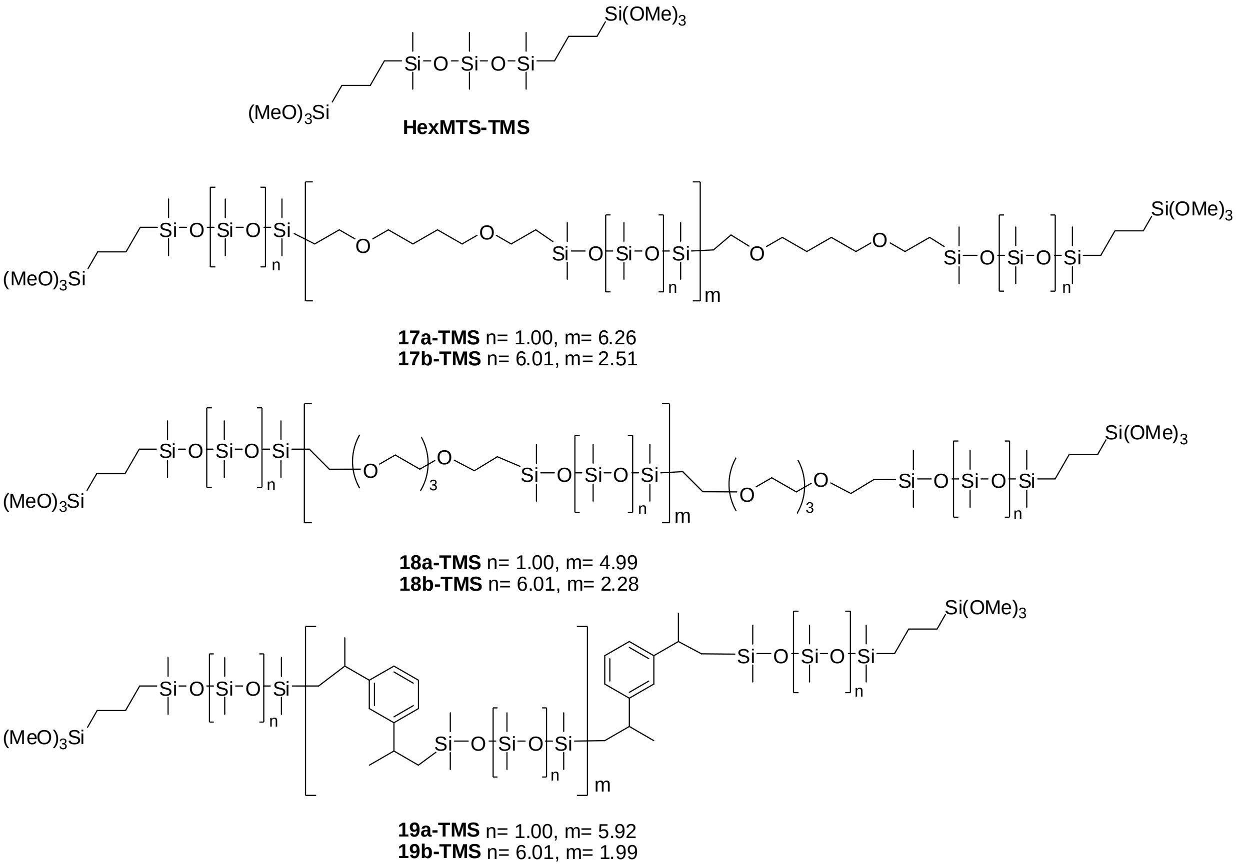
Figures 5.19. Cross section of a coated plate using **15b-NH_2**.

As can be seen, good wetting, as a result of the high spreading capability of the hybrid silicone telomere was achieved but no penetration of the binder into the concrete substate could be observed.

5.3 Preparation and Curing of Trimethoxysilyl-functional Hybrid Silicones

Trialkoxysilyl-functionalized hybrid silicones can be conveniently prepared by hydrosilylation of α,ω-dihydropolysilalkylene siloxanes with allyl or vinyl trialkoxysilanes. The use of the allyl compound is slightly preferred because its hydrosilylation proceeds smoothly without byproduct formation and exclusively yields the terminal (*anti-Markovnikov*) hydrosilylation product. Because of steric effects, methoxy groups hydrolyse faster and were therefore chosen in preference to triethoxy silyl groups.

Six different trimethoxysilyl-telechelic hybrid silicones with different silicone content and different organic spacers were synthesized *via* a *Karstedt*-catalyzed polyhydrosilylation reaction and subsequently functionalized with allyl trimethoxysilane. Again, the silicone character was varied by using 1,1,3,3,5,5-hexamethyltrisiloxane (HexMTS) and α,ω-dihydropoly(dimethylsiloxane) (PDMS-H_2, M_n= 580 g/mol) as siloxane spacers. 1,4-butanediol divinyl ether, triethylene glycol divinyl ether and 1,3-diisopropenylbenzene were used as organic building blocks. Additionally, a very short trimethoxysilyl-telechelic siloxane, **HexMTS-TMS**, was prepared from allyl trimethoxysilane and HexMTS. The obtained trimethoxysilyl-functionalized hybrid silicones are shown in figure 5.20, their composition and molecular weight is given in table 5.12.



HexMTS-TMS

17a-TMS n= 1.00, m= 6.26
17b-TMS n= 6.01, m= 2.51

18a-TMS n= 1.00, m= 4.99
18b-TMS n= 6.01, m= 2.28

19a-TMS n= 1.00, m= 5.92
19b-TMS n= 6.01, m= 1.99

Figure 5.20. Trimethoxysilyl-telechelic hybrid silicones **17a-TMS–19b-TMS**.

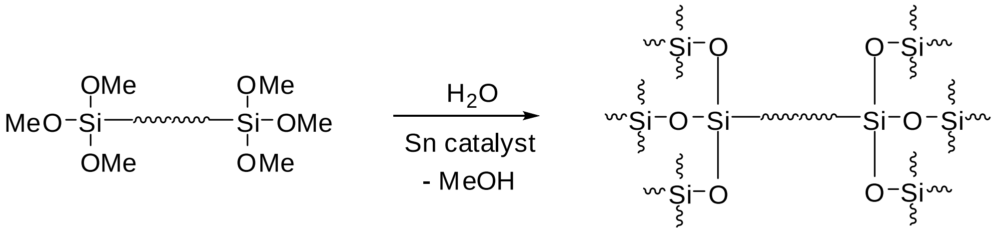
Table 5.12. Composition and molecular weight of trimethoxysilyl-telechelic hybrid silicones **17a-TMS–19b-TMS**.

Compound	Siloxane	Diene	m[a]	M[a] (g/mol)
HexMTS-TMS	HexMTS	-	-	533
17a-TMS	HexMTS	1,4-butandiol divinyl ether	6.26	3080
17b-TMS	PDMS	1,4-butandiol divinyl ether	2.51	3440
18a-TMS	HexMTS	triethylene glycol divinyl ether	4.99	2990
18b-TMS	PDMS	triethylene glycol divinyl ether	2.28	3470
19a-TMS	HexMTS	1,3-diisopropenyl benzene	5.92	3070
19b-TMS	PDMS	1,3-diisopropenyl benzene	1.99	3110

a: Determined by ^{1}H-NMR spectroscopy, error: ± 5%.

The trimethoxysilyl-functional hybrid silicones can be used as basis for one- or two-part room temperature vulcanizing (RTV-1 or RTV-2) silicone rubbers.[96],[97] The crosslinking, i.e. curing or vulcanization, of RTV-1 silicone rubber grades takes place upon exposure to atmospheric moisture. It starts with the formation of a skin on the surface of the silicone rubber and gradually works its way into the compound.

During the curing process, methanol is released. An organotin compound, such as dibutyl tin diketonate can be employed as a catalyst (scheme 5.4).



Scheme 5.4. Condensation curing of RTV-silicone rubber.

By virtue of their diverse and excellent properties, such as outstanding thermal, chemical and weathering resistance, excellent bonding to a variety of substrates and excellent environmental compatibility, RTV silicone rubber compounds have a wide variety of bonding, sealing, and coating applications.[97]

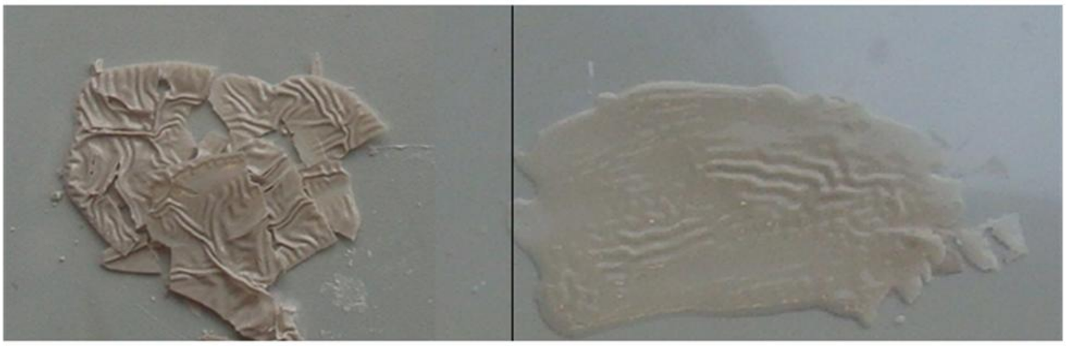
First tests of room temperature vulcanizing hybrid silicones were performed with **HexMTS-TMS** and **17a-TMS** in the presence of 0.1% BNT-CAT® 440 (dibutyl tin diketonate) and moisture. With **HexMTS-TMS** the skin-over time was <10 min and a brittle, clear and transparent film with a corrugated surface was obtained.

The corrugation of the surface is possibly a result of shrinkage due to the high density of trimethoxysilyl groups in the monomer and thus the release of large amounts of methanol. With **17a-TMS** a plain and even, transparent and flexible foil was obtained as shown in figure 5.21.

Figure 5.21. Foil (400 µm) obtained from **17a-TMS** with 0.1% BNT-CAT 440.

To both systems different filling materials such as fumed silica, barite or quartz flour can be added. The addition of iorganic fillers improves the mechanical strength of the silicone rubber and reduces shrinkage and costs of the adhesive or sealant. The cured films of **HexMTS-TMS** and **17a-TMS** with different amounts of quarz or barite powder using 0.1% BNT-CAT® 440 are shown in figure 5.22.

a) 17a-TMS + barite powder (1:2) **b) 17a-TMS** + barite powder (1:3)



c) HexMTS-TMS + barite powder (1:3) **d) 17a-TMS** + quarz powder (1:1)

Figure 5.22. Filled films of **HexMTS-TMS** and **17a-TMS**.

17a-TMS could be cured in the presence up to 3 weight equivalents barite powder (figure 5.22a and 5.22b), to give beige-colored, soft, elastic but to some extent fragile films. With one weight equivalent quarz powder the surface of the cured film was slightly corrugated (figure 5.22d). When **HexMTS-TMS** was used instead of **17a-TMS**, a very hard, brittle and wrinkled film was obtained, due to the higher density of -Si(OMe)$_3$ present in the system (figure 5.22c). In all cases skin-over times of 1–7 min were achieved.

In order to compare their curing behavior and the resulting film properties, the trimethoxysilyl-telechelic copolymers **17a-TMS**, **17b-TMS, 18a-TMS** and **19b-TMS** were tested as monomers in the moisture-curing of silicone rubbers.

To achieve skin-over times which allow reasonable processing, two different organotin compounds, TIB 208 (dioctyltin di-(2-ethylhexanoate)) and TIB 223 (dioctyltin diketonoate) were tested as catalysts for condensation-curing. The experiments were first of all performed in pure, non-filled systems and later on expanded to filled systems using different filling materials. The results for the non-filled systems are given in table 5.13.

Table 5.13. Moisture curing of trimethoxysilyl-functional hybrid silicones **17a-TMS**, **17b-TMS, 18a-TMS** and **19b-TMS**.

Entry	Polymer	Catalyst (0.1%)	Skin-over Time	Film Properties
1	**17a-TMS**	TIB 208	> 240 min	film spreads, brittle, bubbles
2	**17a-TMS**	TIB 223	165 min	no spreading, brittle, bubbles
3	**17b-TMS**	TIB 208	> 240 min	film spreads, brittle, bubbles
4	**17b-TMS**	TIB 223	110 min	film slightly spreads, brittle, bubbles
5	**18a-TMS**	TIB 208	> 240 min	no spreading, brittle, bubbles
6	**18a-TMS**	TIB 223	150 min	no spreading, brittle, bubbles
7	**19b-TMS**	TIB 208	> 240 min	film spreads, brittle, bubbles
8	**19b-TMS**	TIB 223	90 min	no spreading, brittle, bubbles

With all hybrid silicones, cured, tack-free, flexible, fragile films (foils) were obtained. Small amounts of air inclusions (bubbles) were visible in all cured products. In general, with TIB 208 and TIB 223, much longer skin-over times were achieved than with BNT-CAT® 440, with TIB 208 beeing less active than TIB 223. Some formulations were very free-flowing so that smeared films were obtained (entry 1, 3, 4, 7).

Afterwards, the experiments were expanded to filled systems using different filling materials, such as barite flour (Barytmehl N), quartz flour (SIKRON® SF 600) or calcium carbonate (Omyalite 95T). Also the influence of different adhesion promoting and crosslinking or surface modifying additives such as *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (DAMO-T), 3-(*N*-methylamino)propyltrimethoxysilane (DN 1146), 3-aminopropyltrimethoxysilane (DN AMMO) or Palatinol® N (low-viscosity plasticizer on phthalic ester basis) was examined. Furthermore, several different catalysts also including dibutyl tin dilaurate (DBTL) were used and compared with respect to the resulting skin-over times. The results are summarized in table 5.14.

Table 5.14. Filled films of trimethoxysilyl-telechelic hybrid silicones **17a-TMS**, **17b-TMS**, **18a-TMS**, and **19b-TMS**.

Entry	**Polymer**	**Catalyst (0.1%)**	**Filler**	**Additives**	**Skin-over Time**	**Properties after 1d**
1	**17a-TMS**	TIB 223	75% quartz flour		30 min	hard, little flexible
2	**17a-TMS**	TIB 208	75% quartz flour		190 min	hard, little flexible
3	**17a-TMS**	TIB 208	75% Omyalite 95 T		>180 min	brittle
4	**17a-TMS**	TIB 223	75% Omyalite 95 T		8 min	brittle
5	**17a-TMS**	TIB 223	75% Barytmehl N		11 min	flexible
6	**17a-TMS**	TIB 223	75% Barytmehl N	1% DAMO-T	8 min	hard, flexible
7	**17a-TMS**	TIB 223	75% Barytmehl N	1% DN 1146	6 min	hard, little flexible
8	**17a-TMS**	TIB 223	75% Barytmehl N	1% DN AMMO	4 min	hart, little flexible
9	**17a-TMS**	TIB 223	65% Barytmehl N	1% DAMO-T; 10% Palatinol N	3 min	brittle, little flexible
10	**17a-TMS**	TIB 208	65% Barytmehl N	1% DAMO-T; 10% Palatinol N	20 min	brittle
11	**17b-TMS**	TIB 223	75% Barytmehl N		3 min	flexible
12	**17b-TMS**	TIB 208	75% Barytmehl N		200 min	flexible
13	**17b-TMS**	BNT 440	75% Barytmehl N		1 min	flexible
14	**17b-TMS**	DBTL	75% Barytmehl N		44 min	flexible
15	**17b-TMS**	TIB 223	65% Barytmehl N	1% DAMO-T; 10% Palatinol N	5 min	brittle
16	**17b-TMS**	TIB 223	75% quartz flour		41 min	hard, little flexible
17	**17b-TMS**	TIB 208	75% quartz flour		>300 min	hard, little flexible
18	**17b-TMS**	TIB 208	75% Omyalite 95 T		>180 min	brittle
19	**17b-TMS**	TIB 223	75% Omyalite 95 T		10 min	brittle
20	**18a-TMS**	TIB 223	60% Barytmehl N		28 min	flexible
21	**18a-TMS**	TIB 223	60% Barytmehl N	0.5% DAMO-T; 0.5% Anti-terra U 80	18 min	flexible
22	**18a-TMS**	TIB 223	65% Barytmehl N	1% DAMO-T; 10% Palatinol N	4 min	flexible
23	**18a-TMS**	TIB 223	75% quartz flour		10 min	hard, little flexible
24	**18a-TMS**	TIB 223	75% Omyalite 95 T	1% DN 1146	2 min	very hard, brittle
25	**18a-TMS**	TIB 223	75% Omyalite 95 T	1% DAMO-T	2 min	very hard, brittle
26	**19b-TMS**	TIB 223	75% Barytmehl N		6 min	flexible
27	**19b-TMS**	TIB 223	75% quartz flour		42 min	hard, little flexible

All hybrid silicone systems can be filled with up to 75% (in total) of a filling material such as barite (Barytmehl N), quartz or calcium carbonate (Omyalite 95 T) to give cured homogeneous silicone rubbers. Depending on the type and amount of filler, free-flowing to pasty formulations were obtained that cured to flexible to brittle films. In general, Omyalite 95 T and SIKRON® SF 600 led to hard and brittle films, while those films containing Barytmehl N were more flexible. The skinning time could be set by variation of the catalyst. With TIB 223 and BNT-CAT® 440 short pot lives of less than 30 min were achieved (table 5.14, entry 11 and 13) while TIB 208 (entry 12) and DBTL (entry 14) needed up to 200 min to achieve skin formation. In general, films containing quartz flour exhibited longer skinning times than those filled with Omyalite 95 T. The fastest curing was achieved in the presence of Barytmehl N. The addition of DAMO-T improved the flexibility of the resulting films while the addition of DN 1146, DN-AMMO or Palatinol N had no positive effect on the film properties. Fluidity could be improved by addition of Anti-terra® U 80 as wetting and dispersing additive.

In summary, best film properties were obtained with 60% Barytmehl N, 0.5% Anti-terra® U 80 and 0.5% DAMO-T (entry 21). 0.05% TIB 223 were used as a catalyst to obtain manageable pot lives. This standard formulation, as summarized in table 5.15, was used to determine and compare the performance of all six different hybrid silicones **14a-NH$_2$–16a-NH$_2$** with respect to their curing and the resulting general coating properties.

Table 5.15. Formulation for the preparation of silicone rubber coatings containing hybrid silicones **14a-NH$_2$–16a-NH$_2$**.

Component	Proportion
Binder	39%
Barytmehl N	60%, added in two portions
DAMO-T	0.5%
Anti-terra® U 80	0.5%
TIB 223	0.05%

The cured hybrid silicone rubbers were designed as floor or roof coverings or concrete coatings and should thus exhibit a certain rigidity, tensile strength and elongation-to-break. To obtain good coating properties on concrete, they should display good wetting and a certain penetration depth into the mineral material and a good pull-off adhesion on concrete.

To examine these properties application-technological tests were performed according to DIN EN 1542 (measurement of bond strength by pull-off), DIN EN ISO 527-1 and -2 (general principles for the determination of tensile properties, test specimen 5A) and DIN EN ISO 868 (determination of indentation hardness by means of a durometer (Shore hardness)). All samples were prepared using the standard formulation listed above (table 5.15) and conditioned at standard climate (23°C, 50% rel. humidity) for 7d.
The resulting values for tensile strengths (F_{MAX}), elongation-to-break (ε-F_{MAX}) and Shore-A-hardness for **17a-TMS–19b-TMS** are summarized in table 5.16.

Table 5.16. Tensile strength, elongation-to-break and Shore-A-hardness for **17a-TMS–19b-TMS**.

Binder	**Composition**	**M[a] [g/mol]**	**Properties after 7d**	**Shore-A-hardness**	**F_{Max} [N/mm^2]**	**ε-F_{max} [%]**
17a-TMS	HexMTS+ BDDVE+	3080	cured, beige	70	1.13	16.6
17b-TMS	PDMS+ BDDVE	3440	cured, beige	67	1.22	16.5
18a-TMS	HexMTS+ TEG-DVE	2990	cured, beige	81	1.66	23.4
18b-TMS	PDMS+ TEG-DVE	3470	cured, dents	72	1.54	21.1
19a-TMS	HexMTS+ DIPB	3070	cured, bubbles	80	0.75	13.5
19b-TMS	PDMS+ DIPB	3110	cured, dents	80	0.88	11.5

a: Determined by ^{1}H-NMR spectroscopy, error: ± 5%.

With all binders firm, flexible, homogeneously cured, tack-free, beige-colored rubber-like products were obtained within 1d at ambient temperature. Nevertheless, according to DIN EN ISO 527-1, the tests were performed after 7d at standard climate. In some cases, a very fast, spontaneous curing of small amounts of the binder was observed during preparation of the formulation. This can be explained by locally high concentrations of water which locally accelerated the curing process and thus lead to an agglomeration within the formulation. The agglomerates, if not removed by filtration, led to dents in the test specimen.

For all binders the hardness Shore A was in the range of 67–81. Thus, the resulting coatings can be regarded as medium soft to hard elastomers. The least hardness was observed for **17b-TMS**, which contains HexMTS and 1,4-butandiol divinyl ether. Excellent tensile strengths (F_{Max}) of 1.66 N/mm^2 and 1.54 N/mm^2 were obtained with **18a-TMS** and **18b-TMS**, respectively, which both contain triethylene glycol divinyl ether as the organic building block. Slightly better results were obtained with **18a-TMS** which contains a short siloxane chain. **18a-TMS** and **18b-TMS** also exhibited the best elongation-to-break with 21 and 23%. It seems, that the combination of non-polar siloxane and polar triethylene glycol divinylether within one molecule leads to outstanding product properties.

With butandiol divinyl ether only moderate tensile-strenghts (1.1–1.2 N/mm^2) and 16% elongation-to-break were obtained (**17a-TMS**, **17b-TMS**). No large influence of the lengths of the siloxane chain could be observed in these cases. Very low tensile-strength and elongation-to-break were achieved with **19a-TMS** and **19b-TMS**. Obviously, the presence of a non-polar organic building block reduces the tensile properties.

For all systems the elongation–to-break is very low in comparison to the desired value of > 100% which is necessary to achieve effective crack bridging in concrete. But, for the very first experiments using a non-optimized formulation, these results are very promising and can possibly be greatly improved if an optimized formulation is used.

The pull-off adhesion on concrete was determined according to DIN EN 1542 as described previously (section 5.2). All concrete plates were stored at standard laboratory climate (23°C, 50% rel. humidity) for 7d. The amount per plate is given in table 5.17. Several different adhesives were tested to adhere the cicular dollies to the surface until sufficient results were obtained with Araldite® 2047-1. Unfortunately, during testing of the different adhesives, the concrete test specimen containing a **19a-TMS** coating was damaged and could not be used for test purposes any more.

The results of the pull-off adhesion tests (f_h: adhesive tensile strength) with **17a-TMS–18b-TMS** and **19b-TMS** and the observed types of failure are summarized in table 5.17.

Table 5.17. Results of the pull-off adhesion test and corresponding type of failure.

Copolymer	**Amount per plate [g]**	f_h **[N/mm²], type of failure [%]**	f_h **[N/mm²], type of failure [%]**	f_h **[N/mm²], type of failure [%]**	f_h **[N/mm²], type of failure [%]**	f_h **[N/mm²], type of failure [%]**
17a-TMS	120	0.837	0.634	1.773	0.342	0.886
		A/B : B	A/B : B : B/C	A/B : B/C	A/B : B	A/B : B : B/C
		70 : 30	20 : 40 : 40	10 : 90	80 : 20	10 : 20 : 70
17b-TMS	100	0.882	0.430	1.119	0.982	0.597
		A/B : B/C	A/B : B/C	A/B : B/C	A/B : B/C	A/B : B/C
		60 : 40	70 : 30	70 : 30	50 : 50	80 : 20
18a-TMS	100	1.914	1.693	1.747	1.743	1.510
		A/B : B/C	A/B : B : B/C	A/B : B : B/C	A/B : B : B/C	A/B : B : B/C
		10 : 90	10 : 20 : 70	20 : 40 : 40	10 : 40 : 50	10 : 80 : 10
18b-TMS	100	1.229	1.488	1.584	1.325	1.055
		A/B : B/C	A/B : B/C	A/B : B/C	A/B : B : B/C	A/B : B : B/C
		60 : 40	10 : 90	10 : 90	10 : 20 : 70	10 : 10 : 80
19b-TMS	100	0.058	0.289	0.728	0.247	0.153
		A/B	A/B : B	A/B : B : B/C	A/B : B	A/B : B
		100	90 : 10	60 : 10 : 30	90 : 10	90 : 10

f_h: adhesive tensile strength;
A/B: adhesion fracture adhesive/coating;
B: cohesion fracture coating;
B/C: adhesion fracture coating/substrate (concrete);
C: cohesion fracture substrate (concrete).

For all tested hybrid silicones **17a-TMS–18b-TMS** and **19b-TMS**, complete wetting of the concrete substrate was observed leading to the formation of a homogeneous elastomeric surface coating. In some cases, dents were visible in the coating due to agglomeration during mixing (table 5.16). Besides that, neither bubbles, cracks nor significant shrinkage were observed. Images of the coated surface obtained from **17a-TMS** before (left) and after (right) the pull-off adhesion test are shown in figure 5.23.

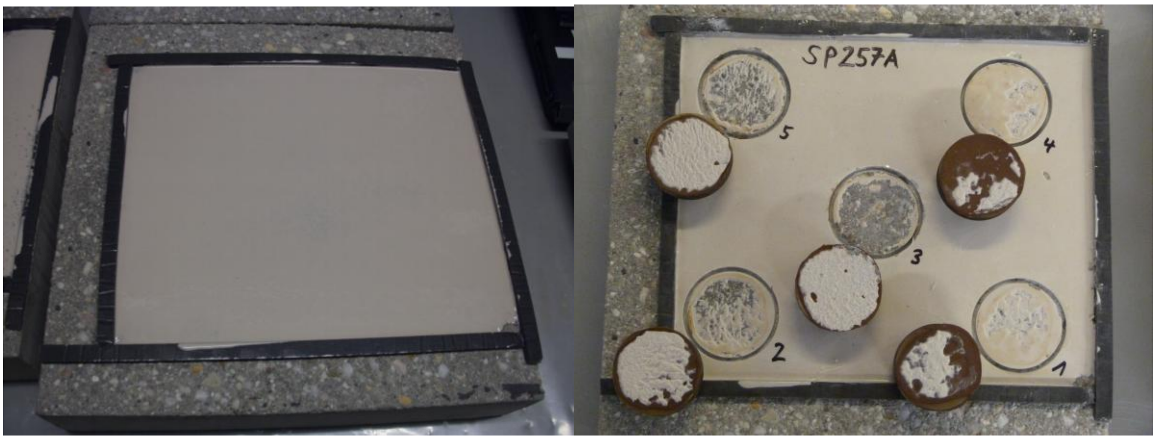
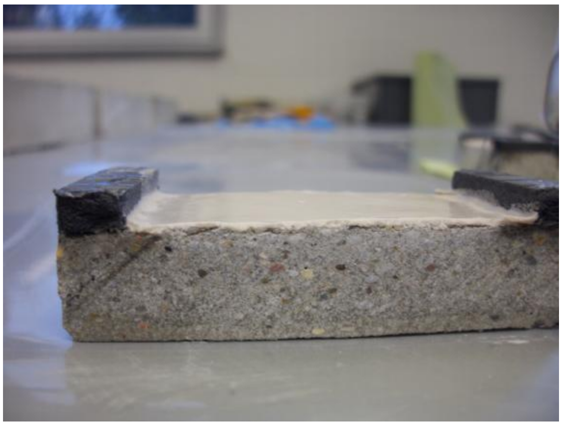


Figure 5.23. Coated surface obtained with **17a-TMS** before (left) and after (right) the pull-off adhesion test.

The best pull-off adhesion of 1.72 N/mm^2 was obtained with **18a-TMS**, followed by **18b-TMS** with 1.34 N/mm^2, which both contain triethylene glycol divinyl ether. These systems also exhibited the best tensile strength and elongation-to-break. Slighly lower values were achieved with **17a-TMS** and **17b-TMS** which contain 1,4-butandiol divinyl ether. As for tensile strength and elongation-to-break, the lowest pull-off adhesion was obtained with **19b-TMS**. The most common types of failure were a break of adhesion between coating and adhesive (A/B) or coating and concrete (B/C). A cohesion fracture of the coating (B) could also be observed.

The penetration depth of the six trimethoxysilyl-functional hybrid silicones into concrete was investigated, using small plates (5x 5 cm) of grit-blasted concrete, which were coated with the hybrid silicones **17a-TMS**–**19a-TMS** using the standard formulation and after complete curing (7d standard laboratory climate) cut into pieces with an angle grinder. Figure 5.24 shows a cross section of the plate coated with **18a-TMS**.



Figures 5.24. Cross section of a plate coated with **18a-TMS**.

Good wetting, as a result of the high spreading capability of the hybrid silicones was achieved but no penetration of the binder into the mineral substrate could be observed.

In conclusion, all trimethoxysilyl-terminated hybrid silicones **17a-TMS–19b-TMS** can be moisture-cured at room temperature in the presence of an organotin catalyt to give homogeneous, firm and flexible films or coatings. The best tensile strength, elongation-to-break and pull-off adhesion was achieved with **18a-TMS**, which contains polar triethylene glycol divinyl ether linkers and short, non-polar siloxane spacers. Obviously, the combination of non-polar siloxane and polar ether units within one molecule leads to outstanding product properties. All general coating properties are in the range of commercially available products.

6. Summary and Conclusion

The Pt-catalyzed hydrosilylation of olefins is one of the most important laboratory and industrial instruments for the preparation of functionalized organosilicon compounds or silicone polymers. Silicones bearing organic, chemically active side groups are of major industrial importance and silane-functionalized olefins, dienes or polymers have gained substantial industrial interest as elastomers, sealants, adhesives or release coatings. The organo-functionalization of silicones and the development of new functional polymers combining the chemical properties of silicones and organic compounds are important strategies for the development of new materials. Polysilalkylene or -arylene siloxanes, so called hybrid silicones, have been developed to avoid the drawback of the depolymerization of classical polysiloxanes and to obtain elastomers with enhanced thermal stability and unique surface properties. They consist of alternating siloxane and organic linker units and exhibit outstanding interfacial properties such as low surface tension, high spreading capability and good penetration into mineral substrates. The synthesis of representatives with strictly linear molecular design can be achieved *via* a Pt-catalyzed polyhydrosilylation reaction of terminal dienes with α,ω-dihydrosiloxanes.

During the course of this work, a synthetic strategy for the preparation of different novel functionalized hybrid silicones as well as a guideline for their potential fields of application should be developed.

First of all, the catalytic activity of six different platinum-based hydrosilylation catalysts was examined and compared. The different catalysts were Pt(0), Pt(II) and Pt(IV) species stabilized by divinyltetramethyldisiloxane, chloro, triphenylphoshine, amino or *N*-heterocyclic carbene ligands. In two model reactions, all different catalysts proved to be active and selective towards *anti-Markovnikov* addition. In general, best results were obtained with *Karstedt's* catalyst [Pt_2(*sym*-tetramethyldivinyldisiloxane)$_3$] (section 2.2).

Compared to homogeneous catalysts, heterogeneous catalysts are rarely used in hydrosilylation reactions, although the separation of the catalyst from the reaction mixture and its recycling would be highly desirable. Accordingly, the catalytic activity and recyclability of solid PtO_2 was examined. NMR and *in situ* IR studies revealed that PtO_2 can be regarded as a “self-dosing” hydrosilylation catalyst precursor. During the hydrosilylation reaction only a small portion of the solid catalyst dissolves and catalyzes the hydrosilylation reaction.

After complete conversion the major part of PtO_2 can be removed from the reaction mixture by simple decantation or filtration and can be utilized for many runs. In the reaction of 1,1,1,3,5,5,5-heptamethyltrisiloxane with *n*-octene turn-over-frequencies of at least 95000/h were obtained (section 2.3).

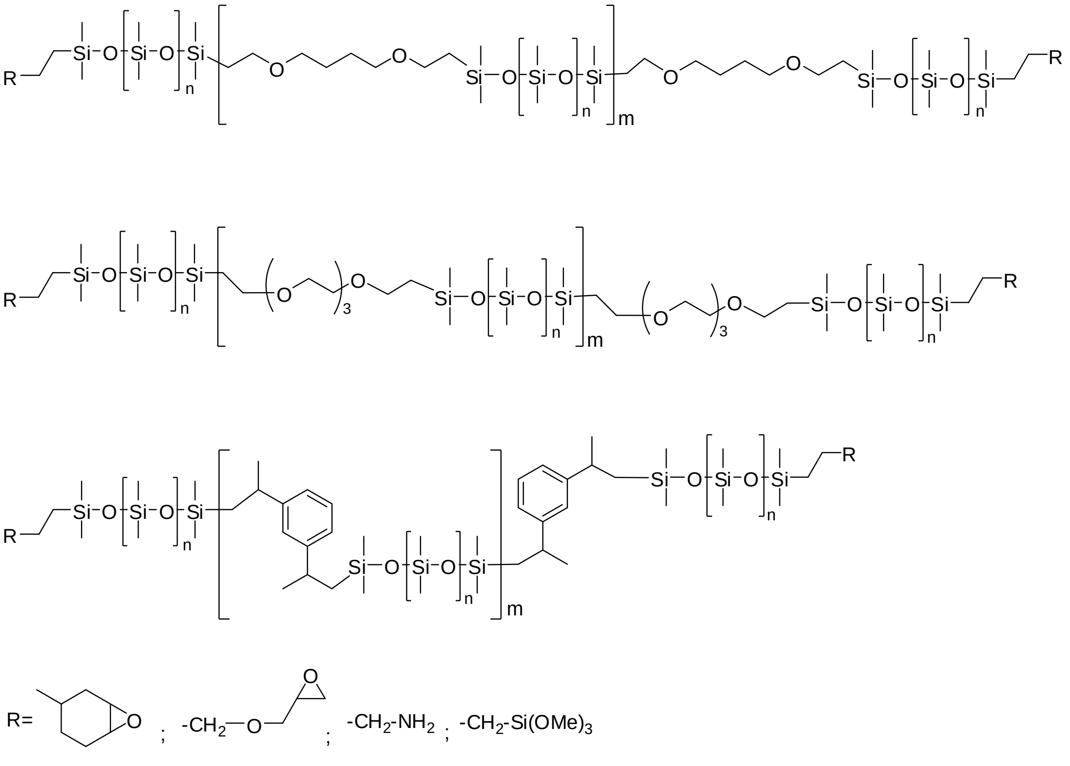
Furthermore, the hydrosilylation of isopropenyl compounds was examined in detail (section 2.4). During the course of this work, a correlation between the byproduct formation in the hydrosilylation of allylic compounds (CH_2=CH-CH_2-X) and the reactivity of the corresponding isopropenyl compounds (CH_2=CH(X)-CH_3) could be established. Thus, the hydrosilylation of allyl acetate and chloride is usually accompanied by the formation of an Si-X product and propene while this C-X bond cleavage reaction occurs exclusively in the hydrosilylation of isopropenyl acetate and chloride. By variation of the substituent of the isopropenyl compound and the catalyst concentration, as well as the use of deuterated silanes and 2-butenyl compounds, two mechanistic approaches for this special reaction pathway could be suggested. Both mechanistic proposals include a C-O bond cleavage reaction (either by a concerted allylic substitution-like mechanism or *via* oxidative addition and β-elimination), the isomerization of the C=C double bond and finally the hydrosilylation of the free propene (section 2.4).

Besides from these fundamental catalytic investigations a synthetic strategy for the preparation of different novel functionalized hybrid silicones could be developed. Several novel differently functionalized hybrid silicones were prepared and characterized with respect to their performance in coating applications.

For this purpose, at first, several different α,ω-dienes were tested in model hydrosilylation reactions to deepen the understanding of their reaction behavior and to determine their suitability as building blocks in the straight-forward synthesis of hybrid silicone backbones. In order to obtain clearly defined copolymer structures and to avoid cost-intensive purification procedures, special attention was paid to high chemo- and stereoselectivity of the hydrosilylation reaction and to minimum byproduct formation. Especially isomerization reactions of terminal double bonds into inactive internal ones and α-addition reactions, which lead to undefined polymer structures needed to be avoided. In conclusion, best results were obtained with 1,4-butandiol divinyl ether, triethylene glycol divinly ether and 1,3-diisopropenylbenzene. All three dienes are commercially available, inexpensive and can be hydrosilylated without byproduct formation to give clearly defined copolymers with high chemical stability (section 3.2 and 4).

All three different organic building blocks could be combined with different siloxane spacers such as α,ω-dihydrotri- or -oligosiloxanes and thus, several different hybrid silicone backbones with different polarity and silicone character could be prepared. Additionally, by variation of the stoichiometry of the two starting materials, the chain lengths and, thus, the molecular weight of the resulting copolymers could be varied.

Several olefins with various functional groups were tested for the functionalization of the resulting Si-H-terminated prepolymers (section 3.3). Like the dienes, the functionalization agents should be inexpensive, non-toxic and easily available and their hydrosilylation needed to proceed smoothly without byproduct formation. From over 40 potential candidates, the most promising results were obtained with vinylcyclohexene oxide, allyl glycidyl ether, allyl amine and allyl trimethoxysilane. Thus, a number of novel α,ω-functionalized hybrid silicone polymers could be prepared and studied as components in the preparation of curable systems (scheme 6.1).



Scheme 6.1. α,ω-Functionalized hybrid silicones.

The epoxy-functional hybrid silicones could be crosslinked photochemically to give stable, soft, elastomeric and transparent films. Best results were obtained with vinylcylohexylepoxy-functional systems in the presence of a highly lipophilic photoinitiator.

The course of photopolymarization was monitored by optical pyrometry, i.e. by following the change in temperature during the photopolymerization reaction in real time with an infrared camera (section 5.1). The glycidyl-functional hybrid silicones could also be cured thermally in the presence of different amine hardeners. These findings suggest their direct application as elastic, highly flexible epoxy-amine coatings or as modifiers for conventional epoxy resins.

The amino-terminated hybrid silicones instead could be efficiently used as binders in epoxy applications. With conventional epoxy resins, the very poor miscibility led to a phase separation prior to curing but with an epoxy-functional trisiloxane all amino-terminated hybrid silicones could be cured to form homogeneous, soft and elastic surface coatings. Those systems containing a short siloxane chain required elevated temperatures to achieve complete and tack-free curing. If this was provided, the best results were obtained with the hybrid silicone, which contains a short siloxane chain and 1,4-butandiol divinyl ether as organic spacer. For all cured systems some general coating properties such as tensile strength, elongation-to-break and pull-off adhesion on concrete could be determined and were quite promising.

The alkoxysilyl-functional hybrid silicone polymers could be moisture-cured in the presence of an organotin catalyst to give homogeneous, firm and flexible films or release coatings. The best general coating properties such as tensile strength, elongation-to-break and pull-off adhesion on concrete were displayed by the most polar hybrid silicone, built up from triethylene glycol divinyl ether and 1,1,3,3,5,5-hexamethyltrisiloxane. Obviously, the combination of non-polar siloxane and polar ether units within one molecule leads to outstanding product properties.

7. Experimental

7.1 General

If no otherwise stated, all reactions and manipulations were carried out in argon atmosphere using standard Schlenk techniques. Solvents were dried by standard procedures [134] or with a *Grubbs*-apparatus using BTS®-catalysts and aluminium oxide [135]. Solvents were stored under an atmosphere of dry argon or nitrogen over 3 or 4 Å molecular sieves. All chemicals were, if not otherwise stated, used as received from commercial sources (*ABCR*, *Alfa Aesar*, *Acros Organics*, *Deutero*, *Sigma Aldrich*, *Umicore*).

NMR spectra were recorded at 298K in $CDCl_3$ (*Deutero*) using a Jeol JMX-GX 400 MHz, a Bruker Avance III 400 MHz or a Bruker AMX 400 MHz nuclear magnetic resonance spectrometer. Chemical shifts δ are given in ppm. For ^{1}H-, ^{2}H- and ^{13}C-NMR the solvent signal was used as internal standard. ^{29}Si-spectra are given relative to TMS as internal standard. The signal assignment was supported by the use of 2-dimensional NMR techniques such as ^{1}H/^{13}C-HMQC or ^{1}H/^{1}H-COSY.

GC-MS experiments were performed in dichloromethane on a Hewlett Packard GC System 6890 with coupled mass selective detector HP 5973 or a Varian CP-3800 GC system with coupled 1200L Quadrupol MS/MS mass detector. IR spectra were obtained from a Varian C-670 IR spectrometer, *in situ* IR studies were performed on a Mettler Toledo ReactIR^{TM}. Gel permeation chromatography (GPC) was conducted on a Waters 2695 alliance system using tetrahydrofuran as the mobile phase. Transmission electron microscopy (TEM) was performed on a Jeol JEM 100CX operated at 100 kV.

The standard laboratory climate is defined as 23°C and 50% relative humidity.

7.2 Comparison of Different Hydrosilylation Catalysts

Catalysts **I–VIIc** were obtained from standard commercial sources and either used respectively, as diluted solutions in hexane (**I**), isopropanol (**II**), dichloromethane (**III**, **V**) or toluene (**IV**) at a concentration of 1 mg Pt/ mL or as solids (**VI**, **VII**). Catalyst **VIId** was prepared from H_2PtCl_6 and $NaNO_3$ according to [31]. For the recycling and leaching experiments, PtO_2 with a platinum content of 81-83% and a surface of > 60 m^2/g (catalyst **VIIa**) was used. Yields were calculated from the ratio of the Si-H signal of the silane at 4.7 ppm and the Si-CH_2 signal of the product at 0.5 ppm in the ^{1}H-NMR spectrum.

The rate of isomerization was determined from the signal of the internal double bond at 5.4 ppm. For the examination of the catalytic activity of PtO_2, all experiments except the recycling experiments were carried out in fresh glassware with a new magnetic stir bar in order to avoid contaminations.

7.2.1 Hydrosilylation of *n*-Octene with PDMS-H_2

10.00 g (14.7 mmol) PDMS-H_2 (M= 680 g/mol) and 3.30 g *n*-octene (29.4 mmol, 2 eq.) were mixed at 40°C and the corresponding amount of catalyst was added. For catalysts **I**–**V**, 10 ppm (0.13 mg Pt) of platinum corresponding to the total amount of substrates were used. For **VI**, 100 ppm (1.3 mg Pt) were used. For *Karstedt's* catalyst (**I**) additionally 2 ppm Pt (0.03 mg Pt) were used. The reaction mixture was carefully heated until the exothermic reaction started. When temperature decreased again, the reaction mixture was stirred for 2h at the given reaction temperature (75-115°C, table 2.1), cooled to room temperature and analyzed by ^{1}H-NMR spectroscopy.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.05 (m, 56H, Si-CH_3), 0.53 (m, 4H, CH_2-Si), 0.88 (t, 6H, CH_3), 1.29 (m, 24H, CH_2) ppm.

7.2.2 Hydrosilylation of Styrene with PDMS-H_2

10.00 g (14.7 mmol) PDMS-H_2 (M= 680 g/mol) and 3.06 g styrene (29.4 mmol, 2 eq.) were mixed at 40°C and 10 ppm (0.13 mg) Pt in the form of catalyst **I**–**V** were added. The reaction mixture was carefully heated until the exothermic reaction started. When temperature decreased again, the reaction mixture was stirred for 2h at the given reaction temperature (75-120°C, table 1.2), cooled to room temperature and analyzed by ^{1}H-NMR spectroscopy.

α-product: ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.06 (m, 56H, Si-CH_3), 1.37 (d, 6H, CH_3), 2.17 (q, 2H, Si-CH), 7.25 (m, 10H, Ar) ppm.

β-product: ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.06 (m, 56H, Si-CH_3), 0.90 (m, 4H, Si-CH_2), 2.65 (m, 4H, CH_2), 7.20 (m, 10H, Ar) ppm.

7.2.3 Comparison of Homogeneous and Heterogeneous Catalysts

4.00 g HMTS (18.0 mmol) and 2.22 g *n*-octene (19.8 mmol, 1.1 eq.) were mixed at room temperature, the corresponding amount of catalyst was added and the reaction mixture was placed into a 80°C preheated oil bath. For the homogeneous catalysts **I**,**II** and **V**, 10 ppm (0.06 mg Pt) of platinum (with respect to the total weight of the reaction mixture) were used. In case of PtO_2 (**VIIa**) 100 ppm (0.622 mg) of platinum (0.8 mg PtO_2, 3.5 µmol) were used.

Samples for ^{1}H-NMR spectroscopy were taken every 15 min.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.02 (s, 3H, Si-CH_3), 0.11 (s, 18H, Si(CH_3)$_3$), 0.47 (m, 2H, Si-CH_2), 0.91 (t, 3H, CH_3), 1.29 (m, 12H, CH_2) ppm.

7.2.4 Comparison of Different PtO_2 Species

4.00 g HMTS (18.0 mmol) and 2.01 g *n*-octene (18.0 mmol) were mixed at room temperature, the corresponding amount of catalyst (**VIIa–VIId**) was added and the reaction mixture was placed into a 100°C preheated oil bath. 100 ppm (0.601 mg) of platinum (0.73–0.76 mg PtO_2) were used. Samples for ^{1}H-NMR spectroscopy were taken after 20, 50, 105 and 225 min.

7.2.5 Determination of TOFs for Different Catalyst Loading

4.00 g HMTS (18.0 mmol) and 2.22 g *n*-octene (19.8 mmol, 1.1 eq.) were mixed at room temperature, the corresponding amount of catalyst was added and the reaction mixture was moved into a 60°C preheated oil bath. 1000 ppm correspond to 7.8 mg (35 µmol) PtO_2, 100 ppm to 0.8 mg PtO_2 (3.5 µmol) and 10 ppm to 0.08 mg PtO_2 (here, approx. 0.1 mg were used).

7.2.6 Recycling and Leaching Experiments

3.00 g HMTS (13.5 mmol) and 1.51 g *n*-octene (13.5 mmol) were mixed at room temperature, 1.4 mg PtO_2 (300 ppm Pt, 6.0 µmol) were added, the reaction mixture was placed into a 85°C preheated oil bath and the *in situ* IR measurement was started. After complete conversion, the clear and colorless product solution was carefully removed with a syringe and fresh substrates (3.00 g HMTS and 1.51 g *n*-octene) were added to the solid catalyst. For the leaching experiments the supernatants of the first 4 cycles were filtered through a 0.45 µm syringe filter, fresh substrates (2.00 g HMTS and 1.01 g *n*-octene) were added and the IR measurement was started. After complete conversion (50 min) the supernatant of cycle 1 was again mixed with fresh substrates (2.00 g HMTS and 1.01 g *n*-octene). This procedure was repeated once again.

7.2.7 Pretreatment of HMTS and *n*-Octene with PtO_2

3.00 g HMTS or 1.51 g *n*-octene, respectively, were stirred with 1.4 mg PtO_2 (**VIIa**) for 2h at 85°C. The liquid phase was removed with a syringe and filtered over a 0.45 µm syringe filter. 1.51 g *n*-octene or 3.00 g HMTS, respectively, were added and the reaction mixture was moved into a 85°C preheated oil bath and the *in situ* IR measurement was started.

7.3 Hydrosilylation of Isopropenyl Compounds

For all reactions, *Karstedt's* catalyst was used as diluted solution (5 mg Pt/mL hexane) as received from Umicore. Et_3SiD was prepared from Et_3SiCl and $LiAlD_4$ (98 atom % D) as described in literature.[136] 2-Methyl-2-propenyl acetate was prepared from 2-methyl-2-propene-1-ol and acetic anhydride as described in [137].

7.3.1 Hydrosilylation Reactions

Under an atmosphere of argon, the corresponding amount of silane was placed in a Schlenk tube with a stir bar and heated to 70°C. In a beaker, the corresponding amount of *Karstedt's* catalyst was added to the isopropenyl compound and the mixture was carefully mixed and added to the silane with a syringe. No increase in temperature was observed. After complete addition, the reaction mixture was stirred at 70°C until the reaction was complete. The reaction progress was monitored by ^{1}H-NMR spectroscopy. Usually, two equivalents of the silane were used to achieve complete olefin conversion.

7.3.1.1 Hydrosilylation of Isopropenyl Acetate with PMDS

3.00 g PMDS (20.2 mmol), 1.01 g isopropenyl acetate (10.1 mmol) and 0.08 mL of a 5 mg Pt/mL hexane solution of *Karstedt's* catalyst (100 ppm Pt per total educts) were used. The reaction was completed within 3.5 h at 70°C.

$AcOSiMe_2OSiMe_3$ (**P1**): ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.12 (s, 9H, $SiCH_3$), 0.26 (s, 6H, $SiCH_3$), 2.06 (s, 3H, CH_3) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 0.28 (Si-CH_3), 1.46 (Si-CH_3), 18.05 (CH_3), 170.78 (C=O) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= –9.35 (SiOAc), 10.14 ($SiMe_3$) ppm. GC-MS (EI, 4.2 min) m/z= 191 $[M-Me]^+$, 149 $[OSiMe_2OSiMe_2]^+$, 133 $[M-SiMe_3]^+$, 43 $[MeCO]^+$.

n-$PrSiMe_2OSiMe_3$ (**P2**): ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.03 (s, 6H, CH_3Si), 0.06 (s, 9H, CH_3Si), 0.51 (m, 2H, CH_2Si), 0.95 (t, 3H, CH_3), 1.35 (m, 2H, CH_2) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 0.34 (Si-CH_3), 2.37 (Si-CH_3), 17.50 (CH_2), 18.32 (CH_3), 21.29 (Si-CH_2) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 6.80 ($SiPrMe_2$), 7.18 ($SiMe_3$) ppm. GC-MS (EI, 2.4 min) m/z=190 $[M]^+$, 175 $[M-Me]^+$, 147 $[SiMe_2OSiMe_3]^+$, 133 $[SiMeOSiMe_3]^+$, 117 $[M-SiMe_3]^+$, 73 $[SiMe_3]^+$.

7.3.1.2 Hydrosilylation of Isopropenyl Acetate with Et_3SiH

250 mg triethylsilane (2.15 mmol), 108 mg isopropenyl acetate (1.07 mmol) and 7.2 µL of a 5 mg Pt/mL hexane solution of *Karstedt's* catalyst (100 ppm Pt per total educts) were used. The reaction was completed within 48h at 70°C.

Et_3SiOAc (**P3**): ^1H-NMR (400 MHz, $CDCl_3$): δ= 0.77 (m, 6H, CH_2), 0.97 (m, 9H, CH_3), 2.06 (s, 3H, CH_3) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 4.40 (CH_2), 6.57 (CH_3), 22.61 (CH_3), 171.75 (C=O) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 25.06 ppm. GC-MS (EI, 7.1 min) m/z= 159 $[M - Me]^+$, 145 $[M – Et]^+$, 115 $[SiEt_3]^+$, 103 $[OSiEt_2]^+$, 75, 59 $[MeCOO]^+$.

n-$PrSiEt_3$ (**P4**): ^1H-NMR (400 MHz, $CDCl_3$): δ= 0.5 (m, 8H, Si-CH_2), 0.97 (m, 12H, CH_3), 1.31 (m, 2H, CH_2), ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 3.69 (CH_2), 7.59 (CH_3), 13.96 (Si-CH_2), 17.03 (CH_2), 18.92 (CH_3) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 6.43 ppm.

GC-MS (EI, 4.2 min) m/z= 158 $[M]^+$, 129 $[M-Et]^+$, 115 $[SiEt_3]^+$, 101 $[M-2Et]^+$, 87 $[SiEt_2]^+$, 71 $[M-3Et]^+$, 59 $[SiEt]^+$, 43 $[CH_3CH_2CH_2]^+$.

7.3.1.3 Hydrosilylation of Isopropenyl Benzoate with PMDS

330 mg isopropenyl benzoate (2.03 mmol), 604 mg PMDS (4.07 mmol) and 19 µL of a 5 mg Pt/mL hexane solution of *Karstedt's* catalyst (100 ppm Pt per total educts) were used. The reaction was completed within 4h at 70°C.

$BzOSiMe_2OSiMe_3$ (**P5**): ^1H-NMR (400 MHz, $CDCl_3$): δ= 0.16 (s, 9H, CH_3), 0.38 (s, 6H, CH_3), 7.44 (q, 2H, Ar), 7.56 (q, 1H, Ar), 8.05 (q, 2H, Ar) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 0.34 (CH_3), 2.04 (CH_3), 133.32–128.38 (Ar), 166.60 (C=O) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= –7.61 (SiOBz), 10.56 ($SiCH_3$) ppm. GC-MS (EI, 13.5 min) m/z= 269 $[M]^+$, 253 $[M-Me]^+$, 133 $[SiMe_2OMe_2]^+$, 105 $[PhCO]^+$, 77 $[Ph]^+$.

Spectroscopic data of *n*-$PrSiMe_2OSiMe_3$ (**P2**) agree with those given in 7.3.1.1.

7.3.1.4 Hydrosilylation of 2-Chloropropene with PMDS

1.55 g 2-chloropropene (20.2 mmol), 4.00 g PMDS (27.0 mmol) and 0.11 mL of a 5 mg Pt/mL hexane solution of *Karstedt's* catalyst (100 ppm Pt per total educts) were used. Because of the high volatility of 2-chloropropene it was used in slight excess and the reaction was performed in a pressure tube at 70°C oil bath temperature. The reaction was complete after 48h.

$ClSiMe_2OSiMe_3$ (**P6**): ^1H-NMR (400 MHz, $CDCl_3$): δ= 0.14 (s, 9H, $SiCH_3$), 0.43 (s, 6H, $SiCH_3$) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 1.83 ($SiMe_3$), 4.42 ($SiMe_2$) ppm.

^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 3.85 (Si-Cl), 11.87 ($SiMe_3$) ppm.

Spectroscopic data of *n*-$PrSiMe_2OSiMe_3$ (**P2**) agree with those given in 7.3.1.1.

7.3.1.5 Hydrosilylation of 2-Chloropropene with Et_3SiH

0.99 g 2-chloropropene (12.90 mmol), 2.00 g Et_3SiH (12.90 mmol) and 0.6 mL of a 5 mg Pt/mL hexane solution of *Karstedt's* catalyst (1000 ppm Pt per total educts) were used. Because of its high volatility, 2-chloropropene was used in excess and the reaction was performed in a pressure tube at 70°C oil bath temperature. After 70h the reaction was still incomplete.

$ClSiEt_3$ (**P7**): ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.82 (q, 6H, Si-CH_2), 1.02 (t, 9H, Si-CH_3) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 6.69 (CH_3), 7.48 (CH_2) ppm.
^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 35.93 ppm.

Spectroscopic data of *n*-$PrSiEt_3$ (**P4**) agree with those given in 7.3.1.2.

7.3.1.6 Hydrosilylation of Isopropenyl Benzyl Ether with PMDS

460 mg PMDS (3.1 mmol), 460 mg isopropenyl benzyl ether (3.1 mmol) and 18 µL of a 5 mg Pt/mL hexane solution of *Karstedt's* catalyst (100 ppm Pt per total educts) were used. The reaction was completed within 4h at 70°C.

$C_{15}H_{28}O_2Si_2$ (**P8**): ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.01 (m, 15H, Si-CH_3), 0.83 (d, 1H, $CH_{cis}Si$), 1.20 (d, 3H, CH_3), 1.44 (d, 1H, $CH_{trans}Si$), 3.63 (m, 1H, CH), 4.40 (q, 2H, ArCH_2), 7.25 (m, 5H, Ar) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 1.61 ($SiCH_3$), 1.88 ($SiCH_3$), 22.4 (CH_3), 27.35 (CH_2Si), 69.73 (CH-O), 72.58 (ArCH_2), 128.11–127.46 (Ar), 139.06 (Ar) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 5.55 ($SiMe_3$), 7.49 ($SiMe_2$) ppm. GC-MS (EI, 15.4 min) m/z= 281 $[M-Me]^+$, 223 $[M-SiMe_3]^+$, 147 $[SiMe_2OSiMe_3]^+$, 91 $[PhCH_2]^+$, 73 $[SiMe_3]^+$.

7.3.1.7 Hydrosilylation of 2-Methyl-2-propenyl Acetate with PMDS

1.95 g PMDS (13.14 mmol), 1.50 g 2-methyl-2-propenyl acetate (13.14 mmol) and 0.07 mL of a 5 mg Pt/mL hexane solution of *Karstedt's* catalyst (100 ppm Pt per total educts) were used. The reaction was completed within 2h at 70°C.

$C_{11}H_{26}O_3Si_2$(**P9**): ^{1}H-NMR (400 MHz, $CDCl_3$): δ= -0.06 (m, 15H, $SiCH_3$), 0.31 (m, 1H, Si-CH_2), 0.51 (m, 1H, $SiCH_2$), 0.85 (d, 3H, CH_3), 1.85 (m, 1H, CH), 1.89 (s, 3H, CH_3), 3.66 (m, 1H, CH_2O), 3.79 (m, 1H, CH_2O) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 0.91 ($SiMe_2$), 1.63 ($SiMe_3$), 19.49 (CH_3), 20.49 (C(O)-CH_3), 22.56 (CH), 28.54 ($SiCH_2$), 71.08 (CH_2-O), 170.33 (C=O) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 6.44 ($SiMe_3$), 7.24 ($SiMe_2$) ppm.
GC-MS (EI, 10.7 min): m/z= 247 $[M-Me]^+$, 191 $[M-MeCOOCH_2]^+$, 147 $[SiMe_2OSiMe_3]^+$, 73 $[SiMe_3]^+$, 43 $[MeCO]^+$.

7.3.1.8 Hydrosilylation of 2-Acetoxy-2-butene with PMDS

786 mg PMDS (5.3 mmol), 605 mg 2-acetoxy-2-butene (5.3 mmol) and 0.03 mL of a 5 mg Pt/mL hexane solution of *Karstedt's* catalyst (100 ppm Pt per total educts) were used. The reaction was finished after 48h at 70°C.

n-BuSiMe$_2$OSiMe$_3$ (**P10**): ^{1}H-NMR (400 MHz, CDCl$_3$): δ= 0.12 (m, 15H, SiCH$_3$), 0.51 (t, 2H, SiCH$_2$), 0.88 (t, 3H, CH$_3$), 1.3 (m, 4H, CH$_2$) ppm. ^{13}C-NMR (100 MHz, CDCl$_3$): δ= 1.37 (SiMe$_3$), 1.76 (SiMe$_2$), 26.25 (CH$_2$), 13.63 (CH$_3$), 22.57 (CH$_2$), 25.42 (SiCH$_2$) ppm. ^{29}Si-NMR (80 MHz, CDCl$_3$): δ= 7.06 (SiBuMe$_2$), 7.72 (SiMe$_3$) ppm. GC-MS (EI, 3.1 min): m/z= 189 [M]$^+$, 147 [SiMe$_2$OSiMe$_3$]$^+$, 133 [SiMeOSiMe$_3$]$^+$, 117 [M-SiMe$_3$]$^+$, 73 [SiMe$_3$]$^+$.

Spectroscopic data of AcOSiMe$_2$OSiMe$_3$ (**P1**) agree with those given in 7.3.1.1.

7.3.1.9 Hydrosilylation of 2-Chloro-2-butene with PMDS

1.64 g PMDS (11 mmol), 0.50 g 2-chloro-2-butene (5.5 mmol) and 0.4 mL of a 5 mg Pt/mL hexane solution of *Karstedt's* catalyst (1000 ppm Pt per total educts) were used. The reaction was almost completed within 48h at 70°C.

Spectroscopic data of ClSiMe$_2$OSiMe$_3$ (**P6**) and *n*-BuSiMe$_2$OSiMe$_3$ (**P10**) agree with those given in 7.3.1.4 and in 7.3.1.8.

7.3.1.10 Hydrosilylation of Isopropenyl Acetate with Et$_3$SiD

500 mg triethyl(silane-d) (4.3 mmol), 427 mg isopropenyl acetate (4.3 mmol) and 18 µL of a 5 mg Pt/mL hexane solution of *Karstedt's* catalyst (100 ppm Pt per total educts) were used. The reaction was completed after 48h at 70°C.

Signals of deuterated propene and H-silane could be observed during the reaction in a sample taken after 24h.

Triethyl(propyl-d^2)silane (Et$_3$SiPr-d^2, **P4-d^2**): ^{2}H-NMR (61 MHz, CDCl$_3$): δ= 0.39 (CH$_2$-Si), 0.86 (CH$_3$), 1.21 (CH$_2$) ppm. ^{1}H-NMR (400 MHz, CDCl$_3$): δ= 0.5 (m, 8H, Si-CH$_2$), 0.95 (m, 12H, CH$_3$), 1.27 (m, 2H, CH$_2$) ppm. ^{13}C-NMR (100 MHz, CDCl$_3$): δ= 3.16 (CH$_2$), 7.41 (CH$_3$), 14.16 (Si-CH$_2$), 17.16 (CH$_2$), 18.61 (CH$_3$) ppm. ^{29}Si-NMR (80 MHz, CDCl$_3$): δ= 25.08 ppm. GC-MS (EI, 4.1 min) m/z= 160 [M]$^+$, 131 [M-Et]$^+$, 115 [SiEt$_3$]$^+$, 103 [M-2Et]$^+$, 87 [SiEt$_2$]$^+$, 73 [M-3Et]$^+$, 59 [SiEt]$^+$, 45 [M-SiEt$_3$]$^+$.

Spectroscopic data of Et$_3$SiOAc (**P3**) agree with those given in 7.3.1.2.

7.3.1.11 Hydrosilylation of Propene with Et_3SiD

In a pressure tube with a propene pressure of 3.0 bar, 0.30 g Et_3SiD (2.6 mmol) and 0.04 mL of a 1 mg Pt/mL hexane solution of *Karstedt's* catalyst (100 ppm Pt per total educts) were stirred for 17h at 75°C.

Triethyl(propyl-d)silane (Et_3SiPr-d, **P4-d**): ^{2}H-NMR (61 MHz, $CDCl_3$): δ= 0.52 (CH_2-Si), 0.95 (CH_3), 1.30 (CH_2) ppm. ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.51 (m, Si-CH_2), 0.93 (m, CH_3), 1.34 (m, CH_2) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 3.34 (CH_2), 7.26 (CH_3), 14.12 ($SiCH_2$), 17.38 (CH_2), 18.46 (CH_3) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 6.32 ppm.

7.3.1.12 Hydrosilylation of Ethyl-1-propenyl ether with PMDS

1.00 g PMDS (6.7 mmol), 0.58 g (6.74 mmol) and 0.32 mL of a 5 mg Pt/mL hexane solution of *Karstedt's* catalyst (1000 ppm Pt per total educts) were used. Even after 70h at 70°C the reaction was incomplete.

$C_{10}H_{26}O_2Si_2$ (**P11**): ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.06 (m, 15H, $SiCH_3$), 0.49 (m, 2H, Si-CH_2), 1.20 (t, 3H, CH_3), 1.59 (m, 2H, CH_2), 3.35 (t, 2H, OCH_2), 3.47 (q, 2H, OCH_2) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 1.44 ($SiCH_3$), 14.05 ($SiCH_2$), 14.86 (CH_3), 23.32 (CH_2), 65.67 (OCH_2), 73.21 ($\underline{C}H_2CH_3$) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 6.89 ($SiMe_3$), 7.62 ($SiMe_2$) ppm. GC-MS (EI, 6.89 min) m/z= 219 $[M\text{-}Me]^+$, 205 $[M\text{-}Et]^+$, 191 $[M\text{-}OEt]^+$, 177 $[M\text{-}CH_2OEt]^+$,147 $[SiMe_2OSiMe_3]^+$, 133 $[SiMe_2OSiMe_2]^+$, 73 $[SiMe_3]^+$.

7.3.2 Kinetic Measurements

Five Schlenk tubes were filled with a mixture of 1.00 g PMDS (6.74 mmol) and 0.34 g (3.37 mmol) isopropenyl acetate, the corresponding amount of catalyst (20, 50, 100, 200, 300 ppm Pt) was added and the reaction mixture was placed into a 70°C preheated oil bath. For example, 300 ppm Pt correspond to 80 µL, 20 ppm Pt to 5.3 µL of a 5 mg Pt/mL hexane solution of *Karstedt's* catalyst. Samples for ^{1}H-NMR spectroscopy were taken every 30 min. Yields were calculated from the ratio of the Si-H signal of the silane at 4.7 ppm and the Si-CH_3 signal of $AcOSiMe_2OSiMe_3$ (**P1**) at 0.3 ppm and the Si-CH_2 signal of $PrSiMe_2OSiMe_3$ (**P2**) at 0.5 ppm, respectively.

7.3.3 Synthesis of Isopropenyl Benzoate

Isopropenyl benzoate was prepared from isopropenyl acetate and benzoyl chloride as described in [138].

Isopropenyl benzoate: ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 2.06 (s, 3H, CH_3), 4.83 (s, 2H, CH_2), 7.47 (m, 2H, Ar), 7.59 (m, 1H, Ar), 8.08 (m, 2H, Ar) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 19.47 (CH_3), 102.15 (CH_2), 133.14–128.29 (Ar), 153.10 (C_q), 164.52 (C=O) ppm.

7.3.4 Synthesis of 2-Acetoxy-2-butene

2-Acetoxy-2-butene was prepared from acetyl chloride and 2-butanone in very low yield as described in [138] with a *trans*:*cis* ratio of about 3:1.

trans-2-Acetoxy-2-butene: ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 1.48 (m, 3H, β-CH_3), 1.86 (m, 3H, α-CH_3), 2.16 (s, 3H, C(O)-CH_3), 5.06 (m, 1H, CH) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 10.44 (β-CH_3), 19.26 (α-CH_3), 20.48 ($\underline{C}H_3$-C(O)), 111.1 (CH), 145.47 (C_q), 168.74 (C=O) ppm.

cis-2-Acetoxy-2-butene: 1.62 (m, 3H, β-CH_3), 1.86 (m, 3H, α-CH_3), 2.10 (s, 3H, C(O)-CH_3), 5.16 (m, 1H, CH) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 11.54 (β-CH_3), 14.61 (α-CH_3), 20.76 ($\underline{C}H_3$-C(O)), 111.76 (CH), 145.71 (C_q), 169.79 (C=O) ppm.

7.4 Synthesis of Different SiH-terminated Hybrid Silicones

Under an atmosphere of argon, m+2 equivalents of 1,1,3,3-tetramethyldisiloxane (TMDS), 1,1,3,3,5,5-hexamethyldisiloxane (HexMTS) or α,ω-dihydropolydimethylsiloxane (PDMS-H_2) were placed into a 250-mL-3-necked round bottom glass flask equipped with reflux condenser, magnetic stirrer, thermo sensor and dropping funnel and heated to 60°C. m+1 Equivalents of the diene were mixed with a corresponding amount of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst to achieve 10 ppm Pt per total substrates and placed into the dropping funnel. With vigorous stirring, the mixture was added dropwise to the siloxane over the course of approximately 1h. The reaction was highly exothermic and the temperature of the reaction mixture was controlled at 60 to 85°C using an ice bath. After completing the addition, the pale yellow mixture was stirred for an additional 1h at 75°C and was then allowed to cool to room temperature. The chain length was determined by ^{1}H-NMR spectroscopy. The integrals of the areas of peaks due to several groups within the molecule are a function of the degree of polymerization m when the integral of the Si-H moiety at 4.7 ppm is set to 2. The average degree of polymerization m was used for the calculation of the molecular weight.

For small amounts (< 20 g in total), the reaction can also be performed in a Schlenk-flask equipped with stir bar, septum and thermo sensor: the corresponding amount of siloxane was heated to 60°C and the diene/catalyst mixture was carefully added with a syringe. Again, the temperature of the reaction mixture was controlled at 60°C to 85°C with an ice bath whereafter, the pale yellow mixture was stirred for an additional 1h at 75°C and was then allowed to cool to room temperature.

7.4.1 Synthesis of Copolymer 1a-SiH

192.8 g (1.44 mmol, 6 eq.) TMDS, 165.5 g 1,9-decadiene (1.20 mmol, 5 eq.) and 3.6 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. Yield: 357.4 g.
M_n (determined by ^{1}H-NMR spectroscopy)= 1500 g/mol.
^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.01 (m, 62H, Si-CH_3), 0.19 (d, 12H, H-Si(C$\underline{H}_3$)), 0.52 (m, 20H, Si-CH_2), 1.29 (m, 81H, CH_2), 4.70 (m, 2H, Si-H) ppm.

7.4.2 Synthesis of Copolymer 1b-SiH

187.7 g (1.40 mmol, 17 eq.) TMDS, 182.0 g 1,9-decadiene (1.32 mmol, 16 eq.) and 3.7 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. Yield: 368.9 g.
M_n (NMR)= 4600 g/mol.
^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.01 (m, 194H, Si-CH_3), 0.19 (d, 12H, H-Si(C$\underline{H}_3$)), 0.52 (m, 66H, Si-CH_2), 1.29 (m, 260H, CH_2), 4.70 (m, 2H, Si-H) ppm.

7.4.3 Synthesis of Copolymer 2a-SiH

4.0 g (19.2 mmol, 3 eq.) HexMTS, 1.77 g 1,9-decadiene (12.8 mmol, 2 eq.) and 0.06 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. Yield: 5.62 g.
M_n (NMR)= 1050 g/mol.
^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.05 (m, 50H, Si-CH_3), 0.19 (d, 12H, H-Si(C$\underline{H}_3$)), 0.50 (m, 9H, CH_2-Si), 1.27 (m, 40H, CH_2), 4.70 (m, 2H, Si-H) ppm.

7.4.4 Synthesis of Copolymer 2b-SiH

4.0 g (19.2 mmol, 17 eq.) HexMTS, 2.50 g 1,9-decadiene (18.1 mmol, 16 eq.) and 0.06 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. Yield: 6.40 g.
M_n (NMR)= 5920 g/mol.
^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.03 (m, 300H, Si-CH_3), 0.19 (d, 12H, H-Si(C$\underline{H}_3$)), 0.53 (m, 65H, Si-CH_2), 1.29 (m, 271H, CH_2), 4.71 (m, 2H, Si-H) ppm.

7.4.5 Synthesis of Copolymer 3a-SiH

5.00 g (8.62 mmol, 3 eq.) PDMS-H_2 (M= 580 g/mol), 0.79 g 1,9-decadiene (5.75 mmol, 2 eq.) and 0.06 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. Yield: 5.65 g. M_n (NMR)= 2220 g/mol.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.04 (m, 146H, Si-CH_3), 0.19 (d, 12H, H-Si(C$\underline{H}_3$)), 0.51 (m, 9H, Si-CH_2), 1.26 (m, 39H, CH_2), 4.71 (m, 2H, Si-H) ppm.

7.4.6 Synthesis of Copolymer 3b-SiH

5.00 g (8.62 mmol, 20 eq.) PDMS-H_2 (M= 580 g/mol), 1.13 g 1,9-decadiene (8.19 mmol, 19 eq.) and 0.06 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. Yield: 6.08 g. M_n (NMR)= 16900 g/mol.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.04 (m, 1148H, Si-CH_3), 0.19 (d, 12H, H-Si(C$\underline{H}_3$)), 0.53 (m, 86H, Si-CH_2), 1.29 (m, 377H, CH_2), 4.71 (m, 2H, Si-H) ppm.

7.4.7 Synthesis of Copolymer 4a-SiH

20.0 g (29.4 mmol, 6 eq.) PDMS-H_2 (M=680 g/mol), 3.19 g 1,9-decadiene (24.5 mmol, 5 eq.) and 0.23 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. Yield: 23.07 g. M_n (NMR)= 4330 g/mol.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.09 (m, 285H, Si-CH_3), 0.19 (d, 12H, H-Si(C$\underline{H}_3$)), 0.91 (m, 14H, CH_2-Si), 1.37 (t, 7H, CH_3), 2.16 (q, 3H, CH), 2.63 (m, 14H, CH_2), 4.72 (m, 2H, Si-H), 6.90-7.18 (m, 18H, Ar) ppm.

7.4.8 Synthesis of Copolymer 5a-SiH

100.0 g (0.48 mol, 6.5 eq.) HexMTS, 64.22 g freshly distilled 1,3-diisopropenylbenzene (0.41 mmol, 5.5 eq.) and 0.33 mL of a 5 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. Yield: 160.90 g. M_n (NMR)= 2800 g/mol.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.00 (m, 137H, Si-CH_3), 0.19 (d, 12H, H-Si(C$\underline{H}_3$)), 0.97 (m, 27H, Si-CH_2), 1.27 (m, 43H, CH_3), 2.90 (m, 14H, CH), 4.70 (m, 2H, Si-H), 7.02-7.17 (m, 28H, Ar) ppm.

7.4.9 Synthesis of Copolymer 5b-SiH

100.0 g (0.15 mol, 3.7 eq.) PDMS-H_2 (M= 680 g/mol), 16.98 g freshly distilled 1,3-diisopropenylbenzene (0.11 mol, 2.7 eq.) and 0.25 mL of a 5 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. Yield: 115.17 g. M_n (NMR)= 3030 g/mol.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.05 (m, 205H, Si-CH_3), 0.19 (d, 12H, H-Si(C$\underline{H}_3$)), 0.95 (m, 11H, Si-CH_2), 1.26 (m, 17H, CH_3), 2.98 (m, 6H, CH), 4.72 (m, 2H, Si-H), 7.00-7.20 (m, 11H, Ar) ppm.

7.4.10 Synthesis of Copolymer 6a-SiH

100.0 g (0.48 mol, 6 eq.) HexMTS, 56.8 g (0.40 mol, 5 eq.) 1,4-butandiol divinyl ether and 1.57 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used.

Yield: 154.96 g. M_n (NMR)= 2520 g/mol.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.06 (m, 128H, Si-CH_3), 0.18 (d, 12H, H-Si(C$\underline{H}_3$)), 0.99 (m, 26H, Si-CH_2), 1.62 (m, 26H, CH_2), 3.39 (m, 27H, CH_2-O), 3.50 (m, 27H, CH_2-O), 4.69 (m, 2H, Si-H) ppm.

7.4.11 Synthesis of Copolymer 6b-SiH

100.0 g (0.15 mol, 3.8 eq.) PDMS-H_2 (M= 680 g/mol), 15.41 g 1,4-butandiol divinyl ether (0.11 mol, 2.8 eq.) and 1.2 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. Yield: 114.08 g. M_n (NMR)= 2880 g/mol.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.07 (m, 193H, Si-CH_3), 0.18 (d, 12H, H-Si(C$\underline{H}_3$)), 0.99 (m, 11H, Si-CH_2), 1.62 (m, 11H, CH_2), 3.39 (m, 10H, CH_2-O), 3.50 (m, 11H, CH_2-O), 4.70 (m, 2H, Si-H) ppm.

7.4.12 Synthesis of Copolymer 7a-SiH

100.0 g (0.48 mol, 5 eq.) HexMTS, 77.61 g triethylene glycol divinyl ether (0.38 mmol, 4 eq.) and 0.36 mL of a 5 mg Pt /mL hexane solution of *Karstedt's catalyst* were used. Yield: 175.91 g. M_n (NMR)= 2300 g/mol.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.05 (m, 93H, Si-CH_3), 0.16 (d, 12H, H-Si(C$\underline{H}_3$)), 1.00 (m, 19H, Si-CH_2), 3.53 (m, 39H, CH_2-O), 3.63 (m, 39H, CH_2-O), 4.68 (m, 2H, Si-H) ppm.

7.4.13 Synthesis of Copolymer 7b-SiH

100.0 g (0.15 mol, 3.6 eq.) PDMS-H_2 (M= 680 g/mol), 21.48 g triethylene glycol divinyl ether (0.11 mol, 2.6 eq.) and 0.5 mL of a 5 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. Yield: 120.09 g. M_n (NMR)= 2910 g/mol.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.09 (m, 186H, Si-CH_3), 0.20 (d, 12H, H-Si(C$\underline{H}_3$)), 1.01 (m, 10H, Si-CH_2), 3.55 (m, 20H, CH_2-O), 3.65 (m, 20H, CH_2-O), 4.72 (m, 2H, Si-H) ppm.

7.4.14 Hydrosilylation of Bisphenol A Diallyl Ether with PMDS

Under an atmosphere of argon, 5.00 g (0.034 mol) PMDS were heated to 40°C and a mixture of 5.19 g (0.017 mol, 2 eq.) bisphenol A diallyl ether and 0.12 mL of a 1 mg Pt/ mL hexane solution of *Karstedt's* catalyst was slowly added with a syringe. After complete addition, the reaction mixture was stirred at 75°C for 2h.

Yield (determined by ^{1}H-NMR spectroscopy): 74%.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.09 (m, 30H, Si-CH_3), 0.62 (m, 4H, Si-CH_2), 1.64 (s, 6H, CH_3), 1.79 (m, 4H, CH_2), 3.90 (t, 4H, CH_2-O), 6.77- 7.15 (m, 8H, Ar) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 0.46 (Si-CH_3), 2.14 (Si-CH_3), 14.41 (Si-CH_2), 23.47 (CH_2), 31.26 (CH_3), 41.50 (C_q), 70.48 (CH_2-O), 113.98 (Ar), 127.79 (Ar), 143.02 (Ar), 157.05 (Ar).

^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 7.58 ppm.

7.4.15 Synthesis of Copolymer 8a-SiH

2-Methyl-3-(2-methylallyloxy)prop-1-en was prepared from 3-bromo-2-methylpropene and 2-methyl-propene-1-ol according to [66].

3.00 g (0.022 mol, 9 eq.) TMDS, 2.51 g (0.020 mol, 8 eq.) 2-methyl-3-(2-methylallyloxy)prop-1-en and 0.05 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. M_n (NMR)= 2400 g/mol.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.07 (m, 111H, $SiCH_3$), 0.16 (d, 12H, $HSiCH_3$), 0.36/ 0.65 (m, 17H, Si-CH_2), 0.94 (d, 53H, CH_3), 1.89 (m, 17H, CH), 3.07/ 3.20 (m, 16/ 17H, CH_2O), 4.69 (m, 2H, Si-H) ppm.

7.4.16 Synthesis of Copolymer 9a-SiH

2-Methyl-4-(2-methyl-allyloxy)but-1-en was prepared from 3-bromo-2-methylpropene and isoprenol as described in [66].

2.00 g (0.015 mol, 9 eq.) TMDS, 1.86 g (0.013 mol, 8 eq.) 2-methyl-4-(2-methyl-allyloxy)but-1-ene and 0.04 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. The reaction was performed in a pressure tube at 100°C for 9d.

M_n (NMR)= 2340 g/mol.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.09 (s, 105H, $SiCH_3$), 0.18 (s, 12H, $HSiCH_3$), 0.43/ 0.63 (m, 16H, $SiCH_2$), 0.96 (d, 51H, CH_3), 1.45/ 1.57/ 1.79/ 1.89 (m, 8H, CH and CH_2), 3.17/ 3.41 (m, 15H, CH_2O), 4.70 (m, 2H, Si-H) ppm.

7.4.17 Attempts of Hydrosilylation of Conjugated and Cyclic Dienes

7.4.17.1 Hydrosilylation of Isoprene

18.00 g (0.026 mol) PDMS-H_2 (M_n=680 g/mol), 2.70 g (0.040 mol, 1.5 eq.) isoprene and 0.20 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. The reaction was performed in a pressure tube at 75°C. A complex product mixture was obtained, which could not be completely analyzed.

7.4.17.2 Hydrosilylation of 1,5-Cyclooctadiene

6.57g (0.049 mol) TMDS, 26.50 g (0.245 mol, 5 eq.) 1,5-COD and 0.33 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. After 24h at 120°C, only the mono-addition product was obtained.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.03 (s, 15H, $SiCH_3$), 0.58 (m, 1H, Si-CH), 1.12- 2.44 (m, 10H, CH_2), 5.66 (m, 1H, CH=CH), 5.80 (m, 1H, CH=CH) ppm.

7.4.17.3 Hydrosilylation of Dicyclopentadiene

15.00 g (0.022 mol) PDMS-H_2 (M_n=680 g/mol), 2.92 g (0.022 mol) dicyclopentadiene and 0.18 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. A complex product mixture was obtained, which could not be completely analyzed.

7.4.17.4 Hydrosilylation of Cyclopentadiene

15.00 g (0.026 mol) PDMS-H_2 (M_n=680 g/mol), 1.46 g (0.040 mol) cyclopentadiene and 0.16 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. No hydrosilylation product was obtained after 24h at 85°C.

7.5 Test Reactions for the Functionalization of SiH-terminated Hybrid Silicones

Under an atmosphere of argon, the corresponding amount of siloxane was placed into a Schlenk tube with a stir bar and heated to 40°C. In a beaker, the corresponding amount of *Karstedt's* catalyst (10 ppm Pt) was added to the functional olefin and the mixture was carefully added to the siloxane using a syringe. If PtO_2 was used, 100 ppm of Pt per total substrates were used and the solid catalyst was directly added to the mixture of siloxane and olefin. Temperature was controlled with a thermo sensor. After complete addition, the reaction mixture was stirred at the given temperature until the reaction was complete. The reaction progress was monitored by ^{1}H-NMR spectroscopy.

7.5.1 Hydrosilylation of Isoprenol with PMDS

5.00 g (0.034 mol) PMDS, 3.19 g (0.037 mol, 1.1 eq.) isoprenol and 0.08 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. For PtO_2, 1.0 mg (100 ppm of Pt) were used. The reaction was complete after 2h at 80°C.

Yield (determined by ^{29}Si-NMR): 81%.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.06 (m, 15H, Si-CH_3), 0.46 (m, 1H, Si-CH'$_2$), 0.63 (m, 1H, Si-CH''$_2$), 0.96 (m, 3H, CH_3), 1.36 (s, br, 1H, OH), 1.47 (m, 1H, CH'$_2$), 1.58 (m, 1H, CH''$_2$), 1.76 (m, 1H, CH), 3.66 (m, 2H, CH_2-O) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 1.93 (Si-CH_3), 22.82 (Si-CH_2), 25.86 (CH), 26.9 (CH_3), 43.23 (CH_2), 60.70 (CH_2-O) ppm. (Small signals of byproducts were visible in the spectrum). ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 7.11 (Si-CH_2), 6.84 (Si-CH_3) ppm. Small signals of an Si-O addition product could be observed at -12.27 and -12.59 ppm. Further signals at 7.64 and 7.44 ppm can be assigned to the Si-C addition product of isoprene.

Comparable results were obtained with PtO_2 and when HexMTS or PDMS-H_2 were used instead of PMDS.

7.5.2 Hydrosilylation of 2-Methyl-3-buten-2-ol with PDMS-H_2

5.00 g (7.35 mmol) PDMS-H_2 (M= 680 g/mol), 1.33 g (15.44 mmol, 2.1 eq.) 2-methyl-3-buten-2-ol and 0.07 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. The reaction was complete after 1.5h at 80°C.

Yield (determined by ^{1}H-NMR): 99%

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.07 (m, 56H, Si-CH_3), 0.55 (m, 4H, Si-CH_2), 1.19 (s, 12H, CH_3), 4.23 (m, 4H, CH_2) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 0.09 (Si-CH_3), 1.10 (Si-CH_3), 12.36 (Si-CH_2), 28.67 (CH_3), 37.26 (CH_2), 71.34 (C_q) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 8.08 (SiO-$\underline{Si}$-CH_2), -21.55 (SiO$\underline{Si}$O), -22.13 (SiO$\underline{Si}$OSi) ppm.

7.5.3 Hydrosilylation of Hydroxybutylvinylether with PMDS

2.00 g (0.013 mol) PMDS, 1.57 g (0.013 mol) hydroxybutylvinylether and 0.04 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. The reaction was complete with respect to Si-H after 2h at 80°C but incomplete concerning the olefin.

Yield (determined by ^{1}H-NMR): 99 % with respect to SiH .

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.06 (m, 15H, Si-CH_3), 0.99 (m, 2H, Si-CH_2), 1.68 (m, 4H, CH_2), 2.69 (s, br, 1H, OH), 3.44 (t, 2H, CH_2-O), 3.52 (m, 2H, CH_2-O), 3.64 (t, 2H, CH_2-OH) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 0.63 (Si-CH_3), 1.65 (Si-CH_3), 19.86 (Si-CH_2), 26.65 (CH_2), 29.91 (CH_2), 62.03 (CH_2-OH), 67.28 (CH_2-O), 70.13 (CH_2-O) ppm.

(Small signals of byproducts were visible in the spectrum). ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 7.51 (Si-CH_2), 5.45 (Si-CH_3) ppm. (Small signals of a Si-O addition product can be seen at -12.67 ppm.) Same results were obtained when PDMS-H_2 was used instead of PMDS.

7.5.4 Hydrosilylation of Trimethylolpropane Monoallyl Ether with PDMS-H$_2$

10.00 g (0.015 mol) PDMS-H_2 (M= 680 g/mol), 5.63 g (0.032 mol, 2.2 eq.) trimethylolpropane monoallyl ether and 0.16 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. The reaction was complete after 2h at 75°C.

Yield of Si-C product (determined by ^{29}Si-NMR): 68%

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.06 (m, 70H, Si-CH_3), 0.49 (m, 4H, Si-CH_2), 0.82 (t, 6H, CH_3), 1.30 (q, 4H, $C\underline{H_2}CH_3$), 1.57 (m, 4H, CH_2), 3.01 (s, br, 4H, OH), 3.35 (t, 4H, CH_2O), 3.39 (s, 4H, CH_2-O), 3.61 (m, 8H, CH_2-O) ppm. (Signals of Si-C and Si-O addition products could hardly be distinguished by ^{1}H-NMR spectroscopy.) ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 7.46 (SiO-$\underline{Si}$-CH_2), -21.49 (SiO$\underline{Si}$O), -22.09 (SiO$\underline{Si}$OSi) ppm. A strong signal at -11.88 ppm indicates the presence of a Si-O addition product (32%).

7.5.5 Hydrosilylation of 2-Allylphenol with PMDS

5.00 g (0.034 mol) PMDS, 4.52 g (0.034 mol) 2-allylphenol and 0.09 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. The reaction was complete after 1h at 75°C. Isolated yield: 89%, b.p.: 60°C/ $1 \cdot 10^{-3}$ mbar.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.06 (s, 15H, SiCH_3), 0.61 (m, 2H, Si-CH_2), 1.68 (m, 2H, CH_2), 2.63 (t, 2H, CH_2-Ar), 4.75 (s, 1H, OH), 6.73-7.13 (m, 4H, Aromat) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$): δ= 0.60 (Si-CH_3), 2.18 (Si-CH_3), 18.33 (Si-CH_2), 23.92 (CH_2), 33.58 (CH_2-Ar), 115.43, 120.87, 127.19, 128.51, 130.32 (Ar), 153.61 (Ar-OH) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 8.11 ($SiMe_2$), 7.90 ($SiMe_3$) ppm.

2-Prop-1-enyl phenol could be identified as a byproduct by ^{1}H-NMR spectroscopy. The same reactivity was observed when PDMS-H_2 was used instead of PMDS. With PtO_2 (100 ppm Pt) and PDMS-H_2, the reaction proceeded in 2h at 120°C.

7.5.6 Hydrosilylation of 4-Vinylepoxycyclohexane with HexMTS

4.00 g (19.0 mmol) HexMTS, 4.77 g (38 mmol, 2 eq) VCO and 0.08 mL of a 1 mg Pt /mL hexane solution of $Pt(PPh_3)_4$ were used. The reaction was complete after 1h at 75°C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.00 (s, 6H, Si-CH_3), 0.04 (s, 12H, Si-CH_3), 0.49 (m, 4H, Si-CH_2), 0.80-2.24 (m, 18H, cHex and cHex-CH_2), 3.13 (m, 4H, epoxy-CH) ppm.

^{29}Si-NMR (80 MHz, $CDCl_3$, δ): -21.21 (Si-CH_3), 7.45 (Si-CH_2) ppm.

Similar results were obtained with PDMS-H_2.

7.5.7 Hydrosilylation of Allyl Glycidylether with HexMTS

4.00 g (19.0 mmol) HexMTS, 5.48 g (48 mmol, 2.5 eq) allyl glycidyl ether and 0.08 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. The reaction was complete after 2h at 75°C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.01 (s, 6H, Si-CH_3), 0.07 (s, 12H, Si-CH_3), 0.53 (m, 4H, Si-CH_2), 1.61 (m, 4H, CH_2), 2.61 (dd, 2H, CH-epoxy), 2.79 (t, 2H, CH-epoxy), 3.15 (m, 2H, epoxy-CH), 3.42 (m, 6H, CH2'-O and O-CH2-CH2), 3.70 (m, 2H, CH2''-O) ppm.

^{29}Si-NMR (80 MHz, $CDCl_3$): δ= -21.16 (Si-CH_3), 7.32 (Si-CH_2) ppm.

Similar results were obtained with PDMS-H_2.

7.5.8 Hydrosilylation of Allyl Amine with PMDS

2.00 g (13 mmol) PMDS, 2.31 g (40 mmol, 3 eq) allyl amine and 0.08 mL of a 5 mg Pt /mL hexane solution of *Karstedt's* catalyst (100 ppm Pt) were used.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.05 (s, 15H, Si-CH_3), 0.50 (m, 2H, Si-CH_2), 1.20 (s, br, 2H, NH_2), 1.44 (m, 2H, CH_2), 2.66 (t, 2H, CH_2-N) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 0.02 ($SiCH_3$), 1.65 ($SiCH_3$), 15.11 (Si-CH_2), 27.46 (CH_2), 45.15 (CH_2-N) ppm.

^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 6.85 ($SiMe_3$), 7.19 ($SiMe_2$) ppm.

Similar results were obtained with PDMS-H_2 or HexMTS.

7.5.9 Hydrosilylation of *N*-BOC Allyl Amine with HexMTS

3.00 g (14 mmol) HexMTS, 4.75 g (30 mmol, 2.1 eq) *N*-BOC allyl amine, dissolved in 10 mL THF and 0.10 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. The slightly exothermic reaction proceeds within 20h at 60°C. The reaction mixture was allowed to cool to ambient temperature and the solvent was removed *in vacuo*.

N-BOC-allyl-amine-HexMTS-adduct: ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.07 (m, 18H, Si-CH_3), 0.51 (m, 4H, Si-CH_2), 1.44 (m, 22H, CH_3 and CH_2), 3.09 (m, 4H, CH_2-N) ppm.

The BOC-protected hydrosilylation product was dissolved in 15 mL dichloromethane at 0°C and 12 mL trifluoro acetic acid (TFA) were added. A strong gas evolution was observed and the reaction mixture was stirred at ambient temperature for 12h. The deprotected product was washed with aq. $NaHCO_3$ and H_2O and dried *in vacuo*.

Isolated yield: 4.69 g (8.9 mmol, 64%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.06 (m, 18H, Si-CH_3), 0.52 (m, 4H, Si-CH_2), 1.60 (m, 4H, CH_2), 2.80 (m, 4H, CH_2-N), 5.67 (s, br, 2H, NH_2) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$): δ= 0.13 ($SiCH_3$), 1.01 ($SiCH_3$), 15.00 (Si-CH_2), 23.98 (CH_2), 43.45 (CH_2-N) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= - 21.68 (Si-CH_3), 7.11 (Si-CH_2) ppm.

7.5.10 Hydrosilylation of 1,4-Vinylaniline with PMDS

0.62 g (4.2 mmol) PMDS, 0.50 g (4.2 mmol) 1,4-vinylaniline (90%) and 0.01 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. The reaction was complete after 6h at 75°C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.07 (m, 15H, Si-CH_3), 0.85 (m, 2H, Si-CH_2), 2.54 (m, 2H, CH_2), 3.53 (s, br, 2H, NH_2), 6.64 (m, 2H, Ar), 6.99 (d, 2H, Ar) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 0.35 ($SiCH_3$), 2.01 ($SiCH_3$), 20.59 (Si-CH_2), 28.35 (CH_2), 115.17, 128.44, 134.79, 144.06 (Ar) ppm. ^{29}Si-NMR (400 MHz, $CDCl_3$): δ= 7.32 (Si-CH_3), 7.44 (Si-CH_2) ppm.

Trace amounts of a Si-N addition product could be observed in all NMR spectra.

7.5.11 Hydrosilylation of 3-Butene-1-amine with PMDS

1.04 g (7.0 mmol) PMDS, 0.50 g (7.0 mmol) 3-butene-1-amine and 0.02 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. The reaction was complete after 12h at 75°C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.04 (s, 6H, Si-CH_3), 0.06 (s, 9H, Si-CH_3), 0.52 (m, 2H, Si-CH_2), 1.02 (s, br, 2H, NH_2), 1.35 (m, 2H, CH_2), 1.46 (m, 2H, CH_2), 2.68 (t, 2H, CH_2-N) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 0.03 ($SiCH_3$), 1.61 ($SiCH_3$), 17.77 (Si-CH_2), 20.23 (CH_2), 37.21 (CH_2), 41.59 (CH_2-N) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 7.00 ($SiMe_3$), 6.71 ($SiMe_2$) ppm.

7.5.12 Hydrosilylation of Allyl Methacrylate with PDMS-H_2

6.00 g (8.8 mmol) PDMS-H_2 (M= 680 g/mol), 2.34 g (18.5 mmol, 2.1 eq.) allyl methacrylate, 1.0 mg BHT (0.01 mol%) and 0.08 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst (**I**) were used. For PtO_2 (**VII**), 1.4 mg (100 ppm Pt) were used. The reaction was complete after 3h at 60°C (**I**) to 90°C (**VII**).

Methacrylpropyl-PDMS: ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.06 (m, 56H, Si-CH_3), 0.57 (m, 4H, Si-CH_2), 1.69 (m, 4H, CH_2), 1.94 (s, 6H, CH_3), 5.54 (s, 2H, C=CH_2), 6.10 (s, 2H, C=CH_2) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 0.10 ($SiCH_3$), 1.07 ($SiCH_3$), 14.16 (Si-CH_2), 18.25 (CH_3), 22.72 (CH_2), 66.90 (CH_2-O), 124.94 (C=$\underline{C}H_2$), 136.32 ($\underline{C}$=CH_2), 167.22 (C=O) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 7.22 (SiO-$\underline{Si}$-CH_2), -21.44 (SiO$\underline{Si}$O), -22.21 (SiO$\underline{Si}$OSi) ppm.

Methacrylic-PDMS: ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.06 (m, 44H, Si-CH_3), 0.32 (s, 12H, ClSi-CH_3) 1.94 (s, 6H, CH_3), 5.60 (s, 2H, C=CH_2), 6.12 (s, 2H, C=CH_2) ppm.

n-Propyl-PDMS: ^{1}H-NMR (400MHz, $CDCl_3$): δ= 0.06 (m, 56H, Si-CH_3), 0.56 (m, 4H, Si-CH_2), 0.95 (t, 6H, CH_3), 1.37 (m, 4H, CH_2) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= -8.82 (Si-OC), -21.71 (SiO$\underline{\text{Si}}$O), -22.19 (SiO$\underline{\text{Si}}$OSi) ppm.

Similar results were obtained with PtO_2.

7.5.13 Hydrosilylation of *t*-Butyl Methacrylate with PMDS

3.00 g (20.2 mmol) PMDS, 2.87 g (20.2 mmol) *t*-butyl methacrylate and 0.06 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. The reaction was complete after 2h at 75°C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.07 (s, 15H, CH_3), 0.64 (m, 1H, $SiCH_2$'), 1.01 (m, 1H, $SiCH_2$''), 1.14 (d, 3H, CH_3), 1.44 (s, 9H, ^{t}Bu-CH_3), 2.44 (m, 1H, CH) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 1.32 ($SiCH_3$), 1.91 ($SiCH_3$), 19.89 (CH_3), 22.84 (Si-CH_2), 27.67 (^{t}Bu-CH_3), 36.35 (CH), 79.17 (C_q-^{t}Bu), 177.31 (C=O) ppm.

^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 7.35 (Si-CH_3), 6.83 (Si-CH_2) ppm.

7.5.14 Hydrosilylation of *t*-Butyl Acrylate with PMDS

3.00 g (20.2 mmol) PMDS, 2.59 g (20.2 mmol) *t*-butyl acrylate and 0.06 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. The reaction was complete after 3h at 75°C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.05 (m, 15H, Si-CH_3), 1.29 (s, 9H, ^{t}Bu-CH_3), 1.41 (d, 3H, CH_3), 3.93 (q, 1H, CH) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 0.88 ($SiCH_3$), 1.86 ($SiCH_3$), 10.83 (CH_3), 28.19 (C_q-^{t}Bu), 29.18 (^{t}Bu-CH_3), 85.68 (CH), 151.42 (C_q-O) ppm.

^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 8.33 (Si-CH_3), -15.23 (Si-O) ppm.

7.5.15 Hydrosilylation of 3-Methyl-3-butenyl Methacrylate with PMDS

3-Methyl-3-butenyl methacrylate was prepared as described in [66].

1.00 g (6.75 mmol) PMDS, 0.52 g (3.37 mmol) 3-methyl-3-butenyl methacrylate and 0.02 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. The reaction was complete after 2h at 75°C. A complex mixture of all three addition types was obtained, which could not be fully assigned.

7.5.16 Hydrosilylation of Nadic Anhydride and Methyl Nadic Anhydride

1.20 g (8.93 mmol) TMDS and 2.93 g (17.87 mmol, 2 eq.) nadic anhydride, suspended in 7.0 mL toluene and 0.01 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. After 12h at 80°C a sticky turbid mixture was obtained which mainly consisted of the substrates. Similar results were obtained with 5.00 g (7.35 mmol) PMDS-H_2 (M_n= 680 g/mol), 2.75 g (15.43 mmol, 2.1 eq.) methyl nadic anhydride and 0.08 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst after 12h at 100°C.

7.5.17 Hydrosilylation of Triethoxy Vinyl Silane with PMDS

2.00 g (13.5 mmol) PMDS, 2.57 g (13.5 mmol) triethoxy vinyl silane and 0.05 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. The reaction was complete after 1h at 75°C. Yield (determined by ^{1}H- and ^{29}Si-NMR): 86% of β-product.
^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.06 (m, 15H, Si-CH_3), 0.54 (m, 4H, Si-CH_2), 1.23 (t, 9H, CH_3), 3.83 (q, 6H, CH_2-O) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 0.57 ($SiCH_3$), 1.77 ($SiCH_3$), 9.22 (Si-CH_2), 18.22 (CH_3), 58.29 (CH_2) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 7.81 (Si-CH_3), 6.74 (Si-CH_2), -45.18 (Si-OEt) ppm.

7.5.18 Hydrosilylation of Allyl Trimethoxy Silane with HexMTS

1.00 g (4.8 mmol) HexMTS, 1.63 g (10.1 mmol, 2.1 eq) allyl trimethoxy silane and 0.03 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. The reaction was complete after 1h at 75°C. Yield: 100%.
^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.03 (s, 6H, Si-CH_3), 0.08 (s, 12H, Si-CH_3), 0.55 (m, 4H, Si-CH_2), 0.61 (m, 4H, Si-CH_2), 1.37 (m, 4H, CH_2), 3.45 (s, 18H, OCH_3) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 0.18 ($SiCH_3$), 1.19 ($SiCH_3$), 13.43 (Si-CH_2), 16.68 (Si-CH_2), 22.37 (CH_2), 50.30 (OCH_3) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 6.56 (Si-CH_2), -21.37 (Si-O-$\underline{Si}$-OSi), -42.09 (Si-$(OMe)_3$) ppm.

7.5.19 Hydrosilylation of Allyl Acetate with PMDS

2.00 g (13.5 mmol) PMDS, 1.63 g (13.5 mmol) allyl acetate and 0.07 mL of a 5 mg Pt /mL hexane solution of *Karstedt's* catalyst (100 ppm Pt) were used. *Acetoxypropylpentamethyldisiloxane*: ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.07 (m, 15H, Si-CH_3), 0.52 (m, 2H, Si-CH_2), 1.66 (m, 2H, CH_2), 2.05 (s, 3H, CH_3), 4.02 (t, 2H, CH_2O) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 0.12 ($SiCH_3$), 1.82 ($SiCH_3$), 14.14 (CH_2), 20.77 (Si-CH_2), 22.62 (CH_3), 67.02 (OCH_2), 170.73 (C=O) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 7.39 (Si-CH_3), 7.06 ($SiCH_2$) ppm.

GC-MS (EI, 13.5 min) m/z= 233 [M-Me]$^+$, 175 [$EtSiMe_2OSiMe_3$]$^+$, 133 [$SiMe_2OSiMe_2$]$^+$, 117 [M-$SiMe_3$-MeCOO]$^+$, 87 [MeCOOEt]$^+$, 73 [MeCOOMe]$^+$.

Spectroscopic data of acetoxypentamethyldisiloxane (**P1**) and *n*-propylpentamethyldisiloxane (**P2**) agree with those given in 7.3.1.1.

The same product distribution was obtained when PDMS-H_2 was employed instead of PMDS and when PtO_2 (100 ppm Pt) was used as a catalyst.

7.5.20 Hydrosilylation of Allyl Benzoate with PMDS

2.00 g (13.5 mmol) PMDS, 2.19 g (13.5 mmol) allyl benzoate and 0.08 mL of a 5 mg Pt /mL hexane solution of *Karstedt's* catalyst (100 ppm Pt) were used. The very exothermic reaction was complete after 1h at 75°C.

Benzoyloxypropylpentamethyldisiloxane: ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.06 (m, 15H, Si-CH_3), 0.62 (m, 2H, Si-CH_2), 1.77 (m, 2H, CH_2), 4.28 (t, 2H, CH_2O), 7.44-8.06 (m, 5H, Ar) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 0.03 ($SiCH_3$), 1.98 ($SiCH_3$), 14.32 (CH_2), 22.85 (Si-CH_2), 67.40 (OCH_2), 128.31-132.66 (Ar), 166.53 (C=O) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 7.88 (Si-CH_3), 7.52 (Si-CH_2) ppm.

Spectroscopic data of benzoyloxypentamethyldisiloxane (**P5**) and *n*-propylpentamethyldisiloxane (**P2**) agree with those given in 7.3.1.3 and 7.3.1.1.

7.5.21 Hydrosilylation of Allyl Phenyl Acetate with PMDS

0.35 g (2.4 mmol) PMDS, 0.42 g (2.4 mmol) allyl phenyl acetate and 0.08 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst (100 ppm Pt) were used. The very exothermic reaction was complete after 1h at 75°C.

Phenylacetoxypropylpentamethyldisiloxane: ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.06 (m, 15H, Si-CH_3), 0.48 (m, 2H, Si-CH_2), 1.63 (m, 2H, CH_2), 3.62 (s, 2H, CH_2-Ar) 4.06 (t, 2H, CH_2O), 7.23-7.39 (m, 5H, Ar) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 0.05 ($SiCH_3$), 1.84 ($SiCH_3$), 14.22 (CH_2), 22.70 (Si-CH_2), 41.30 (CH_2-Ar), 67.12 (OCH_2), 126.91-134.44 (Ar), 171.12 (C=O) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 7.54 (Si-CH_3), 7.25 (Si-CH_2) ppm.

Phenylacetoxypentamethyldisiloxane: ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.06 (m, 9H, Si-CH_3), 0.24 (m, 26H, Si-CH_3), 7.23-7.39 (m, 5H, Ar) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 0.03 ($SiCH_3$), 1.50 ($SiCH_3$), 42.77 (CH_2-Ar), 126.91-134.44 (Ar), 170.90 (C=O) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 10.33 (Si-CH_3), -8.56 (Si-O) ppm.

Spectroscopic data of *n*-propylpentamethyldisiloxane (**P2**) agrees with that given in 7.3.1.1.

7.5.22 Hydrosilylation of 3-Methyl-3-butenylacetate with PMDS

3-Methyl-3-butenyl acetate was prepared from isoprenol and acetic anhydride as described in [137].

0.35 g (2.4 mmol) PMDS, 0.42 g (2.4 mmol) 3-methyl-3-butenyl acetate and 0.08 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst (100 ppm Pt) were used. The reaction was complete after 1h at 75°C. Yield: 100%.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.04 (m, 15H, Si-CH_3), 0.36 (m, 1H, Si-CH_2'), 0.53 (m, 1H, Si-CH_2''), 0.87 (d, 3H, CH_3), 1.38 (m, 1H, CH_2'), 1.53 (m, 1H, CH_2''), 1.66 (m, 1H, CH), 1.90 (s, 3H, C(O)CH_3), 3.97 (t, 2H, CH_2-O) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 1.11 ($SiCH_3$), 1.70 ($SiCH_3$), 20.59 (CH), 22.25 (C(O)$\underline{C}H_3$), 25.88 (CH_3), 26.45 (Si-CH_2), 38.57 (CH_2), 62.61 (OCH_2), 170.46 (C=O) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 6.96 (Si-CH_3), 6.42 (Si-CH_2) ppm.

Spectroscopic data for the hydrosilylation of 2-methyl-2-propenyl acetate with PMDS is given in 7.3.1.7.

7.5.23 Hydrosilylation of Allyl Polyethers with PDMS-H_2

1.67 g (2.5 mmol) PDMS-H_2 (M= 680g/mol), 11.85 g (6.4 mmol, 2.6 eq.) PEO-PPO-allylpolyether (IV=13.7, M=1850 g/mol) and 0.14 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. The initially turbid reaction mixture clears during reaction (2h at 75°C).

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.03 (m, 68H, Si-CH_3), 0.48 (m, 4H, Si-CH_2), 1.09 (m, 265H, PEO-CH_3), 1.56 (m, 4H, CH_2), 3.50 (m, 323H, PEO-CH_2, EO-CH_2, CH_2O) ppm. Small signals at 6.19, 5.92, 4.71, 4.33 and 1.56 ppm indicate the presence of 2-propenyl groups. The same reactivity was observed with a longer PEO-PPO-allyl polyether (IV=16.7) and in the presence of **III** or **VII**.

7.5.24 Hydrosilylation of Isobutyl Vinyl Ether with PMDS

5.00 g (33.7 mmol) PMDS, 3.38 g (33.7 mmol) isobutyl vinyl ether and 0.08 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. The reaction was complete after 1.5h at 75°C. Isolated yield: 8.19 g. b. p.= 30°C (1• 10^{-3} mbar).

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.07 (s, 9H, Si-CH_3), 0.08 (s, 6H, Si-CH_3), 0.90 (d, 6H, CH_3), 0.97 (t, 2H, Si-CH_2), 1.84 (m, 1H, CH), 3.15 (d, 2H, CH_2-O), 3.49 (t, 2H, CH_2-O) ppm.

7.5.25 Hydrosilylation of 4-Benzyloxy-2-methyl-1-butene with PMDS

4-Benzyloxy-2-methyl-1-butene (benzyl isoprenyl ether) was prepared according to [104]. 4.00 g (27.0 mmol) PMDS, 4.75 g (27.0mmol) benzyl isoprenyl ether and 0.09 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. The reaction was complete after 4h at 80°C. Isolated yield: 8.64 g. b. p.= 72°C (1• 10^{-3} mbar).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.07 (s, 15H, $SiCH_3$), 0.43 (m, 2H, Si-CH_2'), 0.63 (m, 2H, Si-CH_2''), 0.94 (d, 3H, CH_3), 1.52 (m, 2H, CH_2'), 1.63 (m, 2H, CH_2''), 1.80 (m, 1H, CH), 3.50 (t, 2H, O-CH_2), 4.50 (s, 2H, Ar-CH_2), 7.26-7.35 (m, 5H, Ar) ppm.

7.5.26 Hydrosilylation of Allyl Phenyl Ether with PMDS

3.00 g (20.2 mmol) PMDS, 2.71 g (20.2 mmol) allyl phenyl ether and 0.06 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. The very exothermic reaction was complete after 1h at 75°C. Isolated yield: 4.59 g. b.p.= 58°C (1• 10^{-3} mbar).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.05 (d, 15H, $SiCH_3$), 0.60 (m, 2H, $SiCH_2$), 1.78 (m, 2H, CH_2), 3.89 (t, 2H, CH_2-O), 6.85-7.26 (m, 5H, Ar) ppm.

Signals at 6.29, 6.18, 5.30, 4.80, 1.63 and 1.58 ppm were used to determine the content of *cis*- and *trans*-2-propenyl groups. The amount of *n*-propylpentamethylsiloxane and the Si-O-adduct was determined from the signals at 0.87 (CH_3) and 0.13 (O-$SiCH_3)_2$) ppm, respectively.

7.5.27 Hydrosilylation of Allyl Benzyl Ether with PMDS

2.00 g (13.5 mmol) PMDS, 2.00 g (13.5 mmol) allyl benzyl ether and 0.04 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. The reaction was complete after 1h at 75°C. Yield (determined by ^{1}H-spectroscopy): 89%

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.08 (d, 15H, Si-CH_3), 0.54 (m, 2H, Si-CH_2), 1.64 (m, 2H, CH_2), 3.46 (t, 2H, CH_2-O), 4.53 (s, 2H, CH_2-Ar), 7.27-7.37 (m, 5H, Ar) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 0.18 ($SiCH_3$), 1.84 ($SiCH_3$), 14.43 (CH_2-Si), 23.65 (CH_2), 72.81 (CH_2-Ar), 73.20 (CH_2-O), 127.44-128.24 (Ar) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 7.48 (Si-CH_3), 6.85 (Si-CH_2) ppm.

Signals at 6.33, 6.04, 4.82, 4.73, 1.60 and 1.58 ppm in the ^{1}H-NMR spectrum were used to determine the content of *cis*- and *trans*-2-propenyl groups.

7.5.28 Hydrosilylation of *n*-Octene with PMDS

5.00 g (33.7 mmol) PMDS, 3.78 g (33.7 mmol) *n*-octene and 0.09 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. The reaction was complete after 1h at 75°C. Isolated yield: 8.11 g. b.p.= 37°C (1• 10^{-3} mbar).

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.04 (s, 6H, $SiCH_3$), 0.06 (s, 9H, $SiCH_3$), 0.50 (m, 2H, $SiCH_2$), 0.89 (t, 3H, CH_3), 1.27 (t, 12H, CH_2) ppm.

7.5.29 Hydrosilylation of α-Methylstyrene with PMDS

5.00 g (33.7 mmol) PMDS, 3.98 g (33.7 mmol) α-methylstyrene and 0.09 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. The reaction was complete after 3h at 75°C. Isolated yield: 8.81 g. b.p.= 46°C (1• 10^{-3} mbar).

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.03 (s, 6H, Si-CH_3), 0.09 (s, 9H, Si-CH_3), 0.98 (m, 2H, Si-CH_2), 1.31 (t, 3H, CH_3), 2.94 (m, 1H, CH), 7.17-7.32 (m, 5H, Ar) ppm.

7.5.30 Hydrosilylation of 4-Vinyl-1-cyclohexene with PDMS-H_2

8.00 g (11.8 mmol) PDMS-H_2 (M_n= 680 g/mol), 2.55 g (23.5 mmol, 2 eq.) 4-vinyl-1-cyclohexene and 0.11 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. The reaction was complete after 2h at 75°C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.07 (m, 56H, $SiCH_3$), 0.55 (m, 4H, Si-CH_2), 1.12-2.16 (m, 18H, CH_2 and cHex), 5.68 (m, 4H, CH) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 8.20 (Si-CH_2), -21.66 (SiO-$\underline{\mathrm{Si}}$-OSi) ppm.

7.5.31 Hydrosilylation of Norbornene with PDMS-H_2

8.00 g (11.8 mmol) PDMS-H_2 (M_n= 680 g/mol), 2.21 g (23.5 mmol, 2 eq.) norbornene and 0.10 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. The reaction was complete after 2h at 75°C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.07 (m, 56H, $SiCH_3$), 0.55 (t, 2H, Si-CH), 1.08-1.60 (m, 18H, nbn), 2.25 (m, 4H, nbn-CH_2) ppm.

7.5.32 Hydrosilylation of Cyclopentene with PDMS-H_2

15.00 g (22.1 mmol) PDMS-H_2 (M_n= 680 g/mol), 3.01 g (44.1 mmol, 2 eq.) cyclopentene and 0.18 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. The reaction was complete after 4h at 75°C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.07 (m, 56H, $SiCH_3$), 0.88 (m, 2H, Si-CH), 1.24-1.85 (m, 16H, cPent) ppm.

7.5.33 Hydrosilylation of 1,1-Diphenylethene with PDMS-H_2

6.00 g (8.8 mmol) PDMS-H_2 (M_n= 680 g/mol), 3.18 g (17.7 mmol, 2 eq.) 1,1-diphenylethene and 0.09 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. The reaction needed almost 48h at 80°C to complete.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.06 (m, 56H, Si-CH_3), 1.43 (d, 4H, Si-CH_2), 4.12 (t, 2H, CH), 7.09-7.31 (m, 20H, Ar) ppm.

7.5.34 Hydrosilylation of Allyl Chloride with PDMS-H_2

20.00 g (0.029 mol) PDMS-H_2 (M= 680 g/mol), 4.95 g (0.065, 2.2 eq.) allyl chloride and 0.25 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. The reaction was performed for 5h at 65°C using a reflux condenser.

Chloro-PDMS: ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.09 (m, 44H, Si-CH_3), 0.46 (s, 12H, ClSi-CH_3) ppm.

Chloropropyl-PDMS: ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.09 (m, 56H, Si-CH_3), 0.68 (m, 4H, Si-CH_2), 1.83 (m, 4H, CH_2), 3.51 (t, 4H, CH_2Cl) ppm.

n-Propyl-PDMS: ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.09 (m, 56H, Si-CH_3), 0.56 (m, 4H, Si-CH_2), 0.98 (t, 6H, CH_3), 1.40 (m, 4H, CH_2) ppm.

7.5.35 Hydrosilylation of Allyl Isocyanate with PMDS

2.00 g (13.5 mmol) PMDS, 1.12 g (13.5 mmol) allyl isocyanate and 0.03 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. The reaction was performed in a pressure tube at 100°C for 72h.

Yield of isocyanatopropyl-PMDS (determined by ^{1}H-NMR spectroscopy): 22%.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.07 (m, 15H, Si-CH_3), 0.55 (m, 2H, Si-CH_2), 1.65 (m, 2H, CH_2), 3.27 (t, 2H, CH_2-N) ppm.

Signals of several byproducts were observed but could not be completely assigned.

7.5.36 Hydrosilylation of Acrolein Diethylacetal with PDMS-H_2

8.00 g (11.8 mmol) PDMS-H_2 (M_n= 680 g/mol), 3.06 g (23.5 mmol, 2 eq.) acrolein diethylacetal and 0.11 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. Yield (determined by ^{1}H-NMR spectroscopy): 97%. The reaction was complete after 2h at 75°C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.04 (m, 56H, Si-CH_3), 0.54 (m, 4H, Si-CH_2), 1.17 (m, 12H, CH_3), 1.59 (m, 4H, CH_2), 3.48 and 3.62 (m, 8H, CH_2-O), 4.37 (t, 2H, CH) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= 7.81 (Si-CH_2), -21.94 (SiO-$\underline{Si}$-OSi) ppm.

7.6 Determination of the Stability of Different Model Compounds

The six model compounds with different functional groups (**A**–**F**, figure 4.1) were synthesized according to 7.5.5, 7.5.24, 7.5.25, 7.5.26, 7.5.28, and 7.5.2 and purified by distillation. To determine their stability towards water, sulfuric acid and sodium hydroxide, 1.5 mL aliquots of each substance were taken and 0.5 mL H_2O (dest.), 0.5 ml sulfuric acid (0.1 M) or 0.5 mL sodium hydroxide (0.1 M) were added, respectively, and the resulting emulsions were heated to 70°C for 14d with regular shaking.

Additionally, 0.95 mL aliquots of each substance were mixed with 0.05 mL 1,8-diazabicycloundec-7-ene (DBU) or 0.05 mL methane sulfonic acid (MSA), respectively, and also heated to 70°C for 14d. Samples were taken after 1, 2, 5, 7 and 14 days and analyzed by ^{1}H-NMR spectroscopy and GC-MS.

7.7 Synthesis and Photochemical Curing of Epoxy-functional Hybrid Silicones

7.7.1 General Method for the Synthesis of Epoxy-functional Hybrid Silicones

The synthesis of the Si-H-terminated prepolymers was performed as described in section 7.4 using either a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst or a 1 mg Pt /mL dichloromethane solution of $Pt(PPh_3)_4$ to achieve 10 ppm Pt per total substrates.

The chain length was determined by ^{1}H-NMR spectroscopy, whereafter the chain-end functionalization with the unsaturated epoxide, 4-vinyl-1,2-epoxycyclohexane (VCO) or allyl glycidyl ether, was performed.

7.7.1.1 Functionalization with Vinylcyclohexene Epoxide (VCO)

Employing the same apparatus as described in 7.4, a stoichiometric amount (2 eq.) of 4-vinyl-1,2-epoxycyclohexane (VCO) was slowly added to the Si-H terminated prepolymer at 60°C *via* the dropping funnel. The reaction was slightly exothermic and the mixture was heated to 75°C for 1h to allow complete conversion. Thereafter, the reaction was allowed to cool to room temperature and all volatile components were removed *in vacuo*. The final products were obtained as pale-yellow oils and their molecular weights were determined by ^{1}H-NMR spectroscopy and gel permeation chromatography.

7.7.1.2 Functionalization with Allyl glycidyl ether (AGE)

Using the apparatus described in 7.4, an excess (2.5 eq.) of allyl glycidyl ether was slowly added to the Si-H terminated prepolymer at 60°C *via* the dropping funnel. The reaction was exothermic and the temperature was maintained at 75°C for 1h to complete the reaction. Thereafter, volatiles and isomerized allyl glycidyl ether were removed *in vacuo* at 60°C. The final products were obtained as pale-yellow oils, their molecular weights were determined by ^{1}H-NMR spectroscopy and gel permeation chromatography.

7.7.2 Synthesis of Epoxy-functional Hybrid Silicones

7.7.2.1 Synthesis of Oligomer 10a-VCO

100.0 g (0.48 mol, 6 eq.) HexMTS, 56.8 g (0.40 mol, 5 eq.) 1,4-butandiol divinyl ether, 1.57 mL of a 1 mg Pt/mL hexane solution of *Karstedt's* catalyst and 14.0 g (0.11 mol, 2 eq.) of 4-vinyl-1,2-epoxycyclohexane (VCO) were used. Yield: 169.0 g as pale-yellow oil.

M_n (determined by ^{1}H-NMR)= 2770 g/mol; M_n (determined by GPC)= 3190 g/mol

^{1}H-NMR (400 MHz, CDCl$_3$): δ= 0.05 (m, 139H, Si-CH$_3$), 0.5 (m, 4H, epoxy-CH$_2$-Si), 0.80-2.24 (m, 18H, cHex and cHex-CH$_2$), 0.99 (m, 26H, Si-CH$_2$), 1.62 (m, 26H, CH$_2$), 3.12 (m, 4H, epoxy-CH), 3.39 (m, 27H, CH$_2$-O), 3.50 (m, 27H, CH$_2$-O) ppm. ^{29}Si-NMR (80 MHz, CDCl$_3$): δ= -21.2 (-SiO-Si-OSi-), -20.9 (epoxy-SiO-Si-OSi-), 5.67 (epoxy-SiO-Si-OSi-CH$_2$), 5.80 (Si-CH$_2$), 7.45 (epoxy-SiO-Si-OSi) ppm.

7.7.2.2 Synthesis of Oligomer 10b-VCO

100.0 g (0.15 mol, 3.8 eq.) PDMS-H$_2$ (M= 680 g/mol), 15.41 g 1,4-butandiol divinyl ether (0.11 mol, 2.8 eq), 1.2 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst and 9.94 g (0.08 mol) 4-vinyl-1,2-epoxycyclohexane (VCO) were used. Yield: 123 g.

M_n (NMR)= 3130 g/mol; M_n (GPC)= 2950 g/mol

^{1}H-NMR (400 MHz, CDCl$_3$): δ= 0.05 (m, 205H, Si-CH$_3$), 0.49 (m, 4H, epoxy-CH$_2$-Si), 0.82-2.22 (m, 18H, cHex and cHex-CH$_2$), 0.99 (m, 11H, Si-CH$_2$), 1.62 (m, 11H, CH$_2$), 3.13 (m, 4H, epoxy-CH), 3.39 (m, 10H, CH$_2$-O), 3.50 (m, 11H, CH$_2$-O) ppm. ^{29}Si-NMR (80 MHz, CDCl$_3$): δ= -22.21 (-SiO-Si-OSi-), -21.61 (epoxy-SiO-Si-OSi-), 5.92 (Si-CH$_2$), 7.44 (epoxy-Si) ppm.

7.7.2.3 Synthesis of Oligomer 10c-AGE

10.0 g (48.0 mmol, 8 eq.) HexMTS, 5.85 g 1,4-butandiol divinyl ether (41.1 mmol, 7 eq.), 0.16 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst and 1.48 g (13.0 mmol) allyl glycidyl ether were used. Yield: 16.6 g.

M_n (NMR)= 3050 g/mol; M_n (GPC)= 3770 g/mol

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.04 (m, 150H, Si-CH_3), 0.53 (m, 4H, CH_2-$C\underline{H}_2$-Si), 0.98 (m, 28H, Si-CH_2), 1.62 (m, 34H, CH_2), 2.60 (m, 2H, CH-epoxy), 2.79 (t, 2H, CH-epoxy), 3.14 (m, 2H, epoxy-CH), 3.40 (m, 32H, CH_2-O and O-$C\underline{H}_2$-CH_2), 3.49 (m, 31H, CH_2-O and epoxy-CH), 3.70 (m, 2H, epoxy-$C\underline{H}_2$-O) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= -20.79 (epoxy-SiO-$\underline{Si}$-OSi-), -20.67 (-SiO-$\underline{Si}$-OSi-),5.72 (epoxy-SiO-Si-O$\underline{Si}$-CH_2), 5.87 (Si-CH_2), 7.58 (epoxy-$\underline{Si}$O-S$\underline{i}$-OSi) ppm.

7.7.2.4 Synthesis of Oligomer 11a-VCO

100.0 g (0.48 mol, 5 eq.) HexMTS, 77.61 g triethylene glycol divinyl ether (0.38 mmol, 4 eq.), 0.36 mL of a 5 mg Pt /mL hexane solution of *Karstedt's* catalyst and 17.30 g (0.14 mmol) 4-vinyl-1,2-epoxycyclohexane (VCO) were used. Yield: 192 g.

M_n (NMR)= 2550 g/mol; M_n (GPC)= 2670 g/mol

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.04 (m, 105H, Si-CH_3), 0.47 (m, 4H, epoxy-CH_2-Si), 0.80-2.24 (m, 18H, cHex and cHex-CH_2), 1.00 (m, 19H, Si-CH_2), 3.12 (m, 4H, epoxy-CH), 3.53 (m, 39H, CH_2-O), 3.63 (m, 39H, CH_2-O) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= -21.24 (epoxy-SiO-$\underline{Si}$-OSi-), -20.97 (-SiO-$\underline{Si}$-OSi-), 5.49 (epoxy-SiO-Si-O$\underline{Si}$-CH_2), 5.64 (Si-CH_2), 7.37 (epoxy-$\underline{Si}$O-S$\underline{i}$-OSi) ppm.

7.7.2.5 Synthesis of Oligomer 11b-VCO

100.0 g (0.15 mol, 3.6 eq.) PDMS-H_2 (M= 680 g/mol), 21.48 g triethyleneglycol divinyl ether (0.11 mol, 2.6 eq), 0.5 mL of a 5 mg Pt /mL hexane solution of *Karstedt's* catalyst and 10.08 g (0.08 mol) 4-vinyl-1,2-epoxycyclohexane (VCO) were used. Yield: 130 g.

M_n (NMR)= 3160 g/mol; M_n (GPC)= 2980 g/mol

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.04 (m, 198H, Si-CH_3), 0.48 (m, 4H, epoxy-CH_2-Si), 0.80 -2.22 (m, 18H, cHex and cHex-CH_2), 1.01 (m, 10H, Si-CH_2), 3.13 (m, 4H, epoxy-CH), 3.55 (m, 20H, CH_2-O), 3.65 (m, 20H, CH_2-O) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= -22.12 (-SiO-$\underline{Si}$-OSi-), -21.42 (epoxy-SiO-$\underline{Si}$-OSi-), 6.54 (Si-CH_2), 5.71 (epoxy-$\underline{Si}$O-Si-OSi) ppm.

7.7.2.6 Synthesis of Oligomer 12a-VCO

100.0 g (0.48 mol, 6.5 eq.) HexMTS, 64.22 g freshly distilled 1,3-diisopropenylbenzene (0.41 mmol, 5.5 eq.), 0.33 mL of a 5 mg Pt /mL hexane solution of *Karstedt's* catalyst and 16.17 g (0.13 mmol) 4-vinyl-1,2-epoxycyclohexane (VCO) were used. Yield: 176 g.
M$_n$ (NMR)= 3050 g/mol; M$_n$ (GPC)= 2950 g/mol
^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.00 (m, 149H, Si-CH_3), 0.49 (m, 4H, epoxy-CH_2-Si), 0.80-2.23 (m, 18H, cHex and cHex-CH_2), 0.97 (m, 27H, Si-CH_2), 1.27 (m, 43H, CH_3), 2.90 (m, 14H, CH), 7.02-7.17 (m, 28H, Ar) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= -21.29 (-SiO-Si-OSi-), -21.17 (epoxy-SiO-Si-OSi-), 6.54 (Si-CH_2), 6.63 (epoxy-SiO-Si-OSi-CH_2), 7.47 (epoxy-SiO-Si-OSi) ppm.

7.7.2.7 Synthesis of Oligomer 12b-VCO

100.0 g (0.15 mol, 3.7 eq.) PDMS-H_2 (M= 680 g/mol), 16.98 g 1,3-diisopropenyl benzene (0.11 mol, 2.7 eq), 0.25 mL of a 5 mg Pt /mL hexane solution of *Karstedt's* catalyst and 9.23 g (0.07 mol) 4-vinyl-1,2-epoxycyclohexane (VCO) were used. Yield: 124 g.
M$_n$ (NMR)= 3280 g/mol; M$_n$ (GPC)= 3280 g/mol
^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.02 (m, 217H, Si-CH_3), 0.49 (m, 4H, epoxy-CH_2-Si), 0.79 -2.20 (m, 18H, cHex and cHex-CH_2), 0.95 (m, 11H, Si-CH_2), 1.26 (m, 17H, CH_3), 2.88 (m, 6H, CH), 3.13 (m, 4H, epoxy-CH), 7.00-7.16 (m, 11H, Ar) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= -22.09 (-SiO-Si-OSi-), -21.75 (epoxy-SiO-Si-OSi-), 6.65 (Si-CH_2), 7.62 (epoxy-SiO-Si-OSi) ppm.

7.7.2.8 Synthesis of Oligomer 13a-VCO

4.0 g (19.2 mmol, 3 eq.) HexMTS, 1.77 g 1,9-decadiene (12.8 mmol, 2 eq.), 0.07 mL of a 1 mg Pt /mL hexane solution of $Pt(PPh_3)_4$ and 1.21 g (9.7 mmol) 4-vinyl-1,2-epoxycyclohexane (VCO) were used. Yield: 6.4 g.
M$_n$ (NMR)= 1266 g/mol; M$_n$ (GPC)= 1780 g/mol
^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.01 (m, 59H, Si-CH_3), 0.52 (m, 13H, Si-CH_2), 0.80-2.23 (m, 18H, cHex and cHex-CH_2), 1.29 (m, 37H, CH_2), 3.13 (m, 4H, epoxy-CH) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= -21.52 (epoxy-SiO-Si-OSi-), -21.37 (-SiO-Si-OSi-), 7.23 (Si-CH_2), 7.33 (epoxy-SiO-Si-OSi-CH_2), 7.37 (epoxy-SiO-Si-OSi) ppm.

7.7.2.9 Synthesis of Oligomer 13b-VCO

5.00 g (8.62 mmol, 3 eq.) PDMS-H_2 (M= 580 g/mol), 0.79 g 1,9-decadiene (5.75 mmol, 2 eq), 0.06 mL of a 1 mg Pt /mL hexane solution of $Pt(PPh_3)_4$ and 0.59 g (4.72 mol) 4-vinyl-1,2-epoxycyclohexane (VCO) were used. Yield: 6.24 g.

M_n (NMR)= 2470 g/mol; M_n (GPC)= 3320 g/mol
^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.06 (m, 158H, Si-CH_3), 0.51 (m, 13H, Si-CH_2), 0.80-2.20 (m, 18H, cHex and cHex-CH_2), 1.29 (m, 39H, CH_2), 3.13 (m, 4H, epoxy-CH) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= -22.93 (-SiO-$\underline{Si}$-OSi-), -21.54 (epoxy-SiO-$\underline{Si}$-OSi-), 7.58 (Si-CH_2), 7.71 (epoxy-$\underline{Si}$O-S$\underline{i}$-OSi) ppm.

7.7.2.10 Synthesis of Oligomer 13c-VCO

4.0 g (19.2 mmol, 17 eq.) HexMTS, 2.50 g 1,9-decadiene (18.1 mmol, 16 eq.), 0.06 mL of a 1 mg Pt /mL hexane solution of $Pt(PPh_3)_4$ and 0.30 g (2.42 mmol) 4-vinyl-1,2-epoxycyclohexane (VCO) were used. Yield: 6.7 g.
M_n (NMR)= 6170 g/mol; M_n (GPC)= 6210 g/mol
^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.03 (m, 312H, Si-CH_3), 0.52 (m, 69H, Si-CH_2), 0.81-2.23 (m, 18H, cHex and cHex-CH_2), 1.29 (m, 271H, CH_2), 3.14 (m, 4H, epoxy-CH) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= -21.42 (-SiO-$\underline{Si}$-OSi-), -21.27 (epoxy-SiO-$\underline{Si}$-OSi-), 7.32 (Si-CH_2), 7.43 (epoxy-SiO-Si-O$\underline{Si}$-CH_2), 7.45 (epoxy-$\underline{Si}$O-S$\underline{i}$-OSi) ppm.

7.7.2.11 Synthesis of Oligomer 13d-VCO

5.00 g (8.62 mmol, 20 eq.) PDMS-H_2 (M= 580 g/mol), 1.13 g 1,9-decadiene (8.19 mmol, 19 eq), 0.06 mL of a 1 mg Pt /mL hexane solution of $Pt(PPh_3)_4$ and 89 mg (0.72 mmol) 4-vinyl-1,2-epoxycyclohexane (VCO) were used. Yield: 6.16 g.
M_n (NMR)= 17150 g/mol; M_n (GPC)= 19400 g/mol
^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.04 (m, 1160H, Si-CH_3), 0.53 (m, 90H, Si-CH_2), 0.77 - 2.24 (m, 18H, cHex and cHex-CH_2), 1.29 (m, 377H, CH_2), 3.13 (m, 4H, epoxy-CH) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= -21.92 (-SiO-$\underline{Si}$-OSi-), -21.53 (epoxy-SiO-$\underline{Si}$-OSi-), 7.58 (Si-CH_2), 7.70 (epoxy-$\underline{Si}$O-S$\underline{i}$-OSi) ppm.

7.7.2.12 Synthesis of Oligomer 13e-AGE

4.00 g (19.2 mmol, 3 eq.) HexMTS, 1.77 g 1,9-decadiene (12.8 mmol, 2 eq.), 0.06 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst and 1.27 g (11.1 mmol) allyl glycidyl ether were used. Yield: 6.89 g.
M_n (NMR)= 1300 g/mol; M_n (GPC)= 1710 g/mol
^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.05 (m, 65H, Si-CH_3), 0.52 (m, 13H, CH_2-Si), 1.27 (m, 40H, CH_2), 1.62 (m, 4H, CH_2), 2.61 (m, 2H, CH-epoxy), 2.79 (t, 2H, CH-epoxy), 3.14 (m, 2H, epoxy-CH), 3.44 (m, 2H, CH_2-O), 3.68 (m, 2H, epoxy-C$\underline{H}_2$-O) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= -21.48 (epoxy-SiO-$\underline{Si}$-OSi-), -21.20 (-SiO-$\underline{Si}$-OSi-), 7.27 (Si-CH_2), 7.34 (epoxy-SiO-Si-O$\underline{Si}$-CH_2), 7.40 (epoxy-$\underline{Si}$O-S$\underline{i}$-OSi) ppm.

7.7.3 Monitoring of the Photopolymerization by Optical Pyrometry

The photoinitiator, *bi*s(dodecylphenyl)iodonium hexafluoridoantimonate (UV 9380C), 50% solution in propylene carbonate, was provided as a gift from the Silicones Department of the General Electric Corporation. This photoinitiator was prepared by the reaction of potassium iodate with a mixture of C10-C14 alkylated benzenes in which the alkyl groups were highly branched.[139] For this reason, photoinitiator UV 9380C consists of a complex mixture of related di(alkylphenyl)iodonium hexafluoridoantimonate salts. (4-*n*-Octyloxyphenyl)phenyliodonium hexafluoridoantimonate (IOC-8) and diphenyliodonium tetrakis(pentafluorophenyl)borate (DPI-TFPB) were prepared as described by *Crivello et al*.[140]

The apparatus and methods employed for the monitoring of the photopolymerizations carried out by optical pyrometry were described by *Crivello et al.* in 2003.[141] Samples for analysis were prepared as follows: homogeneous solutions of the desired epoxy functional hybrid silicone with the designated photoinitiator (2 wt%) were prepared (usually 0.5 g of epoxy functional hybrid silicone were used). A 10 µm thick fluorinated polyethylene film was first laid down and a thin polyester fiber mesh, serving as a spacer, was placed on top of the polymer film. The liquid sample was placed onto this assembly and an identical layer of fluorinated polyethylene film was placed over the top. The resulting sample sandwich was mounted in a 2.0 cm x 2.0 cm plastic slide holder and irradiated with UV light from a UVEX SCU-110 mercury lamp and directed *via* a 95-cm liquid light pipe onto the sample. The wavelengths transmitted through the liquid optic light guide are from 220-650 nm. The end of the wand was placed at a predetermined distance and directed at an incident angle of 45° onto the sample window. A Raytek Marathon Series MM Infrared Thermometer (Raytek, Co., Champlain, NY) was used to monitor the temperature of the sample in real-time. This instrument has a sensitivity of ±0.5°C with an operating temperature range of -40 to 800°C, a response time of 120 ms and the capability of 10 temperature measurements per second. The instrument is responsive to infrared radiation in the range of 8-14 µm. Using a laser aligner, the focal point of the sensor of the OP instrument was centered in the middle of the sample window. All optical pyrometry experiments were conducted at ambient temperature (21–25°C). In each case, the samples were allowed to equilibrate and establish a flat baseline for 20 s before UV irradiation was started. Temperature data were collected at a rate of one measurement per second and were directly recorded and downloaded to a Lenovo ThinkPad personal computer for analysis. All experiments were performed at a light intensity of 2340 mJ/cm^2 min.

7.8 Thermal Curing of Epoxy-functional Hybrid Silicones

7.8.1 Attempts of Curing of Epoxycyclohexyl-functional Hybrid Silicones 10a-VCO–12b-VCO with DETA

10.00 g (3.6 mmol) **10a-VCO** (M= 2770 g/mol), 0.15 g diethylenetriamine (1.44 mmol, 0.4 eq.), 1.00 g benzylalcohol (10 wt%) and 0.33 g Ancamine K54 (3 wt%) were mixed in a plastic vial for 5 min and the resulting turbid mixture was cast on a teflon plate or a PE-foil with a thickness of 200 µm with a drawdown bar. Especially on teflon, no complete wetting was obtained, because of contraction of the liquid. The films were stored either at ambient (25°C) or elevated temperature (100°C) for 7d. In both cases, no curing or change in viscosity was observed. Monitoring the reaction by ^{1}H-NMR spectroscopy revealed no epoxy-ring opening reaction after 7d at 100°C.

Also with all other hybrid silicones **10b-VCO–12b-VCO**, which were treated in the same way, no curing occurred. The use of $BF_3 \bullet Et_2O$ instead of Ancamine K54 led to a spontaneous crosslinking of the hybrid silicone.

7.8.2 Attempts of Curing of 50/50 Mixtures of Epoxycyclohexyl-functional Hybrid Silicones 10a-VCO–12b-VCO and Conventional Epoxy Resins

7.8.2.1 Mixtures with Poly(phenylglycidyl ether)-*co*-formaldehyde

4.00 g (1.4 mmol) **10a-VCO** (M= 2770 g/mol), 4.00 g poly(phenylglycidyl ether)-*co*-formaldehyde (Novolak-glycidyl ether, M= 570 g/mol, functionality= 3.2), 0.52 g diethylenetriamine, 0.85 g benzylalcohol (10 wt%), 0.28 g Ancamine K54 (3 wt%) and 0.03 g Byk 354 (0.3 wt%) were mixed in a plastic vial for 5 min. Very poor miscibility was observed even when the mixture was heated to 80°C. The resulting turbid mixture was cast on a teflon plate or a PE-foil with a thickness of 200 µm with a drawdown bar and the resulting films were stored at ambient (25°C) or elevated (100°C) temperature. After 50 min a skin formation of the poly(phenylglycidyl ether)-*co*-formaldehyde component was observed and a highly inhomogeneous film with brittle islands of cured Novolak-glycidyl ether within the liquid hybrid silicone was obtained. No curing of the hybrid silicone component occurred within 5d at elevated temperatures (100°C).

Same results were obtained with hybrid silicones **10b-VCO–12b-VCO**. The best miscibility was obtained with **12a-VCO**. All attempts to improve the miscibility of the two components by addition of dipropylene glycol dimethyl ether (Proglyde-DMM, 5 wt%), xylene (2.5 wt%) or Byk 57 (0.3 wt%) failed.

7.8.2.2 Mixtures with *bis*-Glycidyl-poly(bisphenol-A-*co*-epichlorohydrin)

4.00 g (1.3 mmol) **12a-VCO** (M= 3050 g/mol), 4.00 g (10.6 mmol) *bis*-glycidyl-poly(bisphenol-A-*co*-epichlorohydrin) (M= 377 g/mol), 0.49 g diethylenetriamine, 0.85 g benzylalcohol (10 wt%), 0.25 g Ancamine K54 (3 wt%) and 0.03 g Byk 354 (0.3 wt%) were mixed in a plastic vial for 5 min. Slightly better miscibility than with Novolak-glycidyl ether was observed, but again a highly inhomogeneous film with brittle islands of cured conventional epoxy resin within the liquid hybrid silicone was obtained.
Same results were obtained with **10b-VCO–12b-VCO**.

7.8.3 Curing of Glycidyl-functional Hybrid Silicones

HexMTS-AGE was synthesized as described in 7.5.7.

7.8.3.1 Curing of HexMTS-AGE with DETA, EDA or IPDA

1.00 g (2.29 mmol) **HexMTS-AGE**, 0.10 g benzylalcohol (10 wt%), 0.03 g Ancamine K54 (3 wt%) and 95 mg DETA (0.92 mmol, 0.4 eq.), 68.5 mg EDA (1.14 mmol, 0.5 eq.) or 194 mg IPDA (1.14 mmol, 0.5 eq.), respectively, were mixed in a glass vial for 5 min and the resulting turbid mixture was poured on a watch glass and stored at 100°C. Best miscibility was observed with IPDA. In all cases, complete curing was achieved in 4h.

7.8.3.2 Curing of 10c-AGE with DETA, EDA or IPDA

1.00 g (0.33 mmol) **10c-AGE** (M= 3050 g/mol), 0.10 g benzylalcohol (10 wt%), 0.03 g Ancamine K54 (3 wt%) and 13.5 mg DETA (0.13 mmol, 0.4 eq.), 9.9 mg EDA (0.16 mmol, 0.5 eq.) or 27.9 mg IPDA (0.16 mmol, 0.5 eq.), respectively, were mixed in a glass vial for 5 min and the resulting turbid mixture was poured on a watch glass and stored at 100°C. Complete curing was achieved in 4h (DETA) to 24h (IPDA).

7.8.3.3 Curing of a 50/50 Mixture of HexMTS-AGE and *bis*-Glycidyl-poly(bisphenol-A-*co*-epichlorohydrin)

1.00 g (2.29 mmol) **HexMTS-AGE**, 1.00 g (2.65 mmol), *bis*-glycidyl-poly(bisphenol-A-*co*-epichlorohydrin), 0.20 g DETA (1.98 mmol, 0.4 eq.), 0.20 g benzylalcohol (10 wt%) and 0.06 g Ancamine K54 (3 wt%) were mixed in a glass vial for 5 min and the resulting mixture was poured on a PE-foil and stored at ambient temperature (25°C). Complete and almost homogeneous curing was achieved in 3d.

7.9 Synthesis and Curing of Amino-terminated Hybrid Silicones

The synthesis of the Si-H-terminated hybrid silicones was performed as described in section 7.4 using *Karstedt's* catalyst. The chain length was determined by ^{1}H-NMR spectroscopy and the resulting average degree of polymerization m was used for the calculation of the molecular weight. Subsequently, the chain-end functionalization was performed by addition of 4 eq. of allyl amine and one drop of an undiluted solution of *Karstedt's* catalyst (21% Pt in xylene). The reaction mixture was heated to 40°C for 12h. Afterwards, excessive allyl amine was removed *in vacuo* and the final molecular weight was determined by ^{1}H-NMR spectroscopy. In all cases, the final degree of polymerization m was somewhat higher than for the Si-H-terminated prepolymers.

7.9.1 Synthesis of Oligomer 14a-NH$_2$

50.0 g (0.24 mol, 9 eq.) HexMTS, 30.31 g 1,4-butandiol divinyl ether (0.21 mmol, 8 eq.) and 0.81 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used for the preparation of the α,ω-SiH-prepolymer. Complete functionalization was achieved using 6.02 g (0.11 mol, 4 eq.) allyl amine and one drop of an undiluted solution of *Karstedt's* catalyst (21% Pt in xylene). Yield: 81 g.

M_n (determined by ^{1}H-NMR)= 3620 g/mol; Degree of functionalization: 100%.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.09 (m, 187H, Si-CH_3), 0.52 (m, 4H, aminopropyl-CH_2-Si), 0.98 (m, 39H, Si-CH_2 and NH_2), 1.44 (m, 4H, aminopropyl-CH_2), 1.61 (m, 38H, CH_2), 2.66 (t, 4H, CH_2-NH_2), 3.38 (m, 38H, CH_2-O), 3.49 (m, 37H, CH_2-O) ppm.

7.9.2 Synthesis of Oligomer 14b-NH$_2$

75.0 g (0.13 mol, 4.5 eq.) PDMS-H_2, 14.30 g 1,4-butandiol divinyl ether (0.10 mol, 3.5 eq.) and 0.89 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used for the preparation of the α,ω-SiH-prepolymer. Complete functionalization was achieved using 6.76 g (0.12 mol, 4 eq.) allyl amine and one drop of an undiluted solution of *Karstedt's* catalyst (21% Pt in xylene). Yield: 92 g.

M_n (NMR)= 3840 g/mol; Degree of functionalization: 100%.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.07 (m, 262H, Si-CH_3), 0.53 (m, 4H, aminopropyl-CH_2-Si), 0.99 (m, 19H, Si-CH_2 and NH_2), 1.45 (m, 4H, aminopropyl-CH_2), 1.62 (m, 18H, CH_2), 2.66 (t, 4H, CH_2-NH_2), 3.39 (m, 17H, CH_2-O), 3.50 (m, 17H, CH_2-O) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= -22.98 (-SiO-$\underline{\text{Si}}$-OSi-), -21.37 (aminopropyl-SiO-$\underline{\text{Si}}$-OSi-), 6.09 (Si-CH_2), 7.65 (aminopropyl-$\underline{\text{Si}}$O-Si-OSi) ppm.

7.9.3 Synthesis of Oligomer 15a-NH$_2$

32.50 g (0.16 mol, 7 eq.) HexMTS, 27.02 g triethylene glycol divinyl ether (0.13 mol, 6 eq.) and 0.59 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used for the preparation of the α,ω-SiH-prepolymer. Complete functionalization was achieved using 5.10 g (89.3 mmol, 4 eq.) allyl amine and one drop of an undiluted solution of *Karstedt's* catalyst (21% Pt in xylene). Yield: 61 g.

M_n (NMR)= 3740 g/mol; Degree of functionalization: 100%.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.05 (m, 174H, Si-CH_3), 0.51 (m, 4H, aminopropyl-CH_2-Si), 1.00 (m, 37H, Si-CH_2 and NH_2), 1.44 (m, 4H, aminopropyl-CH_2), 2.66 (t, 4H, CH_2-NH_2), 3.54 (m, 63H, CH_2-O), 3.64 (m, 67H, CH_2-O) ppm.

7.9.4 Synthesis of Oligomer 15b-NH$_2$

60.0 g (0.10 mol, 4 eq.) PDMS-H_2 (MW=580 g/mol), 15.69 g triethylene glycol divinyl ether (77.6 mmol, 3 eq.) and 0.76 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used for the preparation of the α,ω-SiH-prepolymer. Complete functionalization was achieved using 5.34 g (93.5 mmol, 4 eq.) allyl amine and one drop of a undiluted solution of *Karstedt's* catalyst (21% Pt in xylene). Yield: 78 g.

M_n (NMR)= 3810 g/mol; Degree of functionalization: 100%.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.06 (m, 259H, Si-CH_3), 0.52 (m, 4H, aminopropyl-CH_2-Si), 1.01 (m, 19H, Si-CH_2 and NH_2), 1.45 (m, 4H, aminopropyl-CH_2), 2.66 (t, 4H, CH_2-NH_2), 3.55 (m, 30H, CH_2-O), 3.63 (m, 31H, CH_2-O) ppm.

7.9.5 Synthesis of Oligomer 16a-NH$_2$

40.0 g (0.19 mol, 6.5 eq.) HexMTS, 25.67 g freshly destilled 1,3-diisopropenylbenzene (0.16 mol, 5.5 eq.) and 0.66 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used for the preparation of the α,ω-SiH-prepolymer. Complete functionalization was achieved using 5.61 g (98.3 mmol, 4 eq.) allyl amine and one drop of a undiluted solution of *Karstedt's* catalyst (21% Pt in xylene). Yield: 68 g.

M_n (NMR)= 3040 g/mol; Degree of functionalization: 100%.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.01 (m, 148H, Si-CH_3), 0.54 (m, 4H, aminopropyl-CH_2-Si), 0.98 (m, 31H, Si-CH_2 and NH_2), 1.28 (m, 43H, CH_3), 1.46 (m, 4H, aminopropyl-CH_2), 2.67 (t, 4H, CH_2-NH_2), 2.90 (m, 14H, CH), 7.00-7.19 (m, 29H, Ar) ppm.

7.9.6 Synthesis of Oligomer 16b-NH_2

50.0 g (86.2 mmol, 4 eq.) PDMS-H_2 (MW= 580 g/mol), 10.23 g freshly distilled 1,3-diisopropenylbenzene (64.7 mmol, 3 eq.) and 0.66 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used for the preparation of the α,ω-SiH-prepolymer. Complete functionalization was achieved using 4.18 g (73.2 mmol, 4 eq.) allyl amine and one drop of an undiluted solution of *Karstedt's* catalyst (21% Pt in xylene). Yield: 62 g.

M_n (NMR)= 3440 g/mol; Degree of functionalization: 100%.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.06 (m, 232H, Si-CH_3), 0.53 (m, 4H, aminopropyl-CH_2-Si), 0.96 (m, 19H, Si-CH_2 and NH_2), 1.26 (m, 23H, CH_3), 1.46 (m, 4H, aminopropyl-CH_2), 2.67 (t, 4H, CH_2-NH_2), 2.89 (m, 7H, CH), 6.99-7.18 (m, 14H, Ar) ppm.

7.9.7 Curing of Amino-termiated Hybrid Silicones with Conventional Epoxy Resins

7.9.7.1 Attempt of Curing Novolak-glycidyl ether with 14a-NH_2

3.62 g **14a-NH_2** (M= 3620 g/mol, f= 4, 1.0 mmol), 0.63 g Novolak-glycidyl ether (M= 570 g/mol, f= 3.6, 1.11 mol), 0.49 g (10 wt%) benzylalcohol and 0.15 g (3 wt%) Ancamine K54 were mixed in a plastic vial for 5 min using a speedmixer and the resulting turbid mixture was poured on a PE-foil and stored at ambient temperature for 7d. Complete phase separation occurred and no cured product was obtained.

7.9.7.2 Attempt of Curing of Glycidyl-BPA with 14a-NH_2, 14b-NH_2 or 15a-NH_2

In a plastic vial, 1.0 mmol of the amino-terminated hybrid silicones **14a-NH_2**, **14b-NH_2** or **15a-NH_2**, respectively, was mixed with a stoichiometric (NH:epoxy=1:1) or substoichiometric amount of *bis*-glycidyl-poly(bisphenol-A-*co*-epichlorohydrin (M= 377 g/mol, f=2), according to table 5.6. 10 wt% of the solvent (isopropanol or benzylalcohol), 3 wt% of Ancamine K54 and, if desired 0.1 % of Byk 354 were added. The resulting turbid mixture was stirred for 5 min in a speedmixer and, thereafter, poured on a PE-foil and stored at ambient temperature for 7d. No cured product was obtained due to phase separation.

7.9.7.3 Curing of HexMTS-AGE with 14a-NH_2, 14b-NH_2 or 15a-NH_2

In a plastic vial, 1.0 mmol of the amino-terminated hybrid silicones **14a-NH_2**, **14b-NH_2** or **15a-NH_2**, respectively, was mixed with a stoichiometric (NH:epoxy=1:1) or substoichiometric amount of **HexMTS-AGE** (M= 436 g/mol, f=2), according to table 5.7. 10 wt% of the solvent (isopropanol, benzylalcohol or methyl *tert*-butyl ether), 3 wt% Ancamine K54 and, if desired, 0.1 % Byk 354 or Byk 57 were added. The resulting turbid mixture was stirred for 5 min in a speedmixer and, thereafter, poured on a PE-foil and stored at standard climate (23°C, 50% rel. humidity) for 7d.

For example, for curing **14a-NH$_2$** with **HexMTS-AGE** according to entry 2, table 5.7, 3.62 g **14a-NH$_2$**, 0.87 g **HexMTS-AGE**, 0.52 g benzylalcohol, 0.15 g Ancamine K54 and 5 mg Byk 354 were used.

7.9.7.4 Preparation of Filled Films using HexMTS-AGE and 14a-NH$_2$, 14b-NH$_2$ or 15a-NH$_2$

1.0 mmol of the amino-terminated hybrid silicones **14a-NH$_2$**, **14b-NH$_2$** or **15a-NH$_2$**, respectively, 0.5 mmol of **HexMTS-AGE**, 10 wt% benzylalcohol, 3 wt% Ancamine K54, 0.1% Byk 354, the corresponding amount of filling material and, if desired Anti-terra U80, according to table 5.8, were mixed in a plastic vial for 5 min using a speedmixer and, thereafter, poured or coated on a PE-foil and stored at standard climate for 7d.

For example, for entry 7 (table 5.8), 3.84 g **14b-NH$_2$**, 0.87 g **HexMTS-AGE**, 0.81 g Aerosil 812S (10 wt%), 0.54 g benzylalcohol, 0.16 g Ancamine K54 and 5 mg Byk 354 were used. For entry 9, table 5.8, 3.84 g **14b-NH$_2$**, 0.87 g **HexMTS-AGE**, 0.54 g benzylalcohol, 0.16 g Ancamine K54, 5 mg Byk 354 and 5.41 g Omyalite 95T (50% in total) were used.

7.9.8 Application-technological Tests for Epoxy-amine Coatings

The following formulation was used for all application-technological tests:

13.5 mmol of the amino-terminated hybrid silicone **14a-NH$_2$–16b-NH$_2$** (1 eq.) and a stoichiometric amount of **HexMTS-AGE** (27.0 mmol, 2 eq.), 10 wt% benzylalcohol, 3 wt% Ancamine K54, 0.1 % Byk 354 and 0.5% Anti-terra U 80 were mixed in a plastic vial using a speedmixer. An equivalent amount of silica flour SIKRON SF 600 was added in two portions; after each addition the mixture was mixed for 5 min.

For example, 48.87 g **14a-NH$_2$**, 11.77 g **HexMTS-AGE**, 6.97 g benzylalcohol, 2.09 g Ancamine K54, 69.70 g SIKRON SF 600, 0.14 g Byk 354 and 0.70 g Anti-terra U 80 were used.

The resulting mixture was either poured on a grit-blasted concrete plate to determine pull-off adhesion and penetration depth or poured into a mold to obtain the test specimen to determine tensile strength and elongation-to-break.

7.9.8.1 Determination of Tensile strength, Elongation-to-break and Shore-A-hardness

Tensile-strength (F_{MAX}) and elongation-to-break (ε-F_{MAX}) were determined on the basis of DIN EN ISO 527-1 using a tensile testing maschine Zwicki 1120 type Z2.5/TN1P with a prestress of 0.2 N and a position-controlled testing speed of 1.0 mm/min. For each hybrid silicone binder **14a-NH_2–16a-NH_2**, three dumb-bell shaped test specimen were prepared according to DIN EN ISO 527-2 (specimen 5A) and the average is reported. The multipurpose test specimen were 75 mm long, with the center section being 4 mm wide, 1.5 - 2.2 mm thick and 20 mm long (gauche lengths). All samples were conditioned at standard climate for 7d. The test specimen of **14a-NH_2**, **15a-NH_2** and **16a-NH_2** were additionally stored at 80°C for 7d.

The test specimen were also used to determine the Shore-A-hardness according to DIN EN ISO 868 using a Zwick 3130 durometer.

7.9.8.2 Determination of Pull-off Adhesion

The pull-off adhesion on concrete was determined on the basis of DIN EN 1542. Six grit-blasted concrete slabs (20x 25 cm test surface) were coated with the six different binders **14a-NH_2**–**16b-NH_2** using the standard formulation described above. The amount per plate is given in table 5.11. All plates were conditioned at standard climate for 28d and at 80°C for additional 7d to achieve complete curing. Five circular steel dollies (Ø = 50 mm) were used per plate and adhered to the surface using a cold curing two-part methacrylate adhesive (Araldite 2047-1). The adhesive was allowed to dry for 2h, whereafter 5 mm deep drill holes were drilled around each dolly. The pull-off adhesion was determined using a BPS Wenningsen’s F15D Easy M200 pull-off equipment with a testing force of 100 N/s.

7.9.8.3 Determination of the Penetration Depth

To determine the penetration depth of the epoxy-amine coatings derived from **14a-NH_2**–**16b-NH_2**, small plates (5x5 cm) of grit-blasted concrete were coated with a thickness of 1-2 mm using the standard formulation and after complete curing (7d standard climate, 7d 80°C) cut into pieces with an angle grinder. Attempts to visualize the penetration by dyeing the mineral substrate failed.

7.10 Synthesis and Curing of Trimethoxysilyl-terminated Hybrid Silicones

The synthesis of the Si-H-terminated prepolymers was performed as described in section 7.4 using *Karstedt's* catalyst. The chain length was determined by ^{1}H-NMR spectroscopy and the resulting average degree of polymerization m was used for the calculation of the molecular weight. Subsequently, the chain-end functionalization was performed by adding 2 eq. of allyl trimethoxysilane. The reaction was slightly exothermic and the reaction mixture was heated to 75°C for 1h to allow complete conversion. Thereafter, the reaction was allowed to cool to room temperature and volatiles were removed *in vacuo*. The final products were obtained as pale-yellow oils. Final degrees of functionalization and molecular weights were determined by ^{1}H-NMR spectroscopy.

7.10.1 Synthesis of HexMTS-TMS

10.00 g (48 mmol) HexMTS, 15.57 g allyl trimethoxy silane (96 mmol, 2 eq.) and 0.3 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst were used. Yield: 15 g.
Degree of functionalization: 100%.
^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.01 (s, 6H, Si-CH_3), 0.06 (m, 12H, Si-CH_3), 0.63 (m, 4H, TMS-propyl-CH_2-Si), 0.72 (m, 4H, $C\underline{H}_2$-Si$(OMe)_3$), 1.47 (m, 4H, TMS-propyl-CH_2), 3.56 (s, 18H, OMe) ppm. ^{13}C-NMR (400 MHz, $CDCl_3$, δ): 0.18 (Si-CH_3), 1.19 (Si-CH_3), 13.43 (Si-CH_2), 16.68 (Si-CH_2), 22.37 (CH_2), 50.30 (OMe) ppm. ^{29}Si-NMR (80 MHz, $CDCl_3$): δ= -42.09 (Si$(OMe)_3$), -21.37 (OSi-O$\underline{Si}$-OSi), 6.56 (Si-CH_2) ppm.

7.10.2 Synthesis of Oligomer 17a-TMS

50.00 g (0.24 mol, 6.3 eq.) HexMTS, 28.69 g 1,4-butandiol divinyl ether (0.20 mmol, 5.3 eq.), 0.79 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst and 9.49 g allyl trimethoxy silane (57.9 mmol, 2 eq.) were used. Yield: 87 g.
M_n (determined by ^{1}H-NMR)= 3080 g/mol; Degree of functionalization: > 97%.
^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.05 (m, 152H, Si-CH_3), 0.63 (m, 4H, $C\underline{H}_2$-$(CH_2)_2$-Si$(OMe)_3$), 0.71 (m, 4H, $C\underline{H}_2$-Si$(OMe)_3$), 0.97 (m, 29H, CH_2-Si), 1.47 (m, 4H, $C\underline{H}_2$-CH_2-Si$(OMe)_3$), 1.61 (m, 29H, CH_2), 3.38 (m, 29H, CH_2-O), 3.49 (m, 29H, CH_2-O), 3.55 (s, 18H, OMe) ppm.

7.10.3 Synthesis of Oligomer 17b-TMS

75.0 g (0.13 mol, 4 eq.) PDMS-H_2 (MW= 580 g/mol), 13.79 g 1,4-butandiol divinyl ether (97.0 mmol, 3 eq.), 0.89 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst and 9.57 g allyl trimethoxy silane (58.9 mmol, 2 eq.) were used. Yield: 96 g.

M_n (NMR)= 3440 g/mol; Degree of functionalization: > 99%.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.07 (m, 229H, Si-CH_3), 0.63 (m, 4H, TMS-propyl-CH_2-Si), 0.72 (m, 4H, $C\underline{H}_2$-Si$(OMe)_3$), 0.99 (t, 14H, CH_2-Si), 1.48 (m, 4H, TMS-propyl-CH_2), 1.62 (m, 14H, CH_2), 3.39 (m, 14H, CH_2-O), 3.50 (m, 14H, CH_2-O), 3.56 (s, 18H, OMe) ppm.

7.10.4 Synthesis of Oligomer 18a-TMS

32.50 g (0.16 mol, 6 eq.) HexMTS, 26.27 g triethylene glycol divinyl ether (0.13 mol, 5 eq.), 0.59 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst and 7.26 g allyl trimethoxy silane (44.7 mmol, 2 eq.) were used. Yield: 65 g.

M_n (NMR)= 2990 g/mol; Degree of functionalization: > 96%.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.06 (m, 126H, Si-CH_3), 0.61 (m, 4H, TMS-propyl-CH_2-Si), 0.71 (m, 4H, $C\underline{H}_2$-Si$(OMe)_3$), 1.00 (t, 24H, CH_2-Si), 1.47 (m, 4H, TMS-propyl-CH_2), 3.55 (m, 65H, CH_2-O and OMe), 3.63 (m, 48H, CH_2-O) ppm.

7.10.5 Synthesis of Oligomer 18b-TMS

60.0 g (0.10 mol, 4 eq.) PDMS-H_2 (MW=580 g/mol), 15.69 g triethylene glycol divinyl ether (77.6 mmol, 3 eq.) and 0.75 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* and 7.75 g allyl trimethoxy silane (47.8 mmol, 2 eq.) were used. Yield: 79 g.

M_n (NMR)= 3470 g/mol; Degree of functionalization: > 97%.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.07 (m, 213H, Si-CH_3), 0.64 (m, 4H, TMS-propyl-CH_2-Si), 0.72 (m, 4H, $C\underline{H}_2$-Si$(OMe)_3$), 1.01 (t, 13H, CH_2-Si), 1.48 (m, 4H, TMS-propyl-CH_2), 3.56 (m, 44H, CH_2-O and OMe), 3.63 (m, 25H, CH_2-O) ppm.

7.10.6 Synthesis of Oligomer 19a-TMS

40.0 g (0.19 mol, 6.5 eq.) HexMTS, 25.69 g freshly distilled 1,3-diisopropenylbenzene (0.16 mol, 5.5 eq.) and 0.66 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst and 7.97 g allyl trimethoxy silane (49.1 mmol, 2 eq.) were used. Yield: 73 g.

M_n (NMR)= 3070 g/mol; Degree of functionalization: > 94%.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.03 (m, 139H, Si-CH_3), 0.64 (m, 4H, TMS-propyl-CH_2-Si), 0.73 (m, 4H, C$\underline{H}_2$-Si$(OMe)_3$), 0.98 (m, 26H, Si-CH_2), 1.27 (m, 41H, CH_3), 1.48 (m, 4H, TMS-propyl-CH_2), 2.92 (m, 14H, CH), 3.57 (s, 18H, OMe), 7.00-7.19 (m, 28H, Ar) ppm.

7.10.7 Synthesis of Oligomer 19b-TMS

40.0 g (69.0 mmol, 3.8 eq.) PDMS-H_2 (MW= 580 g/mol), 8.18 g freshly destilled 1,3-diisopropenylbenzene (51.7 mmol, 2.8 eq.), 0.48 mL of a 1 mg Pt /mL hexane solution of *Karstedt's* catalyst and 5.57 g allyl trimethoxy silane (34.4 mmol, 2 eq.) were used.

Yield: 52 g. M_n (NMR)= 3110 g/mol; Degree of functionalization: > 97%.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.05 (m, 199H, Si-CH_3), 0.64 (m, 4H, TMS-propyl-CH_2-Si), 0.72 (m, 4H, C$\underline{H}_2$-Si$(OMe)_3$), 0.96 (m, 12H, Si-CH_2), 1.26 (m, 18H, CH_3), 1.49 (m, 4H, TMS-propyl-CH_2), 2.89 (m, 6H, CH), 3.57 (s, 18H, OMe), 6.99-7.18 (m, 12H, Ar) ppm.

7.10.8 Preparation of un-filled Films of HexMTS-TMS and 17a-TMS–19b-TMS

1.00 g of the corresponding hybrid silicone and 0.01 g (0.01 wt%) of the organotin catalyst (BNT-CAT 440, TIB 223 or TIB 208) were mixed in a plastic vial for 5 min using a speedmixer and the resulting clear mixture was cast on a PE-foil with a thickness of 400 µm with a drawdown bar. The films were stored at ambient temperature (25°C).

7.10.9 Preparation of filled Films of HexMTS-AGE and 17a-TMS–19b-TMS

1.00 g of the corresponding hybrid silicone, 0.01 g (0.01 wt%) of the organotin catalyst (BNT-CAT 440, TIB 223, TIB 208 or DBTL), the given amount of the corresponding filling material (Barytmehl N, quartz powder or Omyalite 95T, 60-75% in total), as depicted in table 5.14 and if desired, 0.5-1.0 wt% of the additives DAMO-T, DN 1146, DN AMMO, Anti-terra U 80 or 10 wt% Palatinol N were mixed in a plastic vial for 5 min using a speedmixer. The resulting mixture was poured on a PE-foil and stored at ambient temperature (25°C).

7.10.10 Application-technological Tests for Silicone Rubber Coatings

The following formulation was used for all application-technological tests:

To 50.0 g **17a-TMS–19b-TMS** (39%), 75.0 g Barytmehl N (60%) were added in two portions. After each addition the mixture was mixed for 5 min using a speedmixer. Subsequently, 0.63 g Dynasilan DAMO-T (0.5%), 0.63 g Anti-terra U 80 (0.5%) and 0.31 g (0.05%) TIB 223 (20% in *t*-butyl methyl ether) were added and the resulting mixture was either poured on a grit-blasted concrete plate to determine pull-off adhesion and penetration depth or poured into teflon molds to obtain the test specimen for the determination of tensile strength and elongation-to-break as described in 7.9.8.

Tensile strength (F_{MAX}), elongation-to-break (ε-F_{MAX}) and Shore-A-hardness were determined after 7d at standard laboratory climate as described in 7.9.8.1. The pull-off adhesion on concrete was determined after 7d at standard laboratory climate as described in 7.9.8.2. Araldite 2047-1 was used as adhesive because several other adhesives on epoxy basis such as MC-Quicksolid, 3M Scotch-Weld DP100 and DELO-Automix 03 rapid did not achieve sufficient adhesion. The penetration depth into concrete was determined after 7d at standard laboratory climate according to 7.9.8.3.

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Eines noch

Nicht mehr gierig sein,
nichts mehr erhoffen, befürchten,
nur noch am Schnittpunkt von Vergangenheit und Zukunft
drauflossitzen und
selbstverständlich werden,
freundlich, aber kein Tölpel,
friedlich, aber nicht harmlos,
gelassen, aber nicht gelangweilt

Am Ende eine Schale Erdbeeren
beim bloßen Betrachten schmecken,
eine frischgemähte Wiese riechen,
indem man gerne an sie denkt

Und dann, nach ein paar Jahren
an Vorlaufzeit mit oder ohne Fasten,
dann einmal noch sich konzentrieren
und den Weßlinger See
mit einem einzigen Schluck
austrinken, das wär's.

Matthias Politycki