

New Strategies for the Achievement of Silylated Polyurethanes with Improved Rheological and Tensile Properties

PhD Dissertation

by

Rok Brišar

**Leibniz Institute for Catalysis
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New Strategies for the Achievement of Silylated Polyurethanes with Improved Rheological and Tensile Properties

Dissertation

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Abstract

A rising number of patents in the field of silicon modified polymers (SMP) as the main component of many sealants, adhesives and coatings in the last two decades are a direct response to an increased demand for those compounds on the market. Most companies enrolled in this field are investing large funds into the development of new adhesives and sealants based on the various types of silicon modified polymers, which makes this emerging field extremely competitive. Organic chemists, polymer chemists and chemical engineers find themselves in the center of all attention as they are responsible for the development and optimization of new SMPs with enhanced properties for specific application.

One of the most commonly used subgroup of SMPs in practice is the silylated polyurethane prepolymers. The popularity of the silicon curable polyurethanes can be justified by their superior adhesion, toughness and the versatility of the silicon cure system. However a few drawbacks are accompanying this technology, the largest of all being the high viscosity of the prepolymers. This thesis summarizes the development of several strategies for overcoming the severe viscosity build-up during the synthetic process and the effect of the modifications on the tensile, adhesive and setting properties of the prepared silylated polyurethanes.

It has been proved that the main reason for the increased viscosity of the prepolymers is a high amount of hydrogen bonding due to urea bond formation during prepolymer method. Thus, methodologies for lowering the viscosity based on the prevention of hydrogen bonding have been developed. Strategies like elimination of urea N-H hydrogen bond donors by hydantoin ring formation, hindering of urea group by using siloxacycloalkenes or the exchange of urea with urethane group by using hydroxyl functional alkoxysilanes proved to be effective. Presented systems show a decrease in the prepolymer viscosity which was the main aim of our investigation. Nevertheless, the influence of the presented methodologies on the curing speed was investigated using time-resolved NMR spectroscopy by which the hydrolysis mechanism was proposed. Furthermore, the lap-shear tests revealed that the modification of the aminofunctional alkoxysilane end-capper, which is later used for the preparation of prepolymers has a positive effect of adhesion to several different materials. Additionally, the cured prepolymers show a comparable elongation strength and improved elasticity compared to standard silylated polyurethanes used in commercial applications.

To attain the above mentioned achievements, several modified aminoalkoxysilanes were developed, which were prepared by optimized synthetic methods and were additionally structurally analyzed. One of the highlights of this work was the preparation of stable hydroxyl functional methoxysilanes which was accomplished by a comprehensive structure-stability investigation. The stability of these compounds was verified by stability tests coupled with NMR spectroscopy. The prepared hydroxyl functional methoxysilanes were employed to

develop a new one-pot prepolymer method, which is not possible by using conventional end-cappers and can therefore raise a great industrial interest.

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List of abbreviations

[M ⁺]	molecular ion peak	etc.	<i>et cetera</i> (and similar)
Å	Ångström	FTIR	fourier transform infrared spectroscopy
ABS	acrylnitril-butadien-styrol-copolymer	g	gram
AFM	atomic force microscopy	GC	gas chromatography
AL	aluminium (99.5)	GC-MS	gas chromatography–mass spectrometry
AMEO	(3-aminopropyl) triethoxysilane	h	hours
AMMO	(3-aminopropyl) trimethoxysilane	HDI	Hexamethylene diisocyanate
aq	aqueous	HMBC	heteronuclear multiple bond correlation
ATR	attenuated total reflectance spectroscopy	HRMS	high resolution mass spectroscopy
CASE	coatings, adhesives, sealants and elastomers	HSQC	heteronuclear single quantum coherence spectroscopy
CHDI	1,4- <i>trans</i> -cyclohexyl diisocyanate	Hz	Herz
CLAB	<i>Candida Antarctica</i> lipase	IPDI	isophorone diisocyanate
COSY	correlation spectroscopy	IR	infrared spectroscopy
CTFA	calcium trifluoroacetate	<i>J</i>	coupling constant
DBTL	dibutyltin dilaurate	J	Joule
DBU	1,8-ciazabicyclo (5.4.0)undec-7-ene	kcal	kilocalorie
DCM	cichloromethane	M	metal
DMC	couble metal cyanide	m	multiplet
DMSO	cimethylsulfoxide	m.p.	melting point
DOTL	cioctyltin dilaurate	MDI	methylene diphenyl diisocyanate
DPD	dissipative particle dynamics	Me	methyl
DSC	differential scanning calorimetry	MeO	methoxy
ESI	electrospray ionization	min	minute
<i>et al.</i>	<i>et alii</i> (and others)	mL	milliliter

MMAO-12	modified methylaluminoxane, type 12	^t Bu	<i>tert</i> -butyl
mmol	millimole	TDI	toluene diisocyanate
<i>m</i> -PPDI	<i>meta</i> -phenylene diisocyanate	TEA	triethylamine
MS	mass spectroscopy	TEAL	triethylaluminum
NMR	nuclear magnetic resonance	THF	tetrahydrofuran
OE _t	ethoxy	TMG	1,1,3,3-tetramethyl- guanidine
P1 ^t Bu	phosphazene base P1- <i>t</i> -Bu	U.S.	United States
PDMS	poly(dimethyl siloxane)	XRD	x-ray spectroscopy
PEG	poly(ethylene glycol)	δ	chemical shift in ppm
PEO	poly(ethylene oxide)		
PMMA	poly(methyl methacrylate)		
PO	propylene oxide		
PPDI	<i>para</i> -phenylene diisocyanate		
PPG	poly(propylene glycol)		
PPO	poly(propylene oxide)		
PTHF	poly(tetrahydrofuran)		
PU	polyurethane		
PVC	poly(vinyl chloride)		
RO	ring opening		
ROP	ring opening polymerization		
rT	room temperature		
SMP	silicon modified polymer		
SOT	skin over time		
STST	stainless steel		
t	time		
T	temperature		
TAS	trialkoxysilane		

1. Introduction

Somewhere, something incredible is waiting to be known.

Carl Sagan, (1934-1996)

1.1. Scope of work

Silicon-curing polyurethanes gained a lot of interest in the sealant and adhesive industry due to their versatility, strength, chemical stability and low price. An intensive research in this field in the last 30 years, allowed the broadening of the application scope to many areas of construction and transportation. Despite an intensive research in this field, there are still major problems to be tackled in order to further expand the applicability of these types of adhesives and sealants.

The largest issue of the current technology is the high viscosity of synthesized silylated polyurethanes, which is mainly the result of strong intramolecular hydrogen bonding and poor reaction selectivity. The aim of this work is to provide several strategies for supplying low viscous silylated polyurethanes by either eliminating hydrogen bonding or by improving the reaction selectivity between polyisocyanates, polyol and silane end-capper.

The first chapter will provide the background in to the silicon modified polyurethane technology. Herein the reasons behind the high viscosity and other physical and chemical properties will be explored and discussed. Based on the presented findings, several methodologies will be proposed, which are based on either elimination or the reduction of the hydrogen bonding as shown in the Figure 1.1.

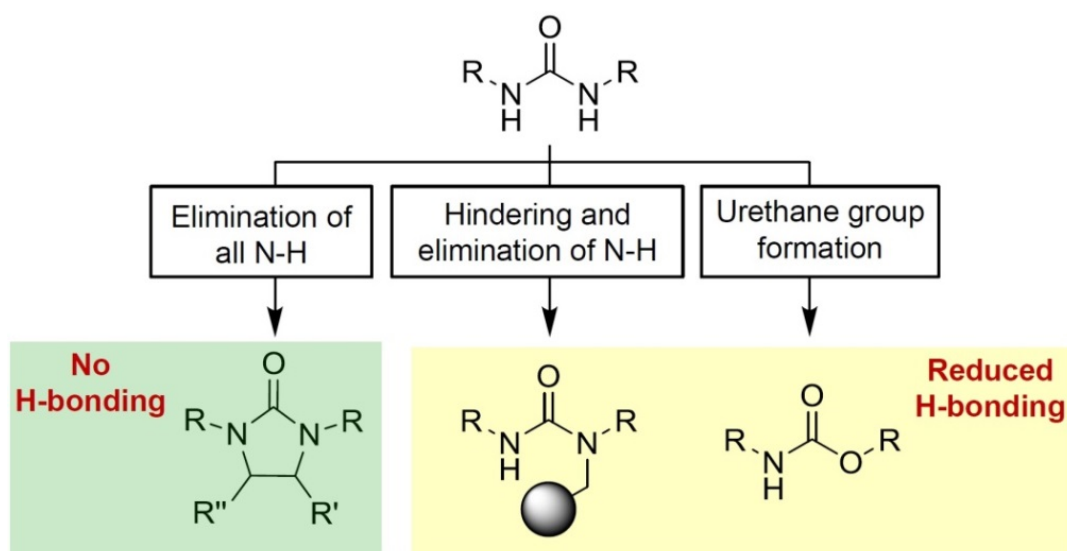


Figure 1.1: Strategies for lowering the viscosity of the prepolymers by influencing the amount of the hydrogen bonding.

The methodologies presented in this work are based on either elimination or on reduction of the amount of hydrogen bonding using different approaches. Chapter 2 deals with the complete elimination of the active hydrogen (N-H) in the urea group by formation of the covalent ring and its influence on the rheological properties of the prepolymer. Following chapters describe the reduction of the hydrogen bonding by either partial elimination of N-H groups and hindering of the remaining ones (Chapter 3) or formation of urethane instead of urea groups, which also reduces the amount of hydrogen bonding (Chapters 4 and 5). Finally the conclusion and outlook of this work is summarized in the in the last part of this thesis.

The results show, that the control of the hydrogen bonding plays an important role not only in the tailoring of the rheological properties of prepolymers, but also in the tensile, adherent and setting characteristic of the cured films.

1.2. Silicon modified polymers

Moisture-curable silicon modified prepolymers (SMP) have been known for several decades and are widely used in many technical applications such as sealants,^[1] adhesives,^[2] coatings,^[3] spray foams^[4] etc. The most commonly used silylated polyurethanes have been developed by Brode and Conte in 1972 to extend the property range of conventional sealant formulations^[5]. These polymers possess alkoxysilane groups, which hydrolyze and crosslink even at room temperature in the presence of atmospheric moisture and a catalyst, eliminating the corresponding alcohols. Depending on the type of the alkoxy groups at the silicon atom and/or functional group on the alkyl chain, the hydrolysis speed can be efficiently controlled.^[6] Methoxy- and ethoxysilanes exhibit the highest hydrolysis speed, therefore they are most commonly used in moisture curable compositions. The crosslinking speed and density of SMP also depends on the nature of the crosslinking catalyst and the curing conditions. In this process, prepolymers form first long chain polymers and later three dimensional networks to obtain highly crosslinked networks with good mechanical strength and superior temperature and chemical stability.^[7]

Coatings, adhesives, sealants and elastomers (CASE) based on polyurethane silicon modified polymers is a steadily growing market due to its broad applicability and robustness. Globally, the overall consumption of formulated adhesives reached 29.4 billion dollars in 2014 and according to the reports published in recent years, the market for adhesives and sealants is to grow steadily by 2.8 – 3 % each year until at least 2023.^[8] The fastest annual growth expected for reactive adhesives and sealants is driven by the rising demand in the Asia-Pacific market and by the trends favoring higher added-value products. The most rapid gains compared to other sealant types were recorded and are still predicted for the silicone and polyurethane sealant types, supported by their superior performance and characteristics. Due to the growing trends of the adhesive and sealant markets, large funds are being invested in to the research and development of new types of silicon modified polyurethanes. This trend can be also witnessed by the growing number of patents from leading companies present in this filed like Henkel Corporation (Germany), Sika A.G. (Switzerland), Bostik (France), Dow Chemical Company (U.S.), 3M (U.S.), H.B. Fuller (U.S.), Wacker Chemie (Germany), Weicon GmbH & Co. KG (Germany), Cemedine (Japan), ThreeBond Group (Japan), and others.^[8c,9]

Silylated polyurethanes have excellent adhesion to a variety of materials commonly used in construction and good chemical and mechanical durability. An especially good feature of these sealants and adhesives is their bonding to plastics (PVC, ABS, polystyrene, acrylates etc.), glass, wood, metals and ceramic materials. Due to these reasons, these one-component sealants and adhesives are used for filling gaps and seals in cars, trucks and

trailers; as well as for vibration mounting mounts and other innumerable applications in the construction industry.^[10]

1.3. Polyether polyols

A polyol, poly glycol or polyether polyol is a polymeric compound, having a polyether backbone with hydroxyl groups on each chain-end of the polymer. The most commonly used polyether polyols are poly(ethylene oxide) (PEO or PEG), poly(propylene oxide) (PPO or PPG) and poly(tetrahydrofuran) (PTHF) (Figure 1.2). They are mostly used in the polyurethane industry with weight fractions ranging from 30 wt% for rigid insulation foams, 70 wt% for flexible foams and up to 90 wt% for low modulus sealants.^[11] The main purpose of the polyether polyol backbone is to provide a polymer matrix with softness and flexibility, while the highly hydrogen-bonded polyurea or polyurethane segment is responsible for stiffness and rigidity. By changing the weight-ratio of polyether vs. polyurethane segments, the properties of the final polymer can be finely tuned to express the specific property desired for the final application.

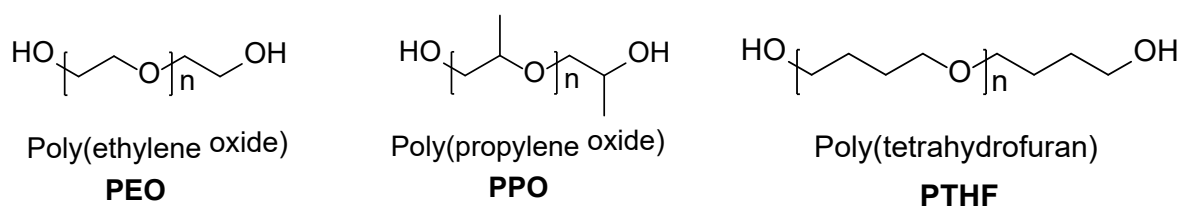


Figure 1.2: Examples of three polyether polyols most commonly used in polyurethane industry.

Poly(propylene glycol) was traditionally produced by anionic polymerization, which involves the use of a dihydroxyl functional oligomer, commonly referred to as a “starter” and a strong base. Typically KOH is reacted with an alcohol to form potassium alkoxide, which initiates living or pseudo living polymerization.^[12] However the main drawback of this polymerization method is the formation of a large number of unsaturation on the chain ends of the polymer. The base is unfortunately also able to isomerize propylene glycol to allyl alcohol, which terminates the chain growth or acts as a monofunctional starter.^[12b,13] This side reaction limits the use of this polymerization process in a large scale, since the preparation of high molecular weight polymer is challenging. For example, the degree of unsaturation of a PPG with a molecular weight of approximately 2000 - 3000 g/mol prepared by this method is so large, that the polymer is unusable in the elastomer production.^[14]

The breakthrough came in 1960s with the discovery of double metal cyanide (DMC) catalyst by General Tire Inc.^[15] In the 1980s, companies like ARCO,^[16] Asahi Glass^[17] and Shell^[17] made large improvements to the catalyst in order to use it in large scale production. The biggest advantage of DMC catalysis over conventional anionic polymerization is that it is less likely to promote the isomerization of propylene oxide to allyl alcohol and therefore the

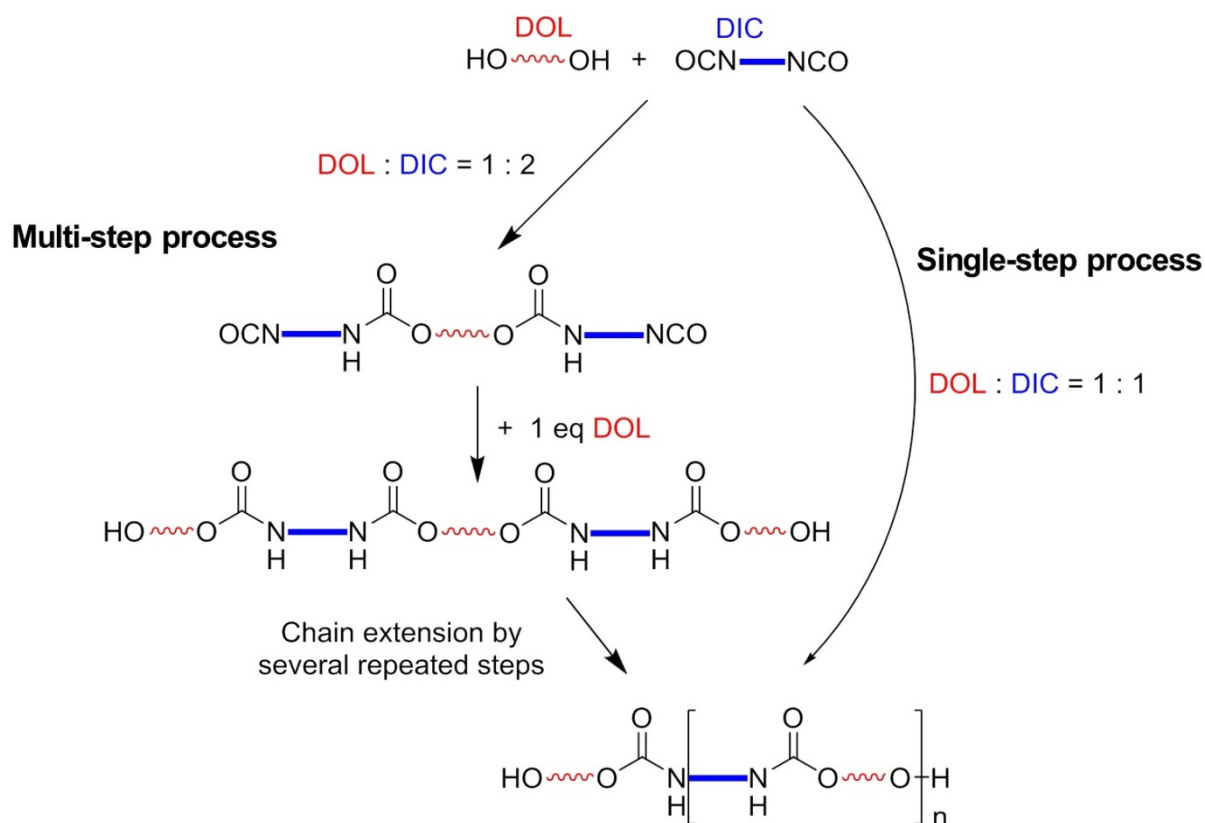
unsaturation level is lowered to the minimum level. The decreased degree of propylene oxide isomerization not only lowers the unsaturation level, but also allows the use of high molecular weight PPGs (>20 000 g/mol) in elastomer preparation.^[18]

Another advantage of DMC catalysis is that the polymerization process is highly controlled and therefore, the produced polyethers contain a narrow molecular weight distribution. This is an especially important parameter, since it has a large influence on the rheological, physical and mechanical properties of the polyurethane based elastomers.

1.4. Polyurethanes

Polyurethanes (PU) are a class of polymeric materials embodying a great chemical stability and mechanical endurance. Due to their good structure/property relationship, the properties of the final PU can be well tailored, which makes them extremely versatile and useful in many applications like paints, elastomers, insulations, fibers, foams etc.^[19] The first polyurethane materials were prepared in the labs of Otto Bayer and his coworkers shortly before Second World War and were immediately a big success.^[20] The basic principle of polyurethane preparation is the single- or multi-step reaction between a diisocyanate and a diol or a diamine to form the corresponding urethane and urea repeating units.^[21] These units are responsible for the superior properties, which are a direct result of the specific micro structure formation consisting of “hard” and “soft” segments. According to the ratio of the “hard” and “soft” segments and the sources from which PU are synthesized, they can be grouped in to several different classes like: rigid, flexible, thermoplastic and water-borne PU as well as binders, coatings, adhesives and elastomers etc.^[22]

The PUs are prepared either by single- or multi-step process (Scheme 1.1). In the latter, a bifunctional chain extender (DOL) is mixed with a small excess of diisocyanate (DIC) in approximately 1:2 ratio to form a diisocyanate functional compound. In the second step, one equivalent of chain extender is added to form hydroxyl or amino functional oligomers. This process is repeated until desired property or molecular weight is achieved.^[23] In a single step process, the bifunctional chain extender is mixed with diisocyanate in approximate 1:1 ratio, at which point polymerization process occurs, forming highly crosslinked polymer.^[24] The multi-step process is generally preferred since it is more controlled and gives polymers of higher quality, however the process is in general technically demanding and involves several steps, which makes it economically less attractive.^[23]



Scheme 1.1: Graphical representation of multi- and single-step process for preparation of polyurethanes.

The choice of the chain extender will determine whether the polymer will be poly(urethane) or poly(urea) or a poly(urethane-urea). If the chain extender is a diol it will be a poly(urethane) and if a chain extender is a diamine it will be a poly(urea). A combination of these two functionalities can be used as well, which is usually named poly(urethane-urea).

1.4.1. Structure/property relationship

The most important factor determining the properties of PU is the microphase-separated structure, which occurs when a block copolymer consists of two chemically incompatible backbones.^[25] The chain extender, which is usually a flexible polyether, polyester or polysiloxane polymer forms a “soft” segment, while the rigid urea or urethane based part forms highly hydrogen bonded “hard” segment.

The initial understanding of the microphase-separation was that the disconnected hard particles are dispersed in a (soft) rubbery medium.^[26] However, measured mechanical modulus of the prepared PU did not exactly match with predicted ones, implying that the proposed model was not correct.^[27] Some years later Wilkes *et al.*,^[28] Macosco *et al.*,^[29] Koberstein *et al.*^[25c,30] and others^[31] showed that the microstructure separation is actually more complex. Koberstein *et al.* showed that the hard segment structure of elastomer transitioned from phase-segregated non-correlated structure to a continuous-phase structure as the hard segment volume increased. His estimation was that the phase separation of hard

segment begins when the hard segment repeat length ($[\text{moles of chain extender}]/[\text{moles of soft segment}]$) is about $3^{[25c]}$. Ryan *et al.* showed that the phase separation is driven primarily by thermodynamic incompatibility rather than the hydrogen bonding and that hard segment hydrogen bonding formation occurs after phase separation.^[31] He proved this by using real time X-ray coupled with *in situ* infrared spectrometer.^[31] The observations by this two authors were also independently confirmed by Wilkes^[28], Runt^[32] and Sonnenschein^[33] (Figure 1.3).

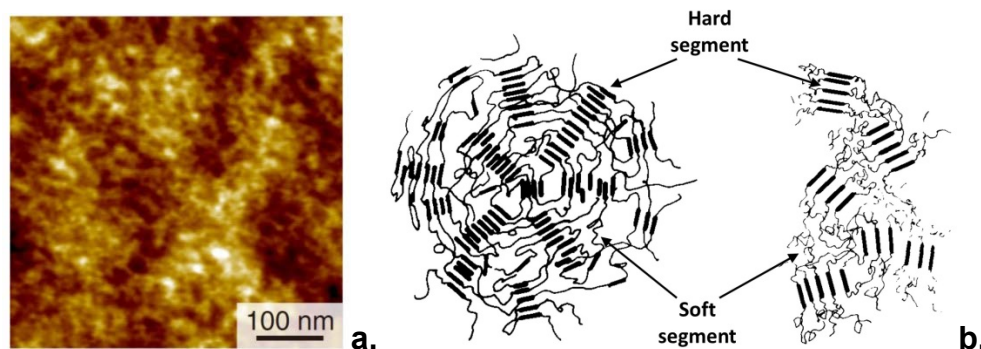


Figure 1.3: a. Atomic force microscopy (AFM) of a PU microphase-structure. The light regions are highly hydrogen bonded hard segments, while darker spots are soft segments. Taken from reference [33c]. b. Schematic representation of the microphase-separation. Taken from reference [34].

In addition to hydrogen bonding, the polarity also plays an important role in microphase separation since it determines the solubility of polar urethane or urea groups in the soft polyether segment. The solubility parameter value for urea group is 45.6 J/cm^3 , while the value for urethane is 37.2 J/cm^3 ,^[35] indicating that latter is significantly more soluble in polyether matrix with solubility parameter of 20.2 J/cm^3 for poly(ethylene oxide)^[36] and 18.9 J/cm^3 for poly(propylene oxide).^[37]

1.4.2. Hydrogen bonding

As mentioned earlier, hard segments are obtained by reacting isocyanate with amine or alcohol to obtain the corresponding urea or urethane group. These groups interact with each other in the form of extended chains, with N-H “donor” groups, hydrogen bonded to C=O “acceptor” groups. The most important difference between urea and urethane groups is the strength of the hydrogen bonding,^[22,35] which directly influences the macroscopic properties like viscosity, mechanic modules, thermal stability etc. There is also a competition between self-association (urea-urea, urea-urethane or urethane-urethane H-bonding) or inter-association, which is for example N-H to ether –O– hydrogen bonding. However, the latter is only a secondary process and is often overlooked due to the poor solubility of polar urea or urethane groups in non-polar polyurethane matrix.^[38] A great deal of research publications on the hydrogen bonding topic in polyurethanes was published by Yilgor,^[37,39] Wilkes,^[35,40] Cooper,^[25b,26] Coleman,^[41] MacKnight,^[42] Sheng-Khan,^[43] and others.

Figure 1.4 graphically presents the types and strength of the hydrogen bonding and the development of the microphase-structure as its direct consequence. Urethane group forms relatively weak “monodentate” or single intermolecular hydrogen bonds (46.5 kJ/mol), while urea forms much stronger “bidentate” or dual intermolecular hydrogen bonds (58.5 kJ/mol).^[39] The reason for the stronger self-association of poly(ureas) is the bidentate hydrogen bonding, which results in an even denser hard segment packing.^[41,44] Based on the same effect, the hydrogen bonding between urea N-H and ether oxygen is also stronger than single urethane N-H/ether oxygen hydrogen bonding. The consequence of this can be observed also on a macroscale level, since urea based materials possess greater Young modules, increased viscosities or higher melting points.

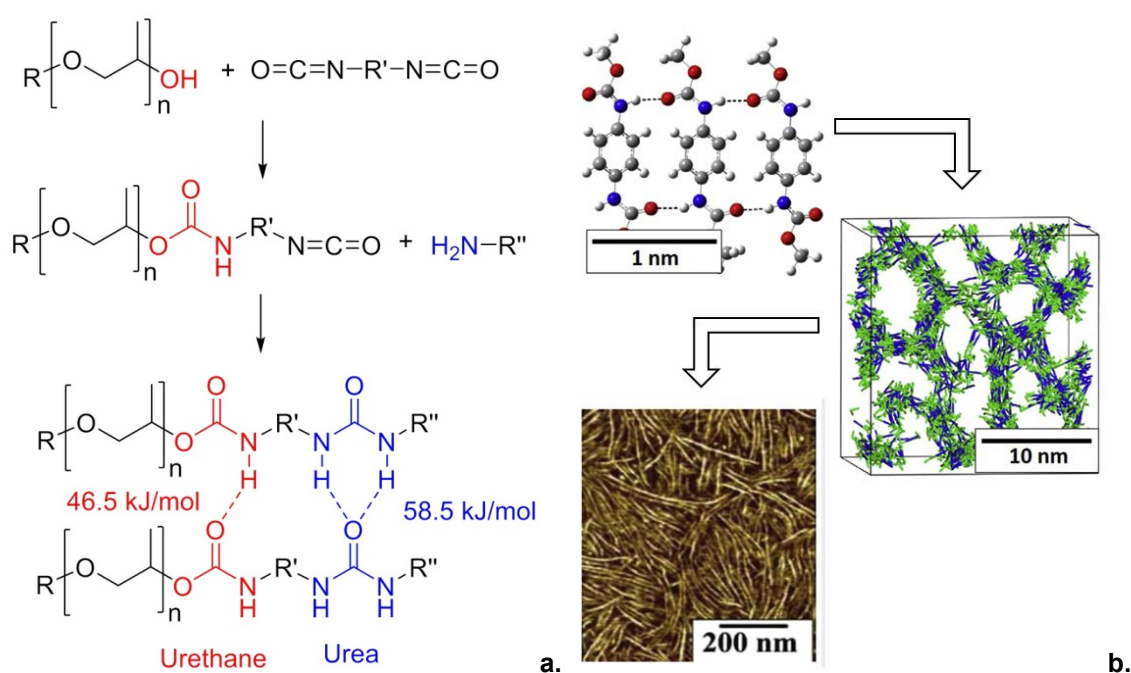


Figure 1.4: **a.** Hydrogen bonding strength between urethane and urea groups. **b.** Hydrogen bonded microstructure formation between urethanes as a consequence of the hydrogen bonding in PU. Taken from reference [35].

Infrared spectroscopy is a common method for detecting the amount of hydrogen bonding, therefore this method is commonly used in the characterization of polyurethanes in wide variety of studies.^[19,35,39,41,42b,43a] A number of vibrational modes are sensitive to hydrogen bonding in PU systems, however the most information can be retrieved from N-H stretching in the region from 3150 - 3400 cm^{-1} and C=O in the region 1550 – 1800 cm^{-1} . Since the N-H stretching region of the IR-spectrum can be very complex, this region cannot be used in a straightforward manner to obtain accurate quantitative data concerning the amount and nature of hydrogen bonding. Due to this reason the researchers most commonly look closely in to the shifts in the carbonyl region, which proved to be complex, especially in dilute solutions or low molecular weight systems.^[38,41] Due to the effect of hydrogen bonding on to the electron distribution in the bonds, one would initially expect to have a lower frequency

band for hydrogen bonded carbonyl stretch and higher frequency band for non-hydrogen bonded ("free") one. However, since hydrogen bonding is a cooperative effect it is also possible to distinguish between hydrogen bonded carbonyl bands in dimers or in "multimeric" crystalline-like structures.^[45] Because of the cooperative effect the strength of the hydrogen bonding is increased and therefore the bands for crystalline-like hydrogen bonded structures appear at lower wavenumbers than for example a dimeric structure.^[45] Furthermore, the carbonyl group stretch in highly diluted solutions, with low amount of hydrogen bonding has its stretching band at a slightly different wavenumber than for example carbonyl group at the end of hydrogen bonded chain. However the precise determination of each version of hydrogen bonded carbonyl bands is not possible, since the frequencies highly depend on the chemical structure of the polyurethane. Polyurethanes containing aromatic groups in the direct contact with urethane groups have the corresponding stretching bands at lower frequencies compared to the aliphatic ones. The characteristic bands of differently hydrogen bonded urethane groups are summarized in the Figure 1.5.

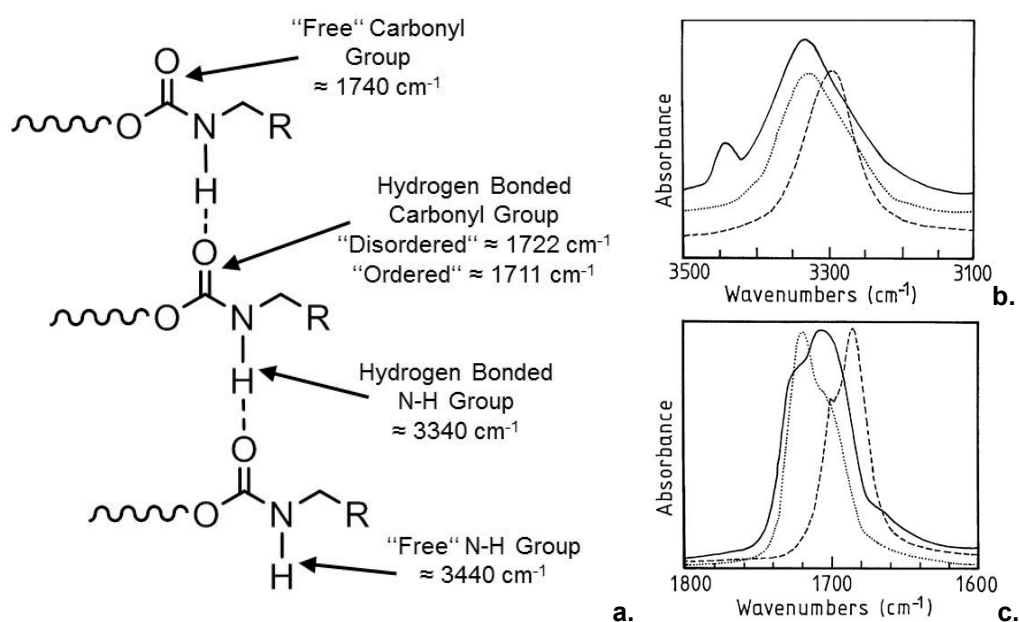


Figure 1.5: a. IR band assignment for hydrogen bonding possibilities in polyurethanes. b. N-H stretching region of urethane. c. Carbonyl stretching region of urethane (- - -), PDMS-Urethane copolymer (—), PEO-Urethane (····). Taken from reference [38,46].

Due to the greater π -electron delocalization of urea groups in polyureas, the carbonyl stretching band can be found at lower wavenumbers compared to polyurethanes. However, the π -electron delocalization has a negligible effect on N-H stretch, therefore only little or no shift can be observed. Due to this reason, it is almost impossible to distinguish between N-H stretch of the urea and urethane in the IR spectra. The hydrogen bonded "ordered" carbonyl stretch bands are also more shifted in the IR spectrum in comparison to the "disordered" since the strength of the bifurcated (2:1 structure) ordered urea bonding is higher. The

characteristic bands of differently hydrogen bonded urea groups are summarized in the Figure 1.6.

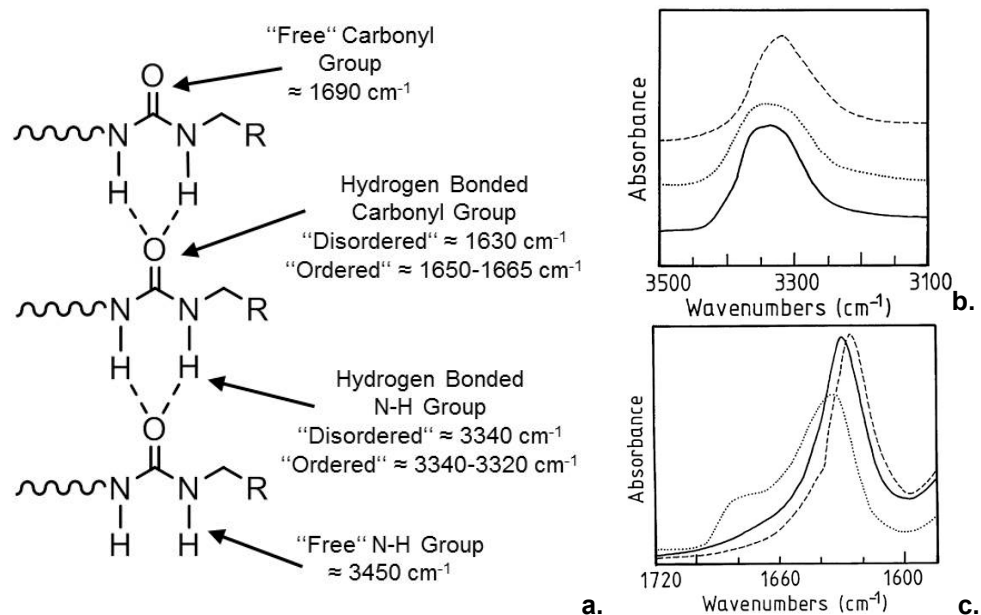


Figure 1.6: a. IR band assignment for hydrogen bonding possibilities in polyureas. b. N-H stretching region of urea. c. Carbonyl stretching region of urea (---), PDMS-urea copolymer (—), PEO-urea (····). Taken from reference [38,46].

Another critical parameter influencing the properties of polyurethanes is the symmetry of the diisocyanate. The structure of commercially available diisocyanates can be divided into two main groups (Figure 1.7): symmetric (e.g., PPDI, HDI, CHDI, MPDI, MDI and HMDI) and asymmetric (e.g., TDI and IPDI). Studies show that the structure and especially the symmetry of diisocyanate plays a crucial role in hard segment formation as well as on the strength of short and long range hydrogen bonding.^[47] Symmetric diisocyanates form long linear polyurethane backbones which easily assemble to form crystalline hard domains. On the other hand, the presence of asymmetric diisocyanates leads to the formation of kinked polymer backbones causing highly tangled (amorphous) structures with lower amounts of highly ordered hard segments. Even diisocyanates with NCO groups on 1,3 position (MPDI) on the benzyl ring form asymmetric, tangled structures with more disorder than in the case of PPDI as shown in Figure 1.7.

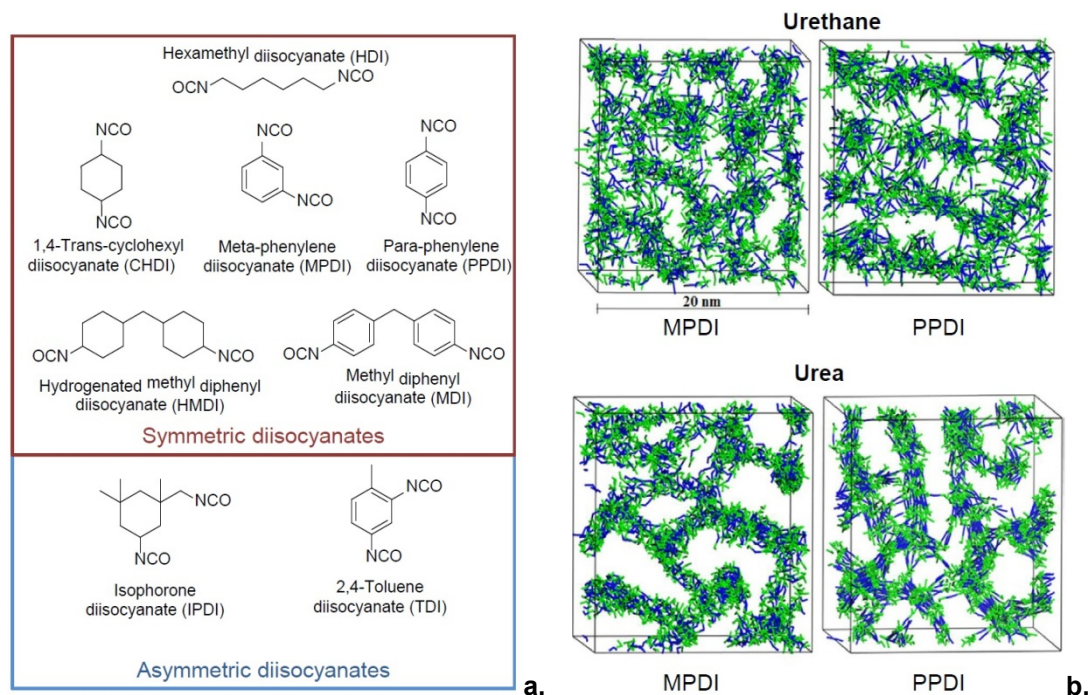


Figure 1.7: **a.** Chemical structures of diisocyanates commonly used for PU preparation. **b.** Dissipative particle dynamics (DPD) simulation of hard segment morphologies of polyurethane (top) and polyurea (bottom) prepared from MPDI on the left and PPDI on the right. Blue: phenyl rings, Green: urea or urethane groups. Taken from reference [48].

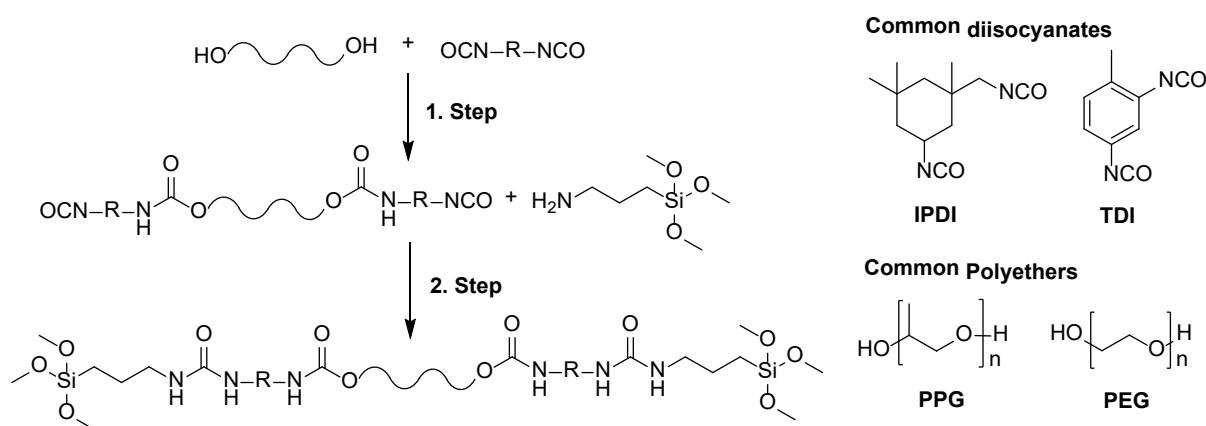
1.5. The Prepolymer method

The most common method used for the preparation of silylated polyurethanes is the two-step prepolymer method. In a first step, an isocyanate-terminated prepolymer is prepared by reacting a high molecular weight polyether with diisocyanate at elevated temperatures.^[49] The ratio of diisocyanate/OH is very important when preparing an NCO terminated polymer. If the ratio is approximately 1, the resulting polymer should have predominantly NCO terminating groups, however in practice large chain-extension can occur.^[50] The undesired consequence of this side reaction is the increase of molecular weight and consequently the build-up of viscosity. The chain-extension is a result of the unselective reaction between polyether chain-end and diisocyanate, therefore the appropriate selection of the diisocyanate and the catalyst is of the major importance. Another way to reduce the chain-extension is to add a slight excess of diisocyanate (1-5 mol%).

Low-viscosity urethane prepolymers are suitable for the production of low-modulus construction sealants and adhesives which can be prepared using diisocyanates having two NCO groups with different reactivity.^[50a] This improves the selectivity of the OH/NCO reaction, since one group is more electrophilic than the other and therefore reacts faster with polymer chain-end than the other, leading to mono addition of diisocyanate to the polyether chain-end. Typical diisocyanates for preparing low-viscosity silylated polyurethanes sealants are toluene diisocyanate (TDI) or isophorone diisocyanate (IPDI). Both diisocyanates are

also asymmetric, which disturbs the hard segment packing and the strength of hydrogen bonding and therefore additionally decreases the viscosity (Figure 1.7).^[50a]

In the second step, the alkoxysilane terminated polymer is prepared by reacting NCO functional polymer from the first step with functional alkylalkoxysilane in the presence of the catalyst (Scheme 1.2). The most commonly used alkylalkoxysilane is (3-aminopropyl)triethoxysilane (AMEO) or (3-aminopropyl)trimethoxysilane (**AMMO**). The amino group reacts rapidly with isocyanate terminated polymer therefore the reaction times are short and no free isocyanate groups are detected after the end-capping.



Scheme 1.2: Left: graphical presentation of the prepolymer method for the preparation of silylated polyurethanes. Right: most common diisocyanates and polyethers for the preparation of latter.

The use of an appropriate catalyst in the prepolymer method is also an important parameter, since it influences the selectivity and the reaction rates of the diisocyanate addition to the polymer chains and the reaction rate of the corresponding NCO terminated polymer with the functional silane. The kinetics and the selectivity of urea and urethane formation under the influence of the catalysts have been extensively studied in the past.^[51] Many metal-based catalysts like Ti,^[52] Ni,^[52] Co,^[53] Fe,^[54] Zn^[55] and Bi^[55-56] acetylacetonates and dilaurates have been used for the synthesis of polyurethanes, however the best performance by far is show by Sn-based catalysts.^[55,57] Due to this reason dibutyltin dilaurate (DBTL) and dioctyltin dilaurate (DOTL) are still the most commonly used catalysts for preparation of silylated polyurethanes as sealants, adhesives, coatings etc.^[58] Another advantage of tin-based catalysts is that they do not only catalyze urea or urethane group formation, but also the hydrolysis and cross-linking of alkoxysilanes, which has a positive effect on the curing speed in the final formulation.^[59]

1.6. Organofunctional alkoxysilane end-cappers

The most important intermediates in silicon chemistry and technology are organochlorsilanes, organosilanols and organoalkoxysilanes. The latter are most commonly used in larger scale due to their ability to be catalytically hydrolyzed with water under mild

conditions to produce silanols, which condense to siloxanes.^[60] Organoalkoxysilanes produce alcohols during hydrolysis, which are usually neither toxic nor corrosive in contrast to the hazardous hydrochloric acid produced by hydrolysis of organochlorsilanes.

When the organoalkoxysilanes or organochlorsilanes ($R-SiX_3$, X being a hydrolyzable group like: Cl, OMe, OEt...) are placed in to the hydrolytic environment, they tend to hydrolyze to produce corresponding silanols.^[61] Even though organosilanols are rarely isolated and characterized, they are key intermediates in the preparation of organosiloxanes. The tendency of silanols to condense with other silanols to form extended siloxane chains, branching and crosslinking, is usefully exploited in sealants, adhesives and coatings. An important parameter is the rate at which alkoxysilanes are converted in to siloxanes. This mostly depends on the structure of the alkoxysilane, its solubility in water and the environmental conditions. Silanols and siloxanols play also a key role in ring opening polymerization (ROP) of cyclic siloxanes to prepare linear or branched polysiloxanes.^[62] Another advantage of organoalkoxysilanes and polysiloxanes is that the decomposition under harsh conditions produces only CO_2 , water and SiO_2 all of which are environmentally friendly.^[63]

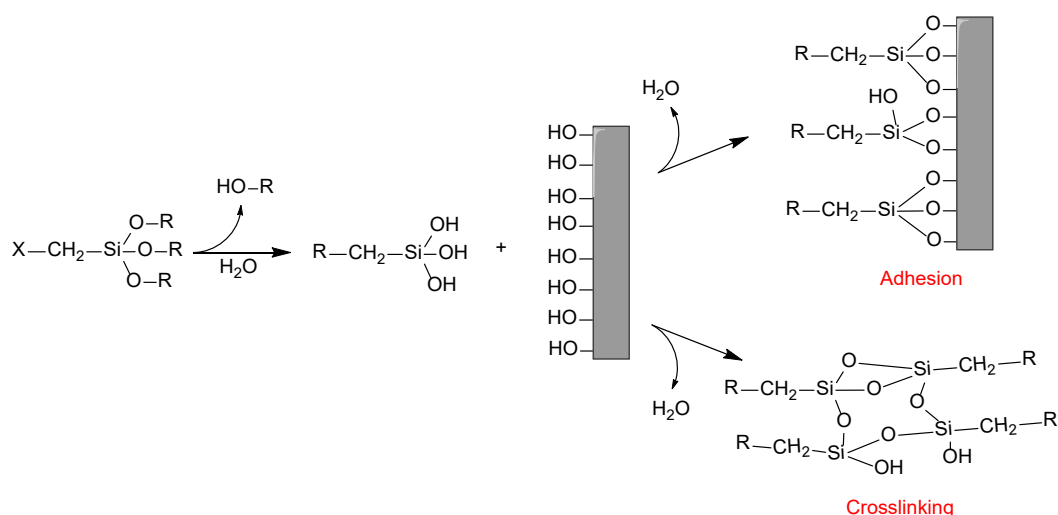
1.6.1. Organoalkoxysilanes

Alkoxysilanes are compounds containing silicon bonded to an organic rest through the oxygen bridge *i.e.*, $Si-O-R'$. The silicon can have one to four alkoxy groups, which can be selected from a wide variety of rests like: alkyl aryl, alkenyl, hydride, etc. In fact a large variety of different alkoxysilanes have been reported in academic and patent literature, however only a small number of alkoxysilanes are used for commercial purposes.^[64] The most common alkoxysilanes are trimethoxysilane and triethoxysilane.

Organoalkoxysilanes can be prepared by three different pathways: by reaction of alcohols with organochlorsilanes,^[65] by reaction of organometallic reagents with alkoxysilanes,^[66] or by hydrosilylation.^[65b,66a] The most common precursors for the preparation of organoalkoxysilanes are chlorosilanes, which are prepared by the famous Müller-Rochow process, commonly known also as the "direct" process.^[67] The chlorosilanes prepared this way are then converted in alkoxysilane precursors like: $HSi(OR')_3$ and $Si(OR')_4$ ($R = CH_3$, CH_2CH_3).^[68] These materials are afterwards functionalized with common methods like hydrosilylation to organoalkoxysilanes for usage in sealant and adhesive industry^[68] or as a liquid source of silicon dioxide.^[69] Both $HSi(OR')_3$ and $Si(OR')_4$ ($R = CH_3$, CH_2CH_3) are made by direct hydrolysis of the appropriate chlorosilane with alcohols. However HCl is produced during the process, which needs to be efficiently removed and recycled. Unfortunately this process is challenging in large scale production sites.^[66a] Furthermore, due to the hydrolytic

instability of alkoxyasilanes and chlorosilanes they need to be handled in closed systems, without any contact with external environment.

Alkoxyasilanes are used in many applications, all of which rely on the hydrolysis of alkoxy groups with water or hydroxyl functional materials. The application of alkoxyasilanes can be divided into several different groups like: adhesion promoters, crosslinkers, water scavengers and surface modifiers.^[70] In some applications alkoxyasilanes are hydrolyzed in order to obtain a solution of silanols prior to their use.^[71] The silanols not only condense with each other, but also with OH-groups on the surface of different materials, which improves the adhesion of the cured film to the surface (Scheme 1.3). The surface can be also pre-functionalized, with alkoxyasilanes, which is the basic working principle of the surface modifiers and adhesion promoters. Especially the adhesion promoters have a strong interaction with the surface and the prepolymer at the same time, which improves adhesion of the cured film to the surface.



Scheme 1.3: Hydrolysis and condensation of organoalkoxyasilanes to promote adhesion and crosslinking.

The functionality on the organic rest connected to the silicon center of the alkoxyasilane also has a major influence on the performance of the organoalkoxyasilane. There are many different functional alkoxyasilanes available on the market today, all of which have a specific behavior in the formulation, which enables one to finely tune the characteristics of the final adhesive or sealant to meet the market's demands. The most common functionalities are: vinyl, epoxy, acrylate, amino and thiol, which improve the interaction to the surface or to the organic matrix through hydrogen bonding, van der Waals forces, dipole-dipole interactions, π -stacking etc. Another important factor is the influence of the organic rest on the hydrolysis rate of the alkoxyasilane groups. It is well established, that exhibit acrylate-, vinyl- and aminosilanes the highest hydrolysis speed due to the electronic effects of these groups on the silicon center. The hydrolysis rate is exponentially enhanced when the number of carbons between silicon and amino or acrylate group is decreased from 3 to 1 ("alpha"

effect).^[6a] A few explanations of this phenomenon were proposed in the academic literature; however a detailed discussion on this topic is yet to be presented.

1.6.2. The role of organoalkoxysilanes in silylated polyurethanes

An important parameter in designing the properties of silylated polyurethanes is the selection of appropriate organoalkoxysilanes used as “end-cappers”. Depending on the type of the end-capper it was possible to influence the properties like curing speed, viscosity, adhesion on different substrates, mechanical properties of cured film, visual appearance, smell, etc. A commonly used end-capper for the preparation of silylated polyurethanes is 3-(trialkoxysilyl)propyl isocyanate. The advantage of this end-capper is its straightforward application in the prepolymer method. The end-capper is simply mixed with the hydroxyl functional polyol at elevated temperatures in a one-step process to obtain an alkoxysilane-terminated polymer.^[72] These prepolymers exhibit low viscosities and rapid curing rates, unfortunately they fail in the field of the mechanical performance of the cured film. Furthermore, high price makes them less appealing for the large scale prepolymer preparation.

The most common method for preparing silylated polymers is the end-capping of isocyanate terminated polymers with organoalkoxysilanes containing nucleophilic groups like amino, thiol or hydroxyl. The most commonly used silane is (3-aminopropyl)trimethoxysilane (AMMO), since the polymers end-capped with aminosilanes have generally good to excellent adhesion to many substrates. Also the high curing rate and low price of aminosilane end-capped prepolymers makes it attractive for their use in large scale production. Nevertheless, these polymer exhibit high viscosities compared to other sealants due to the highly hydrogen-bonded urea network.^[42a,73] Another disadvantage of primary aminosilanes is its susceptibility to be oxidized with air, which makes the product slowly turn yellow over time. This phenomenon is also known as the yellowing effect.^[74] The mentioned disadvantages of primary aminosilanes can be overcome by using secondary amines, or branched amines on *beta* position of the alkyl spacer between amine and silicon center.^[75] The branching of the alkylene bridge on the *beta* position of the amino group retards the oxidation and therefore slows or even completely prevents the yellowing.^[50a] Secondary aminosilane reacts slowly with isocyanate terminated polymers, but does not cause a major increase in the viscosity due to the steric hindrance of the N-substituted group.^[50a] The N-substituted group can have also other advantages; for example, polymers end-capped with N-phenyl-(3-aminopropyl)trimethoxysilane exhibit 4 to 8 times faster tack-free time and better mechanical properties.^[76]

Primary aminosilanes are often modified to secondary amines using Michael addition. Schmalstieg *et al.* prepared Michael adducts resulting from the mixture of the alkyl maleate

and primary aminosilane, which has been used to end-cap NCO terminated polymers.^[77] This kind of aminosilanes are commonly used in automotive applications due to their good mechanical and thermal properties.^[50a]

Another used functionality of organoalkoxysilanes is also a thio group, which is rarely used in consumer applications, due to the unpleasant smell during longer storage or decomposition.^[78] Furthermore, the reaction with the isocyanate terminated polymer is usually slower than with aminosilanes.^[50a] Other functionalities of organoalkoxysilanes used for many specific applications are urea, amide, hydroxyl, epoxy, and so on, which are presented in a Table 1.1.

Table 1.1: Common organoalkoxysilanes used for preparation of silylated polymers.

Entry	Structure	Name	Reference
Amino alkoxysilane			
1		(3-aminopropyl)triethoxysilane	[79]
2		(aminomethyl)triethoxysilane	[6a]
3		Bis-(3-trimethoxysilylpropyl) amine	[80]
4		<i>N</i> -butyl-(3-aminopropyl)triethoxysilane	[81]
5		(2-aminoethyl)aminopropyl trimethoxysilane	[82]
Isocyanate alkoxysilane			
6		(3-isocyanatopropyl)triethoxysilane	[83]
7		(isocyanatomethyl)triethoxysilane	[84]
Other alkoxysilanes			
8		(3-mercaptopropyl)triethoxysilane	[78,85]
9		1-(3-(trimethoxysilyl)propyl)urea	[86]
10		<i>N</i> -(3-(trimethoxysilyl)propyl)acrylamide	[87]
11		4-hydroxy- <i>N</i> -(3-(trimethoxysilyl)propyl)pentanamide	[88]
12		3-glycidoxypropyl trimethoxysilane	[89]

1.7. Adhesion of the silylated polyurethanes

Silylated polyurethanes are an important class of adhesives and sealants for a variety of applications like: joining, gap filling or structural bonding of various materials. To fulfill these functions, the prepolymers need to retain cohesive integrity as well as adhere to the joined substrates throughout the lifetime of the sealed or bonded structure. During the service of the cured sealant or adhesive, they are exposed to a range of static and dynamic stresses imposed by external forces like: mechanical stress, radiation, temperature fluctuation, moisture penetration etc. A combination of these factors frequently leads to changes in the material's internal structure and consequently in its mechanical properties.^[90] Hence the examination of the latter is a crucial technique for the development of new, high performance silylated polyurethanes.

Both sealants and adhesives operate primarily by adhesion, which is the attraction between the substrate and the cured polymer resulting from strong intermolecular forces. This is distinctively different from cohesion, which involves only intermolecular attractive forces within a single substance, typically cured polymer.^[91] A good indication of the mechanical behavior of the cured prepolymer can be obtained by inspecting the type of failure after the mechanical testing. Adhesive failure is an interfacial bond failure between the adhesive and the adherent. Cohesive failure of the adhesive occurs when stress fracture within the adhesive material allows a layer of adhesive to remain on both substrates, indicating that the attachment of the polymer to the substrate is stronger than the internal strength of the cured prepolymer itself.^[91] However, in some cases a structural failure is also possible, meaning that the adhesive and cohesive strength of the adhesive material is stronger than the testing material itself (Figure 1.8).^[92]

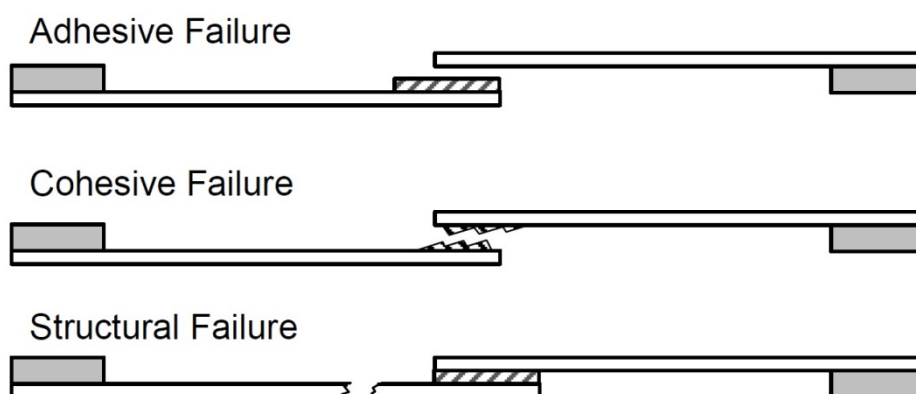


Figure 1.8: Failure types in adhesives during lap shear test.

1.7.1. Adhesion theory

Adhesion is an important factor in determining a sealant's adhesive performance and is primarily affected by the physio-chemical interaction between the cured polymer and the surface of the material to which it is applied. Although several studies describe the bonding

of the polymer to the surface there is no adhesion theory, which would precisely predict and explain all interactions that take place in the contact interphase of the substrate and the adhesive^[7].

Both, adhesive and cohesive forces can be attributed to either short or long range molecular interactions or so-called primary and secondary bonds. Primary forces are characterized as covalent, ionic or coordinative bonds, while secondary are weaker van der Waals forces, hydrogen bonding, dipole-dipole interactions etc^[10]. However, the chemical interaction with the surface is not the only factor influencing the adhesion, therefore, parameters like viscosity, polarity and curing rates also need to be considered. Two theories relevant to this work describing the adhesion of the silylated polyurethanes to the surface are briefly discussed in the following text.

- Adsorption theory

The adsorption theory states that adhesion results from molecular contact between two materials and the surface forces that develop. Adhesion results from the adsorption of adhesive molecules onto the substrate and the resulting attractive forces, usually designated as secondary or van der Waals forces. For these forces to develop, the respective surfaces must not be separated more than five angstroms (Å) in distance. Therefore, the adhesive must make intimate, molecular contact with the substrate surface.^[93]

The process of establishing continuous contact between an adhesive and the substrate is known as “wetting”. Good wetting results when the adhesive flows into the valleys and crevices on the substrate surface, while in contrast poor wetting results when the adhesive bridges over the valleys formed by these crevices.^[94] An important parameter for improving the “wettability” of the surface are the viscosity and the curing rate of the prepolymer. If the viscosity is low, the surface area is generally higher, since small air pockets and voids can easily be filled at the interface. However, if the curing rate is fast, the viscosity might rise rapidly, preventing an efficient spreading of the adhesive on the surface. Wetting ability is also dependent on other physical properties like surface tension of the prepolymer.

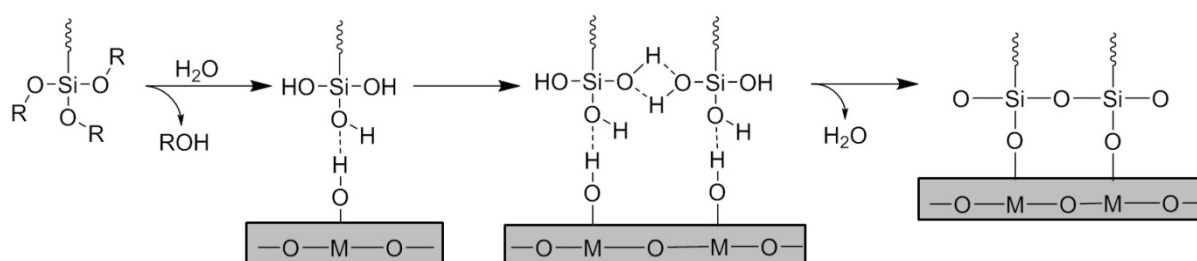
- Diffusion theory

The fundamental concept of the diffusion theory is that adhesion arises through the inter-diffusion of molecules in the adhesive and substrate. The diffusion theory is most commonly applicable when both the adhesive and substrate are polymeric, having compatible long-chain molecules capable of movement. The key is that the adhesive and the substrate must be chemically compatible in terms of diffusion, miscibility or solubility.^[10]

The proposed mechanism involves the migration of polymer silane terminal group to the interface between the adhesive and substrate, where it reacts with absorbed moisture to produce silanol groups, which allow the bonding to the surface. The amount of silane needed may be low enough to produce a monomolecular film on the interphase surface. Because the process involves migration of the silane terminal group to the surface, it is necessary to permit sufficient time for reaction to occur at the surface, therefore low curing rates are more preferred in this case.^[95] Furthermore, viscosity plays an important role in controlling the diffusion rates as lower prepolymer viscosity allows faster diffusion of the silicon reactive terminal groups on to the substrate surface.^[96]

1.7.1.1. Adhesion to mineral surface

A mineral surface is generally considered as an oxide surface such as silicate (glass), nevertheless most of the metals contain a thin oxide layer on its surface, therefore they are also often regarded as materials with mineral surfaces. The generally accepted mechanism for adhesion of alkoxy-silanes terminated polymers to the mineral surface consists of several steps. In the first step is the hydrolysis of alkoxy-silanes groups by adsorbed or atmospheric water.^[6] The produced silanol groups may first form hydrogen bonds with the surface, but during evaporation of the corresponding alcohol they condense to siloxane structures chemically bonded to the surface (Scheme 1.4). The extent of adhesion of the silane primer film with the polymer matrix then determines the ultimate bond strength.^[97]



Scheme 1.4: Bonding of silane terminated prepolymers to a mineral surface.

It was shown that alkoxy-silanes form strongly adsorbed polysiloxane films on ceramic and metal surfaces. Especially strong bonding of the alkoxy-silane terminated polymers are formed with glass, since the silanol groups on the glass surface react readily with alkoxy-silane groups forming strong Si-O-Si bonds (23.6 kcal/mol).^[98] The “oxane” bond between silicon and iron or aluminum on the other hand are significantly weaker and are not resistant to hydrolysis even at ambient conditions, therefore the adhesion to metal surfaces is generally lower compared to the one with glass.^[95b] However, the chemical and mechanical integrity of these films are highly dependent on the application parameters such as concentration of the alkoxy-silane groups in the prepolymer, pH, curing time and temperature.^[10]

In the case of the adhesion of alkoxy-silane-terminated polymers to mineral materials, van der Waals forces and hydrogen bonding do not play a major role. The adhesion strength is mostly determined by the covalent (glass) or coordination (metals), therefore only small improvement can be made by modifying the chemical structure of the polyurethane.^[99]

1.7.1.2. Adhesion to polymeric surface

Silylated polyurethanes exhibit a great adhesion to many polymeric materials, even in cases where the chemical structures have nothing in common on the first glance. The reason is that all polymeric materials have fundamental similarities, which are important for adhesion. For instance, surface energies are in the same order of magnitude for most polymers and are controlled largely by the general chemical composition of the polymer molecules. Factors such as the polarity and surface functionality of the molecules affect the surface tension and often account for a great improvement in adhesion. These properties are usually determined by the main polymer backbone in the adhesive or sealant formulation.^[10]

Addition of the carboxyl groups to the polymers is well known as an efficient adhesion promotion mechanism for polar substrates. This C=O groups improve the adhesion to polyesters, acrylates or even olefin polymers to the substrates. Other electronegative atoms such as chlorine and nitrogen, have been noticed to improve the adhesion *via* hydrogen bonding across the interface.^[10] In the case of silylated polyurethanes; a strong bidentate hydrogen bonding of the urea N-H groups to acrylate C=O accounts for a significant improvement of adhesion, while crosslinking of alkoxy-silane groups only serves as a mechanical anchoring in the small micro voids.^[100]

Morris *et al.* investigated the adhesion between different polymers and observed, that adhesion mechanism involves also an interchain entanglement and not chemical bonding, however the latter is largely dependent on the solubility of polymers in each other.^[101] A series of studies have also been published on mechanical coupling or interlocking as another adhesion mechanism, which is based on locking of the cured prepolymer on to the rough surface of polymer.^[102] This mechanism is largely dependent on the surface of the materials rather than its chemical structure. The current debate surrounding mechanical adhesion concerns the significance of the interlocking in explaining surface adhesion of polymers.^[103]

1.8. Tensile properties of cured silylated polyurethanes

The physical properties of many prepolymers end-capped with various organofunctional silanes have been often evaluated in the past. It was found, that not only the structure of the prepolymer determines the mechanical properties of the cured elastomer but also the structure of the silane crosslinker.^[7] The silane crosslinking part of the silylated prepolymer

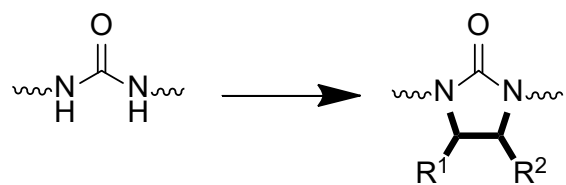
has an influence on viscosity, stability, curing rate and amount of crosslinking, which indirectly influence the physical properties of the cured polymer.

As mentioned earlier, the properties of polyurethane sealants depend strongly on their polymeric backbone. Poly(propylene glycol), which is the most commonly used polymer backbone in polyurethane sealants, offers good hydrolysis resistance, low-temperature flexibility, and lower cost as other alternative polyols.^[104] Furthermore, the typical polyurethane structure of soft and hard segments can be used to dramatically vary physical properties such as modulus, flexibility, and strength, which makes this class of sealants unique.^[104]

2. Alkyne amide functional alkoxysilanes and its application in SMP technology

2.1. Project outline

The conventional method for preparing silylated polyurethane prepolymers involves reacting an isocyanate terminated polymer with aminoalkylalkoxysilane. The resulting urea group can form strong intermolecular hydrogen bonds, causing an undesired viscosity build-up. On the other hand, low viscous moisture curable prepolymers are of high interest in the sealant industry due to the easier processability. The most effective strategy for avoiding viscosity build-up during the prepolymer method proved to be the prevention of hydrogen bonding. The preparation of a functional alkoxysilane, which can completely prevent the hydrogen bonding of the urea group by the formation of intramolecular covalent ring (Scheme 2.1) is discussed in this chapter.

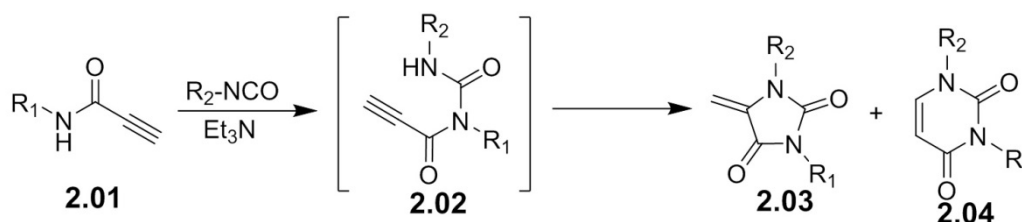


Scheme 2.1: Prevention of the hydrogen bonding by urea annulation.

The prepared functional alkoxysilane is to be used as an end-capper for the preparation of silylated polyurethane prepolymers. The effect of the intramolecular ring formation on the rheological properties of prepolymer will be outlined and discussed in this chapter.

2.2. Background

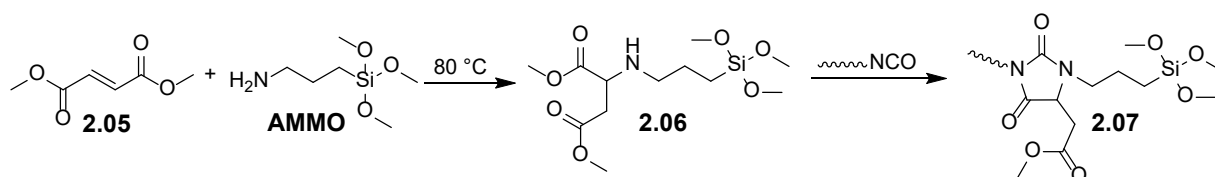
Amide-substituted alkynes are most commonly associated with Huisgen's cycloaddition, or "click" reaction, where the activated triple bond reacts with an azide to form triazole.^[105] Another kind of "click" reaction was also explored also by Damon and Coppola. They investigated the reaction between amide alkynes (**2.01**) and isocyanates in the presence of an organic base. The most common organic base employed is triethylamine which catalyzes the reaction between amide and isocyanate to produce an intermediate (**2.02**).^[106] Cyclization can occur either at *beta* carbon to produce hydantoin (**2.03**), or at the terminal carbon to produce uracil (**2.04**) as shown in Scheme 2.2. Surprisingly, the reaction is selective towards the former to produce **2.03** in up to 82 % yield.



Scheme 2.2: Formation of hydantoin cycle **2.03**.

Said and Savage extended the scope of the reaction also to alkyl amides to produce hydantoin cycles which are further converted to 5-spyro hydantions for the use in the pharmaceutical industry.^[107]

An important advantage of this type of cyclization is that it completely eliminates the hydrogen bond donor functionality (N-H) and therefore prevents all possible hydrogen bonding of the urea group. The first attempts to prevent the hydrogen bonding by forming an hydantion ring was reported by Siranovich *et al.*, they reacted isocyanate terminated polymer with alkoxy silane containing ester groups (**2.05**).^[108] By heating maleic ester modified alkoxy silane (**2.06**) with isocyanates, a hydantoin cycle (**2.07**) is formed, which completely eliminates hydrogen bonding of the urea group (Scheme 2.3).^[109] Consequently, the viscosity of the prepared silylated polymer was significantly reduced. However, an alcohol is being expelled during this reaction, which can further react with isocyanates and prevent complete end-capping of the prepolymer with the alkoxy silane end-capper. Furthermore, the removal of alcohol after the reaction requires an additional purification step, which is not desired in the large scale prepolymer preparation.



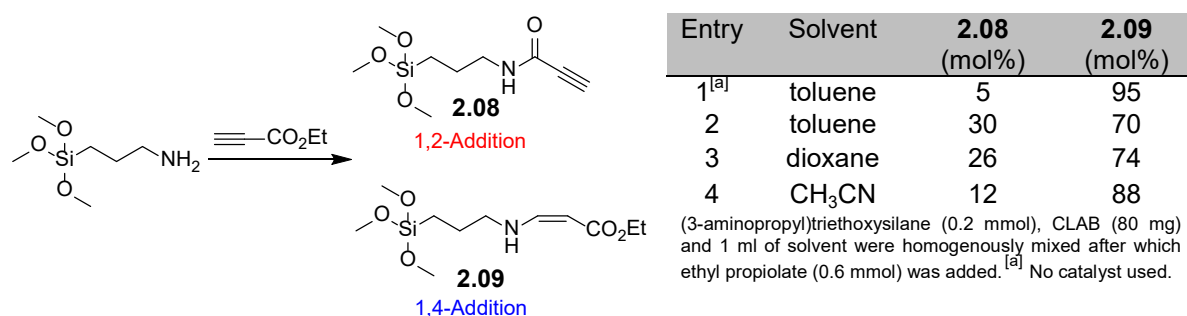
Scheme 2.3: End-capping of an isocyanate terminated polymer by forming a hydantoin cycle (**2.07**) as reported by Schmalstieg.^[109]

2.3. Results and discussion

2.3.1. Preparation of amide alkyne functional alkoxysilane

Previous publications in the field of the hydantoin cycle formation to eliminate hydrogen bonding provided an inspiration to apply this chemistry in the SMP sealant technology.^[76-77] In the first step, the preparation of amide alkyne functional alkoxysilane was necessary. The synthesis of amide alkyne compound can be achieved by several pathways like ester aminolysis^[107,110] or by the reaction of activated carboxylic acids with amines.^[111] Both approaches were tested in the lab in order to find the optimal synthetic methodology.

Demeunyck *et al.* reported the preparation of propyolamides by reaction of aliphatic amines with ethyl propiolate catalyzed by *Candida Antarctica* lipase (CLAB).^[112] The attempt to reproduce the same reaction using aminoalkoxysilane is presented in the Scheme 2.4. Controlling the chemoselectivity of ethyl propiolate to the amine proved to be challenging, since many side products can be formed because of the competition between 1,2- and 1,4-addition reactions. Contrary to the literature findings, it was not possible to shift the chemoselectivity towards the desired product (**2.08**). Instead high amounts of 1,4-addition product (**2.09**) was obtained, which were very difficult to remove from the reaction mixture due to the sensitivity of compound **2.08** towards heat, air and moisture. After several experiments, the decision was made not to pursue this method further.



Scheme 2.4: Left: reaction of aminoalkoxysilane with ethyl propiolate. Right: solvent influence on the reaction selectivity.

Gonzalez *et al.* published the preparation of amide alkyne functional alkoxysilanes as a solid support in affinity chromatography using carbodiimide to activate the carboxylic acid.^[113] By modifying the reported procedure, it was possible to prepare amide-alkyne (**2.10-2.12**) and amide-alkene functional alkoxysilanes (**2.13, 2.14**) in higher yields. The products were analyzed by NMR spectroscopy, GC-MS and electrospray ionization mass spectroscopy (ESI-MS) and are presented in the Table 2.1.

Table 2.1: Synthesis of different amide alkyne and alkene functional alkoxy silanes.

$$\text{R-O-Si(R)(O-R)}_2\text{-(CH}_2\text{)}_3\text{NH}_2 + \text{HO-C(=O)-R'} \xrightarrow[23\text{ }^\circ\text{C / 3h}]{\text{DCC / CH}_2\text{Cl}_2, 0\text{ }^\circ\text{C / 1h}} \text{R-O-Si(R)(O-R)}_2\text{-(CH}_2\text{)}_3\text{NH-C(=O)-R'}$$

Entry	Substrates	Product	Yield (%) ^[a]
1		2.10	95
2		2.11	92
3		2.12	88
4		2.13	95
5		2.14	91

^[a] The yields were determined by gas chromatography and verified by NMR spectroscopy.

2.3.2. Formation of hydantoin rings with isocyanates

The formation of hydantoin cycles was studied in the presence of the organic base triethylamine (TEA). When an equimolar amount of amide alkene functional alkoxy silane **2.10** and phenyl isocyanate (**2.15**) was stirred together at room temperature, an exothermic reaction took place (Figure 2.1). The resulting brown liquid was analyzed with the help of COSY, HSQC and HMBC NMR techniques to confirm the hydantoin ring formation. HMBC NMR experiments revealed the long range coupling of the methylene protons (position 3, Figure 2.1) with both carbons containing carbonyl groups (position 1 and 2, Figure 2.1), implying the urea group formation as a result of the reaction of amide with isocyanate. The formation of the hydantoin ring can finally be confirmed by the coupling of the vinyl protons (position 4, Figure 2.1) only with the carbon of the amide carbonyl group (position 2, Figure 2.1).

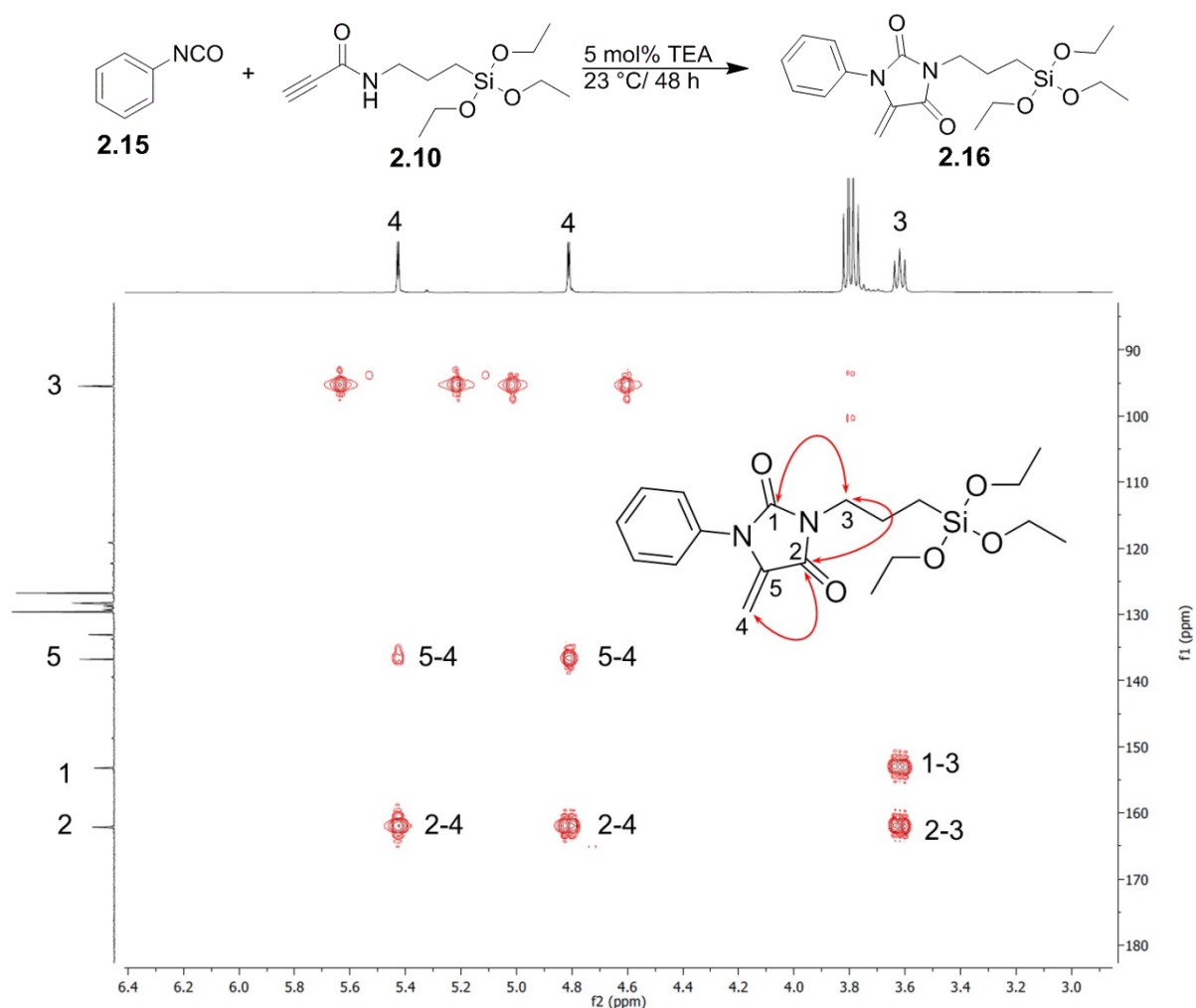
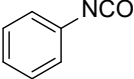
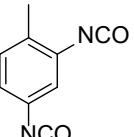
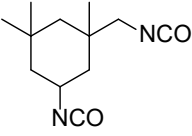
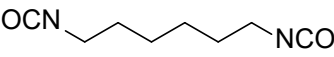


Figure 2.1: The formation of hydantoin ring proven by HMBC NMR experiment performed in CDCl_3 as a solvent.

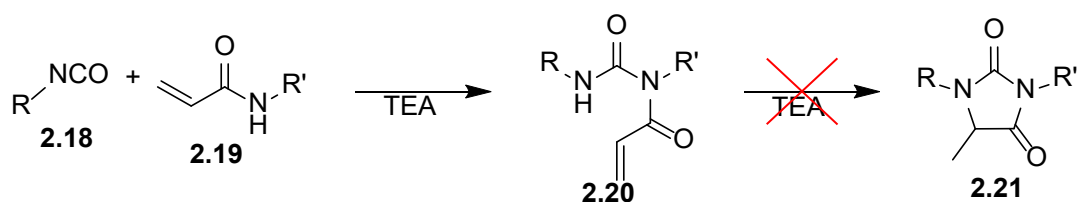
Having the practical protocol for the hydantoin ring formation in hand, the scope of the reaction with other diisocyanates commonly used in the SMP technology was studied. The formation of hydantoin cycle appears general with the use of aryl isocyanates (**2.15**, **2.16**) and results in excellent yields, however the use of bulky alkyl isocyanates like **IPDI** results only in good to moderate yields (Table 2.2).^[113] Less bulky isocyanates like hexamethylene diisocyanate (**2.17**) tend to form oligomers or polymers, which was observed also by other authors.^[107,113] A plausible explanation is that the increased basicity of the nitrogen atom bearing the alkyl group causes intermolecular interactions leading to the oligomerization and polymerization.^[106]

Table 2.2: The scope of the reaction using different (di)isocyanates.

Isocyanate	Structure	Yield (%) ^[a]
phenyl isocyanate		98
toluene diisocyanate (TDI)		83
isophorone diisocyanate (IPDI)		79
hexamethylene diisocyanate (HDI)		Oligomers

[a] Equimolar amounts of selected (di)isocyanate and compound **2.10** (NCO:**2.10** = 1:1) were mixed in THF at 23 °C for 48 h in the presence of 5 mol% TEA. ^[a] Isolated yields.

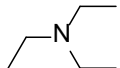
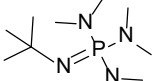
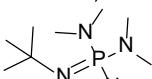
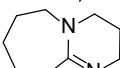
An attempt towards hydantoin ring formation was made by reacting isocyanate and alkene functional alkoxysilanes (**2.13**, **2.14**) which are significantly cheaper and less toxic. By employing the developed reaction conditions as described above and using TEA as base, the coupling of alkoxysilane (**2.13**) and aromatic isocyanate (**2.15**) was possible, however the formation of the hydantoin ring (**2.21**) was not detected. A plausible explanation is that since sp^2 hybridized carbon of the double bond is significantly less nucleophilic than sp hybridized carbon of the triple bond, which is not able to perform a successful nucleophilic attack to N-H of the urea intermediate (**2.20**). Consequently, the N-H deprotonation of the formed urea group on **2.20** is not possible; therefore the reaction is halted after the first step and the double bond is left unreacted.

**Scheme 2.5:** Schematic representation of the reaction between isocyanate **2.18** and alkene functional alkoxysilane **2.19** which does not proceed to form hydantoin ring **2.21**.

Another important aspect of the hydantoin ring formation is the use of an organic base as a catalyst. The most commonly used base for this type of the reactions is triethylamine, however, the unpleasant smell and low boiling point (101 °C) makes it less attractive for use in the consumer products. In the hope of finding an alternative catalyst a screening using optimized reaction protocol was performed, which provided us with two alternative catalysts

(Table 2.3). 1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU) and phosphazene base *tert*-Butylimino-tris(dimethylamino)phosphorane (P_1 *t*-Bu) are commonly used catalysts in organic synthesis and perform well also in our system. The reaction proceeded efficiently with both alternative catalysts resulting in completely reacted NCO groups, which was verified by NMR and IR spectroscopy. The singlet at 2.73 ppm of the triple bond in the NMR spectra completely disappeared, while doublets in the region from 4.8 to 5.5 ppm appeared, indicating that the hydantoin ring was formed. Another advantage of the presented catalysts (P_1 *t*-Bu and DBU bases) is that they are much more basic according to their pK_a values,^[114] which gives the possibility to lower the concentration of the catalyst to only 1 mol% (Table 2.3, entry 4).

Table 2.3: Base screening for the reaction of hydantoin ring formation.

Entry	Base	Structure	pK_a [114]	Concentration (mol%)	ΔT [°C] ^[a]	IR spectroscopy ^[b]
1	/				0	NCO band present
2	TEA		4.2	5	37	No NCO band observed
3	P_1 <i>t</i> -Bu		17.0	5	41	No NCO band observed
4	P_1 <i>t</i> -Bu		17.0	1	17	No NCO band observed
5	DBU		14.2	5	39	No NCO band observed

Equimolar amounts of phenyl isocyanate (**2.15**) and compound **2.10** were mixed in THF at 23 °C for 48 h in the presence of 5 mol% the selected base. ^[a] The exothermic reaction was monitored by inserting a temperature sensor directly in to the reaction mixture. ^[b] ATR spectra of was recorded after the reaction. NCO band appeared at 2254 cm^{-1} .

2.3.3. Prepolymer preparation

After the synthesis of different amide alkyne functional alkoxysilanes and the confirmation of the hydantoin cycle formation, the prepared end-cappers were tested in the conventional prepolymer synthesis.

The isocyanate functional polyol (**2.22**) was prepared by mixing an appropriate amount of isophorone diisocyanate (**IPDI**) and polypropylene glycol in the presence of DBU catalyst. Afterwards, the alkyne functional alkoxysilane (**2.10**) was added as it is shown in the Figure 2.2. After the reaction, the prepolymer was analyzed by NMR and IR spectroscopy to verify that all NCO groups reacted and to confirm the formation of the hydantoin ring. According to the IR spectrum of the reaction mixture, it was concluded that no free NCO (detection limit 0.5 % of all NCO groups^[115]) and alkyne groups are present in the prepolymer since the bands at 2257 cm^{-1} (NCO) and 2104 cm^{-1} (alkyne) disappeared after the reaction.

Furthermore, the intensity of N-H stretch band at around 3300 cm^{-1} is significantly decreased compared to the conventional end-capping with aminosilanes (Figure 2.2C). This indicates that the number of N-H groups was significantly reduced in the case of amide alkyne functional alkoxy silane (**2.10**) due to the hydantoin ring formation.

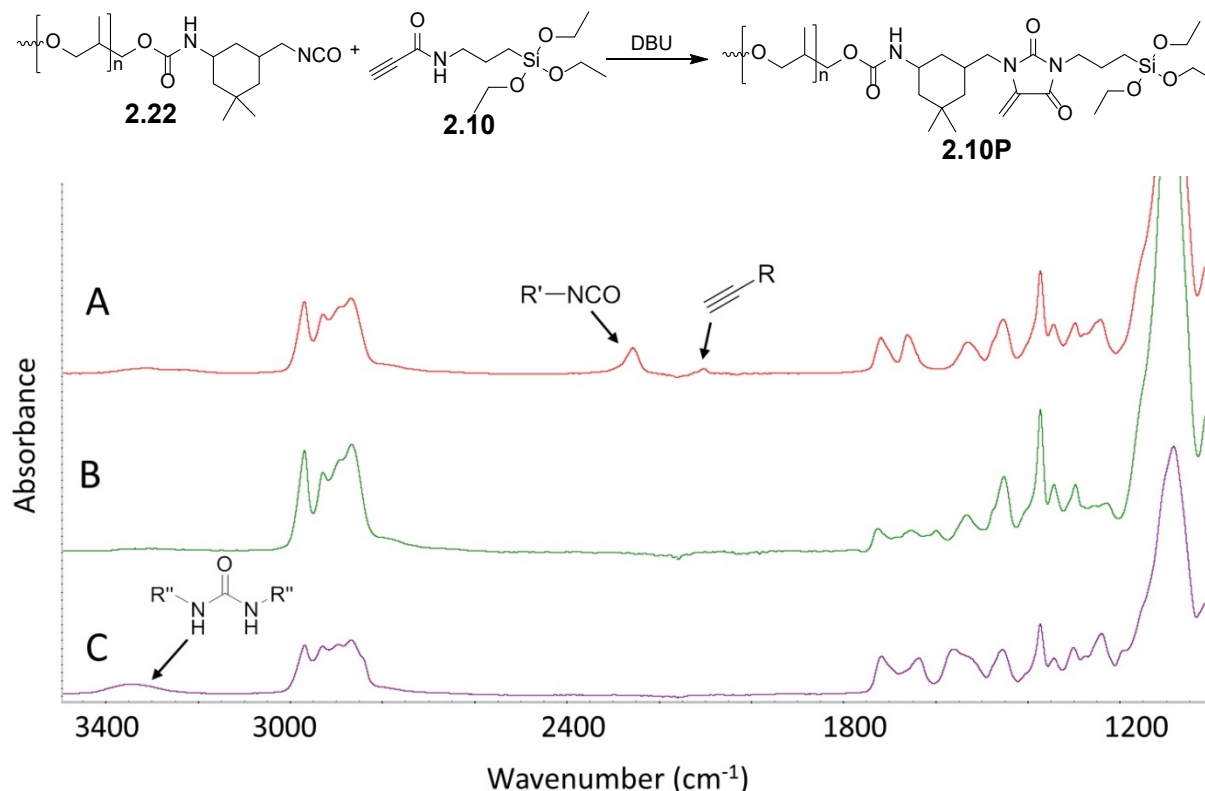


Figure 2.2: Preparation of silylated polyurethane (**2.10P**) using amide alkyne functional alkoxy silane (**2.10**) as an end-capper. **A:** IR spectrum of the reaction mixture of NCO terminated polymer (**2.22**) and **2.10** before the reaction. **B:** IR spectrum of the reaction mixture after the end-capping with **2.10**. **C:** IR spectrum of the reaction mixture after the end-capping with (3-aminopropyl)triethoxysilane (**AMEO**).

2.3.4. Rheological considerations

The viscosity of the prepolymers was measured after each synthetic step of the prepolymer method to follow the effect of the polymer modification on the hydrogen bonding. The viscosity build-up during the conventional prepolymer end-capping using aminosilane depends on many factors such as the molecular weight of the soft segment (PPG) etc. ^[116] In this particular case, the viscosity increase was 300 to 500 %, when using aminosilane as an end-capper. This is the consequence of the strong bidentate hydrogen bonding of the formed urea group. However, when amide alkyne functional alkoxy silanes (**2.10** and **2.12**) was employed as an end-capping agent, the viscosity increase was only 20-50 % (prepolymers **2.10P** and **2.12P**), which is a major improvement compared to other known methods (Figure 2.3). A minor rise of viscosity of prepolymers **2.10P** and **2.12P** can be attributed to the polymer chain extension due to the addition of the end-capper to the polymer chain ends and not to the hydrogen bonding. Prepolymer chain is elongated by the addition of the end-

copper from the both chain ends, which increases the viscosity slightly due to the well know relationship between polymer molecular weight and viscosity.^[117]

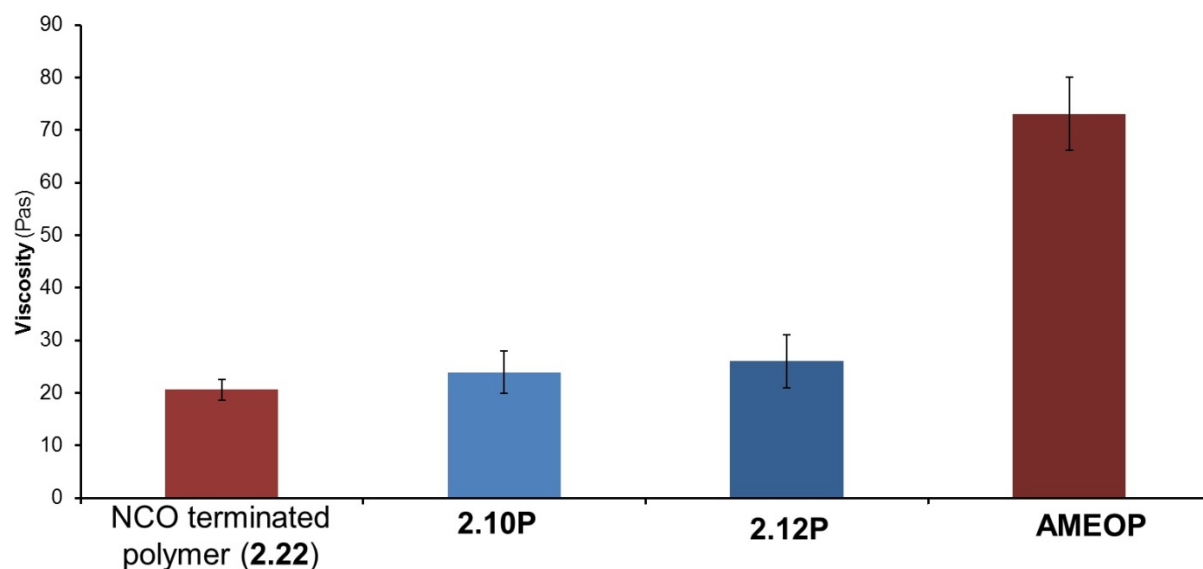


Figure 2.3: Viscosity of the prepared prepolymers before (**2.22**) and after end-capping with alkyne functional alkoxysilanes (**2.10** and **2.12**) or **AMEO** to produce corresponding prepolymers **2.10P**, **2.12P** and **AMEOP**. The prepolymers were prepared using standard prepolymer method and by using PPG with molecular weight of 4000 g/mol. The synthesis was reproduced three times and the viscosity value was averaged.

2.4. Conclusion

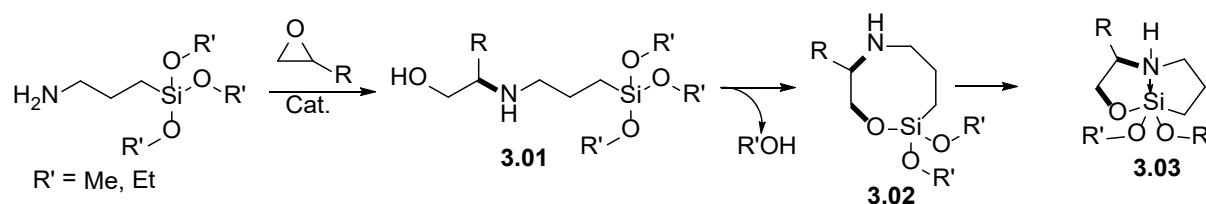
In summary, a new alkyne amide functional alkoxysilane coupling reagents were developed (**2.10-2.12**) using optimized reaction conditions in good to excellent yields. This facile coupling reagent is able to produce hydantoin cycles with isocyanates to completely eliminate the N-H hydrogen donor groups. The substrate scope of the developed methodology was investigated during this investigation, which showed high yields of hydantoin cycles for aromatic isocyanates, while aliphatic isocyanates give only moderate to low yields.

The ability of alkyne amide functional alkoxysilane to prevent hydrogen bonding of the urea group was exploited to prepare low-viscous silylated polyurethanes which are the first of its kind according to our knowledge.

3. Prepolymers end-capped with siloxacycloalkanes

3.1. Project outline

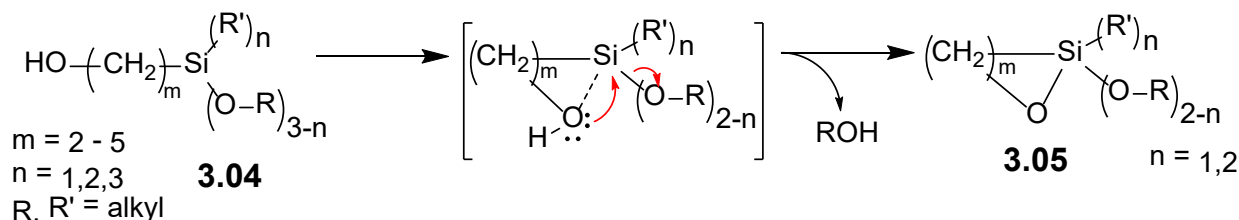
The search for alternative silicon-containing heterocyclic coupling reagents (from now on referred to as siloxacycloalkanes (**3.02**) or silatranes and (**3.03**)) represents a growing field in silicon chemistry and has a tremendous impact on adhesive and sealant industry.^[118] These versatile reagents can be implemented in various ways to enhance the performance of polymeric materials, like their adherence to the surface or to improve the curing speed of sealants.^[119] By combining current trends in organosilane chemistry with the need to produce low viscous silylated polyurethanes, new siloxacycloalkane end-cappers were developed. The aim was to prepare compounds by ring opening of epoxides with aminosilanes in the first step, which cyclize to yield siloxacycloalkane rings (**3.02**) as presented in the Scheme 3.1. The prepared coupling reagents are to be used further to prepare silylated polyurethanes in order to investigate their influence on rheological, curing, adhesive and tensile properties.



Scheme 3.1: Ring opening of epoxides to prepare siloxacycloalkanes (**3.02**) and silatranes (**3.03**).

3.2. Background

Reports show that intramolecular coordination between oxygen and silicon in silicon containing heterocycles on the ground state enhances the replacement of the alkoxy group by other electron withdrawing groups to form a cycle.^[120] Thereby the electron accepting ability of the silicon atom is increased. The importance of such interaction lies in the instability of hydroxyl functional alkoxy-silanes, which readily decompose and produce cyclic products.^[121] Among these products are siloxacycloalkanes (**3.05**), which are cyclic alkoxy-silanes, formed as a result of the cyclization of hydroxyl-functional alkoxy- or chlorosilanes (**3.04**). The formation of siloxacycloalkanes is a consequence of the hydrolytic instability of alkoxy- or chlorosilane groups, which are being intramolecularly hydrolyzed by the hydroxyl group. Koerner and Rossmly were the first to synthesize five and six membered alkylalkoxycyclosiloxanes by the transesterification reaction to obtain a primary alcohol in the first step. They proposed that the primary alcohol is not stable in the presence of alkoxy-silanes and therefore tends to cyclize, eliminating the corresponding alcohol (Scheme 3.2).^[122] An intermolecular condensation of the hydroxyl functional alkoxy-silanes is also a possibility, which results in the formation of oligomers and polymers, however this has not been observed in practice. The cyclization reaction was explained by Spier *et al.*, who proposed that the weak intramolecular coordination between oxygen and silicon might be responsible for decomposition to cyclic product and not to long chain oligomers and polymers, which one might also expect.^[123]



Scheme 3.2: Cyclization of the hydroxyl functional alkoxy-silane (**3.04**) to form siloxacycloalkane (**3.05**).

The same observation was also reported by Kuwajima *et al.*, who prepared 5, 6 and 7-membered siloxacycloalkane rings, synthesized by intramolecular cyclization of primary alcohols with alkoxy-silanes.^[124] Others also proved the instability of secondary and tertiary alcohols in the presence of alkoxy-silanes, which results in the formation of a variety of siloxacycloalkanes.^[121,125]

Lukevits *et al.* reported the formation of a $\text{N} \rightarrow \text{Si}$ dative bond in the siloxacycloalkane rings.^[126] They discovered that the formation of the $\text{N} \rightarrow \text{Si}$ dative bond is a result of the donation of the nitrogen lone pair to the silicon atom to form a pentavalent silatrane compound (**3.05**). Considerable attention was also placed on the length of $\text{N} \rightarrow \text{Si}$ bond and its effect on the stability of the silatrane compounds. An important observation regarding the

structural characteristics of these compounds is the relationship between the Si-X (X being methoxy, hydroxyl group or halogen) and Si-N distances: the longer the Si-X bond length (implying a weaker Si-X bonding interaction) generally results in a shorter Si-N distance (suggesting a stronger Si-N bonding interaction) and vice versa (Figure 3.1).^[127] These findings indicate that by changing the substitution on the Si or N atom one can influence the strength of the N→Si dative bonding, which consequently influences the stability of the silatranes.^[128]

Jensen *et al.* investigated the effect of the substitution on the relationship of N→Si dative bond vs. Si-X bond on the axial position. Specifically they focused on the relationship between the number of the bridges (n) and the interaction between Si and nitrogen.^[127a] They found that as n increases, more charge is accumulated in the Si-O and Si-N bonding region. As n is decreased from 3 to 1 the axial Si-O bond weakens and the Si-N bond strengthens. These findings indicate, that the bridging in the silatrane compounds is of key importance for the formation of the N→Si dative bond. However, if the number of bridges is too high, they tend to stabilize the pentavalent silicon compound resulting in lower hydrolysis rates. It was pointed out long time ago that triple bridged ($n = 3$) silatranes are relatively stable to the atmospheric moisture and were more difficult to hydrolyze than the corresponding derivatives of triethoxysilanes.^[129]

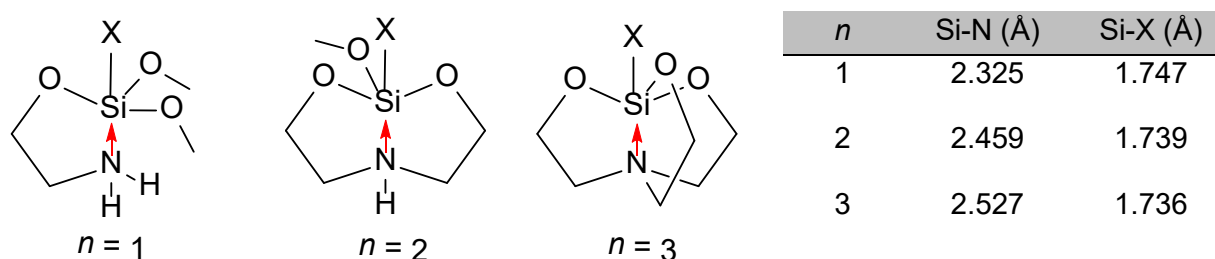


Figure 3.1: Representative structures of alkoxy-silatrane compounds taken from the reference [127a]. The bond distances were obtained from corresponding XRD structures. n = number of bridges between Si and N atoms; X = group on the axial position to the Si-N dative bond (-OH in this above described case).

In order to obtain versatile silane coupling reagents for the use as adhesive promoters or as end-cappers, it is advantageous to prepare compounds with fast hydrolysis rate. This goal can be achieved by using pentavalent silatranes containing minimal number of bridges ($n = 1$ or 2). A number of patents and research papers report the use of siloxacycloalkane rings as volatile coupling reagents in nanotechnology,^[118] surface treatment,^[130] end-capping,^[119] etc.

Azasilanes are cyclic silanes containing Si-N bond in the place of Si-O bond of siloxacycloalkane ring. They emerged as volatile surface treatment reagents, which react exothermically with hydroxyl groups on the surface of the materials by a ring opening reaction.^[118] The ring opening produces amine functionality, which can be then further

3.3. Results and discussion

3.3.1. Preparation of siloxacycloalkanes

Semlalia *et al.* demonstrated the catalytic efficiency of calcium trifluoroacetate $\text{Ca}(\text{CF}_3\text{CO}_2)_2$ (CTFA) for selective ring opening of epoxides by amines.^[133] The catalyst proved to be selective towards the production of β -aminoalcohols in stoichiometric yields. Larger amount of this catalyst was prepared by a modified literature report,^[134] which was later used for selective ring opening of epoxides with aminosilanes. The reaction products were analyzed by GC and GC-MS, which allowed the determination of the reaction selectivity (Table 3.1 and Table 3.2).

First, several experiments were performed in order to optimize the reaction conditions for the sake of increasing the reaction yield. During this investigation the reaction temperature and the molar ratio of reactants for each type of epoxide were screened. This allowed the development of optimal reaction conditions for each epoxide, maximizing the reaction yield and selectivity, along with minimizing several potential work-up steps. An example of optimization for the reaction between (3-aminopropyl)triethoxysilane (**AMMO**) and propylene oxide (**PO**) to prepare siloxacycloalkane (**3.06**) is shown in the Table 3.1. A detailed process on the reaction optimization is described in the appendix (A3.1).

Table 3.1: Reaction selectivity of the propylene oxide (**PO**) ring opening by (3-aminopropyl)triethoxysilane (**AMMO**).

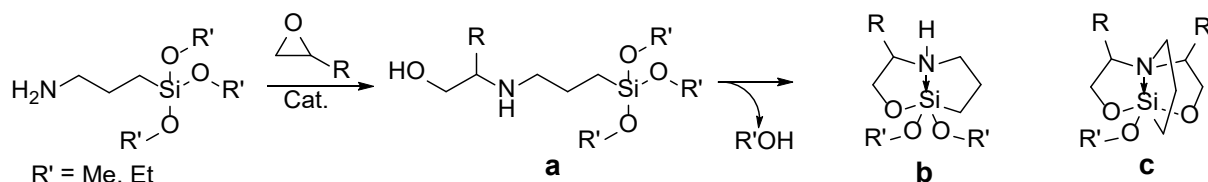
Entry	Temperature [°C]	Ratio AMMO : PO	3.06	3.07	Conversion [%] ^[a]
1	23	1 : 1	64	6	70
2	23	1 : 2	3	96	99
3	0	1 : 1	77	4	81
4	0	1 : 2	92	6	98

^[a] The conversion refers to the consumption of the **AMMO**, which was determined by integrating the peaks of GC chromatography.

The reaction of aminosilane with epoxides under mild conditions provided excellent conversions to the corresponding aminoalcohol in each case. The produced hydroxyl group performs a nucleophilic attack on to the alkoxy silane to form a siloxacycloalkane ring. However, the latter process proved to be less efficient in the case of ethoxysilanes, where the major product is the hydroxyl functional alkoxy silane (Table 3.2, entry 1 and 2). It is well established that the hydrolytic stability of alkoxy silanes increases by increasing the number of carbon atoms of the alkoxy groups due to the steric and inductive effects,^[135] meaning that the hydrolysis of methoxysilane groups is up to 10 times faster than the equivalent

ethoxysilane groups.^[6f] Due to this reason, the conversion of ethoxysilanes (**AMEO**) to corresponding siloxacycloalkane is lower in comparison to methoxysilanes (**AMMO**). This observation indicates that the nucleophilic attack of the hydroxyl functional alkoxy silane is the rate determining step for producing siloxacycloalkanes.

Table 3.2: Reaction selectivity of the epoxide ring opening by aminosilanes.



Entry	R'	Epoxide	Products ^[a] [mol%]			Conversion ^[b] [mol%]
			a	b	c	
1	Et		78	16	0	94
2	Et		42	41	0	83
3	Me		0	99	0	99
4	Me		0	92	6	98
5	Me		0	95	3	98
6	Me		0	61	36	97
7	Me		0	95	2	97
8	Me		0	97	1	98

2 mol % of CTFA, aminosilane and epoxide were mixed for 48 h at room temperature. Afterwards the produced alcohol was removed and the product was analyzed with NMR and gas chromatography.^[a] The results of the reaction selectivity were determined by GC.^[b] The conversion refers to the consumption of the appropriate aminosilane, which was determined by integrating the peaks of GC chromatography.

Based on the performed experiments, it was concluded that the reaction of the epoxides with aminosilanes showed good to excellent selectivity towards mono-addition to produce product **b** as shown in the Table 3.2. Ordinarily, if the purity of the alkoxy silane is in the range for 90 to 95 mol% it can be used for the preparation of the silylated polyurethanes without further purification. That means that most of the prepared end-cappers can be employed in the prepolymer method directly after their synthesis. However, to test the real performance of the end-capper in the prepolymer system, it was necessary to purify the products *via* vacuum

distillation. This process significantly lowered the yields due to the large amount of crosslinking during the heating. The yields after purification are presented in the Figure 3.2.

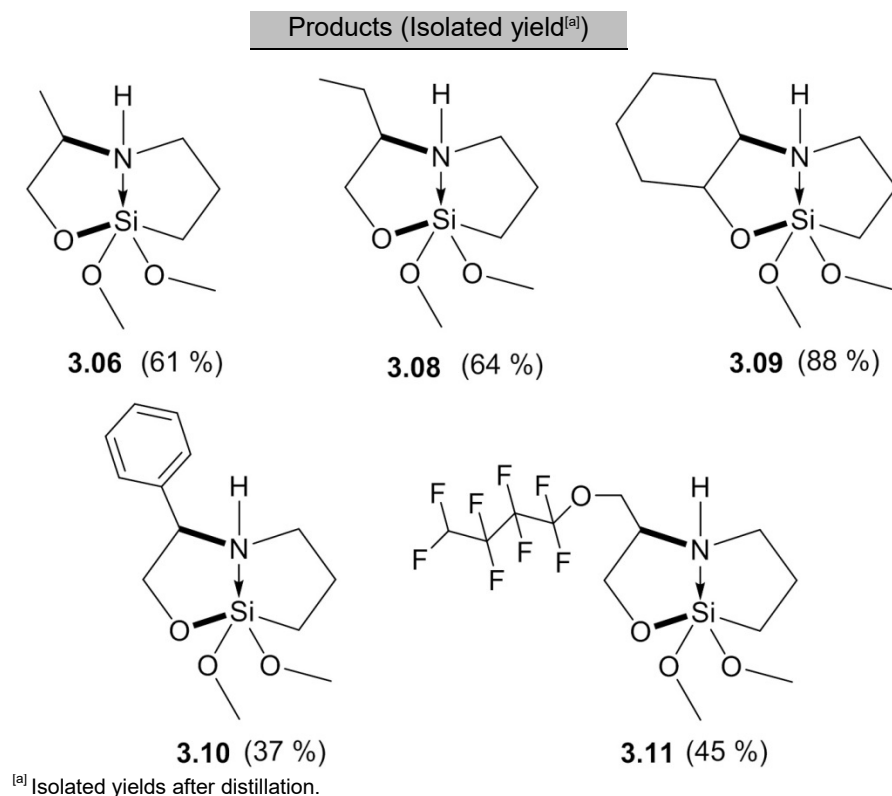


Figure 3.2: Prepared siloxacycloalkenes (**3.06**, **3.08-3.11**) and their corresponding isolated yields.

3.3.2. Structural considerations

The siloxacycloalkane end-capper (**3.09**) prepared from cyclohexene oxide is a crystalline solid at room temperature; therefore it was possible to characterize it using single crystal X-ray diffraction (Figure 3.3).

The coordination geometry of the silicon atom is a trigonal bipyramid, as is observed in most silatranes.^[127b,136] The length of the N→Si dative bond is 2.259 Å, which is in the same range as in the reported data.^[127] The weak coordination of the nitrogen lone pair to the silicon changes the electronic state of the silicon by reducing the partial positive charge on silicon, which strongly influences the Si–O bond lengths. The Si1–O2 bond on the axial position is the longest compared with the other two equatorial Si1–O1 and Si1–O3 bonds, since the length of this bond is strongly dependent on the strength of the N→Si dative interaction. According to literature findings, as the N→Si coordination strengthens, the Si1–O2 bond weakens.^[127a] This phenomenon was explained by Jensen *et al.*, who based the explanation on the charge localization between N→Si1–O2 bonds. As more charge is accumulated in the N→Si dative bond, implying a stronger bond, less charge is in the Si1–O2 bonding region leading to decrease in bond strength.^[127a,129] The influence of the N→Si dative bond on the

Si-O bonding is of particular interest since the interaction of Si and oxygen is important for the hydrolytic stability of the end-capper.

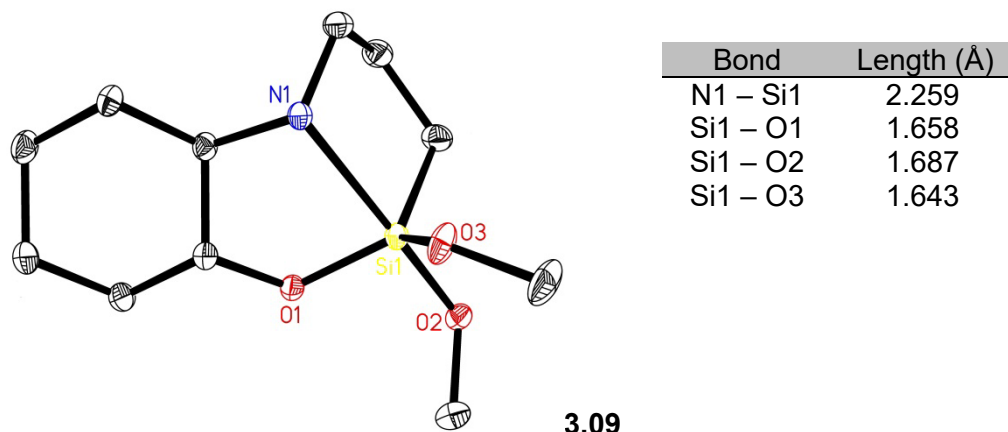


Figure 3.3: ORTEP diagram of the structure of *N*-methylcyclohexene-8,8-dimethoxy-1-oxa-4-aza-8-sila (**3.09**). Displacement ellipsoids correspond to 30 % probability. The carbon atom labels and hydrogens are omitted for clarity.

In order to investigate the effect of the N→Si dative bond on the hydrolytic stability of siloxacycloalkane, the interest was in comparing the strength of the Si-N interaction in the prepared end-cappers. Unfortunately the crystallization of other siloxacycloalkanes was not achieved, since the melting points were well below the room temperature. To compare the interaction between Si and N, the investigation of the shifts in the ^{29}Si NMR spectra of all prepared siloxacycloalkanes was undertaken. A large up-field shift in the ^{29}Si NMR spectra for siloxacycloalkane compared to related trimethoxysilane could be observed, as showcased in Figure 3.4 Right.

Shevchenko suggested that the positive charge at a silicon in silatranes is higher than in trialkoxysilanes, which could explain the up-field shift in the ^{29}Si NMR spectra of the silatranes, due to the well-known relationship between chemical NMR shift and Si effective charge.^[137] However, a straightforward correlation of the ^{29}Si NMR shifts and the length of the N→Si dative bond proved difficult to assess. The influence of the group in the axial position has a strong effect on the N→Si dative bond, which can be also detected in the shift of the alkoxy silane signal in the ^{29}Si NMR spectra and can deviate from 11 to 25 ppm.^[137] On contrary, the substitution on the amino group has only a small influence on the N→Si interaction, therefore characterization with ^{29}Si NMR is challenging, since the ^{29}Si NMR shifts deviate only around 1–4 ppm.^[136] Based on the measured ^{29}Si NMR spectra presented in the Figure 3.4 Left, we can conclude, that only a small up-field shift can be observed for electron donating Me- (**3.06**) and Et- (**3.08**) groups on the α -position next to the amino group, compared to electron withdrawing ones like phenyl (**3.10**) or fluoroether (**3.11**). The changes in ^{29}Si NMR shifts indicate that the N→Si dative bond length might vary slightly, but is in the same length range. A larger down-field shift for the cyclohexane derivative (**3.09**) can be

explained by a combination of steric and electronic reasons. The coordination of N to Si atom is in this case more difficult due to the rigidity of the cyclohexene ring, which restricts the proximity of the N atom to the Si and therefore the electron withdrawing effect of N to Si is in this case weaker.

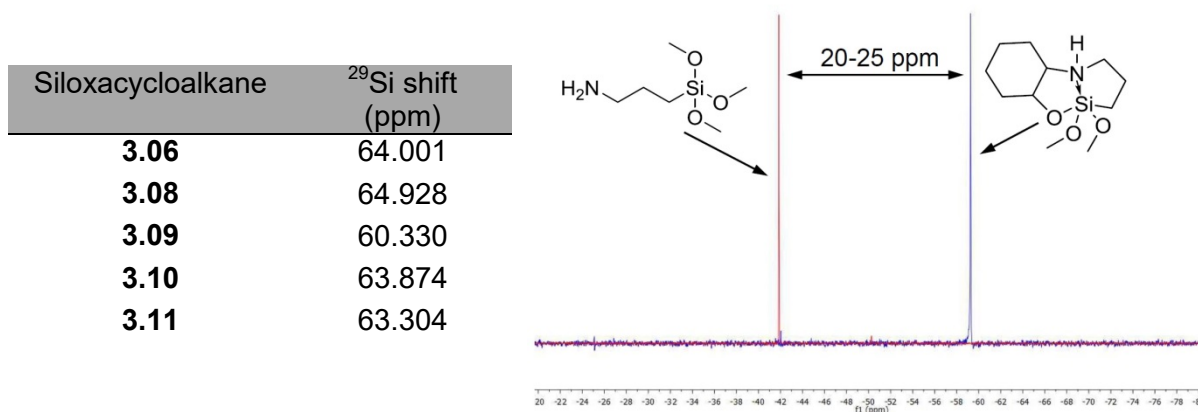


Figure 3.4: Left: ^{29}Si NMR shifts of prepared siloxacycloalkanes. Right: Comparison between trimethoxysilane and siloxacycloalkane **3.09** ^{29}Si NMR shifts.

3.3.3. The reactivity of siloxacycloalkenes with isocyanates

A side effect of the N \rightarrow Si dative bond is a decrease in the nucleophilicity of the amine group, since the nitrogen lone pair is coordinated to the silicon atom and is therefore unavailable for the nucleophilic attack. This can prove problematic in the prepolymer method, where the amine functional end-capper is reacted with NCO functional prepolymer. In order to test if the developed end-capper is able to react with the isocyanate, the compound **3.09** was reacted with phenyl isocyanate, which resulted in a product **3.12** in 99 % yield. After the recrystallization, the obtained product was characterized with single crystal X-ray diffraction (Figure 3.5).

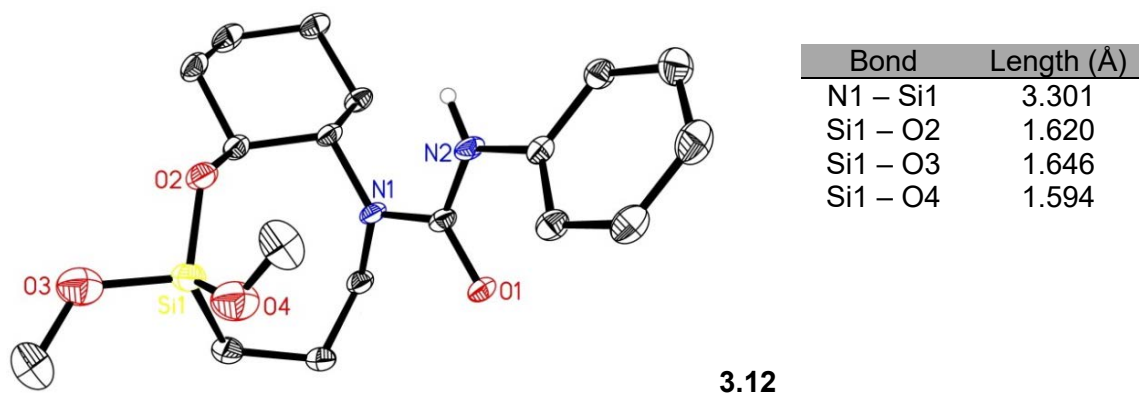


Figure 3.5: ORTEP diagram of the structure of **3.09** reacted with phenyl isocyanate to obtain **3.12**. Displacement ellipsoids correspond to 30 % probability. The carbon atom labels and hydrogens are omitted for clarity.

The crystal structure shows a tetravalent siloxacycloalkane compound (**3.12**) with slightly distorted tetrahedral geometry around the silicon, which was determined by measuring bonding angles. The most important observation is that the N→Si dative bond is broken, when an electrophile is reacted with a silatrane compound. The break is a consequence of the nucleophilic attack of the amino group on to the NCO. In order to achieve a successful reaction, the lone pair on nitrogen becomes available by breaking N→Si dative bond.^[138] The distance between Si and N atom is elongated from 2.259 to 3.301 Å. Consequently, the geometry and distance of Si-O bonds change. The distance of the most Si-O bonds is slightly shortened, which indicates a stronger Si-O interaction and therefore stronger bonds. The break of the N→Si dative bond indicates the improvement of the hydrolytic stability of the developed end-capper, which might result in slower curing speed of the silylated polyurethanes end-capped with siloxacycloalkanes compared to established **AMMO** end-capped prepolymer.

3.3.4. Hydrolytic stability of siloxacycloalkenes

The kinetic and mechanistic investigation in to the hydrolytic stability of prepared siloxacycloalkanes was conducted with the help of the NMR spectroscopy. The sample of the siloxacycloalkanes was dissolved in D₃-acetonitrile and placed in to the NMR spectrometer. Directly before the measurement, 1 % aqueous solution of formic acid was added to the reaction mixture to initiate the hydrolysis of the alkoxysilane groups. The process could be well followed by recording one ¹H and ²⁹Si NMR measurement every hour. The ²⁹Si NMR spectra were exploited to determine the concentrations of TAS (non-hydrolyzed compound), M (one hydrolyzed methoxy group), D (two hydrolyzed methoxy groups) and T (three hydrolyzed methoxy groups) structures. Each of these structures has a characteristic shift in the ²⁹Si NMR spectra: ≈ -40 ppm TAS, ≈ -49 ppm for M structure, ≈ -59 ppm for D structure and ≈ -65 ppm for T structure, as is shown in the Figure 3.6.^[6e]

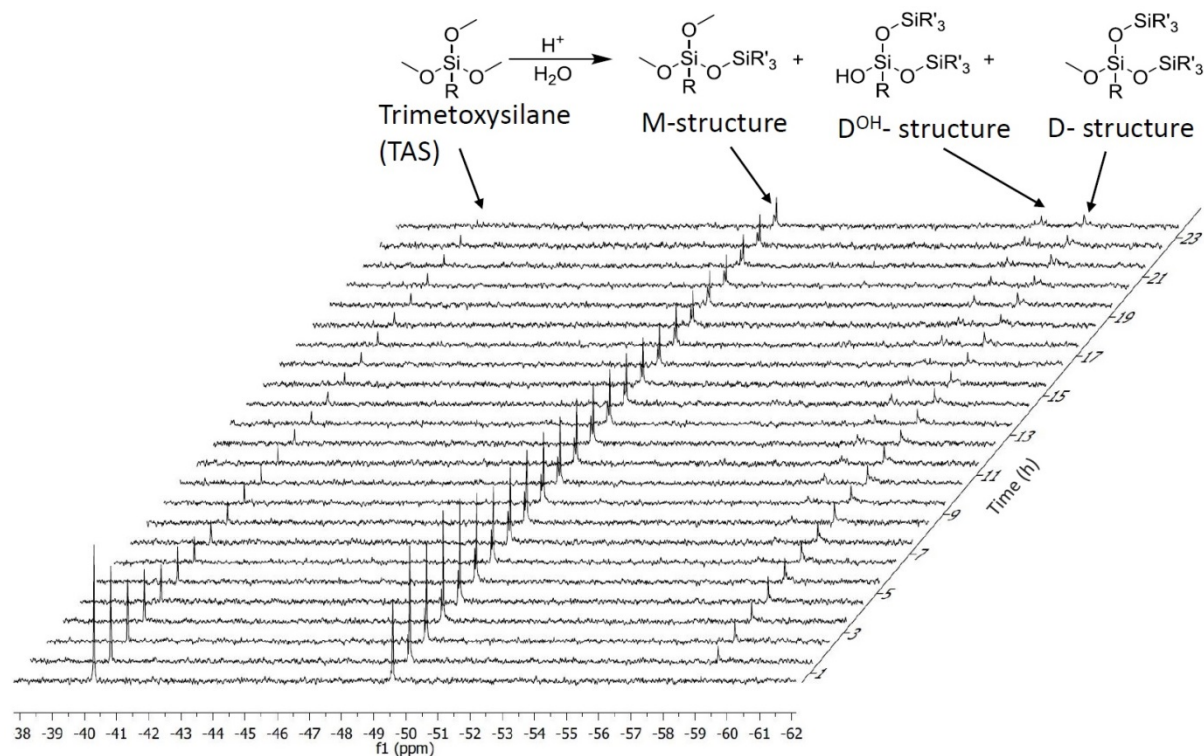


Figure 3.6: Recorded ^{29}Si NMR spectra of the compound **3.09** during hydrolysis relative to time.

According to the literature findings, the signals at -40.1, -49.3 and -59.2 ppm were assigned to TAS, M and D silane structures. In the case of siloxacycloalkanes **3.09** and **3.11**, T structures, which should have the highest up-field shift were not observed.^[6e] The unusual increase of the signal intensity at -57.8 ppm was attributed to the D-silane structure containing an additional silanol group. It is well established, that the transition from Si-OR to the corresponding Si-OH gives a shift to lower fields due to the stronger -OH electron withdrawing character compared to the methoxy group.^[6e,139]

The electron density of the Si center in silatranes is increased due to the N electron pair donation, which usually results in the shift of the ^{29}Si NMR signal up-field from -40 to about -60 ppm. However, the addition of a small amount of aqueous acid solution resulted in the down-field shift of ^{29}Si signal back to -40 ppm, indicating the break of the N→Si dative bond. The splitting of the dative bond is a consequence of the nitrogen atom protonation rather than the breaking of the endocyclic Si-O bond as was proposed previously.^[140] Since no signal at around -60 ppm for the Si atom with the dative bond was observed in the early stages of experiment, it was assumed that this is first step of the hydrolytic process.

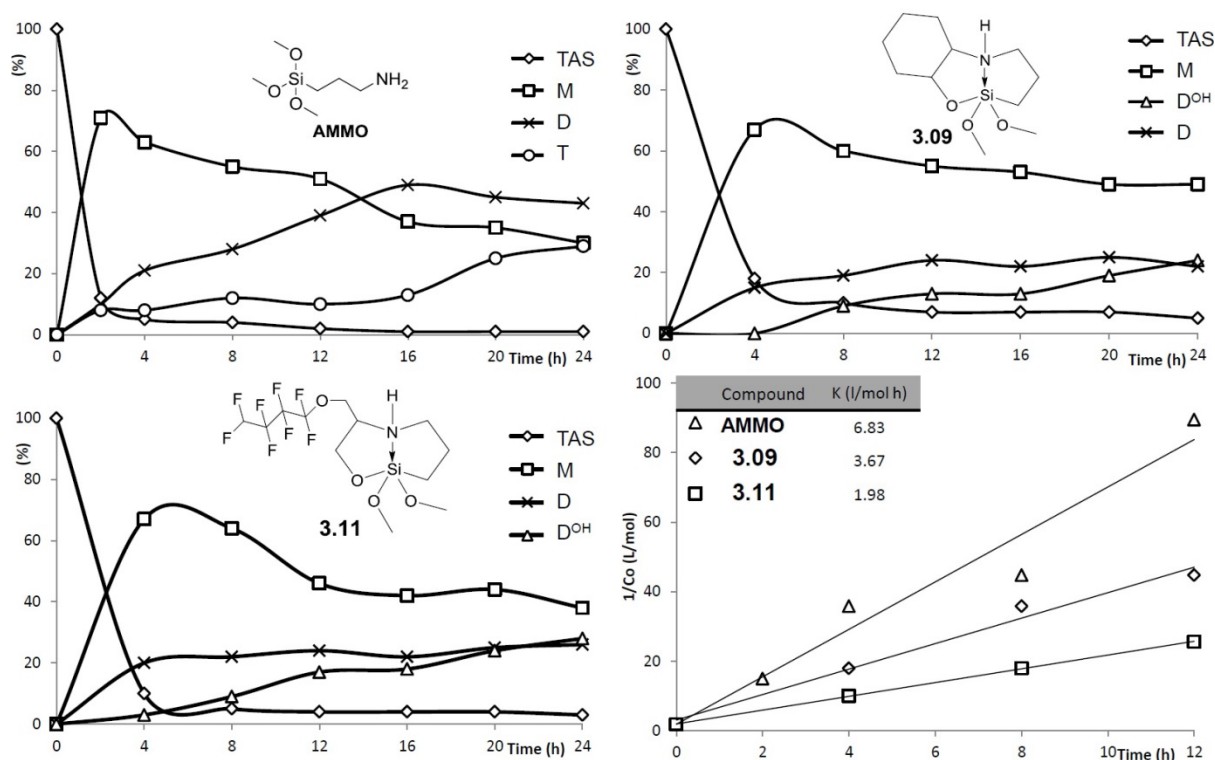


Figure 3.7: Hydrolytic kinetic curves of alkoxy silanes in acidic media extrapolated from time resolved ^{29}Si NMR spectra. **Bottom right:** linearized kinetic curves of the TAS (non hydrolyzed structure) according to the second order kinetics.

The hydrolysis curves of the three studied silanes were obtained by signal integration in the ^{29}Si NMR spectra. In all cases, the resolution of the NMR spectra gradually decreased overtime; therefore the analysis of the products over longer time ($> 20\text{h}$) is no longer reliable.

The best indication of the hydrolytic speed can be estimated by following the decline in the concentration of trialkoxysilane (TAS) signal, which can be well correlated by the second order kinetics.^[129] This indicates, that the reaction is of bimolecular type, where the concentration of silane (TAS) and H_3O^+ ions is of great importance. Due to this reason the hydrolysis speed is highly dependent on the pH of the solution as discussed in the literature.^[129]

The reaction rate constant was determined for all three alkoxy silanes, which shows that the kinetic behavior of silatrane hydrolysis (**3.09** and **3.11**) in acidic media is slower compared to the linear aminosilane (**AMMO**). At least three factors can be attributed to the increase of hydrolytic stability of silatrane compounds:

The presence of the $\text{N} \rightarrow \text{Si}$ interaction decreases the partial positive charge on the Si atom and hampers the nucleophilic attack by water or other anions.^[6d]

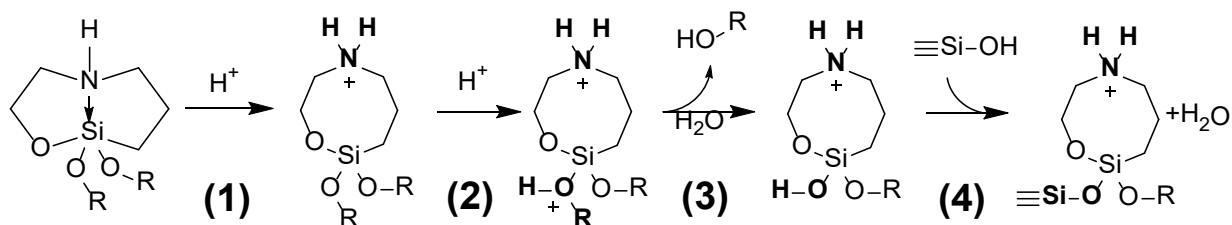
Bulky groups of silatranes like cyclohexene ring of compound **3.09** hinder the electrophilic attack of the hydroxonium ion (H_3O^+).^[6d] This can be well correlated with the fact that the hydrolysis rate of the less bulky silatrane **3.11** is higher than its bulky variation **3.09**.

The effect of the leaving group plays probably the most important role, since it is well known that the relative rate of hydrolysis increases with the number of smaller, less electron donating groups. For example, relative rates of alkyltrimethoxy, alkylethoxydimethoxy and alkylmethoxydiethoxy decreases in that order.^[141] This indicates that the ring of the siloxacycloalkene stabilizes the structure and suggests that the ring opening of the structure is the final hydrolytic step, however it was not possible to prove this claim so far.

As shown in the Figure 3.7, **AMMO** and both silatranes (**3.09** and **3.11**) underwent hydrolysis in a similar manner, since the kinetic curves of the TAS, M and D species show similar trends. However, T structures can only be observed in the ²⁹Si NMR spectra of **AMMO**, while in the spectra for silatrane compounds a signal for D^{OH} appeared. The formation of relatively stable silanol groups indicates that the formation of a completely crosslinked network in these compounds is slow, since only 2 alkoxy groups are condensed to form Si-O-Si bonds. This leads to the formation of linear oligomers or polymers. In order to achieve effective crosslinking three Si-O-Si bonds need to be formed per every silane.^[142]

Based on the presented hydrolytic study of double-bridged silatranes in acidic medium and reported literature findings, the following reaction mechanism has been proposed (Scheme 3.4):

1. Protonation of the nitrogen atom and concerted cleavage of the intramolecular N→Si dative bond.^[143]
2. An electrophilic attack of the hydroxonium ion on to one of the alkoxy-oxygen. The protonation of the oxygen becomes slower after the first, second and third groups are hydrolyzed.^[141a]
3. Cleavage of one of the Si-O bond followed by the formation of the silanol group and corresponding alcohol as a leaving group.
4. The condensation of silanol to produce siloxane polymer chain.



Scheme 3.4: Proposed mechanism for the acid catalyzed hydrolysis of silatranes.

Since silanol-functional alkoxy silane was detected in the ²⁹Si NMR spectra and it was gradually increasing with the progress of the reaction, it was suggested that the condensation of silanols to siloxanes is the rate determining step of the overall reaction.

The goal of the presented investigation was to obtain a mechanistic insight in to the hydrolysis of siloxacycloalkenes and possibly correlate this behavior in to the prepolymer curing process. The performed study of hydrolysis of siloxacycloalkenes in acidic media gives us a good indication in to the hydrolytic performance of the prepared compounds compared with conventional silanes. Even though the nature of the environment during the hydrolytic study is different to the one in the prepolymer system, it is expected to witness the analogous curing trend.

3.3.5. Prepolymer preparation

Having assessed a practical protocol for the preparation of siloxacycloalkanes, they were employed as end-cappers for the preparation of moisture curable polyurethanes. All prepolymer reactions utilizing siloxacycloalkanes proceed smoothly at 80 °C for 3 hours, and were seemingly unaffected by the electronic or steric nature of the end-cappers. However, it seems that the siloxacycloalkane end-capping reaction rate is lower compared to the conventional aminosilane end-capping. An attempt was made to shorten the reaction time from 3 to 2 hours, which resulted in unreacted NCO groups detected by IR spectroscopy. A reasonable explanation is that the N→Si dative bond of the siloxacycloalkanes decreases the nucleophilicity of the amine group, since the nitrogen lone pair is coordinated to the silicon atom and is therefore unavailable for the nucleophilic attack on to the isocyanate as was already discussed in the chapter 3.3.3.

Figure 3.8 shows the viscosities of the prepared prepolymers containing siloxacycloalkane end-cappers compared to conventional **AMMO** end-capping. A positive trend was noted, since the viscosities of most prepoylmers are lower compared to the conventional system. Only in the case of siloxacycloalkane containing cyclohexane ring (**3.09**) the viscosity is higher, which can be attributed to a high melting point (55 °C) of the employed end-capper, while other end-cappers have melting points well below room temperature. Therefore, most of the end-cappers can be used in a liquid form, while siloxacycloalkane containing cyclohexane ring (**3.09**) must be melted beforehand.

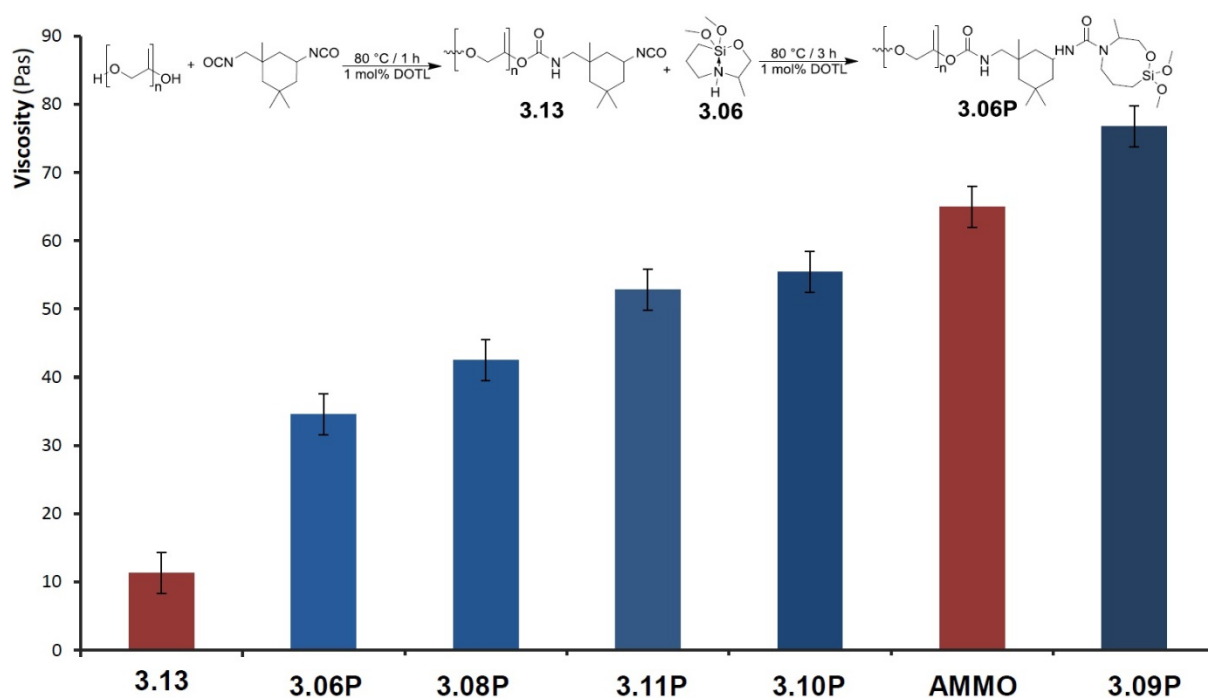


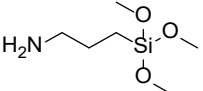
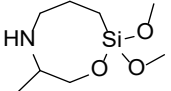
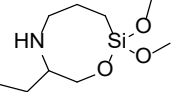
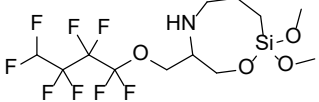
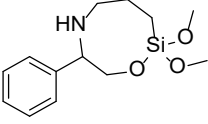
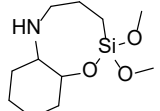
Figure 3.8: Viscosities of prepolymers end-capped with different siloxacycloalkenes. The synthesis was reproduced three times and the viscosity value was averaged.

A decrease in the viscosity of the prepolymers can be attributed to several factors. The most obvious explanation is the absence of active hydrogen in the urea group, which is a result of the reaction of the secondary amine group with the isocyanate. In this way, bidentate hydrogen bonding is prevented, resulting in weaker polyurea hard-segment packing leading to a decrease in the prepolymer viscosity. Another reasonable explanation could also be hindering of the remaining N-H by bulky groups of the end-capper, however this proved be a minor factor, since it is obvious from the Figure 3.8 that bulkier end-cappers (**3.09**, **3.10** and **3.11**) lead to higher viscosity.

Another important property of any moisture curable adhesive or sealant is its curing speed in the hydrolytic environment. Tests on the adhesives to determine their curing or setting behavior are for example tack-free time, pot life or skin-over time (SOT), which are usually determined visually or mechanically.^[144] The most commonly used method for determining the curing speed of silylated polyurethanes is the SOT determination. The SOT of prepared prepolymers was estimated by spreading them on a glass surface and visually determining when a thin solid (cured) layer is formed over the polymer film. It is evident from Table 3.3 that all siloxacycloalkane end-cappers exhibit slower curing rates compared to the conventional **AMMO** end-capper. This is consistent with our time resolved NMR study of the hydrolytic behavior of siloxacycloalkanes, which revealed that siloxacycloalkanes are more hydrolytically stable than conventional aminotrialkoxysilanes. Moreover, the hydrolytic behavior also depends on the substitution of the siloxacycloalkane cycle. Less sterically

demanding groups have a positive effect on the hydrolytic speed of the alkoxy silane groups as is evident from the Table 3.3.

Table 3.3: Skin over time (SOT) of the prepolymers end-capped with presented siloxacycloalkanes (PPG 4000 g/mol). Standard deviation is ± 0.5 h.

Entry	Prepolymer	End-capper	SOT (h)
1	AMMOP		0.5
2	3.06P		2.5
3	3.08P		2
4	3.11P		2
5	3.10P		6
6	3.09		12

It is noteworthy to mention that many prepolymers end-capped with siloxacycloalkanes remained slightly tacky even after several days at atmospheric conditions, while conventional silylated polyurethanes completely cure in 24 hours. Tackiness is the result of incompletely hydrolyzed alkoxy silane groups of the siloxacycloalkanes on both chain ends as was shown during hydrolytic test followed by time resolved NMR measurement.

3.3.6. Hydrogen bonding in prepared prepolymers

To investigate the effect of the hydrogen bonding on the viscosity and potentially on the mechanical properties of the cured film, the infrared spectra of the prepared prepolymers was closely investigated. Infrared spectroscopy is very sensitive to the hydrogen bonding and is a technique of choice in the characterization of wide range of polyurethanes.^[45,145]

The first step in our investigation of the hard segment self-association in the prepolymer matrix was the review of the IR band assignment as many authors have reported before.^[45,146] Despite the fact that many vibrational modes are sensitive to hydrogen bonding, the most commonly studied bonds are N-H and C=O at 3150-3400 and 1550-1800 cm^{-1} respectively. However, since N-H stretching in the IR spectrum appears as a very broad band, a high concentration of urethane and urea groups is required in the sample to obtain a

reliable result. This is unfortunately not the case in prepolymers which were prepared during this investigation. Due to this fact, the focus was on to the carbonyl group band assignment.

Two bands appeared in the regions 1690-1740 and 1600-1680 cm^{-1} , which were assigned to urethane and urea carbonyl stretch respectively. Both bands were mathematically corrected by the help of the Fourier deconvolution in order to obtain a better resolution of the IR spectra for further deconvolution.^[147]

Many authors have discussed the urea and urethane IR spectra and its mathematical resolution in great lengths, therefore the bands were assigned according to the accepted methods and reported data.^[38,41,148] By closely examining the carbonyl stretch of the urethane group it can be seen that there are three overlapping bands centered near 1720 cm^{-1} (Figure 3.9). The curve can be fitted in to three Gaussian bands at 1708, 1720 and 1730 cm^{-1} , which correspond to the hydrogen bonded "ordered", "disordered" and non-hydrogen bonded or "free" carbonyl groups respectively. One would expect that the amount of "free" carbonyl groups would be the highest, since all prepolymers manifest as liquids, however contrary to our expectations a high amount of ordered hydrogen bonded structures appears to be in the prepolymer matrix. This indicates that hydrogen bonding plays a major role in the formation of hard segments on the molecular level, determining the rheological and mechanical properties of the silylated polyurethanes.

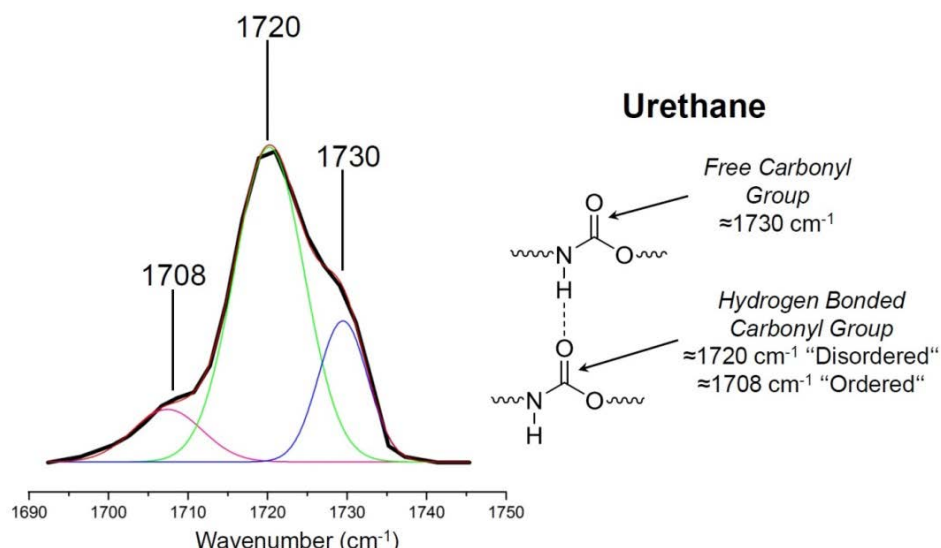


Figure 3.9: Carbonyl stretching region of the urethane group in the prepolymer based in the 4200 g/mol poly propylene glycol, **IPDI** and **3.09** corrected by the Fourier deconvolution and band assignment for corresponding carbonyl stretching modes.

By performing a similar examination on the carbonyl stretch of the urea group, three overlapping bands centered near 1645 cm^{-1} (Figure 3.10) were also found. The curve was fitted in to three Gaussian bands at 1622, 1645 and 1660 cm^{-1} , which correspond to the hydrogen bonded "ordered", "disordered" and non-hydrogen bonded or "free" carbonyl

groups respectively. It is well established that urea group forms well defined ordered hard segments, due to its bidentate hydrogen bonding.^[148] However despite the fact that this strong bidentate urea interaction is prevented in our case, relatively high amount of “ordered” hydrogen-bonded urea structures and relatively low amount of “free” urea groups can still be observed.

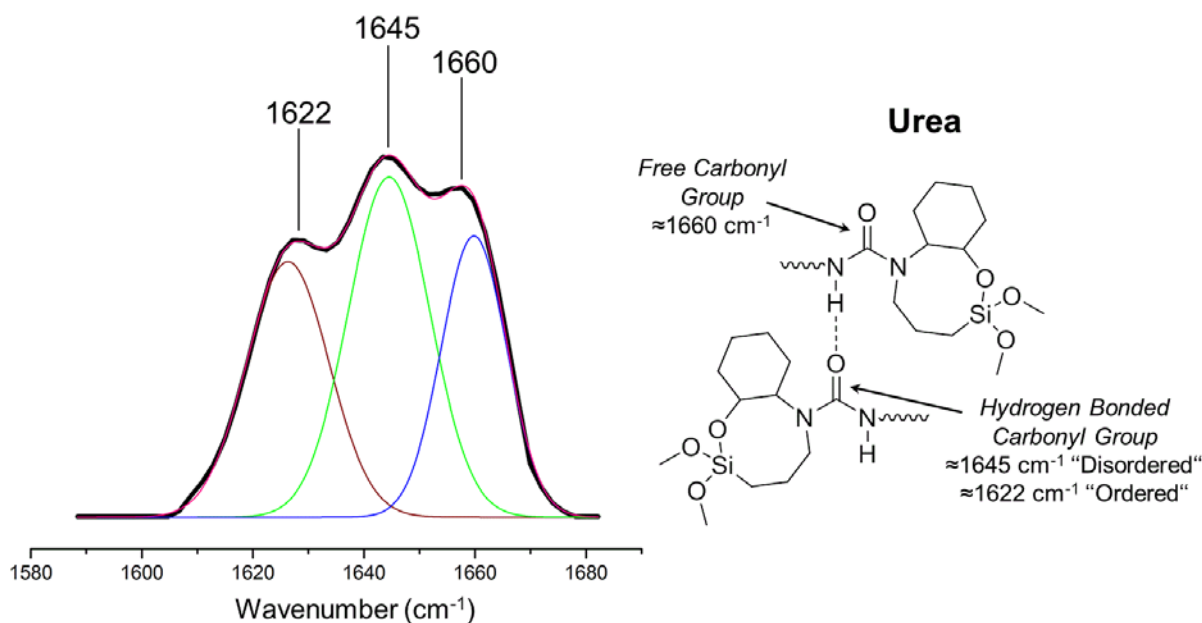


Figure 3.10: Carbonyl stretching region of the urea group in the prepolymer based in the 4200 g/mol poly propylene glycol **IPDI** and **3.09** corrected by the Fourier deconvolution and band assignment for the corresponding carbonyl stretching modes.

The band assignment discussed above is based on the reasonable predictions and on reported literature, however no prove was given in the process. Accordingly, the preparation of silylated polyurethanes with different amounts of soft segments was undertaken. The amount of soft segments was varied by using polypropylene glycol (PPG) of different molecular weights (≈ 2000 , 4000 and 1200 g/mol). The urethane and urea carbonyl stretching in the IR spectrum of prepared prepolymers is shown in the Figure 3.11. As expected, the amount of “free” urethane carbonyl band increases as the relative amount of PPG is raised, while the amount of “ordered” carbonyl groups decreases at the same time. A similar, but more distinct trend is observed in the case of urea carbonyl stretch. When the molecular weight of the PPG is raised from 2000 to 12000 the “ordered” urea segments significantly lower, while “free” carbonyl stretch rises above all other. Such changes are a result of the N-H hydrogen bonding of the urea and urethane groups to the ether oxygen as the concentration of latter increases, thus leaving carbonyl with fewer potential bonding partners.^[38] These findings also serve as a practical prove for the band assignments discussed previously, since the amount of “free” and hydrogen bonded carbonyl groups clearly depends on the concentration of urea and urethane groups in silylated polyurethanes.

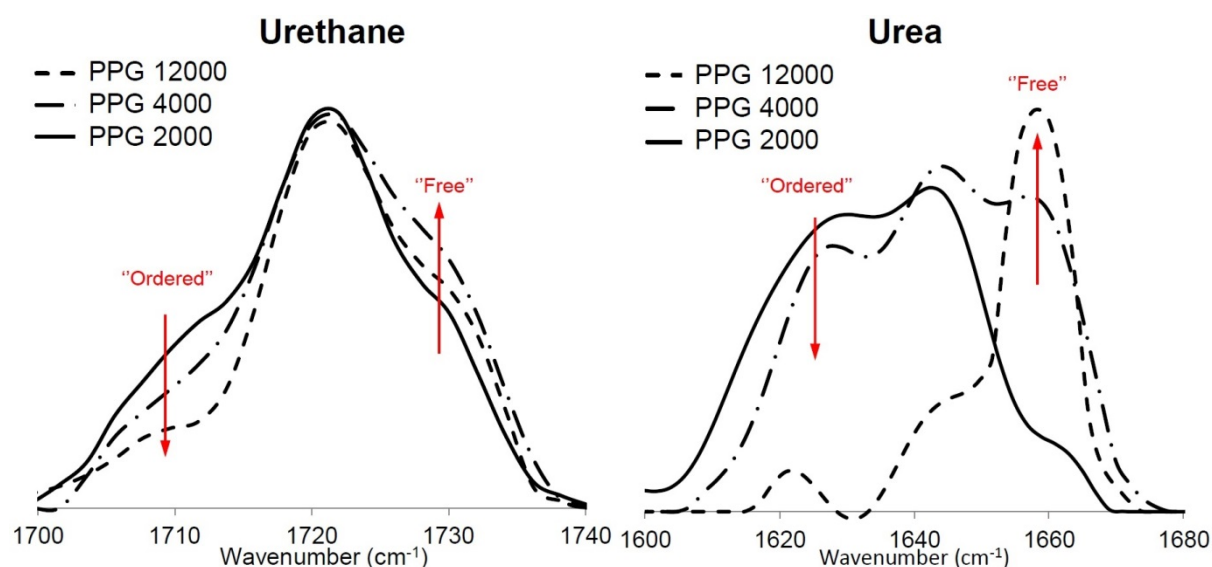


Figure 3.11: Carbonyl stretching region of urethane and urea of the prepared silylated polyurethanes prepared with polypropylene glycol (PPG) of different molecular weights (2000, 4000 and 12000 g/mol), **IPDI** and end-capper **3.09**.

Finally, the investigation of the end-capper influence on the hydrogen bonding in the silylated polyurethane matrix was undertaken, by comparing prepolymers of same molecular weight, but end-capped with different aminosilanes. A closer look in to the carbonyl stretch region of the IR spectrum revealed no major differences in urethane C=O stretch, while urea C=O stretch significantly varied depending on the type of the end-capper, which is also presented in the Figure 3.12. The most obvious difference is the fact that prepolymer end-capped with conventional primary aminosilane (**AMMO**) contain the highest amount of “ordered” hydrogen bonded carbonyl groups, since the band at 1622 cm^{-1} is the dominant one. IR spectra of the prepolymers end-capped with siloxacycloalkenes show higher amount of “free” and “disordered” carbonyl groups compared to **AMMO** end-capped prepolymer indicating that the amount of hydrogen bonding in these polymers is significantly lower. Furthermore, the formation of well-defined hard segments is less probable. Instead, disordered and thermodynamically less stable structures are formed, allowing the polyether chains to flow with lower restrictions.^[48] This observation is consistent with rheological findings described in the chapter 3.3.5, where it was described that the prepolymers end-capped with siloxacycloalkenes exhibit generally lower viscosities. The only siloxacycloalkene end-capped prepolymer which exhibit higher viscosity than conventional system is the one containing cyclohexane ring (**3.09**). The IR spectra of the latter show a remarkably high amount of “ordered” and “disordered” hydrogen bonded-carbonyl groups and low concentration of “free” carbonyl groups compared to other siloxacycloalkene end-cappers.

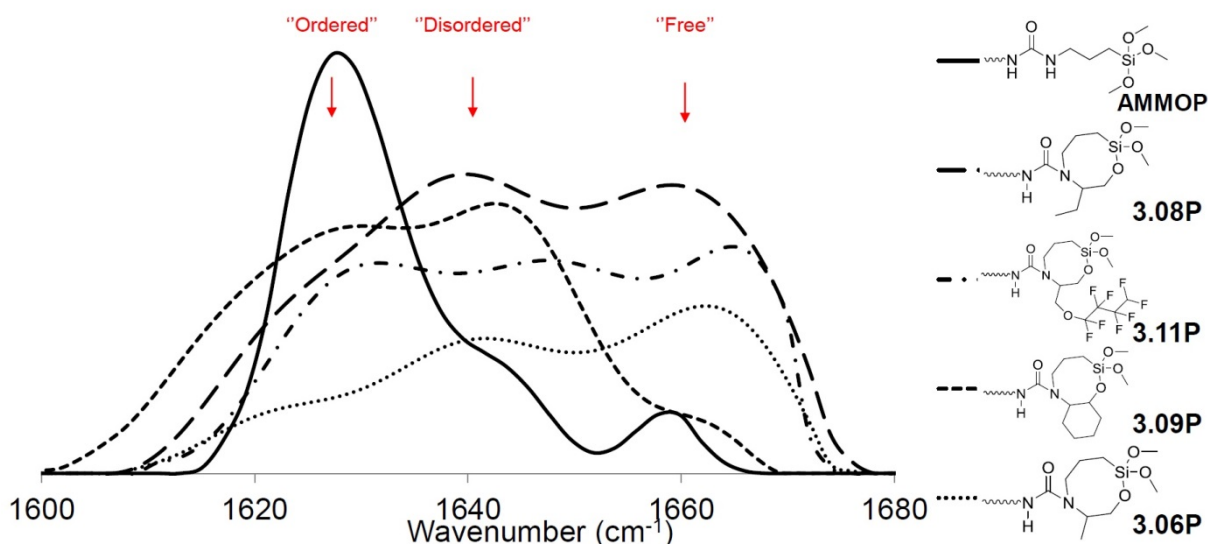


Figure 3.12: Carbonyl stretching region of the urea of the silylated polyurethanes prepared with PPG of 4000 g/mol, **IPDI** and different end-cappers.

Slight shifts of the IR bands can be visible for different end-cappers, which was attributed to the influence of the side groups of the siloxacycloalkenes on the electronic structure of the urea group.^[38] In addition to the inductive effect, also steric hinderance plays an important role, which might attribute to the slight shifts in the IR band wavelengths.

3.3.7. Adherence of prepared prepolymers to different materials

The effect on adhesion of siloxacycloalkane end-capped polyurethanes on different materials was investigated using lap-shear tests. The lap-shear tests are similar to peel tests although this method of adhesion measurement is more commonly quantitative in nature.^[103] The results of mean lap-shear measurements composed of 4 prepolymer types and 6 different substrates are shown in Figure 3.13. Several different substrates representing different types of commonly used materials in construction were selected. The materials can be grouped as following: metals (AL= aluminum, STST= stainless steel), polymers (PMMA= Poly(methyl methacrylate), PVC= poly(vinyl chloride)) and natural materials (glass and wood).

The results obtained from adhesion tests presented in Figure 3.13 seem somehow random; however, by closely examining the shear strength values and the failures types several conclusions can be withdrawn.

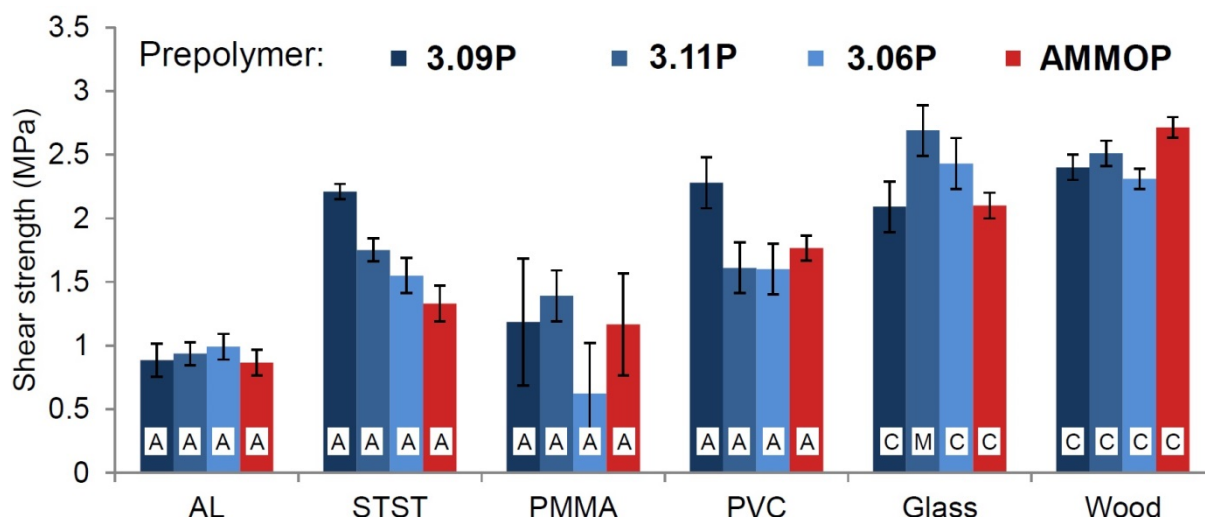


Figure 3.13: Mean lap-shear values of silylated prepolymers tested on different materials. Type of failure: adhesive (A), cohesive (C), material (M). The prepolymers were prepared using standard prepolymer method and using PPG with molecular weight of 12000 g/mol).

The relationship between the shear strength of the silylated polyurethanes to different materials show that the highest adherence strength can be achieved with materials like wood and glass, while metals exhibit only good to poor adherent bonding. Further evidence of this claim is also the type of failures observed, as wood and glass show mostly cohesive break, while metals and plastics show adhesive failure. Even though the values for the shear strength on natural materials seem similar, there are fundamental differences on the mechanism of adhesive bonding to these materials.

Gupta *et al.* showed that the adhesion mechanism underlying the interaction between wood fibers and thermoplastic composites is through surface roughness and in turn mechanical interlocking, while polar interactions play a less significant role.^[149] Furthermore, the hydroxyl groups on the surface of wood fibers are able to hydrolyze the alkoxysilane groups to form a covalent bonding of the silylated polyurethanes to the surface, which further increases the adhesive bonding.

In contrast to wood, the adhesion of silylated polyurethanes to the surface of glass proceeds primarily through covalent bonding and not through mechanical interlocking. The formation of covalent Si-O-Si bonds between glass and the alkoxysilane groups was discussed by many authors, and is generally accepted as a predominant bonding mechanism.^[95,150]

As mentioned earlier, the adhesion of silylated polyurethanes to metals is generally weaker than to glass or wood. However, a simple explanation of this is difficult to give, since the bonding of the polymers to metals surfaces is a complex process and is still an object of an intensive discussion in the scientific literature.^[97] Nevertheless, several factors may be responsible for weaker adhesive bonding, most important being the poor strength of Si-O-M (M= metal) bond. The formation of this bond was proposed by Watts *et al.*, however the

thermodynamic stability of this bond is low, therefore it is easy to be broken or hydrolyzed.^[151] The mechanical interlocking also plays a part in the adhesive bonding of polymers to metals, which was also observed in our investigation. The results show, that the adhesion of the prepolymers to rough surface generally results in higher shear strength value. This might be also a good explanation why the adherence to well-polished aluminum plates was weaker as to slightly rough stainless steel plates (appendix). Furthermore, it is known that surface of the aluminum is passivated by a thin layer of aluminum oxide, while stainless steel contains no oxide coating. This might lead to fundamental difference of the adhesion to these materials, which were observed during adherence testing.

The mechanism behind the adhesive bonding of silylated polyurethanes to plastics is difficult to assess to a single type of surface interaction. Several possibilities like interdiffusion,^[152] mechanical interlocking,^[94] hydrogen bonding,^[10] acid-base interactions^[94] and dipole-dipole forces^[153] contribute to the strengthening of adhesive bonding. In the case of PMMA, the most dominant bonding interaction can be assigned to the hydrogen bonding between acrylate carbonyl groups and urea and urethane groups of silylated polyurethanes; however a partial chain entanglement is also a possibility.^[154] The strength of adhesive bonding to PVC was found to be surprisingly high, especially because of its incompatibility with silylated polyurethanes.

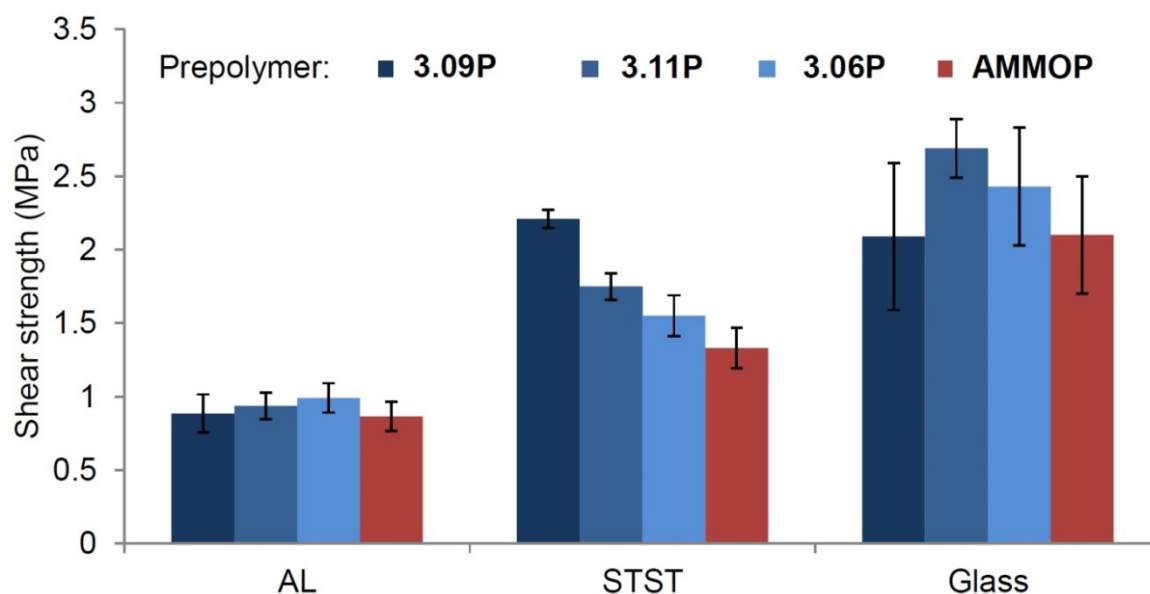


Figure 3.14: Mean lap-shear values of silylated prepolymers tested on aluminium (AL), stainless steel (STST) and glass. The prepolymers were prepared using standard prepolymer method and using PPG with molecular weight of 12000 g/mol, **IPDI** and end-cappers as indicated.

The influence of polyurethane end-capper on the adhesive bonding to different materials is another aspect which was explored during this investigation. It was noticed that siloxacycloalkane end-cappers have a positive influence on the adhesive bonding to aluminum, stainless steel and glass. In all cases the primary adhesion mechanism is through

the covalent bonding of the adhesive to the substrate, meaning that latter was improved by using siloxacycloalkane end-cappers.^[151] This result can be explained by several effects:

- Improved wettability: an important parameter for good wettability is the ability of the adhesive to establish a good contact by filling the holes and voids on the surface of the substrate and so maximizing the contact surface area.^[93] Since the developed prepolymers exhibit lower viscosity, the wettability is improved since the diffusion of the polymer chains in to the holes is easier.
- Reduced curing rates: the diffusion of the reactive alkoxy silane terminating groups of the silylated polyurethanes to the substrate surface is of fundamental importance for good adhesion.^[95b] The reduced curing rates of the alkoxy silane groups allow better diffusion of the alkoxy silanes to the surface and thereby increase the density of the covalent bonding to the surface of the substrate.
- Formation of the hydroxyl groups during the curing process: the hydrolysis of the developed silylated polyurethanes results in the ring opening of the siloxacycloalkane rings and consequently in the formation of the aliphatic hydroxyl group. The formed –OH group can form hydrogen bonding to urea or urethane groups and so increase the strength of the polymer adhesive layer. Another possibility is the interaction of hydroxyl group to the surface of the substrate material; however, this claim is difficult to elaborate.

It is worth to mention that the adhesive bonding to the glass was so strong in some cases, that it lead to the material break. This result means that the adhesive and cohesive strength of the adhesive is stronger than the strength of the substrate material itself.

3.3.8. Tensile properties of the cured films

Tensile properties of the prepared films were tested to study the effect of the siloxacycloalkane end-capping and the results are given in Figure 3.15. The obtained stress-strain curves demonstrate the significant impact of the end-capping type on the tensile properties of the casted film, cured under atmospheric conditions. It was observed, that the tensile strength and the elongation at break of the cured prepolymers end-capped with siloxacycloalkanes are generally higher than the standard **AMMOP** prepolymer. The only prepolymer with lower tensile strength was the one prepared with the fluorinated end-capper (**3.11P**), however its maximum elongation is still higher than for the standard **AMMOP** system.

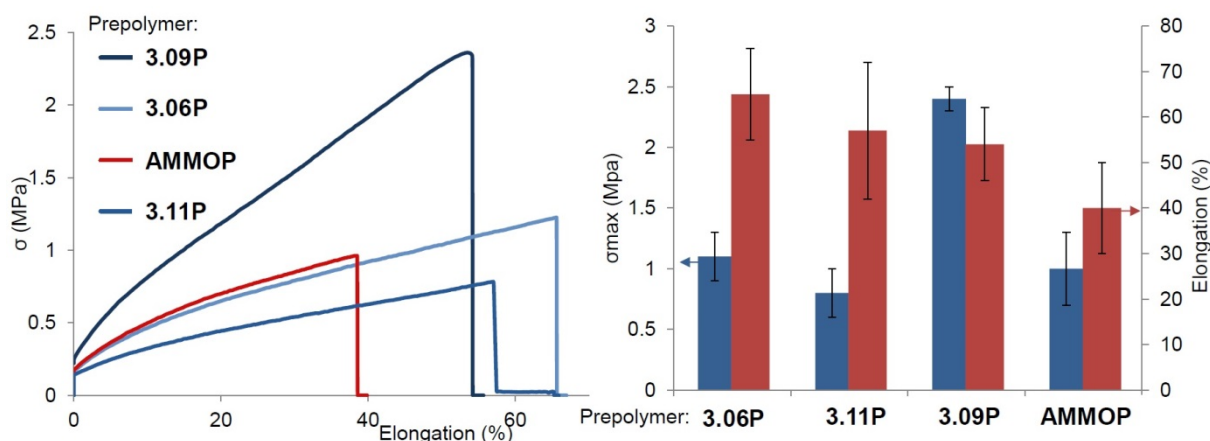


Figure 3.15: Mechanical properties of the cured films of the prepolymers end-capped with siloxacycloalkanes **3.06**, **3.09** and **3.11**. Right: Representative stress-strain curves of the cured films. Left: Average values for the tensile strength and elongation break of the cured films. The prepolymers were prepared using standard prepolymer method and using PPG with molecular weight of 1200 g/mol, **IPDI** and end-cappers indicated.

The increase of tensile strength and elongation at break of the prepared prepolymers may be attributed to the increased amount of hydrogen bonding or other van der Waals forces in the prepolymer after curing. As mentioned in the chapter 3.2, the result of the siloxacycloalkene hydrolysis is the ring opening of the structure by the formation of the hydroxyl functionality. The $-OH$ group can form intramolecular hydrogen bonds with urea and urethane groups of other prepolymer chains, resulting in the enhanced prepolymer network. The increase of the elongation values can be also ascribed to a less crosslinked network due to the lower hydrolysis rate of the end-capper during curing as was observed during time resolved NMR measurements in the chapter 3.3.4.

The prepolymer functionalized with the end-capper containing the cyclohexane ring (**3.09P**) showed superior properties, since the values for tensile strength are more than twice as high compared to the standard system. The increase in the tensile strength and elongation break can be assigned to several factors. One of them is the viscosity of the uncured prepolymer, which is higher compared to other prepolymers (Chapter 3.3.5). Higher viscosity is most probably the result of stronger hydrogen bonding in the prepolymer matrix, as was shown in the chapter 3.3.6 using IR spectroscopy. The higher amount of hydrogen bonding contributes to the tensile strength of the cured prepolymer as was shown before by other authors.^[40] Furthermore, this particular end-capper is a crystalline solid in its pure form, while other end-cappers are liquids at room temperature. This indicates that dense packing of the end-capped prepolymer chain-ends during or after the curing results in a formation of the dense hard-segments, which are known to enhance the tensile strength of the polyurethanes.^[155] Furthermore, the produced hydroxyl functionality during the curing process is able to additionally enhance the secondary forces in the hard segments, leading to the strengthening of the polymer matrix.

It is worth to mention that the curing of the casted films was extended from 1 to 2 weeks, since the prepolymers end-capped with siloxacycloalkenes required longer time to achieve tack-free state, than the standard **AMMO** end-capped prepolymers.

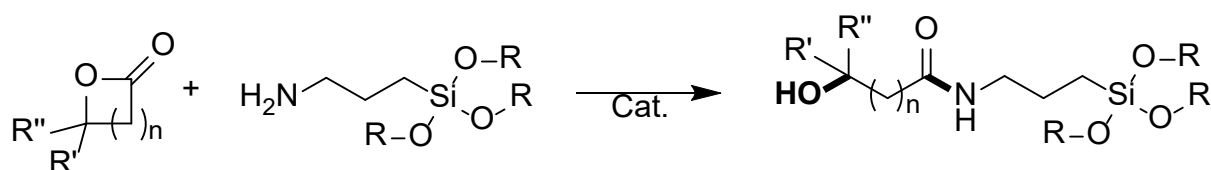
3.4. Conclusion

The formation of N→Si dative bond in siloxacycloalkenes and its influence on the amine reactivity and alkoxysilane hydrolysis was investigated during this study. The results revealed that the prepared siloxacycloalkenes have the potential to be powerful silane coupling reagents, which can be utilized in many ways like surface treatment, water scavenging or polyurethane modification. The latter proved to be effective, since the prepared silylated polyurethanes exhibit reasonable curing speeds and significantly lower viscosities compared to currently commercially available moisture curable polyurethanes. Studies of urea and urethane carbonyl stretching by IR spectroscopy revealed that the formation of the highly hydrogen bonded hard segments is disturbed in the case of siloxacycloalkane end-capping, which has a positive effect on the rheological properties of the silylated polyurethane. The use of siloxacycloalkanes in the prepolymer system leads to the enhanced adhesion to glass, aluminum and stainless steel, which was shown by lap-shear tests. Furthermore elongation testing shows an improvement in tensile strength and elongation values for variety of cured siloxacycloalkanes end-capped prepolymers.

4. Hydroxyl-functional alkoxy silane end-cappers

4.1. Project outline

Inspired by the results presented in previous chapter, it was intriguing to further expand the understanding it to the stability of the hydroxyl functionality in the presence of trimethoxysilane. However, contrary to the work discussed in the chapter 4, the focus was on preventing the self-dealcoholization reaction instead of inducing it in order to obtain a stable hydroxyl-functional alkoxy silane (Scheme 4.1).



Scheme 4.1: Preparation of hydroxyl functional alkoxy silanes.

The first and main objective of this investigation was thus to develop a simple, efficient and mild synthetic procedure to yield a stable hydroxyl-functional silane, which can be stored and handled under atmospheric conditions. This was achieved by a comprehensive kinetic and structural investigation using *in situ* IR and NMR spectroscopy.

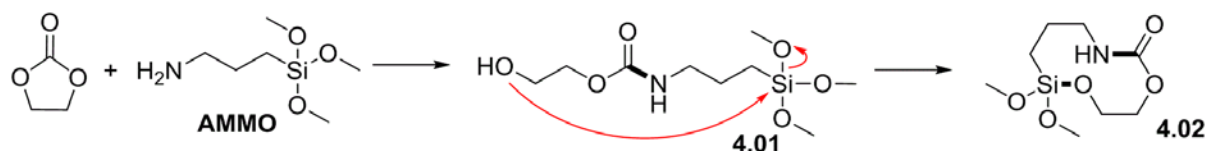
The currently used prepolymer method to produce silylated polyurethanes consists of several steps at high temperature (80 - 100 °C) and remained practically unchanged for several decades now.^[156] The optimization of the currently used prepolymer process in the large-scale manufacture is of high interest in the polyurethane industry. However, using the most popular aminosilane end-cappers (**AMMO** and **AMEO**), this goal is difficult to achieve. Accordingly, the decision was made to use stable hydroxyl functional alkoxy silane to develop a one pot prepolymer method for the preparation of low-viscosity silylated polyurethanes. The adhesive and tensile properties of the prepared prepolymers were analyzed in detail using common techniques. The optimization process, scope and limitations will be discussed after a short introduction in to the current state of the art.

4.2. Background

Although a wide range of organofunctional alkoxysilanes are available on the market today, there are still challenges in the field of hydroxyl functional alkoxysilanes. The hydroxyl functionality is of great interest in the polyurethane technology, since the reaction of OH with isocyanates results in an urethane group, which forms weaker hydrogen bonds compared to urea groups.^[43a] Polyurethanes derived from hydroxyl functional compounds generally exhibit lower viscosity; therefore, they are mechanically easier to handle.^[88] The main reason for the lack of commercially available hydroxyl functional alkoxysilanes is their instability due to the probability of the self-dealcoholization reaction to produce intramolecular rings and oligomers. Most of the commercially available hydroxyl functional alkoxysilanes are diluted in alcohols like methanol or ethanol to stabilize alkoxysilane groups. However, if the solvent is removed they tend to form cycles and oligomers, which prevent their usage for preparation of silylated polyurethanes. The rest of the commercially available hydroxyl-functional alkoxysilanes are prepared as ethoxysilanes or propoxysilanes (not methoxysilanes), which is undesired for the preparation of silylated polyurethanes, since the curing speed after the end-capping is generally too slow for the needs of consumer applications.^[157] Therefore, a need exists for the preparation of the stable hydroxyl functional methoxysilanes, which can be stored as pure substance for longer time under ambient conditions and which can readily be used in the prepolymer method for the preparation of silylated polyurethanes.

Moren *et al.* were the first to present a method for preparing hydroxyl-functional alkoxysilanes, which were used as an end-capper for the preparation of silylated polyurethanes^[158] or as a water soluble hydrolyzed silanes.^[159] The end-capper was prepared by a reaction between aminosilane and cyclic carbonate at high temperatures. They noticed that the stability of the hydroxyl functional ethoxysilane is suitable for prepolymer preparation, however methoxysilane version (**4.01**) proved to be unstable. According to the ²⁹Si NMR analysis, it was shown that 46 % of the methoxysilane groups underwent alcohol interchange with the hydroxyl group (Scheme 4.2) to form cyclic alkoxysilane (**4.02**).^[158]

Many patents have been published in the last decade on the topic of hydroxyl functional alkoxysilanes preparation. Most of the disclosed silanes are produced for the use in the preparation of silylated polyurethanes for sealants and adhesives. Methods for preparing of hydroxyl functional alkoxysilanes comprise mostly of ring opening of epoxides,^[160] cyclic lactides,^[161] lactones^[162] and so on.



Scheme 4.2: Preparation of hydroxyl functional alkoxy silane (**4.01**) and its self-delacoholization reaction by forming **4.02**.

The most promising approach so far proved to be ring opening of cyclic lactides and lactones, since the nucleophilicity of the hydroxyl group can be tuned by selecting appropriate substitution on the lactide or lactone.^[162] Mono-substituted lactides and lactones proved especially effective in stabilization of the hydroxyl group, since the nucleophilicity of the produced secondary alcohol is significantly lower than the primary OH group, as can be seen in Table 4.1.^[35] However, even though the reactivity of the hydroxyl group is lower, it is still possible to detect an amount of self-deacoholization reaction at increased temperatures or at longer storage time^[88]. This is a serious problem, which occurs during the synthesis of the end-capper or for large-scale sealant preparation, where end-cappers are exposed to high temperatures (up to 80 °C) and strong catalysts.

Table 4.1: Relative reactivity of an aromatic isocyanate with alcohols. Taken from reference [35].

Alcohol	Chemical structure	Relative reaction rate
Primary	R-OH	100
Secondary	R ₂ -OH	30
Tertiary	R ₃ -OH	0.5
Water	H ₂ O	100

To prepare high quality end-cappers with the highest amount of unreacted hydroxyl groups it is important to use mild synthetic procedures. This requires a strong catalyst to lower the activation energy of reaction, while it does not promote the self-deacoholization reaction. Many authors have reported the catalytic ring opening of lactones with amines under mild conditions, with Lewis acids like aluminum chloride,^[163] alkylaluminumium,^[164] lithium bis(trifluoromethanesulfonimide)^[165] etc. However, the use of the Weinreb reagents coming from the reaction of trimethylaluminum with an amine, or the use of 2-hydroxypyridine have been considered as being the most popular.^[164,166]

4.3. Results and discussion

Based on the reported literature it was shown that for the preparation of stable hydroxyl functional alkoxy silanes it is necessary to consider two key factors: synthetic procedure and the structure of prepared end-capper. In the first part of this investigation the focus was on the optimization on the synthetic procedure, while in the second part the structure-stability relationship was closely examined.

4.3.1. Optimization of the reaction conditions

In situ infrared (IR) spectroscopy was used to follow the disappearance of the carbonyl band of the lactone at 1800 cm^{-1} or appearance of the amide bands at 1600 and 1530 cm^{-1} , which allowed the monitoring of a reaction conversion and possible side reactions. By using this method, it was possible able to determine the kinetic factors for each lactone and catalyst used. The reaction followed second order kinetics irrespective to the lactone or catalyst type, which was confirmed by integrating the obtained concentration vs. time curve. The optimal reaction temperature proved to be $50\text{ }^{\circ}\text{C}$, since at these conditions the reaction speed and the amount of side reaction show a good compromise (Appendix A4.1).

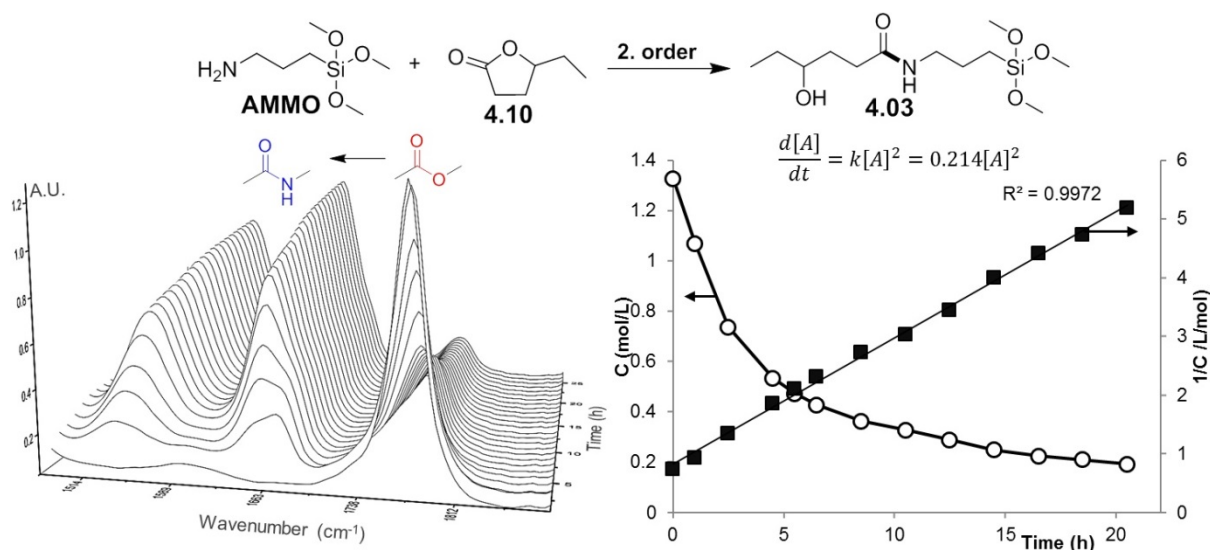


Figure 4.1: Left: time-resolved *in situ* IR analysis for the reaction of **AMMO** with lactone to prepare hydroxyl functional alkoxy silane **4.03**. Right: Determination of the reaction rate and reaction rate constant.

4.3.2. Catalyst screening

On order to find the optimal catalyst to accelerate the reaction between (3-aminopropyl)trimethoxysilane (**AMMO**) and γ -hexalactone (**4.10**), several common Lewis acids and bases were screened. Afterwards, the reaction rate constants for each catalyst were determined, which is provided in the Figure 4.2. It was showed that Lewis acids and bases have a positive effect on the reaction kinetics compared to the non-catalyzed reaction. Especially, Lewis acids like triethylaluminium (TEAL) show up to 130 times increase in reaction rate. According to the literature findings, trialkylaluminium species reacts with

primary and secondary amines to form an active aluminum intermediate, which is extremely reactive towards electrophiles like esters.^[164,166] During this process a small amount of alkane (ethane in our case) is produced in the reaction mixture, which was noticed since bubbling was observed when TEAL and aminosilane were mixed.

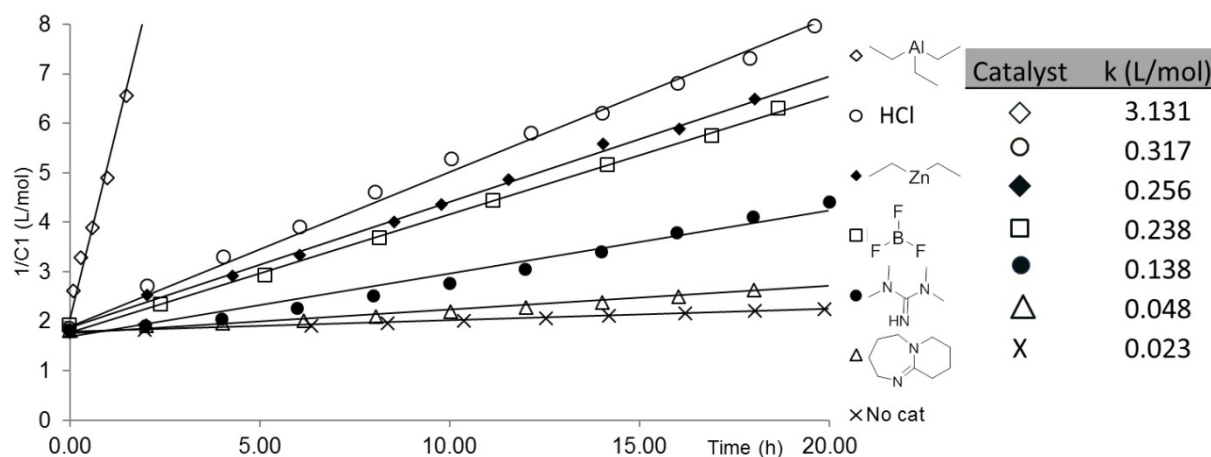


Figure 4.2: Determination of the reaction rate constants for different catalysts using time-resolved *in situ* IR analysis.

In addition to the increase in the reaction rate, reaction selectivity towards the desired product is also of an interest. Therefore, every reaction mixture produced during catalyst screening was analyzed using GC-MS and NMR techniques (Figure 4.3). According to the obtained data, it was concluded that aluminum and titanium Lewis acids have a positive effect on the reaction selectivity, which is in correlation with the reaction rate presented above. In case of high reaction rate, an improvement in the reaction selectivity was noticed. In case of TEAL and MMAO-12^[167] catalyst full conversion is achieved in less than 3 hours, compared to other catalysts, by which high conversions (< 90 %) are achieved only after 20 hours or even longer. The most probable explanation is, that the exposure to increased temperatures for longer times increases the self-dealcoholization, therefore this time must be shortened to a minimum. Furthermore, catalysts like BF₃,^[6b] DBU,^[6b,61b] TMG^[61b] are known to promote hydrolysis of the alkoxysilane groups, which induces the self-dealcoholization reaction of hydroxyl functional alkoxysilanes.

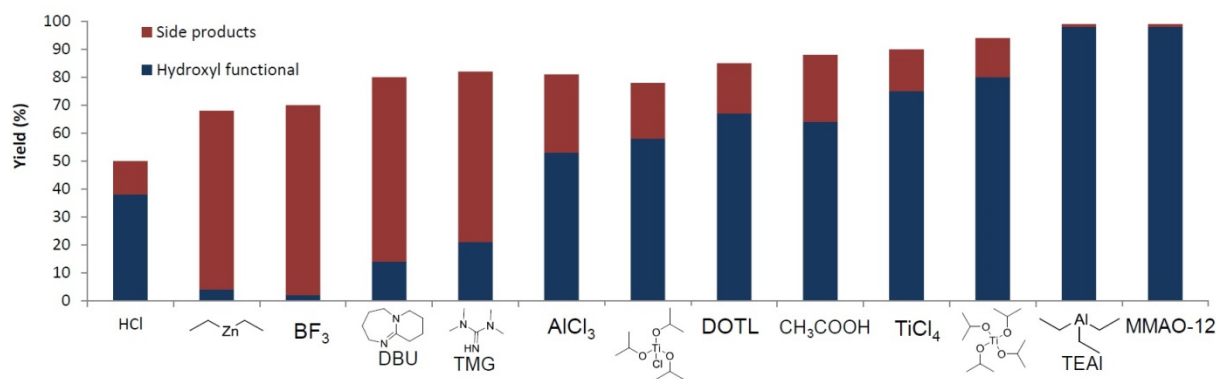


Figure 4.3: Investigation of the reaction selectivity towards hydroxyl functional alkoxy silanes by using different catalysts.

Based on the performed experiments, it was shown that organoaluminium compounds are superior compared to any other catalyst to produce hydroxyl functional alkoxy silanes. In addition to the short reaction time, they also exhibit exceptional reaction selectivity, which has economic and practical benefits. However, the main disadvantage of organoaluminium compounds is their difficult handling in the large scale. Organoaluminium catalysts like TEAL and MMAO are corrosive to many materials and they readily decompose on air, which leads to safety hazards. To minimize the safety difficulties during the preparation of hydroxyl functional alkoxy silanes several experiments with lower catalyst concentration were performed (Figure 4.4). Unfortunately, the decrease in catalyst concentration had a negative effect on the reaction yield. When 0.5 mol% of TEAL was used, the reaction was significantly slower, resulting in only 63 % yield after 5 hours, while 0.1 mol% of the TEAL resulted in only 32 % yield. After the linearization of the reaction curves for the reaction with 0.1 mol% of TEAL it was confirmed, that the reaction still follows second order kinetics, although the reaction rate constant corresponds to that of the uncatalyzed reaction, which indicates the deactivation of the catalyst (Figure 4.4). In the case of the 0.5 mol% of TEAL it was evident that the initial reaction constant is in the expected range for the catalyzed reaction, however after several minutes the reaction rate slows down until it reaches the one for the uncatalyzed reaction.

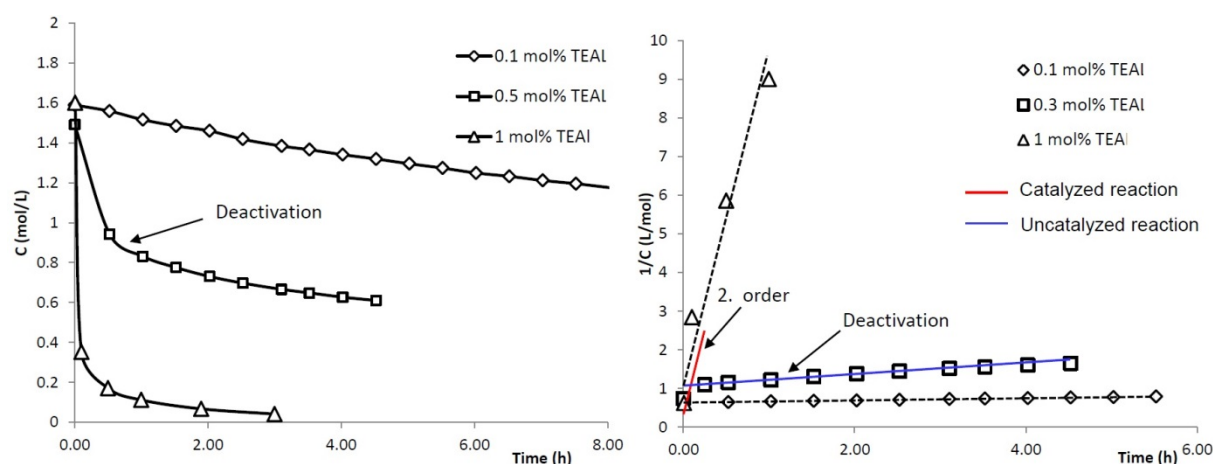
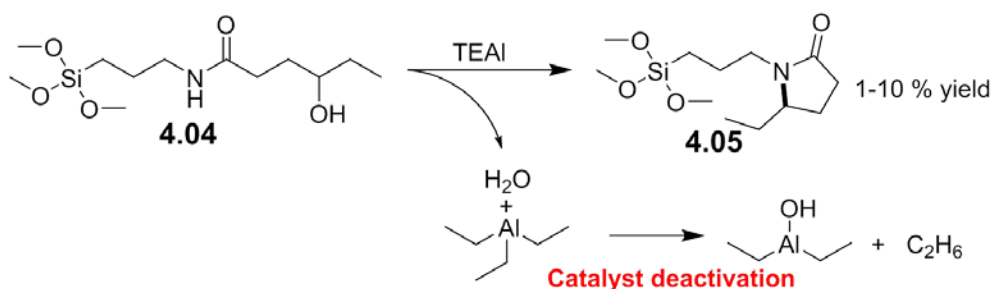


Figure 4.4: Preparation of hydroxyl functional alkoxysilanes by using reduced amount of TEAL catalyst. Left: Consumption of lactone during the reaction. Right: Linearized reaction rate curves.

The change of the reaction rate and order during the reaction indicates that a side product is being formed, which is deactivating the catalyst.^[168] After thorough analysis of the reaction product, it was discovered that a small amount (< 2 mol%) of lactame (**4.05**) side product is being formed.^[169] During the lactamization of amidoalcohols, water is being produced, which reacts with TEAL to produce catalytically inactive aluminum hydroxide as presented in the Scheme 4.3. This side reaction is proceeding regardless of the catalyst concentration. However, when the catalyst concentration is higher, the amount of produced water is most probably not high enough to completely deactivate the catalyst. In conclusion, it was discovered that the most appropriate catalysts for the preparation of stable hydroxyl functional alkoxysilanes are organoaluminium compounds like TEAL or MMAO with a concentration of at least 1 mol%.



Scheme 4.3: Deactivation of the catalyst due to the water formation as a side product during the reaction.

4.3.3. Lactone screening

In order to understand the structure / stability relationship of the hydroxyl functional alkoxysilanes, a broad substrate screening was performed. During the catalyst screening it was discovered that the reaction rate of the lactone ring opening is one of the main determining factors for the stability of the hydroxyl functional alkoxysilane. Therefore, it was determined the reaction rate constants for a range of different lactones (Figure 4.5). The outcome of the lactone screening showed that the dominating factors for the lactone ring

opening with aminosilanes are the ring strain and the substitution of the lactone ring. For example, β -Butyrolactone (**4.06**) reacts exothermically with aminosilane even in absence of the catalyst due to its high ring strain. However, γ -Methyl decalactone (**4.12**) shows a very slow reaction rate without the addition of the catalyst, indicating that sterically demanding hexyl and methyl groups hinder the nucleophilic attack of the aminosilane.

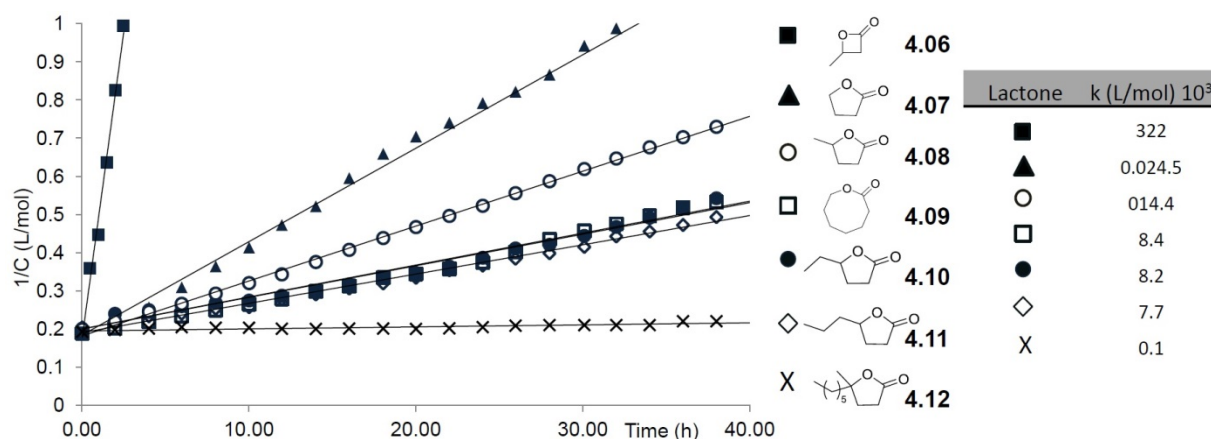


Figure 4.5: Determination of the reaction rate constants for ring opening of different lactones with aminosilanes. Reaction was conducted at 25 °C without catalyst.

Further investigation on the structure / stability relationship was conducted by ring opening of a wide variety of lactones with aminosilanes under the optimized conditions developed during the catalyst screening. Most of the lactones reacted readily at 50 °C to achieve good to excellent yields; however, some of the products remained unstable and further reacted to form cyclic silanes. The obvious difference between the stability of hydroxyl functional ethoxysilanes and methoxysilane is a result of higher hydrolytic stability of ethoxysilane groups. However, methoxysilanes are highly desired for the preparation of silylated polyurethanes, therefore the stabilization of the latter was our priority.

The structure of the lactone also plays an important role in the stability of the OH group towards the self dealcoholization reaction. Based on the Figure 4.6 it is evident, that the products from substituted lactones exhibit excellent stability compared to those from the unsubstituted lactones. The reasonable explanation is that the reaction product between an unsubstituted lactone and an aminosilane contains a primary hydroxyl group, which is significantly more nucleophilic than secondary or tertiary and is therefore more prone to the nucleophilic attack on to the alkoxysilane groups or other side reactions.^[35] Further stabilization can be achieved by using more sterically demanding groups like ethyl, propyl and hexyl, which are attached to the gamma position of the lactone. Hence, the highest yields were obtained with disubstituted lactones, containing bulky groups.

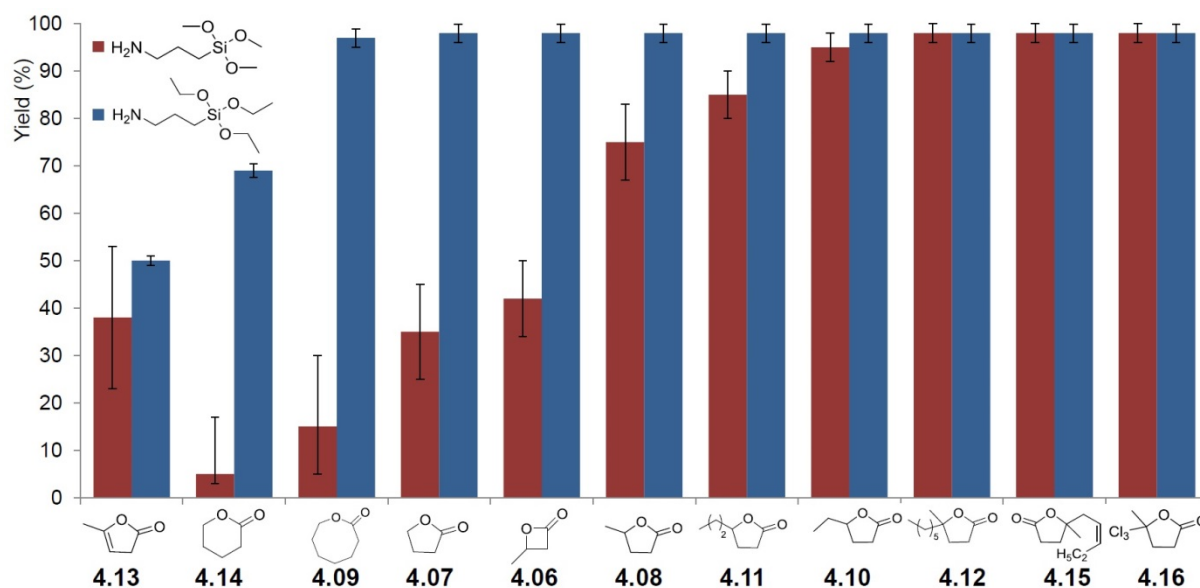


Figure 4.6: Lactone screening for the preparation of hydroxyl functional alkoxy-silanes under optimized conditions (50 °C, 1 mol% TEAL).

4.3.4. Stability of hydroxyl functional alkoxy-silanes

From the general industrial practice, it is known that when the compound is produced in the large scale it is usually stored in liter bottles or even in large (200 L) barrels until further use. This process may take up to several months, during which the compounds may alter their chemical structure. This concern also applies for the preparation of the alkoxy-silane end-cappers in the large scale, in which case compounds can be stored for longer time. The reactive compounds need to remain stable during the storage and transportation time, which include mechanical and thermal stress. The stability of the hydroxyl functional alkoxy-silanes proved to be the limiting factor for usage of this end-capper type in big scale production. Although several hydroxyl-functional methoxy-silanes were prepared, the stability of the prepared compounds under longer storage conditions had to be verified. By exposing the compounds to 50 °C for 8 days, it is possible to estimate the stability of the end-capper for 1 year at room temperature^[170]. This procedure is a common method used by many companies for estimating the stability of their products.

By following the change of the prepared end-cappers during the stability tests using NMR spectroscopy, it was possible to identify the type and extend of the side reactions. Figure 4.7 shows the ¹H NMR spectra of the hydroxyl functional end-capper over 8 days at 50 °C. Firstly the rising of the doublet at 1.3 ppm and a multiplet at 4.1 ppm can be observed, which correspond to the CH₃ and CH of the lactam functional alkoxy-silane (**4.18**). The formation of lactam functionality was also supported by GC-MS analysis. Since water is produced during lactamization, further hydrolysis of the alkoxy-silane groups is initiated. This is witnessed by the rising of the singlet for methanol and other small signal around 3.6 ppm. The self-

dealcoholization reaction was not detected in ^1H NMR spectra, even though it was detected in by GC-MS analysis.

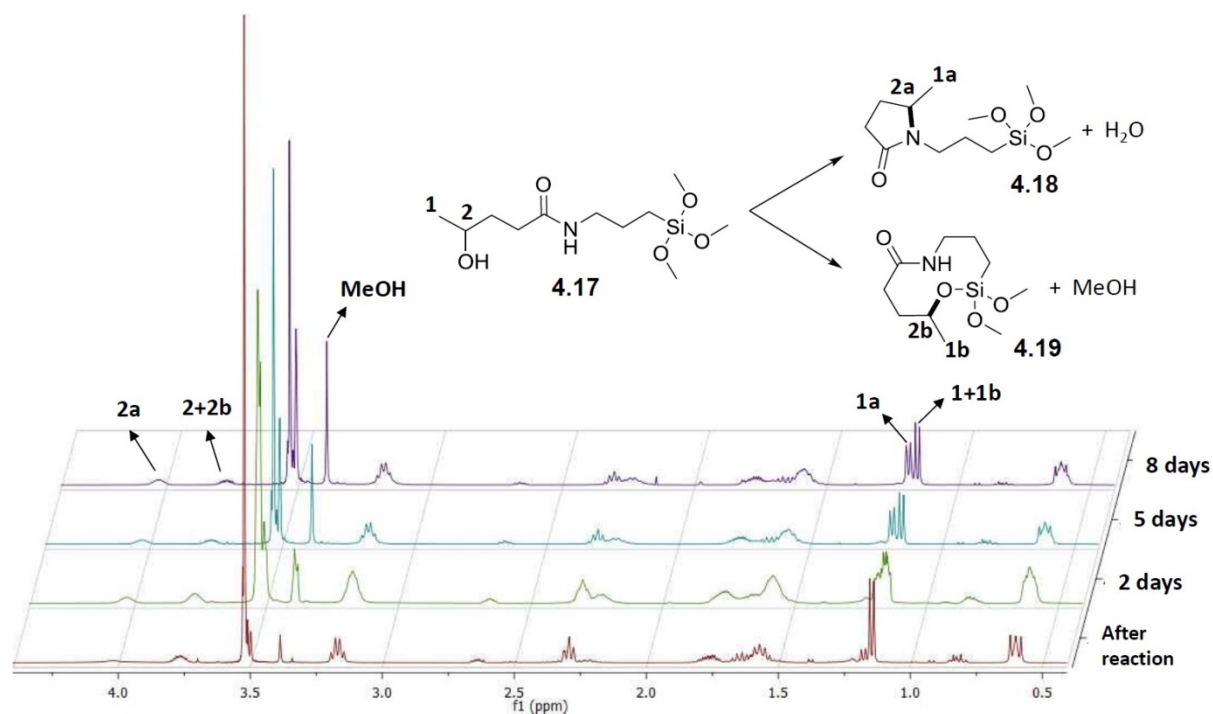


Figure 4.7: ^1H NMR spectra of the hydroxyl functional end-capper **4.17** over 8 days at 50 °C. NMR spectra were measured using CDCl_3 as a solvent at 23 °C.

^{29}Si NMR spectra showed signals appearing around -44 ppm, which belong to the hydrolyzed silanol and Si-O-Si groups, which is the consequence of the produced water (Figure 4.8). Additionally, a signal at -41.6 ppm appears, which can be assigned to the self-dealcoholization product (**4.19**).

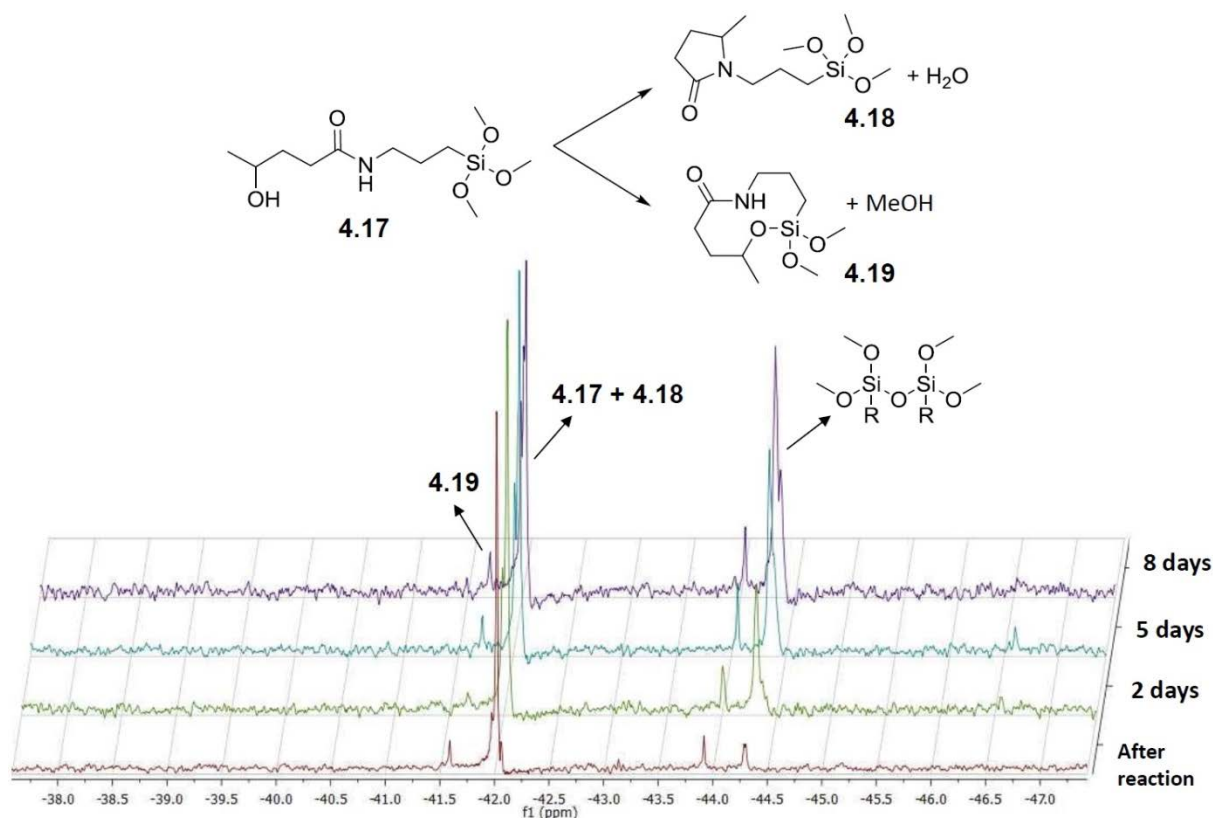


Figure 4.8: ^{29}Si NMR spectra of the hydroxyl functional end-capper **4.17** over 8 days at 50 °C. NMR spectra were measured using CDCl_3 as a solvent at 23 °C.

According to the NMR findings described above, it was possible to well estimate the extent and the nature of side reactions during the storage of the end-capper. The same experiments were also performed with other hydroxyl functional methoxysilanes to determine their stability. By integration of the NMR multiplets, it was possible to determine the purity of the end-cappers over the time. It is evident from the Figure 4.9, that tertiary hydroxyl functional methoxysilanes (**4.20**, **4.21**) exhibit superior stability in comparison to primary (**4.23**, **4.24**) and secondary ones (**4.04**, **4.17** and **4.22**). Furthermore, steric hindering additionally contributes to the stability of the hydroxyl group, since the stability of more sterically hindered secondary hydroxyl groups is significantly higher.

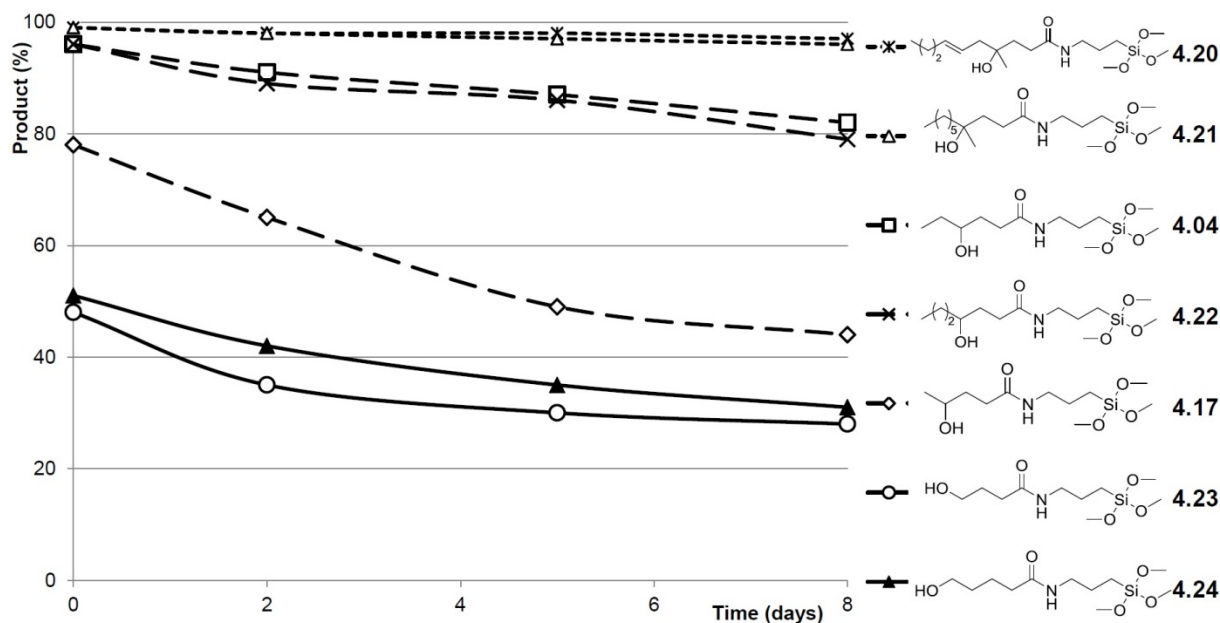


Figure 4.9: Stability of the prepared hydroxyl functional methoxysilanes over 8 days at 50 °C (— primary OH, — secondary OH, ---- tertiary OH).

A kinetic investigation into the conversion of the hydroxyl functional methoxysilanes into the side products revealed that the reaction follows first order kinetics. The combined reaction rate constants for the side reactions is in the range from 2.5 to $3.3 \times 10^{-3} \text{ h}^{-1}$ for primary hydroxyl group (compounds **4.23**, **4.24**), 0.8 to $3.5 \times 10^{-3} \text{ h}^{-1}$ for secondary hydroxyl group (compounds **4.04**, **4.17** and **4.22**) and around $0.1 \times 10^{-3} \text{ h}^{-1}$ for the tertiary group (compounds **4.20**, **4.21**) at 50 °C.

Another stability test commonly used is to expose the material to 80 °C for 1 hour.^[171] This test provides the information on how the material behaves under severe short lasting temperature shocks, which can occur for example during transportation. This test was also used to verify the stability of the hydroxyl functional methoxysilanes. No major changes have been observed in the samples before and after the experiments, which leads to the conclusion that hydroxyl functional methoxysilanes can survive short term temperature stress. ^1H and ^{29}Si NMR spectra obtained during short term stability tests are presented in the appendix.

4.3.5. Hydrolytic stability of hydroxyl functional alkoxysilanes

For industrial applications of organofunctional alkoxysilanes, both the hydrolytic rate and the reaction mechanism are of fundamental importance. In this study, hydrolysis was investigated using time resolved ^1H and ^{29}Si NMR, by help of which, the kinetic curves were drawn using the same methodology as was earlier described in the chapter 3.3.4 (Figure 4.10).

The best indication of the hydrolytic speed can be estimated by following the drop in the concentration of trialkoxysilane (TAS) signal. By linearizing the TAS kinetic curve it was

confirmed, that the reaction follows second order kinetics, which is consistent with the literature findings for the acid catalyzed hydrolysis of organoalkoxysilanes.^[129] Another important observation is that the hydrolysis rate of **4.21** is lower than for hydroxyl functional alkoxysilane. The rate of hydrolysis depends on many factors, one of which is also the surrounding groups near to the silicon center. Many researchers came to the conclusion that the highest hydrolysis speed is obtained by aminosilanes, while amidosilanes exhibit generally lower reaction rates. One of the proposed explanations is the unavailability of the lone pair on the nitrogen of the amide group due to the resonance with the carbonyl group, while the amine lone pair is able to coordinate with the silicon atom and so influence the hydrolysis rate.^[6a]

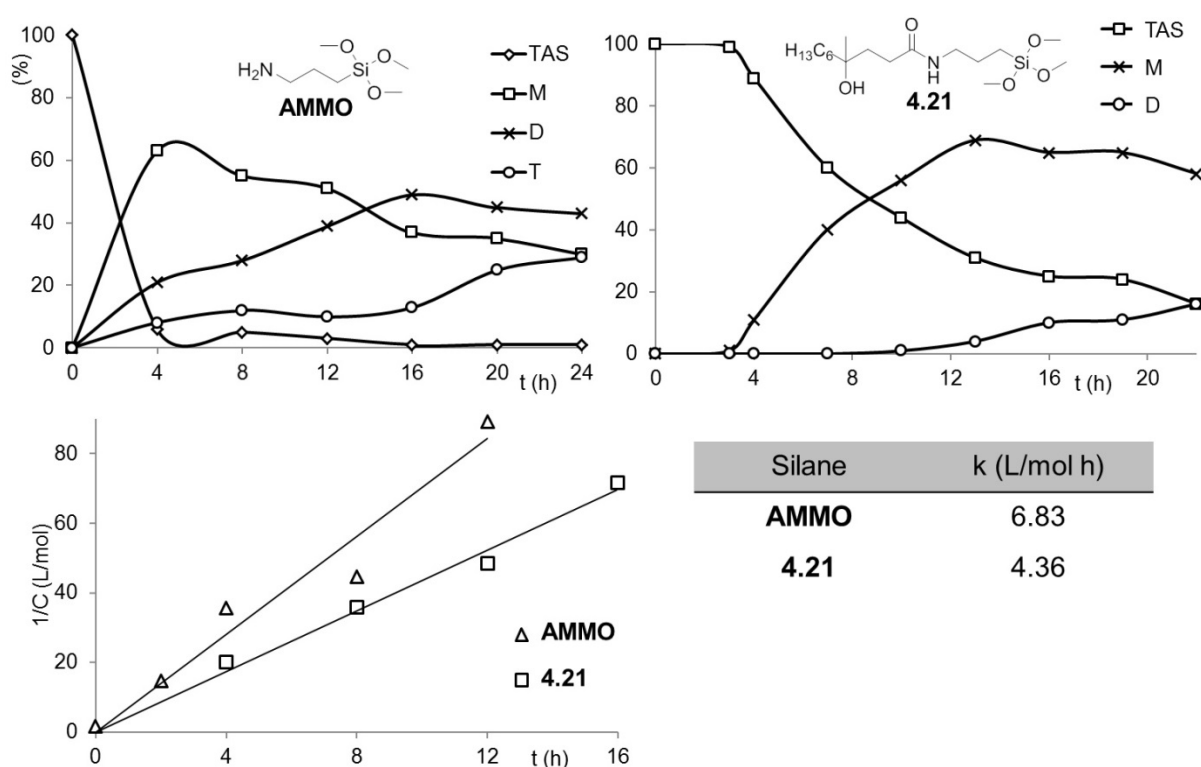
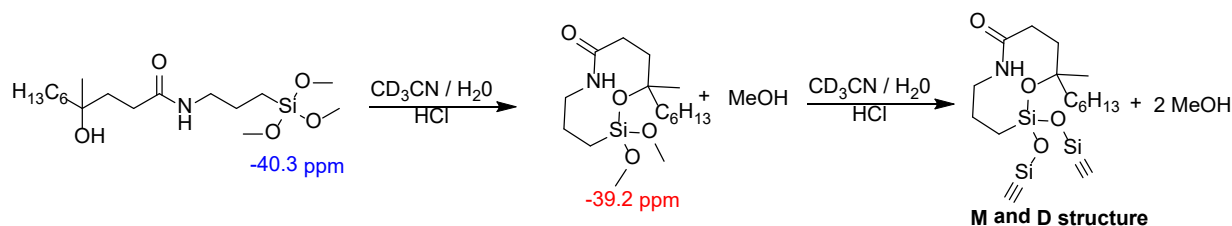


Figure 4.10: Hydrolytic kinetic curves of alkoxysilanes in acidic media extrapolated from time resolved ^{29}Si NMR spectra. **Top:** kinetic curves of the functional alkoxysilane hydrolysis. **Bottom:** linearized curves of the TAS kinetic curves for both silanes.

The comparison of the hydrolytic behavior between **AMMO** and **4.21** shows several fundamental differences. A peculiar induction time in the hydrolysis of the **4.21** alkoxysilane implies a secondary process which is induced by water or acid. After a closer look in to the time resolved ^{29}Si NMR spectra of the **4.21** hydrolysis, it was observed that a signal at -40.3 ppm for TAS group slowly disappears in the course of 4 hours, while a new signal at -39.2 ppm appears at the same time. A small shift indicates a minor change of the trimethoxysilane environment resulting in a slight increase of electron density of the silicon center. The change can be reasonably assigned to the self dealcoholization reaction, which is catalyzed by a small amount of acid in the reaction media forming a siloxacycloalkane ring as

presented in Scheme 4.4. Furthermore, a down-field shift of the methoxy signal in the ^1H NMR spectra supports the proposed hydrolytic mechanism.



Scheme 4.4: Proposed mechanism responsible for induction time of the **4.21** hydrolysis.

The absence of the signal for the T structure in the ^{29}Si NMR spectra can be assigned to at least two factors:

1. a gradual decrease of the ^{29}Si NMR resolution due to the formation of highly crosslinked networks towards the end of our experiment,
2. ring stabilization of the alkoxy-silane, resulting in an immense decrease of the hydrolysis rate of the formed siloxacycloalkene ring: The ring opening requires the breaking of a third, highly sterically shielded alkoxy group.

The unusual hydrolytic behavior of hydroxyl functional alkoxy-silanes could be usefully exploited in applications where the curing must be delayed for a particular amount of time. For instance, a potential application of the developed end-capper (**4.21**) is for coatings that need to be spread evenly on the surface, after which the curing is self-initiated.^[172] However, further implementation of the developed compounds was not pursued.

4.3.6. Prepolymer preparation

The core of the effort to develop a stable hydroxyl functional alkoxy silane lies in the need to prepare urea-free moisture curable silylated polyurethanes. All prepolymer reactions utilizing hydroxyl functional alkoxy silane as end-cappers proceed smoothly at 80 °C over 3 hours, and were seemingly unaffected by their electronic or steric nature. It was expected that the reaction rate of the end-capping with hydroxyl functional alkoxy silane would be lower compared to the conventional aminosilane end-capping, since alcohols are weaker nucleophiles than amines and are known to react slower with isocyanates.^[22] Contrary to the expectations, it was found that 3 hours are sufficient to completely react all NCO groups as it is the case in the conventional prepolymer process.

After the preparation of each prepolymer end-capped with a different hydroxyl functional alkoxy silanes, the viscosities were measured, which is showcased in the Figure 4.11. The viscosity of urea-free silylated polyurethanes is up to 6 times lower than the conventional aminosilane end-capped prepolymers. The outcome indicates that the elimination of the urea groups from the polymer matrix has a positive effect on the rheological properties of the prepared prepolymers. This can be attributed to the absence of strong bidentate hydrogen bonding of the urea group^[148]

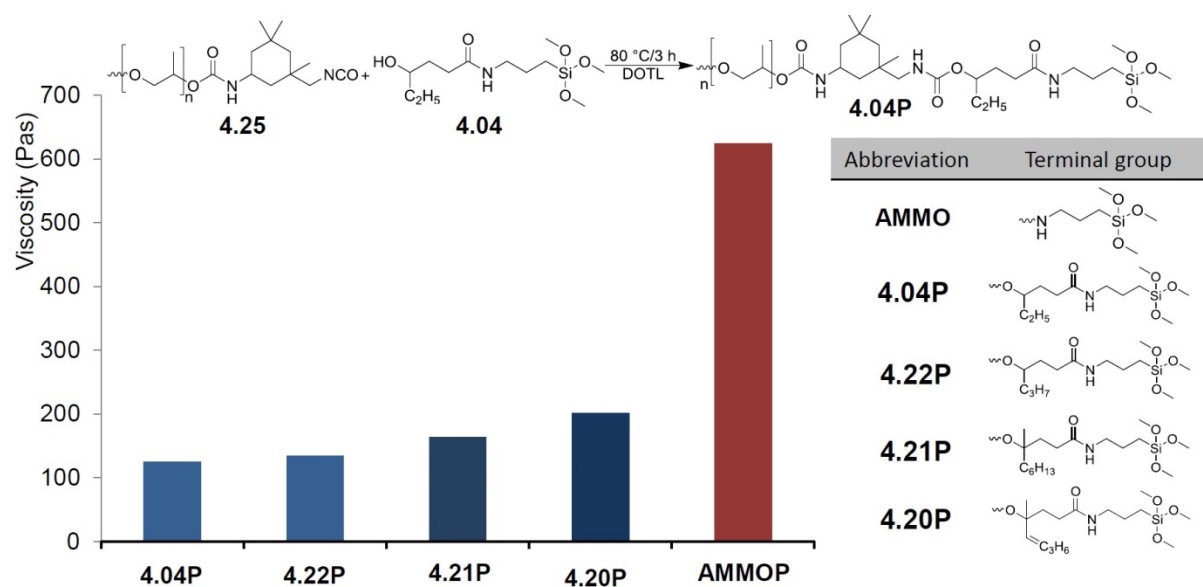


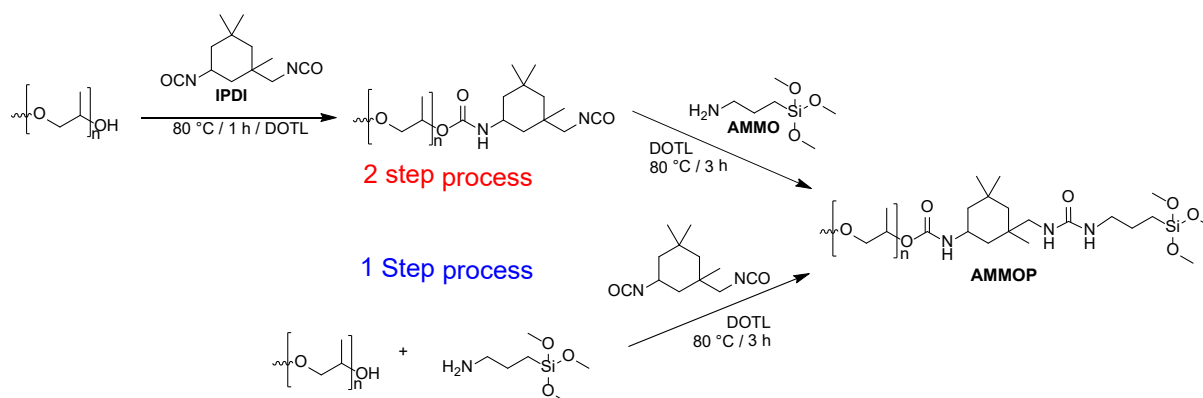
Figure 4.11: Viscosities of prepolymers end-capped with different hydroxyl functional alkoxy silanes as shown in the legend on the right. The prepolymers were prepared using standard prepolymer method and using PPG with molecular weight of 12000 g/mol.

Interestingly, the lowest viscosities are observed in the case of prepolymers containing secondary alcohol end-cappers (**4.04P** and **4.22P**) and which have less sterically demanding side groups compared to the **4.20P** and **4.21P** prepolymers. It is possible that small changes arise from the fact that **4.20** and **4.21** end-cappers have higher viscosities than **4.04** and **4.22**. Another reasonable explanation is also that sterically more demanding groups of

tertiary hydroxyl functional end-cappers **4.04** and **4.22** increase the chain entanglement, which obstructs the polymer backbone chain flow leading to slight increase in viscosity.

4.3.7. Optimization of the prepolymer method

The currently used method for the preparation of silylated polyurethanes in a multi-ton scale consist of two steps as described in chapter 1.5.^[72a,80] In order to simplify the production process and consequently bring further economic advantages to the table, a new one-step prepolymer method was developed (Scheme 4.5). The improved prepolymer method comprises of mixing a dry hydroxyl functional polymer with a stable hydroxyl functional alkoxy silane at 80 °C. Shortly afterwards, a diisocyanate (**IPDI**) and a catalyst (**DOTL**) were added to the mixture and stirred vigorously until all the NCO groups were reacted (3h). After the reaction, the viscosity was measured and compared to prepolymers made by the conventional two-step method (Scheme 4.5).



Scheme 4.5: Schematic representation of one- and two-step methods used for the preparation of silylated polyurethanes.

Obtained viscosity values revealed that the one-step method is not appropriate in case of primary aminosilane (**AMMO**) end-capping, since the prepolymers exhibit viscosities above 1000 Pas. High viscosities are undesired for final application, since those prepolymers are difficult to handle.^[73] Furthermore, the prepolymer becomes highly turbid immediately after diisocyanate addition. The turbidity arises from the double addition of aminosilane to diisocyanate, which is insoluble in the polyether matrix. The remaining diisocyanate reacts with terminal OH-groups of the PPG, leading to a severe chain extension resulting in uncontrolled viscosity increase.

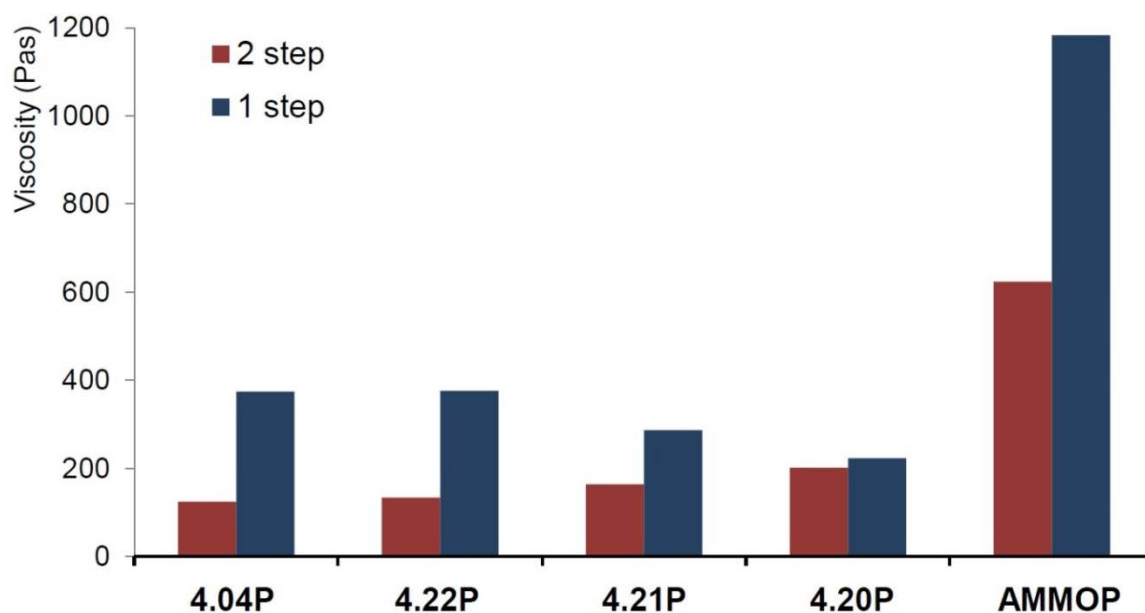


Figure 4.12: Viscosities of prepolymers end-capped with different hydroxyl functional alkoxysilanes prepared by two-step (red) and one-step (blue) prepolymer method. Standard deviation is ± 1 h.

A more encouraging result was achieved by using hydroxyl functional end-cappers. The prepolymers produced were clear, with only slightly higher viscosity than the ones prepared by the conventional method. The viscosity increase was higher in the case of secondary hydroxyl functionality (**4.04P** and **4.22P**), indicating a partial di-addition of the end-capper to the diisocyanate as was described in the case of primary aminosilane (**AMMO**). The latter process is not as probable for the less nucleophilic tertiary alcohol, therefore the diisocyanate first attacks the terminal OH of the PPG chain and then reacts with remaining OH groups of the end-capper.^[35]

The described one-step prepolymer method has many advantages over the conventional synthetic methods for the preparation of silicon modified polymers (SMP). The overall reaction time of the disclosed method is thus significantly shortened which increases the economic viability of the process.

4.3.8. Curing/setting behavior of the prepared silylated polyurethanes

The curing speed/setting speed is another good indicator of the quality of the silylated polyurethanes. To obtain a reasonably good idea about the curing behavior the skin over time (SOT) of all the prepared prepolymers was determined (Figure 4.13).

By assessing the SOT values of the prepolymers prepared by two-step process, one can conclude that the prepolymer containing **AMMO** end-capper cured faster than all other urea-free prepolymers. It is well established that amino functional alkoxysilanes exhibit higher curing speeds compared to alkoxysilanes with functionalities like: amide, acrylate, ester etc.^[6a,50b] However this property of aminosilanes cannot be assigned to a single effect. Factors like electronic and steric effects, pD dependence, van der Waals and hydrogen bonding

interactions between amino group and alkoxy leaving group work in the work in synchrony, making aminosilane the most prone to hydrolysis during curing with water.^[6a] Another important parameter, which influences the curing rate of the adhesive or sealant, is its viscosity. When the viscosity of the prepolymers is lower, the SOT values are generally higher, since higher crosslinking density is required to form a solid film, compared to highly viscous prepolymers. Due to this reason, longer time is required to achieve higher crosslinking density in the thin film on the surface of the specimen.^[10] This is consistent with our results, since the urea-free prepolymers which exhibit lower viscosity show higher SOT values.^[173]

It is necessary to mention, that all prepolymers prepared by one-step method exhibit higher SOT values, however for most of them, the increase was only slight. According to our expectations, the prepolymer end-capped with **AMMO** in a one-step process displayed extremely low curing speeds and remained tacky even after several weeks at atmospheric conditions. This result even elaborates the fact, that primary aminoalkoxysilanes are not appropriate agents for preparation of silylated polyurethanes using this method. The argumentation for the decline in the curing rates lies in poor reaction selectivity during end capping reaction as was described in the chapter 4.3.7.

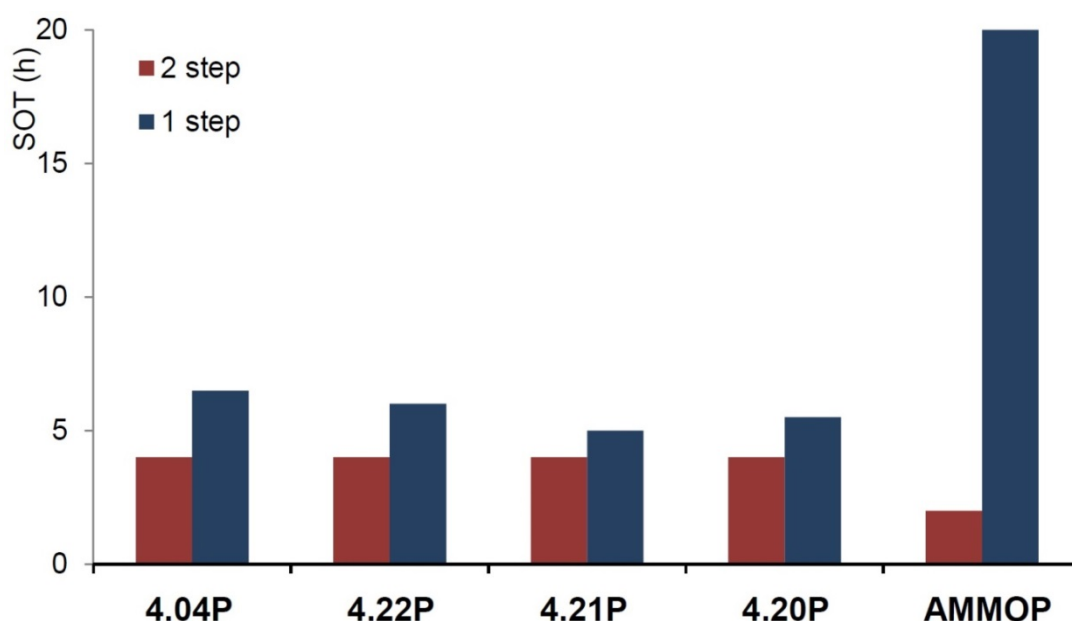


Figure 4.13: Skin over time of prepolymers end-capped with different hydroxyl functional alkoxy silanes prepared by two-step (red) and one-step (blue) prepolymer method.

4.3.9. Adherence of urea-free prepolymers to different materials

The effect on adhesion of urea-free polyurethanes prepared with hydroxyl functional alkoxy silanes (**4.04P** and **4.20P** - **4.22P**) on different materials was investigated using lap-shear tests. The prepared silylated polyurethane was placed between two plates of the same material and cured for 1 week at atmospheric conditions. Afterwards the lap-shear tests were

performed, the results of which are presented in the Figure 4.14. In addition to the shear strength values, the type of failure on the substrate specimen was also examined. In the case of glass and wood a cohesive break was observed, which indicates, that the adhesive strength of the cured prepolymer exceeds its cohesive bonding. This was expected, since bonding of the silylated polyurethanes to natural materials relies on the covalent type connection as was described in the chapter 1.7.1.1. Furthermore, the adhesive bonding to wood is further enhanced by mechanical interlocking of the adhesive with wood fibers and voids.

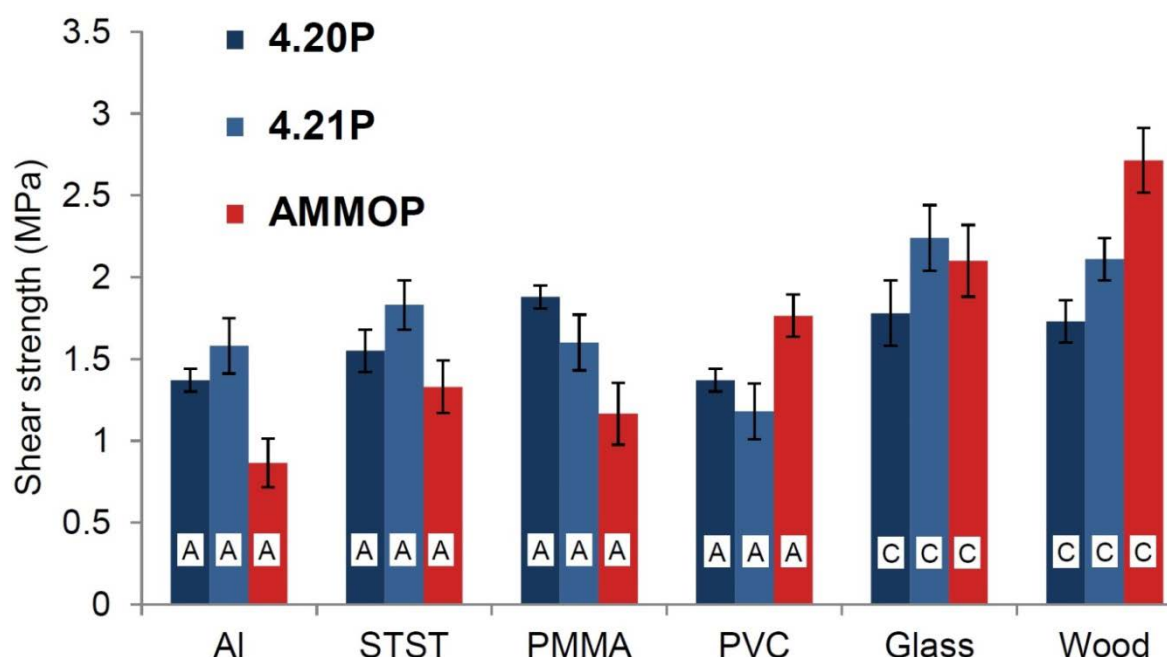


Figure 4.14: Mean lap-shear values of urea-free silylated prepolymers (**4.20P** and **4.21P**) tested on different materials. Type of failure: adhesive (A), cohesive (C). The prepolymers were prepared using standard prepolymer method and using PPG with molecular weight of 12000 g/mol.

The results obtained during the lap-shear tests showed, that the modification of the silane end-capper has a significant effect on its adherent properties. Interestingly, the elimination of the urea group and the introduction of the less polar alkyl chain in to the prepolymer structure have a varying effect on the adherence strength. In the case of the materials which have commonly poor adherence to silylated polyurethane like aluminum (AL), stainless steel (STST) and poly(methyl methacrylate) (PMMA) the properties were considerably improved. In the case of more polar materials like glass, wood and poly(vinyl chloride) (PVC), the adherence deteriorated. One possible explanation for this kind of response is the elimination of the urea group, which plays an important role in adherent bonding. Urea group is known for the superior adhesion to polar surfaces due to its strong bidentate hydrogen bonding.^[174] Another reason could also be the introduction of the less polar alkyl chains, which prevents a good wettability of the polar substrate due to their chemical incompatibility.

On the other hand the diffusion theory developed by Vyutskii assumes that the adhesion is directly related to the ability of the polymer molecules to interdiffuse into a substrate.^[175] The interdiffusion into the pores of the substrate is promoted, when the chain flow is allowed. In the case of aminosilane end-capped prepolymer (**AMMOP**) the highly hydrogen bonded polymer matrix does not allow the polymers to flow as easily as in urea-free polyurethanes, therefore the diffusion is not as efficient. On the other hand, the urea-free prepolymers (**4.20P** and **4.21P**) with sterically demanding alkyl groups surrounding the urethane functionality prevent a great amount of hydrogen bonding as shown in chapter 4.3.6, while the coordination of N-H to the metal centers is still possible. This effect might be responsible for the improvement of the adhesive bonding of the developed silylated polyurethanes to metals. In the case of urea-containing polymers the absence of the sterically demanding groups promotes the intramolecular hydrogen bonding to form the hard segments rather than hydrogen bonding or coordination of the polar urea groups to the surface of the metals and polymers.

It is noteworthy to mention, that the adhesion strength of **4.20P** and **4.21P** is in most of the cases in the same order of magnitude, which can be due to the very similar chemical structure of the end-cappers.

4.3.9.1. Adhesion of the prepolymers made with one-step method

To simplify the production process and consequently bring further economic advantages in to the large-scale process, a new one-step prepolymer method was developed and described in chapter 4.3.7. The analysis of the rheological and curing properties showed some differences between one- and two-step process, which arise from the reaction selectivity between the OH/NH₃ and NCO groups. The results showed that the one-step reaction is not appropriate for the commonly used **AMMO** end-capper, while the developed hydroxyl functional alkoxysilanes (**4.04** and **4.20-4.22**) show excellent results. To test the adherence of the developed silylated polyurethanes we performed lap-shear test of **AMMOP** and **4.20P** prepolymers made by both prepolymer methods. The results of these tests are presented in the Figure 4.15.

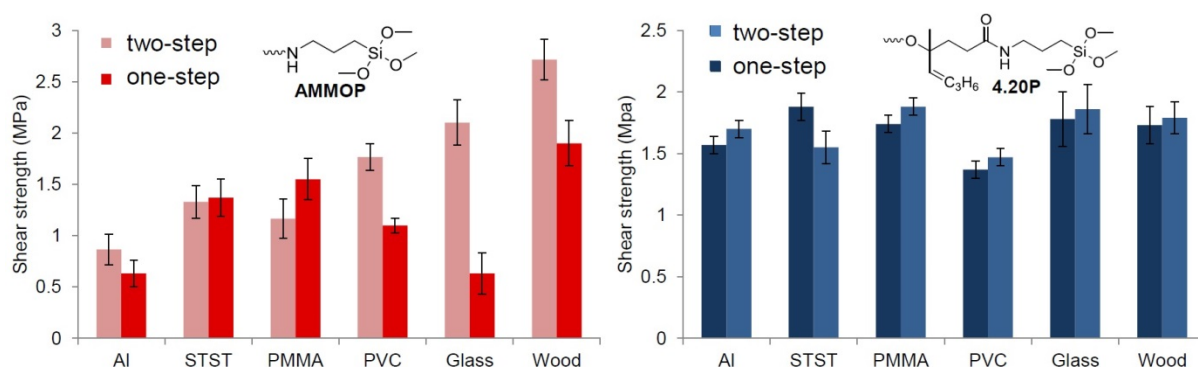


Figure 4.15: Mean lap-shear values of silylated prepolymers **AMMOP** (left) and **4.20P** (right) tested on different materials. The prepolymers were prepared using one- and two-step prepolymer method and by using PPG with molecular weight of 12000 g/mol.

The prepolymers prepared with **AMMO** in the one-step prepolymer method proved to be highly viscous, turbid and exhibited slower curing. Due to this reasons, the results for the lap-shear tests showed a generally negative trend compared to the standard two-step prepolymer method. Another observation was that the films containing **AMMO** prepared by the one-step method were still tacky after breaking the specimen apart, which is the consequence of the poor curing speeds.

For the testing of the prepolymers terminated with hydroxyl functional alkoxyasilanes, the end-capper **4.20** was selected, since it showed the best results in the previous lap-shear tests. To the pleasant surprise, the prepolymers prepared employing hydroxyl functional alkoxyasilane (**4.20P**) as an end-capper showed excellent reproducibility and were completely cured even in the center of the specimen, where diffusion of moisture from the air is a rate determining step for the curing process. Furthermore, only slight differences in the values for shear strength were noticed and remained in the error range of the measurement.

4.3.10. Tensile strength of urea-free prepolymers prepared by two-step method

The tensile properties of the cured films prepared by two step method were tested to study the effect of the elimination of the urea groups form the prepolymer system. The results of the performed elongation tests are given in Figure 4.16, which were obtained from stress-strain curves. The comparison between the measured values for **4.20P**, **4.21P** and **AMMOP** demonstrate a minor impact of the urea group elimination on the tensile properties of the casted film, cured under atmospheric conditions during 7 days. It was observed that the tensile strength (σ_{max}) of the cured films remains in the same order of magnitude or is slightly decreased, while the values for the elongation are generally higher compared to standard **AMMO** prepolymer type.

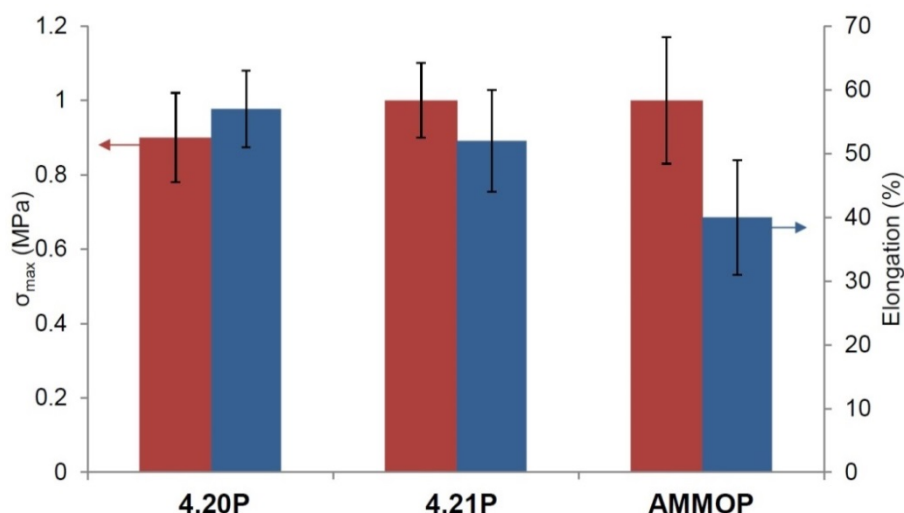


Figure 4.16: Mean values of the elongation tests of the silylated prepolymers end-capped with **AMMOP**, **4.20P** and **4.21P**. The prepolymers were synthesized using PPG with molecular weight of 12000 g/mol.

Considering the peculiar increase of the elongation at break, while the tensile strength remains about the same for the urea-free prepolymer, the decision was made to explore this further. The swelling test to determine the crosslinking density of the cured prepolymers were performed (Table 4.2). The results show that the crosslinking density of the urea-free prepolymers are generally lower than the corresponding **AMMO** end-capped prepolymer. This is consistent with our previous findings described in the chapter 4.3.8, where it was shown; that the curing of urea-free prepolymer is slower, therefore lower crosslinking density are achieved.

Table 4.2: Left: Results of the swelling test performed with the cured prepolymers (PPG 12000 g/mol) end-capped with **AMMOP**, **4.21P** and **4.20P**. **Right:** Calculation of the degree of crosslinking.

Prepolymer	Degree of crosslinking [/]		Calculation
	one-step	two-step	
AMMOP	/ ^[a]	0.243	
4.21P	0.198	0.151	$Swelling [\%] = \frac{Ws - Wd}{Wd} \times 100$ [1]
4.20P	0.184	0.157	$Deg. of crosslinking [/] = \frac{1}{Swelling}$ [2]

A part of the cured prepolymer was placed in toluene for 4 days after which the amount of swelling was determined gravimetrically.

^[a] the sample disintegrated during the swelling test, therefore the evaluation was not possible.

Wd = Weight of dry polymer

Ws = Weight of swollen polymer

However, one may argue that the determination of the crosslinking density by swelling test of different termosets is not an appropriate method as the penetration of the solvent in to the polymer chains depends on the polymer polarity and other structural features. Due to this reason toluene was selected as a solvent, since it is known to be less dependent on the polymer structure compared to other solvents since it does not form any hydrogen bonds or van der Waals interactions with the polar urea, urethane groups or polyether backbone. ^[176]

Based on the obtained results presented above it was concluded, that the combination of the crosslinking density and hydrogen bonding is the most probable reason for the increase in the elongation at break of the cured prepolymers. As discussed previously, the elimination of the urea group and steric shielding of the remaining urethane groups results in the facilitated movement of the polymer chains. In contrary to that statement the urea-containing prepolymers contain highly hydrogen bonded hard-segments which restrict the soft-segment movement. This generally results in high tensile strength, but low elongation at break. In this work it was possible avoid this effect by eliminating the urea group which was only possible by introducing hydroxyl functional alkoxysilane as an end-capper. Furthermore, lower crosslinking density leads to lower stiffness of the cured polymer; therefore, it allows the polymer resin to achieve higher deformation, before the break.

4.3.10.1. Comparison of the tensile strength of the prepolymers prepared with one- and two-step method

To compare the tensile properties of the prepolymers synthesized by one- and two- step procedure the elongation test were performed on **AMMOP** and **4.20P** prepolymers made by using both methodologies. The results of these tests are presented in the Figure 4.17.

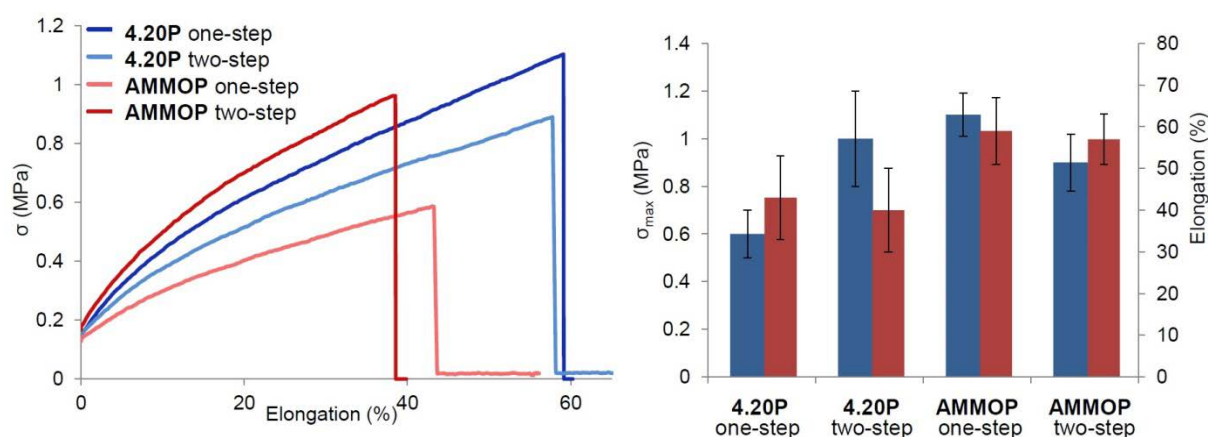


Figure 4.17: Mean values of the elongation tests of the **AMMOP** and **4.20P** prepolymers prepared by one- and two-step prepolymer method. The prepolymers were synthesized using PPG with molecular weight of 12000 g/mol.

As expected, the sample prepared using one-step method with **AMMO** end-capper, show poor properties, since the curing is not completed as was shown before. However, an encouraging result was visible in the case of urea-free (**4.20P**) prepolymers. It was observed that the tensile strength was slightly improved by one-step prepolymer method, while the elongation break remained in the same range. Based on the obtained results it was concluded, that one-step prepolymer method has a positive effect on the mechanical properties of the cured films, since the tensile strength and elongation break are well balanced between each other.

4.4. Conclusion

The main object of this study was to prepare hydroxyl-functional methoxysilanes. The aim of was achieved by ring-opening of lactones with aminoalkoxysilanes. However, in order to prepare a few truly stable hydroxyl functional methoxysilanes, an extensive catalyst and lactone screening was performed with the help of *in situ* IR and NMR spectroscopy. With the performed stability tests, it was confirmed that secondary and tertiary hydroxyl functionality remains stable for longer time at increased temperatures.

Having several stable hydroxyl functional methoxysilanes in hand, it was possible to utilize them as end-cappers for the preparation of silylated polyurethanes. These prepolymers exhibit low viscosities and reasonable curing rates. Furthermore, it was shown that these silane coupling reagents can be used in a one-step prepolymer method, since the nucleophilicity of the OH functionality of developed end-capper is similar or lower to the one of the polyether terminal OH. This method has economic and practical advantages for preparation of silylated polyurethanes in the multi-ton scale.

Furthermore, the cured urea-free prepolymers prepared by one- and two-step methods showed an improved adherence strength to materials like aluminum, stainless steel and poly(methyl methacrylate). Additionally, an improvement in tensile strength and elongation break was shown during our investigation.

5. Phenoxy-functional alkoxysilane end-cappers

5.1. Project outline

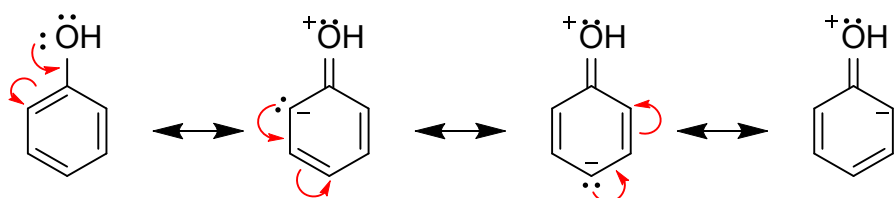
The preparation of highly desirable hydroxyl functional alkoxysilanes proved challenging according to the published patent and scientific literature. Since it is well established that hydroxy groups connected directly to phenyl rings (phenoxy) are significantly less nucleophilic, it was decided to use this property as an advantage. In this chapter, the preparation of stable phenoxy-functional alkoxysilanes is presented and discussed.

The aim of our investigation is to develop a new end-capping procedure by applying phenoxy-functional alkoxysilanes to prepare low viscous silylated polyurethanes with reasonable curing properties. The adhesive and tensile strength of the cured polymers were analyzed to identify the influence of the incorporation of the phenyl group in to the prepolymer matrix.

5.2. Background

Phenols are aromatic compounds containing hydroxyl group attached directly to an aromatic sp^2 hybridized carbon, commonly referred to also as enols. The combination of the hydroxyl group and the aromatic ring modifies the properties of both partners and creates a functional group which differs significantly in many of its properties and reactions from its two constituents. Phenols are important in industry, in agriculture, in medicine, in chemical synthesis and in polymer chemistry.^[177] The hydroxyl group of phenol determines its acidity whereas the benzene ring characterizes its basicity, thus it is formally the enol form of the carbonyl group.^[178]

Phenol can be considered as the enol of cyclohexadienone. While the tautomeric keto–enol equilibrium lies far to the ketone side in the case of aliphatic ketones, for phenol it is shifted almost completely to the enol side. The reason of such stabilization is the formation of the aromatic system. The resonance stabilization is very high due to the contribution of the *ortho*- and *para*-quinonoid resonance structures. In the formation of the phenolate anion, the contribution of quinonoid resonance structures can stabilize the negative charge (Scheme 5.1).^[178] Due to the stabilization of the negative charge by the aromatic system, phenols are considered to be less nucleophilic compared to the aliphatic alcohols. The latter are also considerably less acidic, therefore they tend not to form salts with alkali metal salts in contrary to phenols.^[179]



Scheme 5.1: Phenol resonance stabilization.

One of the common phenols is salicylic acid, which was first used in 19th century as a painkiller. In 1897 a research group in the company Bayer synthesized acetylsalicylic acid, which was two years later offered on the market under the trade name Aspirin®.^[180] The success of Aspirin was terrific. In 1994 the *Medical Sciences Bulletin* reported, that more than 50 nonprescription drugs contain aspirin as the principal ingredient in United states alone.^[180-181] This caused not only a severe drop of the price of acetylsalicylic acid but also of its derivatives. One of the most common derivatives of the latter is salicylaldehyde, whose price is steadily dropping over the last 5 years.^[182] The main industrial significance of salicylaldehyde is for the formation of phenol-imine resins. For example, 2-hydroxy-1,5-benzenetricarbaldehyde undergoes polymerization with primary diamines in the presence of acid catalysts forming phenol-imine resins, which are used as cross-linkers in a variety of polymers.^[183]

Furthermore, salicylaldehyde imines have become very important in asymmetric catalysis and a variety of polydentate ligands prepared from chiral monoamines and diamines are employed in oxidation reactions, carbenoid reactions and Lewis acid catalyzed reactions (Figure 5.1).^[184] An imine derived from a chiral 1-phenethylamine and salicylaldehyde (**5.02**) was employed in the copper catalyzed asymmetric cyclopropanation by Nozaki, Noyori and coworkers in 1966, which is the first example of the asymmetric catalysis in a homogeneous system.^[184-185] Salicylaldehyde imines with ethylenediamine (salen) have also been studied extensively by Jacobsen and Katsuki and their coworkers since 1990 in asymmetric catalysis (Figure 5.1 Left).^[186] Salen complexes (**5.01**) derived from salicylaldehyde imines are also commonly used for ring-opening copolymerization of carbon dioxide and epoxides.^[187]

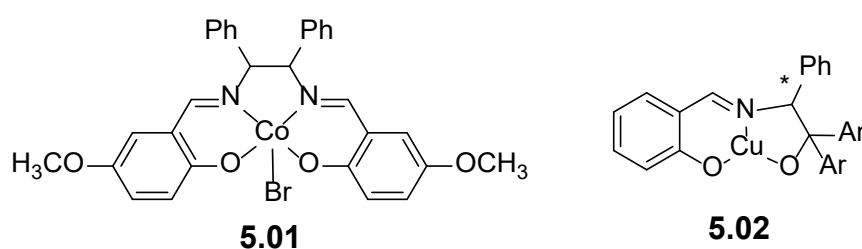
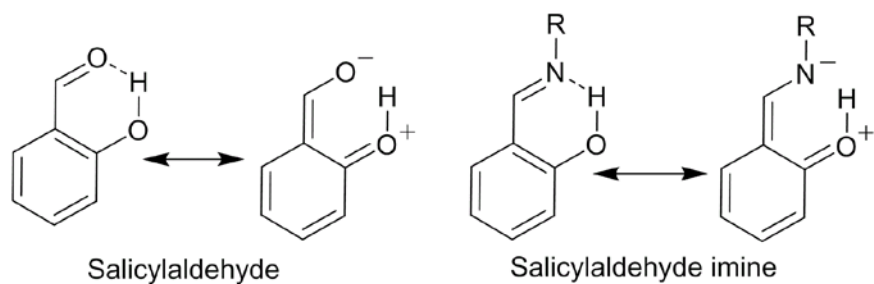


Figure 5.1: Left: Cobalt salen complex (**5.01**). Right: Asymmetric ligand for Copper catalysis derived from salicylaldehyde (**5.02**).

Phenolic compounds are promising materials for the preparation of stable hydroxyl functional alkoxy silanes due to the lower nucleophilicity of the phenolic hydroxyl group. However, due to the high stability of the phenolic compounds the reaction of the phenolic -OH with the isocyanates during the end-capping might be considerably slower compared to the currently used end-cappers. Gelderen showed that the reaction of aryl isocyanates with primary and secondary aliphatic alcohols proceeds smoothly, while the reaction of tertiary alcohols and phenols takes place only with great difficulty without the use of any catalyst.^[188] Later on, Yezrielev *et al.* investigated the reaction selectivity between aliphatic isocyanates and phenolic and aliphatic alcohols under the influence of different catalysts.^[189] With the organotin catalysts like dibutyltin dilaurate (DBTDL) the aliphatic OH reacts first. When tertiary amines, triphenylphosphine or even when no catalyst was employed at room temperature the phenolic -OH reacted preferably, however the reaction was 3-4 times slower than the DBTDL-catalyzed reaction. Another important factor is the use of the appropriate solvent, which plays an important role in the rate of the isocyanate-phenol reaction. The reaction is largely accelerated in polar media, since the O-H bond is more polarized under the influence of polar solvents. More polar groups of the solvent generate loose ion-pair of the hydroxyl, which attacks the nitrogen atom of the NCO more easily to produce the urethane group.^[190]

However, in the case of salicylaldehyde and salicylaldehyde imine, the nucleophilicity of the phenolic -OH group is further compromised by the resonance stabilization with the aldehyde or imine group as shown in the Scheme 5.1.



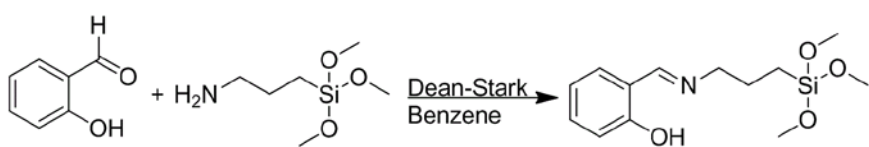
Scheme 5.1: The stabilization of the phenolic hydroxyl group of the salicylaldehyde and salicylaldehyde imine through resonance and intramolecular hydrogen bonding.

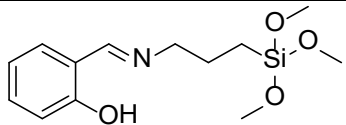
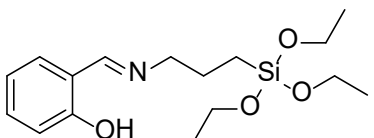
5.3. Results and discussion

5.4. Preparation of phenol functional alkoxyasilanes

There are many ways to prepare phenolic functional alkoxyasilanes. The selected path involved the preparation of salicylaldehyde imines by reacting salicylaldehyde and aminosilane. The reason for selecting salicylaldehyde as a phenolic compound is its low price and the fact that it is readily available on the market. Furthermore, the stability of prepared imines is also a factor to take into account, however, the stability of aromatic imines is high, compared to aliphatic ones, therefore the hydrolysis of the imine group with water is less possible. Especially salicylaldehyde imines exhibit remarkable stability, which is enhanced by the resonance between the imine and hydroxyl group through the phenyl ring. [191]

Table 5.1: Prepared phenol functional alkoxyasilanes and corresponding isolated yields.



Compound	Product	Yield (%) ^[a]
5.03		96
5.04		97

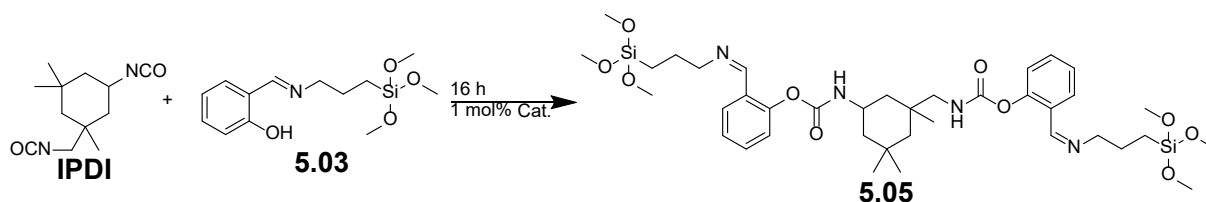
^[a] Isolated yields.

The end-capper containing salicylaldehyde imine was prepared by mixing salicylaldehyde and (3-aminopropyl)triethoxysilane (**AMEO**) in a Dean-Stark apparatus using benzene as a solvent. The reaction proceeds smoothly in excellent yields. However, the crucial factor for high yields and good purity is the removal of water by the azeotropic mixture of H₂O/benzene. If the removal of the produced water during the imine formation is not fast enough, the hydrolysis of alkoxyasilane groups is induced, resulting in oligomerization or even polymerization of the end-capper. In that case, a distillation is needed after the synthesis in order to obtain a pure product. By carefully adjusting the reaction parameters it was possible to prepare the final product in good purity without the need to distill it afterwards.

5.4.1. Catalyst screening

Aromatic isocyanates are generally more reactive than aliphatic isocyanates. The presence of electron-withdrawing substituents on the isocyanates like the phenyl ring increases the reactivity, whereas the electron donors decrease the reactivity.^[192] Furthermore, bulky substituents adjacent to isocyanate groups tend to decrease reactivity due to the steric hindrance in the addition to the inductive effect.^[193] The most commonly used isocyanate for the preparation of silylated polyurethanes is isophorone diisocyanate (**IPDI**) due to the positive effect on the viscosity and mechanical properties. Therefore, it is highly desired to use it as a standard compound for prepolymer preparation. However, **IPDI** is known as one of least reactive diisocyanates due to its bulky aliphatic groups. In order to increase the reactivity of **IPDI** in the prepolymer different Lewis acids and bases can be used.

In order to simulate the reactivity of prepared end-cappers in the prepolymer process, they were first reacted with **IPDI** in neat conditions, to verify the coupling between NCO groups and the OH groups of the end-capper. Using **IPDI** and phenol functional alkoxyisilane (**5.03**) as standard compounds, the relationship between the reaction yield and the catalyst employed to produce reaction product **5.05** was investigated (Scheme 5.2). The ATR IR spectra were recorded after the reaction in order to verify the disappearance of the NCO stretching bands and the appearance of urethane bands. The detection of the phenolic OH-band disappearance proved to be difficult to follow by IR spectroscopy, since it is overlapping with urethane N-H stretching band, which is being formed during the same reaction.



Scheme 5.2: The reaction between isophorone diisocyanate (**IPDI**) and phenol functional alkoxyisilane to prepare **5.05**, in order to test the reactivity of prepared end-capper.

The reaction product **5.05** was obtained by the reaction of 2 : 1 molar ratio of **IPDI** : **5.03**. When the above reaction was carried out in the presence of 1 mol% of Lewis bases like DBU or TMG the NCO absorbance band completely disappeared, indicating that the reaction is completed. In the case of DOTL as a catalyst, the NCO absorbance band was still clearly visible, meaning that this particular Lewis acid is not the best choice for the catalyst. However since DOTL has a very positive effect on the curing speed in the final formulation, therefore it is of high interest to perform the reaction with this catalyst. In order to increase the reaction rate, the reaction temperature was increased to 120 °C, which lead the reaction to completion (Figure 5.2).

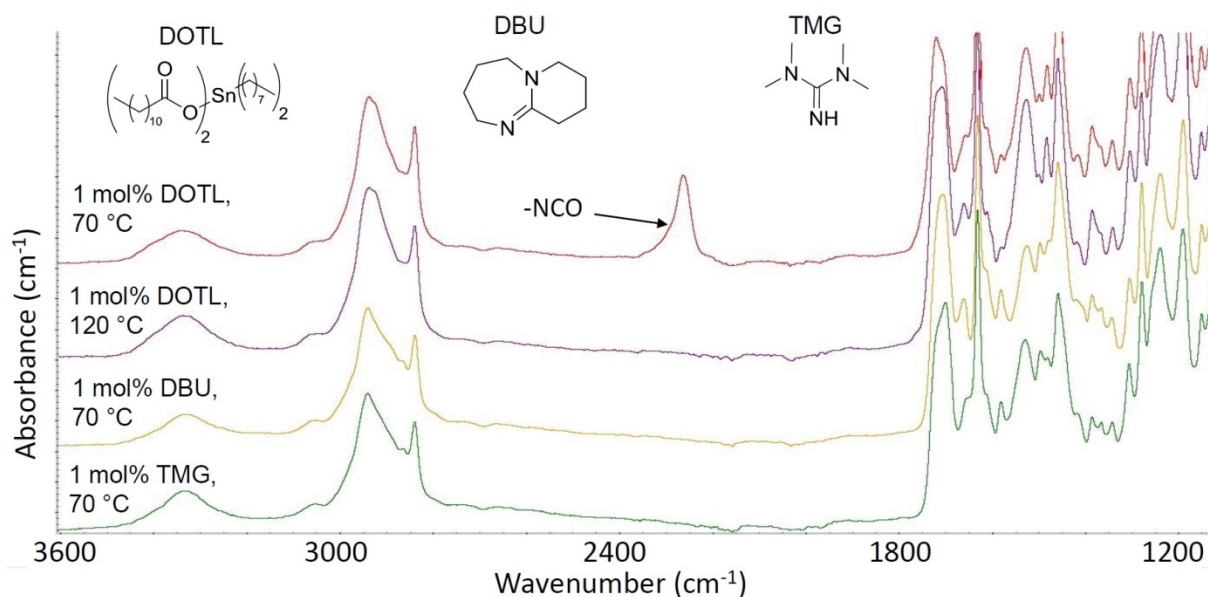


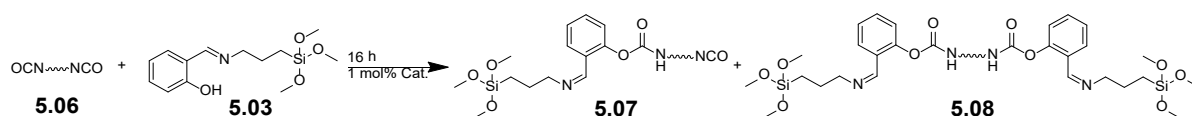
Figure 5.2: IR spectra of the final reaction mixture after the reaction between **IPDI** and **5.05**. Reaction conditions: DOTL (1 mol%, 70 °C or 120 °C, 16 h), DBU (1 mol%, 70 °C, 16 h) and TMG (1 mol%, 70 °C, 16 h).

5.4.2. Prepolymer preparation

During the catalyst screening it was discovered, that the prepared end-cappers (**5.03** and **5.04**) are significantly less reactive than other conventional amino or hydroxyl functional alkoxy silanes like **AMMO**, **4.20** or **4.21** (Chapter 4). Experiments showed that the conventional end-capping method employing DOTL as a catalyst at 80 °C was not sufficient to completely react with all NCO groups of the prepolymer, since the NCO absorbance band could still be visible in the IR spectrum. Ying Li *et al.* described the influence of the reaction environment (solvent) on the reaction rate of phenols with isocyanates.^[190a] They describe, that the reaction is faster in polar solvents like DMF or DMSO, which are able to partially polarize the phenolic OH to generate loose ion-pair. In the second step, the loose ion-pair attacks the NCO to generate a urethane bond. This process is significantly slower in less polar environment like polypropylene glycol (PPG). Therefore, the end-capping reaction needs longer time to be completed. Due to the lower reactivity of phenols in the polypropylene glycol matrix, the search for alternative end-capping methods was embarked on.

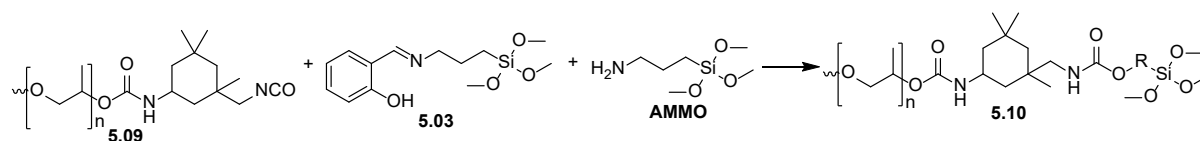
One possible option for completely functionalizing the polyol with phenoxy functional alkoxy silanes is to selectively react the prepared end-capper with desired diisocyanate in order to obtain NCO-functional alkoxy silane **5.07** (Scheme 5.3). This diisocyanate could be then directly used in the prepolymer method by adding it directly to the polyol. One of the advantages of this process is that theoretically no chain extension of polyol occurs during this process, which additionally lowers the viscosity. Furthermore, the proposed process would reduce the reaction time of the overall prepolymer method since only one reaction step

instead of two is required. An attempt was made to develop this approach, by reacting the **IPDI** with compound **5.03** in 1 : 1 ratio at 70 °C using various catalysts. The obtained reaction mixture exhibited very high viscosity and was difficult to handle under inert conditions. Especially, the addition of highly viscous liquids to the polyol during the prepolymer method is technically difficult and is therefore not desired. Furthermore, in order to determine the reaction selectivity, a quantitative analysis was required. The analysis of the reaction mixture proved challenging, since the obtained compounds have molecular weight in the range from 400-600 g/mol for mono-addition product (**5.07**) and from 700 to 1000 g/mol for di-addition product (**5.08**) as showed in the Scheme 5.3. The compounds of this size are not appropriate for the analysis with classic GC or GC-MS methods, while other chromatographic methods require calibration beforehand. This procedure requires standards which are extremely difficult to prepare. Furthermore, liquid chromatography of alkoxyasilanes is challenging, since these compounds can react with the stationary phase and block or damage the column.



Scheme 5.3: Pre-functionalization of the end-capper (**5.03**) with diisocyanate (**5.06**) to produce NCO-functional alkoxyasilane **5.07** and di-addition product **5.08**.

Another possible approach for preparing NCO-free silylated polyurethanes is to prepare NCO-terminated prepolymer (**5.09**) in the first step and then in the second step add an amount of phenoxy functional alkoxyasilane. The ratio of OH : NCO should be lower than 1 in order to have an excess of the NCO groups during the first end-capping step. Thereby, most of the OH should react faster, which would increase the end-capping reaction rate and force all of the phenol groups to react. In the last step, an amount of the aminoalkoxyasilane is added in order to react the remaining NCO groups (Scheme 5.4).



Scheme 5.4: Preparation of the silylated polyurethane (**5.10**) by using a combination of **AMMO** and **5.03**.

In order to find the optimal compromise between reaction time, prepolymer viscosity and prepolymer curing speed, the ratio of phenolic alkoxyasilane and aminosilane end-capper was investigated. NCO-terminated polyol (**5.09**) was prepared by reacting 4200 g/mol polyol with **IPDI** in the presence of 1 mol% DOTL catalyst under standard conditions (80 °C, 1 h). Desired amount of compound **5.03** was added to the mixture and stirred for 16 hours at 80 °C. Afterwards an amount of **AMMO** was added in order to react with all remaining NCO

groups. The sum of moles of **5.03** and **AMMO** was equivalent to the moles of all NCO groups of the **5.09** before the end-capping reaction.

The preparation of moisture curable prepolymers using the combination of phenolic alkoxy silane and aminosilane as end-cappers was successful, since no unreacted NCO groups were visible in the IR spectrum after the reaction. In the case, when only phenol functional alkoxy silane was used as an end-capper, it was still possible to detect a small amount of free NCO groups after the prepolymer method using IR spectroscopy.

After each reaction, the viscosity of the prepolymer was measured and a film was casted in order to examine its skin-over time. Figure 5.3 presents the results obtained for different ratios of **5.03** : **AMMO**. The viscosity of the prepolymer was positively influenced by the addition of **5.03**, since a higher amount of presented end-capper resulted in a prepolymer viscosity decrease. The formation of urethane groups instead of urea groups reduces the amount of hydrogen bonding, which leads to weaker intermolecular interaction, leading to a decrease of prepolymer viscosity. Unfortunately the curing speed is adversely affected by the higher amount of **5.03**, as the addition of presented end-capper slows the curing rate. Valerrian found that the introduction of phenyl groups in to the prepolymer backbone have a great drop in water vapor transmission rates compared to other aliphatic groups.^[194] The decrease in water permeation in to the prepolymer matrix is one possible explanation for the decrease of the curing speed of prepared prepolymers. Another reason lies in the effect of the functional groups on the hydrolysis speed of alkoxy silanes.^[6e] It is well established, that aminoalkoxy silanes exhibit good curing speeds, however any modification of the amine groups usually results in the decrease of the alkoxy silane hydrolysis rates.

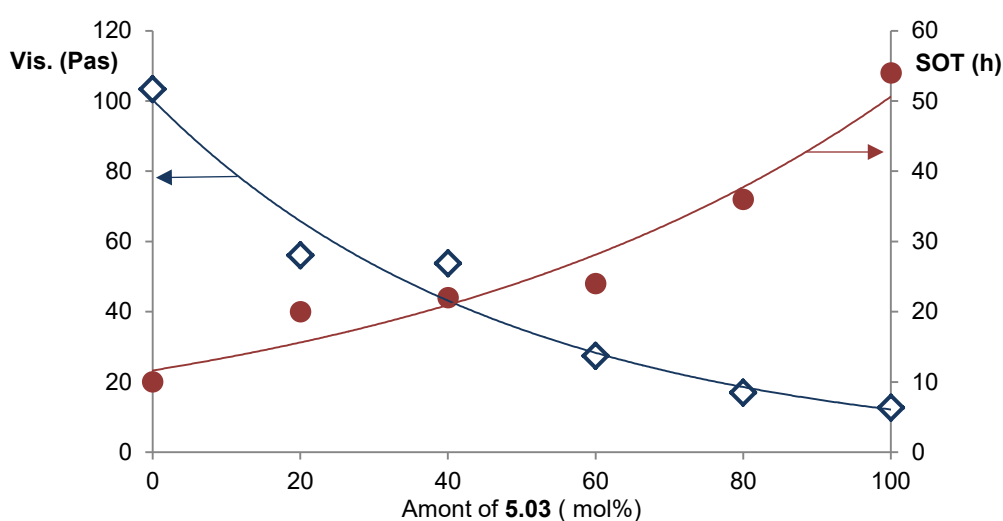


Figure 5.3: Optimization of the end-capping process using the mixture of phenolic silane and aminosilane. Graph shows the amount the mol% of end-capper **5.03** according to the total amount required. The remaining amount was compensated with **AMMO**. The prepolymers were prepared using standard prepolymer method and by using PPG with molecular weight of 4000 g/mol.

The optimal ratio of the **5.03** : **AMMO** was determined to be 40 : 60 mol%, since this is the point where the correlated curves for viscosity and the skin-over time intersect. In this point the positive effect of viscosity decrease is the highest and the negative effect of the increase of the skin-over time is the minimal. By using the described combination of both phenolic and amino functional alkoxysilane end-cappers it was possible to obtain low viscous prepolymers with reasonable curing speed.

5.4.3. Adhesion of the prepolymers prepared using phenol functional alkoxysilane

The combination of the phenol functional alkoxysilane (**5.03**) and aminosilane (**AMMO**) as end-cappers proved effective as the prepolymers show reduced viscosity values and reasonable curing speed. However, the introduction of the phenyl rings in to the prepolymer formulation may have a substantial effect on the properties of the cured material; hence it was decided to test the adherent properties of the developed silylated polyurethane. Each prepolymer containing different ratio of **5.03** : **AMMO** was casted on to selected substrate material and cured for 3 weeks at ambient conditions. The results of the lap-shear test performed on the cured prepolymers are showcased in the Figure 5.4 and Figure 5.5.

As presented in the Figure 5.4, it is obvious, that the introduction of the phenol functional alkoxysilane in to the prepolymer formulation has a peculiar effect on the adherent strength to different materials. For example, the adherence of the prepolymer to the PVC plastic is not largely affected by varying the ratio of **5.03** : **AMMO** (Figure 5.4). Nevertheless, in the case of glass, the adherence was substantially improved by using a higher amount of **5.03** as an end-capper. The increase in adhesive bonding can be justified by the fact, that the hydrolysis speed of the developed end-capper is relatively slow (chapter 5.4.2), therefore, the migration of the aminosilane chain-ends to the glass surface is more effective. Silanol groups on the surface of the glass are able to hydrolyze the alkoxysilane groups to form Si-O-Si bonds to the surface as is proposed by the diffusion theory.^[175] As a result of that, the overall binding density to the surface is higher compared to conventionally used aminosilane end-cappers (**AMMO**).

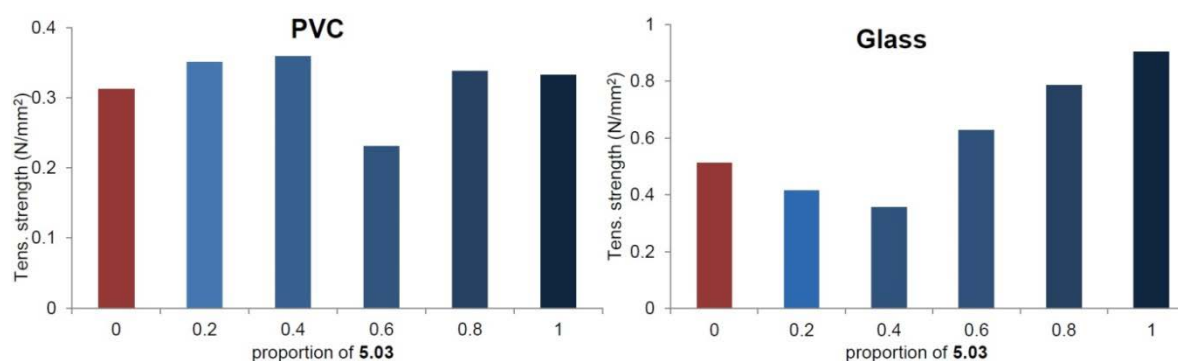


Figure 5.4: Tear strength values obtained by lap-shear tests performed on phenol containing silylated prepolymers casted on PVC and glass. The prepolymers were prepared using different ratios of **14** : **AMMO** at standard conditions and PPG with molecular weight of 4000 g/mol.

The adherence strength of the developed silylated polyurethanes to PMMA shows a negative trend in respect to the addition of **5.03** as an end-capper (Figure 5.5). This clearly shows, that an increased amount of non-polar phenyl rings and the absence of the urea bonds disturbs the interaction of the prepolymer to the surface, since hydrogen bonding and van der Waals forces are the primary binding mechanism of polyurethanes to the PMMA surface.^[100]

Contrary to the results obtained in the case of PMMA, Figure 5.5 shows that the adherence of the prepolymers containing **5.03** as an end-capper improves the adherent bonding to wood. Low viscosity of the prepolymers allow them to penetrate deep in to the wood pores and cure faster and more efficient, since the diffusion of water through pores is possible, contrary to other materials like PMMA, PVC, glass or metals.^[195] Seemingly the decreased polarity due to the incorporation of the phenyl rings and the absence of the urea groups in the presented prepolymers did not play a major role in the diffusion of the prepolymer in to the highly polar wood pores.

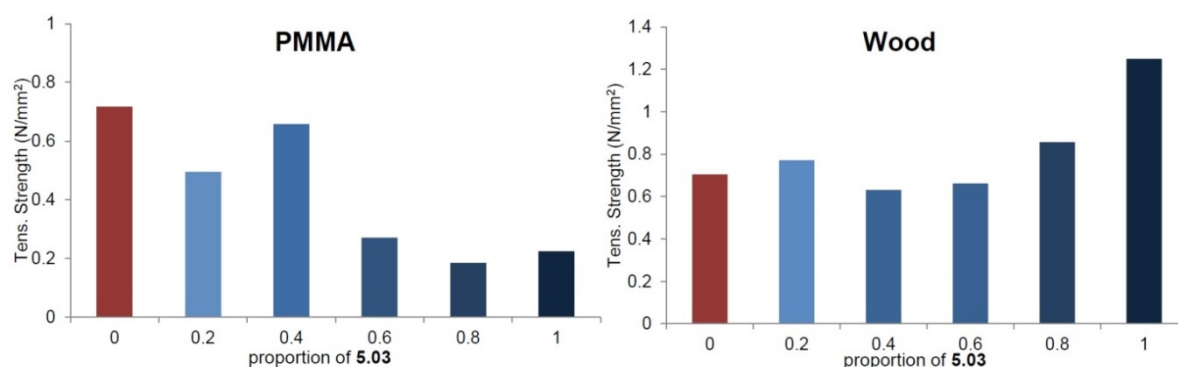


Figure 5.5: Tear strength values obtained by lap-shear tests performed on phenol containing silylated prepolymers casted on PMMA and wood. The prepolymers were prepared using different ratios of **5.03**: **AMMO** at standard conditions and PPG with molecular weight of 4000 g/mol.

5.4.4. Tensile strength of the prepolymers prepared using phenol functional alkoxy silane

The tensile properties of the prepared films were tested to study the effect of the phenyl ring incorporation and the removal of the urea groups from the prepolymer. The results of the performed elongation tests are given in the Figure 5.6. Stress-strain curves demonstrate an impact of the introduction of the phenoxy functional alkoxy silane as an end-capper on the tensile properties of the casted film, cured under atmospheric conditions in the course of 3 weeks. It was observed that there is a strong dependency between the tensile properties and the amount of **5.03** used as an end-capper. A higher amount of **5.03** leads to the decrease of the tensile strength while the value for the elongation at break increases. When only **5.03** was employed as an end-capper the films remained tacky after longer time, due to the incredibly slow curing rate as was discussed previously. These films broke easily, hence their mechanical properties were poor.

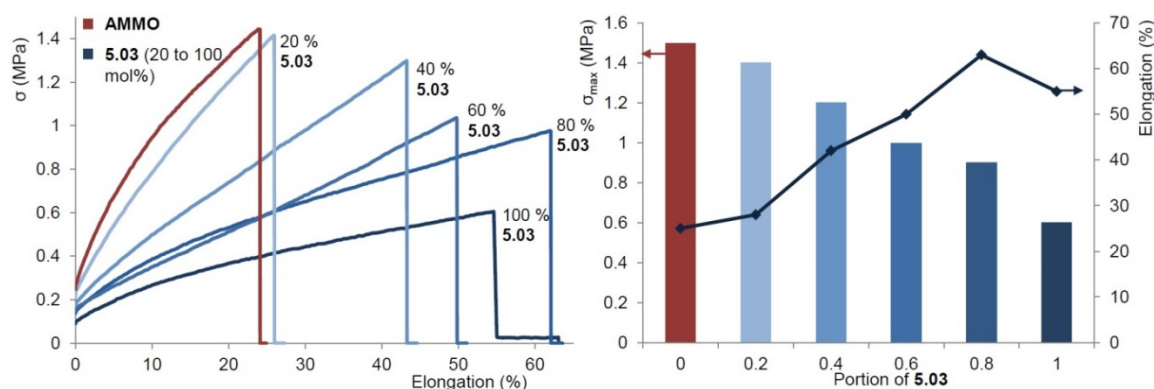


Figure 5.6: Left: Elongation tests results of the silylated prepolymers end-capped with different ratios of **5.03** : **AMMO**. The prepolymers were synthesized using PPG with molecular weight of 4000 g/mol. Left: stress-strain curves. Right: values obtained from stress-strain curves.

The tensile properties of the cured film are dependent on the crosslinking density as well as on the interaction between the polymer chains on the molecular level like hydrogen bonding or van der Waals interactions.^[196] In the chapter 5.4.2 it was shown, that the viscosity of the prepolymer end-capped with **5.03** is strongly decreased due to the elimination of the urea groups and the introduction of less polar phenyl ring. This leads to the decrease in the amount of hydrogen bonding and van der Waals interactions, allowing the polymer chains to flow with less restriction. In the case of setting materials this behavior leads to the increase in the elongation at break and many times to the decrease in tensile strength.^[197]

5.5. Conclusion

Structural and electronic properties of phenols were exploited to prepare extraordinary stable hydroxyl functional alkoxysilanes by a straightforward methodology. Despite the fact that phenolic hydroxyl group is less nucleophilic than aliphatic alcohols; this work presents a method for successfully reacting phenoxy functional alkoxysilanes with aliphatic isocyanates in high yields.

The developed methodology for Lewis base catalyzed reaction of phenols with isocyanates provided us with the possibility to end-cap NCO-terminated polyethers with phenolic functional alkoxysilanes. However, it was found that end-capping process during the prepolymer method is too slow; therefore a new 2-stage end-capping method was developed. By tuning the ratio between phenol functional alkoxysilanes and **AMMO**, it was possible to prepare prepolymer with improved rheological properties (up to 80 % viscosity decrease) and good curing rates comparable to currently available silylated polyurethanes (SOT \approx 10 h).

Several prepared prepolymers were cured, in order to measure their adhesive and tensile properties. The results show a drop in tensile strength, while the elongation is strongly increased when phenol functional alkoxysilane is used as an end-capper. Furthermore, the adhesion to natural materials like glass and wood was improved by introducing phenyl functionality in to the prepolymer structure.

6. Summary

Silylated polyurethanes are often the main components of many sealants and adhesives. However, the main drawback accompanying these products is the high viscosity of the prepolymers after their synthesis. Several attempts into lowering the viscosity were made, however a simple and efficient methodology has not been provided until now. This thesis summarizes the development of several strategies for overcoming the severe viscosity buildup during the synthetic process.

It has been proved in this work that the main reason for the increased viscosity of the prepolymers is the high amount of hydrogen bonding. The urea and urethane groups are responsible for the formation of highly hydrogen-bonded hard segments, which increase the viscosity of the prepolymer. Thus, developed methodologies for lowering the viscosity are based on either elimination or the reduction of the amount of hydrogen bonding.

In chapter 2 new alkyne-amide functional alkoxysilane (**2.10-2.12**) coupling reagents are presented, which are able to completely prevent urea hydrogen bonding by intramolecular annulation reaction. The substrate screening of the developed methodology exhibits high yields (up to 98 %) of hydantoin cycle formation for aromatic isocyanates, while aliphatic isocyanates give only moderate to low yields (> 80 %). The complete prevention of the hydrogen bonding of the urea group resulted in up to 75 % decreased viscosity of the prepared prepolymers.

Other methodologies presented in this work focused on the overall reduction of the hydrogen bonding. The first approach dealt with the hindering of the urea group, while the second approach focused on the replacement of urea by the urethane group.

Chapter 3 described the preparation of at least seven different siloxacycloalkane end-cappers with the aim to utilize them as polymer end-capping reagents. These compounds are able to hinder the urea group and so prevent hydrogen bonding. The latter proved to be effective, since the prepared silylated polyurethanes exhibit up to 40 % lower viscosities compared to currently commercially available moisture curable polyurethanes. Studies of the urea and urethane carbonyl stretching by IR spectroscopy revealed that the formation of the highly hydrogen-bonded hard segments is disturbed in the case of siloxacycloalkane end-capping, which has a positive effect on the rheological properties of the silylated polyurethane.

The last approach described in the chapters 4 and 5 utilizes about 15 different stable hydroxyl functional alkoxysilanes, which form urethane instead of urea groups with isocyanate terminated polymers. This work showed that urea-free silylated polyurethanes

exhibit up to 70 % lower viscosities compared to similar urea containing prepolymers. Furthermore, a one-step prepolymer method was developed during this investigation, which provides further economic advantages compared to currently used two-step prepolymer method.

Most of the prepared prepolymers were also casted and cured, in order to measure their adhesive and tensile properties. The results showed that several prepared end-cappers exhibit enhanced mechanical and adhesive properties of the corresponding prepolymers.

This work proved that the control of the amount of hydrogen bonding in the silylated polyurethanes plays an important role in determining their rheological, curing, mechanical and adhesive properties. It was shown, that the complete or at least partial elimination of the hydrogen bonding reduces the prepolymer viscosity, which is an important parameter in for preparation of high quality adhesives or sealants.

We shall not cease from exploration, and the end of all our exploring will be to arrive where we started and know the place for the first time.

T. S. Eliot, (1888-1965)

7. References

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A1. Appendix

A1.1. General methods

The reactions involving moisture or air sensitive compounds were performed under argon atmosphere by using conventional Schlenk techniques. Argon was dried by passing it through the phosphorous pentoxide filled column. All glassware, syringes, needles, rubber tubes etc. that came in contact with sensitive substances were evacuated or flushed with argon prior to usage.

A1.2. Vacuum

All pressures for distillations and evacuation were measured using CVC 3000 Vacuubrand pressure sensors. Standard vacuum pressure: membrane pump: ≥ 20 mBar, oil pump: ≥ 0.01 mBar.

A1.3. Solvents

Solvents for moisture or oxygen sensitive reactions were dried, distilled or degassed and stored under inert atmosphere following the known procedures in organic or inorganic chemistry.

Following solvents were used for synthetic, storage or stabilization purposes: water, ethanol, methanol, isopropanol, dimethylsulfoxide (DMSO), ethyl acetate, chloroform, dichloromethane, benzene, tetrahydrofuran, toluene, heptane, hexane, pentane, diethyl ether etc.

A1.4. Infrared spectroscopy (IR)

ATR infrared spectra of the samples were measured on Bruker Alpha-P spectrometer. All samples were measured neat. Liquid samples were measured in a film, while solid samples were pressed directly on to the IR-detector window. Adsorption bands are given in wave numbers (cm^{-1}) and were measured in the range from 400 to 4000 cm^{-1} .

Time resolved measurements for kinetic purposes were recorded by using Mettler Toledo React IR 15 with diamond window probe. The adsorption region measured is from 650 to 2500 cm^{-1} with phase correction.

The abbreviations used to describe band intensity are: s (strong), m (medium), w (weak).

A1.5. Nuclear magnetic resonance spectroscopy (NMR)

NMR spectra of the samples were measured on Bruker 300 MHz (AV300 or Fourier 300: ^1H = 300 MHz, ^{13}C = 75 MHz) or on Bruker 400 MHz (AV400: ^1H = 400 MHz, ^{13}C = 101 MHz, ^{19}F = 282 MHz, ^{29}Si = 79 MHz) spectrometers. The time-resolved measurements were

performed on Bruker 250 MHz (AVANCE 250 II: ^1H = 250 MHz, ^{13}C = 63 MHz, ^{29}Si = 79 MHz). Spectra shifts are reported as δ -values in ppm relative to the deuterated solvent shift(s). Following solvents were used for referencing NMR spectra:

d_1 -chloroform (^1H = 7.26 ppm, ^{13}C = 77 ppm), d_8 -toluene (^1H = 2.08, 6.97, 7.01, 7.09 ppm, ^{13}C = 137.48, 128.87, 127.96, 125.13, 20.43 ppm), d_3 -acetonitrile (^1H = 1.94 ppm, ^{13}C = 1.32, 118.26 ppm), d_2 -water (^1H = 4.79 ppm), d_6 -dimethylsulfoxide (^1H = 2.49 ppm, ^{13}C = 7.0 ppm).

The abbreviations used to describe the multiplicity of the spectra peaks are: s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quadruplet), dd (doublet of doublets), dt (doublet of triplets), ddd (doublet of doublets of doublets) and m (multiplet), etc. Coupling constant J is reported in Hertz (Hz).

A1.6. Ionization techniques

Samples for mass spectrometry were dissolved in tetrahydrofuran (THF). Mass spectra were obtained by using Finnigan MAT 95 (200 eV, EI-MS) or LCQ (70 eV, ESI-MS). High resolution mass spectrometry (HRMS) analysis was performed on Bruker APEX IV (7 T, FTICR).

A1.7. Crystal structure analysis

Crystallographic data were obtained on a Bruker KAPPA APEX II DUO diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares procedures on F_2 with the SHELXTL software package XP (Bruker AXS) was used for graphical representation. Displacement of ellipsoids are drawn at the 30 % probability.^[198]

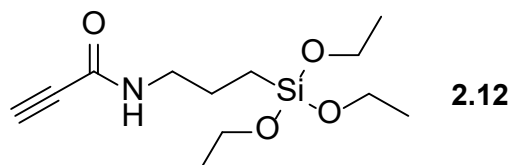
A1.8. Viscosity measurement

Rheological properties of the samples were measured using Anton Paar MCR 302 Rheometer at 25 ± 0.5 °C. All measurements were performed in neat conditions using PP25/TG stirring plate. Each measurement consisted of 25 single measurements, which were averaged in to a final result.

A2. Appendix to Chapter 2

A2.1. Synthesis of the amide alkyne functional alkoxy silanes

Synthesis of N-(3-(triethoxysilyl)propyl)propiolamide



Representative procedure A:

70 ml of dry dichloromethane, 10.721 g (46.5 mmol) of (3-aminopropyl) triethoxysilane (**AMEO**) and 3.420 g (48.8 mmol) of propiolic acid was added in to the evacuated 100 ml Schlenk flask. The mixture was cooled to 0 °C under vigorous stirring, after which 10.07 g (46.5 mmol) of dicyclohexylcarbodiimide was slowly added in the course of 30 minutes. The mixture was stirred for 1 hour at 0 °C and then slowly warmed up to the room temperature. A white precipitate was filtered off using Schlenk technique. Solvent was removed by co-evaporation with toluene to afford a yellowish product in 95 % yield.

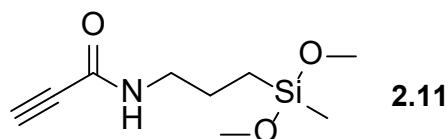
¹H NMR (300 MHz, Chloroform-*d*) δ 6.83 (s, 1H), 3.75 (q, *J* = 7.0 Hz, 6H), 3.22 (q, *J* = 6.9 Hz, 2H), 2.79 (s, 1H), 1.65 – 1.53 (m, 2H), 1.16 (t, *J* = 7.0 Hz, 9H), 0.58 (t, *J* = 7.0 Hz, 2H).

¹³C NMR (75 MHz, CDCl₃) δ = 152.2, 77.5, 72.9, 58.4, 42.0, 22.3, 18.1, 7.7.

²⁹Si NMR (79 MHz, CDCl₃) δ = -46.3.

ESI-TOF/MS *m/z* calcd. for C₁₂H₂₃NO₄Si [M+Na]⁺: 296.12886; found: 296.12917.

Synthesis of N-(3-(trimethoxysilyl)propyl)propiolamide



12.32 g (57.3 mmol) of yellow oily liquid was synthesized in (92 % yield) according to the representative procedure A, using 4.203 g (60.1 mmol) of propiolic acid and 9.787 g (60.0) of (3-aminopropyl)dimethoxymethylsilane.

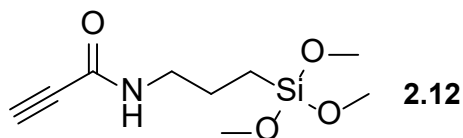
¹H NMR (300 MHz, Chloroform-*d*) δ 6.82 (s, 1H), 3.41 (s, 6H), 3.17 (q, *J* = 7.1 Hz, 2H), 2.71 (s, 1H), 1.62 – 1.58 (m, 2H), 0.51 (t, *J* = 7.0 Hz, 2H), 0.05 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ = 153.18, 77.47, 72.90, 50.03, 43.09, 27.97, 15.09, -2.11.

^{29}Si NMR (79 MHz, CDCl_3) $\delta = -46.3$.

ESI-TOF/MS m/z calcd. for $\text{C}_9\text{H}_{17}\text{NO}_4\text{Si}$ $[\text{M}+\text{Na}]^+$: 238.0870; found: 238.0863.

Synthesis of N-(3-(trimethoxysilyl)propyl)propiolamide



12.32 g (53.3 mmol) of brown oily liquid was synthesized in (89 % yield) according to the representative procedure A, using 4.203 g (60.1) of propiolic acid and 10.741 g (60.0 mmol) of (3-aminopropyl)trimethoxysilane (**AMMO**).

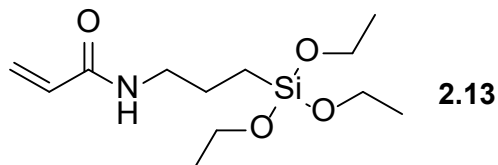
^1H NMR (300 MHz, Chloroform- d) δ 6.71 (s, 1H), 3.47 (s, 9H), 3.12 (q, $J = 7.1$ Hz, 2H), 2.73 (s, 1H), 1.64 – 1.51 (m, 2H), 0.57 (t, $J = 7.0$ Hz, 2H).

^{13}C NMR (75 MHz, CDCl_3) $\delta = 153.2, 77.5, 72.9, 49.8, 42.0, 24.5, 6.7$.

^{29}Si NMR (79 MHz, CDCl_3) $\delta = -40.8$.

ESI-TOF/MS m/z calcd. for $\text{C}_9\text{H}_{17}\text{NO}_4\text{Si}$ $[\text{M}+\text{Na}]^+$: 254.08191; found: 254.122191.

Synthesis of N-(3-(triethoxysilyl)propyl)acrylamide



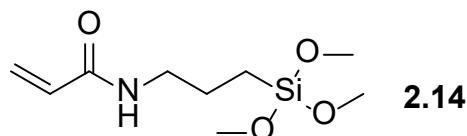
2.6 g (9.5 mmol) of yellowish liquid was synthesized in (95 % yield) according to the representative procedure A, using 0.721 (10 mmol) g of acrylic acid and 2.21 g (10 mmol) of (3-aminopropyl)triethoxysilane (**AMEO**).

^1H NMR (300 MHz, Chloroform- d) δ 6.62 (s, 1H), 6.30 – 5.93 (m, 2H), 5.52 (dd, $J = 9.7, 2.3$ Hz, 1H), 3.74 (q, $J = 7.0$ Hz, 6H), 3.24 (q, $J = 7.0, 2\text{H}$), 1.69 – 1.52 (m, 2H), 1.15 (t, $J = 7.0$ Hz, 9H), 0.67 – 0.43 (m, 2H).

^{13}C NMR (75 MHz, CDCl_3) $\delta = 165.5, 131.1, 125.6, 58.3, 41.8, 22.7, 18.2, 7.7$.

^{29}Si NMR (79 MHz, CDCl_3) $\delta = -46.4$.

ESI-TOF/MS m/z calcd. for $\text{C}_{12}\text{H}_{25}\text{NO}_4\text{Si}$ $[\text{M}+\text{Na}]^+$: 298.14451; found: 298.14492.

Synthesis of N-(3-(trimethoxysilyl)propyl)acrylamide

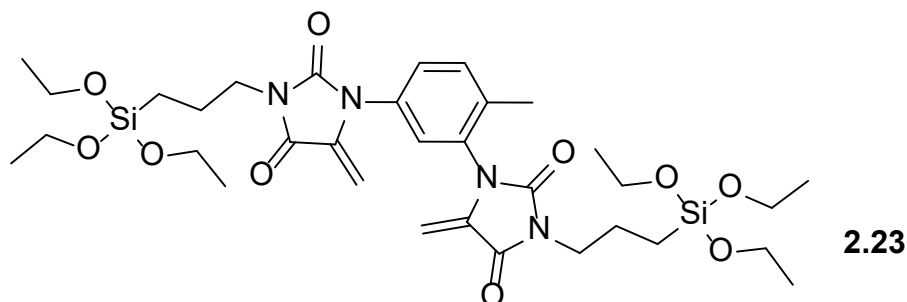
2.1 g (9.1 mmol) of yellowish liquid was synthesized in (91 % yield) according to the representative procedure A, using 0.721 g (10 mmol) of acrylic acid and 1.79 g (10 mmol) of (3-aminopropyl)trimethoxysilane (**AMMO**).

¹H NMR (300 MHz, Chloroform-*d*) δ 6.58 (s, 1H), 6.27 – 5.90 (m, 2H), 5.50 (dd, *J* = 9.6, 2.2 Hz, 1H), 3.47 (s, 9H), 3.12 (q, *J* = 7.1 Hz, 2H), 1.67 – 1.50 (m, 2H), 0.55 (t, *J* = 7.0 Hz, 2H).

¹³C NMR (75 MHz, CDCl₃) δ = 162.5, 129.4, 123.6, 48.3, 41.3, 23.4, 6.4.

²⁹Si NMR (79 MHz, CDCl₃) δ = -41.9.

ESI-TOF/MS *m/z* calcd. for C₉H₁₉NO₄Si [M+Na]⁺: 256.09756; found: 256.09731.

Synthesis of N-(3-(triethoxysilyl)propyl)propiolamide and toluene diisocyanate adduct**Representative procedure B:**

20 ml of dry tetrahydrofuran (THF), 2.971 g (10.9 mmol) of compound **2.10** and 0.946 g (10.9 mmol) of toluene diisocyanate (TDI) was mixed in to the evacuated 25 ml Schlenk flask. The mixture was cooled to 0 °C under vigorous stirring, after which 0.036 g (0.35 mmol) of triethylamine was slowly added. The mixture was stirred for 2 hours at 0 °C and then slowly warmed up to the room temperature and kept stirring for 48 hours. Solvent was removed by using high vacuum to afford a dark brown product in 83 % yield.

¹H NMR (300 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.3 Hz, 1H), 7.29 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 5.40 (dd, *J* = 14.3, 2.3 Hz, 1H), 5.13 (d, *J* = 2.9 Hz, 0H), 4.51 (d, *J* =

2.3 Hz, 0H), 3.80 – 3.68 (m, 6H), 3.22 (t, $J = 6.9$ Hz, 2H), 2.14 (s, 1H), 1.81 – 1.71 (m, 2H), 1.20 – 1.06 (m, 9H), 0.56 (t, $J = 7.2$ Hz, 2H).

^{13}C NMR (75 MHz, CDCl_3) $\delta = 152.1, 137.0, 136.1, 132.6, 131.9, 127.3, 126.7, 96.0, 91.4, 72.8, 58.5, 34.2, 21.7, 18.2, 7.7$.

^{29}Si NMR (79 MHz, CDCl_3) $\delta = -46.2$.

ESI-TOF/MS m/z calcd. for $\text{C}_{33}\text{H}_{52}\text{N}_4\text{O}_{10}\text{Si}_2$ $[\text{M}+\text{Na}]^+$: 743.31143; found: 743.28312.

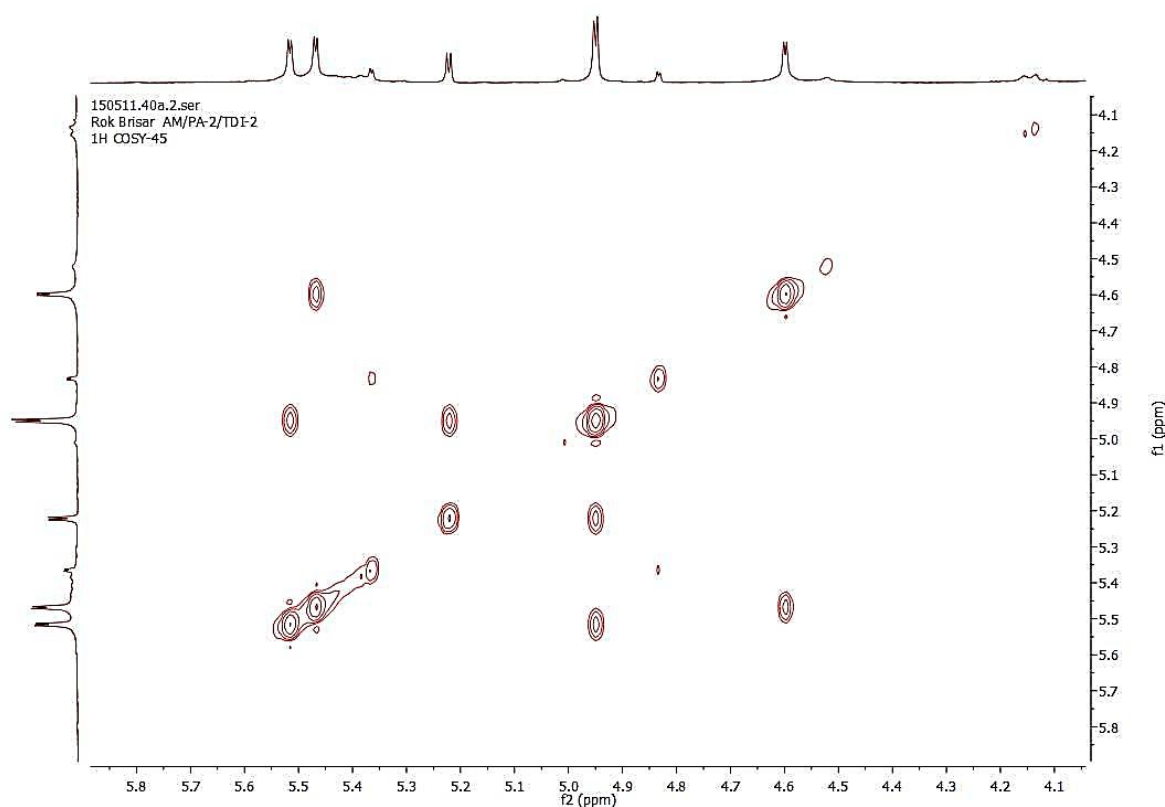


Figure A 5.5.1: COSY NMR spectra of the compound **2.23** in CDCl_3 .

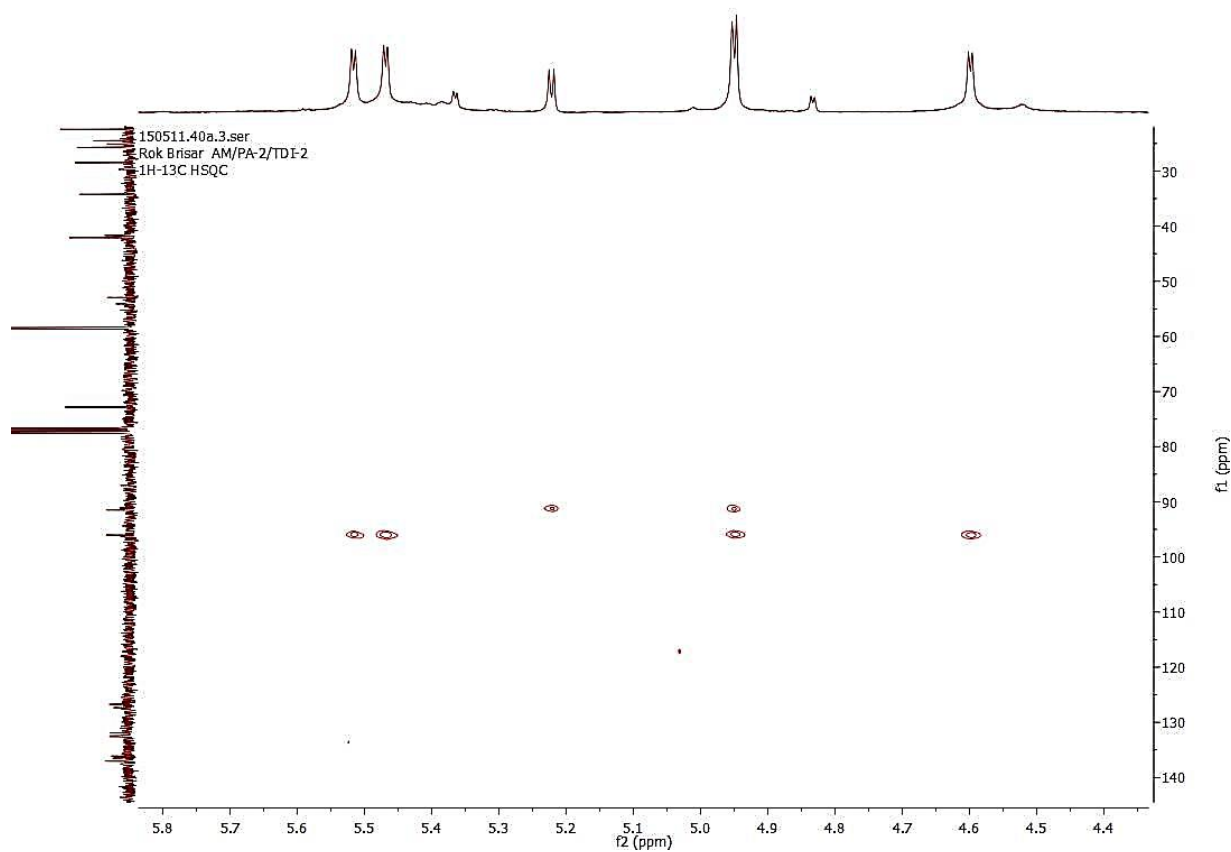


Figure A 5.5.2: HSQC NMR spectra of the compound **2.23** in CDCl_3 .

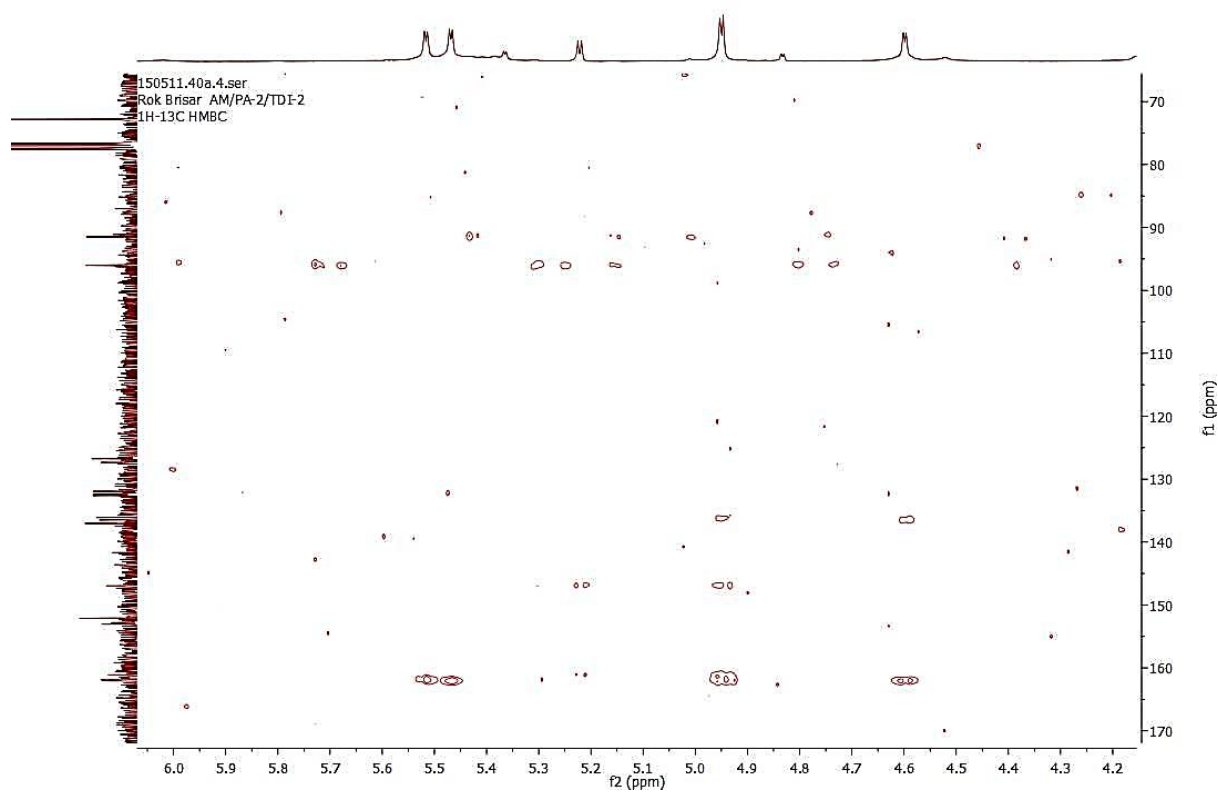
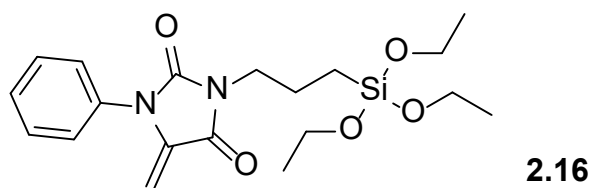


Figure A 5.5.3: HMBC NMR spectra of the compound **2.23** in CDCl_3 .

Synthesis of N-(3-(triethoxysilyl)propyl)propiolamide and toluene diisocyanate adduct

0.7 g (1.78 mmol) of brown viscous liquid was synthesized in 98 % yield according to the representative procedure B, using 0.218 g (1.83 mmol) of compound **2.10** and 0.5 g (1.83 mmol) of phenyl isocyanate and 0.001 (5 mol%) g of triethylamine.

¹H NMR (400 MHz, Chloroform-d) δ 7.47 – 7.41 (m, 1H), 7.35 (dd, J = 7.0, 0.9 Hz, 2H), 7.30 (dd, J = 8.5, 1.3 Hz, 2H), 5.42 (d, J = 2.1 Hz, 1H), 4.80 (d, J = 2.1 Hz, 1H), 3.79 (q, J = 7.0 Hz, 6H), 3.65 – 3.57 (m, 2H), 1.79 (m, 2H), 1.18 (t, J = 7.0 Hz, 9H), 0.69 – 0.60 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ = 162.1, 153.2, 136.7, 133.0, 129.6, 128.2, 126.7, 95.4, 58.4, 41.6, 21.8, 18.3, 7.8.

²⁹Si NMR (79 MHz, CDCl₃) δ = -46.5.

ESI-TOF/MS m/z calcd. for C₁₉H₂₈N₂O₅Si [M]: m/z : 392.17675; found: m/z : 392.17613.

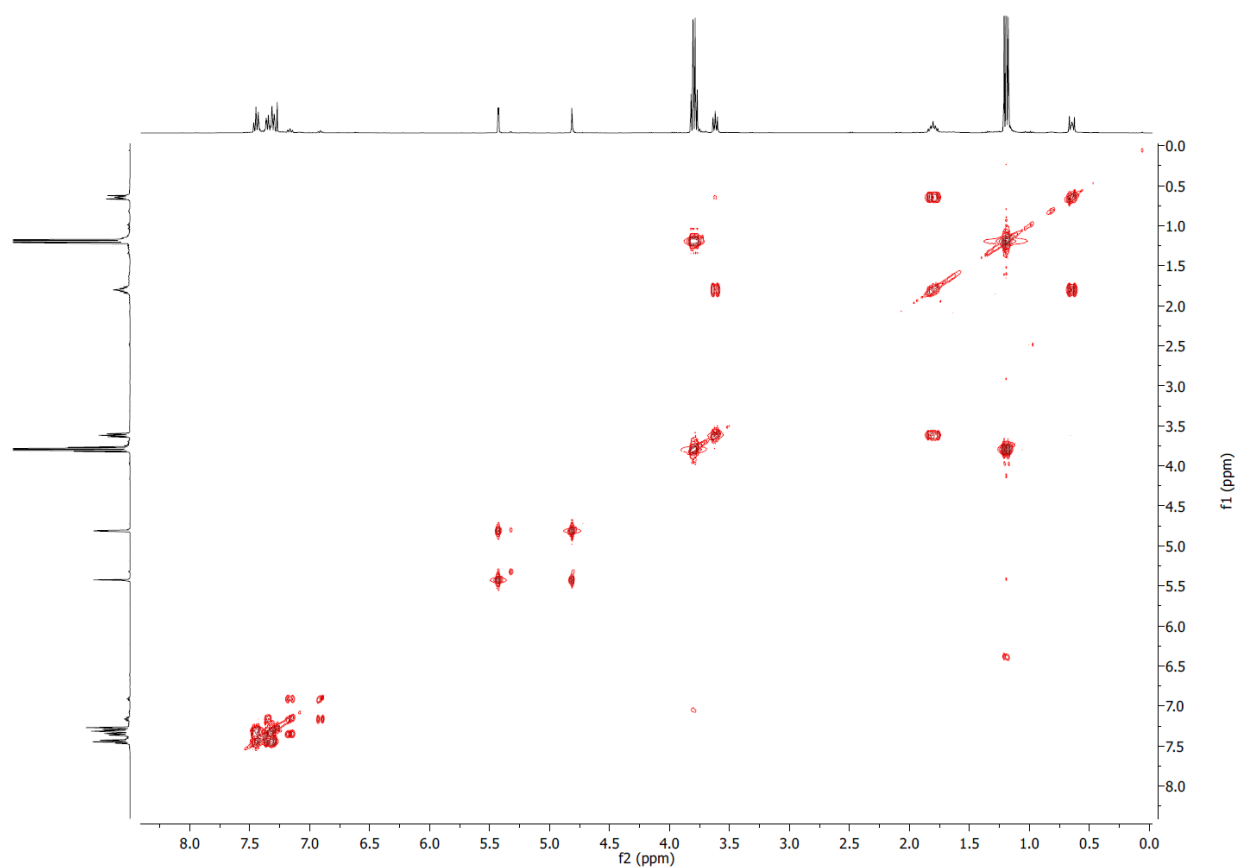


Figure A 5.5.4: COSY NMR spectra of the compound **2.16** in CDCl_3 .

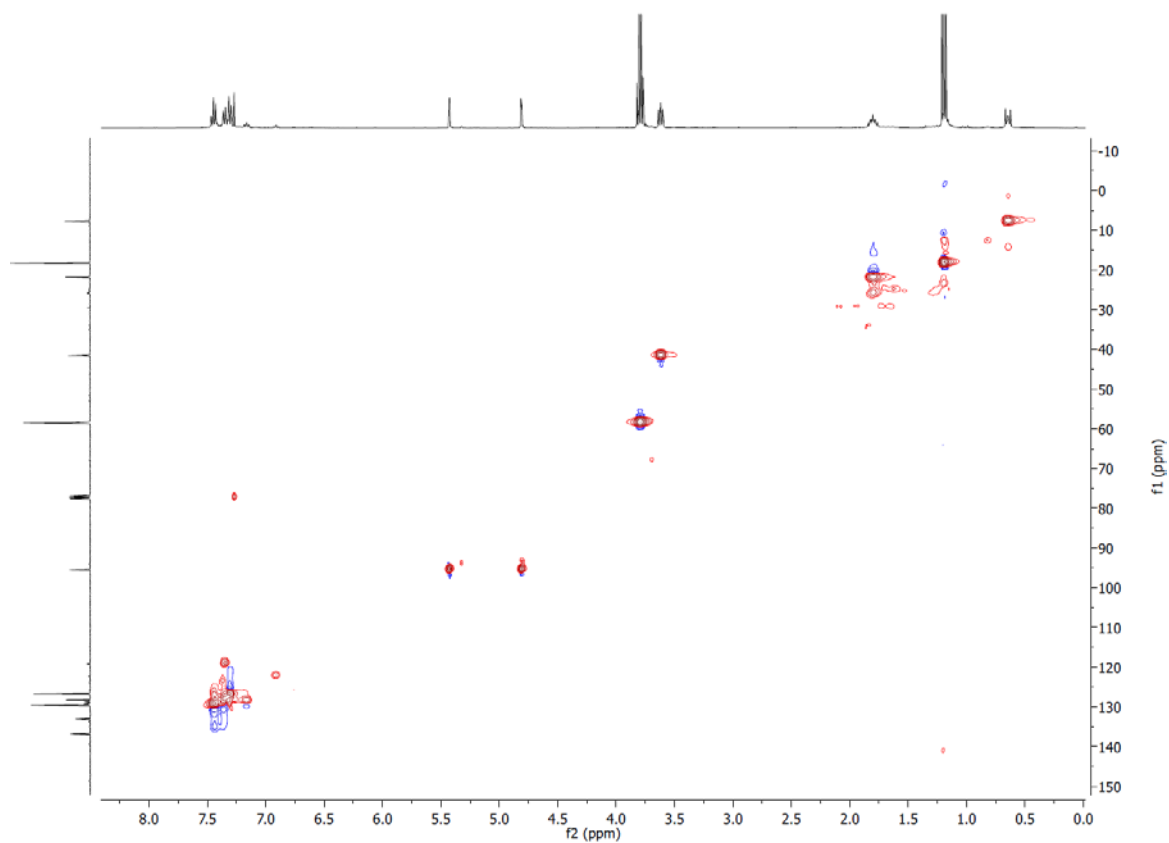


Figure A 5.5.5: HSQC NMR spectra of the compound **2.16** in CDCl_3 .

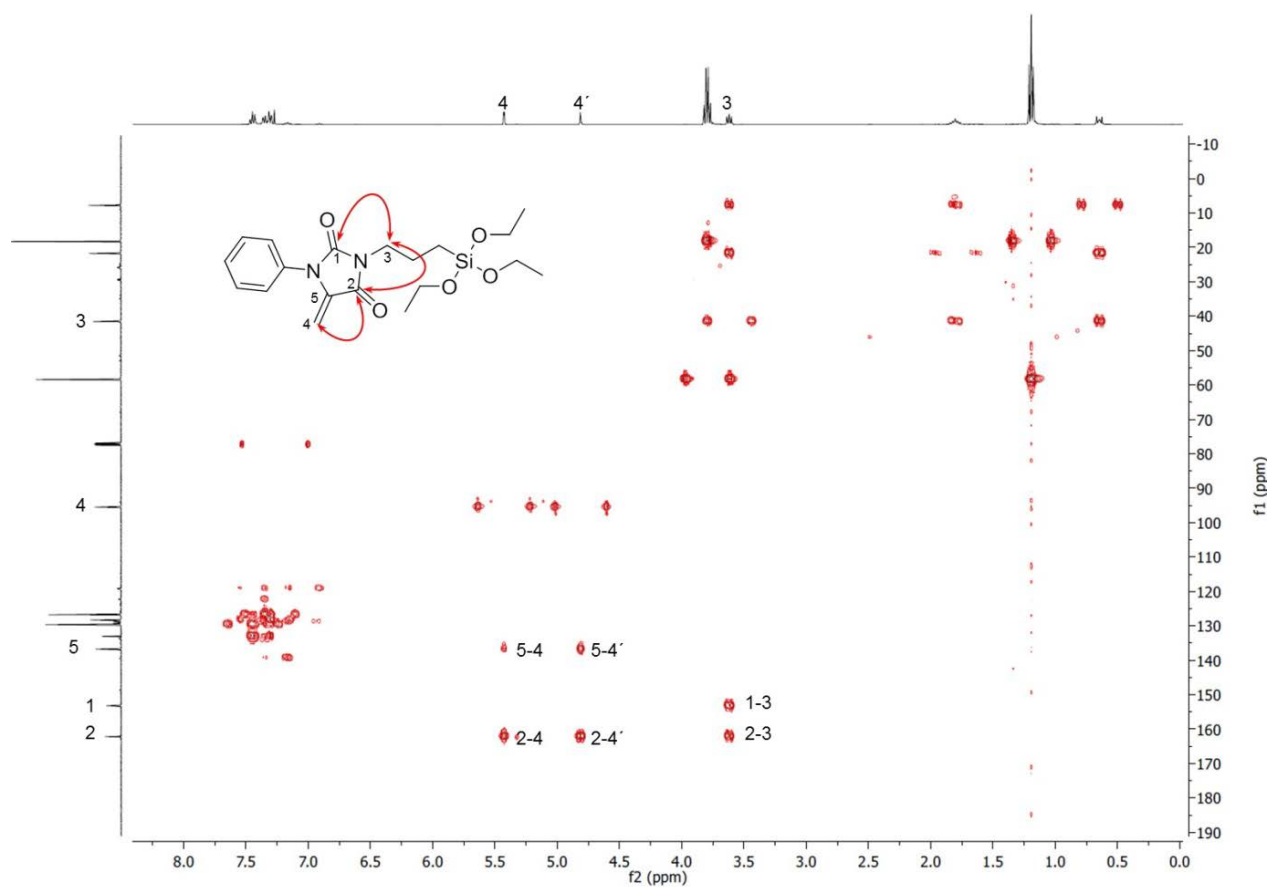
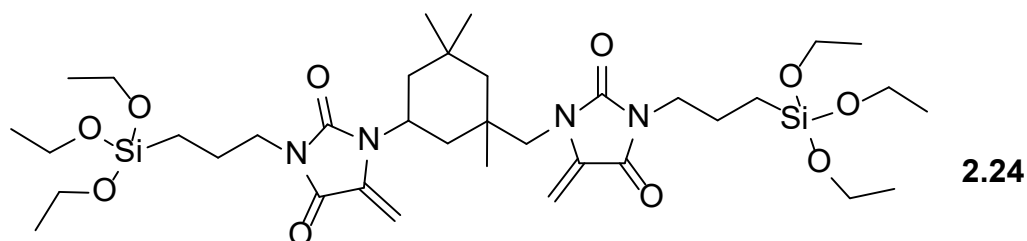


Figure A 5.5.6: HMBC NMR spectra of the compound **2.16** in CDCl_3 .

Synthesis of N-(3-(triethoxysilyl)propyl)propiolamide and isophorone diisocyanate adduct



5.2 g of dark brown solid was synthesized in 79 % yield according to the representative procedure B, using 2.500 g (9.2 mmol) of compound **2.10**, 1.220 g (5 mmol) of isophorone diisocyanate (**IPDI**) and 0.093 g of triethylamine.

^1H NMR (300 MHz, Chloroform-*d*) δ 5.40 (bm, 1H), 4.79 (bm, 1H), 3.84 – 3.73 (m, 6H), 3.54 (m, , 2H), 3.36 – 3.24 (m, 1H), 3.04 (s, 1H), 1.74 (m, 2H), 1.24 – 1.16 (m, 9H), 1.15 – 1.05 (m, 3H), 1.04 – 0.87 (m, 3H), 0.65 – 0.50 (m, 2H).

^{13}C NMR (75 MHz, CDCl_3) δ = 152.1, 137.0, 136.1, 132.6, 131.9, 127.3, 126.7, 96.0, 91.4, 72.8, 58.5, 34.2, 21.7, 18.2, 7.7.

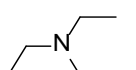
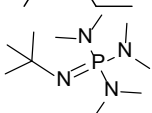
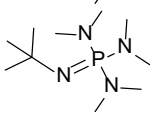
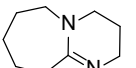
^{29}Si NMR (79 MHz, CDCl_3) δ = -46.10.

ESI-TOF/MS m/z calcd. for $\text{C}_{36}\text{H}_{64}\text{N}_4\text{O}_{10}\text{Si}_2$ $[\text{M}+\text{Na}]^+$: 791.40533; found: 791.40587.

Catalyst screening

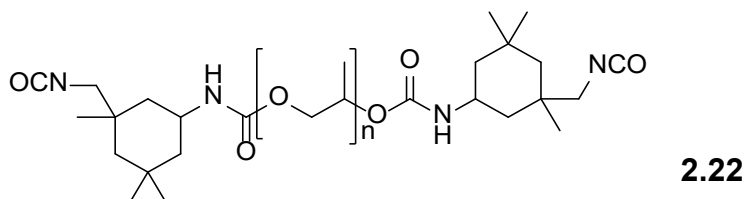
10 ml of dry tetrahydrofuran (THF), 2.033 g (7.4 mmol) of compound **2.10** and 0.648 g (3.7 mmol) of toluene diisocyanate (TDI) was mixed in to the evacuated 25 ml Schlenk flask. The mixture was cooled to 0 °C under vigorous stirring, after which 1-5 mol% of selected catalyst was slowly added. The mixture was stirred for 2 hours at 0 °C and then slowly warmed up to the room temperature and kept stirring for 48 hours. Solvent was removed by using high vacuum to afford a dark brown product. The completion of the reaction was determined by analyzing IR spectrum (Table A 5.5.1).

Table A 5.5.1: Results of the catalyst screening

Entry	Base	Structure	pK_a [114]	Concentration (mol%)	ΔT [°C]	IR spectroscopy
1	/	/	/	/	0	NCO band present
2	TEA		4.2	5	37	No NCO band
3	P_1 t-Bu		17.0	5	41	No NCO band
4	P_1 t-Bu		17.0	1	17	No NCO band
5	DBU		14.2	5	39	No NCO band

A2.2. Prepolymer preparation

Preparation of the -NCO terminated polymer

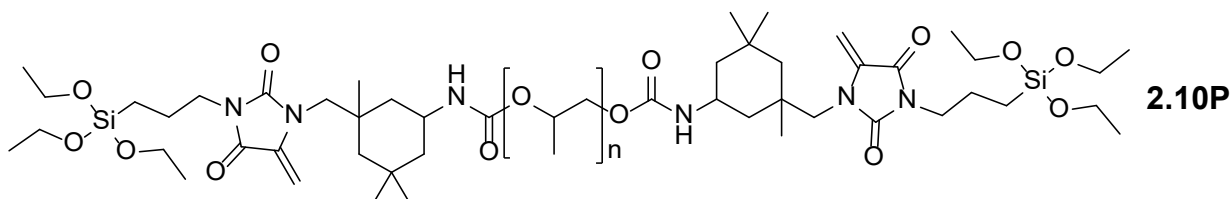


Representative procedure C:

10 g of poly(propylene glycol) (PPG) (Acclaim 4200, 4000 g/mol, 28 ± 1.5 mg KOH/g) was added in to the evacuated 25 ml Schlenk flask. The temperature was raised to 80 °C during which vacuum was applied for 1 hour. Afterwards 1.11 (5 mmol) g of isophorone diisocyanate (**IPDI**) and 0.0076 g (1 mol%) of DBU were added to the mixture and kept under vigorous stirring for 1 hour. The product **2.22** was analyzed using IR spectroscopy. After the reaction the viscosity was measured to be 20.61 Pas.

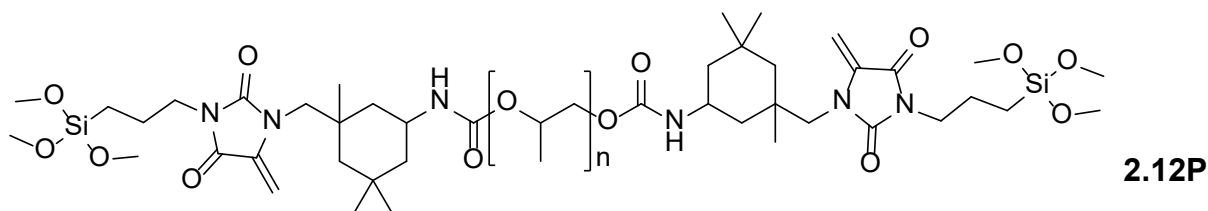
IR (ATR, neat, cm^{-1}): 3332.17 (w), 2969.59 (s), 2929.74 (s), 2867.37 (s), 2264.66 (s), 1718.79 (s), 1523.88, (m), 1452.67 (m), 1372.27 (s), 1343.57 (m), 1298.13 (m), 1238.19 (m), 1093.97 (s), 1014.22 (m), 925.76 (m), 864.99 (w), 578.31 (w), 455.15 (w)

Preparation of the alkoxy silane terminated prepolymer using end-capper 2.10



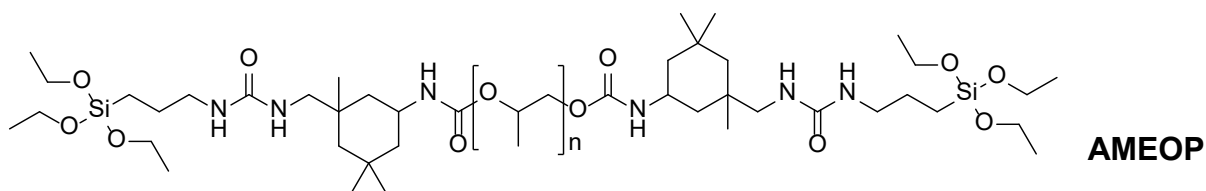
Approximately 12 g of yellowish viscous liquid was synthesized by adding 1.370 g (50 mmol) of compound **2.10** to 11.11 g of NCO terminated polymer (**2.22**) prepared according to the representative procedure C. No NCO band was detected by IR spectroscopy, therefore we concluded, that the end-capping reaction is completed. After the reaction the viscosity was measured to be 22.51 Pas.

IR (ATR, neat, cm^{-1}): 2969.95 (s), 2929.94 (s), 2867.27 (s), 1725.79 (m), 1653.23 (m), 1599.21 (m), 1532.92 (m), 1451.63 (m), 1372.34 (s), 1343.06 (m), 1296.24 (m), 1228.25 (m), 1094.26 (s), 1012.81 (m), 926.60 (m), 867.12 (w), 823.08 (w), 665.86 (w), 460.70 (w),

Preparation of the alkoxy silane terminated prepolymer using end-capper 2.12

Approximately 12 g of yellowish viscous liquid was synthesized by adding 1.155 g (50 mmol) of compound **2.12** to 11.11 g of NCO terminated polymer (**2.22**) prepared according to the representative procedure C. No NCO band was detected by IR spectroscopy, therefore it was concluded, that the end-capping reaction is completed. After the reaction the viscosity was measured to be 25.33 Pas.

IR (ATR, neat, cm^{-1}): 2970.11 (s), 2929.77 (s), 2868.13 (s), 1719.09 (m), 1651.00 (m), 1532.20 (m), 1452.84 (m), 1372.46 (s), 1343.03 (m), 1297.26 (m), 1241.07 (m), 1097.09 (s), 1013.86 (m), 930.46 (m), 866.58 (w), 778.14 (m), 666.37 (w), 464.62 (w).

Preparation of the alkoxy silane terminated prepolymer using AMEO end-capper

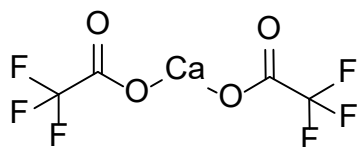
Approximately 12 g of colourless viscous liquid was synthesized by adding 1.105 g (50 mmol) of **AMEO** to 11.11 g of NCO terminated polymer prepared according to the representative procedure C. No NCO band was detected by IR spectroscopy, therefore it was concluded, that the end-capping reaction is completed. After the reaction the viscosity was measured to be 76.09 Pas.

IR (ATR, neat, cm^{-1}): 3353.96 (w), 2969.96 (s), 2929.43 (s), 2867.88 (s), 1719.41 (m), 1638.93 (m), 1552.58 (m), 1452.38 (m), 1372.45 (s), 1343.12 (m), 1297.58 (m), 1240.53 (m), 1097.36 (s), 1013.56 (m), 930.17 (m), 865.96 (w), 777.38 (m), 663.62 (w), 447.93 (w), 415.74 (w).

A3. Appendix to Chapter 3

A3.1. Preparation of siloxacycloalkanes

Synthesis of Calcium bistrifluoroacetate



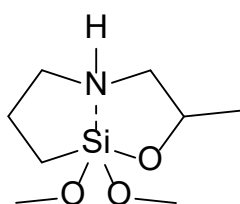
CaTFA

The following procedure is adapted from literature reports^[133]. In an evacuated round bottom flask under argon atmosphere 1.05 g (0.025 mol) of calcium hydride suspended in 20 ml of dry tetrahydrofuran were added. In the next step 17.1 g (0.15 mol) of trifluoroacetic acid were added slowly over the course of one hour. A milky mixture was obtained. The solvent and excess of acid was removed using vacuum. The remaining white solid was washed 3 times with diethyl ether and dried under vacuum. The title product was obtained as a white solid (4.9 g) in 74 % yield.

¹³C NMR (75 MHz, D₂O) δ 162.96 (q, J = 35.5 Hz), 116.23 (q, J = 291.5 Hz).

¹⁹F NMR (282 MHz, D₂O) δ = -75.32.

Synthesis of 2-methyl-8,8-dimethoxy-1-oxa-4-aza-8-sila



3.06

Representative procedure D:

In an evacuated round bottom flask under the argon atmosphere 1.06 g (0.4×10^{-3} mol) of the calcium bistrifluoroacetate was mixed with 35.8 g (0.2 mol) of 3-aminopropyl)trimethoxysilane and 13.9 g (0.24 mol) of propylene oxide. The reaction mixture was stirred over two days at 4 °C. Then, the excess of propylene oxide and the produced methanol were evaporated at 50 °C and under vacuum to obtain 25.0 g (0.121 mol) of colorless liquid was synthesized in (61 % yield).

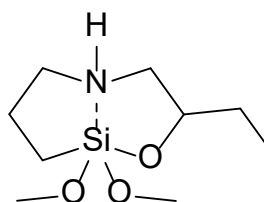
^1H NMR (400 MHz, Chloroform-*d*) δ 3.41 (ddd, J = 10.1, 6.1, 3.9 Hz, 1H), 2.96 (s, 6H), 2.33 (dd, J = 12.0, 3.8 Hz, 1H), 2.29 – 2.22 (m, 1H), 2.02 – 1.83 (m, 1H), 1.71 (t, J = 11.1, 4.3 Hz, 1H), 1.17 (dtd, J = 8.9, 4.6, 2.6 Hz, 1H), 1.04 (dtd, J = 10.4, 5.5, 4.6, 1.8 Hz, 1H), 0.69 (d, J = 0.7 Hz, 3H), 0.26 – 0.12 (m, 1H), 0.04 (ddd, J = 15.4, 10.7, 6.7 Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ = 66.46, 52.71, 50.07, 46.10, 22.52, 20.37, 7.80.

^{29}Si NMR (79 MHz, CDCl_3) δ = -64.0.

ESI-TOF/MS m/z calcd. for $\text{C}_8\text{H}_{19}\text{NO}_3\text{Si}$ $[\text{M}+\text{H}]^+$: 205.11342 found: 205.11423

Synthesis of 2-ethyl-8,8-dimethoxy-1-oxa-4-aza-8-sila



3.08

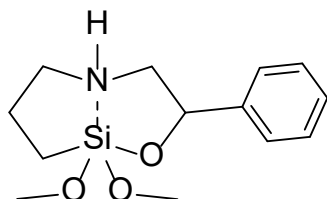
28.0 g (0.128 mol) of colorless liquid was synthesized in (64 % yield) according to the modified representative procedure D, by mixing 21.6 g of butylene oxide (0.3 mol) and 35.8 g (0.2 mol) of (3-aminopropyl)trimethoxysilane at 23 °C in the presence of the catalyst (**CaTFA**).

^1H NMR (400 MHz, Chloroform-*d*) δ 3.19 – 3.09 (m, 1H), 2.92 (d, J = 2.4 Hz, 6H), 2.29 (d, J = 8.8 Hz, 1H), 2.20 (t, J = 4.0 Hz, 1H), 1.95 – 1.82 (m, 1H), 1.78 – 1.65 (m, 1H), 1.12 (dd, J = 6.8, 3.0 Hz, 1H), 1.00 – 0.89 (m, 2H), 0.46 (t, J = 7.0, 3H), 0.19 – 0.09 (m, 1H), 0.06 – -0.08 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ = 71.5, 50.8, 49.9, 46.1, 27.9, 22.4, 9.7, 7.9.

^{29}Si NMR (79 MHz, CDCl_3) δ = -65.9.

ESI-TOF/MS m/z calcd. for $\text{C}_9\text{H}_{21}\text{NO}_3\text{Si}$ $[\text{M}+\text{H}]^+$: 220.13242 found: 220.13233

Synthesis of 2-benzyl-8,8-dimethoxy-1-oxa-4-aza-8-sila**3.10**

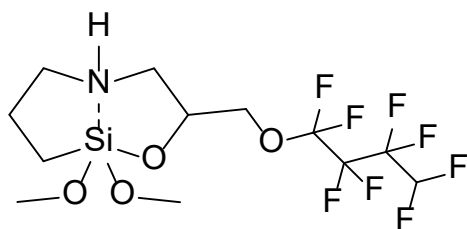
52.0 g (0.194 mol) of yellowish liquid was synthesized in (97 % yield or 37 % after distillation) according to the modified representative procedure D, by mixing 24.0 g (0.2 mol) of epoxybenzene and 35.8 g (0.2 mol) of (3-aminopropyl)trimethoxysilane at 23 °C in the presence of the catalyst (**CaTFA**).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.39 (m, 2H), 7.36 (td, J = 5.3, 2.7 Hz, 2H), 7.28 (m, 1H), 4.93 – 4.81 (m, 1H), 3.57 (d, J = 6.0 Hz 6H), 3.08 (d, J = 7.6 Hz, 1H), 2.84 – 2.73 (m, 1H), 2.59 – 2.32 (m, 2H), 1.73 (dd, J = 6.8, 4.2 Hz, 1H), 1.67 – 1.50 (m, 1H), 0.90 – 0.80 (m, 1H), 0.74 – 0.59 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ = 142.3, 128.2, 127.2, 125.3, 72.5, 53.5, 50.6, 50.5, 46.3, 22.8, 8.2.

²⁹Si NMR (79 MHz, CDCl₃) δ = -63.8.

ESI-TOF/MS m/z calcd. for C₁₃H₂₁NO₃Si [M+H]⁺: 268.13242 found: 268.13249

Synthesis of 2-octafluoromethoxy -8,8-dimethoxy-1-oxa-4-aza-8-sila**3.11**

80.1 g (0.190 mol) of yellowish liquid was synthesized in (95 % yield, or 45 % after distillation) according to the modified representative procedure D, by mixing 54.8 g (0.2 mol) of 2,2,3,3,4,4,5,5-octafluoropentyl glycidyl ether and 35.8 g (0.2 mol) of (3-aminopropyl)trimethoxysilane at 23 °C in the presence of the catalyst (**CaTFA**).

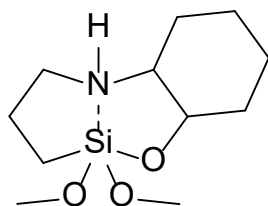
¹H NMR (400 MHz, Chloroform-*d*) δ 6.04 (tt, J = 51.9, 5.5 Hz, 1H), 3.91 (m, 1H), 3.61 (d, J = 4.6 Hz, 2H), 3.40 (s, 6H), 2.80 – 2.66 (m, 2H), 2.52 – 2.30 (m, 2H), 1.61 (ddd, J = 9.1, 6.8, 3.4 Hz, 1H), 1.55 – 1.39 (m, 1H), 0.71 – 0.58 (m, 1H), 0.58 – 0.44 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ = 115.3, 107.6, 105.0, 74.7, 70.0, 68.3, 50.2, 50.1, 47.3, 46.2, 22.4, 7.8.

^{29}Si NMR (79 MHz, CDCl_3) δ = -63.3.

ESI-TOF/MS m/z calcd. for $\text{C}_{12}\text{H}_{19}\text{F}_8\text{NO}_4\text{Si}$ $[\text{M}+\text{H}]^+$: 422.09892 found: 422.09735

Synthesis of N-methylcyclohexene-8,8-dimethoxy-1-oxa-4-aza-8-sila



3.09

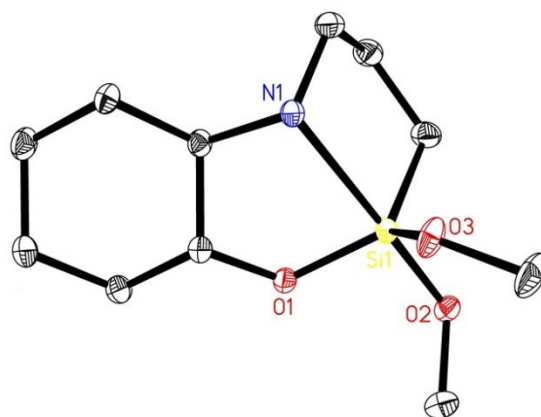
43.1 g (0.176 mol) of white needles were synthesized in (88 % yield) according to the modified representative procedure D, by mixing 39.2 g (0.4 mol) of cyclohexene oxide and 35.8 g (0.2 mol) of (3-aminopropyl)trimethoxysilane at 23 °C in the presence of the catalyst (**CaTFA**).

^1H NMR (400 MHz, Chloroform- d) δ 3.44 (s, 3H), 3.40 (s, 3H), 3.28 – 3.18 (m, 2H), 2.66 – 2.43 (m, 2H), 2.07 – 1.98 (m, 1H), 1.97 – 1.84 (m, 2H), 1.70 – 1.63 (m, 1H), 1.61 – 1.45 (m, 1H), 1.37 (bs, 1H), 1.31 – 1.11 (m, 4H), 1.02 (td, J = 12.0, 3.3 Hz, 1H), 0.69 – 0.58 (m, 2H), 0.52 – 0.40 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ = 75.6, 61.7, 50.5, 50.0, 43.8, 33.3, 30.7, 25.4, 24.2, 22.9, 7.5.

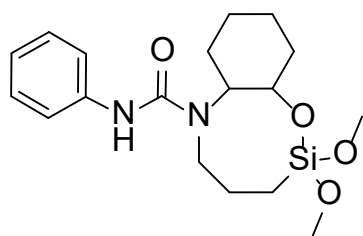
^{29}Si NMR (79 MHz, CDCl_3) δ = -60.3

ESI-TOF/MS m/z calcd. for $\text{C}_{11}\text{H}_{23}\text{NO}_3\text{Si}$ $[\text{M}+\text{H}]^+$: 246.14472 found: 246.15231



Empirical formula	C ₁₁ H ₂₃ NO ₃ Si
Formula weight	244.38
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	C2/c
Unit cell dimensions	a = 26.320(3) Å (90°) b = 6.0848(7) Å (110.4223°) c = 17.581(2) Å (90°)
Volume	2624.8(6) Å ³
Density (calculated)	1.237 Mg/m ³
Absorption coefficient	0.173 mm ⁻¹
F(000)	1064
Crystal size	0.394 x 0.114 x 0.086 mm
Theta range for data collection	1.660 to 27.999°
Index ranges	-34 ≤ h ≤ 34, -7 ≤ k ≤ 8, -23 ≤ l ≤ 21
Reflections collected	13012
Independent reflections	468 [R(int) = 0.0359]
Completeness to theta	= 25.242° 100.0 %
Absorption correction	Semi-empirical from equivalents
Data / restraints / parameters	3165 / 0 / 151
Goodness-of-fit on F²	1.040

Synthesis of N-methylcyclohexene-8,8-dimethoxy-1-oxa-4-aza-8-sila and phenyl isocyanate adduct



3.12

In an evacuated round bottom flask under the argon atmosphere 1.5 g (6 mmol) of compound **3.09** was dissolved in 10 ml of dry chloroform. 0.729 g (6 mmol) of phenyl isocyanate was slowly added to the solution. The reaction mixture was stirred for 12 hours at room temperature. The solvent was evaporated at 50 °C and under vacuum to obtain 2.2 g of

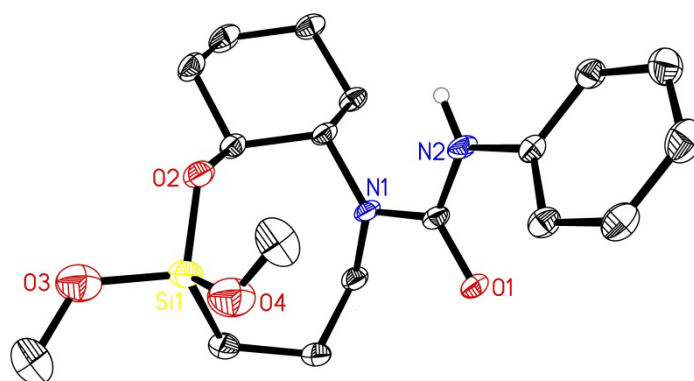
a white solid in 98 % yield. The solid was crystalized in $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ mixture to obtain transparent needles, which were submitted for XRD structure determination.

^1H NMR (400 MHz, Chloroform- d) δ 7.14 (t, J = 7.8 Hz, 2H), 6.96 (t, J = 7.9 Hz, 2H), 6.51 (t, J = 8.0 Hz, 1H), 3.87 – 3.77 (m, 1H), 3.42 – 3.37 (m, 1H), 3.37 (s, 3H), 3.31 (s, 3H), 2.63 (t, J = 13.8 Hz, 2H), 1.60 (m, 4H), 1.40 (q, J = 11.4, 10.2 Hz, 2H), 1.26 – 1.02 (m, 3H), 0.62 – 0.48 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ = 157.1, 137.4, 128.2, 125.3, 120.2, 72.5, 62.0, 50.76, 50.2, 34.7, 31.6, 28.9, 24.4, 22.7, 21.4, 6.9.

^{29}Si NMR (79 MHz, CDCl_3) δ = -41.6.

ESI-TOF/MS m/z calcd. for $\text{C}_{18}\text{H}_{28}\text{N}_2\text{O}_4\text{Si}$ $[\text{M}+\text{Na}]^+$: 365.18519 found: 365.18579



Empirical formula	$\text{C}_{18}\text{H}_{28}\text{N}_2\text{O}_4\text{Si}$
Formula weight	364.18
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	P c
Unit cell dimensions	$a = 10.0880(8)$ Å $b = 13.378(1)$ Å $c = 9.0659(7)$ Å
Volume	$1146(15)$ Å ³
Density (calculated)	1.056 Mg/m ³
Absorption coefficient	0.123 mm ⁻¹
F(000)	392
Crystal size	0.488 x 0.438 x 0.258 mm
Theta range for data collection	1.97 to 27.998°.
Index ranges	-12 ≤ h ≤ 12, -17 ≤ k ≤ 17, -11 ≤ l ≤ 11
Reflections collected	5005
Independent reflections	4741 [$R(\text{int}) = 0.0519$]
Completeness to theta	26.988° 100.0 %
Absorption correction	Semi-empirical from equivalents
Data / restraints / parameters	2896 / 0 / 151
Goodness-of-fit on F2	1.033

A3.2. Hydrolytic considerations of siloxacycloalkenes

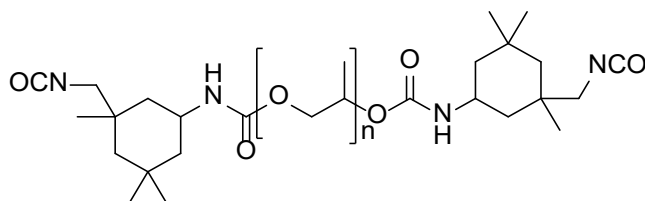
All ^1H and ^{29}Si NMR spectra for the kinetic studies were obtained at 25 °C using Bruker 250 MHz AVANCE 250 II spectrometer.

Siloxacycloalkene (0.3 mmol) was dissolved in 0.5 ml of CD_3CN , which was placed in the NMR tube. Firstly, the spectrometer's probe was tuned and matched to this solution after which the machine was also shimmed. Subsequently, 0.5 ml of H_2O with 1 % HCl was added into the NMR tube and ^1H and ^{29}Si NMR measurement of the locked sample was started using the acquisition time of 6.3 s and a sweep width of 5165 Hz for ^1H NMR measurement and acquisition time of 15 s and a sweep width of 19960 Hz for ^{29}Si NMR measurement. The starting interval of each ^1H and ^{29}Si NMR acquisition were set up to be 1 hour and were completed automatically.

The values for plotting the kinetic hydrolysis curves were obtained by integrating the signals in the NMR spectrum, which were converted into the molar concentration for kinetic purposes.

A3.3. Prepolymer preparation

Preparation of the -NCO terminated polymer

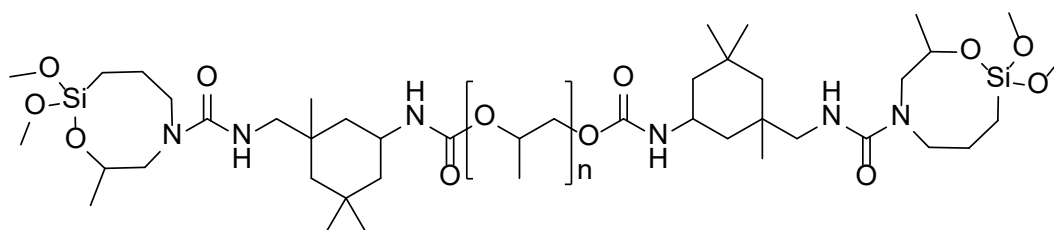


3.13

Representative procedure E:

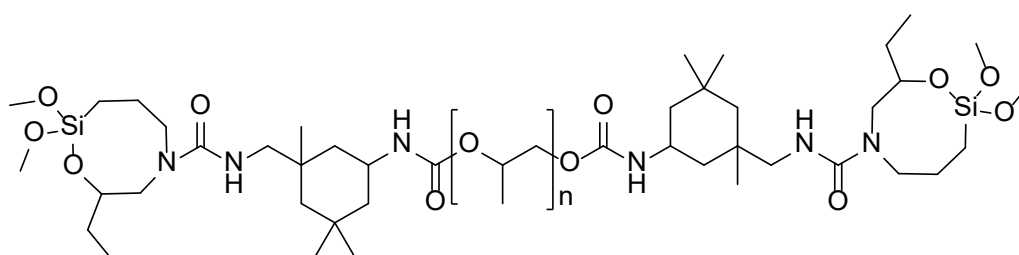
10 g of poly(propylene glycol) (PPG) (Acclaim 4200, 4000 g/mol, 28 ± 1.5 mg KOH/g) was added into the evacuated 25 ml Schlenk flask. The temperature was raised to 80 °C during which vacuum was applied for 1 hour. Afterwards 1.11 g (5 mmol) of isophorone diisocyanate (IPDI) and 0.03 g (1 mol%) of DOTL were added to the mixture and kept under vigorous stirring for 1 hour. The product **3.13** was analyzed using IR spectroscopy. After the reaction the viscosity was measured to be 20.03 Pas.

IR (ATR, neat, cm^{-1}): 3332.17 (w), 2969.59 (s), 2929.74 (s), 2867.37 (s), 2264.66 (s), 1718.79 (s), 1523.88 (m), 1452.67 (m), 1372.27 (s), 1343.57 (m), 1298.13 (m), 1238.19 (m), 1093.97 (s), 1014.22 (m), 925.76 (m), 864.99 (w), 578.31 (w), 455.15 (w).

Preparation of the alkoxy silane terminated prepolymer using end-capper 3.06.**3.06P**

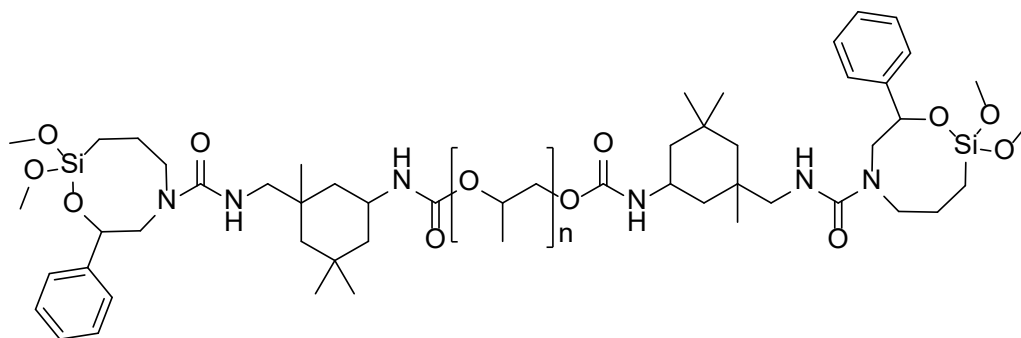
Approximately 12 g of colorless viscous liquid was synthesized by mixing 1.027 g (5 mmol) of compound **3.06** and 11.11 g of NCO terminated polymer (**3.13**) prepared according to the representative procedure E for 3 hours at 80 °C. No NCO band was detected by IR spectroscopy, it was concluded that the end-capping reaction is completed. After the reaction the viscosity was measured to be 34.58 Pas.

IR (ATR, neat, cm^{-1}): 3349.37 (w), 2969.41 (s), 2929.79 (s), 2867.33 (s), 1719.66 (m), 1655.16 (m), 1526.28 (m), 1453.58 (m), 1372.40 (s), 1343.85 (m), 1297.71 (m), 1241.58 (m), 1085.89 (s), 1012.72 (s), 925.84 (s), 865.39 (w), 820.70 (m), 788.24 (w), 761.59 (w), 448.06 (w).

Preparation of the alkoxy silane terminated prepolymer using end-capper 3.08.**3.08P**

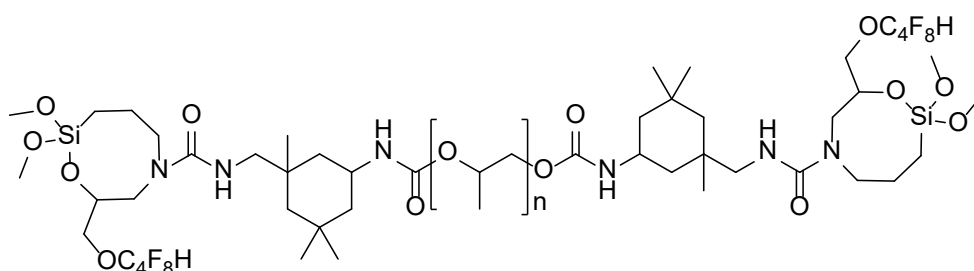
Approximately 12 g of colorless viscous liquid was synthesized by mixing 1.10 g (5 mmol) of compound **3.08** and 11.11 g of NCO terminated polymer (**3.13**) prepared according to the representative procedure E for 3 hours at 80 °C. No NCO band was detected by IR spectroscopy, therefore it was concluded that the end-capping reaction is completed. After the reaction the viscosity was measured to be 42.46 Pas.

IR (ATR, neat, cm^{-1}): 3342.27 (w) 2969.34 (s), 2929.71 (s), 2867.64 (s), 1719.50 (m), 1649.25 (m), 1523.94 (m), 1453.90 (m), 1372.28 (s), 1343.27 (m), 1297.84 (m), 1240.69 (m), 1086.70 (s), 1012.83 (m), 927.70 (s), 865.97 (w), 819.88 (m), 765.25 (w), 663.40 (w).

Preparation of the alkoxy silane terminated prepolymer using end-capper 3.10.**3.10P**

Approximately 12 g of colorless viscous liquid was synthesized by mixing 1.335 g (5 mmol) of compound **3.10** and 11.11 g of NCO terminated polymer (**3.13**) prepared according to the representative procedure E for 3 hours at 80 °C. No NCO band was detected by IR spectroscopy, therefore it was concluded that the end-capping reaction is completed. After the reaction the viscosity was measured to be 55.43 Pas.

IR (ATR, neat, cm⁻¹): 3338.25 (w), 2969.57 (s), 2929.80 (s), 2867.78 (s), 1719.47 (m), 1526.07 (m), 1452.99 (m), 1372.40 (s), 1343.10 (m), 1298.31 (m), 1240.16 (m), 1090.87 (s), 1014.49 (m), 926.25 (s), 865.22 (w), 817.33 (m), 754.66 (w), 700.96 (m), 666.72 (w), 448.70 (w).

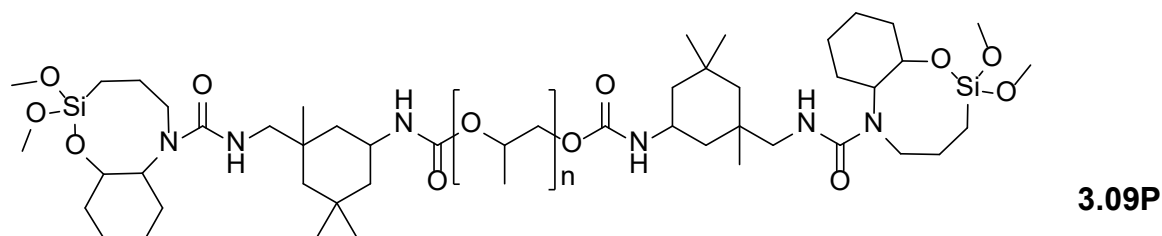
Preparation of the alkoxy silane terminated prepolymer using end-capper 3.11.**3.11P**

Approximately 12 g of colorless viscous liquid was synthesized by mixing 2.153 g (5 mmol) of compound **3.11** and 11.11 g of NCO terminated polymer (**3.13**) prepared according to the representative procedure E for 3 hours at 80 °C. No NCO band was detected by IR spectroscopy, therefore it was concluded that the end-capping reaction is completed. After the reaction the viscosity was measured to be 52.78 Pas.

IR (ATR, neat, cm⁻¹): 3336.38 (w), 2970.00 (s), 2930.11 (s), 2868.48 (s), 1717.16 (m), 1652.34 (m), 1523.53 (m), 1456.04 (m), 1372.73 (s), 1343.48 (m), 1297.77 (m), 1242.03 (m),

1087.71 (s), 1013.31 (m), 926.21 (s), 866.46 (m), 807.05 (m), 762.63 (m), 661.88 (w), 544.14 (w), 450.19 (w), 419.82 (w).

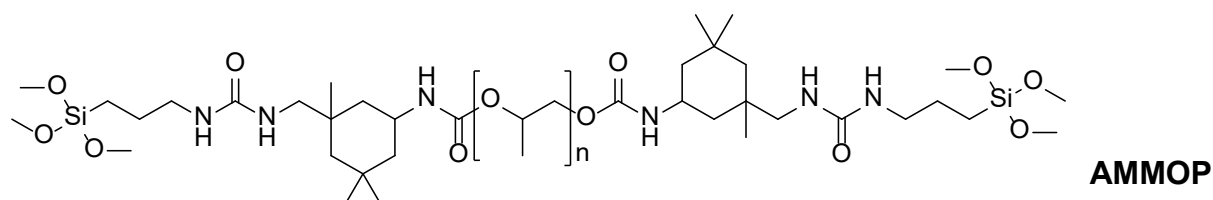
Preparation of the alkoxy silane terminated prepolymer using end-capper 3.09.



Approximately 12 g of slightly yellowish viscous liquid was synthesized by mixing 1.225 g (5 mmol) of compound **3.09** and 11.11 g of NCO terminated polymer (**3.13**) prepared according to the representative procedure E for 3 hours at 80 °C. No NCO band was detected by IR spectroscopy, therefore it was concluded that the end-capping reaction is completed. After the reaction the viscosity was measured to be 76.78 Pas.

IR (ATR, neat, cm⁻¹): 3343.25 (w), 2969.52 (s), 2930.15 (s), 2865.97 (s), 1719.21 (m), 1641.33 (m), 1524.19 (m), 1452.30 (m), 1372.37 (s), 1343.40 (m), 1298.04 (m), 1240.67 (m), 1086.31 (s), 1013.35 (m), 926.09 (m), 867.99 (w), 823.00 (m), 694.54 (w), 450.12 (w).

Preparation of the alkoxy silane terminated prepolymer using AMMO end-capper.



Approximately 12 g of colorless viscous liquid was synthesized by mixing 0.897 g (5 mmol) of **AMMO** and 11.11 g of NCO terminated polymer (**3.13**) prepared according to the representative procedure E for 3 hours at 80 °C. No NCO band was detected by IR spectroscopy, therefore it was concluded that the end-capping reaction is completed. After the reaction the viscosity was measured to be 64.96 Pas.

IR (ATR, neat, cm⁻¹): 3350.47 (w), 2969.72 (s), 2930.25 (s), 2867.74 (s), 1718.34 (m), 1638.51 (m), 1560.45 (m), 1454.38 (m), 1372.52 (s), 1343.19 (m), 1298.20 (m), 1086.92 (s), 1013.87 (m), 925.98 (m), 865.83 (m), 820.87 (m), 664.67 (w), 441.08 (w).

A3.4. Determining the skin over time of the casted prepolymer

Prepared prepolymer was casted on the aluminum plate in 2 mm thickness at 23 °C and atmospheric conditions (relative humidity ca. 40-60 %). The curing of the casted sample was tested every 5 minutes with the steel spatula by probing the surface for the formation of the

thin solid film. When thin film was formed, the time was noted and the sample was left to cure until it reached tack-free state at which point the sample was stored or used for further experiments.

A3.5. Resolving of the IR spectra for the determination of the hydrogen bonding

IR spectra of the raw samples were obtained using Bruker Alpha-P spectrometer. The prepolymers were casted on a clean KBr disc and measured in 2 cm^{-1} resolution in minimum of 64 scans per measured point. Afterwards the obtained data were imported in to the OMNIC 7.3 ThermoFischer Scientific software, where the spectra were processed using Fourier deconvolution to obtain better resolution and clear band splitting. Final band deconvolution was achieved using Origin 9.1 software using Gaussian distribution.

A3.6. Lap-shear tests

The substrates (except wood) for the lab shear tests were soaked and cleaned with isopropanol before usage. The prepared prepolymers were casted on the substrate in 500 mm^2 ($25 \times 20\text{ mm}$) surface area and in 1-2 mm thickness (Figure A 2.2.1). The prepolymers were covered from both sides with the same substrate material and cured for 2 weeks at 23°C and atmospheric conditions (relative humidity cca. 40-60 %). The materials used:

- PMMA: Poly(methyl methacrylate)
- PVC: Poly(vinyl chloride)
- AL: Aluminum 99.5 %
- STST: Stainless steel V2A 4301
- Wood: Plywood
- Glass

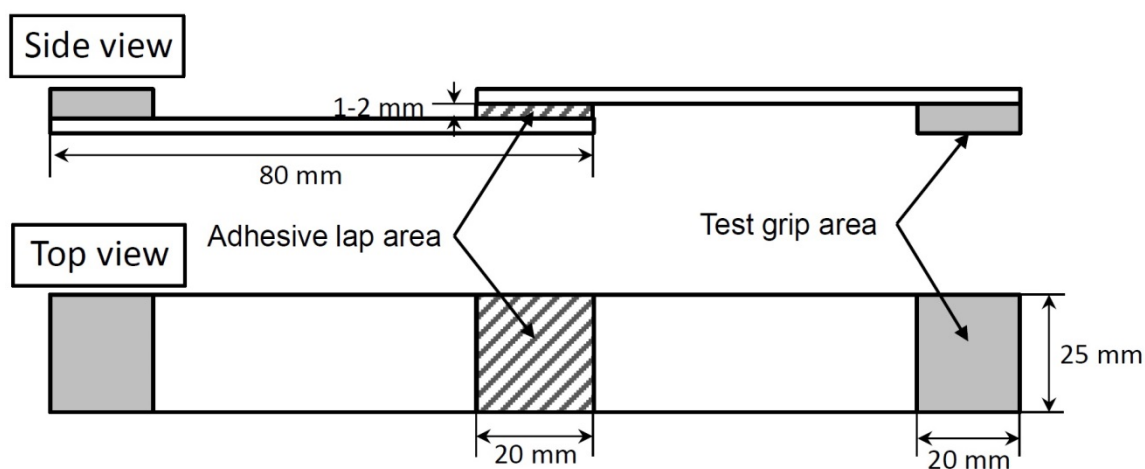


Figure A 2.2.1: Illustration of the specimen for tensile shear bond strength measurements.

After the curing of the prepolymer the specimen was inserted in to the Zwick 0.5/1.5 kN and tested according to the DIN EN 1465 standard. After the destructive measurement was performed, the type of the failure was determined as is exemplary presented in the Figure A 2.2.2.

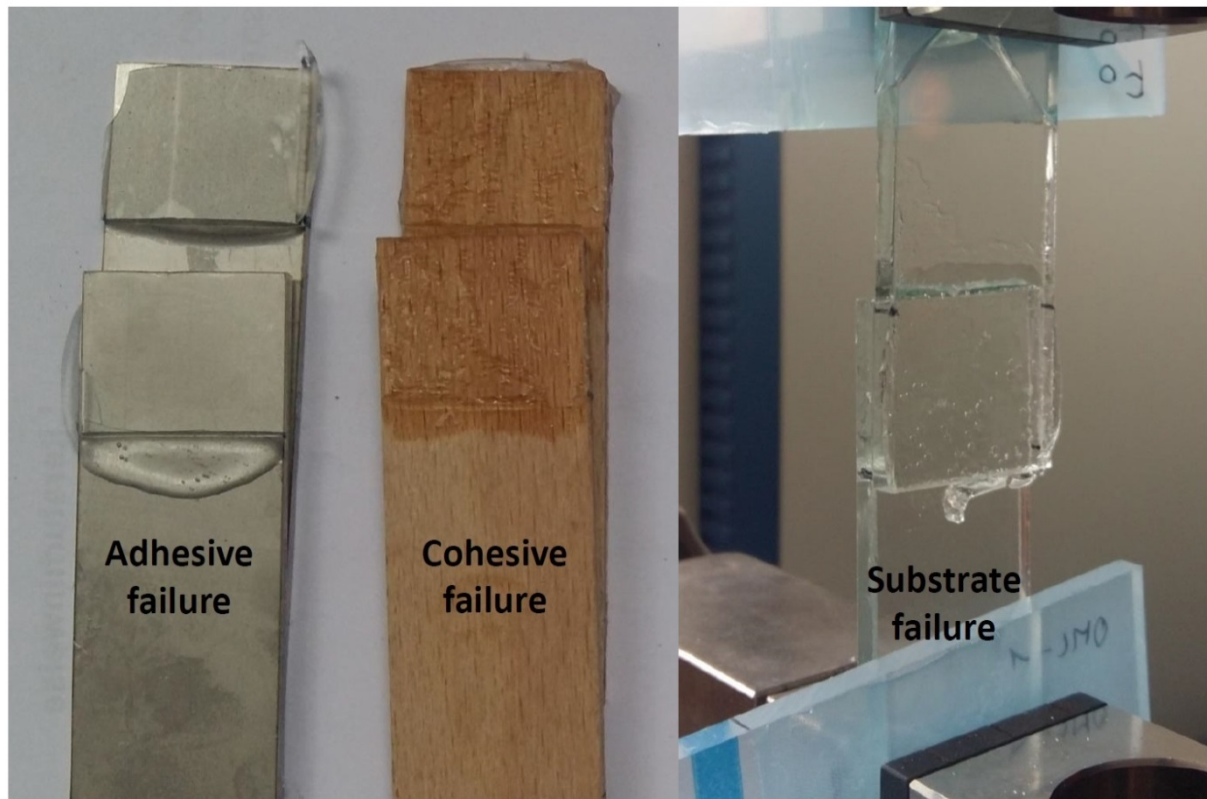


Figure A 2.2.2: Types of the failures during lap-shear tests.

A3.7. Tensile strength test cured prepolymers

Method A:

The prepared prepolymers were evenly casted on the plastic foil surrounded with 2 mm thick aluminum plate in the 65 cm² (5 x 13 cm) surface area. The prepolymers were cured for 2 weeks at 23 °C and atmospheric conditions (relative humidity cca. 40-60 %). Afterwards the films were cut in to the dogbone shape to meet the desired specifications as showcased in the Figure A 2.2.3.

Method A:

The prepared prepolymers were evenly casted in to the PTFE mold containing indentations, which meet the required specifications presented in the Figure A 2.2.3. The prepolymers were cured for 2 weeks at 23 °C and atmospheric conditions (relative humidity ca. 40-60 %).

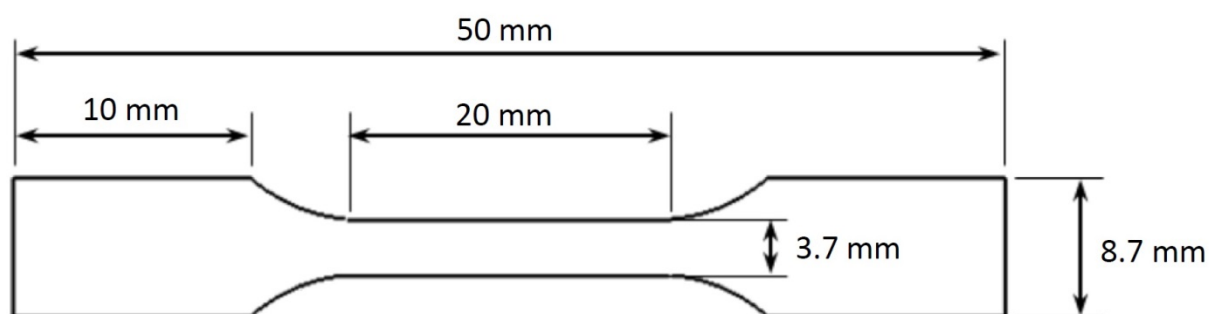


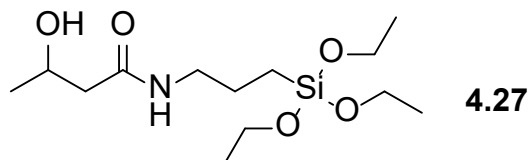
Figure A 2.2.3: Illustration of the specimen for tensile strength (elongation) measurements.

After the curing of the prepolymer the specimen was inserted in to the Zwick 0,5/1, 5 kN and tested according to the DIN 53504 standard, having the preload of 0.1 MPa and elongation speed of 200 mm/min. The software automatically calculated the elongation break (%) and the tensile strength (N/mm²) from the obtained elongation curve.

A4. Appendix to Chapter 4

A4.1. Synthesis of hydroxyl functional alkoxy silanes

Synthesis of 3-hydroxy-N-(3-(triethoxysilyl)propyl)butanamide



Representative procedure F:

2.21 g (0.01 mol) of (3-aminopropyl)triethoxysilane and 0.1 ml (0.1 mmol) of 1 molar solution of trimethylaluminium were mixed in an evacuated Schlenk tube and heated to 50 °C. Afterwards 0.86 g (0.01 mol) of β -butyrolactone was slowly added and stirred for 3 hours. Afterwards the heating was removed to afford a product as a yellowish liquid in 94 % yield.

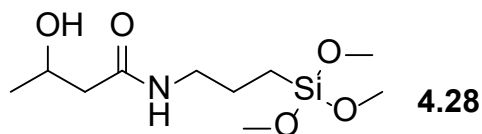
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 6.99 (s, 1H), 3.93 (m, 1H), 3.71 – 3.58 (m, 6H), 3.06 (m, 2H), 2.23 – 2.08 (m, 2H), 1.43 (m, 2H), 1.08 (d, J = 6.4 Hz, 3H), 1.05 – 0.97 (m, 9H), 0.53 – 0.43 (m, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ = 172.2, 64.6, 58.2, 44.0, 41.6, 22.9, 22.5, 18.1, 6.3.

$^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ = -46.0.

ESI-TOF/MS m/z calcd. for $\text{C}_{13}\text{H}_{29}\text{NO}_5\text{Si}$ $[\text{M}+\text{H}]^+$: 308.18485 found: 308.18477.

Synthesis of 3-hydroxy-N-(3-(trimethoxysilyl)propyl)butanamide



2.65 g (0.01 mol) of yellow viscous liquid was synthesized in 35 % purity according to the representative procedure F, by mixing 1.79 g (0.01 mol) of (3-aminopropyl)trimethoxysilane, 0.1 ml (0.1 mmol) of trimethylaluminium and 0.86 g (0.01 mol) of β -butyrolactone. Further purification of the compound was not conducted due to the instability of the desired product.

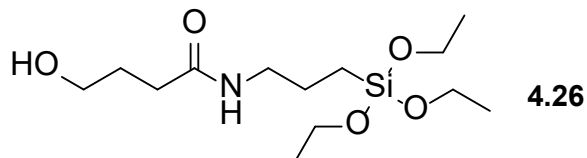
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 6.91 (s, 1H), 5.01 (s, 1H), 3.98 (m, 1H), 3.40 (s, 9H), 3.06 (m, 2H), 2.23 – 2.08 (m, 2H), 1.45 (m, 2H), 1.05 (d, J = 6.4 Hz, 3H), 0.53 – 0.43 (m, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ = 172.4, 64.6, 50.3, 44.0, 41.6, 22.8, 22.5, 6.3.

$^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ = -42.3.

ESI-TOF/MS m/z calcd. for $C_{10}H_{23}NO_5Si$ $[M+H]^+$: 266.13790 found: 266.13801.

Synthesis of 4-hydroxy-N-(3-(trimethoxysilyl)propyl)butanamide



3.02 g (9.3 mmol) of yellow liquid was synthesized in 98 % yield according to representative procedure F, by mixing 2.21 g (0.01 mol) of (3-aminopropyl)triethoxysilane, 0.1 ml (0.1 mmol) of trimethylaluminium and 0.86 g (0.01 mol) of γ -butyrolactone. Further purification of the compound was not needed.

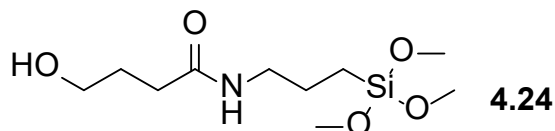
1H NMR (300 MHz, Chloroform- d) δ 6.87 (t, J = 5.5 Hz, 1H), 4.30 (bs, 1H), 3.66 – 3.53 (m, 6H), 3.41 (t, J = 5.9 Hz, 2H), 2.98 (q, J = 6.7 Hz, 2H), 2.11 (t, J = 7.0 Hz, 2H), 1.70 – 1.53 (m, 2H), 1.46 – 1.33 (m, 1H), 1.05 – 0.94 (m, 9H), 0.46 – 0.37 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.8, 67.0, 50.4, 41.91, 34.5, 33.1, 23.4, 22.6, 6.4.

^{29}Si NMR (79 MHz, $CDCl_3$) δ = -46.3.

ESI-TOF/MS m/z calcd. for $C_{13}H_{29}NO_5Si$ $[M+H]^+$: 308.18485 found: 308.18588.

Synthesis of 4-hydroxy-N-(3-(trimethoxysilyl)propyl)butanamide



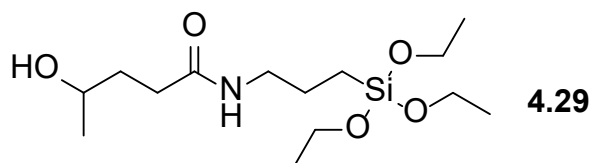
2.65 g (0.01 mol) of yellow viscous liquid was synthesized in 53 % purity according to the representative procedure F, by mixing 1.79 g (0.01 mol) of (3-aminopropyl)trimethoxysilane, 0.1 ml (0.1 mmol) of trimethylaluminium and 0.86 g (0.01 mol) of γ -butyrolactone. Further purification of the compound was not conducted due to the instability of the compound.

1H NMR (400 MHz, Chloroform- d) δ 6.71 (s, 1H), 3.71 – 3.60 (m, 1H), 3.43 (s, 9H), 3.14 – 2.99 (m, 2H), 2.18 – 2.09 (m, 2H), 1.84 – 1.62 (m, 2H), 1.58 – 1.37 (m, 2H), 0.57 – 0.43 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.6, 61.9, 50.4, 41.9, 32.6, 28.3, 22.5, 6.4.

^{29}Si NMR (79 MHz, $CDCl_3$) δ = -42.1.

ESI-TOF/MS m/z calcd. for $C_{10}H_{23}NO_5Si$ $[M+H]^+$: 266.13790 found: 266.13745.

Synthesis of 4-hydroxy-N-(3-(triethoxysilyl)propyl)pentanamide

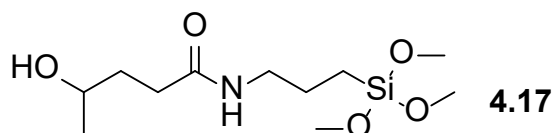
3.21 g (0.01 mol) of colorless liquid was synthesized in 85 % purity according to the representative procedure F, by mixing 2.21 g (0.01 mol) of (3-aminopropyl)triethoxysilane, 0.1 ml (0.1 mmol) of trimethylaluminium and 1.0 g (0.01 mol) of γ -valerolactone. Further purification of the compound was not conducted due to the instability of the compound.

^1H NMR (300 MHz, Chloroform-*d*) δ 6.77 (bs, 1H), 3.70 - 3.89 (m, 6H), 3.59 (q, J = 7.0 Hz, 2H), 3.23 - 3.05 (m, 2H), 2.32 - 2.21 (m, 2H), 1.80 - 1.62 (m, 2H), 1.49 - 1.62 (m, 2H), 1.34 (d, J = 6.2 Hz, 3H), 1.26 - 1.04 (m, 9H), 0.47 - 0.72 (m, 2H).

^{13}C NMR (75 MHz, CDCl_3) δ = 173.7, 66.7, 58.1, 49.7, 41.7, 32.8, 28.8, 23.1, 17.9, 7.4.

^{29}Si NMR (79 MHz, CDCl_3) δ = -46.4.

ESI-TOF/MS m/z calcd. for $\text{C}_{14}\text{H}_{31}\text{NO}_5\text{Si}$ $[\text{M}+\text{H}]^+$: 322.20050 found: 322.20048.

Synthesis of 4-hydroxy-N-(3-(trimethoxysilyl)propyl)pentanamide

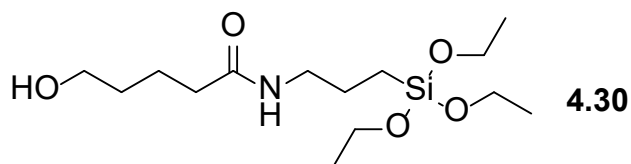
2.79 g (0.01 mol) of yellow viscous liquid was synthesized in 85 % purity according to the representative procedure F, by mixing 1.79 g (0.01 mol) of (3-aminopropyl)triethoxysilane, 0.1 ml (0.1 mmol) of trimethylaluminium and 1.05 g (0.01 mol) of γ -valerolactone. Further purification of the compound was not conducted due to the instability of the compound.

^1H NMR (400 MHz, Chloroform-*d*) δ 6.70 (t, J = 5.8 Hz, 1H), 3.70 - 3.78 (m, 1H), 3.50 (s, 9H), 3.10 - 3.22 (m, 2H), 2.33 - 2.23 (m, 2H), 1.68 - 1.78 (m, 2H), 1.47 - 1.58 (m, 2H), 1.12 (d, J = 6.2 Hz, 3H), 0.61 - 0.54 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ = 173.8, 67.0, 50.4, 41.9, 34.5, 33.1, 23.4, 22.6, 6.4.

^{29}Si NMR (79 MHz, CDCl_3) δ = -42.2.

ESI-TOF/MS m/z calcd. for $\text{C}_{10}\text{H}_{23}\text{NO}_5\text{Si}$ $[\text{M}+\text{H}]^+$: 280.15355 found: 280.15298.

Synthesis of 5-hydroxy-N-(3-(triethoxysilyl)propyl)pentanamide

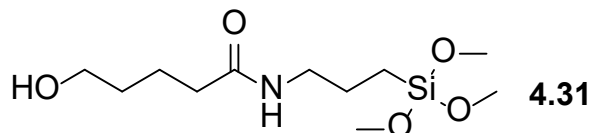
3.19 g (0.01 mol) of colorless liquid was synthesized in 98 % yield according to the representative procedure F, by mixing 2.21 g (0.01 mol) of (3-aminopropyl)triethoxysilane, 0.1 ml (0.1 mmol) of trimethylaluminium and 1.05 g (0.01 mol) of δ -valerolactone. Further purification of the compound was not needed.

^1H NMR (400 MHz, Chloroform-*d*) δ 6.31 (s, 1H), 3.77 – 3.59 (m, 6H), 3.53 – 3.41 (m, 1H), 3.03–3.10 (m, 2H), 2.12 – 2.01 (m, 2H), 1.61 – 1.37 (m, 6H), 1.37 – 1.19 (m, 2H), 1.10 (t, J = 9.2, 9H), 0.57 – 0.44 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ = 173.2, 61.8, 58.2, 41.7, 36.4, 32.2, 25.4, 22.7, 18.1, 7.6.

^{29}Si NMR (79 MHz, CDCl_3) δ = -46.2.

ESI-TOF/MS m/z calcd. for $\text{C}_{14}\text{H}_{31}\text{NO}_5\text{Si}$ $[\text{M}+\text{H}]^+$: 322.20050 found: 322.20072.

Synthesis of 5-hydroxy-N-(3-(triethoxysilyl)propyl)pentanamide

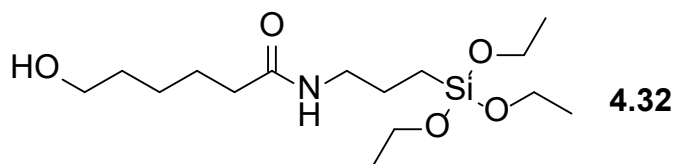
2.76 g (0.01 mol) of yellowish viscous liquid was synthesized in 52 % purity according to the representative procedure F, by mixing 1.79 g (0.01 mol) of (3-aminopropyl)trimethoxysilane, 0.1 ml (0.1 mmol) of trimethylaluminium and 1.05 g (0.01 mol) of δ -valerolactone. Further purification of the compound was not conducted due to the instability of the compound.

^1H NMR (400 MHz, Chloroform-*d*) δ 6.58 (s, 1H), 3.70 – 3.58 (m, 1H), 3.46 (s, 9H), 3.16 – 3.04 (m, 2H), 2.10 (td, J = 7.4, 3.5 Hz, 2H), 1.67 – 1.54 (m, 2H), 1.54 – 1.43 (m, 4H), 0.59 – 0.47 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ = 173.4, 62.2, 61.5, 50.4, 41.7, 31.9, 22.6, 22.0, 6.3.

^{29}Si NMR (79 MHz, CDCl_3) δ = -42.1.

ESI-TOF/MS m/z calcd. for $\text{C}_{11}\text{H}_{25}\text{NO}_5\text{Si}$ $[\text{M}+\text{H}]^+$: 280.15355 found: 280.15289.

Synthesis of 6-hydroxy-N-(3-(trimethoxysilyl)propyl)hexanamide

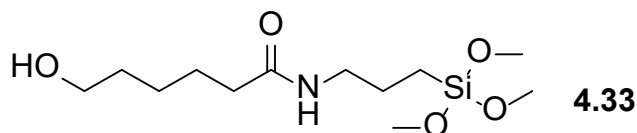
3.26 g (0.01 mol) of yellow viscous liquid was synthesized in 97 % yield according to the representative procedure F, by mixing 2.21 g (0.01 mol) of (3-aminopropyl)triethoxysilane, 0.1 ml (0.1 mmol) of trimethylaluminium and 1.14 g (0.01 mol) of ϵ -caprolactone. Further purification of the compound was not needed.

^1H NMR (400 MHz, Chloroform-*d*) δ 6.85 (s, 1H), 3.81 – 3.61 (m, 9H), 3.07 (q, J = 7 Hz, 2H), 2.22 (t, J = 4.4, 2H), 1.72 - 1.60 (m, 2H), 1.61 – 1.40 (m, 4H), 1.16 – 1.01 (m, 13H), 0.58 – 0.45 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ = 173.8, 66.8, 58.2, 41.9, 34.5, 33.0, 23.3, 22.7, 18.14, 7.6.

^{29}Si NMR (79 MHz, CDCl_3) δ = -46.3.

ESI-TOF/MS m/z calcd. for $\text{C}_{12}\text{H}_{27}\text{NO}_5\text{Si}$ $[\text{M}+\text{H}]^+$: 294.16920 found: 294.16899.

Synthesis of 6-hydroxy-N-(3-(trimethoxysilyl)propyl)hexanamide

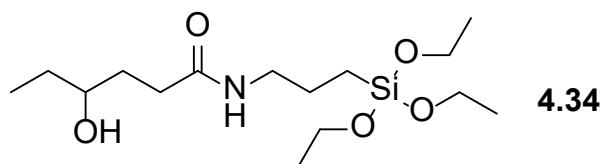
2.89 g (0.01 mol) of yellow viscous liquid was synthesized in 31 % purity according to the representative procedure F, by mixing 1.79 g (0.01 mol) of (3-aminopropyl)trimethoxysilane, 0.1 ml (0.1 mmol) of trimethylaluminium and 1.14 g (0.01 mol) of ϵ -caprolactone. Further purification of the compound was not conducted due to the instability of the compound.

^1H NMR (400 MHz, Chloroform-*d*) δ 6.58 (s, 1H), 3.68 – 3.52 (m, 2H), 3.39 (s, 9H), 3.07 – 2.97 (m, 2H), 2.20 – 2.10 (m, 2H), 1.45 – 1.31 (m, 2H), 1.22 (tq, J = 6.9, 2.2 Hz, 2H), 0.50 – 0.40 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ = 173.4, 62.2, 61.5, 50.4, 41.7, 31.9, 22.6, 22.0, 6.3.

^{29}Si NMR (79 MHz, CDCl_3) δ = -42.3.

ESI-TOF/MS m/z calcd. for $\text{C}_{12}\text{H}_{27}\text{NO}_5\text{Si}$ $[\text{M}+\text{H}]^+$: 294.16920 found: 294.16899.

Synthesis of 4-hydroxy-N-(3-(triethoxysilyl)propyl)hexanamide

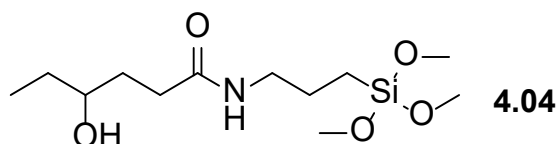
3.30 g (0.01 mol) of yellow viscous liquid was synthesized in 98 % yield according to the representative procedure F, by mixing 2.21 g (0.01 mol) of (3-aminopropyl)triethoxysilane, 0.1 ml (0.1 mmol) of trimethylaluminium and 1.14 g (0.01 mol) of γ -caprolactone. Further purification of the compound was not needed.

^1H NMR (400 MHz, Chloroform-*d*) δ 6.91 – 6.69 (bs, 1H), 4.23 – 3.94 (bs, 1H), 3.79 – 3.62 (m, 6H), 3.35 – 3.52 (m, 2H), 3.11 (q, J = 6.4 Hz, 1H), 2.31 – 2.18 (m, 2H), 1.73 (m, 2H), 1.60 – 1.44 (m, 2H), 1.44 – 1.29 (m, 2H), 1.19 – 1.04 (m, 9H), 0.90 – 0.78 (m, 3H), 0.58 – 0.45 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ = 173.9, 72.2, 58.2, 41.9, 33.0, 32.3, 30.2, 22.7, 18.1, 9.9, 7.7.

^{29}Si NMR (79 MHz, CDCl_3) δ = -46.1.

ESI-TOF/MS m/z calcd. for $\text{C}_{15}\text{H}_{33}\text{NO}_5\text{Si}$ $[\text{M}+\text{H}]^+$: 336.21615 found: 336.21686.

Synthesis of 4-hydroxy-N-(3-(triethoxysilyl)propyl)hexanamide

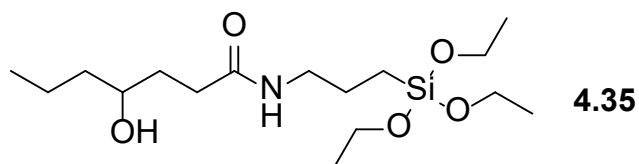
2.90 g (0.01 mol) of colorless liquid was synthesized in 99 % yield according to the representative procedure F, by mixing 1.79 g (0.01 mol) of (3-aminopropyl)trimethoxysilane, 0.1 ml (0.1 mmol) of trimethylaluminium and 1.14 g (0.01 mol) of γ -caprolactone. Further purification of the compound was not needed.

^1H NMR (400 MHz, Chloroform-*d*) δ 6.55 (bs, 1H), 3.78 (bs, 1H), 3.53 (s, 9H), 3.18 (q, J = 7.1, 2H), 2.32 (t, J = 6.7 Hz, 2H), 1.93 - 1.79 (m, 2H), 1.67 – 1.52 (m, 2H), 1.50 – 1.37 (m, 2H), 0.90 (t, J = 7.5 Hz, 3H), 0.65 – 0.58 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ = 173.9, 72.4, 50.5, 41.9, 33.1, 32.2, 30.3, 22.6, 9.9, 6.4.

^{29}Si NMR (79 MHz, CDCl_3) δ = -42.1.

ESI-TOF/MS m/z calcd. for $\text{C}_{12}\text{H}_{27}\text{NO}_5\text{Si}$ $[\text{M}+\text{H}]^+$: 294.16920 found: 294.16893.

Synthesis of 4-hydroxy-N-(3-(triethoxysilyl)propyl)heptanamide

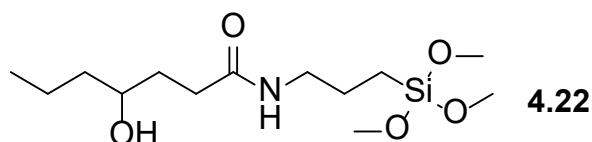
3.30 g (0.01 mol) of colorless liquid was synthesized in 96 % yield according to the representative procedure F, by mixing 2.21 g (0.01 mol) of (3-aminopropyl)triethoxysilane, 0.1 ml (0.1 mmol) of trimethylaluminium and 1.28 g (0.01 mol) of γ -heptalactone. Further purification of the compound was not needed.

^1H NMR (400 MHz, Chloroform-*d*) δ 6.96 (bs, 1H), 4.14 (bs, 1H), 3.69 (qd, J = 7.0, 1.8 Hz, 6H), 3.57 – 3.37 (m, 1H), 3.08 (q, J = 6.6 Hz, 2H), 2.35 – 2.46 (m, 1H), 1.79 – 1.89 (m, 2H), 1.59 – 1.64 (m, 2H), 1.42 – 1.18 (m, 2H), 1.23 – 1.03 (m, 9H), 0.86 – 0.72 (m, 2H), 0.58 – 0.41 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ = 173.9, 70.5, 58.2, 41.9, 39.6, 33.0, 22.7, 18.8, 18.1, 13.9, 7.6.

^{29}Si NMR (79 MHz, CDCl_3) δ = -46.2.

ESI-TOF/MS m/z calcd. for $\text{C}_{16}\text{H}_{35}\text{NO}_5\text{Si}$ $[\text{M}+\text{H}]^+$: 350.23180 found: 350.23153.

Synthesis of 4-hydroxy-N-(3-(triethoxysilyl)propyl)heptanamide

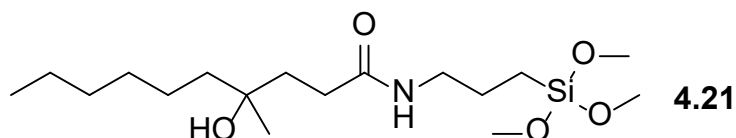
2.92 g (0.01 mol) of colorless liquid was synthesized in 95 % yield according to the representative procedure F, by mixing 1.79 g (0.01 mol) of (3-aminopropyl)trimethoxysilane, 0.1 ml (0.1 mmol) of trimethylaluminium and 1.28 g (0.01 mol) of γ -heptalactone. Further purification of the compound was not needed.

^1H NMR (400 MHz, Chloroform-*d*) δ 6.66 (bs, 1H), 3.86 (bs, 1H), 3.51 (s, 9H), 3.15 (td, J = 7.3, 5.8 Hz, 2H), 2.29 (t, J = 6.8, 2H), 1.66 – 1.49 (m, 4H), 1.46 – 1.23 (m, 4H), 0.90 – 0.81 (m, 3H), 0.62 – 0.56 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ = 173.9, 70.7, 50.4, 41.9, 39.7, 33.1, 32.8, 22.6, 18.8, 14.0, 6.4.

^{29}Si NMR (79 MHz, CDCl_3) δ = -42.2.

ESI-TOF/MS m/z calcd. for $\text{C}_{13}\text{H}_{29}\text{NO}_5\text{Si}$ $[\text{M}+\text{H}]^+$: 308.18485 found: 308.18463.

Synthesis of 4-hydroxy-N-(3-(triethoxysilyl)propyl)heptanamide

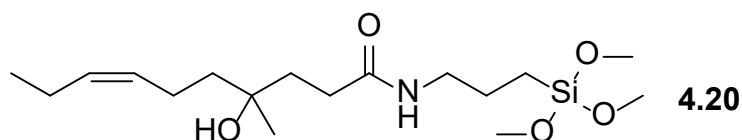
3.57 g (0.01 mol) of colorless liquid was synthesized in 98 % yield according to the representative procedure F, by mixing 1.79 g (0.01 mol) of (3-aminopropyl)trimethoxysilane, 0.1 ml (0.1 mmol) of trimethylaluminium and 1.84 g (0.01 mol) of γ -methyl decalactone. Further purification of the compound was not needed.

^1H NMR (400 MHz, Chloroform-*d*) δ 6.34 (bs, 1H), 3.56 (s, 9H), 3.21 (td, J = 7.1, 5.8 Hz, 2H), 2.30 (td, J = 7.3, 1.7 Hz, 2H), 1.84 – 1.68 (m, 2H), 1.60 (p, J = 7.4 Hz, 2H), 1.47 – 1.40 (m, 2H), 1.36 – 1.22 (m, 8H), 1.13 (s, 3H), 0.91 – 0.82 (m, 3H), 0.63 (t, J = 8.3, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ = 174.0, 71.6, 50.5, 42.5, 41.9, 36.6, 31.8, 31.1, 29.9, 26.5, 24.0, 22.6, 22.6, 14.0, 6.4.

^{29}Si NMR (79 MHz, CDCl_3) δ = -42.2.

ESI-TOF/MS m/z calcd. for $\text{C}_{17}\text{H}_{37}\text{NO}_5\text{Si}$ $[\text{M}+\text{H}]^+$: 364.24745 found: 364.25137.

Synthesis of 4-hydroxy-4-methyl-N-(3-(trimethoxysilyl)propyl)dec-7-enamide

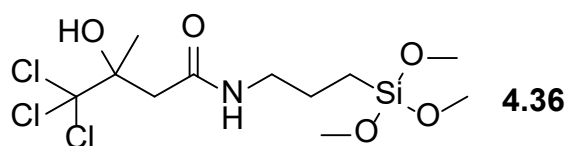
3.57 g (0.01 mol) of colorless liquid was synthesized in 98 % yield according to the representative procedure F, by mixing 1.79 g (0.01 mol) of (3-aminopropyl)trimethoxysilane, 0.1 ml (0.1 mmol) of trimethylaluminium and 1.82 g (0.01 mol) of 4-Hydroxy-4-methyl-7-decenoic acid γ -lactone. Further purification of the compound was not needed.

^1H NMR (400 MHz, Chloroform-*d*) δ 6.56 (bs, 1H), 5.33 – 5.19 (m, 1H), 3.49 (s, 9H), 3.14 (q, J = 6.7 Hz, 2H), 2.30 – 2.19 (m, 2H), 2.09 – 1.87 (m, 4H), 1.80 – 1.62 (m, 2H), 1.60 – 1.48 (m, 2H), 1.47 – 1.37 (m, 2H), 1.10 (s, 3H), 0.88 (td, J = 7.6, 2.1 Hz, 3H), 0.61 – 0.51 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ = 174.0, 131.6, 128.9, 71.3, 50.4, 42.3, 41.9, 36.7, 30.9, 26.3, 22.6, 21.8, 20.4, 14.2, 6.4.

^{29}Si NMR (79 MHz, CDCl_3) δ = -42.2.

ESI-TOF/MS m/z calcd. for $\text{C}_{17}\text{H}_{35}\text{NO}_5\text{Si}$ $[\text{M}+\text{H}]^+$: 362.23180 found: 362.23239.

Synthesis of 4-hydroxy-4-methyl-N-(3-(trimethoxysilyl)propyl)dec-7-enamide

1.79 g (0.01 mol) of (3-aminopropyl)trimethoxysilane was stirred in an evacuated Schlenk tube at room temperature. Afterwards 2.03 g (0.01 mol) of 4-methyl-4-(trichloromethyl)-2-oxetanone was slowly added and stirred for 3 hours. Afterwards the heating was removed to afford a product as a yellowish liquid in 98 % yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 6.83 (bs, 1H), 3.57 (s, 9H), 3.31 – 3.19 (m, 2H), 3.04 – 2.59 (m, 2H), 1.71 – 1.59 (m, 5H), 0.70 – 0.61 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ = 171.1, 107.8, 81.5, 50.6, 41.9, 40.8, 23.3, 22.4, 6.5.

²⁹Si NMR (79 MHz, CDCl₃) δ = -42.4.

ESI-TOF/MS *m/z* calcd. for C₁₁H₂₂Cl₃NO₅Si [M+H]⁺: 383.0303 found: 383.0311.

A4.2. Monitoring the progress of the lactone RO with aminosilanes

In order to monitor a reaction conversion and possible side reactions, an *in situ* infrared (IR) spectroscopy was used to follow the disappearance of the carbonyl band of the lactone at 1800 cm⁻¹ or appearance of the amide bands at 1600 and 1530 cm⁻¹.

The FTIR spectrometer was stabilized for at least 1 hour and the diamond probe was cleaned with acetone before usage. Afterwards the diamond window on end of the probe was inserted directly in to the reaction medium at which point the reaction was initiated. It was necessary to keep the FTIR probe under cca. 70-80° angle to prevent bubble formation over the FTIR diamond window. The obtained spectra were further processed with the help of the concentration/signal intensity calibration curve, which was obtained beforehand, to obtain the kinetic plots.

A4.3. Catalyst screening

1.79 g (0.01 mol) of (3-aminopropyl)triethoxysilane and 0.1 mmol of selected catalyst were mixed in an evacuated Schlenk tube and heated to 50 °C. Afterwards 1.14 g (0.01 mol) of γ -hexalactone was slowly added and stirred for 20 hours or less if reaction was completed sooner. The reaction was monitored using *in situ* IR spectrometer. Afterwards the heating was removed to afford a reaction mixture, which was analyzed by GC and NMR techniques in order to determine the yield and the amount of the side products formed.

A4.4. Stability test

Longstanding stability

The hydroxyl functional methoxysilanes were synthesized by optimized procedure using triethylaluminium at 50 °C. The samples were placed in the Schlenk flasks under argon atmosphere, which were stored in an oven at 50 °C for 8 days. Small amount of sample for GC-MS and NMR analysis was withdrawn immediately after the reaction and after 3, 5 and 8 days. Results are presented in the Figure A 2.2.1 -Figure A 2.2.14.

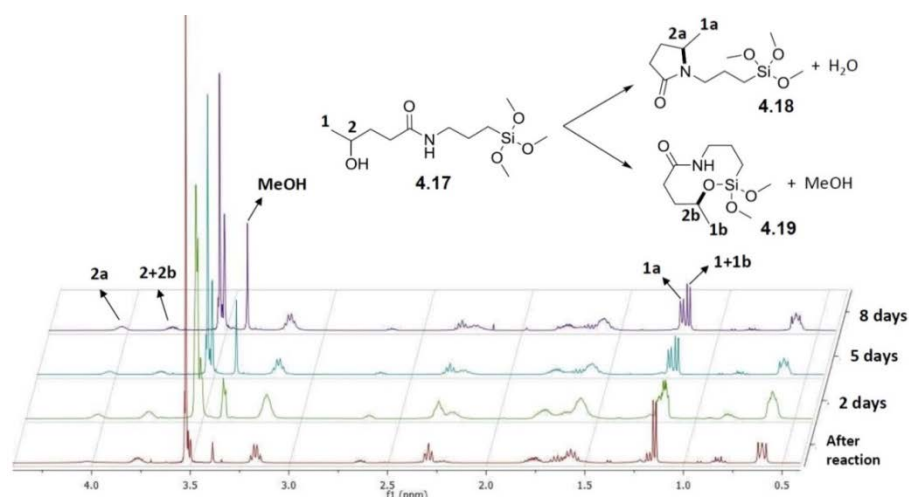


Figure A 2.2.1: Longstanding stability of the compound 4.17 at 50 °C, and the graphical representation of the side reactions analyzed by 1H NMR in CDCl₃.

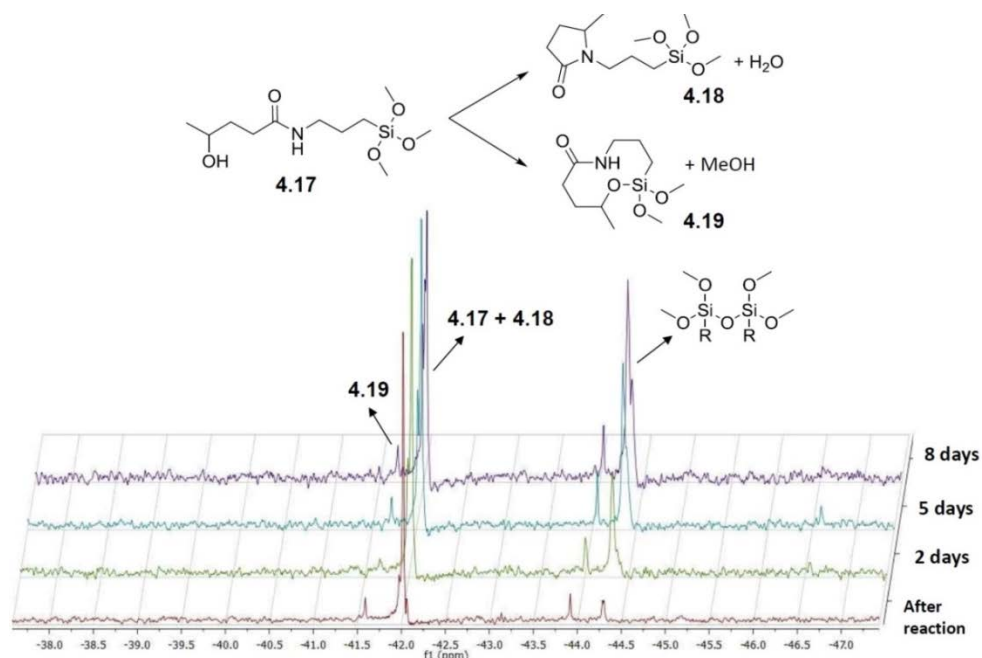


Figure A 2.2.2: Longstanding stability of the compound 4.17 at 50 °C, and the graphical representation of the side reactions analyzed by 29Si NMR in CDCl₃.

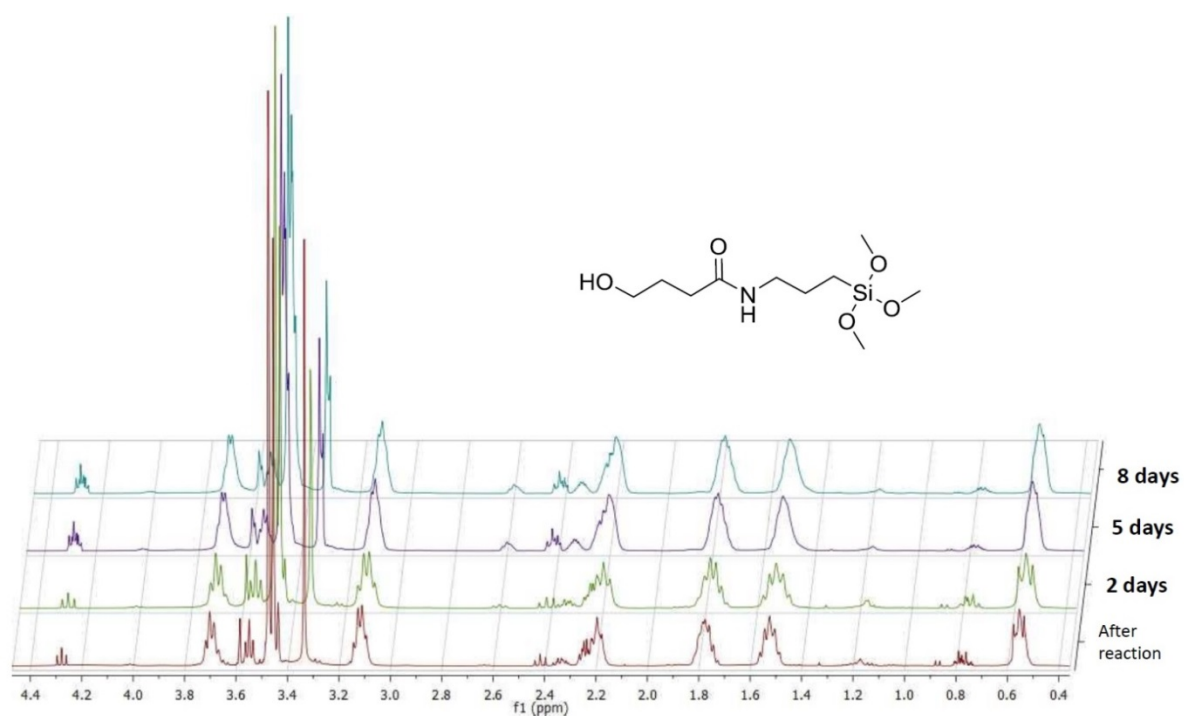


Figure A 2.2.3: Longstanding stability of the compound **4.23** at 50 °C analyzed by ¹H NMR in CDCl₃.

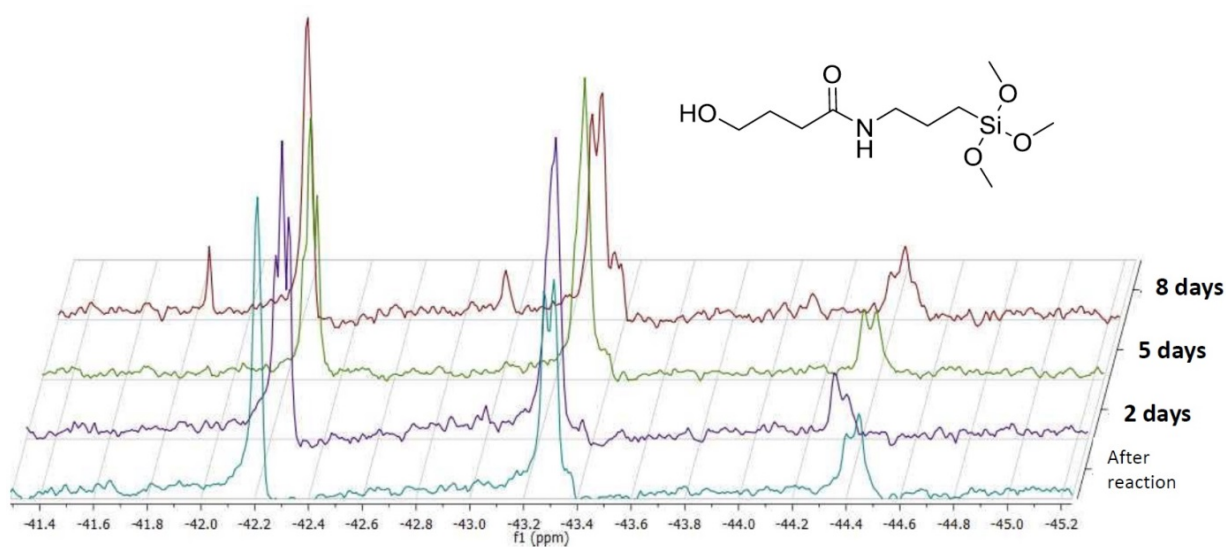


Figure A 2.2.4: Longstanding stability of the compound **4.23** at 50 °C analyzed by ²⁹Si NMR in CDCl₃.

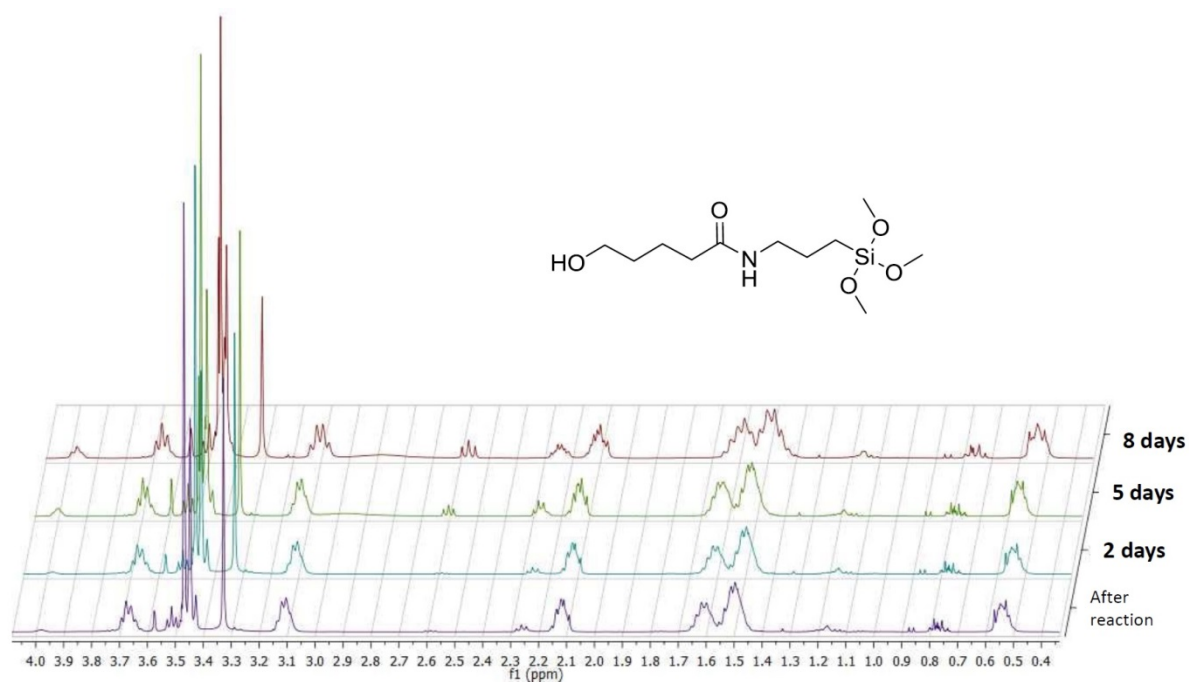


Figure A 2.2.5: Longstanding stability of the compound 4.24 at 50 °C analyzed by ^1H NMR in CDCl_3 .

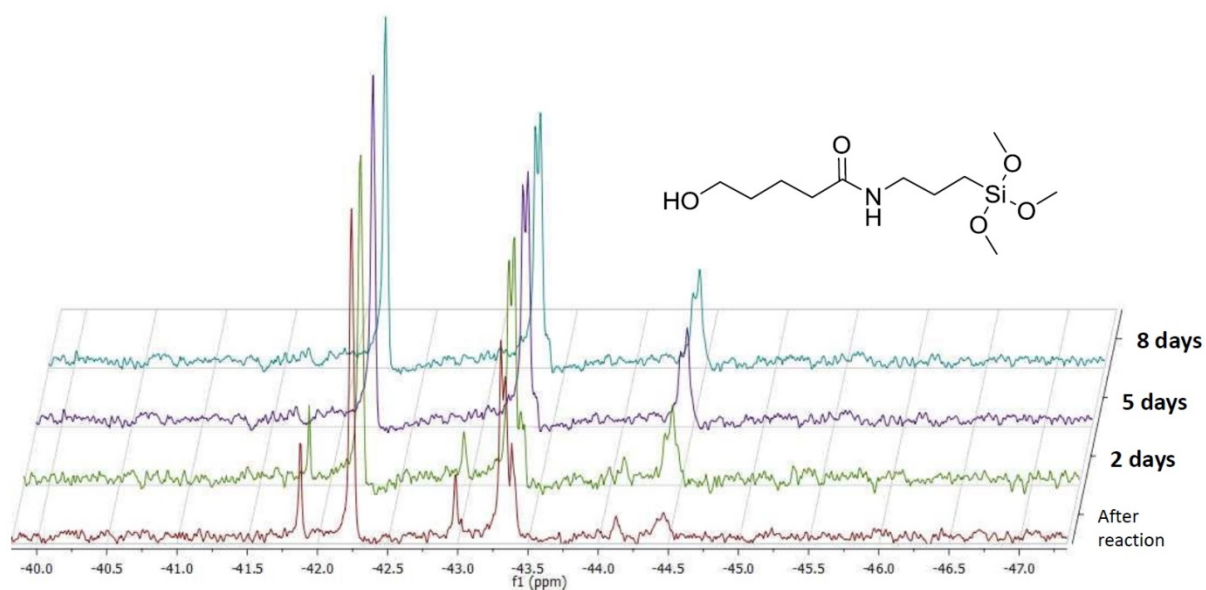


Figure A 2.2.6: Longstanding stability of the compound 4.24 at 50 °C analyzed by ^{29}Si NMR in CDCl_3 .

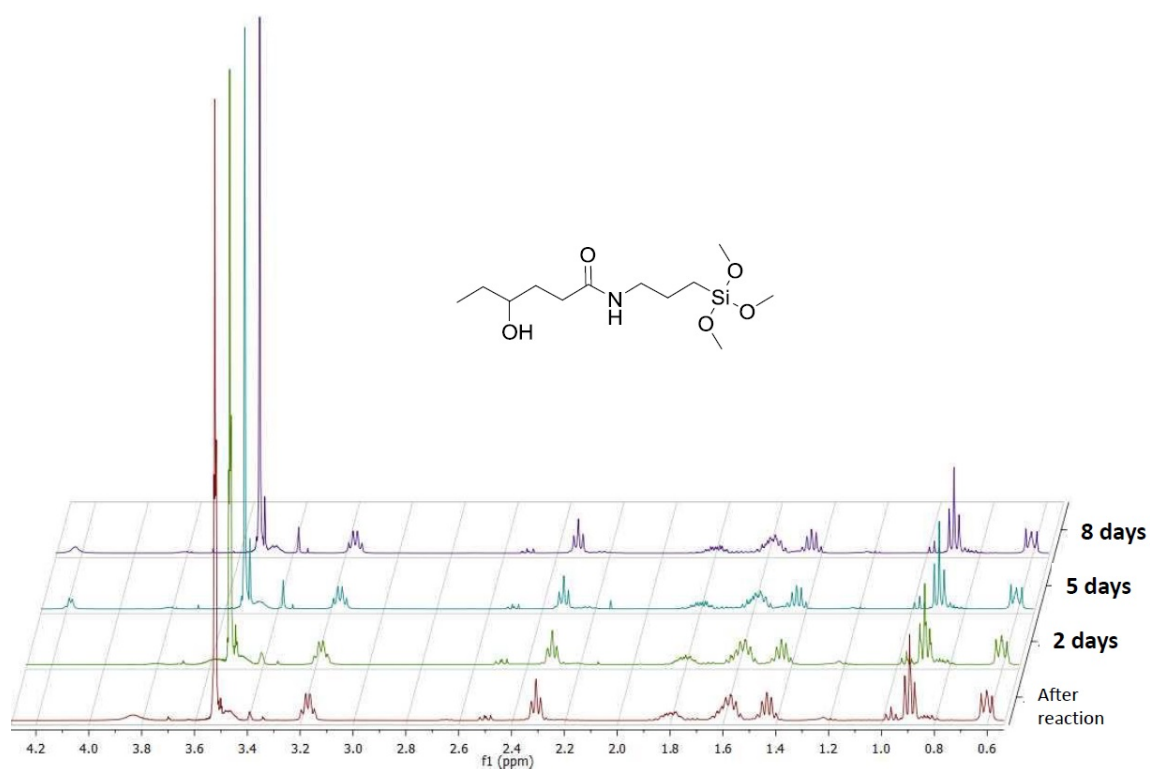


Figure A 2.2.7: Longstanding stability of the compound 4.04 at 50 °C analyzed by ¹H NMR in CDCl₃.

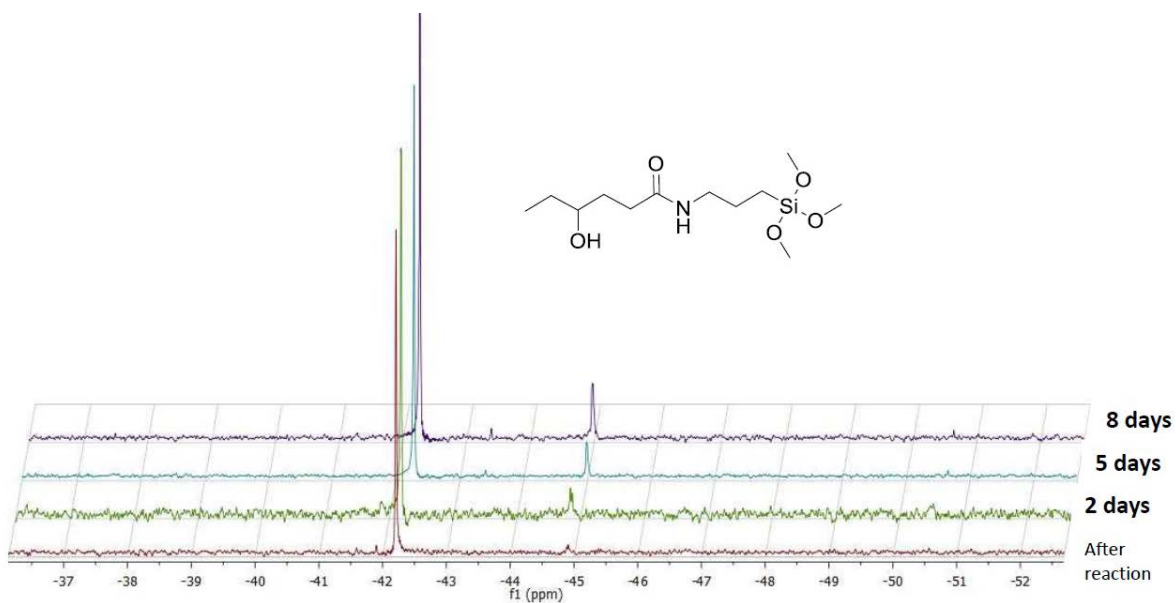


Figure A 2.2.8: Longstanding stability of the compound 4.04 at 50 °C analyzed by ²⁹Si NMR in CDCl₃.

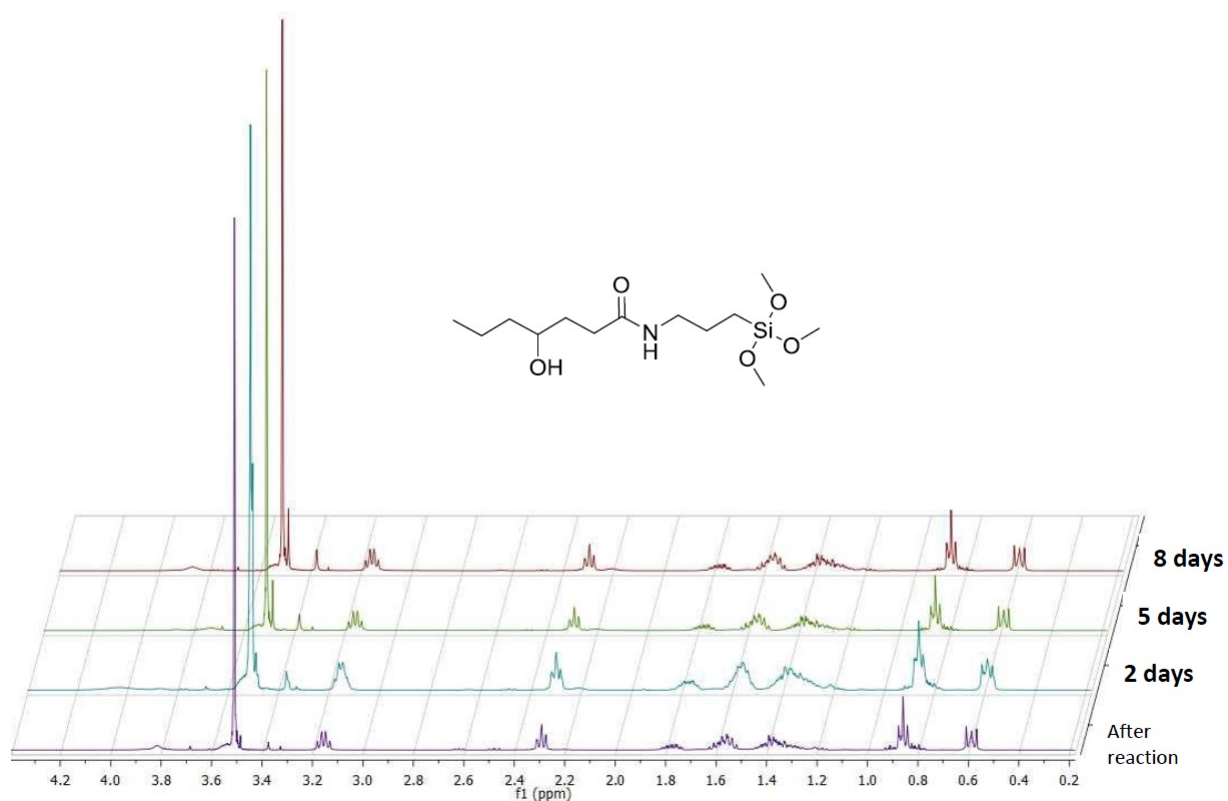


Figure A 2.2.9: Longstanding stability of the compound **4.22** at 50 °C analyzed by ^1H NMR in CDCl_3 .

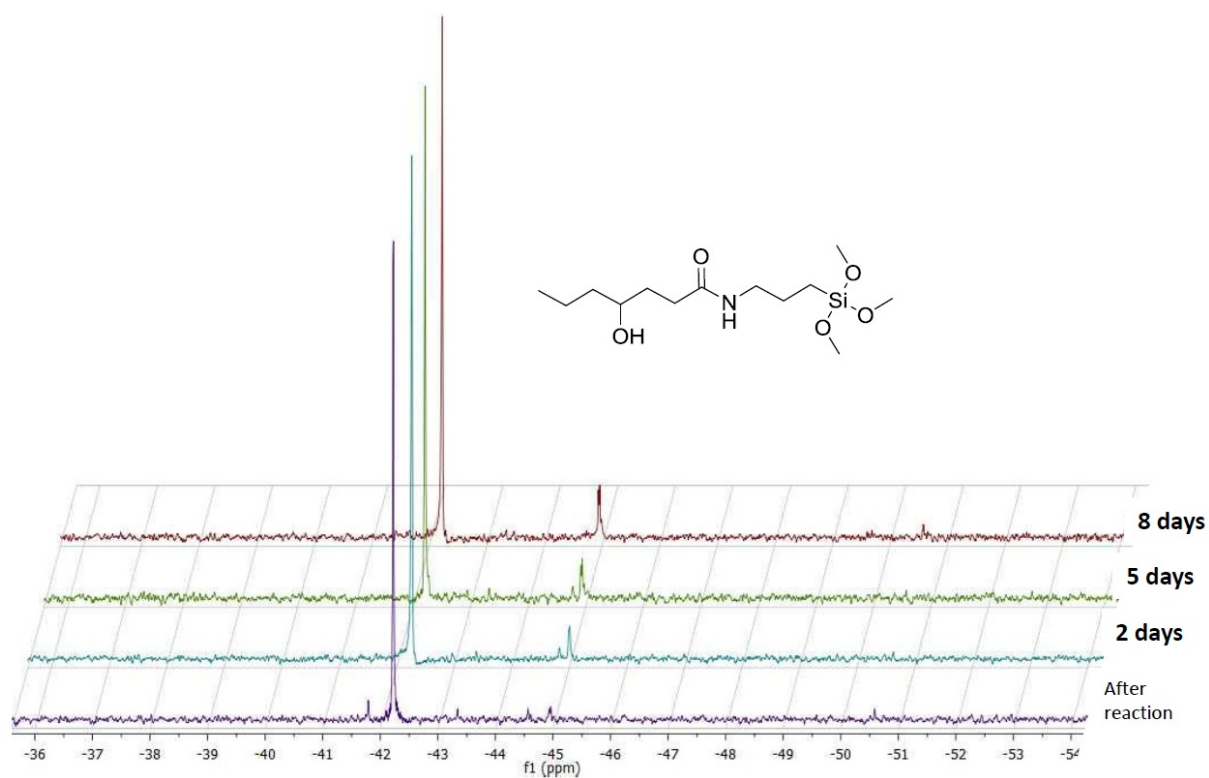


Figure A 2.2.10: Longstanding stability of the compound **4.22** at 50 °C analyzed by ^{29}Si NMR in CDCl_3 .

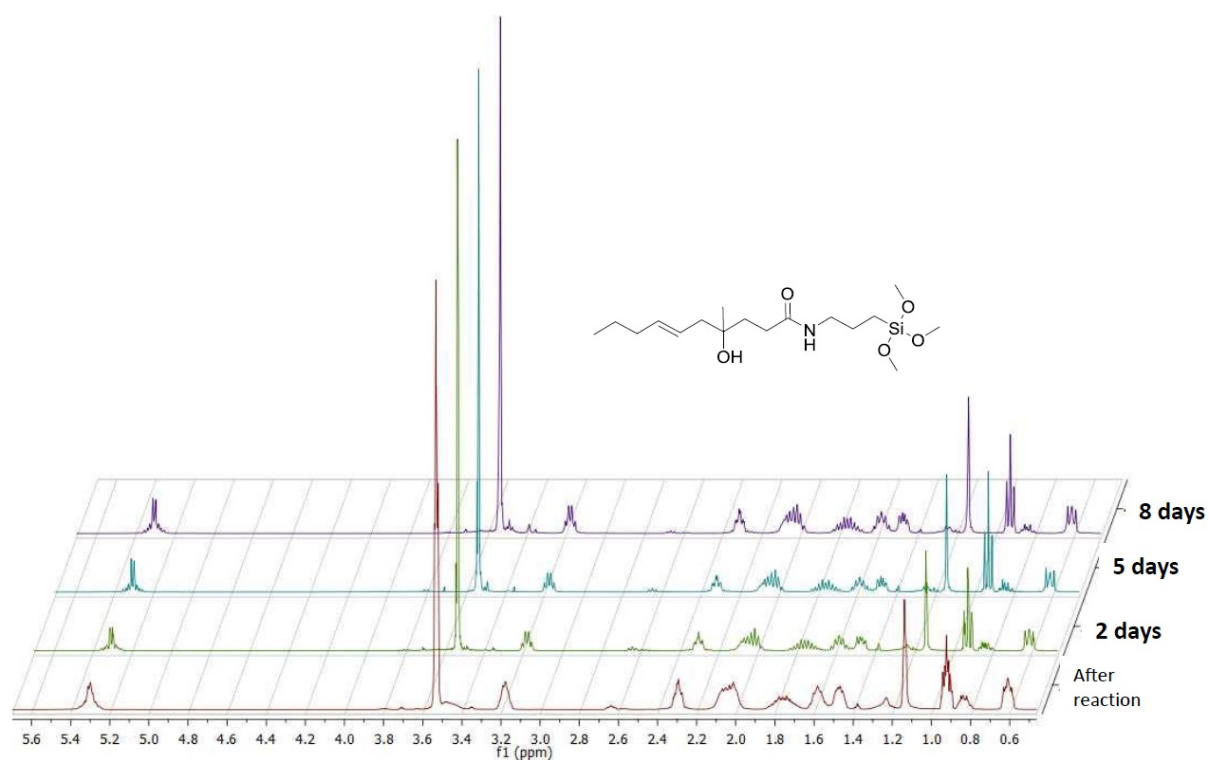


Figure A 2.2.11: Longstanding stability of the compound **4.20** at 50 °C analyzed by ¹H NMR in CDCl₃.

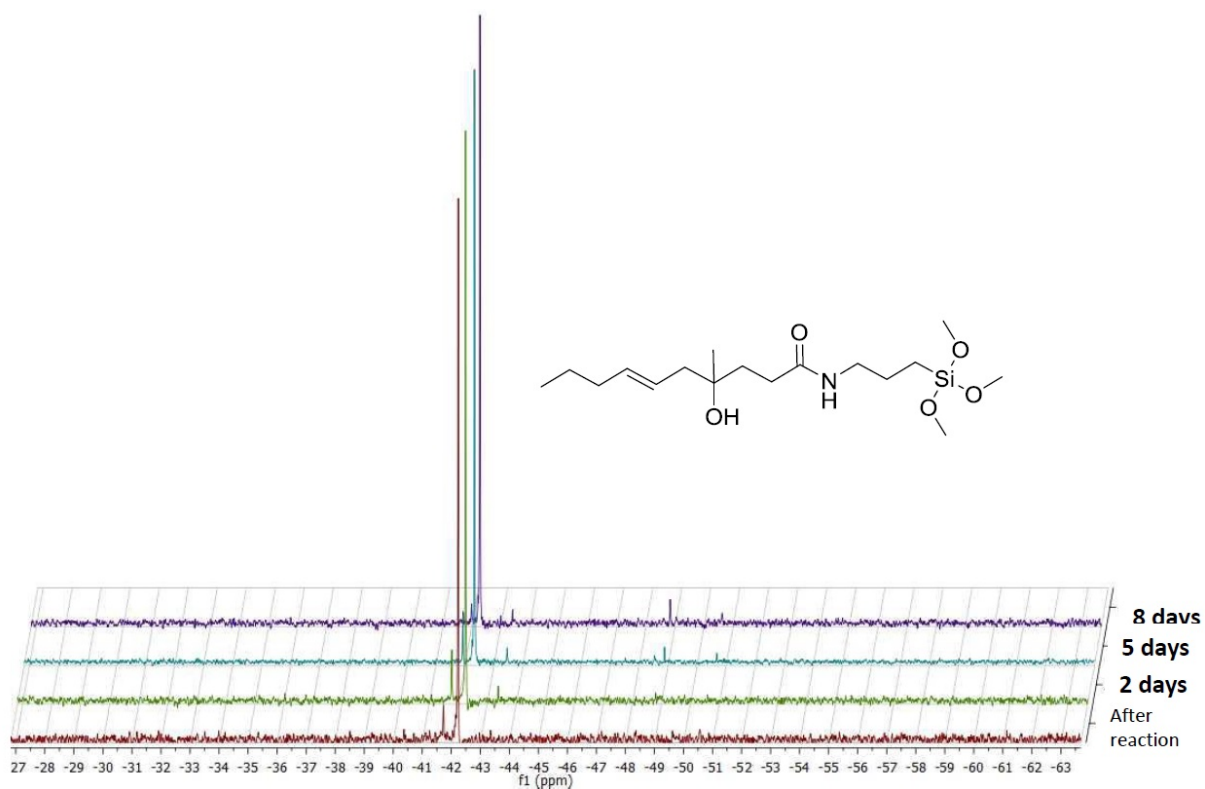


Figure A 2.2.12: Longstanding stability of the compound **4.20** at 50 °C analyzed by ²⁹Si NMR in CDCl₃.

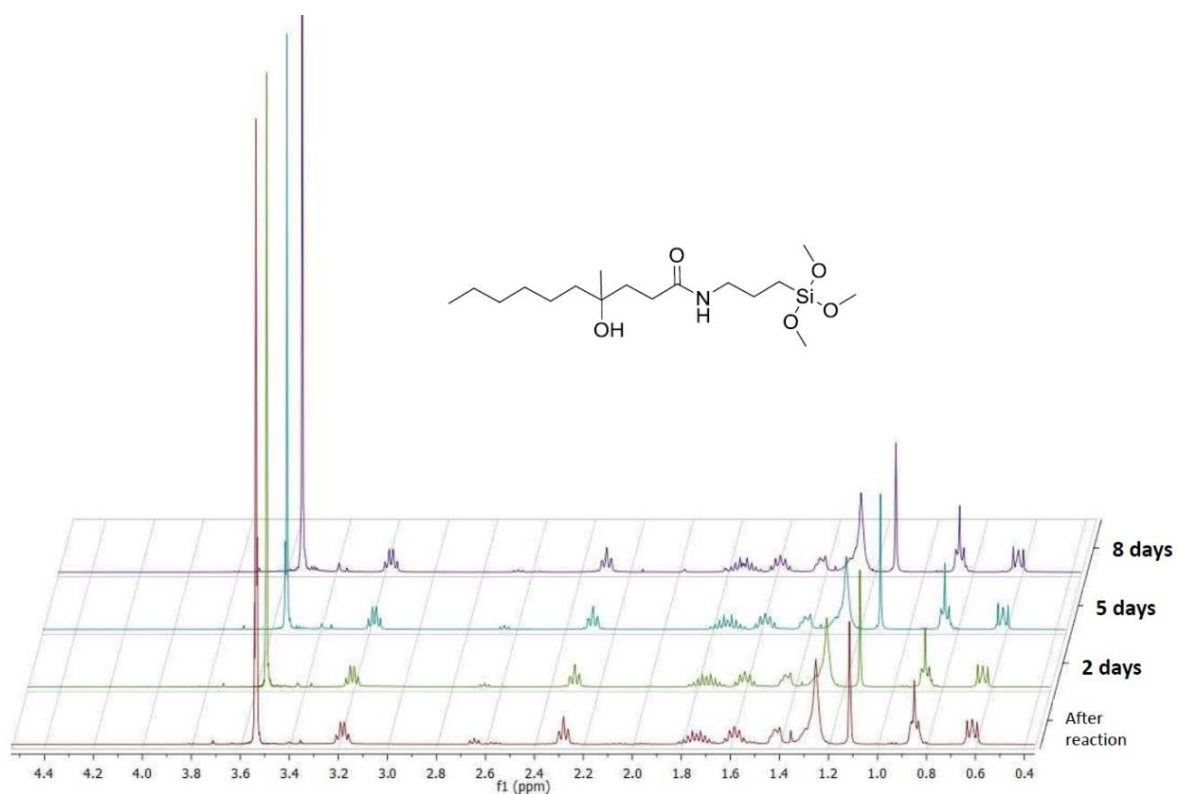


Figure A 2.2.13: Longstanding stability of the compound **4.21** at 50 °C analyzed by ¹H NMR in CDCl₃.

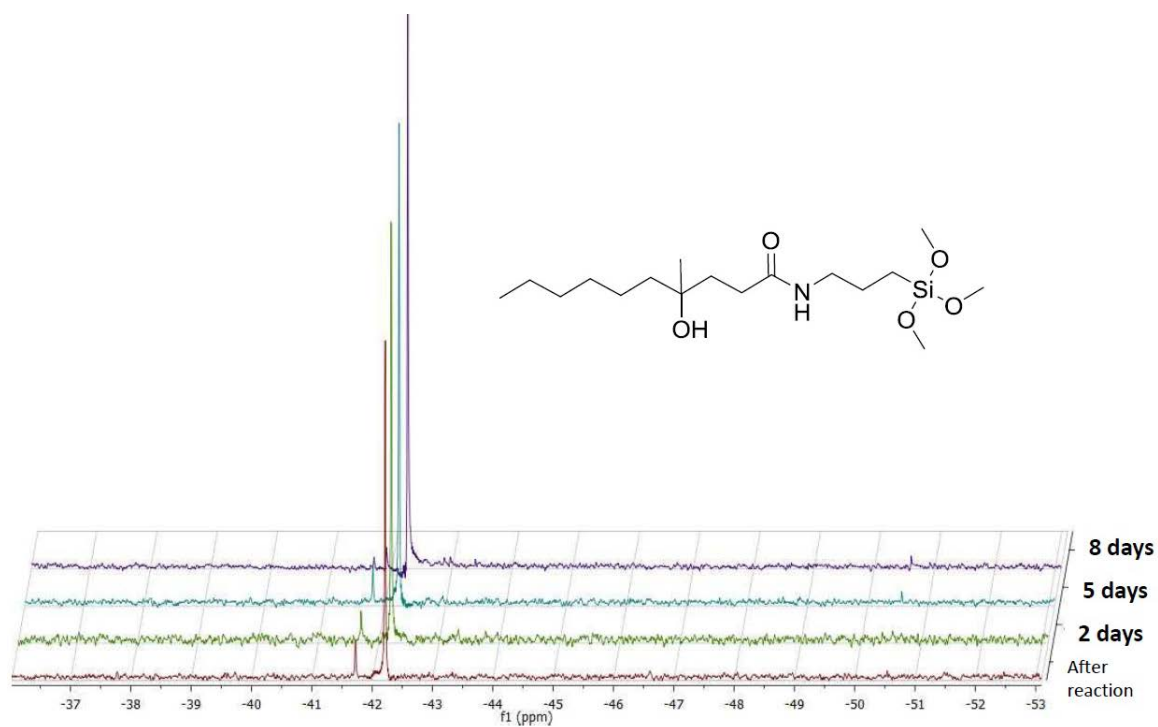


Figure A 2.2.14: Longstanding stability of the compound **4.21** at 50 °C analyzed by ²⁹Si NMR in CDCl₃.

Short standing stability

The hydroxyl functional methoxysilanes were synthesized by optimized procedure using triethylaluminium at 50 °C. The samples were placed in the Schlenk flasks under argon atmosphere, which were stored in an oven at 80 °C for 1 hour. Samples for GC-MS and NMR analysis were withdrawn before and after the stability test. Results are presented in the Figure A 2.2.15 to Figure A 2.2.19.

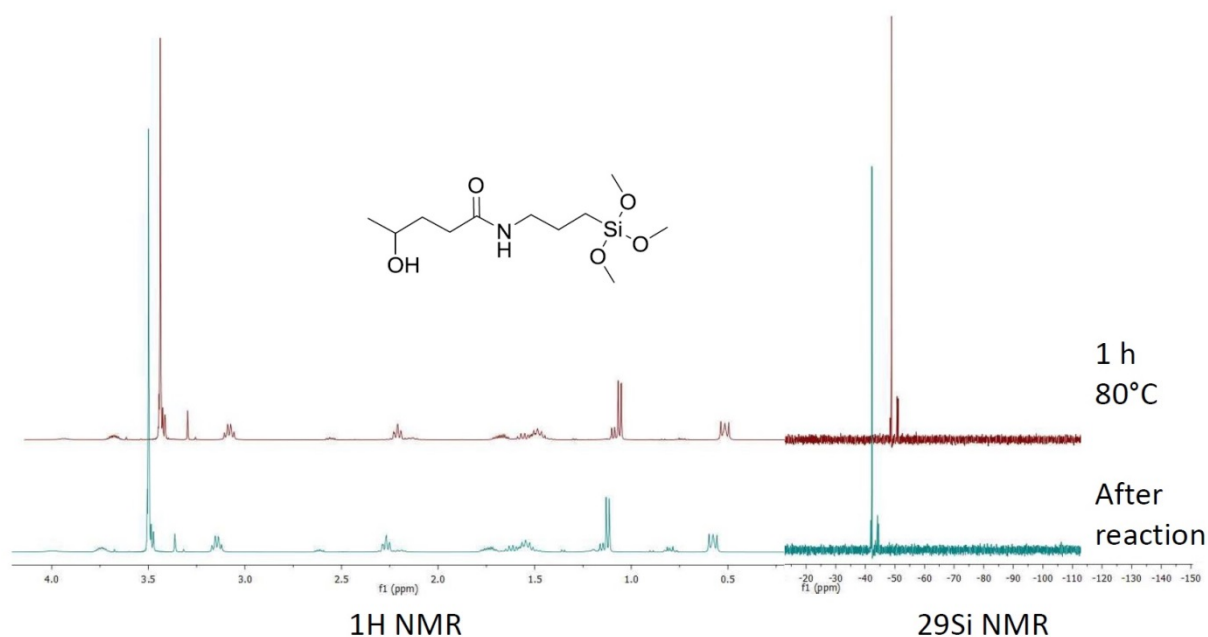


Figure A 2.2.15: Short standing stability of the compound **4.17** at 50 °C analyzed by ¹H and ²⁹Si NMR in CDCl₃.

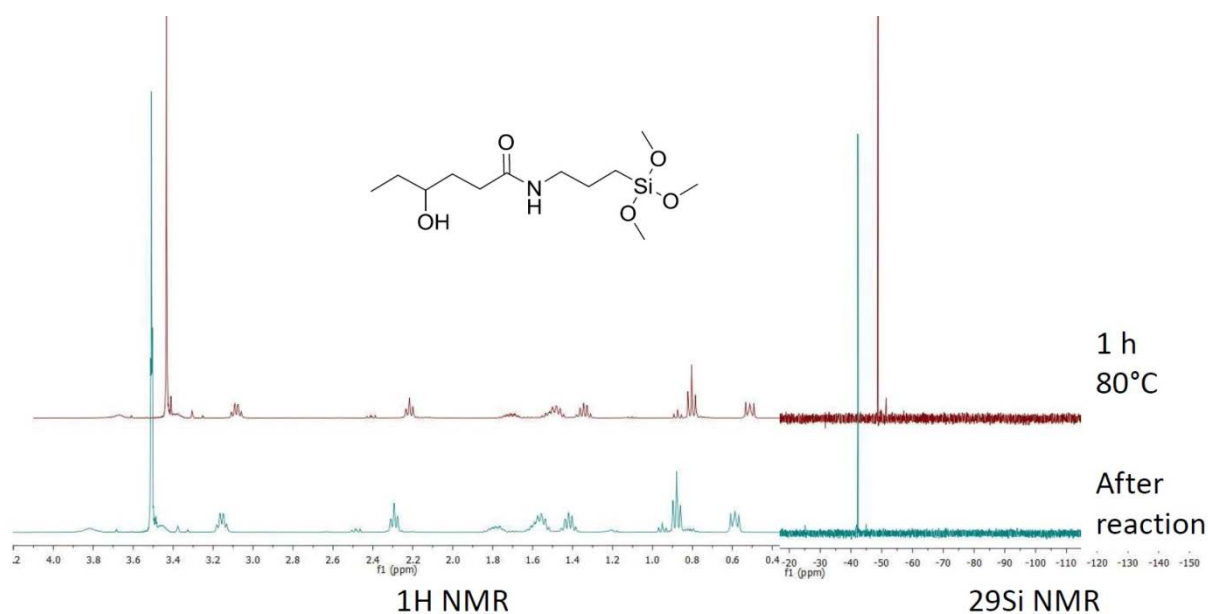


Figure A 2.2.16: Short standing stability of the compound **4.04** at 50 °C analyzed by ¹H and ²⁹Si NMR in CDCl₃.

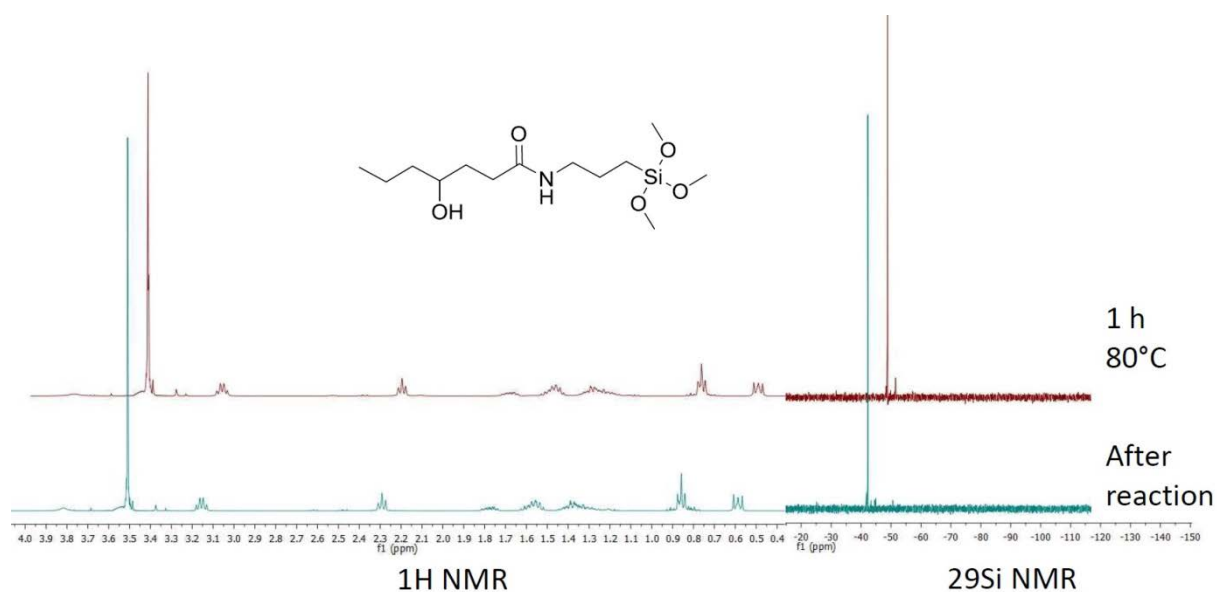


Figure A 2.2.17: Short standing stability of the compound **4.22** at 50 °C analyzed by ¹H and ²⁹Si NMR in CDCl₃.

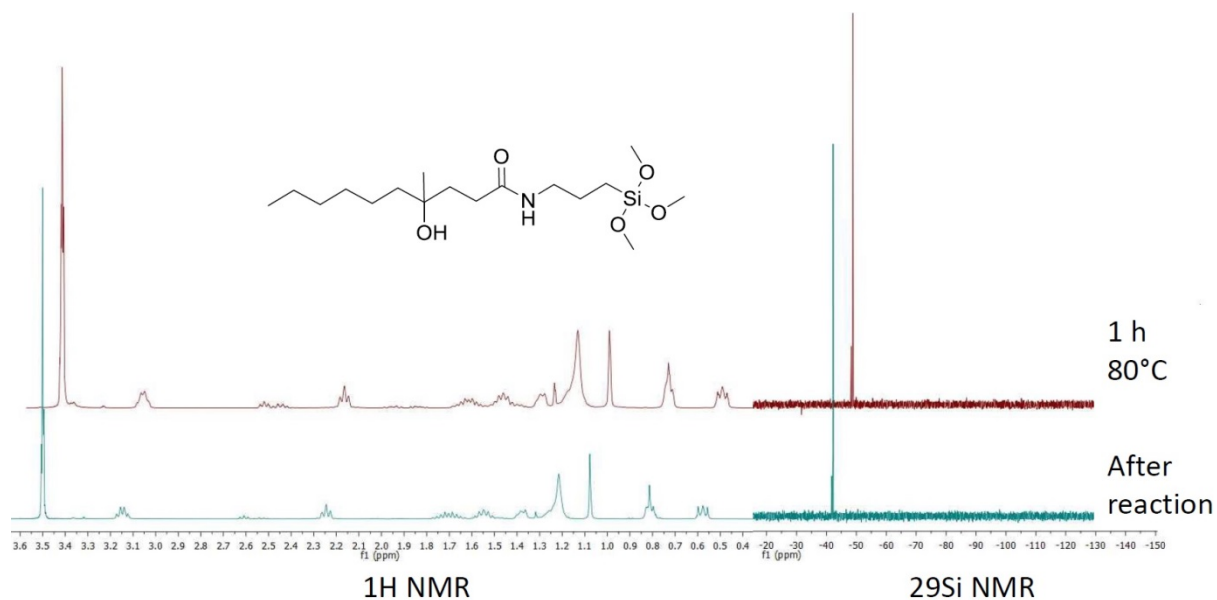


Figure A 2.2.18: Short standing stability of the compound **4.21** at 50 °C analyzed by ¹H and ²⁹Si NMR in CDCl₃.

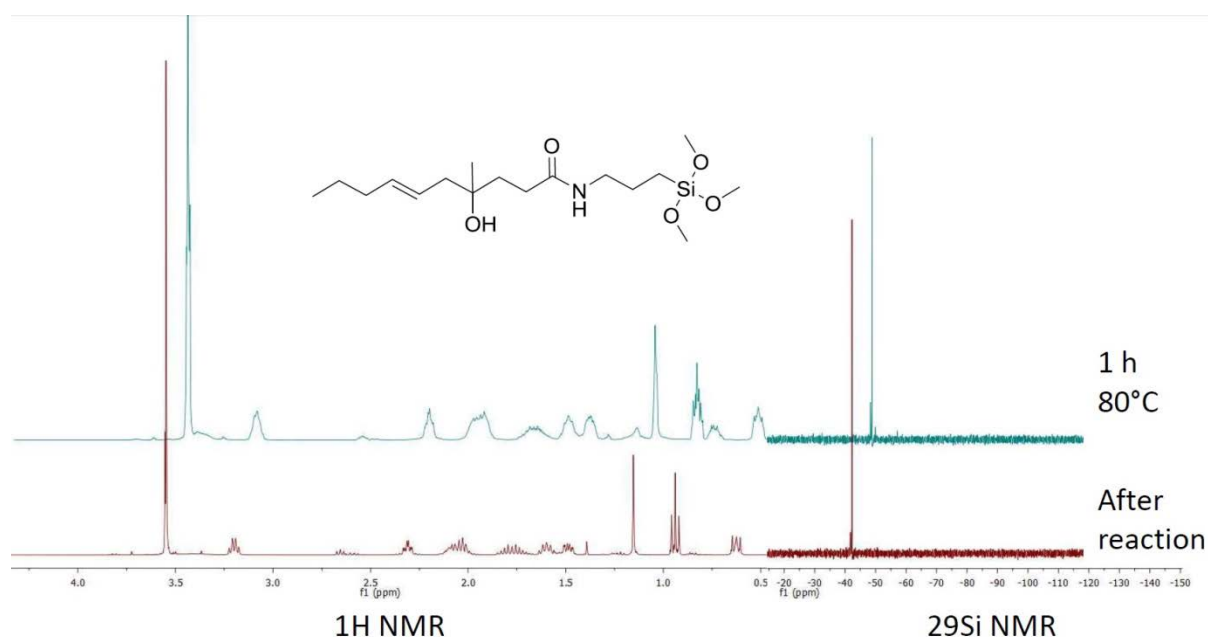


Figure A 2.2.19: Short standing stability of the compound **4.20** at 50 °C analyzed by ^1H and ^{29}Si NMR in CDCl_3 .

A4.5. Kinetic investigation of the side reactions

By analyzing the ^1H and ^{29}Si NMR spectra and with the help of the GC-MS, it was possible to identify the side reactions. The lactamization reaction produces water as a side product, which hydrolyzes alkoxy silane groups leading to oligomerization. Self-dealcoholization reaction is a result of the nucleophilic attack of the hydroxyl group on to the alkoxy silane to form a cyclic silane and alcohol. The extent of both reactions was determined by integrating multiplets in ^1H and ^{29}Si NMR and plotted against time. Afterwards the curves were linearized and the kinetic factors were determined.

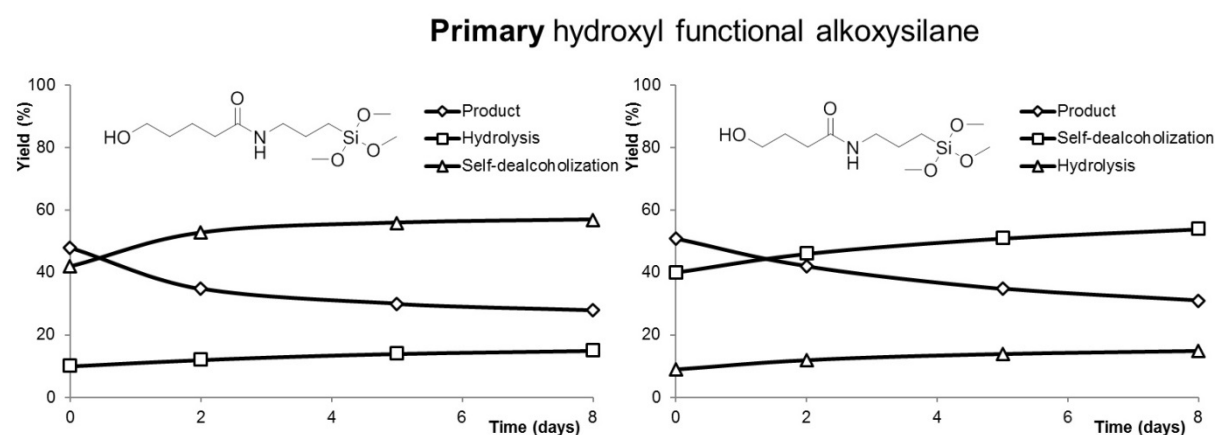


Figure A 2.2.20: Stability testing of the primary hydroxyl functional methoxysilanes over 8 days at 50 °C.

Secondary hydroxyl functional alkoxy silane

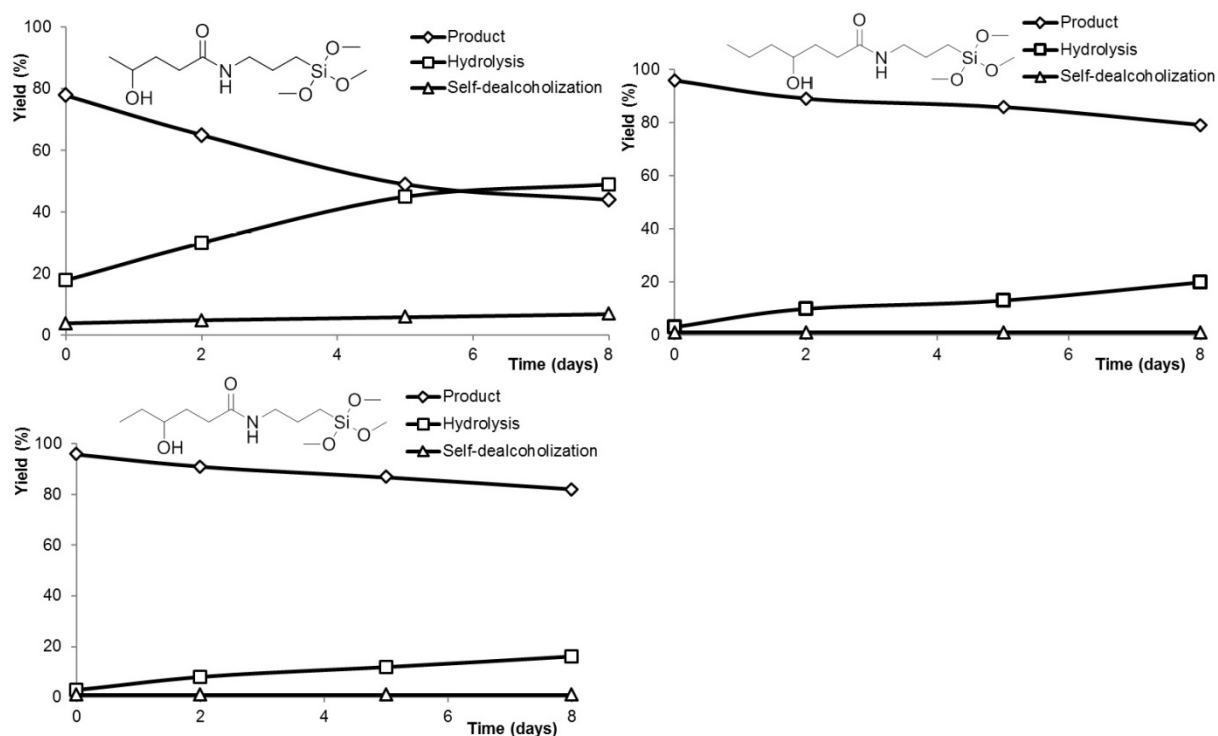


Figure A 2.2.21: Stability testing of the secondary hydroxyl functional methoxysilanes over 8 days at 50 °C.

Tertiary hydroxyl functional alkoxy silane

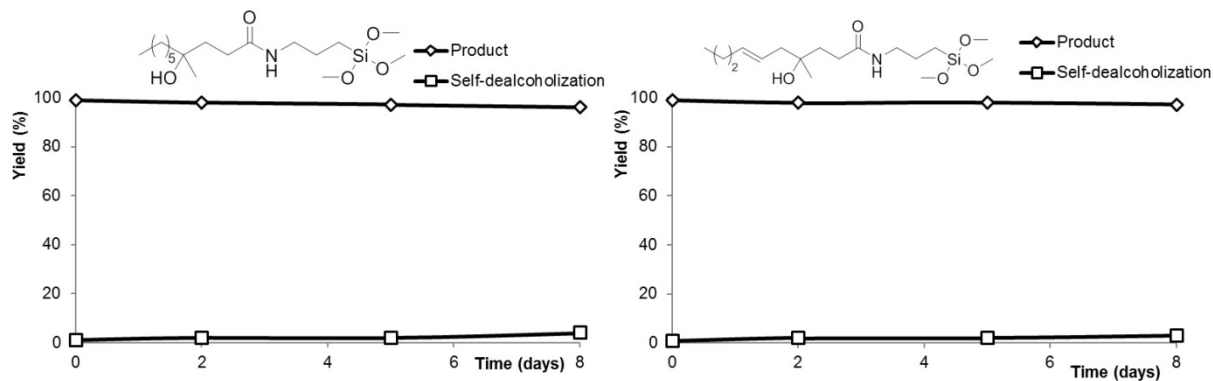


Figure A 2.2.22: Stability testing of the tertiary hydroxyl functional methoxysilanes over 8 days at 50 °C.

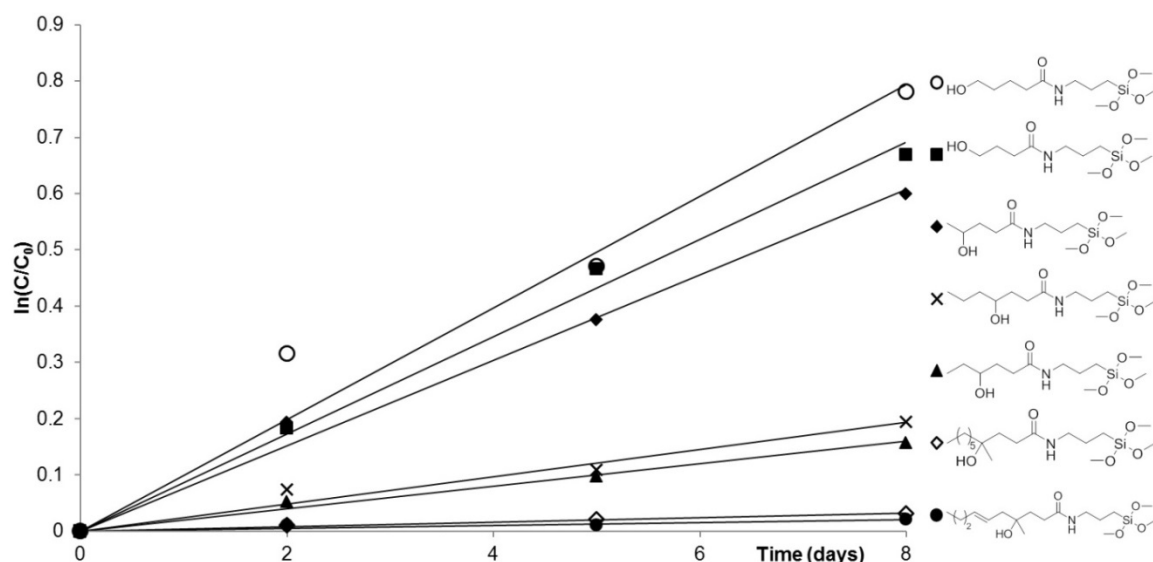


Figure A 2.2.23: Linearized curves of the hydroxyl functional methoxysilane conversion to side products over 8 days at 50 °C.

A4.6. Hydrolytic investigation of hydroxyl functional alkoxy silanes

All ^1H and ^{29}Si NMR spectra for the kinetic studies were obtained at 25 °C using Bruker 250 MHz AVANCE 250 II spectrometer. Hydroxyl functional alkoxy silane (0.3 mmol) was dissolved in 0.5 ml of CD_3CN , to which 0.5 ml of H_2O with 1% HCl was added just before the kinetic evaluation. The experiment was performed according to the procedure described in the chapter A3.2.

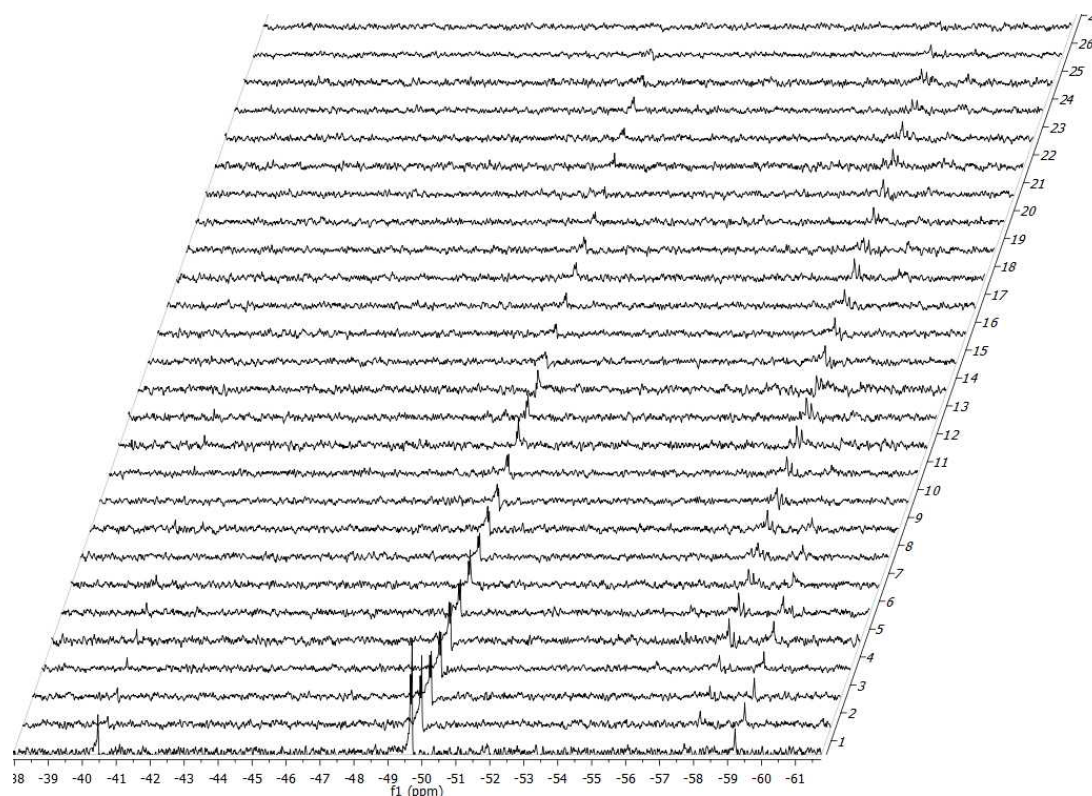


Figure A 2.2.24: Recorded ^{29}Si NMR spectra of AMMO during hydrolysis relative to time (27h).

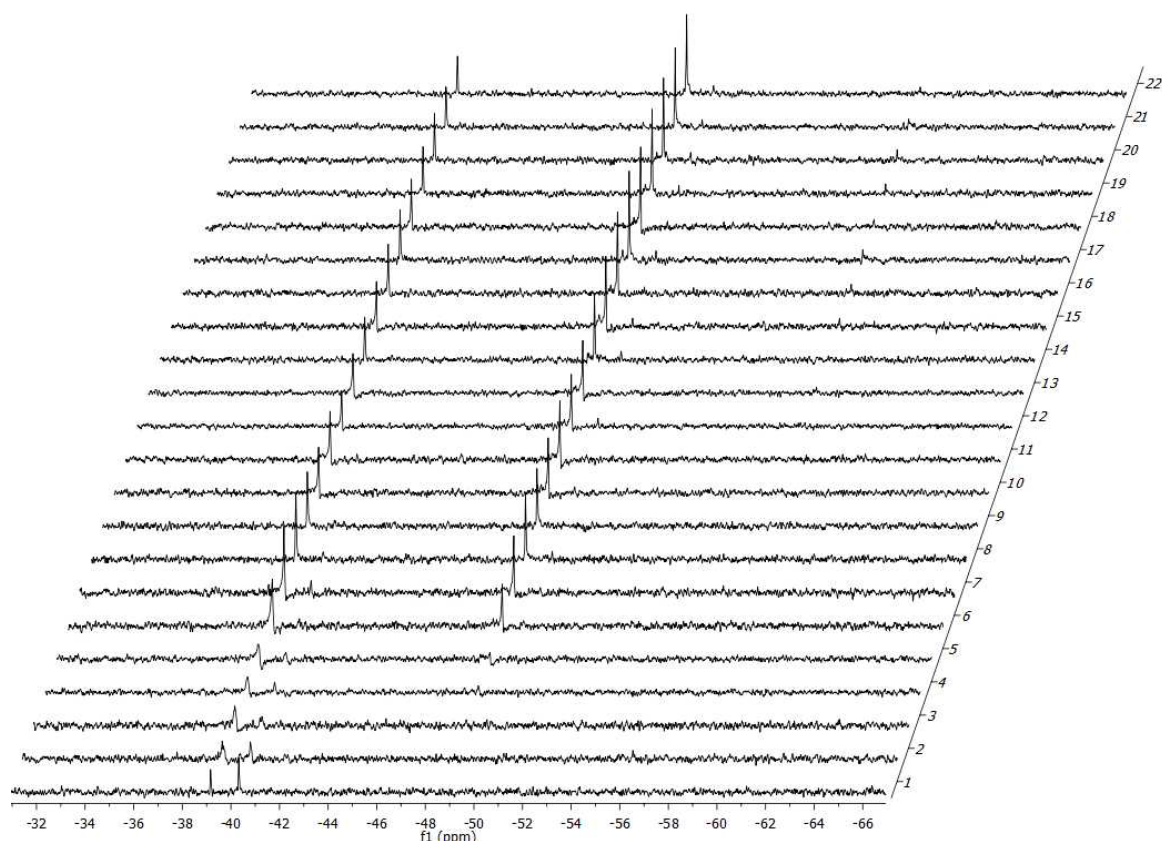
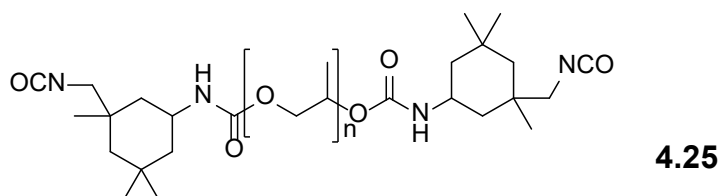


Figure A 2.2.25: Recorded ^{29}Si NMR spectra of the compound **4.21** during hydrolysis relative to time (27h).

A4.7. Prepolymer preparation

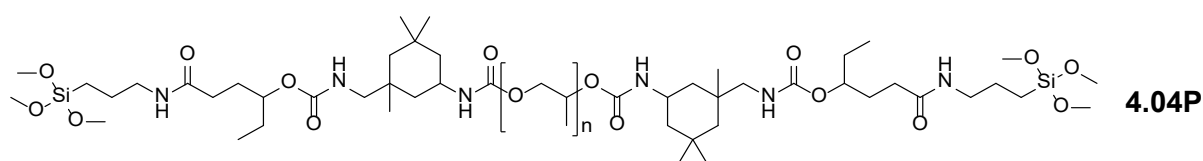
Preparation of the -NCO terminated polymer



Representative procedure G:

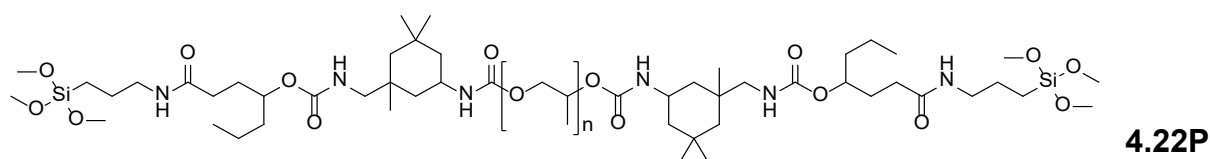
20 g of poly(propylene glycol) (PPG) (Acclaim 12200, 12000 g/mol, 10 ± 1.5 g KOH/g) was added in to the evacuated 50 ml three neck flask equipped with a mechanical stirrer. The temperature was raised to 80 °C during which vacuum was applied for 1 hour. Afterwards 0.87 g (3.9 mmol) of isophorone diisocyanate (IPDI) and 0.06 g (1 mol%) of DOTL were added to the mixture and kept under vigorous stirring for 1 hour. The product **4.25** was analyzed using IR spectroscopy. After the reaction the viscosity was measured to be 53.42 Pas.

IR (ATR, neat, cm^{-1}): 3332.17 (w), 2969.59 (s), 2929.74 (s), 2867.37 (s), 2264.66 (s), 1718.79 (s), 1523.88, (m), 1452.67 (m), 1372.27 (s), 1343.57 (m), 1298.13 (m), 1238.19 (m), 1093.97 (s), 1014.22 (m), 925.76 (m), 864.99 (w), 578.31 (w), 455.15 (w).

Preparation of the 4.04P prepolymer end-capped with 4.04.

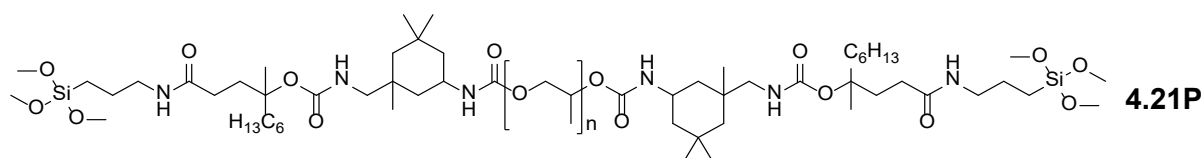
Approximately 22 g of colorless viscous liquid was synthesized by mixing 1.135 (3.9 mmol) g of compound **4.04** and 20.87 g of NCO terminated polymer (**4.25**) prepared according to the representative procedure G for 3 hours at 80 °C. No NCO band was detected by IR spectroscopy, therefore it was concluded that the end-capping reaction is completed. After the reaction the viscosity was measured to be 124.68 Pas.

IR (ATR, neat, cm⁻¹): 3342.68 (w), 2969.64 (s), 2929.94 (s), 2867.47 (s), 1721.80 (m), 1655.4 (w), 1528.60 (m), 1453.09 (m), 1372.25 (s), 1343.30 (m), 1296.91 (m), 1241.23 (m), 1091.88 (s), 1013.38 (m), 925.42 (m), 866.41 (m), 824.39 (m), 662.48 (w), 446.90 (w).

Preparation of the 4.22P prepolymer end-capped with 4.22

Approximately 22 g of colorless viscous liquid was synthesized by mixing 1.190 g (3.9 mmol) of compound **4.22** and 20.87 g of NCO terminated polymer (**4.25**) prepared according to the representative procedure G for 3 hours at 80 °C. No NCO band was detected by IR spectroscopy, therefore it was concluded that the end-capping reaction is completed. After the reaction the viscosity was measured to be 134.26 Pas.

IR (ATR, neat, cm⁻¹): 3334.60 (w), 2969.54 (s), 2930.06 (s), 2867.81 (s), 1719.71 (m), 1649.75 (w), 1530.38 (m), 1453.35 (m), 1372.53 (s), 1343.10 (m), 1298.40 (m), 1240.56 (m), 1092.44 (s), 1014.59 (m), 926.16 (m), 865.46 (m), 821.68 (m), 453.17 (w).

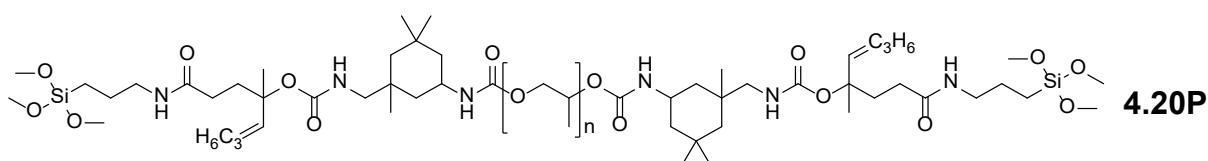
Preparation of the 4.21P prepolymer end-capped with 4.21

Approximately 22 g of colorless viscous liquid was synthesized by mixing 1.405 g (3.9 mmol) of compound **4.21** and 20.87 g of NCO terminated polymer (**4.25**) prepared according to the representative procedure G for 3 hours at 80 °C. No NCO band was detected by IR

spectroscopy, therefore it was concluded that the end-capping reaction is completed. After the reaction the viscosity was measured to be 164.37 Pas.

IR (ATR, neat, cm^{-1}): 3339.43 (w), 2969.57 (s), 2929.92 (s), 2867.03 (s), 1717.27 (m), 1673.42 (m), 1527.27 (m), 1452.95 (m), 1372.32 (s), 1343.18 (m), 1296.87 (m), 1241.65 (m), 1090.25 (s), 1013.30 (m), 866.15 (m), 822.85 (m), 444.50 (w).

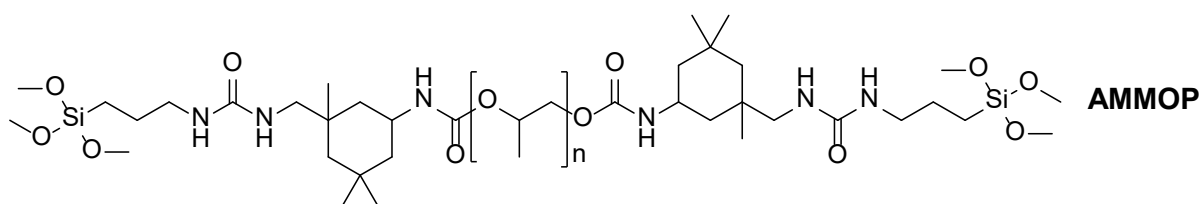
Preparation of the 4.20P prepolymer end-capped with 4.20



Approximately 22 g of colorless viscous liquid was synthesized by mixing 1.395 g (3.9 mmol) of compound **4.20** and 20.87 g of NCO terminated polymer (**4.25**) prepared according to the representative procedure G for 3 hours at 80 °C. No NCO band was detected by IR spectroscopy, therefore it was concluded that the end-capping reaction is completed. After the reaction the viscosity was measured to be 201.24 Pas.

IR (ATR, neat, cm^{-1}): 3350.47 (w), 2969.72 (s), 2930.25 (s), 2867.74 (s), 1718.34 (m), 1638.51 (m), 1560.45 (m), 1454.38 (m), 1372.52 (s), 1343.19 (m), 1298.20 (m), 1086.92 (s), 1013.87 (m), 925.98 (m), 865.83 (m), 820.87 (m), 664.67 (w), 441.08 (w).

Preparation of the silylated prepolymer end-capped with AMMO



Approximately 22 g of slightly yellowish viscous liquid was synthesized by mixing 0.693 g (3.9 mmol) of compound **AMMO** and 20.87 g of NCO terminated polymer (**4.25**) prepared according to the representative procedure G for 3 hours at 80 °C. No NCO band was detected by IR spectroscopy, therefore it was concluded that the end-capping reaction is completed. After the reaction the viscosity was measured to be 624 Pas.

IR (ATR, neat, cm^{-1}): 3351.24 (w), 2969.82 (s), 2930.12 (s), 2867.11 (s), 1718.44 (m), 1640.60 (m), 1557.89 (m), 1453.70 (m), 1372.43 (s), 1343.18 (m), 1296.88 (m), 1242.72 (m), 1094.02 (s), 1013.35 (m), 925.67 (m), 866.46 (m), 824.21 (w), 664.57 (w), 452.02 (w).

A4.7.1. Preparation of the silylated polyurethanes by one-step prepolymer method

20 g of prepolymers (PPG) (Acclaim 12200, 12000 g/mol, 10 ± 1.5 mg KOH/g) was poured in to the evacuated 50 ml three neck flask. The temperature was raised to 80 °C during which vacuum was applied for 1 hour. Afterwards the flask was equipped with mechanical stirrer and 4 mmol g of selected end-capper with 0.06 g (1 mol%) of DOTL were added to the polymer and homogenously mixed. Finally 0.86 g (3.9 mmol) of IPDI was added and stirred at 80 °C for 3 hours. The product was analyzed using IR spectroscopy. After the reaction the viscosity was measured, which is showcased in the Table A 2.2.1.

Table A 2.2.1: Viscosity and the appearance of silylated polyurethanes prepared by one-step prepolymer method

Product structure	Viscosity	Appearance
4.04P	374.32	Slightly turbid viscous liquid
4.22P	376.24	Slightly turbid viscous liquid
4.21P	287.18	Transparent viscous liquid
4.20P	223.69	Slightly yellowish viscous liquid
AMMOP	1183.3	Highly turbid viscous liquid

A4.8. Lap-shear testing of the cured prepolymers

The substrates (except wood) for the lab shear tests were soaked and cleaned with isopropanol before usage. The prepared prepolymers were casted on the substrate 1-2 mm thickness and covered from both sides with the same substrate material. The prepolymers were cured for 2 weeks at 23 °C and atmospheric conditions (relative humidity ca. 40-60 %). After the curing of the prepolymer the specimen was tested according to the DIN EN 1465 standard using the same methodology as previously described in the chapter A3.6.

A4.9. Tensile strength test cured prepolymers

After the curing of the prepolymer the specimen was inserted in to the Zwick machine and tested according to the DIN 53504 standard, as was previously described in the chapter A3.7.

A4.10. Swelling tests

The swelling degree of silylated polyurethanes with toluene films were tested as follows: pre-weighed dry slabs (ca. 5 mm x 5 mm in size) were immersed in toluene, at 25 °C for 4 days.^[199] After immersing, the samples were blotted with laboratory tissue and weighed. The swelling degree (solvent uptake) was expressed as the weight ratio of toluene in the swollen sample:

$$\text{Swelling degree} = \frac{W_S - W_D}{W_S} \left[\frac{g_{\text{solvent}}}{g_{\text{swollen sample}}} \right] \quad (1)$$

where, W_D is the weight of the dry sample and W_S is the weight of the swollen sample.

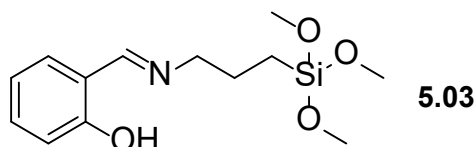
The crosslinking density was calculated as the reciprocal value of swelling degree of the particular sample:

$$\text{Crosslinking density} = \frac{1}{\text{Swelling degree}} \quad [/\quad] \quad (2)$$

A5. Appendix to Chapter 5

A5.1. Preparation of phenol functional silanes

Synthesis of 2-(((3-(trimethoxysilyl)propyl)imino)methyl)phenol



Representative procedure H:

100 ml of benzene and 14.2 g (0.12 mol) of salicylaldehyde were mixed in the evacuated Dean-Stark apparatus. The mixture was brought to the reflux conditions after which 20.8 g (0.12 mol) of **AMMO** was slowly added. The mixture was kept stirring for 3 hours at reflux conditions. Afterwards the solvent was removed via vacuum distillation to afford a product as a yellow liquid. The obtained liquid exhibited 96 % purity and was suitable for further use, however in order to obtain 99 % purity the reaction product was distilled to afford yellow liquid product in 82 % yield.

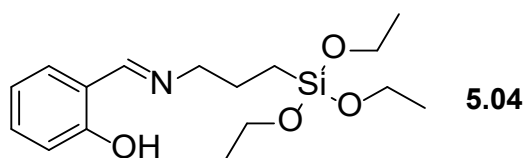
¹H NMR (400 MHz, Chloroform-*d*) δ 13.59 (s, 1H), 8.33 (s, 1H), 7.34 – 7.27 (m, 1H), 7.25 (d, J = 7.7 Hz, 1H), 6.97 (d, J = 8.5 Hz, 1H), 6.90 – 6.85 (m, 1H), 3.59 (s, 9H), 3.58 (m, 2H), 1.91 – 1.76 (m, 2H), 0.75 – 0.70 (t, J = 8.3 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ = 164.9, 161.3, 132.0, 131.1, 118.8, 118.3, 116.9, 61.8, 50.5, 24.1, 6.6.

²⁹Si NMR (79 MHz, CDCl₃) δ = -42.2.

ESI-TOF/MS m/z calcd. for C₁₃H₂₁NO₄Si [M+H]⁺: 284.12734 found: 284.12811.

Synthesis of 2-(((3-(triethoxysilyl)propyl)imino)methyl)phenol



15.4 g (0.047 mol) of yellow liquid was synthesized in 97 % yield according to the representative procedure H, by mixing 10.8 g (0.049 mol) of **AMMO** and 4.1 g (0.049 mol) of salicylaldehyde in Dean-Stark apparatus under reflux for 4 hours.

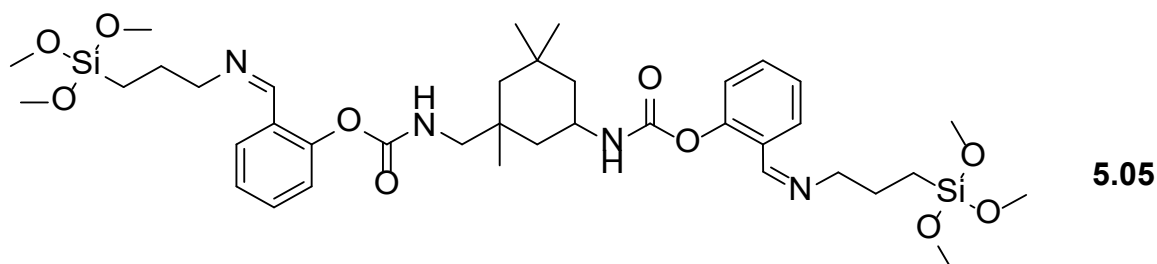
^1H NMR (400 MHz, Chloroform-*d*) δ 13.68 (s, 1H), 8.42 (s, 1H), 7.42 – 7.31 (m, 1H), 7.05 (d, J = 7.7 Hz, 1H), 6.75 (d, J = 8.5 Hz, 1H), 6.73 – 6.66 (m, 1H), 3.81 (q, J = 7.1 Hz, 6H), 3.68 (t, J = 6.8 Hz, 2H), 1.94 – 1.73 (t, J = 7.0 Hz, 9H), 0.79 – 0.68 (t, J = 8.4 Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ = 164.7, 161.3, 133.6, 131.1, 118.7, 118.3, 116.9, 61.4, 58.3, 24.3, 18.2, 7.9.

^{29}Si NMR (79 MHz, CDCl_3) δ = -46.1.

ESI-TOF/MS m/z calcd. for $\text{C}_{16}\text{H}_{27}\text{NO}_4\text{Si}$ $[\text{M}+\text{H}]^+$: 326.17429 found: 326.17101.

Catalyst screening for the reaction between 5.05 and IPDI



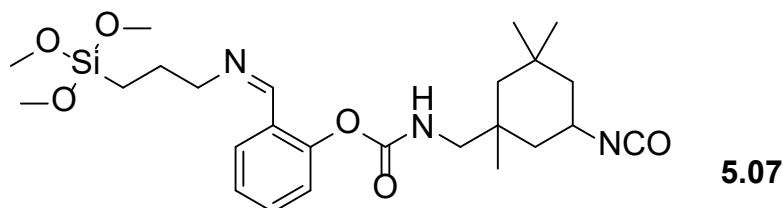
1 g of phenol functional alkoxy silane (**5.05**) was added in to the 25 ml Schlenk flask and heated to desired temperature at which point 0.39 g of **IPDI** and 1 mol% of selected catalyst was added. The reaction mixture was stirred for 16 hours. The obtained product was analyzed by NMR and IR spectroscopy in order to verify the completion of the reaction.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.29 (s, 1H), 7.24 – 7.17 (m, 1H), 6.95 – 6.87 (m, 1H), 6.87 – 6.78 (m, 1H), 3.88 – 3.71 (m, 1H), 3.63 – 3.58 (m, 3H), 3.53 (s, 9H), 2.87 (s, 1H), 2.81 – 2.74 (m, 2H), 2.66 (m, 2H), 1.87 – 1.72 (m, 2H), 1.72 – 1.62 (m, 2H), 1.26 – 1.08 (m, 2H), 1.08 – 0.94 (m, 3H), 0.89 (s, 6H), 0.71 – 0.61 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ = 232.4, 164.7, 160.8, 157.4, 132.0, 131.2, 120.4, 118.8, 118.5, 116.8, 62.0, 54.7, 52.0, 50.5, 39.6, 38.8, 36.4, 35.0, 31.8, 27.6, 24.1, 23.2, 18.3, 6.6.

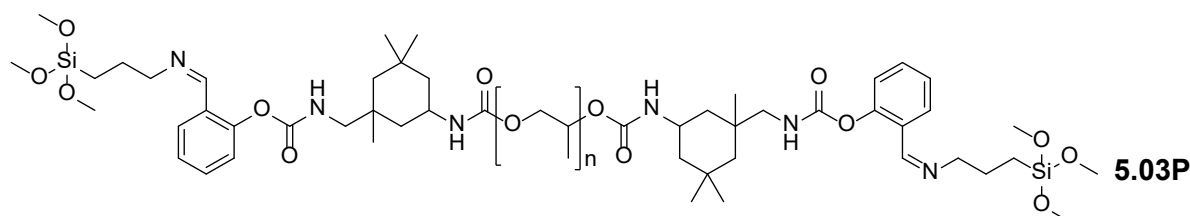
^{29}Si NMR (79 MHz, CDCl_3) δ = -42.2.

IR (ATR, neat, cm^{-1}): 3339.88 (m), 2938.85 (s), 2840.10 (s), 1719.92 (m), 1632.06 (m), 1527.26 (m), 1481.89 (w), 1459.03 (m), 1385.58 (w), 1341.92 (w), 1304.15 (w), 1279.37 (w), 1234.89 (m), 1189.29 (m), 1076.38 (s), 868.14 (w), 814.75 (s), 754.81 (s), 640.09 (w), 444.44 (s).

A5.2. Preparation of the –NCO functional alkoxy silane

1 g (3.5 mmol) of phenol functional alkoxy silane (**5.07**) was added in to the 25 ml Schlenk flask and heated to desired temperature at which point 0.78 g of **IPDI** (3.5 mmol) and 1 mol% DOTL was added. The reaction mixture was stirred for 16 hours. The obtained product was analyzed by IR spectroscopy in order to verify the completion of the reaction. Further analysis of the product by GC-MS, NMR, ESI and GPC did not gave a complete picture of the selectivity between mono- and diaddition of the phenol functional alkoxy silane to the diisocyanate, therefore the investigation was aborted at this point.

IR (ATR, neat, cm^{-1}): 3339.88 (m), 2938.85 (s), 2840.10 (s), 2263.6 (m), 1719.95 (m), 1632.07 (m), 1527.23 (m), 1481.92 (w), 1459.05 (m), 1385.61 (w), 1341.89 (w), 1304.11 (w), 1279.17 (w), 1234.79 (m), 1189.19 (m), 1076.38 (s), 868.14 (w), 814.77 (s), 754.80 (s), 640.01 (w), 444.42 (s).

A5.3. Prepolymer preparation**Preparation of the silylated prepolymer end-capped with 5.03**

Approximately 12 g of colorless viscous liquid was synthesized by mixing 1.415 g (5 mmol) of compound **5.03** and 11.11 g of NCO terminated polymer (**5.07**) prepared according to the **Representative procedure E** for 16 hours at 70 °C. An NCO band was detected by IR spectroscopy, therefore it was concluded that the end-capping reaction is not completed. After the reaction the viscosity was measured to be 16.69 Pas.

IR (ATR, neat, cm^{-1}): 3340.88 (m), 2969.71 (m), 2930.35 (m), 2867.81 (m), 2265.83 (m), 1719.64 (m), 1633.08 (m), 1525.35 (m), 1455.21 (m), 1372.47 (s), 1343.07 (m), 1298.69 (m), 1280.47 (w), 1238.83 (m), 1086.92 (s), 1014.07 (m), 926.07 (m), 867.27 (m), 821.47 (m), 757.80 (m), 640.00 (w), 447.45 (w).

Preparation of the silylated prepolymer end-capped with the combination of **5.03** and **AMMO**

Approximately 12 g of yellow viscous liquid was synthesized by mixing a desired amount of compound **5.03** and 11.11 g of NCO terminated polymer (**5.07**) prepared according to the representative procedure E for 16 hours at 70 °C. Afterwards the remaining **AMMO** was added to react remaining NCO groups. No NCO band was detected by IR spectroscopy, therefore it was concluded that the end-capping reaction is completed. After the reaction the viscosity was measured and the skin over time (SOT) was determined, which is presented in the Table A 2.2.1.

Table A 2.2.1: Viscosity and SOT of the prepolymers synthesized with the different ratios of **AMMO** : **5.03** end-cappers

Entry	Ratio		Viscosity (Pas)	SOT (h)
	AMMO	5.03		
1	0	100	12.65	54
2	20	80	16.96	36
3	40	60	27.41	24
4	60	40	53.75	22
5	80	20	65.02	20
6	100	0	100.32	10

A5.4. Lap-shear testing of the cured prepolymers

The substrates (except wood) for the lab shear tests were soaked and cleaned with isopropanol before usage. The prepared prepolymers were casted on the substrate 1-2 mm thickness and covered from both sides with the same substrate material. The prepolymers were and cured for 3 weeks at 23 °C and atmospheric conditions (relative humidity ca. 40-60 %). After the curing of the prepolymer the specimen was tested according to the DIN EN 1465 standard using the same methodology as previously described in the Chapter A3.6.

A5.5. Tensile strength test cured prepolymers

After the curing of the prepolymer, a proper shape of the specimen was inserted in to the Zwick machine and tested according to the DIN 53504 standard, as was previously described in the Chapter A3.7.

8. Curriculum Vitae

Rok Brisar,
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18055 Rostock,
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Education:

- | | |
|------------------|---|
| 01.2015- 12.2017 | PhD
University of Rostock, Leibniz Institute for Catalysis (LIKAT),
Rostock, Germany. |
| 09.2012-11.2015 | Master's degree in Chemical engeneering,
University of Ljubljana,
Ljubljana, Slovenia. |
| 09.2009-11.2012 | Bachelor's degree in Chemical engeneering,
University of Ljubljana,
Ljubljana, Slovenia. |

Awards and Achievements:

- | | |
|-----------------|--|
| 10.2014 | Freshhh 2014 , MOL Group, participation,
Ljubljana, Slovenia (International) |
| 09.2014 | Henkel Innovation Challenge , final,
Düsseldorf, Germany. |
| 06.2014 | Henkel Innovation Challenge , 1. Place,
Ljubljana, Slovenia. |
| 09.2012-11.2014 | Scholarship for talented students , Group Lasko,
Ljubljana, Slovenia. |

Work Experience:

- | | |
|-----------------|---|
| 03.2011-12.204 | Research Assistant , Institute Jozef Stefan,
Ljubljana, Slovenia. |
| 06.2006-06.2010 | Production Assistant , Renault Nissan Slovenia,
Novo mesto, Slovenia. |

Conferences and Workshops:

- 06.11.2017 **N² Science Communication Conference**, Berlin, Germany.
R. Brisar, D. Hollmann, E. Mejia.
Metal-free Amine Oxidation by Using Pyrazine Radical Cations
- 29.08.2016 **8th European Silicon Days**, Poznan, Poland.
R. Brisar, E. Mejia, U. Kragl.
"Preparation of stable hydroxyl functional alkoxysilanes by lactone ring opening; a kinetic study" (Poster presentation)
- 20.07.2015 **Liverpool Summer School in Catalysis**, RSC, Liverpool, England.
R. Brisar, E. Mejia, U. Kragl.
"Process development for copolymerization of CO₂ and propylene oxide using Cr(III)(salen)Cl" (Poster presentation)
- 07.07.2014 **Bioinspired Materials for Solar Energy Utilization**, Esrasmus intensive programme, Crete, Greece.
R. Brisar, L. Wibmer, C. Legendre.
"Solar driven reduction of CO₂" (Oral presentation)

Publications:

R. Brisar, D. Hollmann, E. Mejia, *Eur. J. Org. Chem.*, 2017, DOI: 10.1002/ejoc.201700949
"Pyrazine Radical Cations as a Catalyst for the Aerobic Oxidation of Amines"

R. Brisar, E. Mejia, J. Damke, J. Klein, Patent app. num. 17182578.9, European patent office, priority date 21.07.2017.
"Curing composition based on SMP with cyclic alkoxysilanes"

R. Brisar, E. Mejia, J. Damke, J. Klein, Patent app. num. 17182575.5, European patent office, priority date 21.07.2017.
"Method for preparing silicon-containing heterocycles"

R. Brisar, E. Mejia, U. Kragl, J. Damke, J. Klein, Patent app. num. 17167870.9, European patent office, priority date 25.04.2017.
"Silane Coupling Agents"