# Ring-opening Polymerization of Siloxanes with Nitrogen Containing Bases

Dissertation

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____________________________

(Theresia Köhler)

:

*“Cuiusvis hominis est errare,*

*nullius nisi insipientis in errore perseverare.“*

Cicero, Philippica 12, 2

*“When everything seems to be going against you,*
*remember that the airplane takes off against the wind,*
*not with it.“*

Henry Ford (1863 – 1947)

# Acknowledgements

> *„Eine wissenschaftliche Entdeckung ist nie die Arbeit von nur einer Person."*
> *(A scientific discovery never is the work of a single person only.)*
> Louis Pasteur (1822 - 1895)

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# Abstract

The anionic ring-opening polymerization (AROP) of cyclosiloxanes is one important route for synthesizing polyorganosiloxanes and several different initiators are well known. Recently, metal-free organocatalysts like phosphazenes, N-heterocyclic carbenes or guanidines are in focus of research. In the scope of this work especially N-Heterocyclic carbenes as well as amines, amidines and guanidines were investigated as suitable initiators and co-initiators respectively.

Focusing especially on 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) a new polymerization process is established, where AROP is taking place in a mechanical stabilized non aqueous emulsion. Regarding this, we were able to confirm the polymerization mechanism for octamethylcyclotetrasiloxane ($D_4$) proposed in the literature, which includes the use of an alcohol as co-initiator. Furthermore, we identified different side reactions which are taking place under ROP conditions leading to α-, ω-di(methoxydimethylsilyl)PDMS.

Furthermore parameters influencing the course of polymerization like reaction temperature, amount of co-initiator and solvent as well as nature of the alcohol were investigated. Additionally it was tried to target molecular weight by adjusting the concentration of alcohol, water or silanol.

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# List of Abbreviations

| | |
|---|---|
| AN | acceptor number |
| AROP | anionic ring-opening polymerization |
| CMC | critcal micelle concentration |
| CROP | cationic ring-opening polymerization |
| $D_3$ | hexamethylcyclotrisiloxane |
| $D^F_3$ | 1,3,5-tri(3,3,3-trifluoropropyl-)-1,3,5-trimethylcyclotrisiloxane |
| $D^R_3$ | organocyclotrisiloxane |
| $D_4$ | octamethylcyclotetrasiloxane |
| $D^R_4$ | organocyclotetrasiloxane |
| $D_5$ | decamethylcyclopentasiloxane |
| $D_6$ | dodecamethylcyclohexasiloxane |
| $D_7$ | tetradecamethylcycloheptasiloxane |
| $D_x$ | cyclosiloxane |
| DBU | 1,8-diazabicyclo[5.4.0]undec-7-ene |
| DN | donor number |
| DOTL | dioctyltinlaureate |
| DVS | 1,3-divinyl-1,1,3,3-tetramethyldisiloxane |
| ESI | electron spray ionization |
| ET(30) | Dimroth-Reichardt solvent parameter |
| GC | gas chromatography |
| GPC | gel permeation chromatography |
| HMBC | heteronuclear multiple bond correlation |
| HMDS | hexamethyldisiloxane |
| HOTf | Trifluoromethane sulfonic acid (also referred to as triflic acid) |
| HTV | high temperature vulcanization |
| iPrOH | *iso*-propanol |
| IUPAC | international union for pure and applied chemistry |
| KHMDS | potassium hexamethyldisilazide |
| KOtBu | potassium tert-butanolate |
| MALDI | matrix assisted laser desorption ionization |
| MeOH | methanol |

| | |
|---|---|
| MM | disiloxane |
| $M_n$ | number averaged molecular weight |
| MS | mass spectroscopy |
| MTBD | 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene |
| $M_w$ | weight averaged molecular weight |
| n-BuOH | butan-1-ol |
| NHC | N-heterocyclic carbenes |
| NMR | nuclear magnet resonance spectroscopy |
| O/W emulsion | Ooil in water emulsion |
| P4-*t*Bu | 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]-2λ5,4λ5-catenadi(phosphazene) |
| PDI | polydispersity index |
| PDMS | polydimethylsiloxane |
| ROP | ring-opening polymerization |
| RTV | room temperature vulcanization |
| RTV-I | one component room temperature vulcanization |
| RTV-II | two component room temperature vulcanization |
| $^{29}$Si(IG)-NMR | inversed gated silicon NMR |
| TBD | 1,5,7-triazabicyclo[4.4.0]dec-5-ene |
| *t*-BuOH | 2-methylpropan-2-ol (also referred to as *tert*-butanol) |
| TfSi-H | trifluoromethanesulfonimide |
| THF | tetrahydrofurane |
| TMDS | 1,1,3,3-tetramethyldisiloxane |
| TMSOC | 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane |
| TMSOH | trimethylsilanol |
| TOF | time of flight |
| W/O emulsion | water in oil emulsion |

# 1 Introduction and Scope of Work

> *"The artificial compounds that have created many new products are the offspring of the marriage of organic to inorganic chemistry."*
>
> Eugene G. Rochow (1909 – 2002)

## 1.1 General introduction and problem

Silicone materials are inorganic polymers whose chains are characterized by alternating silicon and oxygen atoms which might be linear or branched (Figure 1-1). They represent an important material class with special properties compared to common organic materials.[1]

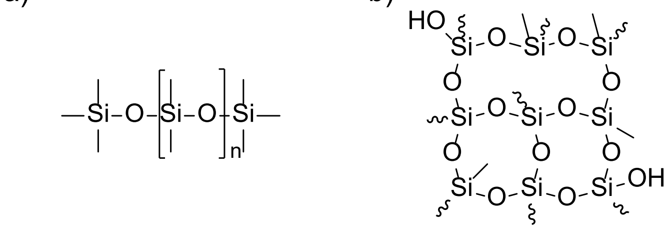


**Figure 1-1: Exemplary structures of silicone materials a) linear polydimethylsiloxane (PDMS) and b) highly branched hydroxy functional silicone resin.**

They are used in the areas of automotive industry, construction materials, electronics, healthcare, personal care as well as in industrial processes. Due to their special properties they are widely used in many different applications such as insulating materials, spreading agents, defoamers, parting agents, implants, drug delivery systems, adhesives and sealants. Most of them are polymerized siloxanes or based on crosslinked derivatives thereof.[2-4]

The term "silicone" was embossed by Frederick S. Kipping[5] who studied silicon and its compounds at the beginning of the 20th century. He called the resin-like materials which he obtained "silicon ketones". Because of their limited variety and the limited possibilities in their reaction Kipping did not foresee any application.[6-7] James F. Hyde produced silicone resins for impregnating and coating glass in the 1930ies building on Kipping's work.[8-9]

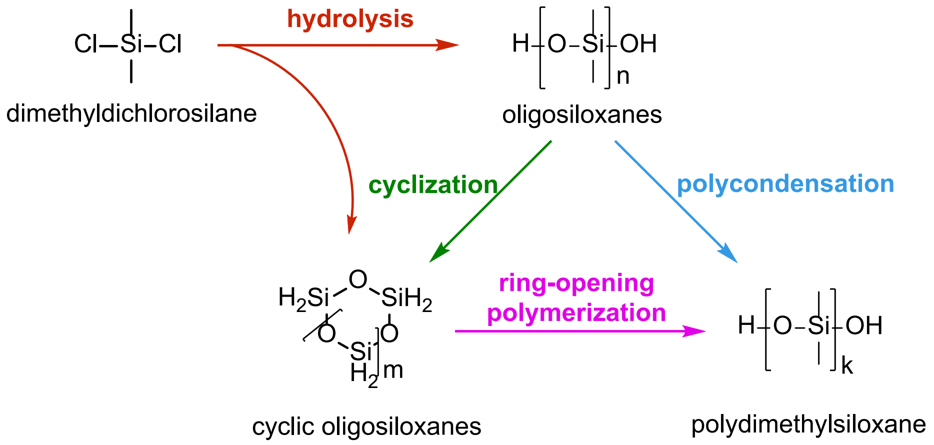
Before the development of the direct synthesis of organohalosilanes[10-11] – also known as Müller-Rochow process – in the 1940ies availability of the raw materials was limited to silica and mineral silicates and lead to a very slow development of the silicone chemistry.[6]

Since then silicones are produced in industrial scale and a fast development of this material class was possible.

Thereby the sale increased strongly first in USA but shortly after also worldwide.[12] In 2008 480000 t/a of basic silicone products were produced by the biggest European silicone producing companies.[13] In 2011 the worldwide production of silicones was around 7.3 million t/a and was increased to 7.4 million t/a in 2017.[14] Other market researches state an increase in sales of approximately 5%/a until 2019[15] or approximately 4%/a until 2024[16]. This indicates a growing demand on basic siloxane products and a constant innovation potential in this area.

One of the basic siloxane products besides cyclic siloxanes or short chained siloxanes are linear polyorganosiloxanes, mainly polydimethylsiloxanes (PDMS). There already exist a lot of processes to obtain these linear polymers and still new processes are being developed.[17-30]

Principally, they are synthesized by hydrolysis and condensation reactions or by ring-opening polymerization (Scheme 1-1).



**Scheme 1-1: Possible synthesis routes for polydimethylsiloxanes starting from dimethyldichlorosilane.**

The synthesis via condensation is not well controlled and leads to broad polydispersities of the obtained polymers. In contrast, via ring-opening polymerization (ROP) of cyclic siloxanes, which also represents the main pathway in industry, silicones with tailored molecular weights can be obtained in a very controlled way. The variety of suitable initiators, end-blocking agents, additives, reaction set up etc. is broad.[31-32] Especially for the anionic ring-opening polymerization new initiators were invented in the past years. Potassium hydroxide which is one of the earliest initiators[22] can be replaced by metal-free initiators such as tetraethylammonium or tetraethylphosphonium compounds and phosphazene bases.[32] Latest research deals with nitrogen containing bases such as N-heterocyclic carbenes[33], bycyclic guanidines[34] or phosphatranes[35].

Still, problems like unfavored side reactions leading to a breakdown of the polymer chain or the termination of the chain in order to gain telechelic polymers are not solved.

The term telechelic polymer defines pre-polymers with reactive chain-ends which can undergo further polymerization reactions or polymer analogue reactions.[36-37] Polymer analogue reactions are defined as reactions in which the structure of the polymer is changed by the reaction of its reactive moieties. The chain length and therefore its degree of polymerization is not changed.[38]

Thereby, it is important to mention that the reactive endgroups in telechelic polymers derive from the initiator, a terminating or a chain-transfer agent but never from the monomer. Polymers having the same reactive moieties at the chain ends are commonly referred to as homotelechelic polymers, whereas polymers with two different reactive chain ends are called heterotelechelic polymers.[37] In silicone chemistry these reactive moieties at the chain ends are commonly hydroxy (silanols), alkoxy, vinyl or hydrido groups. These groups are especially important for curing these polymers to obtain solid silicone rubbers (Figure 1-2).[39]

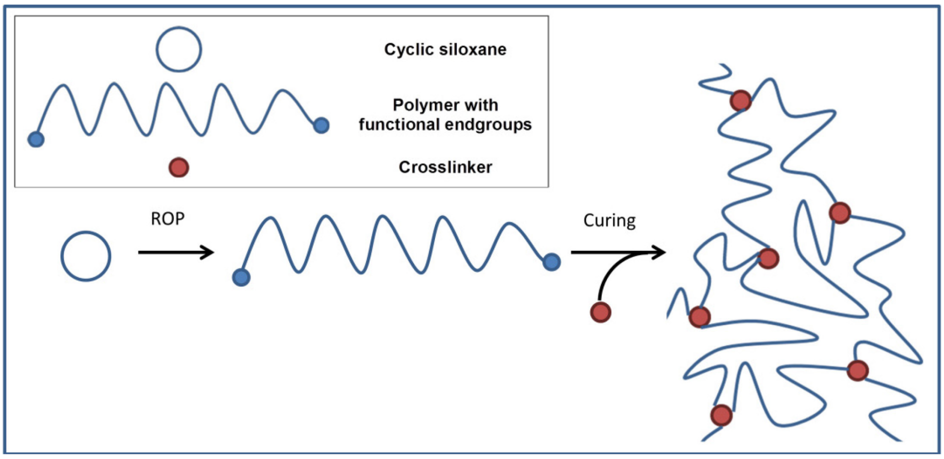


**Figure 1-2: Schematic presentation from cyclic siloxane to cure silicone rubber.**

## 1.2 Scope of work and methodology

In the framework of this research a new process for the synthesis of telechelic siloxanes shall be developed. The process should be controllable in way that the results are reproducible, that the resulting silicone show small polydispersity and that the molecular weigth of the polymer can be tailored. For its successful application in current adhesive and sealant applications, the reactive chain ends of the silicone should be most preferably silanol groups. If this is not the case, at least they should be able to undergo curing.

It was decided to limit the approaches to the anionic ring-opening polymerization.

For this purpose a nitrogen-containing, metal-free catalyst for the ring-opening polymerization of cyclic siloxanes leading to a telechelic linear siloxane with small polydispersity needed to be found.

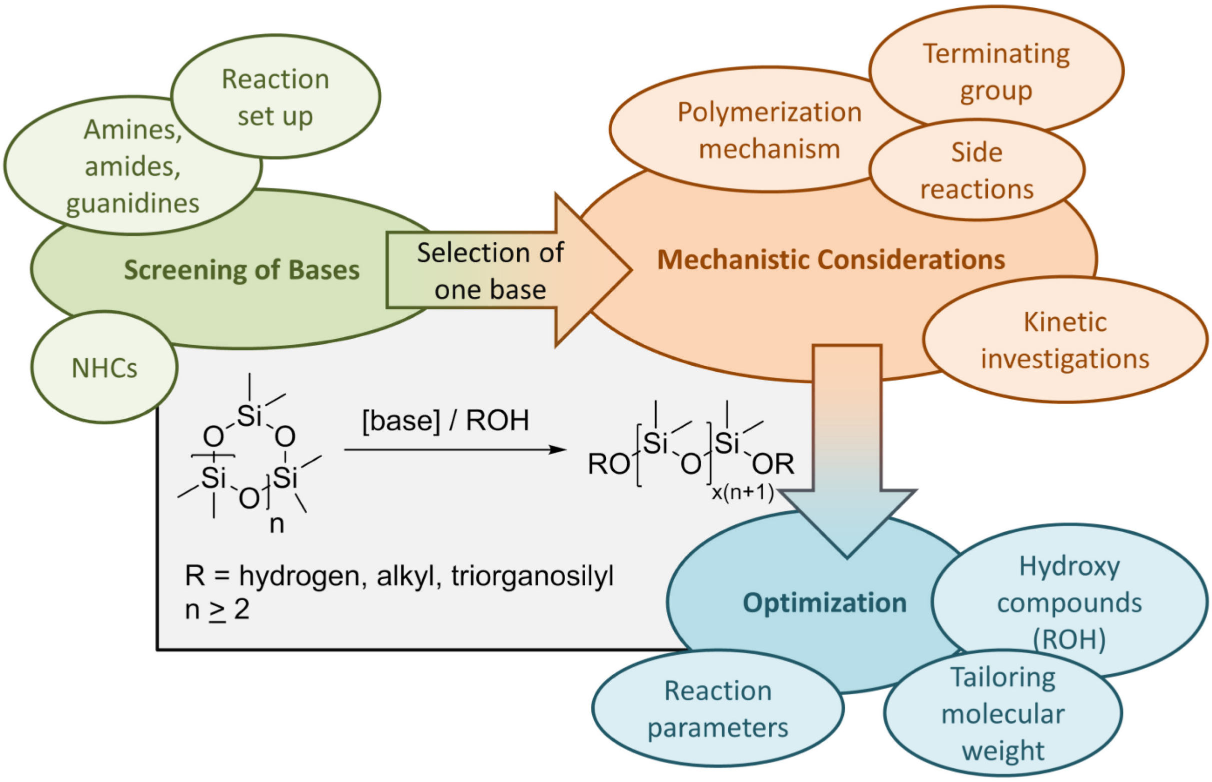


**Figure 1-3: Schematic presentation of the methodology to reach the defined scope of work.**

Therefore, as presented in Figure 1-3, firstly a screening of different nitrogen containing bases was undertaken and compared to the state of the art. Thereby it was focused on N-heterocyclic carbenes and the group of amines, amides and guanidines. The latter ones also necessitated the setup of a new process. After this screening one base identified as most promising was investigated in depth.

Therefore the general polymerization mechanism was investigated. Surprising findings when characterizing the terminating groups of the polymer necessitated a deep understanding of the mechanism and justified investigations of possible side reactions. In order to round off kinetic investigations were undertaken.

To complete different hydroxy compounds investigated, among them acohols, triogranosilanols and water, in order to introduce the designated terminating groups and to tailor the molecular weight of the polymers. Parallel to this reaction conditions such as reaction temperature, concentration of the base and the solvent were optimized which is especially important for possible upscaling experiments.

# 2 Theoretical Background

> *“Most if not all of the known types of organic derivatives of silicon have now been considered and it may be seen how few they are in comparison with those which are entirely organic; as moreover the few which are known are very limited in their reactions, the prospect of any immediate and important advance in this section of organic chemistry does not seem to be very hopeful.”*
>
> Frederic Stanley Kipping (1863 – 1949)

## 2.1 Silicone materials

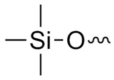
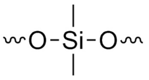
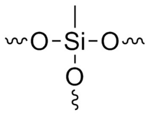
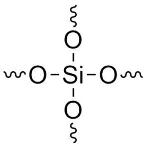
“Siloxane”, traditionally “silicone”, is a collective term for linear or cyclic silicone fluids and oils, branched silicone resins as well silicone elastomers and rubbers.[40] According to the latest IUPAC definition the term “silicone” is only valid for linear polyorganosiloxanes.[41]

Despite the great variety of available silicone products they consist of just four building blocks deriving from the corresponding organochlorosilanes, which are divided into siloxy, siloxane, silsesquioxane and silicate species, of the general formula $R_mSiO_{(4-m)/2}$. Thereby every oxygen atom bound to the silicon atom is counted as ½ due the fact that two silicon atoms “share” it.[42]

To simplify the naming of silicone compounds the MDTQ nomenclature is used. Herein the different building blocks are shorthanded to the letters M, D, T and Q referring to their functionality (Table 2-1). Subscripts and superscripts refer to the number of units and their attached organic moieties respectively.[42] Main organic moieties are hydrido groups, methyl, phenyl- or vinyl moieties.[31]

As example $D_4$ represents the cyclic compound 1,1,3,3,5,5,7,7-octamethylcyclotetrasiloxane, which consists out of four D-units. A MM-compound on the other side represents a disiloxane such as hexamethyldisiloxane consisting out of two M units.

**Table 2-1: Siloxanes building blocks of the general formula $R_mSiO_{(4-m)/2}$ and their shorthand notation.**

| | | | | |
|---|---|---|---|---|
| **Building block** |  |  |  |  |
| **Species** | siloxy | siloxane | silsesquioxane | silicate |
| **Funtionality** | mono | di | tri | tetra |
| **Nomenclature** | M | D | T | Q |

The variety of possible organic moieties and the versatile possible combinations of building blocks leads to this variety of silicone products. Silicone oils and fluids represent linear polyorganosiloxanes of the general structure $MD_xM$.[31] The most important are polydimethylsiloxanes (PDMS). Silicone resins represent highly branched, and high viscous materials consisting mainly out of T and Q units versatile combined with M and D units.[43]

Due to their inorganic backbone and their organic moieties, silicones represent a unique material class with unique properties which are mostly attributed to the special characteristics of the Si-O bonding.[1]

Silicone materials show only slight changes of their physical properties over broad temperature ranges as well as high gas permeability and low glass transition temperatures resulting from the high flexibility of the silicone chains.[44-45] The Si-O bonding is longer than the C-O bonding which results additionally in a wider Si-O-Si bond angle.[46-47] The angle might change with organic moieties attached to the silicon atoms. Both the longer bonding as well as the wider angle allow easier rotation of the moieties attached to the silicon atoms leading to said high flexibility of the silicone chains.[47]

Silicones show good dielectric behavior due to the partial ionic character of the Si-O bond which is determined to ~50% due to its high difference in electronegativity ($\Delta EN_{Si\text{-}O}$ = 1.76).[48] Therefore they are used as insulator materials.[39]

Moreover, the partial ionic character is a very effective tool for the synthesis and modification of silicone polymers through so called “equilibration” or “redistribution” reactions in the presence of strong acids or bases. This also allows the preparation of telechelic or organofunctional terminated silicones.[47]

Furthermore, silicones show high thermal and oxidative stability which results from the high dissociation energy of the Si-O bond ($E_{Si\text{-}O}$ = 460 kJ/mol). In comparison, the dissociation energy of the C-O bond is much lower ($E_{C\text{-}O}$ = 318 kJ/mol).[46-47]

Silicone oils – especially fluids with methyl groups or fluorinated side groups – show low surface tension and high spreading power resulting from the nonpolar organic groups inhibiting intermolecular interactions as well as the high chain flexibility. This is why methylsilicone oils are used as defoamers, mold release agents, spreading agents and hydrophobizing agents.[44]

All these properties make silicones very valuable materials which are applied in many fields of our everyday life.[4]

## 2.2 From silicon to silicone

Although it was already developed independently by E. Rochow[11] and R.Müller[10] in the early 1940ies, organochlorosilanes are mainly produced by direct synthesis – also known as "Müller-Rochow-Process" – until today. Herein, elementary silicon is reacted with chloroalkanes in the presence of a copper catalyst in fluidized bed reactors. The silanes which can be obtained are mainly hydrido-, methyl, ethyl and phenylchlorosilanes. Silanes with higher alkyl or with unsaturated moieties show low yield and are not applicable in this process. They can be obtained via Grignard reaction, hydrosilylation or radical additions.[49-50]

In the following, the direct process is described in more detailed using as example the synthesis of methylchlorosilanes. The main reaction in the direct process leads to dimethyldichlorosilane (Scheme 2-1, a):[49]

$$\text{a)}\quad 2\,CH_3Cl + Si \longrightarrow (CH_3)_2SiCl_2$$

$$\text{b)}\quad 3\,CH_3Cl + Si \longrightarrow (CH_3)SiCl_3 + 2\,{\cdot}CH3$$

$$\text{c)}\quad 3\,CH_3Cl + Si \longrightarrow (CH_3)SiCl_3 + Cl_2$$

$$\text{d)}\quad 2\,Cl_2 + Si \longrightarrow SiCl_4$$

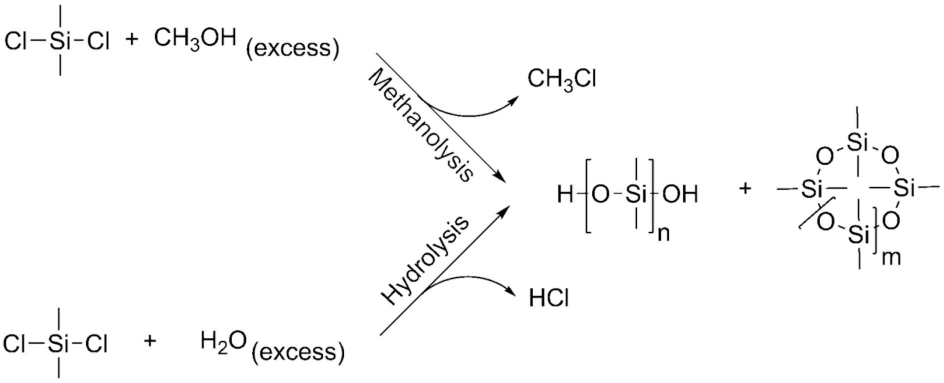
**Scheme 2-1: Basic reactions of the direct synthesis of methylchlorosilanes.**

Other methylchlorosilanes are products of side reactions (Scheme 2-1, b-c) leading to a broad mixture of silanes (also referred to as "crude silane") which has to be purified via complex distillation procedures. However, through adjustment of reaction temperature and the usage of promotors, the composition of the different silanes can be influenced. Anyhow, the main product always is dimethyldichlorosilane. An exemplary composition is given in Table 2-2.[51]

**Table 2-2: Examplary composition of the crude silane (Reaction conditions: 0,5 – 3 wt% copper catalyst; zinc or zinc oxide as promotor; 280 – 320 °C).[51]**

| Methylchlorosilane | Relative amount in the "crude silane" [%] |
|---|---|
| **$(CH_3)_2SiCl_2$** | 80 |
| **$(CH_3)SiCl_3$** | 10 – 15 |
| **$(CH_3)_3SiCl$** | 3 – 4 |

Organochlorosilanes are very sensitive to decomposition in the presence of protic compounds such as water or alcohols under release of hydrochloric acid or chloroalkanes, respectively. This behavior is utilized for the synthesis of polymeric silicone materials. Therefore, the purified organochlorosilanes are used in versatile combinations and are reacted to cyclic siloxanes, linear[39, 52-53] or branched polyorganosiloxanes or highly branched silicone resins[54] via methanolysis or hydrolysis reactions.[4]



**Scheme 2-2: Methanolysis and hydrolysis of dichloromethylsilane.**

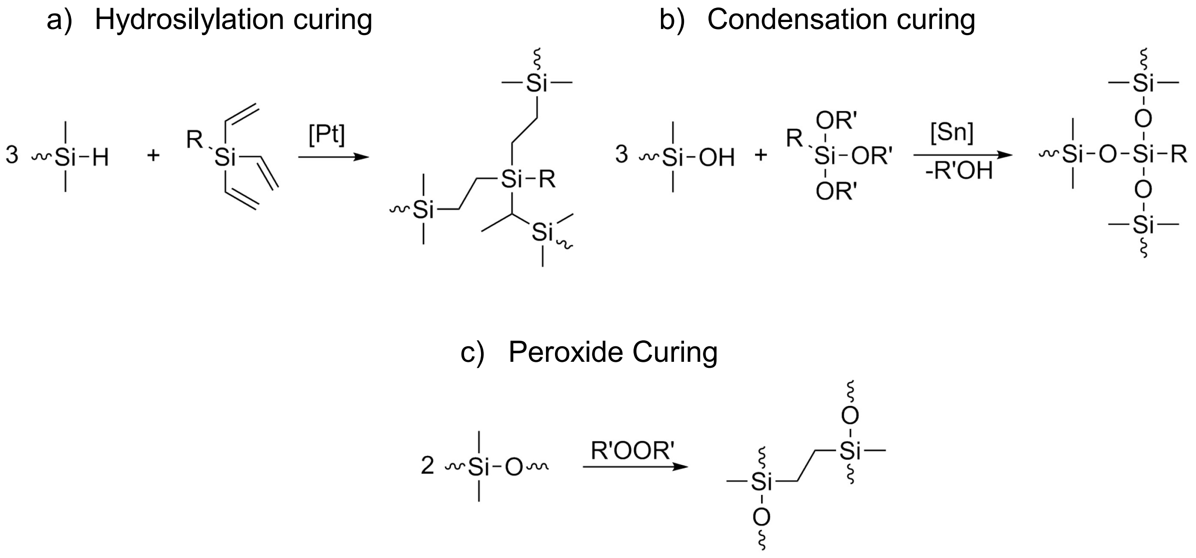
Linear polyorganosiloxanes – also referred to as silicone oils or fluids – are commonly produced in a two-step process starting from dichlorosilanes. The first step is the hydrolysis or methanolysis of dichlorosilane which leads to a mixture of linear and cyclic oligomeric siloxanes (Scheme 2-2).[39, 52-53] Hydrolysis or methanolysis respectively can be performed in a way that either nearly pure linear or nearly pure cyclic oligomeric siloxanes are obtained.[21] Both linear and cyclic oligomers can be also inter-converted into each other.[55-56] The hydrolysate is then further reacted to a high weight polymer by polycondensation or ring-opening polymerization respectively.[39, 52-53]

Highly branched, brittle resins are obtained by hydrolysis or condensation of trichlorosilanes. By combining trichlorosilanes with dichlorosilanes or tetrachlorolsilanes softer or hard resins are obtained respectively. Common combinations are DT resins and MQ resins.[3] Other combinations such as MDT-, MTQ-, QDT-resins are also of industrial interest (see nomenclature explained in Table 2-1.[57-58]

The obtained silicone polymers can be mixed with fillers to obtain liquid silicone rubbers or elastomers. They can be vulcanized (vulcanized = cured = crosslinked) to solid silicone rubbers and elastomers, which are very elastic.[3-4]

In general, main curing processes are differentiated in high temperature vulcanizing (HTV) and room-temperature vulcanizing (RTV). Crosslinking can be carried out via radical curing with peroxides in HTV processes, hydrosilylation curing (in RTV and HTV) as well as condensation curing (in RTV) as shown in Scheme 2-3.

In the condensation curing (cf. Scheme 2-3, b) typically a silanol or a silicone polymer terminated with hydrolysable groups reacts with a silane crosslinker having three to four hydrolysable groups –OR' attached to the silicon atom under release of R'OH.[4] Common hydrolysable groups are alkoxy- (typically methoxy), carboxy- (typically acetoxy), oximo-, amino-, amido- (e.g. N-methylacetamido, N-methylbenzamido) or alkenoxy moieties.[39, 59]



a) Hydrosilylation curing

b) Condensation curing

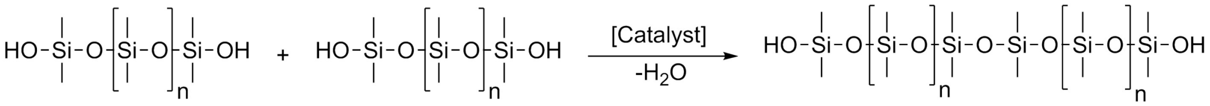
c) Peroxide Curing

**Scheme 2-3: Curing types – a) Hydrosilylation curing, b) Condensation curing, c) Peroxide curing.**

RTV-products are divided in one or two-component RTV (RTV-I; RTV-II) formulations. In RTV-I, all parts of the formulation – polymer, crosslinker, catalyst, fillers and other additives – are mixed together from the beginning and curing starts immediately when getting into contact with air and moisture. In RTV-II, the crosslinker and the polymer are mixed directly before application. The catalyst, additives and fillers are either premixed with the crosslinker or the polymer. RTV-II formulations can be cured either via condensation or hydrosilylation.[4, 39, 59]

## 2.3 Polycondensation of oligomeric silicones

Linear polyorganosiloxanes can be prepared by polycondensation of oligomeric siloxane diols to obtain high molecular weight polymers in the presence of a suitable catalyst (Scheme 2-4). In literature, acidic catalysts such as phosphorous chloronitriles, preferably polychlorophosphazenes, are described.[18, 29, 60] Also bases such as potassium hydroxide or phosphazene bases are effective catalysts.[23-24, 27]



**Scheme 2-4: Polycondensation of oligomeric siloxanes leading to polyorganosiloxanes.**

Polycondensation must be performed under vacuum at elevated temperatures. The water which is released during the reaction should be removed continuously. After reaching the desired molecular weight the reaction can be quenched by amines or ammonia. Moreover, the reaction can be quenched with silylamines or disilazanes, which also act as terminating agents due to silylation of the silanol end groups.[39]

The high reaction speed and the small percentage of cyclic siloxanes in the final product are the most important advantages of this process. However, polydispersities of the obtained polymers are generally broad (PDI = 2 – 50).[52]

## 2.4 Ring-opening polymerization of cyclic siloxanes

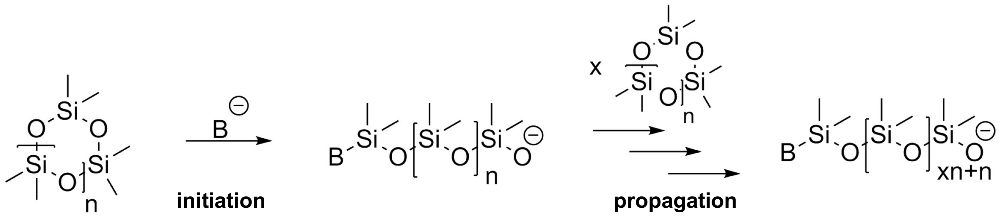
The ring-opening polymerization (ROP) of cyclic organosiloxanes is used to prepare functionalized silicone oils. The polymerization mechanism is based on the cleavage of the Si-O-bonding. The cyclic monomers used are mainly organocyclotetrasiloxane ($D^R_4$) or organocyclotrisiloxane ($D^R_3$). Other monomers include cyclic carbosiloxanes such as 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentante. Known ROP techniques are: ionic, radical or plasma-initiated.[45]

The ionic ROP can be initiated either by strong bases or acids. If the polymerization is initiated by strong bases an anionic mechanism (AROP) takes place. Initiation with strong acids leads to a cationic (CROP) mechanism.[45]

### 2.4.1 Anionic ROP

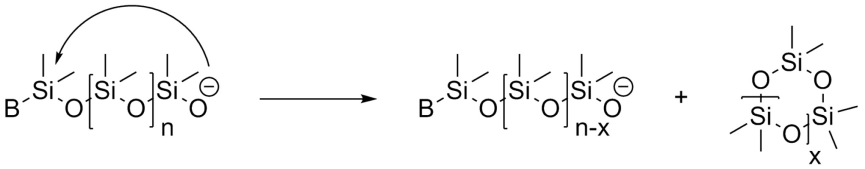
The anionic route is often used for the synthesis of high molecular weight polymers and its mechanism is well understood.[61]

The initiation step requires a base and leads to the formation of silanolate anions, which represent the active center in the propagation reaction (Scheme 2-5), in which the chain length is extended.



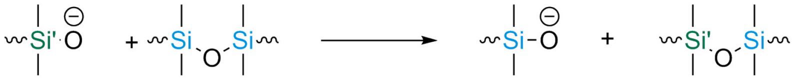
**Scheme 2-5: Initiation reaction by formation of silanolate anions and propagation of the anionic ring-opening polymerization.**

One problem which occurs with the AROP is the so-called back-biting reaction. It represents the reversed reaction of propagation and leads to breakdown of the polymeric chain.
Herein the active center reacts with the growing chain by cleaving the siloxane bond under formation of cyclic siloxanes. As a consequence, smaller and bigger cyclic siloxanes are generated as by-products when equilibrium is achieved (Scheme 2-6).[32] This can be avoided under certain conditions by stopping the reaction directly when equilibrium is achieved and is commonly called non equilibrium polymerization.[62]



**Scheme 2-6: Back-biting reaction which generates macrocyclic siloxanes as undesired byproducts and represents the back reaction of the propagation.**

Chain transfer is another side reaction which can occur. Herein, the active center attacks the siloxane bond of another polymer chain which leads to chain randomization which is also called equilibration.



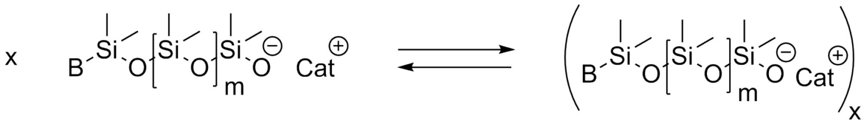
**Scheme 2-7: Chain transfer reaction in anionic ring-opening polymerization.**

As long as the active center is not deactivated, the polymerization proceeds without termination which also enhances the described side reactions.

Chain termination occurs always as side reaction in AROP due to traces of protonic impurities (water e.g.) in the reaction. It can also be forced by using the initiator in an aqueous solution or by quenching the reaction, for instance with water or alcohols.[53] The molecular weight can be controlled by the used amount of water.[63]

An alternative is the usage of end-capping agents which typically are disiloxanes like tetramethyldisiloxane (TMDS), hexamethyldisiloxane (HMDS) or divinyltetramethylsdisiloxane (DVS).[28] Those end-capping agents may be also used to regulate the molecular weight of the polymer and/or to add a functionality e.g vinyl end-groups.[64]

The key factor for the ring-opening polymerization is the silanolate counterion interaction leading to the formation of aggregates as presented in Scheme 2-8, which are inactive in AROP.



**Scheme 2-8: Silanolate cation interaction leading to formation of aggregates, which are not active in ring-opening polymerization. Cat$^+$ represents the counterion. In the case of Cat$^+$ = K$^+$ x equals 2[65] but if Cat$^+$ = Li$^+$ x equals 3 or 4 respectively provided that the concentration of SiO$^-$Li$^+$ is higher than 10$^{-2}$ mol/L[66].**

The polymerization rate is depending on many factors like initiator, polymerization medium as well as the chosen monomer:

*(i) Initiators*

Many different initiators are well known for this route. Widely described are alkali metal or alkali earth metal hydroxides (e.g. KOH, NaOH),[22] alcoholic complexes thereof, alkali metal or alkali earth metal silanolates,[67] tetraammonium hydroxide, phosphazene bases[68] and lately, N-heterocyclic carbenes[33] or bicyclic guanidines.[32, 69]

The polymerization rate increases with the size of the counterion: $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+ \sim Et_4N^+ \sim Et_4P^+$. With rising size, the cations get less electrophilic and therefore the concentration of free anions is increased. The most active initiators therefore are phosphazenes.[65]

Potassium hydroxide is one of the earliest initiators used for the ROP of cyclic siloxanes. Its usage dates back to 1948, when the ring-opening polymerization with alkali metals was first patented.[22] Potassium hydroxide is neither soluble in the monomer nor in the polysiloxane. Therefore, it needs to be dispersed in the reaction system and high temperatures of >150 °C have to be applied to start the polymerization.[25] Nowadays, potassium silanolates are often used as initiators for the synthesis of silicones. They represent a KOH-like initiator which is soluble in siloxanes[70-71] and may be also used for polycondensation.[71] They can be obtained by reacting potassium hydroxide with siloxanes.[67]

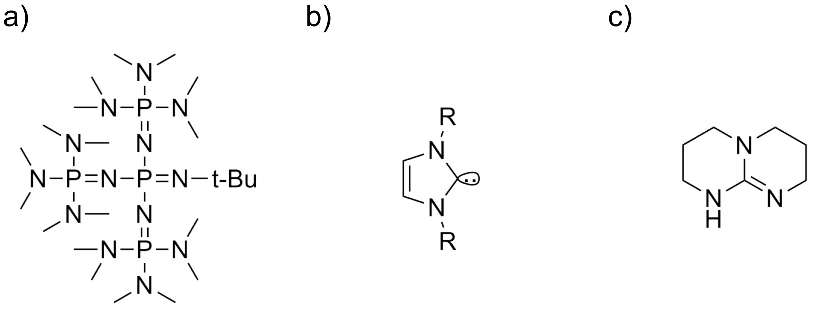


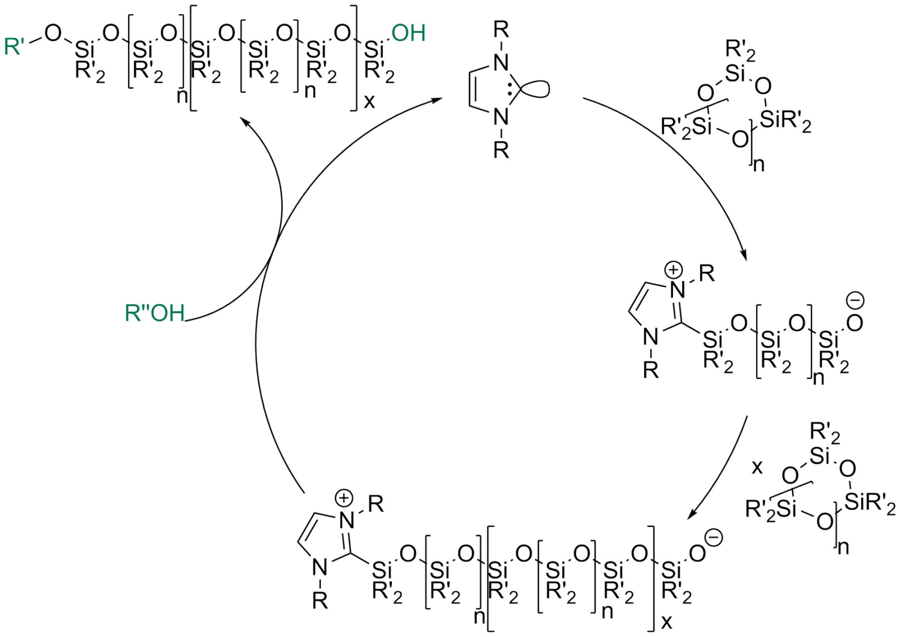
**Figure 2-1: Modern initiators for ROP of cyclosiloxanes a) exemplary molecular structure of a phosphazene: (1-*tert*-Butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranyliden-amino]-2$\Lambda^5$,4Λ5-catenadi(phosphazene)) ($P_4$-*t*Bu phosphazene), b) general molecular structure of a N-heterocyclic carbene (NHC), c) molecular structure of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD).**

Phosphazene bases (Figure 2-1, a), which belong to the class of so-called superbases, are a relatively new class of initiators in the ROP of cyclic siloxanes. They are very efficient initiators for the ring-opening polymerization, especially in the presence of proton donors such as methanol or traces of water.[68] The interaction with proton donors leads to the formation of silanolates with a very bulky and soft counterion in which the positive charge is delocalized. Phosphazene bases can also catalyze condensation reactions when equilibrium is achieved.[24, 27, 72] For example, Möller *et al.* showed that $P_4$-*t*Bu phosphazene is very active at room temperature in very low concentrations ($10^{-3}$ mol/L). Polymerization of $D_4$ starts immediately and equilibrium is achieved after 1 min.[68, 73-74]

In the past years, the initiation *via* Lewis bases became of a special interest in the research. Especially metal-free organocatalysts like N-heterocyclic carbenes (NHCs) or guanidines are used. Thereby, they have been used successfully in the ROP of other cyclic monomers such as caprolactones.[75]

In literature, NHCs with cyclohexyl or *tert*-butyl moieties are described as active initiators for the ROP of cyclic oligosiloxanes. As co-initiators, primary alcohols like methanol or benzyl alcohol are used.[33]

NHCs act as Brønstedt bases and can be utilized as a nucleophilic initiator. Herein, the electron rich carbon of the NHC attacks a silicon atom of the cyclic monomer and binds to it while the monomer is ring-opened. The formed zwitterionic intermediate contains the silanolate center which is needed for the chain propagation described above. The alcohols which are described as co-initiators are necessary for chain termination. By releasing the initiator they form a heterotelechelic silicone which is alkoxy end-capped on the one side and silanol terminated on the other.[76-77]



**Scheme 2-9: Proposed reaction mechanism for the NHC initiated ring-opening polymerization of cyclic siloxanes by monomer activation.**

NHCs (Figure 2-1, b) have the great disadvantage that they are very sensitive to moisture. In literature, $CO_2$-protected NHCs are described, which are deprotected at slightly elevated temperatures (~60 °C) and allow a premixing of the reactants under normal conditions. This is especially advantageous for industrial applications.[78]

Molecules such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) (Figure 2-1, c) have been successfully used for the ROP of cyclic carbosiloxanes like 2,2,5,5-Tetramethyl-1-oxa-2,5-disilacyclopentane or hexamethylcyclotrisiloxane. *Hedrick et. al.* used TBD in a concentration of 1.2 mol% in combination with an alcohol. They confirmed via NMR the obtained heterotelechelic polymers with one alkoxy and one silanol terminated chain end. TBD acts in this polymerization as co-initiator by deprotonation of the added alcohol. The formed alcoholate acts then as initiator for the ring opening polymerization.[69]

TBD is less active than NHCs but the obtained polymers show a narrow polydispersity which indicates a more controlled process.[79] Sivasubramanian *et al.* (Momentive) report [34] a process for generating silicones by polymerizing cyclosiloxanes in the presence of bicyclic guanidines especially TBD. Alcohols are not necessarily used and additionally disiloxanes are used as end-capping agents.[34]

Surprisingly, 7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), which is the methylated analogue of TBD, is reported to be not active in the ROP of cyclic siloxanes.[69]

### *(ii) Influence of solvents and activators*

The polymerization itself can be carried out neat, in solvents or in emulsion. The solubility of the initiator in the reaction medium is also very important regarding the kinetics. Common solvents are liquid hydrocarbons such as hexane or silicone fluids.[28]

In some examples THF is used as solvent in combination with a hard counter-ion, namely $Li^+$, in ROP of $D_3$.[80-84] Reaction conditions are described avoiding backbiting reactions and chain transfer reactions and yielding polymers with very narrow polydispersities (< 1.1). Advantageous to this process is the abstinence of any additives which could contaminate the polymer. An explanation for these results is the favored interaction of the counter-ion with the solvent instead of the active center, leading to less aggregation.[82]

Morton and Bostick reported a solution polymerization of $D_4$ in THF, showing 71 % of conversion after 24 h at 60 °C. Under neat conditions, a reaction temperature of 140 °C was necessary, demonstrating that the choice of solvent can have an accelerating effect on the reaction speed.[85-86]

Various additives and co-initiators have been described which improve the polymerization rate. Among these are hexamethylphosphoric triamide[87-89], dimethyl sulfoxide[87, 90-93], 2,5,8-trioxanonane (diglyme)[94], 2,5,8,11-tetraoxadodecane (triglyme)[95], 1,2-dimethoxyethane[87], dimethylformamide[96], N-methylpyrrolidone[97] which act as activators. The counter-ion interacts stronger with these activators than with the active center of the polymer chain.[89, 92, 98-100] Crown ethers complex the counter-ion and thereby reduce the silanolate-cation interaction and the formation of aggregates (Scheme 2-8) which results in an increase in polymerization rate.[101]

Some of these additives and some other polar aprotic substances such as acetonitrile and acetone where studied in the ROP of 1,3,5-tri(3,3,3-trifluoropropyl-)-1,3,5-trimethylcyclotrisiloxane ($D^F_3$) with sodium siloxanolate as initiator. The reaction is of first order in monomer if no additive is used. Some of these results are summarized in Table 2-3.[96, 102]

**Table 2-3: Reported relative rates $k/k_0$ of polymerization of $D^F_3$ initiated by Sodium siloxanolate ($c = 2\cdot10^{-2}$ mol/L) in the presence of different activators. Variable $k_0$ is the observed first-order rate constant in the absence of an activator.[96, 102]**

| activator | $c_{Additive}$ [mol/L] | T [°C] | $k/k_0$ |
|---|---|---|---|
| **Nitrobenzene** | 0.1 | 40 | 2.1 |
| **Tetrahydrofurane** | 0.1 | 40 | 10.5 |
| **Acetonitrile** | 0.1 | 40 | 34 |
| **Acetone** | 0.1 | 40 | 95 |
| **Dimethylformamide** | 0.01 | 40 | 150 |
| **Dimethylsulfoxide** | 0.01 | 40 | 155 |
| **Hexamethylphosphortriamide** | 0.001 | 40 | 28 |
| **Diglyme** | 0.001 | 40 | 28 |

*(iii) Monomer interaction*

The reactivity of the monomers decreases with increasing ring size: $D_3$ >> $D_4$ > $D_5$ > $D_6$. Hexamethyltrisiloxane ($D_3$) has the largest ring strain among cyclic siloxanes and a planar conformation and shows very high reactivity in ring-opening polymerization.[103] Therefore, $D_3$ is often used in non-equilibrium polymerization processes. This has the advantage that minimal back-biting and chain randomization takes place.[32] Nevertheless, the preparation of $D_3$ is complex and therefore its commercial availability is limited.[52]

The order of $D_x$ is reversed if polymerization is performed neat or in a non-polar solvent in combination with an alkali metal silanolate.[53, 104] This might be explained by the formation of crown ether-like complexes due to a multidentate interaction of $D_6$ or $D_7$ with the cation.[105]

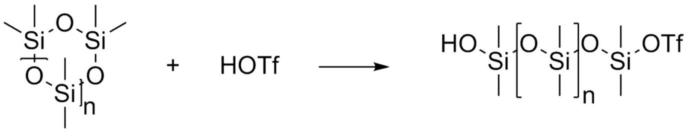
### 2.4.2 Cationic ROP

The CROP is initiated either by Brønstedt or Lewis acids and it is used for monomers with functional groups like SiH or SiCl, which are not stable in the presence of strong bases. Disadvantageous to this process is the simultaneously generation of linear polymers and cyclic oligomers.[106]

The polymerization mechanism is complex and discussed controversially in literature.[107-110] Still some details of the mechanism are not fully explained due to the fact that some unusual kinetic behaviors have been observed. These are for instance a negative order in monomer concentration[108], negative activation energy[108] or the role of water in the polymerization process since water acts both as promotor and inhibitor in the CROP.[106]

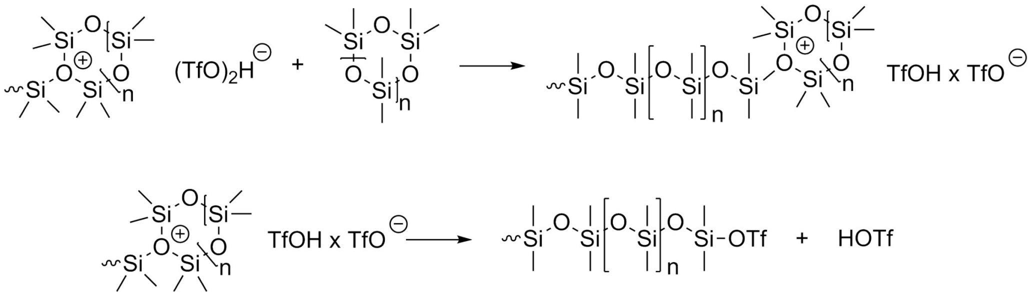
The polymerization mechanism was studied in depth for triflic acid as initiator, which serves as example for the following mechanistic considerations.[107, 111]

In general, it is accepted that the Si-O-bonding is cleaved by strong protic acids during the initiation reaction. Thereby, the corresponding silyl ester silanol is formed which starts the chain propagation (Scheme 2-10).[106]



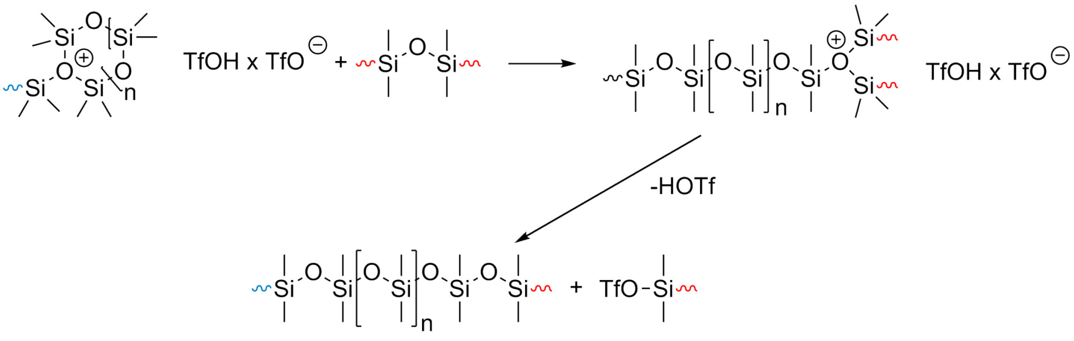
**Scheme 2-10: Initiation reaction of cationic ROP with triflic acid under formation of a silyl triflate silanol.**

It is proposed that homocomplexes of the acid (TfOH x $TfO^-$; $[(TfO_2)H]^-$) or the hydrate ($[TfO \times H_2O]^-$) of the acid are formed and act as initiators since the ester group is inactive.[112] Toskas *et al.* proposed that chain propagation is based on the formation of trisiloxonium ions (Scheme 2-11). [109]



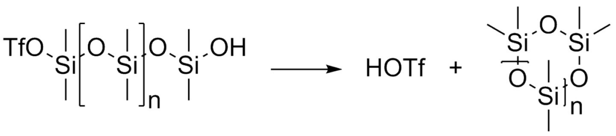
**Scheme 2-11: Mechanism of chain propagation as postulated by Toskas *et al*.**

One important part of the CROP are chain transfer reactions which occur as side reactions (Scheme 2-12).[113]



**Scheme 2-12: Mechanism of chain transfer in CROP.**

Back-Biting reactions which are observed in the AROP occur in the CROP as well. Unlike the AROP, backbiting takes place via intramolecular condensation processes (Scheme 2-13).[106, 109]



**Scheme 2-13: Intramolecular condensation process occurring simultaneously to chain propagation in CROP. This leads to a product mixture of macrocyclic rings and linear polymers.**

Strong protic acids like sulfuric acid[20, 114], sulfonic acids[26, 109, 111, 115] as well as perchloric acid, are used as initiators in the CROP.[102] Sulfuric acid was one of the earliest initiators for CROP of cyclic siloxanes.[114] Effective sulfonic acids, which are described in literature, are triflic acid (HOTf)[109] as well as bis(trifluoromethyl)sulfonimide (TFSI-H) (Figure 2-2).[116]

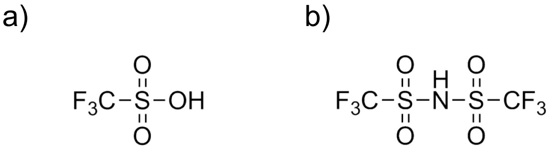


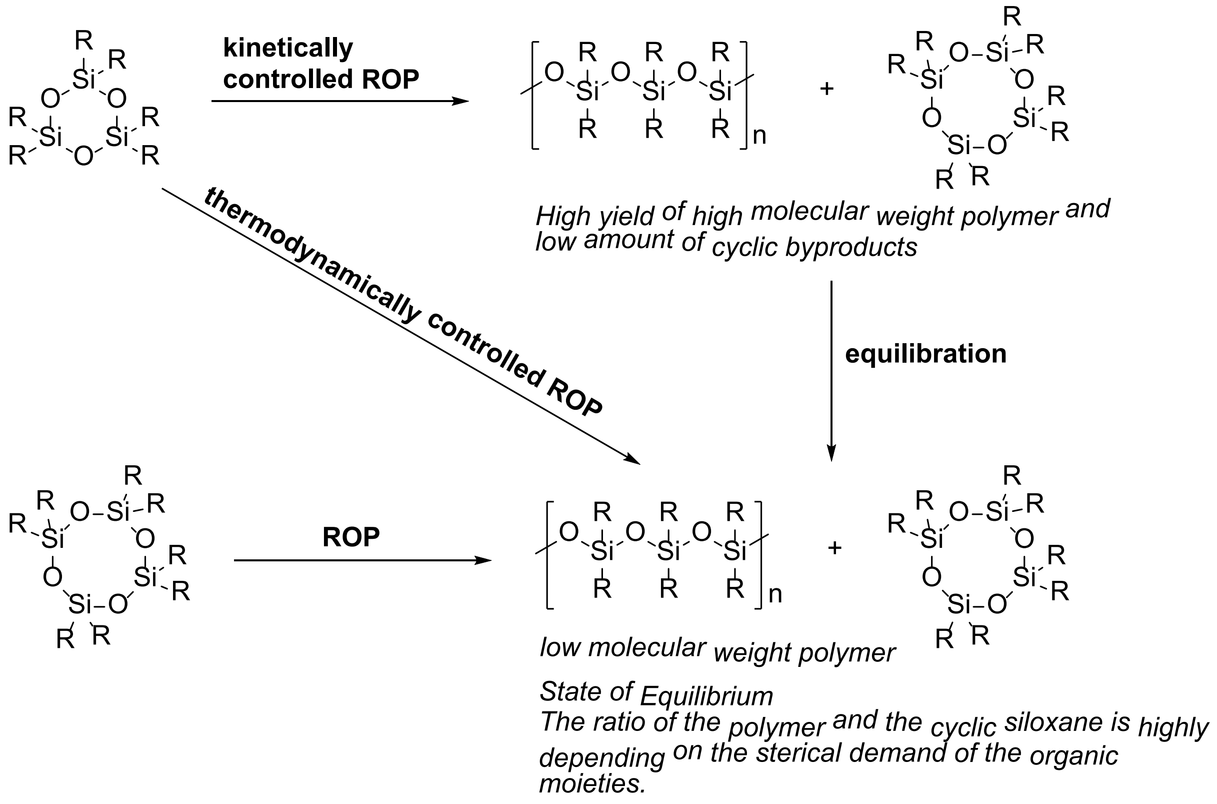
**Figure 2-2: Molecular structure of a) triflic acid (HOTf) and b) bis(trifluoromethyl)sulfonimide (TFSI-H).**

Heterogeneous initiators such as ion exchange resins, acid treated graphite[117] or acid treated clays[118] can be used in CROP.[102] They bear the advantage that they can be easily recovered after the reaction.[119]

A new way for initiating the CROP is the generation of trisiloxonium ions by an *in-situ* Cory hydride transfer. This leads to the great advantage that a simple addition polymerization takes place due to the fact that the propagation of the chain takes place only in one direction.[110] Another way might be the CROP of $D_3$ with trimethylsilyl triflate in the absence of strong protic acids.[120]

### 2.4.3 Thermodynamically vs. kinetically controlled ROP

ROP of both strained ($D_3$) and unstrained ($D_4$ and higher) cyclic siloxanes either anionically or cationically initiated, lead to the same equilibrium in which the polymer and cyclic byproducts exist side by side. Nevertheless, the mechanism leading to this equilibrium is different, which also allows to two possible methods for ROP.[62]



High yield of high molecular weight polymer and low amount of cyclic byproducts

low molecular weight polymer

State of Equilibrium
The ratio of the polymer and the cyclic siloxane is highly depending on the sterical demand of the organic moieties.

**Scheme 2-14: Differences between thermodynamically and kinetically controlled ROP. The figure is based on Beckmann *et al.*[103].**

The thermodynamically controlled ROP leads to the parallel formation of cyclic oligosiloxanes and linear polymers, whereas the kinetically controlled ROP firstly leads to linear polymers and, in a second step, equilibration processes take place.[62]

*(i) Thermodynamically controlled ROP*

The thermodynamically controlled ROP is entropy driven and is mainly applied for the polymerization of cyclotetrasiloxanes or higher cyclosliloxanes because all bonds in both monomer and polymer are thermodynamically the same.[121] This leads to the parallel formation of linear polymer and oligocyclosiloxanes. Thereby, the polymer concentration increases untill equilibrium is achieved. This kind of polymerization is also known as equilibrium polymerization or equilibration because it is stopped after reaching the equilibrium state.[62]

Advantageous to this process is that it is not dependent on the nature of the used initiators. Therefore, initiators can be chosen which achieve equilibrium fast and under mild conditions, do not interact with the monomer and can be separated easily from the product. Furthermore, the polymerization does not have to be quenched at a certain moment.[62]

Limiting to this approach is the formation of oligo cycles. Therefore, the thermodynamically controlled ROP should be used for polymerizations which give a high yield of polymer in the equilibrium state. The ratio of linear polymer and cyclic oligomers in equilibrium is especially influenced by the polarity and bulkiness of the substituents at the silicon atoms. This method is also not recommended for polymers with very low polydispersities and for copolymers which should have a specific structure (e.g alternating).[62]

*(ii) Kinetically controlled ROP*

The kinetically controlled ROP is characterized by the fact that the chain propagation proceeds much faster than the back-biting or chain transfer reactions. This applies only for strained cyclotrisiloxanes where the ROP is not entropy- but enthalpy-driven, whereby the ring strain release is the driving force of the reaction.[62]

The reaction has to be quenched directly after reaching the highest monomer conversion in order to avoid equilibration reactions (c.f. Scheme 2-14). In this case the reaction is stopped before equilibrium is formed and a high molecular weight polymer with only small amounts of cyclic byproducts is obtained.[62]

Advantageous to this process is that polymers with controlled structures and in higher yields can be obtained. Converselly, the processes requires more expensive monomers, very pure reactants and only selected initiators can be used.[62]

## 2.5 Emulsion polymerization

Polymerization can be conducted in dispersed systems as heterophase polymerization. To these belong, among others, suspension polymerization, which is defined as the polymerization in monomer droplets without the usage of a surfactant, as well as precipitation polymerization, which starts from one phase and the polymer precipitates from this phase.[122] One important kind is the emulsion polymerization which was developed during World War I in order to replace the latex of natural rubber by artificial latex[123-126] and represents one of the most important industrial processes.[127]

In general, the emulsion polymerization is often performed with water as continuous phase in which the monomer is emulsified. Surfactants in concentrations above critical micelle concentration (CMC) are used in order to stabilize the emulsion and to form micelles.[128]

A micelle is a colloidal particle with a spherical shape formed by aggregation of surfactant molecules.[122] The micelles represent the main location where polymerization takes place changing to polymer filled latex particles.[128]

Although the first developments were made for radical emulsion polymerization, the basic principles apply for any kind of emulsion polymerization in which the latex particle is acting like a “micro-reactor”.[128] The process can be divided into three stages:

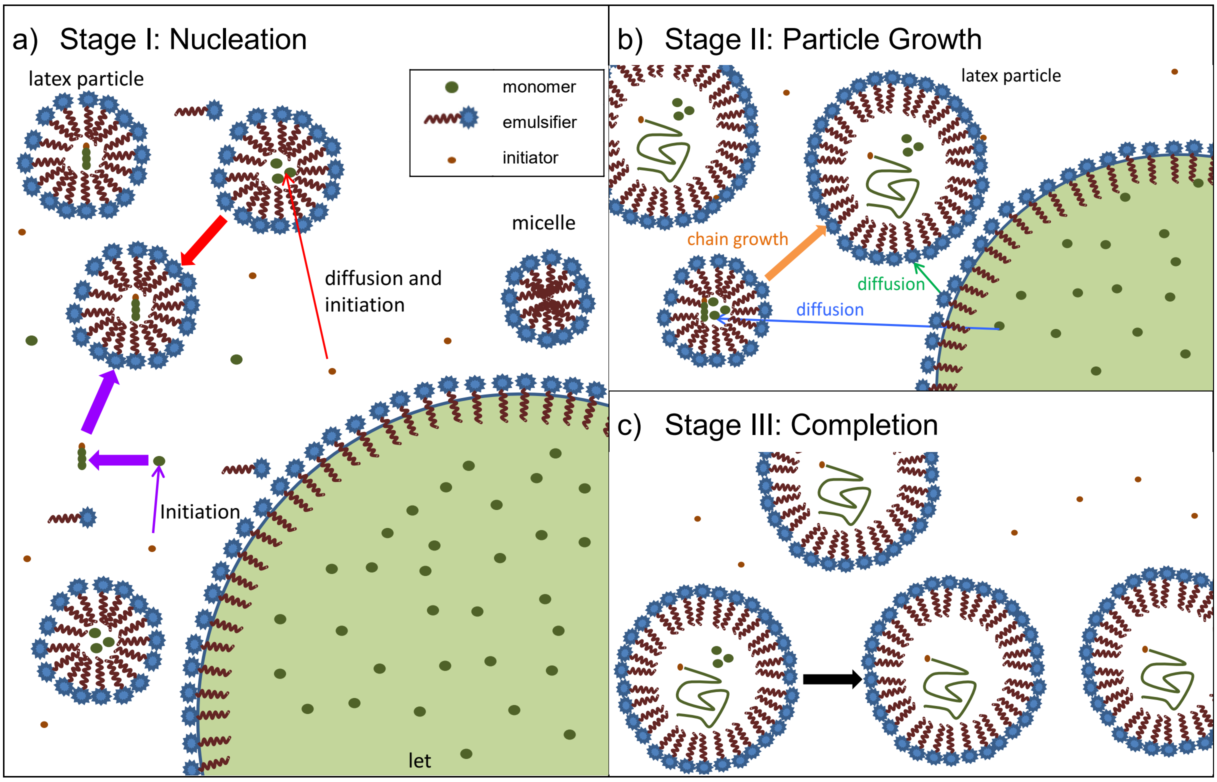


**Figure 2-3: Schematic presentation of the three stages of emulsion polymerization. a) representing homogeneous nucleation and heterogeneous nucleation; b) representing particle growth and c) representing completion of polymerization. Figure was modified according to Yamak[127].**

*Stage I* represents the initial stage and is called "particle formation" or "nucleation" and deals basically with the polymerization initiation (Figure 2-3, a). According to the "micellar nucleation mechanism" or "heterogeneous nucleation model" radicals diffuse into monomer swollen micelles and initiate the polymerization. The micelle is changed into a latex particle instantaneously. Nucleation stops if the surfactant concentration drops below CMC by adsorption of surfactant on the growing latex particles.[129-133] Another proposed nucleation mechanism is the "homogeneous nucleation model". There, the radicals react with dissolved monomer molecules under formation of oligomers. When the oligomer reaches a length where it is not soluble in the continuous phase latex particles are formed.[134] The latter applies especially for monomers which show a high degree of aqueous solubility.[135]

In *Stage II* ("Particle growth stage") nucleation is completed and polymerization proceeds in the latex particles. The polymerization rate is constant because the monomer concentration in these particles remains constant due to diffusion of monomer from the monomer droplets into the latex particle (Figure 2-3 b)). This is also one of the main advantages of the emulsion polymerization. While the monomer droplets decrease in size the polymer particles increase in size and absorb surfactant molecules which are released from the surface of the monomer.[127]

*Stage III* ("Completion") starts when all monomer droplets disappeared and the polymer particles contain all the remaining monomer (Figure 2-3 c)). While monomer concentration in the latex particles is decreasing the polymer rate slows down. Finally a mixture is obtained in which small polymer particles are emulsified in the continuous phase. [127]

Of course, emulsion polymerization is influenced by the rate of diffusion of initiator, monomer and other species throughout the different phases.[128]

As mentioned before, in contrast to that classical emulsion polymerization, mini emulsion polymerization represents a special case. For this kind, typically a combination of emulsifier and hydrophobic coemulsifier is used in order to prevent micelle formation. Initiation (droplet nucleation) and propagation take place in the monomer droplet, which functions as "microreactor" instead of the described micelles. Therefore there is no Stage II since the kinetic model does not apply here. After nucleation Stage III starts immediately.[136]

### 2.5.1 Emulsion Polymerization in Silicone Chemistry

The polymerization of silicones either by ROP[26, 115] or polycondensation[137-138] in aqueous emulsion is of great importance regarding sustainability[32] and was first patented in 1959[139]. As a product, silicone emulsions of polyorganosilanols in water are obtained which can be used in disperse dyes[140], disperse adhesives[141], in personal[142] or home care applications[143].

This chapter mainly focuses on emulsion polymerization of cyclic siloxanes. The process itself and the mechanism behind the process are very complex. The process underlies both chemical reactions as well as physico-chemical phenomena such as diffusion processes, phase equilibria as well as the nature of the interface.[53]

Favored surfactants which are used in the emulsion polymerization of cyclic siloxanes are fatty sulfonic acids (anionic) such as dodecylbenzenesulfonic acid or quaternary ammonium surfactants (cationic) such as dodecylbenzyldimethylammonium hydroxide. These surfactants can already initiate the polymerization themselves. Nevertheless they may be used in combination with classic initiators. Cationic emulsifiers may be used in addition with basic initiators whereas anionic emulsifiers are used in combination with acidic initiators.[53]

Besides the basic reactions – initiation, chain growth, termination of the ROP, which are, condensation reactions of the OH-terminated oligomers and polymers occur. Other side reactions are of course back-biting and redistribution as well as depolymerization reactions.

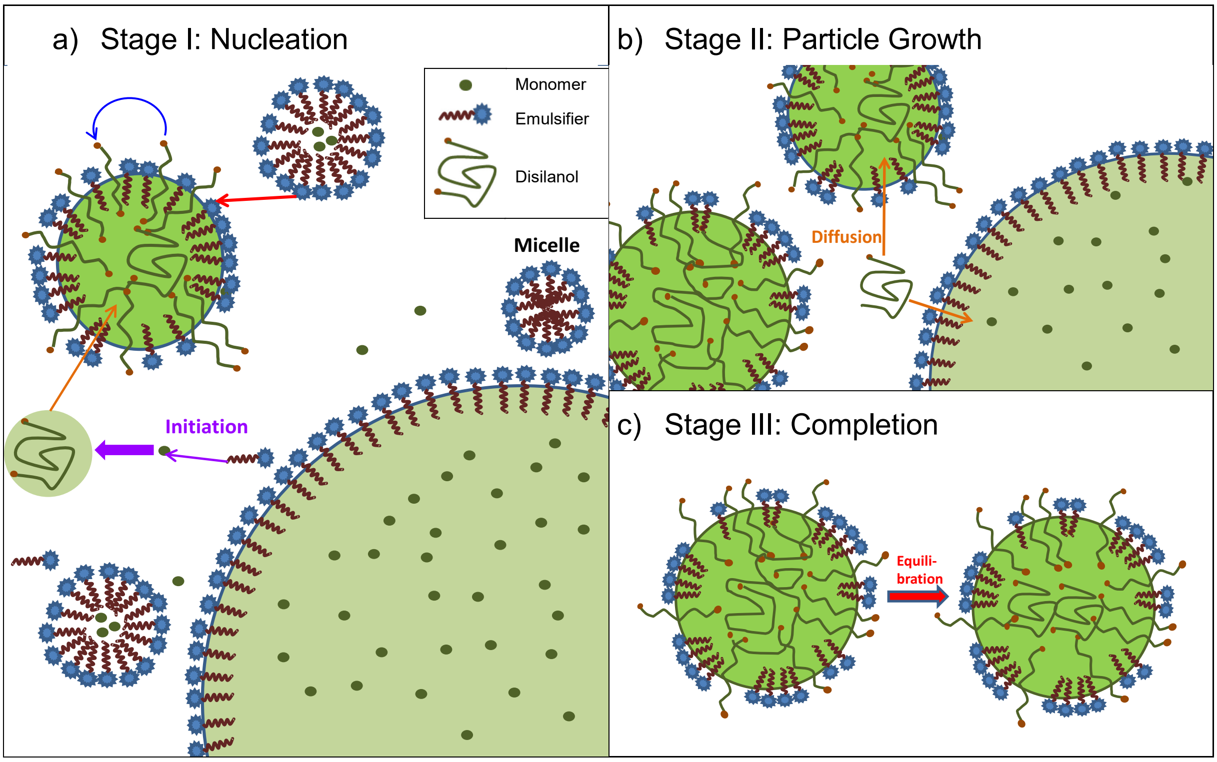


**Figure 2-4: Schematic presentation of the three stages of emulsion polymerization of cyclic siloxanes as for example $D_4$: a) representing homogeneous nucleation b) representing particle growth and c) representing completion of polymerization. Figure was modified according to Gee *et al.*[144-145].**

Latest reports[144-145] propose that initiation and propagation of ROP of cyclic siloxanes take place via homogeneous nucleation in the continuous phase.

In *Stage I* ROP is initiated by the emulsifier itself, leading to small oligomeric silanolates which undergo propagation until the chain gets too hydrophobic and forms a coil, leading to precursor particles becoming polymer particles by coagulation and further stabilization from surfactant molecules diffusing from the micelles. When the growing polymer chain is terminated by water the resulting disilanols can undergo condensation reactions at the polymer particle surface.

*Stage II* starts when micelles are absent. Then no new polymer particles can be formed and newly formed chains diffuse into the polymer particles or monomer droplets, whereby the particles grow.

*Stage III* is characterized by a constant number and size of particles. Only the molecular weight of the polymer changes to an equilibrium value via equilibration.

The possibility of micelle nucleation is neglected, due to the fact that is leading to step growth polymerization via condensation of small oligomers which later on form macro cyclic siloxanes by intramolecular condensation.[144-145]

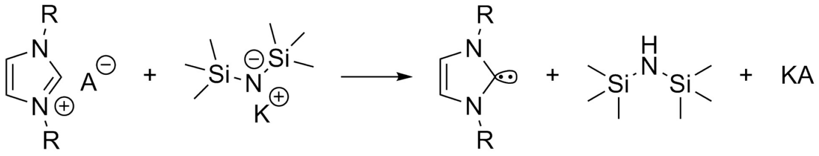
# 3 Ring-opening polymerization of cyclosiloxanes with nitrogen-containing bases

In this chapter several nitrogen containing bases were screened in the ROP of cyclosiloxanes and their general initiating properties were assessed. Thereby, they were differentiated into the class of N-hetercyclic carbenes and the group of amines, amides and guanidines. The different initiators were not only screened but first optimizations of reaction set up in choice of solvent as well amount of co-initiator were also undertaken.

## 3.1 N-Heterocyclic carbenes*

When investigating N-heterocyclic carbenes as suitable initiators, it was focused on the usage of imidazolin-2-ylidenes and dihydroimidazolin-2-ylidenes, which can be obtained by deprotonation of the corresponding imidazolium salts by using a strong base such as KO*t*Bu[146], metal hydrides[147-148], alkyllithiums[149] or potassium disilazide[150].

Therefore, an equimolar solution of the imidazolium salt and potassium hexamethyldisilazide (KHMDS) in THF is prepared. After stirring overnight the orange to brown solution can be used as obtained without any further purification. Stored under argon, the solution is stable over several weeks.



**Scheme 3-1: Generation of N-Heterocyclic carbenes via deprotonation of imidazolium salts in the presence of a strong base.**

All polymerization reactions are performed under argon and moisture-free conditions. The NHC solution in THF and an alcohol are added to the dry monomer octamethylcyclotetrasiloxane ($D_4$).

The use of benzoic acid in order to quench the polymerization is described in literature.[33] A test comparing quenched and unquenched samples via GPC show that quenching has no effect. On the contrary, it seems that the polymers in quenched samples decompose as their molecular weight decreases from ~350000 g/mol to ~200000 g/mol (Chart 3-1).

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* The experiments have been performed in the framework of Annika Dietrich's master thesis, University of Rostock.

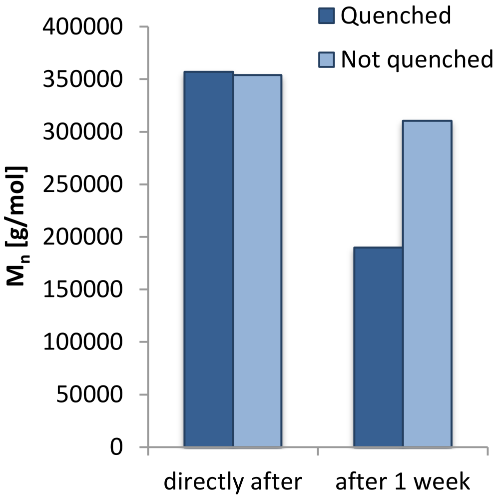
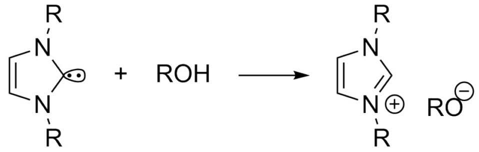


**Chart 3-1: Comparison of the molecular mass of two samples directly after stopping the reaction (fresh) and after one week. Polymerization experiments are carried under inert, moisture free conditions out using 0.1 mol% of 4.1 and 0.1 mol% MeOH related to the amount of $D_4$. Molecular weight is determined by GPC using PDMS standards and toluene as eluent.**

Therefore it is concluded that quenching is not necessary due to the fact that moisture inhibits the initiator as presented in Scheme 3-2: This can be seen by the color change of the reaction mixture from yellow to colorless, when exposed to atmospheric moisture.



**Scheme 3-2: Proposed quenching mechanism with protic molecules such as water or alchols. Molecular weights were determined by GPC using PDMS standards and toluene as eluent.**

First experiments are conducted based on the reaction conditions of Bacereido *et al.*[33] using 1-decyl-3-methylimidazolin-2-ylidene (***3.1***) obtained from 1-decyl-3-methylimidazolium chloride (***3.1a***) and benzyl alcohol (BnOH). The reaction is performed neat using 0.1 mol% ***3.1*** and 0.1 mol% benzyl alcohol as co-initiator at 80 °C (oil bath temperature). After 24 h of reaction time, conversion is determined to 95°% (calculated from $^{29}$Si(IG)-NMR). Number averaged molecular weight is followed by taking samples during reaction and determined by GPC measurements. In the beginning a strong increase in molecular weight can be observed which is expressed by a visible increase in viscosity. After 3 h of reaction time, a local maximum at ~300000 g/mol in molecular weight is observed and equilibrium is established with a slight negative slope, speaking for back-biting processes which occur (cf. Chart 3-2). Polydispersity of the polymer is increasing over time which is also reported by Bacareido as a consequence of intra- and intermolecular transesterification reactions mediated by the carbenes or the terminal siloxides of growing zwitterions.[33]

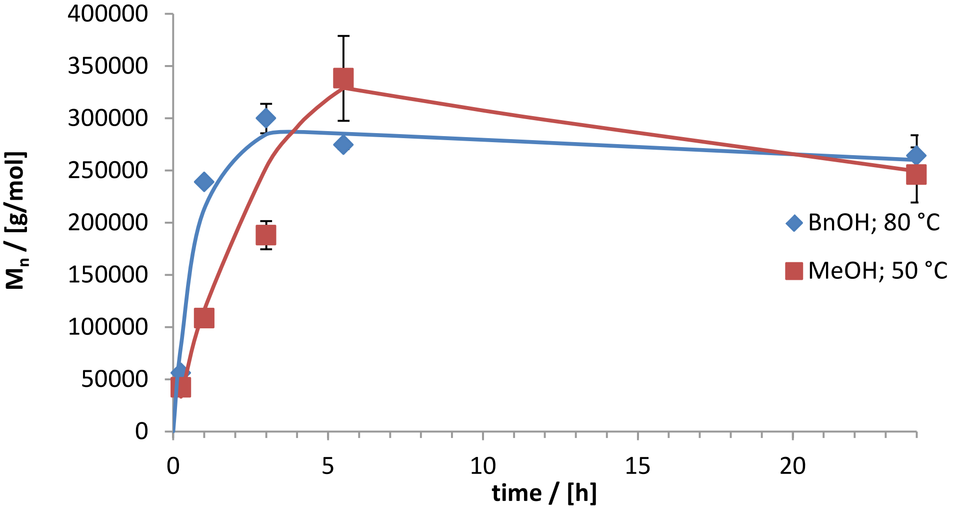


**Chart 3-2: Polymerization experiments using 0.1 mol% of 4.1 and 0.1 mol% alcohol related to the amount of $D_4$. Experiments are carried out under inert, moisture free conditions. Denoted temperatures are related to oil bath temperature. Molecular weight is determined by GPC using PDMS standards and toluene as eluent.**

First results using methanol (MeOH) as co-initiator show high molecular weights ($M_n$ > 300000 g/mol) obtained in between the first five hours. Due to the strong increase in molecular weight, viscosity increases as well. Therefore, homogenous mixing could not be guaranteed and local concentration gradients might have formed. This might also serve as explanation for the high standard deviations observed.

These molecular weights are far too high and therefore influence of temperature, influence of the solvent and influence of alcohol concentration are investigated in order to be able to control the molecular weights.

### 3.1.1 Influence of the solvent

As already discussed, the first polymerization results show high viscosity due to the resulting high molecular weights after 24 hours. In experiments using methanol as co-initiator even gelation of the polymers are observed. Therefore, different solvents are tested in which the polymer is soluble to ensure homogenous mixing throughout the whole reaction. Furthermore, it is suggested that due to the dilution, polymerization proceeds more controlled as expressed by a slower chain growth. Chart 3-3 shows the dilution effect on the molar masses in which toluene acts as solvent and benzyl alcohol as co-initiator.

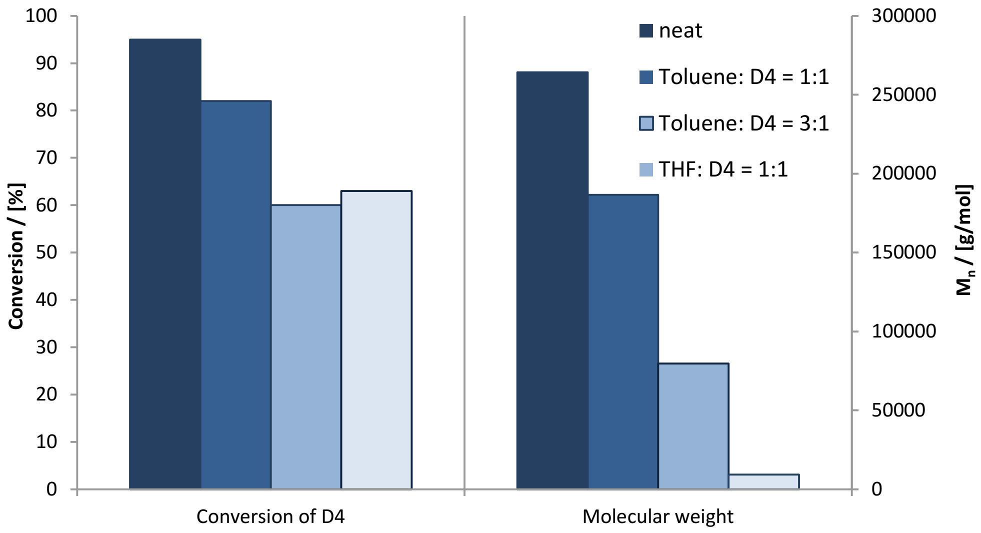


**Chart 3-3: Results of polymerization experiments of $D_4$ using 0.1 mol% of *4.1*, 0.1 mol% of benzyl alcohol related to the amount of $D_4$ in different solvents at 80 °C. All experiments are carried out under inert conditions for 24 h. Molecular weights are determined by GPC using PDMS standards and toluene as eluent. Conversion is calculated from $^{29}$Si(IG)-NMR.**

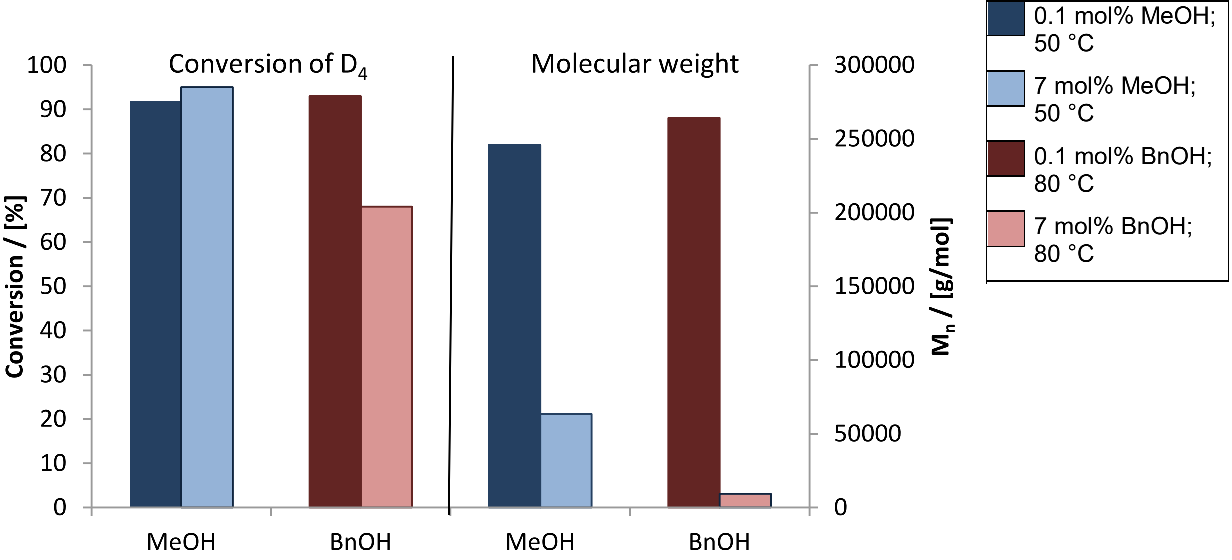
As suggested, molecular weight decreases with increasing solvent concentration, when using toluene, compared to a neat reaction set up. On the other hand, dilution has also an effect on conversion. Interestingly, molecular weights are especially low if using toluene. With an increasing amount of solvent also the conversion decreases from 90 % down to 60 %. The same trend is found when using methanol instead of benzyl alcohol as co-initiator.

This behavior is explained by the increasing dilution of the reaction system and the lower probability of collision of the monomer and the active center of the polymer chain. Another reason for this finding might be that in the apolar solvent aggregation of the zwitterionic polymer chain, (as proposed by Bacareido *et al.*)[33] occurs and therefore chain growth is inhibited.

Interestingly, the usage of THF inhibits chain growth to a high extent, as expressed by lower molecular weights and conversion than those obtained with toluene. This is quite surprising since it was expected that THF as a polar, aprotic solvent would enhance conversion due to a lower aggregation tendency of the active center of the growing chain and the counter ion. Yet the reason for this behavior is still elusive.

### 3.1.2 Influence of the co-initiator

We hypothesize that the use of higher concentration of the alcohol shall result in lower molecular weights. As shown in the presented polymerization mechanism in Scheme 2-9 (p.14) the alcohol acts solely as terminating agent. Therefore, chain termination should happen more frequently because of the higher alcohol concentration and smaller molecular weights should be obtained without affecting conversion.


a) neat

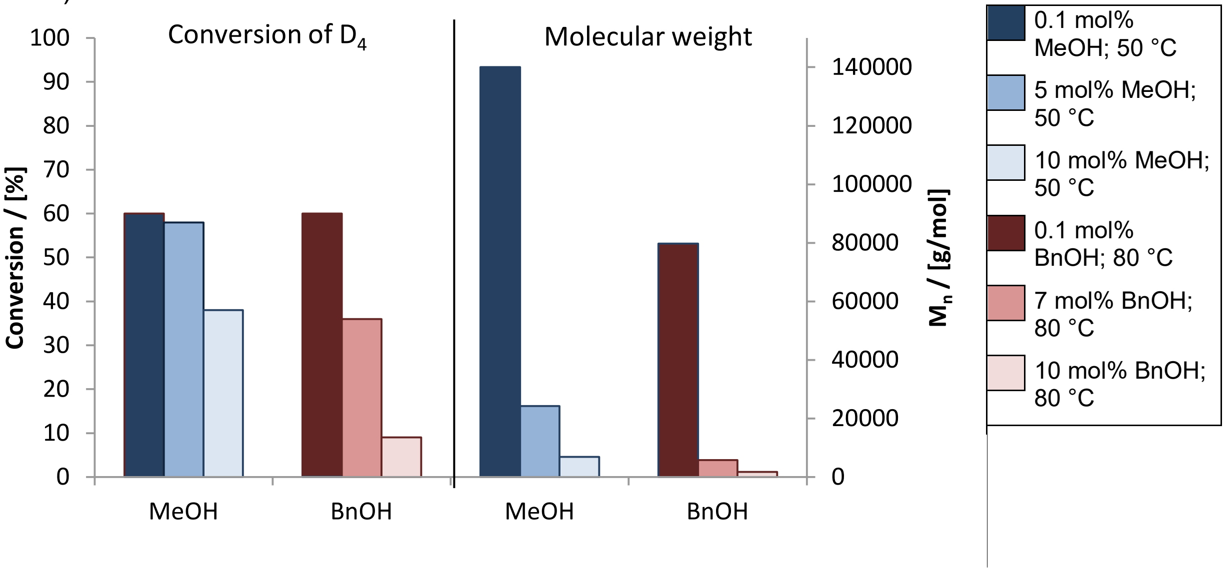

b) in toluene

**Chart 3-4: Influence of the concentration of the alcohol used as coinitiator. All experiments are carried out under inert conditions for 24 h using 0.1 mol% of 4.1 related to the amount of $D_4$ either a)neat or b) in toluene (Toluene: $D_4$ = 3:1). Conversion is calculated from $^{29}$Si(IG)-NMR. Molecular weight is determined by GPC using PDMS standards and toluene as eluent.**

As presented in Chart 3-4, increasing co-initiator concentration results in lower molecular weights and unexpectedly in lower conversions of the monomer $D_4$.

This derives most probably from an inhibition of ***4.1***. Instead of reacting with the monomer, the NHC deprotonates the alcohol and gets inactivated as it is described in Scheme 3-2: under formation of alcoholate anions.[151] It is suggested that the formed alcoholate initiates polymerization itself as shown in Scheme 2-5 (p. 11).[61] In conclusion, this would lead to a change in initiation mechanism in which the used NHC does not act as initiator anymore but as a base which deprotonates the used alcohol.

Especially in higher concentrations, the use of methanol results in higher conversion and higher molecular weights than with benzyl alcohol although reaction temperature is lower. This results from the higher nucleophilicity of methanol. The effect of the nature of the alcohol is especially investigated in later experiments using TBD as co-initiator and is discussed in depth in chapter 5.1.1 (p.73).

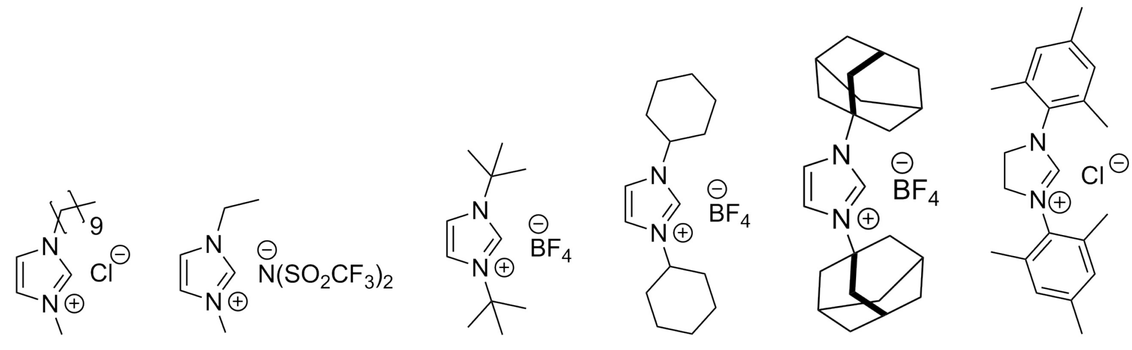
Interestingly, the increase in methanol concentration from 0.1 mol% to 5 mol% in toluene and 7 mol% in a neat setup does not have a significant effect on the monomer conversion, while at the same time; it results in a dramatic drop of the molecular weight (c.f. Chart 3-4). Further increase in methanol concentration leads to a drastic decrease in conversion to 38 % and further decrease in molecular weight which is also observed with benzyl alcohol. This might be explained by the competition between the two initiation mechanisms taking place in the presence of high amounts of alcohols. It is expected that the NHC can only irreversibly deprotonate an equimolar amount of the alcohol and hence cannot be reactivated leading to lower conversion.

As a conclusion, the molecular weight cannot be controlled by the molar amount of alcohol.

### 3.1.3 Screening of different NHCs

In a last step, in order to gain better control over the polymerization, different NHCs are tested. NHCs having an imidazol core (***3.1*** – ***3.5***) as well as one NHC having an imidazolidin core (***3.6***) are tested. Among these are asymmetric NHCs moieties just as the already tested ***3.1*** but also symmetric NHCs such as ***3.3*** used by Bacareido *et al*. in his work.[33]

The different NHCs are obtained by deprotonation of the corresponding imidazolium (***3.1a*** – ***3.5a***) and imidazolinium salts (***3.6a***) with KHMDS in THF (c.f. Figure 3-1). Imidazolium tetrafluoroborates ***3.3a***, ***3.4a*** and ***3.5a*** are synthesized according to Cheng[152], Herrmann[153] and Nakao[154] *et al*.



**3.1a** **3.2a** **3.3a** **3.4a** **3.5a** **3.6a**

**Figure 3-1: Imidazolium and imidazolinium salts which act as precursor for the NHCs generated by deprotonation with potassium disilazide.**

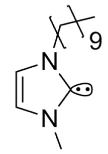
It is hypothesized that symmetric NHCs are more stable than asymmetric ones, which should have an influence on conversion and molecular masses. Furthermore, the influence of the different organic substituents attached to the NHCs having different steric and electronic properties was tested.

As a result from the previous subchapters 3.1.1 and 3.1.2 it is decided to use 0.1 mol% initiator (NHC) and 5 mol% of benzyl alcohol as co-initiator for the screening of the different NHCs. Polymerizations are performed in toluene (Toluene : $D_4$ = 3:1) at 80 °C oil bath temperature.

As presented in table Table 3-1, symmetric NHC ***3.3***, ***3.4*** and ***3.5*** show higher conversion of $D_4$ and the obtained polymers show higher molecular weight compared to the asymmetric NHCs (***3.1*** and ***3.2***). This might indicate a higher stability of the symmetric NHC under ring-opening polymerization conditions. But it can be also related to a prevention of premature deactivation of the NHC by protonation due to a higher steric hindrance by the bigger moieties shielding the NHC core more effectively. NHCs ***3.4*** and ***3.5*** show similar course of molecular weight, when tracking over time (c.f. A3.1.4.2, Scheme A3-1), which results also in similar final molecular weights after 24 h of reaction time and similar conversion. This can be explained by the similar structures of 1-adamantyl and cyclohexyl respectively attached to the nitrogen atoms of the imidazole core, having comparable electronic properties. Controversially, ***3.3*** shows the same conversion as ***3.4*** and ***3.5*** but higher molecular weights. This might be explained by a lower rate in chain-exchange reactions during ROP caused by less sterical hindrance. However the results are in agreement with Baceiredo's work[33], who reported NHC with *tert*-butyl groups as most successful initiator.

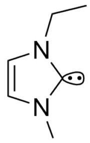
**Table 3-1: Results for the ROP of $D_4$ using different NHCs as initiators. Experiments are carried out using 0.1 mol% of NHC and 5 mol% of benzyl alcohol (both related to the amount of $D_4$) in toluene (Toluene : $D_4$ = 3:1) at 80 °C oil bath temperature for 24 h. Results of the experiments are given under the molecular structure of the NHC as follows: Conversion of $D_4$; $M_n$ (PDI). Conversion is calculated from $^{29}$Si(IG)-NMR and $M_n$ and PDI are determined by GPC measurements using toluene as eluent and PDMS standards.**

**Unsymmetrical limidazolin-2-ylidenes**



**3.1**

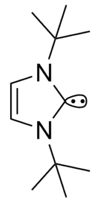
36 %; 5800 g/mol (1.48)



**3.2**

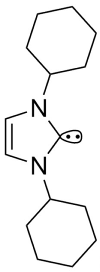
22 %; 1500 g/mol (1.72)

**Symmetrical limidazolin-2-ylidenes**



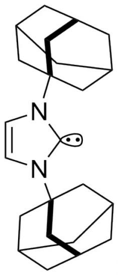
**3.3**

64 %; 9600 g/mol (1.27)



**3.4**

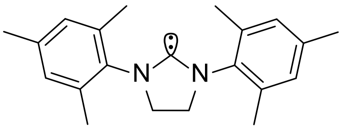
65 %; 8500 g/mol (1.33)



**3.5**

66 %; 8300 g/mol (1.32)

**Symmetrical Imidazolidin-2-ylidenes**



**3.6**

no reaction

Surprisingly, initiator ***3.6*** is not active in ROP and therefore no polymer is formed during reaction. Via NMR measurements, it is proven that the formation of ***3.6*** from ***3.6a*** via deprotonation with KHMDS was successful (c.f. in appendix A3.1.4.1 Figure A3-6). It is reported that imidazole based carbenes (***3.1*** - ***3.5***) are more stable than their dihydro analogues (like ***3.6***) due to fulfillment of Hückel-type aromacity.[155-156] Still, the thermodynamical stability of these dihydrodimidazolin-2-ylidenes is controversially discussed.[157-158] Therefore, it is supposed that the dihydrodimidazolin-2-ylidenes are not as stable as the imidazolin-2-ylidenes which might result in a premature deactivation during ROP.

More likely it might be that the high steric hindrance stemming from the methyl groups at the ortho-positions renders the carbene to be a very poor nucleophile which results in an inhibition of the nucleophilic attack at the cyclic siloxane.

Asymmetrical NHC ***3.2*** shows lower conversion of $D_4$ and polymers with lower molecular weights are obtained not only in comparison to the symmetric NHC but also to NHC ***3.1***. It is assumed, as already mentioned before, that due to the smaller moieties an effective shielding of the NHC core is not possible which is why premature deactivation by protonation takes place as discussed in the previous chapter 4.1.2.

In conclusion symmetrical NHCs are more active in ROP of cyclic siloxanes compared to asymmetric NHCs due to their stability and symmetrical charge distribution. Sterical hindrance due to bulkier moieties attached to the nitrogen atoms seem as far as noticed to be important in terms of shielding the NHC core.

## 3.2 Amines, amidines, guanidines

### 3.2.1 Influence of solvent

The choice of solvent can have a great effect on the reaction system. First polymerization experiments utilizing TBD **(3.14)** as base are performed in toluene and show only low conversion (24 % after 24 h). Moreover only low molecular weight polymers are obtained (c.f. Chart 3-5). Therefore, a solvent screening is performed. Three different solvents, namely acetonitrile, THF and toluene, are tested showing different polarity, acidity and basicity properties (Table 3-2). Additionally, the polymerization is carried out neat without any solvent.

The Dimroth-Reichardt parameter ($E_T(30)$) deriving from the energy for exiting an electron in a model dye compound[159] and the acceptor number (AN) based on the $^{31}P$-NMR shifts deriving from the electrophilic solvent interaction with triethylphosphine oxide[160] are popular measures of the acidity of solvents. The analogue parameter to AN is the donor number (DN) for the determination of the basicity of solvents deriving from the reaction heat of $SbCl_5$ and the solvent in 1,2-dichloroethane.[161-162] Both AN and DN are recommended measures for assessing the basic and acidic properties of solvents based on the comparison with $B_P$ and $A_P$ scales deriving from the Gibbs solvation energy of alkaline metal halides. Therefore, they are not suitable for weakly polar or apolar solvents.[162] Instead, the dielectric constant ($\varepsilon_r$) is here used as measure for the polarity of solvents.

**Table 3-2: Reported polarity expressed by dielectric constant, basicity expressed by DN and acidity expressed by AN and $E_T$ (30) of the screened solvents.**

| Solvent | DN[163] | AN[163] | $E_T$(30) [163] | $\varepsilon_r$[164] |
|---|---|---|---|---|
| Toluene | 1 | --- | 33.9 | 2.38 (25 °C) |
| THF | 20.0 | 8.0 | 37.4 | 7.52 (20 °C) |
| Acetonitrile | 14.1 | 18.9 | 45.6 | 36.64 (20 °C) |
| $D_4$ | --- | --- | --- | 2.39 (20 °C)[165] |
| $D_5$ | --- | --- | --- | 2.50 (20 °C)[165] |

In general TBD, methanol and the solvent are mixed in an argon-flushed, oven-dried flask. $D_4$ as monomer is added under vigorous stirring and the reaction is started by dipping into preheated oil bath (65 °C). After 24 h samples are taken for NMR and GPC analysis in order to determine molecular weight and conversion.

The results are summarized in Chart 3-5:

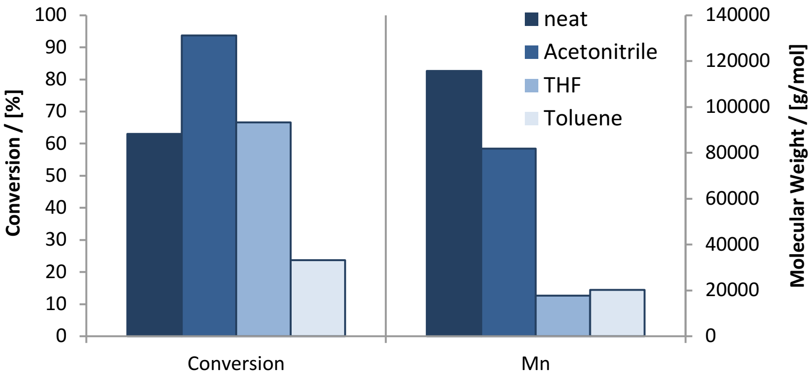


**Chart 3-5: Results of polymerization experiments of $D_4$ using 2 mol% of methanol and 2 mol% of TBD related to the amount of $D_4$. All experiments are carried out under inert conditions in different solvents (Solvent : $D_4$ = 1.5:1) at 65 °C for 24 h. Molecular weights are determined by GPC using PDMS standards and toluene as eluent and conversion is determined by $^{29}$Si(IG)-NMR.**

Compared to toluene, the use of acetonitrile leads to a great increase of conversion from 24 % to 94 %, although $D_4$ and acetonitrile are not miscible. Follow up reactions in acetonitrile showed that equilibrium is already reached after 5 h. Also the usage of THF, which is not as polar as acetonitrile, leads to an increase in conversion from 24 % to 60% when compared to toluene.

The increase in conversion is expected as it is already described in literature that small amounts of a polar aprotic additive such as THF or acetonitrile enhance polymerization speed.[96, 102] Conversion increases in line with the acidity of the solvents represented by $E_T$(30) and AN ( Table 3-2).

Interestingly, the experiments which are performed under neat conditions show higher conversion than in toluene and comparable conversion as in THF. This might be due to the dilution of the reactions system when using THF or toluene since both, monomer and polymer are miscible in these solvents, whereas acetonitrile leads to a biphasic reaction system which might be more comparable to a neat system.

Furthermore, acetonitrile as polar solvent helps to stabilize the formed ions and to avoid the formation of ion pairs and aggregates in order to obtain free ions or at least solvent separated ion pairs.[166] This explains why the reaction in acetonitrile shows higher conversion compared to the neat system.

Additionally, the choice of solvent has a high influence on the $pK_a$ value of the chosen base TBD as presented in Table 3-3.[167] This explains the observed conversions in the different solvents since TBD has a higher basicity in acetonitrile than in THF. It is assumed that the $pK_a$ value of TBD in toluene is even lower than the $pK_a$-value of it in THF. This is based on the fact that toluene itself has a lower polarity compared to THF. For the ring-opening polymerization where TBD acts as co-initiator, high $pK_a$ values are necessary to shift effectively the deprotonation equilibrium of the alcohol towards the alcoholate to initiate the ROP.

**Table 3-3: Reported $pK_a$-value of TBD in THF and acetonitrile.**

| Solvent | $pK_a$[167] |
|---|---|
| THF | 21.0 |
| Acetonitrile | 25.96 |

Surprisingly, there is no correlation between the obtained molecular weights of the polymers, the conversion and the chosen solvent (c.f. Chart 3-5). Experiments where toluene or THF are used lead to lower molecular weights than in acetonitrile or neat which can be again related to the dilution mentioned before.

The usage of acetonitrile might also allow weaker and maybe cheaper bases to be used as co-initiators, which would be of great advantage and would lead to a huge innovation potential. This will be discussed in subchapter 3.2.3.

### 3.2.2 Advantages of using acetonitrile as solvent for ROP of $D_4$

As shown in the previous subchapter 3.2.1, acetonitrile has a great effect on the conversion of $D_4$ under ROP conditions and thus on the reaction speed. The advantages towards the polymerization process will be discussed in this chapter.

It was already mentioned that both $D_4$ and the obtained polymer are not miscible with acetonitrile, which is not surprising due to the difference of their dielectric constants (c.f. Table 3-2). So the whole polymerization takes place in a two phase system. This is more precisely described as an emulsifier-free mechanically-stabilized emulsion polymerization. Via the conductivity method, acetonitrile is determined as the continuous phase, meaning that $D_4$ is dispersed in acetonitrile. For this purpose the conductivity of acetonitrile ($\kappa = 0.3$ µS), $D_4$ ($\kappa = 0$ µS) and a mechanically-stabilized emulsion of both ($\kappa = 0.2$ µS) is measured.

The conductivity method states that W/O emulsions where water is dispersed in oil show lower conductivity than O/W emulsions where water acts as continuous phase.[168] Applied to the here presented non-aqueous or in other words oil-in-polar-solvent emulsion it is expected that, if $D_4$ is the continuous phase, the conductivity of the emulsion would be $\kappa \approx 0$ µS. Since this is not the case it is concluded that $D_4$ represents the dispersed phase. This conclusion is validated by adding tab water to the acetonitrile phase. Water which is not soluble in $D_4$ but in acetonitrile boosts the latter's conductivity and therefore also the conductivity of the emulsion increases, which confirms that acetonitrile acts indeed as the continuous phase.

The biphasic emulsifier-free reaction set up is advantageous to the polymerization process especially because phase separation takes place immediately after stirring is stopped. TBD, which is insoluble in both the monomer and in the polymer, stays in the acetonitrile phase and the reaction does not need to be quenched. This leads to an easier workup: Quenching the reaction with an acid leads to an additional filtration step in order to remove the precipitated salts which can be very challenging for high viscous high molecular weight polymers. Furthermore, the polymer is easily isolated via phase separation. The unreacted monomer, which is dissolved in the polymer, can be removed with high vacuum at elevated temperatures or by solvent extraction with methanol. Actually, it is preferred to wash the polymer with methanol in order to remove remaining traces of the base or the solvent, although experiments showed that this is not necessary.

The simple decantation of the polymer phase leads to a facile reuse of the whole solvent phase in which methanol, TBD and eventually little $D_4$ are dissolved remaining from the polymerization. Therefore, a recycling experiment is designed.

The working sequence is presented in Figure 3-2.

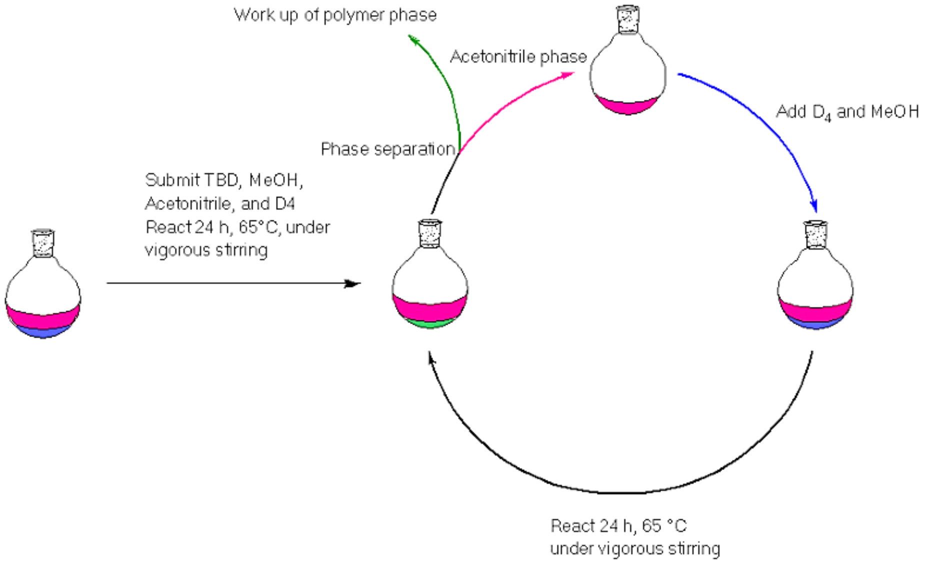


**Figure 3-2: Figure of the working sequence for recycling experiments.**

For the initial experiment (***P3.32***) 2 mol% TBD and 50 mol% methanol related to the amount of $D_4$ and acetonitrile (acetonitrile:$D_4$ = 3:1) are mixed. After adding $D_4$, reaction is conducted for 24 h at 65 °C. After phase separation, the polymer phase is worked up separately by washing with methanol and the solvent phase is transferred into an argon flushed three-neck flask. Fresh $D_4$ and methanol (50 mol% related to the amount of $D_4$) are added again. The reaction mixture is stirred 24 h at 65 °C. Then the reaction mixture is allowed to cool down to room temperature and the phases are separated. Again, the polymer phase is precipitated in methanol and the solvent phase is reused another time. The solvent phase is reused 5 times altogether (experiment ***P3.32a–e***).

From Chart 3-6 we can clearly see that the conversion, which is calculated from $^{29}$Si(IG)-NMR, stays the same and is not decreasing. After reusing the solvent phase 3 times it becomes slightly yellowish, which might be an indication that TBD is somehow affected for example by oxidation or carboxylation reactions. The solvent phase partially evaporates when recycling it although it does not seem to influence the conversion. Furthermore, the polydispersity of the obtained polymers is not affected.

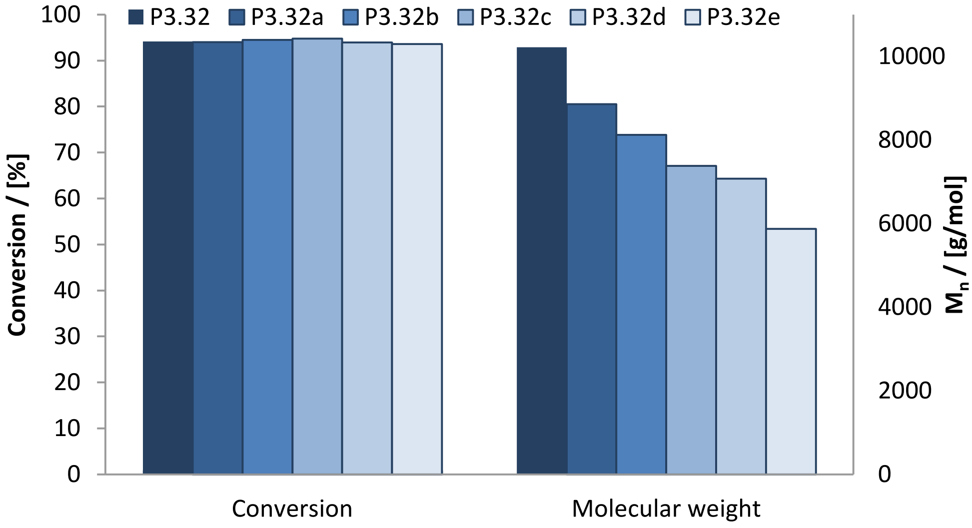


**Chart 3-6: Results of recycling experiments. For the initial experiment 2 mol% of TBD and 50 mol% of methanol are used (related to the amount of $D_4$) and acetonitrile is used in a ratio of acetonitrile : $D_4$ = 1.5:1. The whole solvent phase is recycled. Only methanol (50 mol% related to the amount of $D_4$) and $D_4$ are added freshly to every experiment. All experiments are carried out under inert conditions at 65 °C for 24 h. Conversion is calculated from $^{29}$Si-IG NMR as described in the experimental part. Molecular weight $M_n$ is determined by GPC using PDMS standards and toluene as eluent.**

Chart 3-6 shows that the molecular weight of the obtained polymers is decreasing with every recycling step. The reason for that could be the methanol concentration. After each reaction some methanol is possibly left in the acetonitrile phase, which is neglected for the calculations of the quantities of methanol added after each cycle. Just the same amount of methanol as used in the starting reaction is added. Therefore, the methanol concentration is slightly increasing in every experiment. Higher alcohol concentrations lead to smaller molecular weights of the polymer as will be discussed in chapter 5.1.4 (p. 82).

### 3.2.3 Screening of amines, amidines and guanidines

Due to the similarities on their polymerization mechanisms, basic co-initiators which are used in the ring-opening polymerization of lactones are often also active in ROP of cyclic siloxanes.

Since it was demonstrated that acetonitrile improves the reactivity of TBD as co-initiator several nitrogen containing bases such as amines, amides and guanidines were screened as suitable co-initiators (c.f. Table 3-6), which partially are also described to be active in ROP of lactones.[169-171] However, phosphazene bases are not tested because their behavior is already studied in depth and it is proven that they are very active in ROP of cyclic siloxanes.[68, 73, 172-176]

All results are compared to potassium hydroxide (**3.7**) which is one of the most important initiators for ring-opening polymerization used in industry and therefore serving as state of the art.[32, 177]

KOH is hygroscopic and forms carboxylates very fast. For polymerization reactions in small scales KOH is needed in pulverized form, hence the pellets are grinded in an oven-dried, argon-flushed Schlenk-tube filled with anhydrous heptane. Afterwards heptane is removed in high vacuum ($<10^{-3}$ mbar) and the grinded KOH is stored under argon. This procedure also has the advantage that water will be carried along with heptane upon evaporation.

KOH is not soluble in acetonitrile and neither in $D_4$ but in methanol solid KOH vanishes. This can be related to the formation of potassium methanolate.[67] Therefore, the first experiments are undertaken using high concentration of methanol leading also to the advantage that small molecular weight polymers are obtained (c.f. Table 3-4) which allows easier work up of the polymer and easier characterization of the terminating groups (c.f. chapter 4.2, p. 51).

**Table 3-4: Results of polymerization using KOH (2 mol%) and different concentrations of methanol in acetonitrile (acetonitrile : $D_4$ = 1.5:1) at 65 °C oil bath temperature. Conversion is calculated from $^{29}$Si(IG)-NMR and $M_n$ as well as PDI are determined by GPC measurements using toluene as eluent and PDMS standards.**

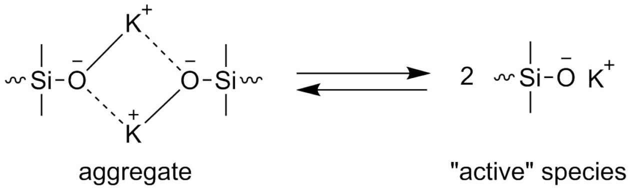
| Reaction | MeOH [mol%] | Conversion [%] | $M_n$ [g/mol] | PDI |
|---|---|---|---|---|
| P3.33 | 2 | 94 | 59000 | 1.73 |
| P3.34 | 200 | 94 | 9500 | 1.37 |
| P3.35 | 400 | 94 | 5500 | 1.39 |

The use of low concentrations of methanol (2 mol%) leads to a heterogeneous biphasic reaction with solid particles. Due to the low concentration of methanol, higher molecular weight polymers are obtained. Interestingly, when using this low concentration of methanol the molecular weight is approximately halved after work up via washing with methanol (c.f. Table 3-5). This behavior was never observed before.

**Table 3-5: Moleuclar weights of polymers before and after processing. Polymerization is performed in the presence of KOH (2 mol%) and methanol (2 mol%) in acetonitrile (acetonitrile : $D_4$ = 1.5:1). Samples of the unprocessed material are taken directly after polymerization whereas molecular weight of the processed material is determined after washing with methanol and stripping in high vacuum at 80 °C. $M_n$ and PDI are determined by GPC measurements using toluene as eluent and PDMS standards.**

| Reaction | | $M_n$ [g/mol] | PDI |
|---|---|---|---|
| P3.33a | Unprocessed raw product | 136500 | 2.20 |
| | Processed polymer | 76100 | 1.73 |
| P3.33b | Unprocessed raw product | 140800 | 2.10 |
| | Processed polymer | 58700 | 1.74 |

One reason for this observation could be that aggregates with potassium are formed during the polymerization process as illustrated in Scheme 3-3. After work up by washing with methanol these aggregates are destroyed and the polymer is finally end-capped.



**Scheme 3-3: Aggregate formation during ring-opening polymerization of cyclic siloxanes if KOH is used as initiator.[178]**

According to literature, 1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU, **3.8**) is not active in the ROP of cyclic esters except in the polymerization of lactides.[170] Surprisingly, when using in our two-phase system in ROP of $D_4$, a conversion of 76 % is achieved. Nevertheless, the conversion of $D_4$ in the presence of DBU is highly depending on the concentration of methanol (c.f. Table 3-7). With lower concentrations of methanol lower conversions are achieved although the obtained molecular weights are not affected significantly. With other co-initiators such as KOH or TBD conversion is independent of the MeOH concentration. Compared to KOH, DBU is less active which results in a lower conversion and molecular weights of the isolated polymers.

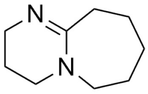
**Table 3-6: Classes of different nitrogen containing bases tested in ROP of $D_4$ as alternative to KOH. Experiments are carried out using 2 mol% of the base and 200 mol% of methanol (both related to the amount of $D_4$) in acetonitrile (acetonitrile : $D_4$ = 1.5:1). Results of the experiments are given under the molecular structure of the base as follows: Conversion of $D_4$; $M_n$ (PDI). Conversion is calculated from $^{29}$Si(IG)-NMR and $M_n$ and PDI are determined by GPC measurements using toluene as eluent and PDMS standards. pKa values in acetonitrile are taken from literature.[167]**

**Alkaline metal hydroxide**

KOH **3.7**

94 %; 9500 g/mol (1.37)

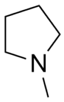
**Amines and amidines**



**3.8**

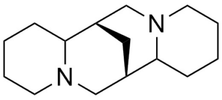
pKa = 24.33

79 %; 2700 g/mol (1.10)



**3.9**

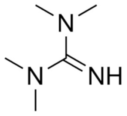
40 %; 2100 g/mol (1.07)



**3.10**

30 %; 2600 g/mol (1.07)

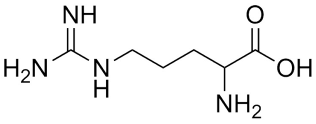
**Acyclic Guanidines**



**3.11**

$pK_a$ = 23.3

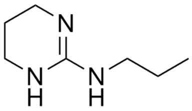
no reaction



**3.12**

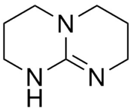
35 %; 2300 g/mol (1.06)

**Cyclic guanidines**



**3.13**

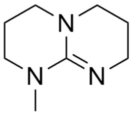
61 %; 1800 g/mol (1.50)



**3.14**

$pK_a$= 25.96

94 %; 5000 g/mol (1.45)

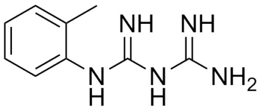


**3.15**

$pK_a$ = 25.43

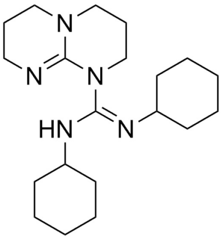
83 %, 5000 g/mol (1.34)

**Biguanidines**



**3.16**

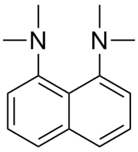
0 %



**3.17**

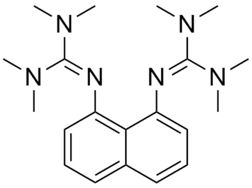
93 %; 6000 g/mol (1.32)

**Proton Sponges**



**3.18**

51 %; 2000 g/mol (1.07)



**3.19**

$pK_a$ = 25.1

90 %; 2000 g/mol (1.67)

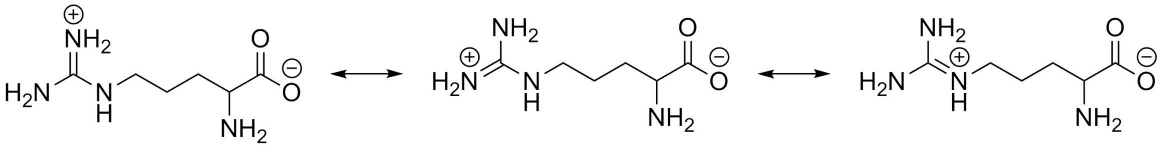
**Table 3-7: Results of polymerization using DBU (2 mol%) and different concentrations of methanol in acetonitrile (acetonitrile : $D_4$ = 1.5:1) at 65 °C oil bath temperature. Conversion is calculated from $^{29}$Si(IG)-NMR and $M_n$ and PDI are determined by GPC measurements using toluene as eluent and PDMS standards.**

| Reaction | MeOH [mol%] | Conversion [%] | $M_n$ [g/mol] | PDI |
|---|---|---|---|---|
| P3.36 | 200 | 76 | 2800 | 1.10 |
| P3.37 | 22 | 22 | 2000 | 1.52 |

(-)-Sparteine (**3.10**), which belongs to the class of alkaloids, can be extracted from scotch broom or a species of lupins, is especially known as ligand in organic chemistry.[179-180] As a chiral diamine, it was originally used in various asymmetric reactions such as lithiations, substitutions, and carbometalations.[181-186] (−)-Sparteine has proven itself to be an extremely effective catalyst for ROP for example in the ROP of lactones.[187] Also N-Methylpyrrolidine (**3.9**) is tested in the ROP of cyclic siloxanes. Both **3.9** and **3.10** are active in ROP of $D_4$ in acetonitrile although the polymers cannot be isolated by "precipitating" in methanol. They have to be washed with water and dried over $Na_2SO_4$. Afterwards, the unreacted $D_4$ is removed in high vacuum at 80 °C. Compared to KOH (94 % of conversion) and to **3.8** (79 % of conversion) both **3.9** and **3.10** show significantly lower conversion (40 % and 30 % of conversion respectively). However, the obtained molecular weights of the isolated polymers are comparable to the one obtained by using DBU (**3.8**).

Surprisingly, tetramethylguanidine (TMG, **3.11**) showed no activity in ROP of cyclic siloxanes whereas arginine showed a conversion of at least 35 % although arginine (**3.12**) is neither soluble in the acetonitrile phase nor in the monomeric phase. Also the polydispersity of the obtained polymer is very low. This might be due to the lower activity of arginine in comparison to TBD (**3.14**) or KOH (**3.7**) which is proven by the rather low conversion. As described above for polymers obtained by using co-initiators **3.9** and **3.10** "precipitation" of the produced polymer in methanol is not possible.

Arginine (**3.12**) is soluble in $H_2O$. Due to this fact it is expected that the usage of $H_2O$ as hydroxy compound leads to an increase in conversion since arginine is partially dissolved in the acetonitrile phase. Surprisingly, polymerization does not proceed. This might be due to the fact that in aqueous solution arginine forms zwitterionic structures (c.f. Scheme 3-4) and is not active in polymerization anymore. The isoelectric point at which arginine is existent in its zwitterionic structure is at pH 10.8.[188] The pH-value – estimated with pH-paper (pH 1-14) – of arginine in water is determined to pH 14 and after adding actetonitrile to pH 10. Thereby the same concentrations as in the polymerization experiments are used. This confirms the assumption of the presence of zwitterionic structure.



**Scheme 3-4: Zwitterionic mesomeric structures of arginine.**

Cyclic guanidines which were tested showed very different results. As already mentioned in previous subchapter 3.2.1, the activity of TBD (**3.14**) in ROP is increased when using polar, aprotic solvents. It shows similar results compared to KOH (conversion = 94 %; $M_n$ = 5000 g/mol). Surprisingly, also the methylated derivative of TBD, 7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD, **3.15**), seems to be active in ROP although Hedrick et. al.[69] reported that MTBD does not initiate ROP of 1-oxa-2,5-disilacyclopentane (TMSOC) under neat conditions. Thereby conversion (83 %) is only slightly lower and molecular weight ($M_n$ = 5000 g/mol) is approximately the same when comparing to TBD. Controversially, **3.13,** a monocyclic guanidine (which is synthesized according to Aoyagi[189] and Cotton[190] *et al.*), is less active expressed by lower conversion of 61 % and low molecular weight (1800 g/mol).

These results suggest that the activity of the co-initiator in ROP is not only depending on its basicity which is expressed by the pKa value but also on its structure and its nucleophilicity.

In the row of different guanidines also biguanidines have been tested. **3.17** is described to be active in ROP of lactides and is more basic than TBD which showed very good results in polymerization of $D_4$.[167] Surprisingly, **3.16** showed no activity in ROP whereas **3.17,** which was synthesized according to Hedrick *et al.*[191-192], showed very good activity, which might be related to its structural similarity of TBD.

Proton sponges have the general feature that they can uptake a proton by forming a stabilized intramolecular hydrogen bond due to the two basic nitrogen moieties and their spatial orientation.[167] Therefore, two different proton sponges with a naphthyl scaffold are tested, having amino and guanidine moieties respectively. **3.19** shows good activity expressed by a conversion of 90 % which is compared to KOH only slightly lower. On the contrary **3.18** shows lower conversion (51 %) which might result from its lower kinetic basicity compared to **3.19**[193]. Although **3.19** has a higher activity compared to **3.18,** both show similar molecular weight although the PDI of the polymer is higher when using **3.19** as co-initiator.

Work up of the polymers using proton sponges especially **3.19** is crucial due to the fact that also small traces of remaining co-initiator color the polymer slightly purple. Over time, the color changes to brown which might be caused by oxidation processes.

After screening all mentioned bases it is decided to have a closer look at those bases which show a conversion higher than 60 %. DBU (**3.8**) is excluded because its conversion is depending on the methanol concentration.

Course of conversion and molecular weight are tracked over 24 h by taking samples each hour. Conversion is determined by $^{29}$Si(IG)-NMR in $CDCl_3$ and $M_n$ by GPC measurement using toluene as eluent and PDMS standards. The presented results in Chart 3-7 and Chart 3-8 represent two experiments except co-initiator **3.17**.

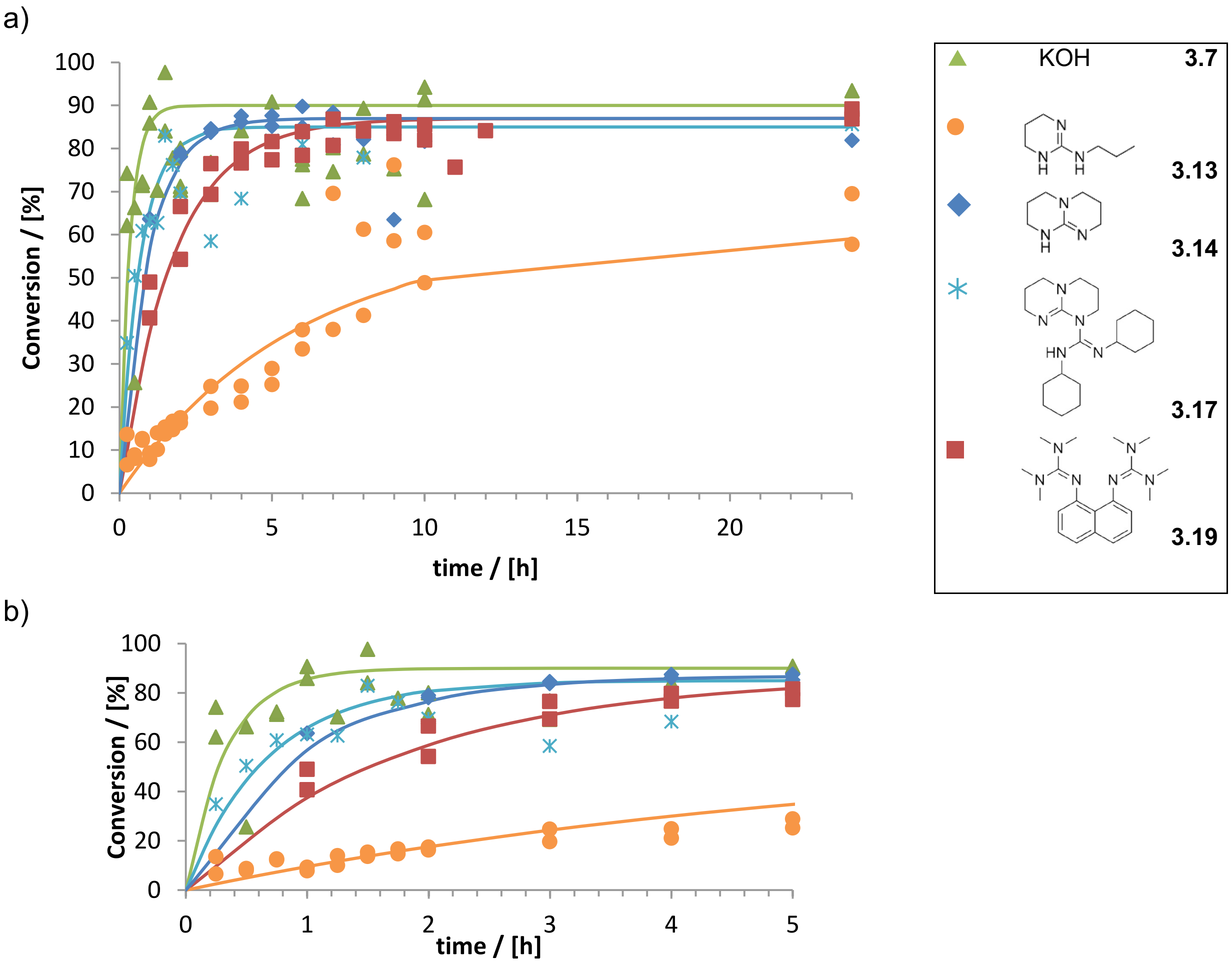


**Chart 3-7: Course of conversion utilizing different initiators a) oververview of the whole experiment (24 h) and b) close up of the first 5 h of reaction. Experiments are carried out using 2 mol% of the base and 200 mol% of methanol (both related to the amount of $D_4$) in acetonitrile (acetonitrile : $D_4$ = 1.5:1). Conversion is calculated from $^{29}$Si(IG)-NMR.**

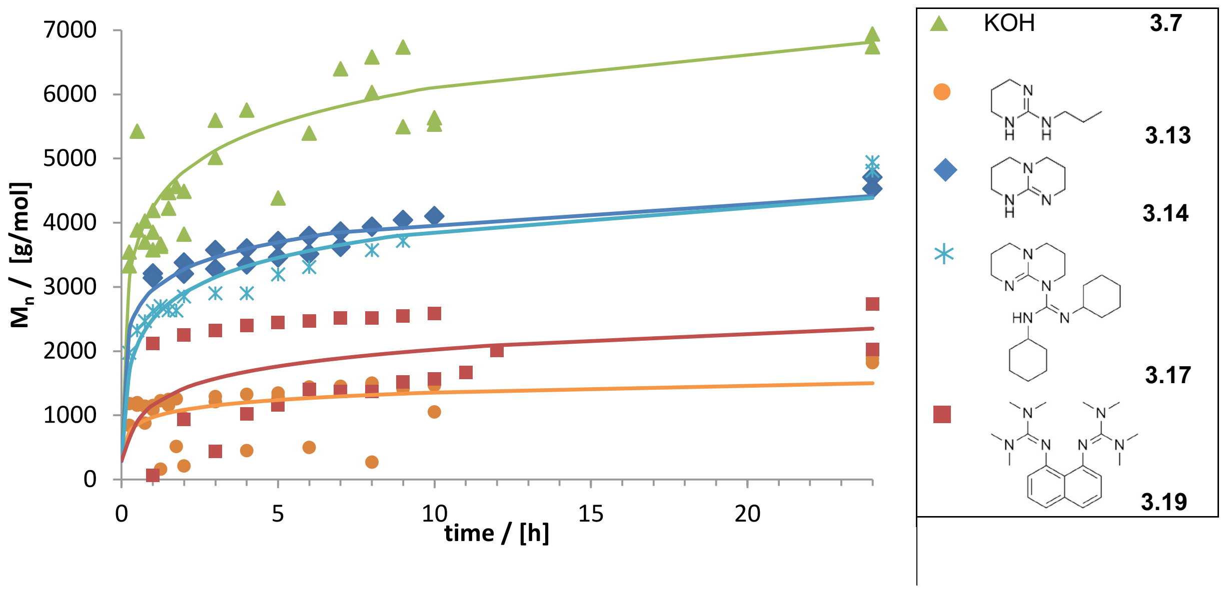
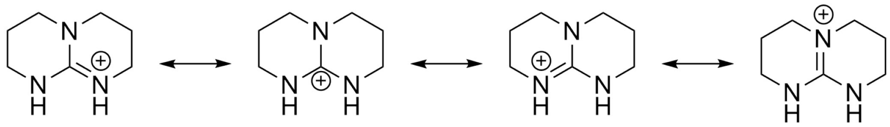


**Chart 3-8: Molecular weight evolution with time when using different initiators. Experiments are carried out using 2 mol% of the base and 200 mol% of methanol (both related to the amount of $D_4$) in acetonitrile (acetonitrile : $D_4$ = 1.5:1). $M_n$ is determined by GPC measurements using toluene as eluent and PDMS standards.**

As can be seen from Chart 3-7 the conversions are very inconsistent which is expressed by the high dispersion of the data points. This might be a problem of sampling which especially occurrs when using KOH (**3.7**). Even though acetonitrile, $D_4$ and PDMS are both soluble in deuterated chloroform, two phases appear in the NMR-tube, which might disturb the measurement.

From Chart 3-7b it seems that **3.13** has lower initial reaction speed compared to **3.14** and **3.17** which show nearly same reaction speed which might be explained by their structural similarity. KOH seems to be faster in the beginning but this is hard to argue due to the high dispersion of the data points.

All the results confirm that the activity of the co-initiator in ROP is not only depending on the basicity which is expressed by the $pK_a$ value but also on sterical demand and nucleophilicity. Another important feature is that these co-initiators need to uptake a proton and have to stabilize the positive charge. Co-initiators **3.13**, **3.14**, **3.17** and **3.19** can stabilize the positive charge via delocalization as presented exemplary in Scheme 3-5. This might be one reason why they show higher conversion than the other co-initiators.



**Scheme 3-5: Mesomeric structures of protonated TBD (3.14).**

The protonation of the co-initiators might be also sterical hindered by moieties attached to the nitrogen such as in molecule **3.13** which is why e.g. planar TBD (**3.14**) shows a higher and faster conversion.

## 3.3 Summary and conclusions

Several nitrogen-containing bases were investigated, whereby this chapter was basically divided into the investigation of NHC and guanidines, amidines and amines as suitable bases for Ring-opening polymerization of octamethylcyclotetrasiloxane ($D_4$). NHCs follow a different polymerization mechanism from those of guanidines, amidines and amines. It is proposed that NHCs act as initiators by attacking the monomer themselves, whereas guanidines, amidines and amines are supposed to act as co-initiators because they deprotonate the present alcohol and the corresponding alcoholate then initiates ROP.

In this context NHCs having an imidazole core were especially investigated.

It was found that NHCs in neat conditions at elevated temperatures show conversions of about 95 % in between 24 h leading to high molecular weight polymers with number averaged molecular weights of about 300000 g/mol. These molecular weights are already achieved after 5 h of reaction which is far too fast to be controllable and lead to a reaction system where the molecular weight cannot be targeted. Therefore, it was tried to slow down the reaction by using solvent and by increasing the concentration of the alcohol which was used in order to terminate the growing chain.

Interestingly, both polar as well apolar aprotic solvents lead to a drastic decrease of conversion which is explained by dilution effects. Increase in concentration of the alcohol lead to inhibition of polymerization by inactivation of the NHCs due to protonation by the alcohol. The formed alcoholates are supposed to initiate polymerization as well promoting a change from NHC initiated zwitterionic ROP towards alcoholate initiated classical AROP or a mixture of both. However, the increase in alcohol concentration induces further decrease of conversion.

Parallel to the screening of NHCs amines, amides and guanidines were investigated as suitable initiators. Thereby in a first step a solvent screening was undertaken since TBD, a so called superbase, showed only moderate conversions under neat conditions and very low conversions in toluene. In contrast to the results obtained when using NHCs in THF the usage of a polar solvent has an accelerating effect on reaction speed here. As a result, polymerization in acetonitrile showed very good results with conversion >90 % in between 24 h, although polymerization proceeded in a biphasic system. The reaction set up was defined as mechanically-stabilized emulsion-polymerization in which acetonitrile acts as the continuous phase. This causes the advantage that quenching of the catalyst is not necessary since it remains in the solvent phase. Furthermore, it was proven that the solvent phase can be recycled and the polymerization proceeds without the necessity of adding new TBD.

The screening of several amines, amides and guanidines showed that TBD (**3.14**) and TBD analogues (**3.15** and **3.17**) have highest conversion in comparison to KOH (**3.7**).

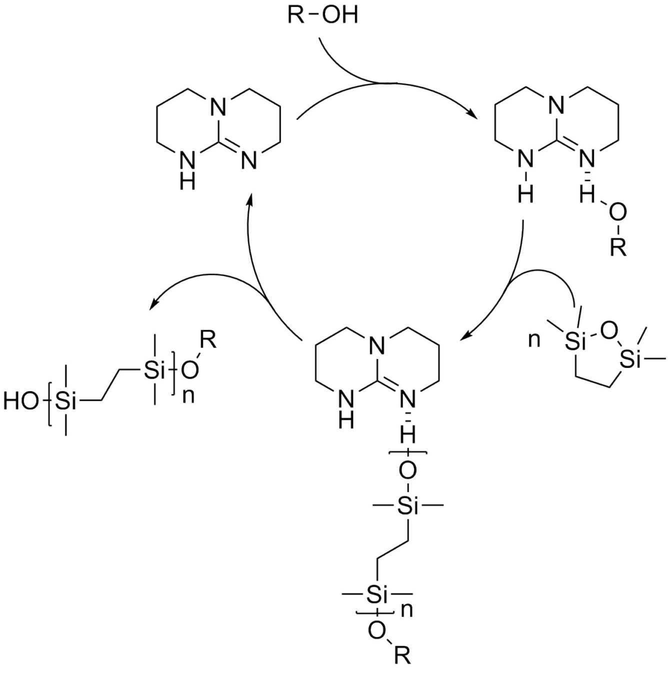
Since it was shown that NHCs are very efficient initiators but are not very well controllable in ROP of cyclic siloxanes, it was decided to undertake further investigations with TBD.

# 4 Mechanistic Considerations

In this chapter we take a deeper look at the polymerization mechanism when using an organocatalyst such as TBD in ring-opening polymerization of cyclic siloxanes. Therefore, in chapter 4.1 the general reaction mechanism is investigated and compared to literature. This is followed by analysis of the obtained polymers paying special attention to the end-groups in chapter 4.2. Due to the finding that surprisingly homotelechelic siloxanes are obtained, possible side reactions are considered and investigated in chapter 4.3.

## 4.1 General reaction mechanism

Hedrick *at al.*[69] investigated the activity of TBD in the ROP of cyclic carbosiloxanes, namely of 1-oxa-2,5-disilacyclopentane (TMSOC), in detail. Using 4-pyrenebutan-1-ol as UV-active initiator they were able to prove its incorporation as terminating group into the polymer backbone. Furthermore, they were able to prove that TBD forms complexes with alcohols and silanols via hydrogen bonding.[69] This might lead to a pseudo-anionic polymerization mechanism as it is suggested in the case of the ROP of strained cyclic esters.[194]

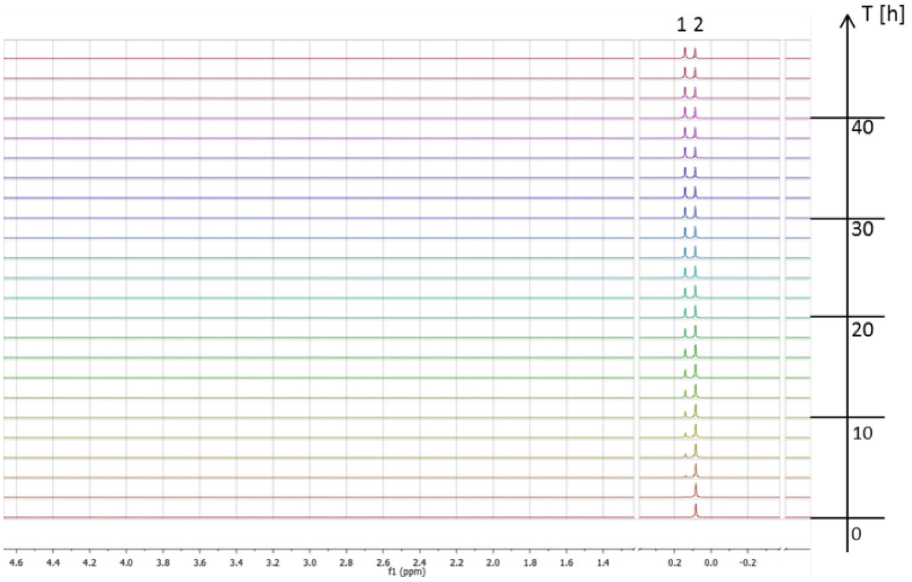


**Scheme 4-1: Proposed pseudo-anionic mechanism of the ROP of TMSOC with TBD as co-initiator and an alcohol based on the results of Hedrick *et al.* [69, 194].**

Based on the work of Hedrick *et al.*[69], polymerization experiment ***P4.1*** is tracked via in-situ $^1$H-NMR and $^{29}$Si(IG)-NMR are performed in deuterated toluene using $D_4$ as monomer instead of TMSOC or $D_3$. For this experiment $D_4$, 2 mol% of TBD, 2 mol% of methanol related to the amount of $D_4$ and deuterated toluene (toluene : $D_4$ = 1.5:1) are used. The NMR spectrometer is preheated to 65 °C and NMR experiments ($^{1}$H, $^{29}$Si(IG)) are performed every 2 h in a Young-NMR-tube for 48 h.

By evaluating the time resolved $^{1}$H-NMR (cf. Figure 4-1 a) and $^{29}$Si(IG)-NMR (cf. Figure 4-1 b) conversion of $D_4$ and growing of the polymer chain is observed. Additionally, the formation of $D_5$ ((cf. Figure 4-1b; Signal 2b) as side product due to back-biting reactions can be observed in time-resolved $^{29}$Si(IG)-NMR.

a) $^{1}$H-NMR



b) $^{29}$Si(IG)-NMR

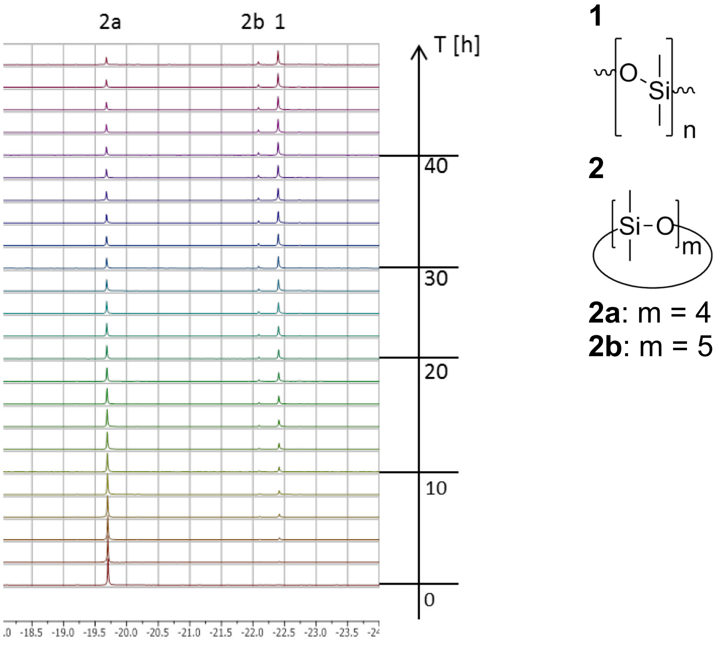


**Figure 4-1: a) $^{1}$H-NMR spectra measured at 400 MHz and b) $^{29}$Si(IG)-NMR spectra measured at 80 MHz of in situ NMR experiment *P4.1* tracked for 48 h at 65 °C. Measurement is undertaken in toluene *d8*.**

By increasing the scale of the signals of time-resolved $^1$H-NMR more details are visible (c.f. Figure 4-2). Signals 3 – 5 and 8 can be related to the protonated initiator (TBDH$^+$) which indicates a classic anionic reaction mechanism. If a complex of either the alcohol or the growing chain with TBD would be present, more signals in $^1$H-NMR would be expected due to the fact that TBD in a complex would not be symmetric like it is in its protonated form. Furthermore, when integrating signal 8 with respect to the other signals related to TBDH$^+$ or TBD, it equals 2 protons. This speaks for a protonated form of TBD and is confirmed by $^1$H-NMR experiments of TBD alone where the integration of the NH-group equals 1 proton (see A4.1.1, Figure A4-1).

Signal 8 (cf. Figure 4-2 b) is shifting from 3.5 ppm to 4.4 ppm during course of the reaction. Here the protonated initiator interacts with both the methanolate as well as the silanolate. At the beginning it interacts with the methanolate anion only but later, when initiation and propagation take place, the active silanolate center can also interact with the protonated initiator. Most probably interaction changes so fast that it cannot be measured by $^1$H-NMR. That is why not two signals can be observed but one as an average of both. Because of the rising concentration of the silanolates the signal is shifting from 3.5 ppm to 4.4 ppm. Signals 6 (3.2 ppm) and 7 (3.4 ppm) are of a special interest due to the fact that they represent the methoxy group in the form of methanol (signal 6) and as chain end group of the polymer (signal 7). Obviously the intensity of signal 6 decreases over time due to the consumption of methanol and its decreasing concentration, whereas the concentration of signal 7 increases over time representing the increasing concentration of polymer chains.

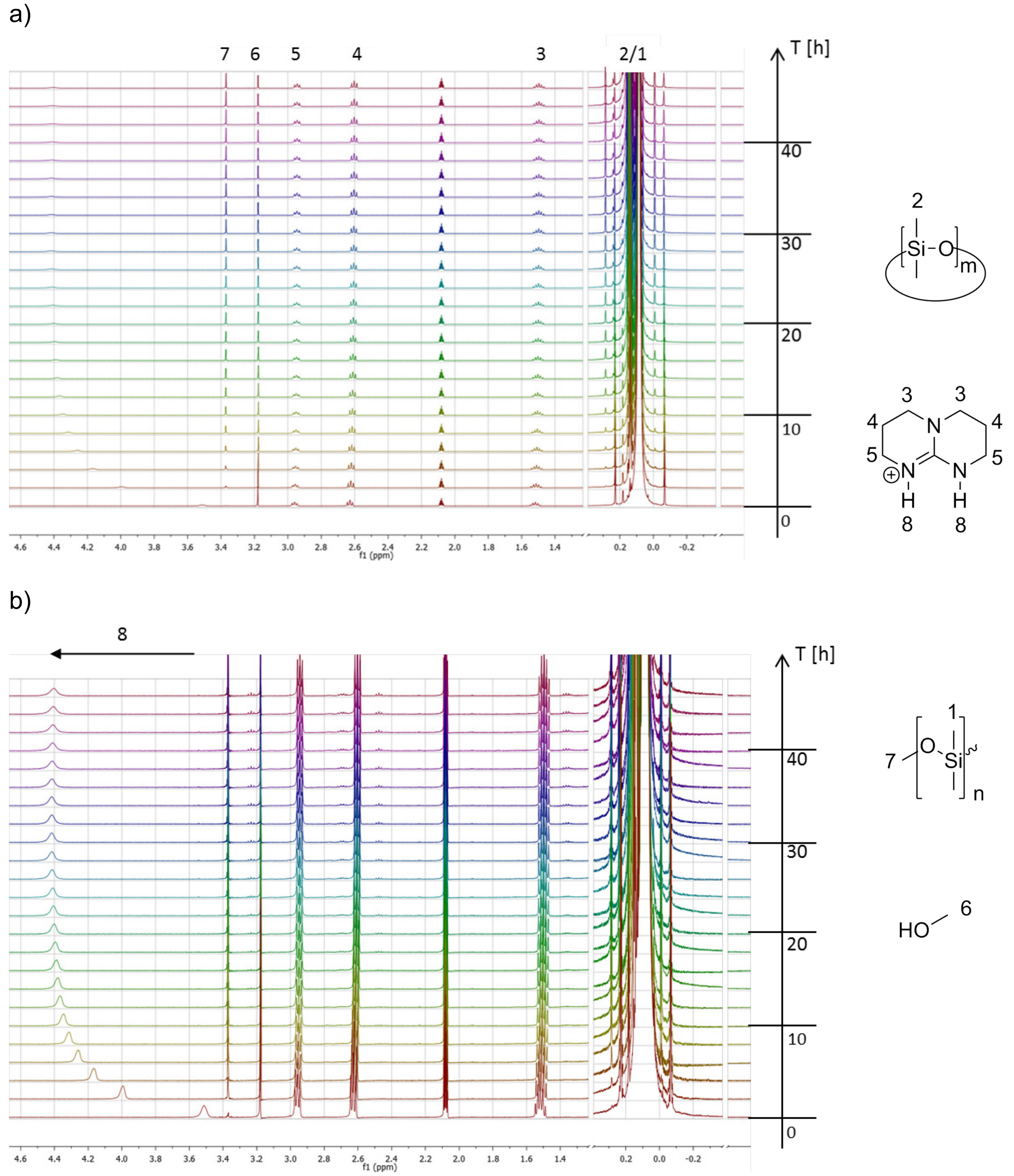
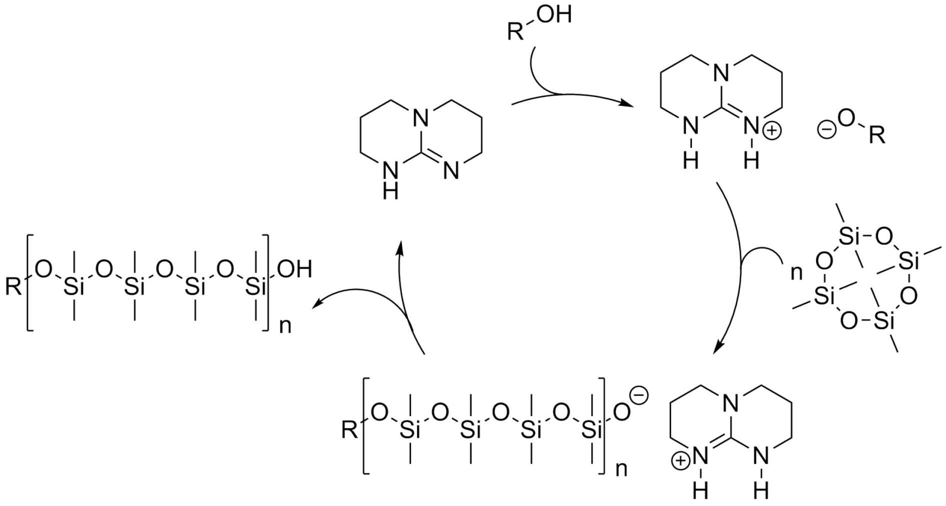


**Figure 4-2: Enlarged time resolved $^{1}$H-NMR spectra of Experiment P4.1. NMR measurements are performed in toluene *d8* at 400 MHz.**

All these findings lead to the conclusion that unlike proposed by Hedrick *et al.*[194], polymerization of $D_4$ follows a classical anionic mechanism (c.f. Scheme 4-2) instead of a pseudo-anionic reaction mechanism.



Scheme 4-2: Proposed reaction mechanism of the ROP of $D_4$ with TBD as co-initiator and an alcohol.

## 4.2 End-group analysis

When using TBD as co-initiator in combination with methanol in ROP of $D_4$ it is expected to obtain hetero-telechelic polydimethylsiloxanes which are *α*-methoxydimethylsilyl-*ω*-hydroxydimethylsilyl terminated as stated by Hedrick et al.[69]. This is why three signals in $^{29}$Si(IG)-NMR of a worked-up polymer are expected: One multiplet for the repeating unit ($Si(CH_3)_2$–O) as well as one signal for each of the two endgroups ($Si(CH_3)_2$–OH and $Si(CH_3)_2$–$OCH_3$). In polymers having high molecular weight only one signal for the repeating unit is observable. Most likely it is not possible to detect the terminating group signals in polymers with high molecular masses due to the low concentration of terminating groups related to the polymer chain.

By synthesizing polymers with a molecular weight below 50000 g/mol it is possible to detect a signal at -11.15 ppm in $^{29}$Si-NMR, which is assigned to one of the possible terminating groups (cf. Figure 4-3).

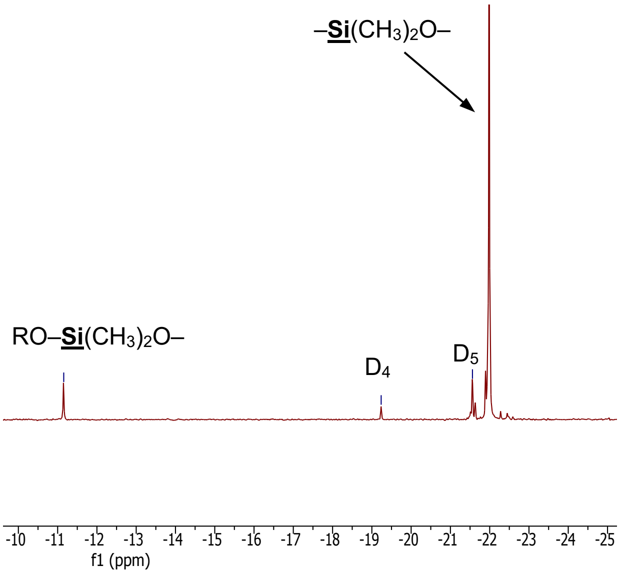


**Figure 4-3: $^{29}$Si(IG)-NMR (80 MHz, 297 K) of P4.2 measured in $CDCl_3$ having following characteristics: $M_n$ = 2600; PDI = 1.42. $M_n$ is determined by GPC measurements using toluene as eluent and PDMS standards.**

It could be that only one overlapping signal appears if the shift of the $Si(CH_3)_2–OH$ and $Si(CH_3)_2–OCH_3$ group are nearly the same but this is contradictory to the results of Cabane *et al.*[195]

Cabane *et al.*[195] followed the polymerization of dimethyldiethoxysilane via $^{29}$Si-NMR. They were able to identify several siloxane species which are formed during the reaction and observed a signal at -13.59 ppm in $^{29}$Si-NMR spectra in a hydroxy terminated oligodimethylsiloxane with four repeating units (cf. Figure 4-4 a) which they related to the Si-OH group. In an oligodimethylsiloxane with three repeating units having one Si-OH and one Si-OEt endgroup they find two signals at -13.17 ppm (Si-OEt) and 13.90 ppm (Si-OH) (cf. Figure 4-4 b) which are related to the terminating groups. They also observe a high-field shift of the signals with increasing chain length of the polymer. This shift is especially strong if the polymer contains two Si-OH terminating groups. But it reaches a plateau if the chain has more than four repeating units.[195]

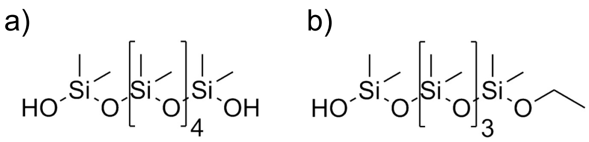


**Figure 4-4: Molecular structure of the polymers mentioned by Cabane et al.[195]**

Taking this into consideration, it is thought that the signals of both endgroups are not overlapping and that the signal at -11.15 ppm in $^{29}$Si(IG)-NMR of ***P4.2*** can be related either to the Si-OH or Si-OMe group of a homotelechelic polymer.

By performing additional 2D-NMR (HMBC: $^1H$, $^{29}Si$) experiments the signal at -11.15 ppm in $^{29}Si$(IG)-NMR can be related to the methoxy group at 3.5 ppm in $^1H$-NMR (c.f. Figure 4-5). Therefore it is confirmed that the signal at -11.15 ppm has to be related to the $-OSi(CH_3)_2-OCH_3$ end-group of the polymer and furthermore it is proven that methanol is incorporated into the polymer, resulting in a homotelechelic *α*,*ω*–di(methoxydimethylsilyl) terminated polydimethylsiloxane.

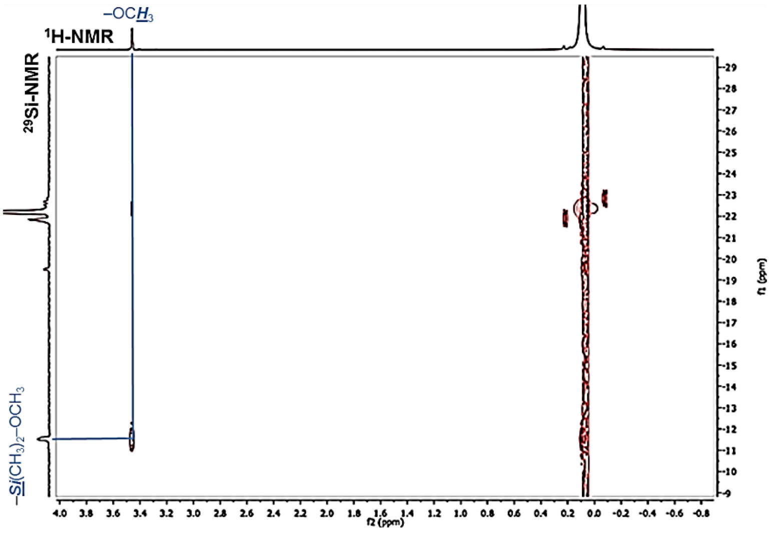


**Figure 4-5: Spectra of HMBC-NMR ($^1H$, $^{29}Si$; 79.5 MHz in $CDCl_3$) of *P4.2*.**

ESI-TOF and MALDI-TOF experiments give evidence that homotelechelic *α*-, *ω*–methoxydimethylsily terminated polydimethylsiloxane are obtained as product of the polymerization of $D_4$ using a combination of TBD and methanol in acetonitrile. Exemplary ESI-TOF spectra of ***P4.2*** (3100 g/mol, PDI = 1.46) show a nearly ideal molecular weight distribution (cf. Figure 4-6 a). Furthermore it is demonstrated that a polymer which is methoxy end-capped on both sides is obtained. Only small signals of heterochelechelic polymers (α-methoxydimethylsilyl-ω-hydroxydimethylsilyl PDMS) can be observed when enlarging the scale of the spectrum as presented in Figure 4-6 b. MALDI-TOF spectra are presented in the appendix (c.f. A4.21, Figure A4-3).

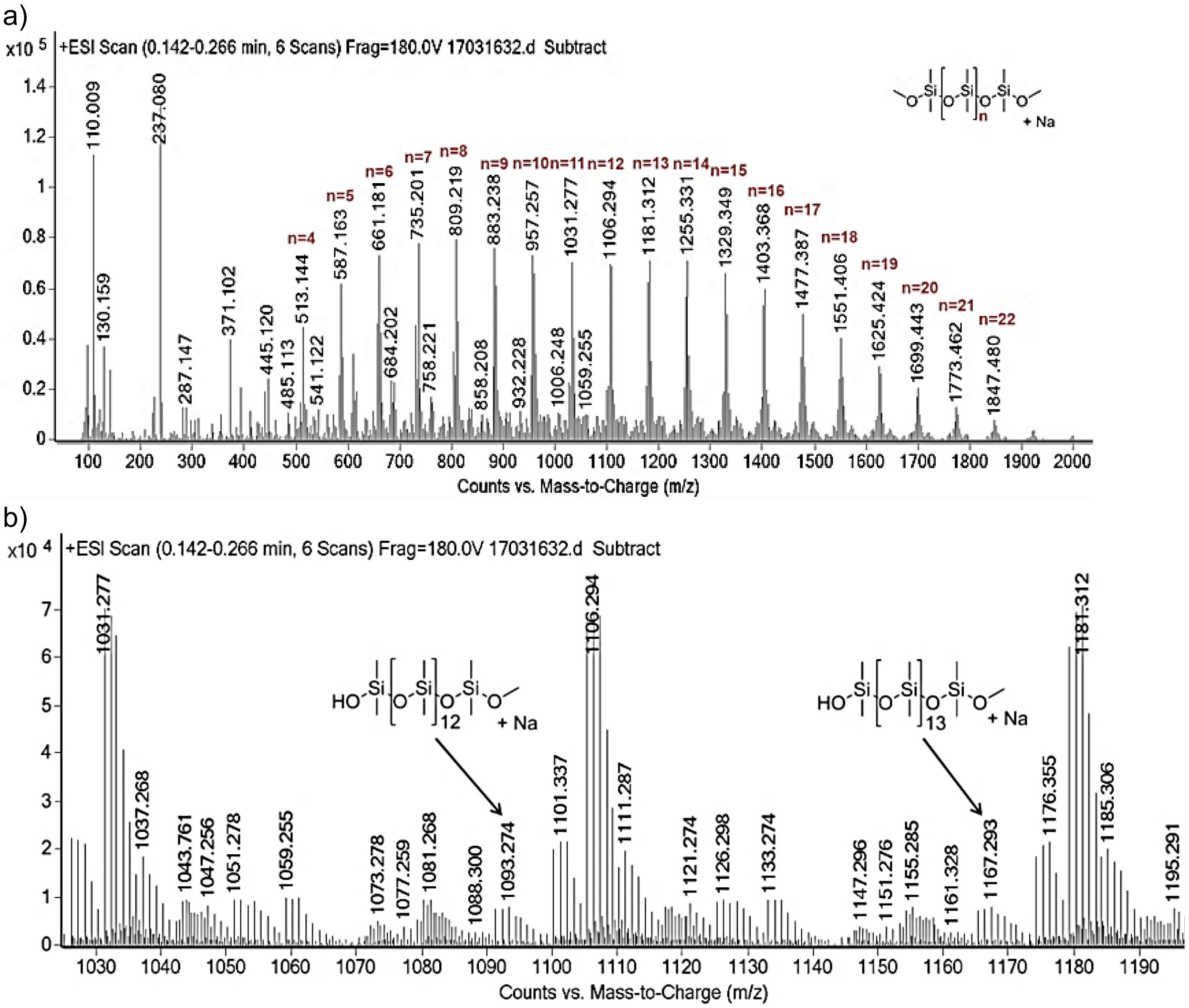


**Figure 4-6: ESITOF MS spectrum of Polymer P4.2: a) as overview and b) detail as zoomed in detail. ESITOF MS is measured in a solution of MeOH containing 0.1% HCOOH in $H_2O$ in a ratio of 90/10.**

Unfortunately, since ESI-TOF is not a quantitative method, the absolute (or relative) amounts of the products cannot be calculated. Therefore, the Si-OH content is determined by preparing an adduct of the silanol with hexafluoroacetone and acquiring $^{19}$F-qNMR spectra of the resulting solution to which an internal standard is added.[196] The measurements show that the Si-OH content of the analyzed polymers ***P4.2*** (3100 g/mol, PDI = 1.46) and ***P4.3*** (13900 g/mol, PDI = 1.64) is below the detection limit (< 10 ppm) confirming that only small traces of heterotelechelic PDMS are to be found in the polymers.*

This and the missing Si-OH signal in $^{29}$Si(IG)-NMR confirms that only a homotelechelic α-, ω-methoxydimethylsilyl terminated polydimethylsiloxane is obtained in polymerization reactions of $D_4$ initiated by a combination of TBD and methanol in acetonitrile. Surprisingly, this has not been mentioned in literature before. Anyhow, this finding is especially important for the scope

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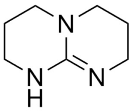
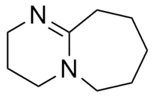
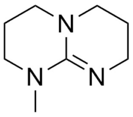
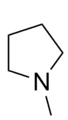
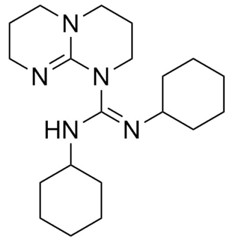
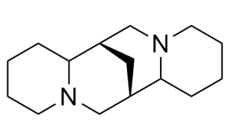
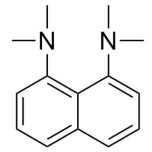
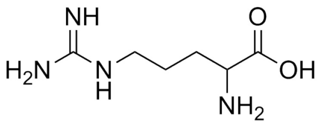
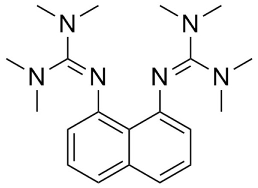
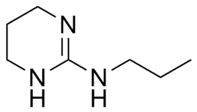
* The determination of the silanol content was performed externally by Lindsey Murphy.

of this work since determination of the end-groups is essential for later follow up reactions such as curing of the materials.

The presented results give reason to re- investigate our initiator screening and it is found that not all tested bases lead solely to a homotelechelic α-, ω –methoxydimethylsilyl terminated PDMS, but also to a mixture of homotelechelic and heterotelchelic PDMS. In conclusion, not all of the tested co-initiators are suitable for the synthesis of homotlechelic α-, ω –methoxydimethylsilyl terminated PDMS, since both endgroups are found in $^{29}$Si(IG)-NMR spectra (c.f. appendix A3.2.7). This could be a hint that side reactions which will be discussed in chapter 4.3.1 (p. 56) are suppressed because equilibrium state is maybe not achieved due to the lower activity of the base.

**Table 4-1: Investigation of terminating groups using different co-initiators which were already presented in 3.2.3 (p. 38). Experiments are carried out using 2 mol% of the base and 200 mol% of methanol (both related to the amount of $D_4$) in acetonitrile (acetonitrile : $D_4$ = 1.5:1). Presence of end-groups is assessed from $^{29}$Si(IG)-NMR spectra.**

| Co-initiator | Structure | Termination | Co-initiator | Structure | Termination |
|---|---|---|---|---|---|
| **3.7** | KOH | SiOMe | **3.14** |  | SiOMe |
| **3.8** |  | SiOMe | **3.15** |  | SiOMe |
| **3.9** |  | SiOH/SiOMe | **3.17** |  | SiOMe |
| **3.10** |  | SiOH/SiOMe | **3.18** |  | SiOH/SiOMe |
| **3.12** |  | SiOH/SiOMe | **3.19** |  | SiOMe |
| **3.13** |  | SiOH/SiOMe | | | |

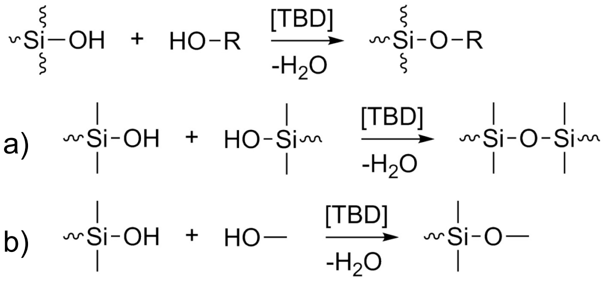
## 4.3 Side reactions

### 4.3.1 Condensation and hydrolysis reactions

In the previous subchapter 4.2 we could prove that, surprisingly, homotelechelic α-, ω – methoxy polydimethylsiloxanes are obtained when performing polymerization in acetonitrile using a combination of TBD/MeOH as initiating system. This is somehow contradictory to the results of Hedrick *et al*. and could not be explained at first sight.[69]

It is well known that bases such as KOH or phosphazenes catalyze condensation processes of oligomeric silanols.[23-24, 27] For instance, Hupfield *et al*. (from Dow corning) reported that phosphazene bases used in ROP of cyclic siloxanes can act as condensation catalysts if equilibrium state in ROP is achieved.[24]

Most probably TBD, which is a strong base as well, catalyzes condensation of silanol end-capped PDMS. In principle two possible reactions resulting from the general interaction between a silanol and a hydroxy functional compound are possible as presented in Scheme 4-3. Herein, a silanol can react with another silanol leading to classical condensation reaction as described in chapter 3.2 (c.f. Scheme 4-3 a) or with an alcohol leading to alkoxylation of the silanol group (c.f. Scheme 4-3 b).



**Scheme 4-3: General reaction of a silanol with a hydroxy compound: a) condensation, b) alkoxylation.**

Too proof this assumption experiments using α-, ω-di(hydroxydimethylsilyl) terminated PDMS are performed as follows:

DMS-S15 (Si-OH terminated polymer of Gelest; $M_n$ = 3300 g/mol), TBD, the alcohol and acetonitrile are mixed in a flask equipped with a reflux condenser. Under vigorous stirring the biphasic reaction mixture is heated to 65 °C oil bath temperature. After 4 h reaction time the reaction is stopped. The experimental results of all experiments are summarized in Table 4-2:

**Table 4-2:Results of condensation experiments concerning the influence of hydroxy compounds by reacting a silanol terminated PDMS (DMS-S15) in the presence of TBD (2 wt%) in acetonitrile (acetonitrile : DMS-S15 = 1.5:1) at 65 °C for 4 h. $M_n$ and PDI are determined by GPC measurements using toluene as eluent and PDMS standards.**

| Starting Material | Reaction | ROH | Ratio TBD:ROH | $M_n$ [g/mol] | PDI |
|---|---|---|---|---|---|
| DMS-S15 | | | | 3300 | 1.90 |
| | P4.5 | --- | --- | 75200 | 1.76 |
| | P4.6 | --- | --- | 56200 | 1.62 |
| | P4.7 | Methanol | 1:8.5 | 27800 | 1.45 |
| | P4.8 | Methanol | 1:200 | 5600 | 1.36 |
| | P4.9 | Eutanol G | 1:8.5 | 17500 | 1.48 |

In experiment ***P4.5*** and its reproduction ***P4.6***, where no additional hydroxy compound is used, the molecular weight increases strongly to an average of ~ 65000 g/mol compared to the molecular weight of the substrate DMS-S15 (3300 g/mol). This is a clear proof that TBD catalyzes also the condensation reaction of silanols.

Also in Experiment ***P4.7*** using methanol in a ratio of TBD : MeOH = 1: 8.5, an increase in molecular weight to ~28000 g/mol is observed which is not as strong as in experiment ***P4.5***. This leads to the conclusion that in this case both condensation and alkoxylation reactions are taking place simultaneously. In $^1$H-NMR the signal representing the methoxy in the polymer is observed. Unfortunately, it is not possible to double-check the presence of this end-group or the presence of Si-OH groups because the molecular weight of the obtained polymer is too high for ESI-TOF experiments as well as for observation of a signal representing a terminating group in $^{29}$Si-NMR experiments.

When comparing the results of experiment ***P4.8*** as well as of experiment **P4.7** with each other it is observed that with higher concentration of methanol (TBD: MeOH = 1:200) lower molecular weights are obtained (~5600 g/mol compared to ~28000 g/mol). This leads to the assumption that with higher concentration of the hydroxy compound alkoxylation is favored. Furthermore, analysis of the final product of experiment (***P4.8***) proves that methanol indeed is incorporated into the polymeric backbone as the characteristic signal is found in $^{29}$Si(IG)-NMR. It seems that alkoxylation is complete since no signal representing a second terminating group was observed.

The usage of 2-Octyldodecanol (Eutanol G) – a fatty alcohol – in (***P4.9)*** results in lower molecular weight of ~18000 g/mol compared to the analogue experiment ***P4.7*** (~28000 g/mol) using methanol. This leads to the conclusion that condensation is taking place but it is slower than analogue reactions with methanol. This behavior can be related to the bulkiness of the alcohol and its steric hindrance.

When plotting the course of reaction (conversion and molecular weight) as presented in Chart 4-1 (representing two experiments) against time at the beginning molecular weight is increasing steadily nearly linear. When conversion reaches approximately 90 % still an increase in molecular weight is observed. It is expected that at this point molecular weight remains constant since the conversion also remains constant and both sides of the chain are methoxy end-capped due to condensation or alkoxylation reaction respectively. This leads to the conclusion that there are still reactive species including hydroxy and methoxy groups.

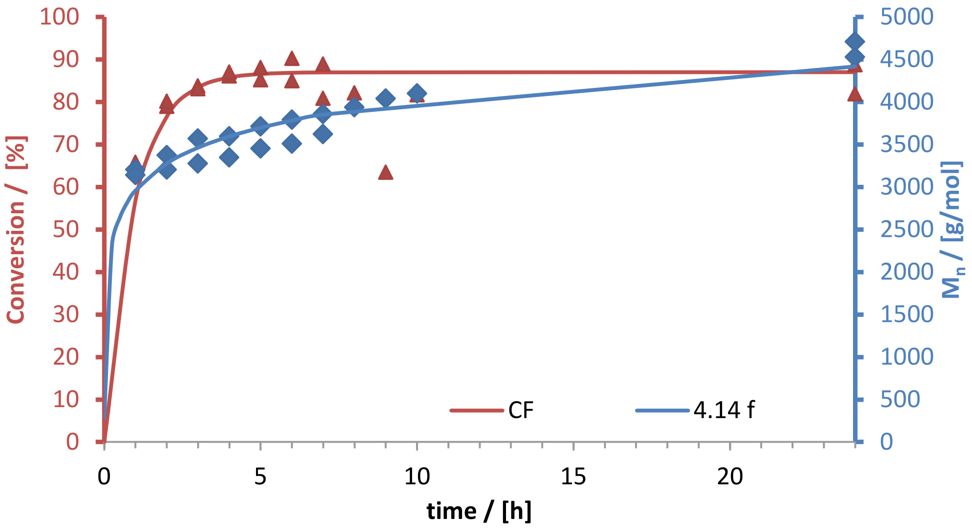
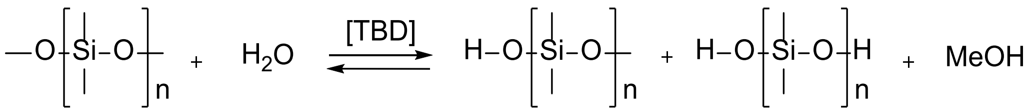


**Chart 4-1: Time-resolved ring-opening polymerization of $D_4$ with TBD (2 mol%) MeOH (200 mol%) in acetonitrile (acetonitrile : $D_4$ = 1.5:1) at 65 °C. Conversion is determined by $^{29}$Si(IG)-NMR in $CDCl_3$ and $M_n$ by GPC measurement using toluene as eluent and PDMS standards.**

Methoxy groups in silicone materials represent reactive functionalities which are often used in sealant formulations which crosslink when getting into contact with moisture.[197] The crosslinking process consists out of two reaction steps. First the methoxy group is hydrolyzed under release of methanol forming a silanol group. In the second step condensation of the silanol group is taking place. Curing reactions of this kind mainly take place only in the presence of water in the form of moisture.

It was already proven that condensation reactions take place in the presence of TBD in acetonitrile. It could be that due to the water which is released during the condensation side reaction methoxy endgroups are partially hydrolyzed to OH-functionalities (cf. Scheme 4-4). This and also the fact that the degree of the described condensation reactions depend on the concentration of methanol implies that the catalytic alkoxylation reaction is an equilibrium reaction.



Scheme 4-4: Possible hydrolysis reaction in the presence of TBD.

The Si-OH groups thus generated can undergo condensation reactions which result in an increase in molecular weight.

To prove this, experiment ***P4.10*** is performed: A *α-, ω*-di(methoxydimethylsilyl) end-capped polymer (***P4.4***), 2 wt% of TBD, $H_2O$ (in a ratio of TBD/$H_2O$ = 1/200) and 15 mL of acetonitrile are reacted at 65 °C. After 4 h a first sample (***P4.10.1***) is taken and analyzed via GPC and NMR. After 24 h the reaction is stopped. The reaction mixture is allowed to cool down to room temperature and phases are separated. A sample of the polymer phase is taken (***P4.10.2***).

In $^{29}$Si(IG)-NMR (c.f. Figure 4-7) of samples ***4.10.1*** and ***P4.10.2*** no end-capping signals neither for methoxydimethylsilyl end-groups nor for hydroxydimethylsilyl end-groups are observed. This can be explained by the increasing molecular weight during this reaction (Table 4-3) which might be explained by condensation reactions of the formed Si-OH groups. Additionally, free methanol is observed in $^1$H-NMR (c.f. in appendix A4.3.1.2, Figure A4-4 and Figure A4-6), proving that hydrolysis reactions take place.

**Table 4-3: Results of substitution experiments using a short chain *α-, ω*-di(methoxydimethylsilyl) end-capped polydimethylsiloxane (P4.4) as starting material which is reacted with $H_2O$ in the presence of TBD (Ratio TBD/$H_2O$ = 1/200). $M_n$ and PDI are determined by GPC measurements using toluene as eluent and PDMS standards.**

| Starting material | Experiment | Reaction time [h] | $M_n$ [g/mol] | PDI |
|---|---|---|---|---|
| P4.4 | | | 4000 | 1.22 |
| | P4.10.1 | 4 | 32400 | 1.41 |
| | P4.10.2 | 24 | 44000 | 1.11 |

During this reaction, also the formation of $D_4$ is observed (c.f. Figure 4-7). In both samples the concentration of $D_4$ is estimated to be 6.9 % (calculated from $^{29}$Si(IG)-NMR) which corresponds approximately to the concentration of $D_4$ when conversion in ROP of $D_4$ remains constant. So it can be said that during this reactions equilibrium between the polymer and $D_4$ is established.

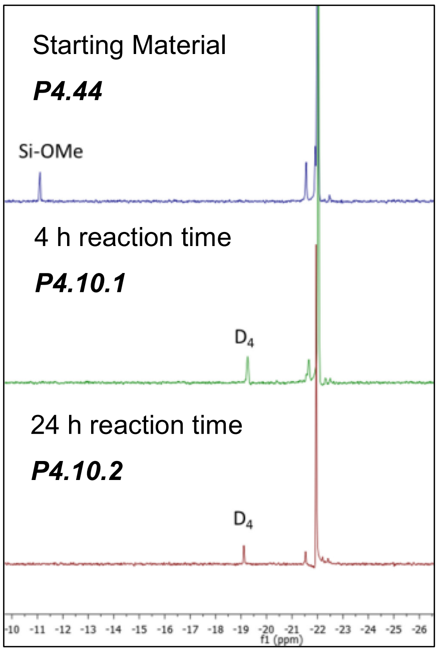
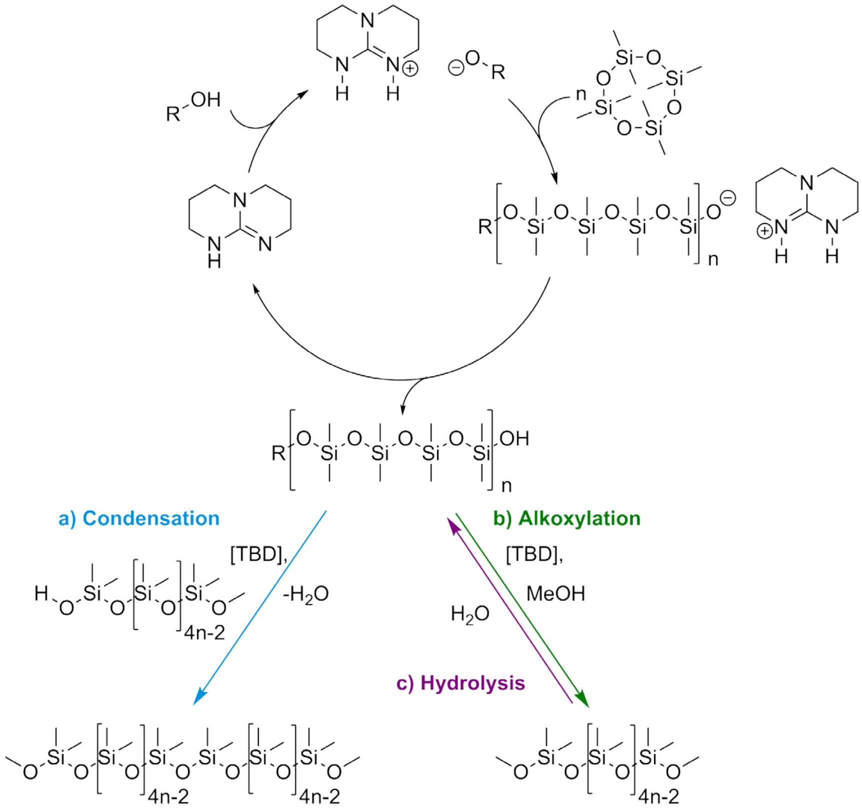


**Figure 4-7:$^{29}$Si(IG)-NMR of the methoxy end-capped starting material *P4.4*, sample *P4.10.1* after 4 h of reaction and *P4.10.2* after 24 h of reaction.**

All the described findings result in the following proposed extended reaction mechanism (Scheme 4-5) disregarding back-biting reactions:



**Scheme 4-5: Proposed mechanism for polymerizing $D_4$ in the presence of TBD which includes the activation of an alcohol leading to a homotelechelic α-, ω- di(methoxydimethylsilyl) terminated PDMS.**

### 4.3.2 Usage of disiloxanes as classic terminating agents

Sivasubramanian and co-workers (from Momentive)[34] reported the polymerization of cyclic siloxanes inititated by TBD in the presence of a disiloxane and eventually an alcohol such as methanol. Disiloxanes (MM) are known to act as end-blockers by equilibration and are often used in ROP of cyclic siloxanes to obtain homotelechelic silicones which are not disilanols.[28]

The combination of a MM-compound with an alcohol which both are acting as terminating agents in the polymerization reaction seemed to be contradictory. The more so that methanol as hydroxy compound is needed as inititator. Thereby it is assumed that either the disiloxane is not active or, if it is active, a mixture of different end-capped polymers is obtained.

Therefore following experiment is performed: TBD, methanol and acetonitrile are mixed in an argon-flushed, oven-dried flask. $D_4$ as monomer and additionally 1,3-divinyl-1,1,3,3-tetramethyldilsiloxane (DVS) as end-capping agent are added under vigorous stirring. The reaction is started by dipping into preheated oil bath (65 °C). The amount of DVS is calculated according to Eq. 4-1 and Eq. 4-2 in order to target a molecular weight of $M_n$ = 2000 g/mol.

$$n_{DVS} : n_{Monomer} = 1 : x \qquad \textbf{Eq. 4-1}$$

$$x = \frac{M_{target} - M_{DVS}}{M_{D4}} \qquad \textbf{Eq. 4-2}$$

*where* $M_{target}$ is desired molecular weight
$M_{D4}$ is molecular weight of $D_4$
$M_{DVS}$ is molecular weight of DVS
$n$ molar amount

After 24 h samples are taken for NMR and GPC analysis in order to determine molecular weight and conversion. Results are presented in Table 4-4:

**Table 4-4: Results of polymerization experiment in the presence of 2 mol% TBD, 400 mol% MeOH and 16 mol% DVS related to the amount of $D_4$ in acetonitrile (acetonitrile : $D_4$ = 1.5:1) at 65 °C oil bath temperature for 24 h. $M_n$ and PDI are determined by GPC measurements using toluene as eluent and PDMS standards. Conversion is calculated from $^{29}$Si(IG)-NMR.**

| Conversion* [%] | $M_n$ [g/mol] | PDI |
|---|---|---|
| 94.0 | 1700 | 1.33 |

Interestingly, in $^{29}$Si(IG)-NMR two signals at -4.3 and -11.3 ppm which can be related to the end-groups can be detected. The signal at -11.3 ppm was already related to the methoxydimethylsilyl endgroup and the signal at -4.3 ppm is related to the vinyldimethylsilyl end-group (cf. A4.3.2). The ratio, which is calculated from $^{29}$Si(IG)-NMR amounts to 61 % Si-Vinyl-groups and 39 % Si-OMe-groups.

It is assumed that the obtained product is a mixture of homotelechelic and heterotelechelic polymers.

Determination of end-groups is carried out via ESI-TOF measurements. The spectra presented in Figure 4-8a) shows a smooth molecular weight distribution and, at first sight, the main signals can be related to a homotelechelic *α-, ω*-vinyldimethylsilyl end-capped polymer.

Calculations of the exact mass of the possible homotelechelic and heterotelechelic polymers – *α-, ω*-methoxydimethylsilyl terminated, *α-, ω*-vinyldimethylsilyl terminated, as well as *α*-methoxydimethylsilyl-*ω*-vinyldimethylsilyl terminated – show that molar masses are quite similar. This and the unusual broad signal groups in ESI-TOF lead to the assumption that there might be overlapping signals.

The detail (c.f. Figure 4-8b) of the marked signal group at 1097.339 m/z in Figure 4-8a shows clearly that there are three different groups of signals overlapping with each other. They can be clearly related to the three possible polymers. This is a proof that the usage of a MM-compound such as DVS in the presence of methanol leads to a mixture of different end-capped polymers.

The mechanism behind the usage of MM-compounds is related to condensation reactions in which OH-functional groups get silylated under release of water. This also applies for silanol groups.[198-200] That is why it is proposed that first *α-, ω*–methoxydimethylsilyl terminated polymers are generated. Due to hydrolysis of the methoxy group, free silanol groups can be obtained which then get silylated. This is a further proof that hydrolysis reactions are taking place during ROP or in equilibrium of the reaction.

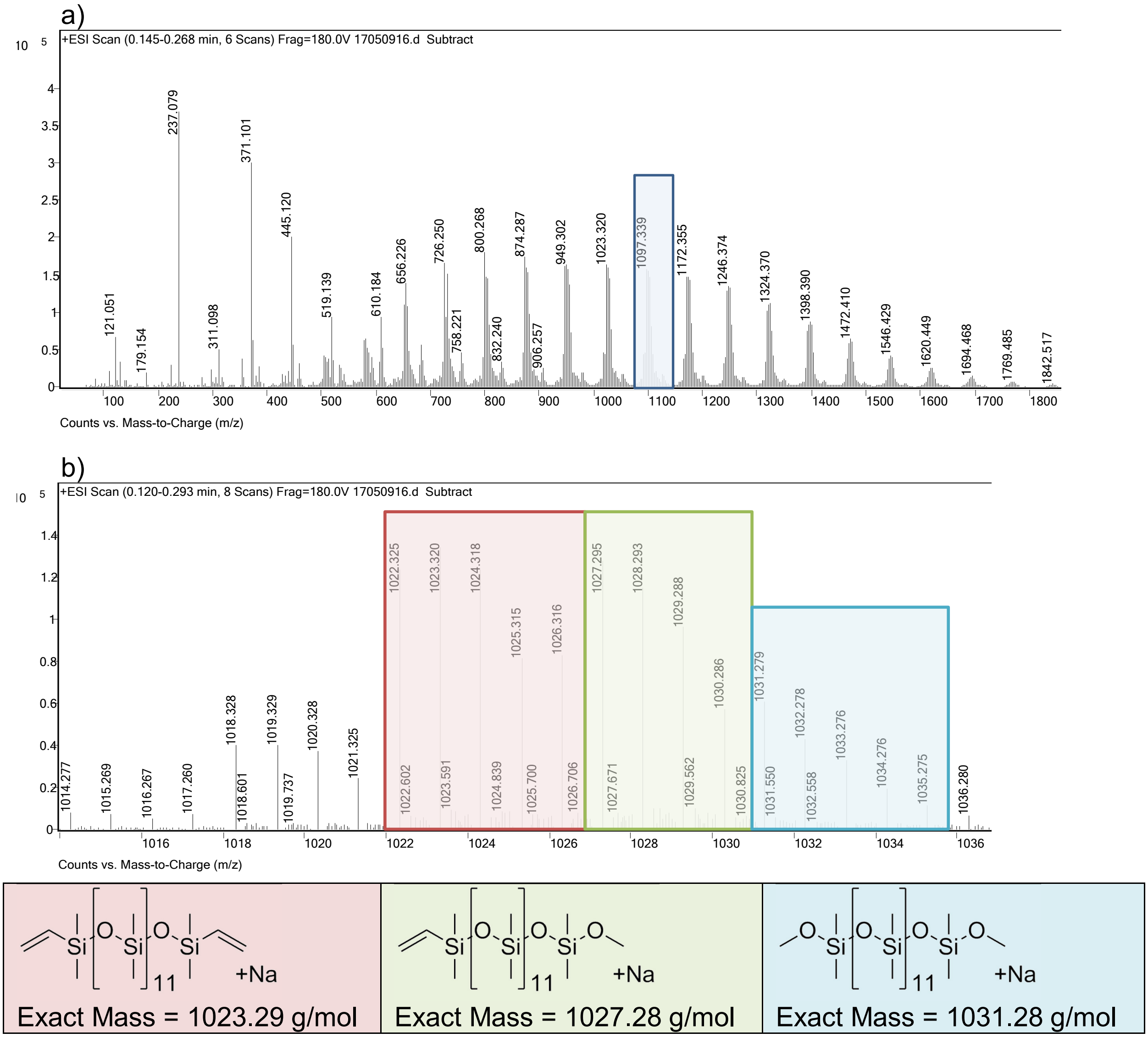
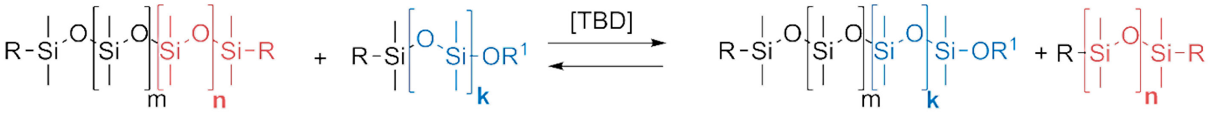


**Figure 4-8:ESI-TOF spectra of polymerization of $D_4$ in the presence of 2 mol% TBD, 400 mol% MeOH and 16 mol% DVS related to the amount of $D_4$ in acetonitrile (acetonitrile : $D_4$ = 1.5:1) at 65 °C oil bath temperature for 24 h : a) complete spectra and b) detail of signal group marked with assignment of polymers.**

### 4.3.3 Equilibration reactions

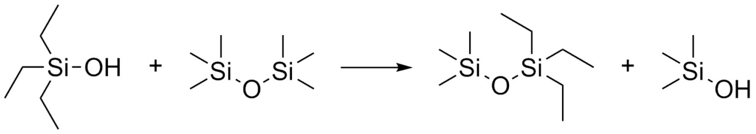
Besides alkoxylation and condensation, equilibration processes represent another possible side reaction which is normally initiated by bases or acids. Often this kind of reaction is described in the context of equilibration of polyorganosiloxanes with halosilanes or alkoxysilanes (c.f.Scheme 4-6).[50]



**Scheme 4-6: Equilibration of polyorganosiloxanes with alkoxysilanes.**

Also the ring-opening polymerization itself is referred to as equilibration polymerization due to the fact that at some point equilibrium between linear siloxane chains and macrocyclic siloxanes ($D_4$ – $D_7$) is formed.[32]

Although *Hedrick et al.*[69] already proved that TBD is not active in equilibration processes when reacting triethylsilanol with hexamethyldisiloxane (HMDS) (Scheme 4-7), equilibration experiments are performed due to the fact that TBD seems to be much more active when used in acetonitrile.



**Scheme 4-7: Expected product of equilibration experiment of Hedrick *et al.*[69].**

A first experiment (***P4.13***) is conducted as described below:

To a 1:1 mixture of **PDMS 14000** and **PDMS 2000** (both trimethylsilyl end-capped PDMS from Alfa Aesar) dry acetonitrile and TBD are added and the reaction mixture is reacted 24 h at 65 °C. After cooling down to room temperature the acetonitrile phase is removed and the polymer phase is worked up.

In a second experiment methanol is added to the reaction mixture described above to see whether the formation of active species like methanolate has an influence on the equilibration process (***P4.14***).

GPC results of both experiments (presented in Table 4-5) show that bimodal peaks are observed. This is not surprising since two different polymers namely **PDMS 2000** and **PDMS 14000** are used, which is demonstrated by preparing a sample where both polymers are mixed in ratio 1:1 (Table 4-5; **PDMS 2000 + PDMS 14000**). A close look onto the molecular weights which are determined via GPC shows that in experiment ***P4.13*** the polydispersities of the two peaks stayed the same and also molecular weights are only slightly changing whereas for experiment ***P4.14*** both polydispersities and molecular weight narrow. This leads to the conclusion that equilibration takes place in presence of methanol and TBD but not in the presence of TBD alone, both in acetonitrile.

**Table 4-5: Results of equilibration experiments P4.13 and P4.14. $M_n$ and PDI are determined by GPC measurements using toluene as eluent and PDMS standards.**

| Starting material | Reaction | Reaction time [h] | $M_n$ [g/mol] | PDI |
|---|---|---|---|---|
| PDMS 2000 | | --- | 1800 | 1.39 |
| PDMS 14000 | | --- | 11600 | 1.65 |
| Mixture of starting materials | | | 16800 | 1.25 |
| (PDMS 2000: PDMS 14000 = 1:1) | | | 2300 | 1.41 |
| | P4.13 | 24 | 14200 | 1.27 |
| | | | 2800 | 1.48 |
| | P4.14 | 24 | 10100 | 1.11 |
| | | | 3700 | 1.21 |

Analysis via $^{29}$Si(IG)-NMR of polymers of experiments ***P4.13*** and ***P4.14*** shows that in polymer ***P4.14*** a new signal at -11 ppm appears, which is related to the methoxydimethylsilyl group. In polymer ***P4.13*** only the trimethylsilyl end-group can be found in $^{29}$Si(IG)-NMR, whereas in polymer ***P4.14*** $CH_3O\text{-}Si(CH_3)_2\text{-}O\text{-}$ terminating group is found as well (c.f. Figure 4-9). This proves that equilibration takes place in the presence of methanol due to the fact that the methanol is incorporated into the polymer backbone.

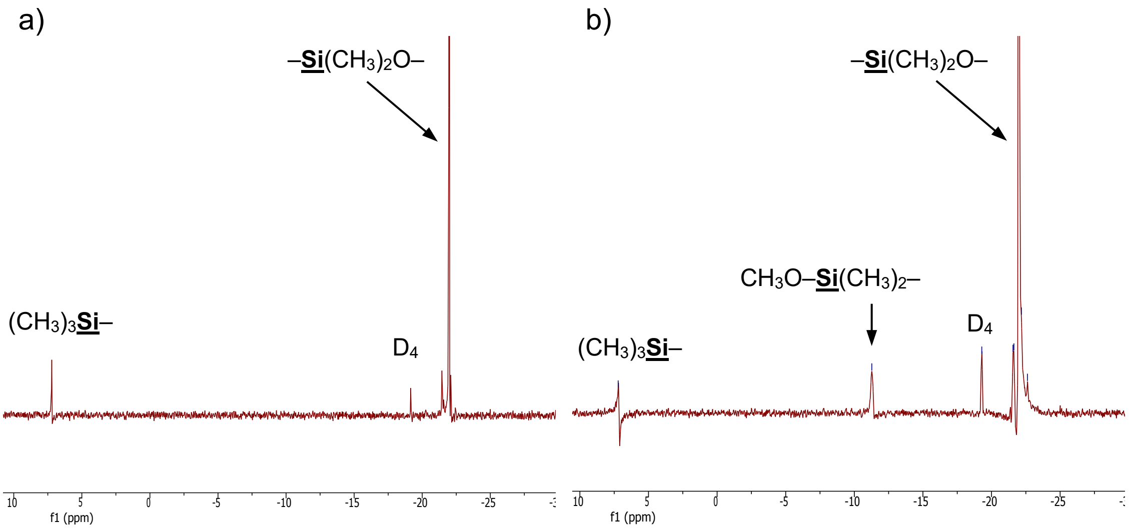
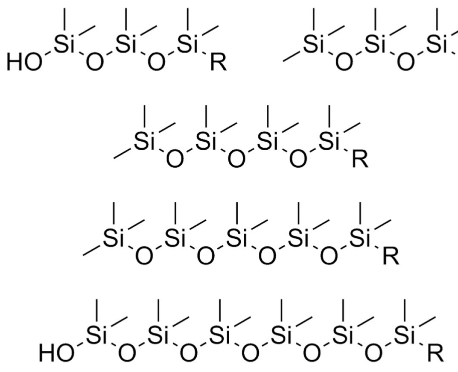


**Figure 4-9: $^{29}$Si(IG)-NMR of equilibration experiments a) polymer P4.13 (in $CDCl_3$, 297 K, 75 MHz)and b) P4.14 (in $CDCl_3$, 297 K, 75 MHz).**

This is further proved by performing GC-MS measurements of the acetonitrile phase of both experiments. Mainly $D_4$ and $D_5$ together with traces of different cyclic siloxanes, namely $D_3$ and $D_6$, are found. GC analysis of the substrates (PDMS 2000 and PDMS 14000) shows only traces of $D_4$ and $D_5$ (cf. in appendix A4.3.3.1; Figure A4-13 and A4-14), which confirms that these cycles are formed during equilibration.

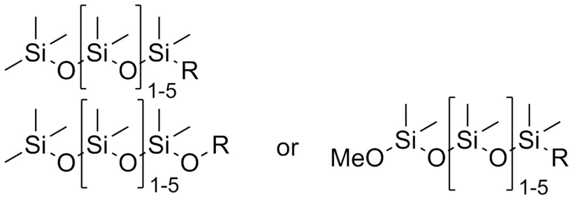
Additionally, traces of small linear oligomers are found (c.f. Figure 4-10).



with R = OH or $CH_3$

**Figure 4-10: Oligomers found in GC-MS spectra of acetonitrile phase of experiment *P4.13*. R cannot be defined because GC-MS spectra showed only fragments. Most likely R is either –OH or $CH_3$.**

In GC-MS spectra of the acetonitrile phase of experiment ***P4.14*** more signals are existent. Besides the above mentioned cycles, traces of different small linear oligomers partially having methoxy terminating groups are found (Figure 4-11).



with R = OH or $CH_3$

**Figure 4-11: Oligomers found in GC-MS spectra of acetonitrile phase of experiment *P4.14*. R cannot be defined because GC-MS spectra showed only fragments. Most probably R is either –OH or $–CH_3$.**

Compared to the results of ***P4.13*** this leads to the assumption that the equilibration process itself is very slow and that active species such as methanolates or silanolates are needed to force equilibration.

## 4.4 Kinetics*

By plotting conversion against time at different reaction temperature it is proven that polymerization proceeds with first order kinetics in monomer as presented in Chart 4-2 until equilibrium is achieved.

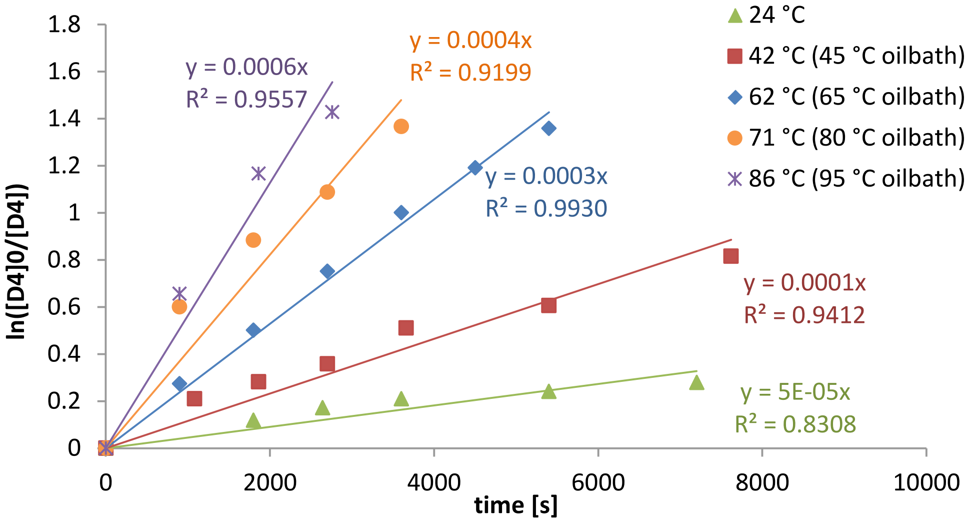


**Chart 4-2: Plot of ln($[D_4]_0/[D_4]$) versus time where $[D_4]_0$ is the initial monomer concentration and $[D_4]$ is the monomer concentration at the time of t. The concentration is $D_4$ is calculated from the conversion which is determined from $^{29}$Si(IG)-NMR.**

By performing experiments using different methanol concentrations it is shown that the concentration of methanol has no influence on the conversion of $D_4$ and it can be said that the reaction is zero order in methanol (c.f. Chart 4-3).. For $H_2O$ we are able to show that its concentration has an effect on the conversion (c.f. 5.1.3, p. 80) and in this case, reaction order in initiator is not supposed to be zero.

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* Part of the presented experiments have been performed in the framework of Lea Grefes research internship, University of Rostock

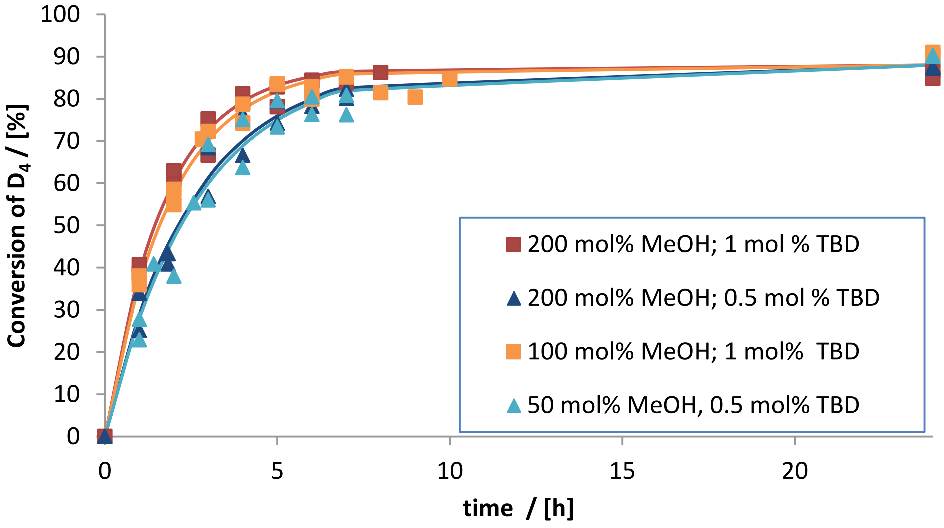

**Chart 4-3: Course of conversion of polymerization using different TBD concentrations and Methanol concentrations in acetonitrile (1.5 the volume of $D_4$) at 65 °C oil bath temperature. Conversion is calculated from $^{29}$Si(IG)-NMR.**

The order in co-initiator is determined using the “method of initial rates”[201]. To identify the initial rates, several polymerizations are conducted changing only co-initiator concentration from experiment to experiment. During polymerization, samples are taken every 15 minutes for 45 minutes, dissolved in $CDCl_3$ and analyzed via $^{29}$Si(IG)-NMR spectroscopy to calculate $D_4$ conversion. Via graphical assessment of the initial rates, rate constant k and order of reaction n in co-initiator can be derived from the intercept and the slope, respectively as shown in Eq. 4-5.

$$v_0 = -\frac{d[D_4]}{dt} \qquad \textbf{Eq. 4-3}$$

$$v_0 = k_{cat}[TBD]_0^n \qquad \textbf{Eq. 4-4}$$

$$lg(v_0) = lg(k_{cat}) + n lg([TBD]_0) \qquad \textbf{Eq. 4-5}$$

*where* $v_0$ is the initial reaction speed
$[D_4]$ is the concentration of $D_4$
$[TBD]_0$ is the initial concentration of TBD
$k_{cat}$ is therate constant in catalyst
$n$ is the reaction order

Reaction order in catalyst is determined to be 0.5 which corresponds to literature and rate constant is assessed to be $k_{cat}$ = 1.778*10*$^{-3}$ mol$^{0.5}$L$^{0.5}$s$^{-1}$ at 62 °C reaction temperature (according to 65 °C oil-bath temperature).

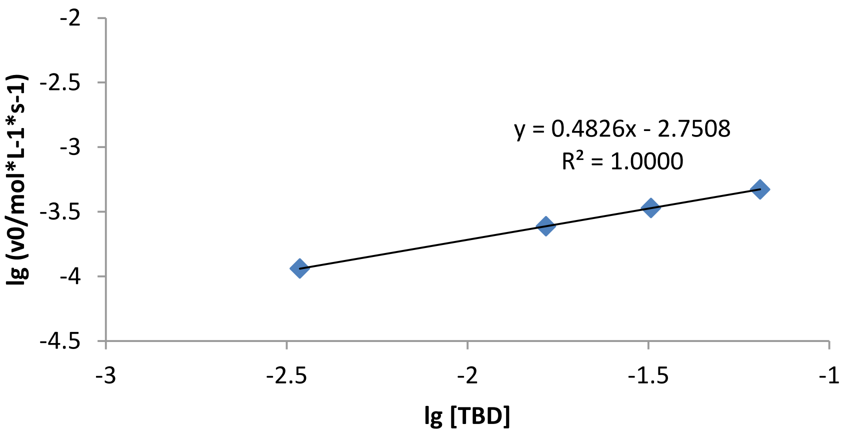

**Chart 4-4: Plot of logarithm of intial reaction speed $v_0$ vs. the logarithm of initial TBD concentration. Order in catalyst was determined from the slope and rate constant $k_{cat}$ (62 °C) was determined from the intercept according to Eq. 4-5.**

These findings are confirmed in literature where it is stated that ring-opening polymerization of $D_4$ follows first order kinetics in monomer and the co-initiator (sometimes referred to as catalyst) has a fractional order of usually 0.5.[102, 173] The fractional order in catalyst is often related to the ionization of the potassium silanolate initiator or the the deaggregation of dormant dimers.[102] Transferred to our polymerization process, this should mean that each molecule of TBD is capable of activating two molecules of initiator. This is in accordance with the finding of Kafka *et al.* who reported the capability of TBD to attack malonate esters nucleophilic with both of its disubstituted nitrogen atoms.[202]

Experiments for the determination of activation energy are performed by using 2 mol% TBD, 200 mol% methanol related to the amount of $D_4$ in acetonitrile (acetonitrile : $D_4$ = 1.5:1) at different reaction temperatures. During polymerization, samples are taken every 15 minutes for 60 minutes, dissolved in $CDCl_3$ and analyzed via $^{29}$Si(IG)-NMR spectroscopy to calculate $D_4$ conversion. Additionally Cr(III)acetylacetonate is used as relaxation agent.

The activation energy is calculated according to Arrhenius law (Eq. 4-6) and also entropy of activation and enthalpy of activation are calculated via graphical assessment.[203]

$$k = Ae^{-\frac{E_a}{RT}} \qquad \textbf{Eq. 4-6}$$

$$ln\,(k) = \left(-\frac{E_A}{RT}\right) + ln(A) \qquad \textbf{Eq. 4-7}$$

*where* $k$ is the rate constant in monomer
$E_A$ is the activation energy
$R$ is the gas constant
$A$ is a pre-exponential factor
$T$ is absolute temperature

If taking the logarithms a plot of ln(k) versus (1/T) gives the activation energy $E_a$ from the slope (cf. Chart 4-5).

The rate constant is also related to the free energy of activation $\Delta G^{\ddagger}$ which can be expressed by $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

$$k = \frac{k'T}{h} e^{-\frac{\Delta G^{\ddagger}}{RT}}$$

**Eq. 4-8**

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$

**Eq. 4-9**

$$k = \frac{k'T}{h} e^{-\frac{\Delta H^{\ddagger}}{RT}} e^{\frac{\Delta S^{\ddagger}}{R}}$$

**Eq. 4-10**

| | | |
|---|---|---|
| *where* | $k$ | is the rate constant in monomer |
| | $k'$ | is Boltzmann's constant |
| | $h$ | is Planck's constant |
| | $R$ | is the gas constant |
| | $T$ | is absolute temperature |
| | $\Delta G^{\ddagger}$ | is free energy of activation |
| | $\Delta H^{\ddagger}$ | is enthalpy of activation |
| | $\Delta S^{\ddagger}$ | is entropy of activation |

Rearrangement and taking the logarithms result in Eq. 4-11 from which $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ can be calculated if ln(k/T) is plotted against (1/T).

$$ln\left(\frac{k}{T}\right) = \frac{-\Delta H^{\ddagger}}{RT} + ln\left(\frac{k'}{h}\right) + \frac{\Delta S^{\ddagger}}{R}$$

**Eq. 4-11**

According to this $\Delta H^{\ddagger}$ can be calculated from the slope and $\Delta S^{\ddagger}$ from the intercept (c.f. Chart 4-6).

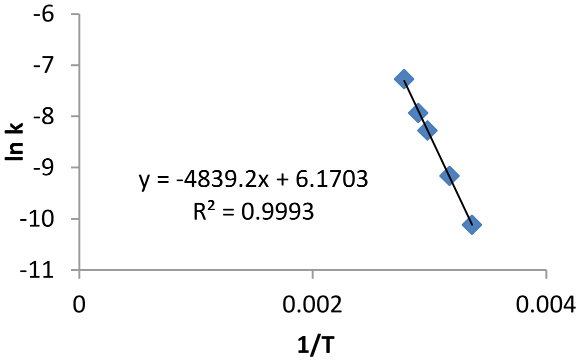

**Chart 4-5: Plot of ln(k) versus 1/T giving the activation energy Ea for the polymerization reaction of $D_4$ with TBD in the presence of methanol in acetonitrile. Ea is determined according to Eq. 4-7 k is determined from the slope of a plot $\ln([D_4]_0/[D_4])$ vs. time (c.f. Chart 4-2).**

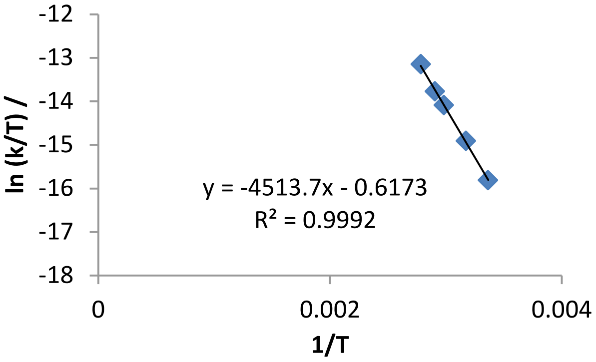

**Chart 4-6: Plot of ln(k/T) versus 1/T giving the enthalpy of activation, $\Delta H^‡$, and entropy of activation, $\Delta S^‡$, of the polymerization reaction of $D_4$ with TBD in the presence of methanol in acetonitrile. k is determined from the slope of a plot $\ln([D_4]_0/[D_4])$ vs. time (c.f. Chart 4-2).**

The determined activation parameters are summarized in Table 4-6.

**Table 4-6: Determined activation parameters of the polymerization of $D_4$ in acetonitrile using Methanol as initiator and TBD as co-initiator.**

| Monomer | $E_A$ | $\Delta H^‡$ | $\Delta S^‡$ |
|---|---|---|---|
| $D_4$ | 40.23 kJ*mol$^{-1}$ | 37.53 kJ*mol$^{-1}$ | -8.45 J*K$^{-1}$*mol$^{-1}$ |

Grzelka *et al.*[173] who investigated the kinetic behavior of the AROP of $D_4$ in the presence of hexapyrrolidinediphosphazenium hydroxide in toluene found values of $E_a$ = 18.1 kcal/mol (~75.9 kJ/mol), $\Delta H^‡$ = 17.5 kcal/mol (~73.3 kJ/mol) and $\Delta S^‡$ = -2.1 eu (~8.8 J*K$^{-1}$*mol$^{-1}$). When compared to the finding presented in Table 4-6 it seems that activation energy and enthalpy of activation are higher suggesting that hexapyrrolidinediphosphazenium hydroxide is less active. But this could be also an effect of the used toluene. As it was described earlier, TBD shows lower reactivity in toluene as well.

Unfortunately the authors did not give any $pK_a$ value for hexapyrrolidinediphosphazenium hydroxide and therefore it is hard to discuss these results. In literature a $pK_a$ value for the similar phenylpentapyrrolidinediphosazenium hydroxide is found which amounts to 27.55 (measured in acetonitrile) and is a bit higher than TBD ($pK_a$ = 25.96 in acetonitrile). Therefore it can be estimated that the higher activation energy results from the lower polarity of the solvent (toluene).

## 4.5 Summary and conclusions

The ring-opening polymerization of $D_4$ initiated by TBD and an alcohol is identified to be a classical anionic polymerization mechanism. Thereby, TBD deprotonates the alcohol and the resulting alcoholate initiates polymerization.

Contrary to Hedrick *et al.*'s results when using TBD as co-initiator, homotelechelic α- ,ω-alkoxydimethylsilyl siloxane polymers are obtained which is proven via 2D-NMR, ESI-TOF and MALDI-TOF experiments. In ESI-TOF also α-methoxy-ω-hydroxy terminated polymers are found but their presence is negligible, as proven by quantification of the Si-OH content. However, their presence is evidence that the resulting homotelechelic siloxane polymers stem from condensation and alkoxylation reactions. It is assumed that these side reactions are especially taking place when equilibrium is reached. Furthermore, equilibration reactions play a minor role and are insignificant.

Kinetic investigations show that the ring-opening polymerization of $D_4$ via methanol in the presence of TBD is of first order in monomer and of fractional order of 0.5 in co-initiator. It is furthermore of zero order in initiator. Additionally activation parameters were determined.

# 5 Investigation of Process Parameters

In this chapter we take a closer look at the reaction parameters. In our previous experiments the initiator was represented by an alcohol, mostly methanol, and it was shown that the initiator acts as terminating group as well. Therefore, in subchapter 5.1 the possibility to target molecular weight of the final polymers by adjusting the concentration of the initiator and the nature of the initiator (which could be either an alcohol, water or a trialkylsilanol) is investigated. In subchapter 5.2 the reaction conditions of our new polymerization process are investigated in depth.

## 5.1 Hydroxy compound as part of the initiating system

Hedrick *et. al.*[69] already described the usage of 4-pyrenebutan-1-ol, ethandiol, triethoxysilanol and hydroxy-terminated macroinitiators such as poly(poly(ethyleneoxide)) (PEO), polystyrene as well as polybutadiene as suitable hydroxy compounds in combination with TBD for the polymerization of $D_3$ and TMSOC. Amines and thiols were inactive in these polymerization experiments.[69]

Therefore, different alcohols, water and silanols were investigated as suitable initiators.

### 5.1.1 Alcohols

Different alcohols – namely methanol (MeOH), *n*-butanol (*n*BuOH), *iso*-propanol (*i*PrOH) as well as *tert*-butanol (*t*BuOH) – are tested to see whether the steric of these has an effect on the course of polymerization.

Therefore, a series of experiments is undertaken using these different alcohols. TBD (2 mol%) and the alcohol (200 mol%) and acetonitrile are mixed in a reaction flask. $D_4$ is added. Reactions are performed at 65 °C. Reactions are tracked subsequently with NMR and GPC experiments by taking samples at define time intervals.

For the determination of conversion via $^{29}$Si(IG)-NMR 0.5 mL of the stirred reaction mixture are taken and measured including the acetonitrile phase in order to eliminate errors by $D_4$ which is dissolved in the acetonitrile phase. For the determination of the molecular weight 0.5 mL of the reaction mixture are taken and the phases are separated. A sample of the polymer phase is then analyzed by GPC.

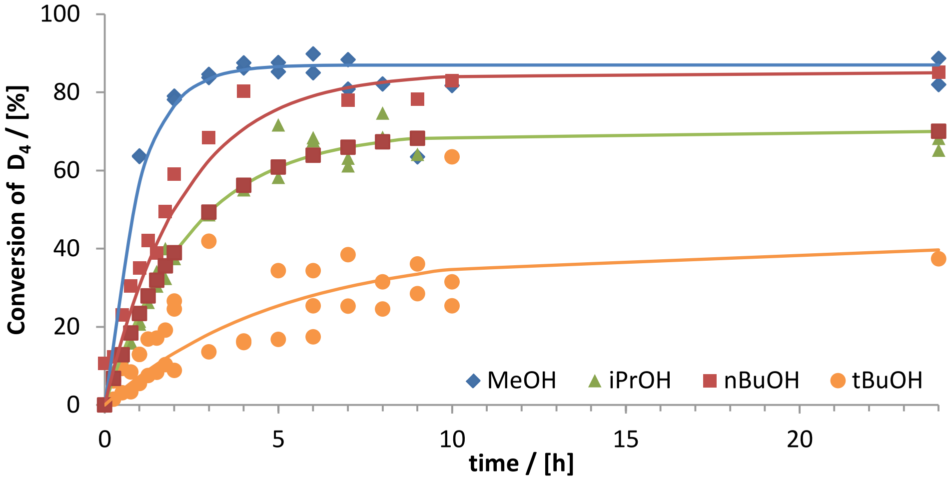

**Chart 5-1: Influence of different alcohols (200 mol% related to the amount of $D_4$) on conversion of $D_4$ during course polymerization where 2 mol % of TBD are used in acetonitrile (acetonitrile : $D_4$ = 1.5:1) at 65 °C oil bath temperature. Conversion is determined from $^{29}$Si(IG)-NMR.**

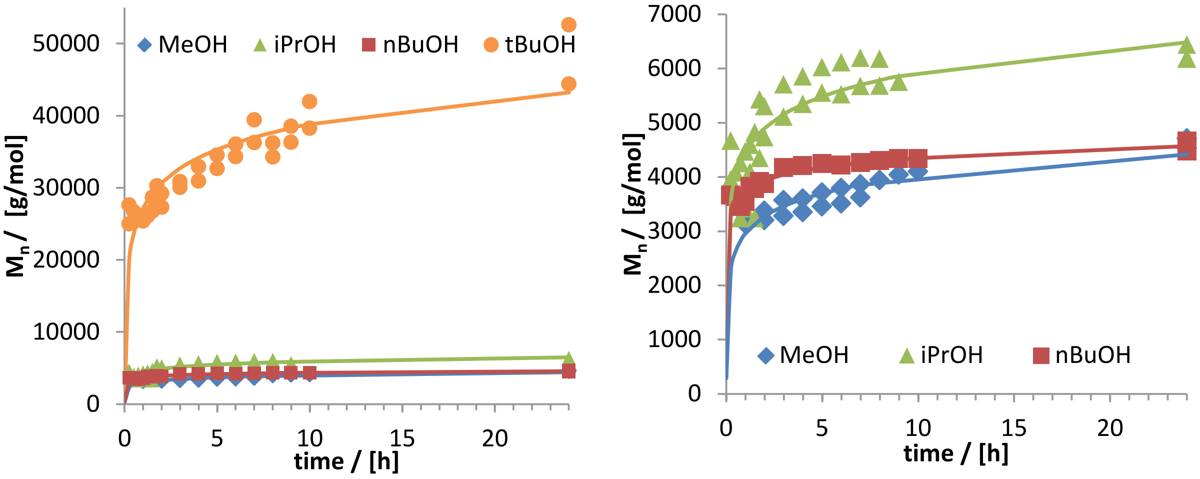

**Chart 5-2: Influence of different alcohols (200 mol% related to the amount of $D_4$) on molecular weight $M_n$ during course polymerization where 2 mol % of TBD are used in acetonitrile (acetonitrile : $D_4$ = 1.5:1) at 65 °C oil bath temperature. $M_n$ is determined via GPC using toluene as eluent and PDMS standards.**

**Chart 5-3: Influence of different alcohols (200 mol%) on molecular weight $M_n$ during course polymerization where 2 mol % of TBD are used in acetonitrile (acetonitrile : $D_4$ = 1.5:1) at 65 °C oil bath temperature. The chart is the same like Chart 5-2 but with smaller scale on y-axis to see differences between experiments using MeOH, *i*PrOH and *n*BuOH. $M_n$ is determined via GPC using toluene as eluent and PDMS standards.**

The results presented in Chart 5-1 to Chart 5-3 show that conversion slows down with increasing chain length and branching of the used alcohol. Interestingly, also differences in the final molecular weight are observed. With increasing branching of the alcohols, higher molecular masses are obtained (up to ~50000 g/mol when using *t*BuOH).

Flory's fundamental principle, published firstly in 1953, suggests that the reactivity of the active center is not controlled by structure or chain length leading to the conclusion that the polymerization process is described by the rate constants of initiation, propagation and termination reactions.[204-205] Therefore, it is assumed that the reactivity of the active silanolate centers in the propagating chain is independent from the starter group. According to this the explanation for the observed difference in conversion might be found in the nature of the chosen alcohol.

The acidity of alcohols decreases with the number of substituents at the α-C-atom, whereas the basicity of alcoholates increases with number of substituents. Therefore, methanol is the strongest acid and *tert*-butanolate is the strongest base within the series of used alcohols and alcoholates (c.f. Figure 5-1).[206]

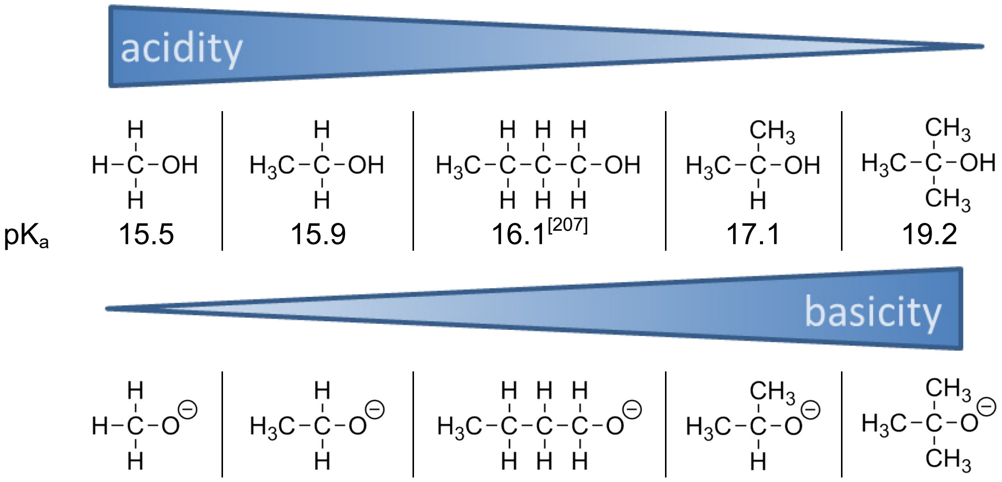

**Figure 5-1: Reported acidity and basicity of selected alcohols. [206]**

Although the basicity of the formed alcoholates increases with number of substituents, nucleophilicity of the same decreases due to steric hindrance.[208] This was also found by Reeve *et al.*[209], who determined the competitive reactivity and the relative nucleophilicity of different alkoxides. From these data, the relative acidity of the corresponding alcohols was calculated. The data are presented in Table 5-1:

**Table 5-1: Reported competitive reactivities, nucleophilicities and acidities of selected alcohols determined by Reeve *et al.*[209] in etherification reactions.**

| Alkoxide | Competitive reactivity | Relative nucleophilicity | Relative acidity of alcohols |
|---|---|---|---|
| Methoxide | 3.6 | 0.82 | 4.4 |
| Ethoxide | 1.0 | 1.0 | 1.0 |
| *iso*-Propoxide | 0.092 | 0.39 | 0.24 |
| *tert*-Butoxide | 0.0089 | 0.043 | 0.21 |

Since the acidity of the used alcohols decreases with increasing branching, the generation of the corresponding alcoholates, which initiate ROP, via deprotonation is slower. This explains the decreasing reactivity of the alcohols in ROP. Another reason is to be found in the bulkiness of the generated alcoholates. With increasing bulkiness of the *in situ* generated alkoxy anion it becomes less nucleophilic and the attack at the cyclic monomer is hindered. As a consequence of both the slower deprotonation as well as the steric hindrance less propagating chains are formed which leads to slower conversion of monomer as well as to higher molecular weights, because of the formation of longer chains.

In $^{29}$Si(IG)-NMR of the polymers obtained when using *n*-butanol and *iso*-propanol, only one signal representing the terminating group at -13.19 ppm representing the *n*-butoxydimethylsilyl group and at -14.93 ppm representing the *iso*-propoxydimethylsilyl group respectively could be found, speaking for the fact that in these cases homotelechelic *α-,ω*-alkoxydimethylsilyl terminated polymers are obtained. This is also proven by ESI-TOF measurements for *n*-butoxydimethylsilyl and *iso*-propoxydimethylsilyl terminated polymers (c.f. in appendix A5.1.1).

When using *tert*-butanol it was not possible to confirm the endgroups via NMR; ESI-TOF or MALDI-TOF due to the high molecular weight of the obtained polymer.

In both MALDI-TOF as well as in ESI-TOF only macrocycles can be found (c.f. in appendix A5.1.1). Macrocycles up to $D_{21}$ are found in all our polymers, even though they were purified in high vacuum at 80 °C (c.f. in appendix A6.1). This is due to backbiting reactions occuring always during thermodynamically controlled ROP.

Measurements of the silanol content showed that in the case of the usage of *n*-butanol and *iso*-propanol SiOH content is below 10 ppm which is the detection limit of the method. For a polymer obtained by initiation with *tert*-butanol silanol content of 239 ± 51 ppm is found.* The theoretical calculated silanol content of the analyzed polymer related to its number averaged molecular weight, provided that it is α-hydroxydimethylsilyl-ω-*tert*-butoxydiemthylsilyl end-capped PDMS, amounts to 274 ppm, which would be in the frame of the determined SiOH content. This suggests that indeed a heterotelechelic α-hydroxydimethylsilyl-ω-*tert*-butoxydimethylsilyl PDMS is obtained and no condensation reactions take place, which might be explained by the slow polymerization rate of this experiment. Literature[23-24, 27] reports, that condensation reactions during ROP are observed at the equilibrium state of the reaction. But when using *t*BuOH as initiator at 65 °C reaction temperature equilibrium is still not achieved after 24 h reaction time and therefore condensation reactions do not take place.

Experiments with *tert*-butanol at reflux conditions show an increase in reactivity expressed by higher conversion after 24 h and unchanged molecular weight compared to reaction

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* The determination of the silanol content was performed externally by Lindsay Murphy.

temperature of 65 °C (c.f. Table 5-2). This suggests that due to the low acidity of *tert*-butanol more energy is required to generate the corresponding alcoholate.

**Table 5-2: Results of polymerization experiments using *tert*-butanol at different reaction temperatures. All experiments are carried out under inert conditions in acetonitrile (acetonitrile : $D_4$ = 1.5:1) for 24 h. 2 mol% of initiator and 200 mol% of *tert*-butanol related to the amount of $D_4$ were used. Conversion is calculated from 29Si(IG)-NMR and $M_n$ and PDI are determined by GPC using toluene as eluent and PDMS standards.**

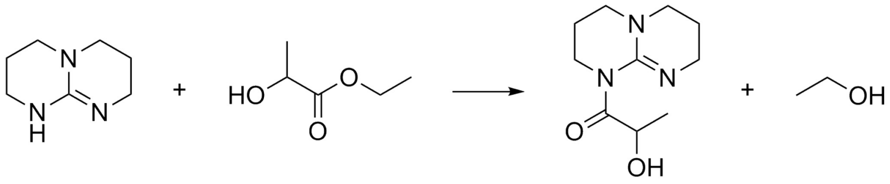
| $T_{oilbath}$ [°C] | Conversion of $D_4$ [%] | $M_n$ [g/mol] | PDI |
|---|---|---|---|
| 65 | 94.5 | 39500 | 1.66 |
| 100 | 91.5 | 41000 | 1.46 |

Experiments using 2-aminoethan-1-ol and 1,3-butandiol were performed in order to assess the effect of additional functionalities in the alcohols.The results of these experiments are listed in Table 5-3 showing that 2-aminoethanol and 1,3-butanediol are suitable alcohols for initiating ROP of cyclic siloxanes leading to slightly higher conversions of 94 % compared to experiments where methanol is used. At the same time 1,3-butane diol leads to higher molecular weights than the usage of 2-aminoethanol (~66000 g/mol vs. ~40000 g/mol).

**Table 5-3: Results of polymerization experiments using different alcohols as initiator. All experiments are carried out under inert conditions in acetonitrile (acetonitrile : $D_4$ = 1.5:1) at 65 °C for 24 h. 2 mol% of initiator and alcohol related to the amount of $D_4$ are used. Conversion is calculated from $^{29}$Si(IG)-NMR and $M_n$ and PDI are determined by GPC using toluene as eluent and PDMS standards.**

| ROH | Concentration of ROH [mol%] | Conversion of $D_4$ [%] | $M_n$ [g/mol] | PDI |
|---|---|---|---|---|
| 2-Aminoethanol | 2 | 94.5 | 39500 | 1.66 |
| 1,3-Butane diol | 2 | 94.4 | 65800 | 1.46 |
| Ethyllactate | 200 | 0 | --- | --- |

Ethyllactate which represents an alcohol with an ester-functionality shows no activity in ROP with TBD. This might be due to the fact that the ester bond might be cleaved in the presence of the strong base. TBD is used in ring-opening polymerization of cyclic esters and the ester bond can be attacked directly. Due to the ester hydrolysis, TBD is acylated and its bacisity is reduced, hampering the deprotonation of the alcohol functionality of the remaining ethyllactate or of the ethanol produced by ester hydrolysis (c.f. Scheme 5-1).[210]



**Scheme 5-1: Possible side reaction of TBD with ethyllactate.**

Furthermore, in literature it is also stated that carboxylates are less nucleophilic than alcohols and therefore less efficient initiators. ROP of cyclic siloxanes such as $D_3$ and $D_4$ can be initiated by carboxylates but so far as known only by benzoates.[208] Therefore even if there is free lactate, as product of the ester hydrolysis, it will not initiate ring-opening.

### 5.1.2 Triorganosilanols*

Triorganosilanolates are often described in literature as efficient initiators for ROP of cyclic siloxanes.[70-71] They can be obtained by reacting potassium hydroxide with silanols forming potassium silanolate.[67]

Therefore triorganosilanols in combination with TBD are used to generate the initiating silanolate *in situ* like it was done with the alcohols in the previous chapter. This bears the advantage that instead of alkoxydimethylsilylgroups, vinyldimethylsilyl groups or trialkylsily groups as terminating groups can be introduced into the silicone polymer. Especially the introduction of vinyldimethyl groups can be utilized for hydrosilylation curing or for analogue reactions.

Time resolved experiments and sample taking for $^{29}$Si(IG)-NMR and GPC measurements is performed as described in chapter 5.1.1 using a silanol instead of an alcohol.

For a test trimethylsilanol (TMSOH) is chosen. In comparison to methanol initiation by TMSOH leads to similar conversions (c.f. Chart 5-4) but to lower molecular weights of the polymer (Chart 5-5). The achievement of lower molecular weights can be explained by the formation of unreactive trimethylsilyl end-groups which cannot hydrolyze as such alkoxy groups. Therefore, the described condensation reactions only occur to a small extend.

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* Parts of the presented experiments have been performed in the framework of Jack Christen's bachelor thesis, University of Rostock.

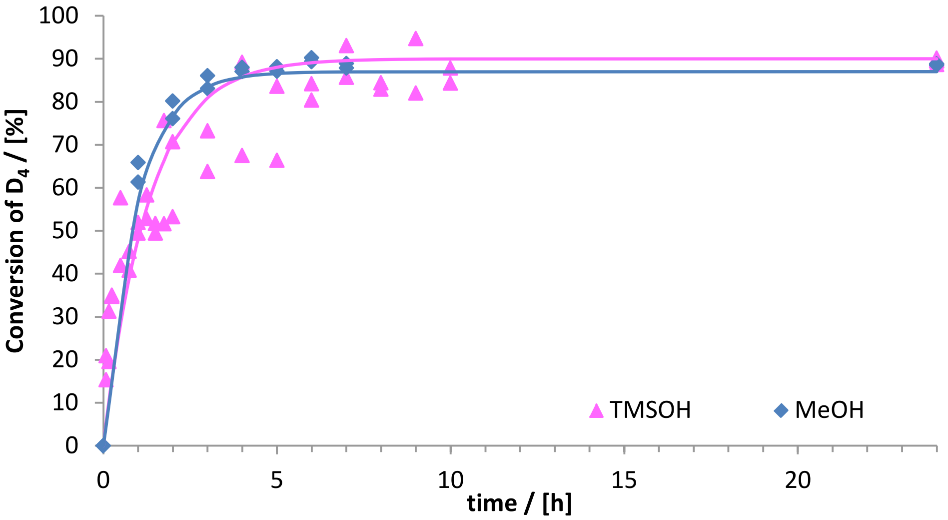


**Chart 5-4: Course of conversion of polymerizations using TMSOH as initiator in comparison to methanol. Presented polymerization reactions are performed using 2 mol% TBD, 200 mol% either TMSOH or MeOH related to the amount of $D_4$ in acetonitrile (acetonitrile : $D_4$ = 1.5:1) at 65 °C oil bath temperature. Conversion of $D_4$ is calculated from $^{29}$Si(IG)-NMR.**

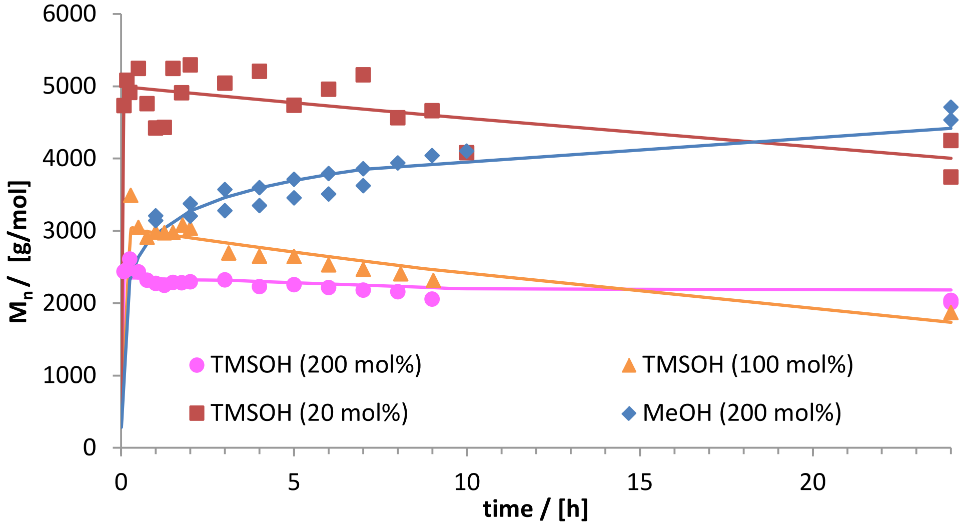
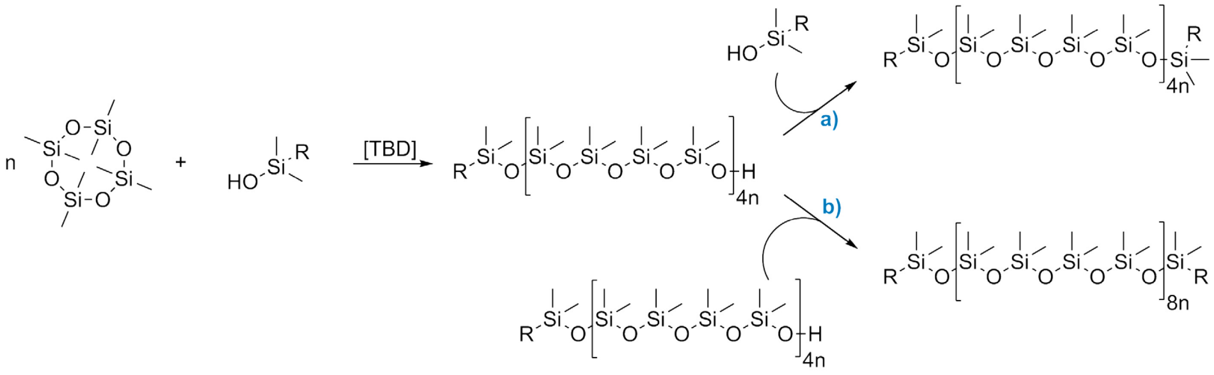


**Chart 5-5: Course of number averaged molecular weight of polymerizations using different concentrations TMSOH compared to MeOH (200 mol%). Presented polymerization reactions are performed using 2 mol% TBD in acetonitrile (acetonitrile : $D_4$ = 1.5:1) at 65 °C oilbath temperature. $M_n$ is determined by GPC using toluene as eluent and PDMS standards.**

Interestingly, molecular weight decreased during course of reaction as presented in Chart 5-5, which can be related to polymer break down. Furthermore, hydrolysis cannot take place. Condensation reactions will take place but only to a certain extend in a way that the intermediate *α*-trimethylsilyl-*ω*-hydroxydimethylsilyl polymers condensate with itself or another trimethylsilanol molecule (Scheme 5-2). Later on, no condensation reactions can take place due to the lack of hydrolysable groups.



**Scheme 5-2: Possible condensation reactions of α-trialkylsilyl-ω-hydroxy terminated polymer as not isolable intermediate of ROP with a) a silanol or b) with itself.**

During polymerization the formation of hexamethyldisiloxane (HMDS) is observed which is generated due the condensation of TMSOH with itself.

### 5.1.3 Water*

When using water as hydroxy compound, silanol terminated polymers are obtained which has the advantage that they can be directly used in curing reactions. Alkoxy end-capped polymers can be also used in these curing reactions but they are slower because in the first step of curing these groups have to be hydrolyzed.[211]

Therefore, a series of experiments is undertaken to investigate the suitability of water as ROP initiator. Time resolved experiments and sample taking for $^{29}$Si(IG)-NMR and GPC measurements are performed as described in chapter 5.1.1 using $H_2O$ instead of an alcohol.

Interestingly, the concentration of $H_2O$ has an influence on the conversion as shown in Chart 5-6 where conversion is tracked over 24 h by taking samples which are analyzed by $^{29}$Si(IG)-NMR. It seems that water has an inhibiting influence on the reaction speed especially if used in high concentrations (1000 mol%). For example Grzelka *et al.*[173] describe that acetonitrile shows an accelerating effect and water an inhibiting effect in polymerizations using phosphazene bases.[173] Therefore, this finding is not surprising, although the exact reason for this effect is still unknown.

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* Parts of the presented experiments have been performed in the frame of Jack Christen's bachelor thesis, University of Rostock.

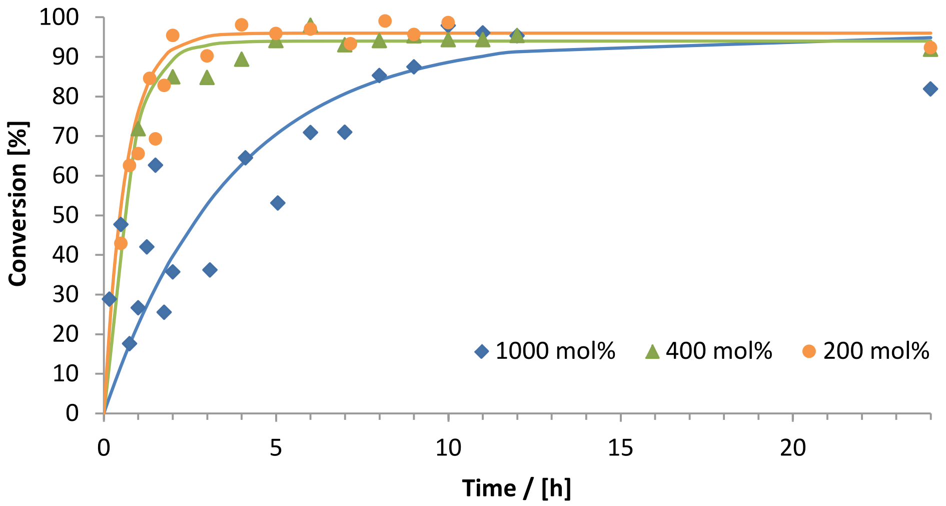

**Chart 5-6: Course of conversion using $H_2O$ as initiator in different concentrations related to the amount of $D_4$. Presented polymerization reactions are performed using 2 mol% TBD related to the amount of $D_4$ in acetonitrile (acetonitrile : $D_4$ = 1.5:1) at 65 °C oilbath temperature. Conversion of $D_4$ is calculated from $^{29}$Si(IG)-NMR.**

Furthermore it seems that conversion drops after 12 h of reaction time from 95 % to 85 % after 24 h of reaction time when using 1000 mol% of $H_2O$. This behavior can be explained due to back-biting reactions in which cyclic species including $D_4$ are formed. The trend is also displayed when tracking molecular weight over time (Chart 5-7). In comparison to MeOH polymers with higher molecular weights are obtained which might result from condensation processes. These condensation processes might take place at the surface of the monomer or polymer droplets which are dispersed in the acetonitrile phase as described by Gee *et al.*[144-145].

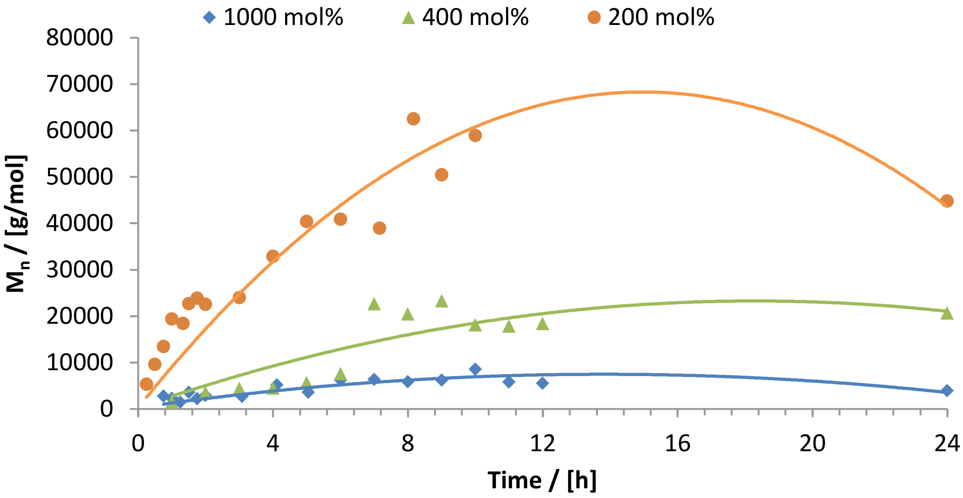

**Chart 5-7: Course of number averaged molecular weight using $H_2O$ as initiator in different concentrations related to the amount of $D_4$. Presented polymerization reactions are performed using 2 mol% TBD related to the amount of $D_4$ in acetonitrile (acetonitrile : $D_4$ = 1.5:1) at 65 °C oilbath temperature. $M_n$ is determined by GPC using toluene as eluent and PDMS standards.**

In all presented experiments sample taking is challenging due to the high viscosity of the obtained polymers which is also displayed by the scattering of the data points in both conversion as well as molecular weight vs. time charts. Moreover, reproduction of the polymerization is not possible due to the uncontrolled polycondensation taking place parallel to ring-opening polymerization.

Therefore, it is thought of lowering the co-initiator concentration to have a more controlled reaction. This leads to a strong decrease in molecular weight but only to a slight decrease in conversion suggesting that condensation reactions are suppressed (c.f. in appendix A6.2.1).

### 5.1.4 Control of molecular weight*

According to the mechanistic investigations, which were discussed in the previous chapter 4, and the proof that the used hydroxy compound like methanol initiates ring-opening polymerization, it is tried to tailor the molecular weight by changing the concentration of the used methanol.

Therefore, experiments are undertaken using different methanol concentrations. Experiments are carried out under moisture-free conditions in an inert argon atmosphere. Resublimed TBD, methanol and the solvent are mixed into an argon-flushed, oven-dried flask. $D_4$ as monomer is added under vigorous stirring and reaction is started by dipping into preheated oil bath. Phases are separated when mixture is cooled down to room temperature. The polymeric phase is washed with methanol.

As presented in Chart 5-8 the concentration of methanol influences the molecular weight. The higher the methanol concentration the lower molecular weight polymers are obtained. Especially in low concentrations (< 50 mol% methanol related to $D_4$) small changes in methanol concentration induce big changes in molecular weight, where as in high concentrations (> 50 mol% methanol related to $D_4$) molecular weight is not strongly affected by changes in methanol concentration leading to a curve with asymptotic behavior.

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* Parts of the presented experiments have been performed in the framework of Jack Christen’s bachelor thesis

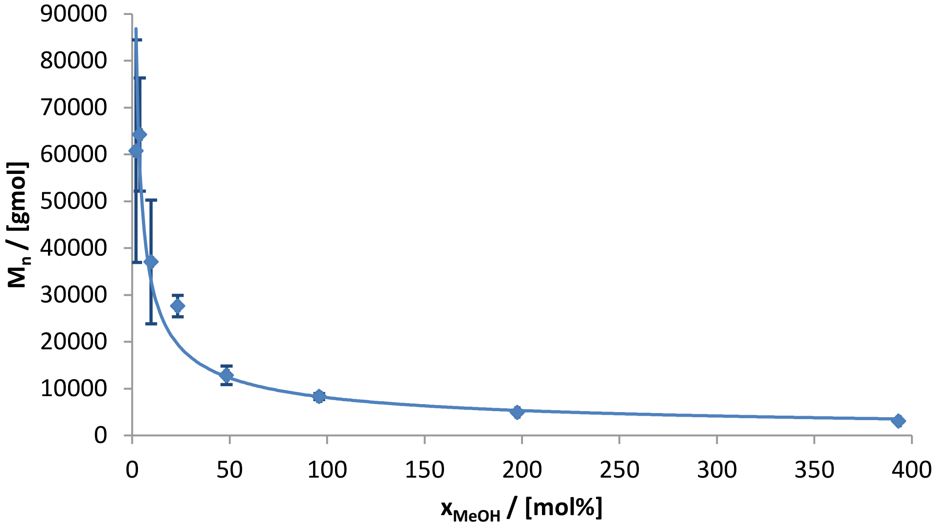

**Chart 5-8: Number averaged molecular weight of polymers depending on the used methanol concentration related to the amount of $D_4$. Experiments are carried out using 2 mol% of TBD in combination with methanol in acetonitrile (acetonitrile : $D_4$ = 1.5:1). $M_n$ is determined by GPC measurements using toluene as eluent and PDMS standards.**

Interestingly, also standard deviation in the first part of the curve is higher due to the steep negative slope. Small changes in methanol concentration lead to big variations in molecular weight. The reason might be the error inherent to the measurement of the required amount of methanol. Another reason might be the high vapor pressure of methanol at the reaction temperature (65 °C). The boiling point of methanol at atmospheric pressure (1 bar) is 64.7 °C, therefore the vapor pressure of methanol in the reaction mixture equals the atmospheric pressure. Although a reflux condenser is used, the methanol is not hold back entirely, leading to these high deviations in molecular weight. A solution to this problem might be the usage of pressure tubes. Since for all reactions a mechanical stirrer is used to ensure homogenous mixing of the biphasic reaction mixture this is not tried.

To prove the hypothesized loss of methanol due to its high vapor pressure, we performed several experiments using 2-octyldodecanol (Eutanol G) as fatty alcohol with higher boiling point. As presented in Chart 5-9 experiments are reproduced four times and standard deviation is calculated. The usage of 2-Octyldodecanol leads to a lower standard deviation in comparison to the usage of methanol for both 4 and 10 mol% of hydroxyl compound (s ~ 600 and 900 g/mol respectively compared to 13200 and 12000 g/mol), which supports our assumption that the high vapor pressure of methanol leads to said high deviations. At the same time, lower molecular weights are obtained when 2-Octyldodecanol is used. The influence of the steric effects of different alcohols is discussed in the previous subchapter 5.1.1 and serves as additional argument in this context.

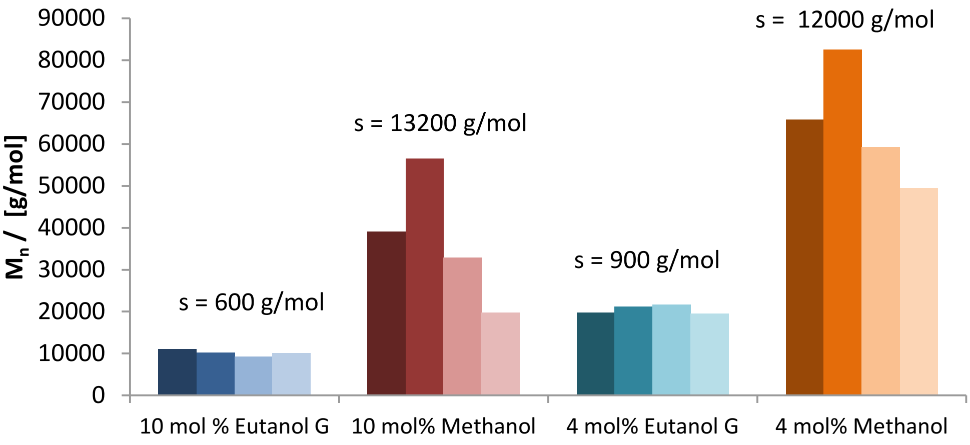

**Chart 5-9: Influence of the choice of alcohol on the reproducibility expressed by the standard deviation. Experiments are carried out using 2 mol% of TBD in combination with either Eutanol G or methanol in acetonitrile (acetonitrile : $D_4$ = 1.5:1). $M_n$ is determined by GPC measurements using toluene as eluent and PDMS standards.**

Targeting molecular weight by using the achieved graphs is not possible(c.f in appendix A5.1.2.3, Chart A5-1). This is most probably due to the described reproducibility problems.

The influence of the concentration of the chosen hydroxy compound is also observed for water and trimethylsilanol showing the same trend as can be seen in Chart 5-10. Thereby, it is evident that in comparison to each other the usage of trimethylsilanol leads to lower molecular weights than the usage of methanol whereas the usage of water leads to higher molecular weights. The higher molecular weights when using water might be explained by the described condensation processes, whereas the lower molecular weights when using TMSOH might be explained by the achievement of “dead” trimethylsilyl chain ends.

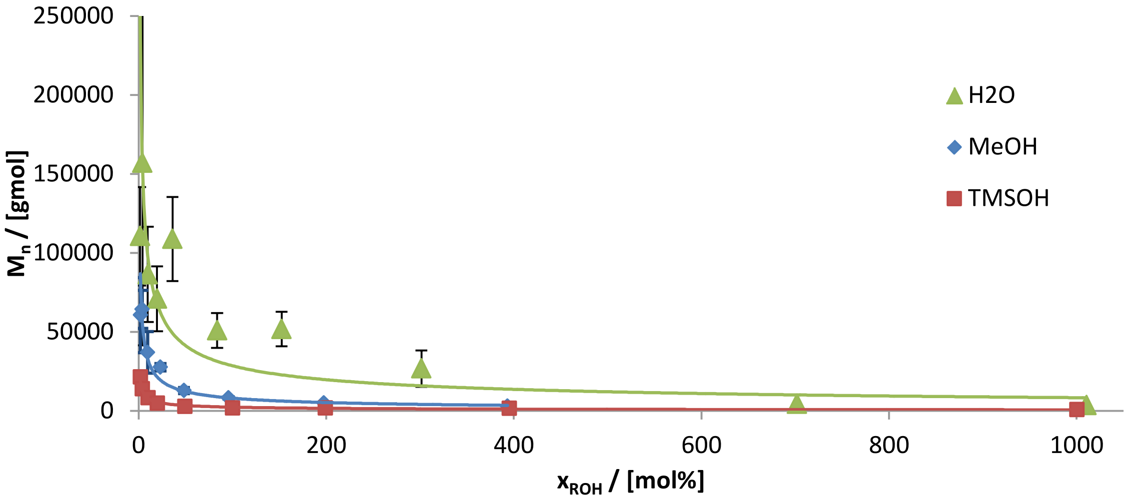

**Chart 5-10: Number averaged molecular weight of polymers depending on the concentration of the used hydroxy functional compound – MeOH, $H_2O$ and TMSOH – related to the amount of $D_4$. Experiments were carried out using 2 mol% of TBD in combination with one of said hydroxy functional compounds in acetonitrile (acetonitrile : $D_4$ = 1.5:1). $M_n$ is determined by GPC measurements using toluene as eluent and PDMS standards.**

## 5.2 Investigation of reaction parameters*

In the course of the process development for polymerizing $D_4$ with an initiating system containing TBD and an alcohol in acetonitrile, reaction conditions should be improved for up-scaling experiments and possible transfer into industrial applications.

It is of special interest to lower the amount of TBD and acetonitrile which are quite cost-intensive besides the monomer, although the solvent phase containing both acetonitrile as well as TBD can be reused.

Anyhow, parameters which had been investigated are reaction temperature, amount of TBD as well as solvent volume. The different parameters are varied one by one while keeping all other parameters constant.

Initially, 2 mol% of TBD related to the amount of $D_4$ and acetonitrile in an amount of $CH_3CN$ to $D_4$ = 1.5: 1. As reaction temperature 65 °C are chosen because of the boiling point of the initial used methanol.

In general, ROP is carried out under moisture-free conditions in an inert argon atmosphere. Resublimed TBD, methanol and the solvent are mixed into an argon-flushed, oven-dried flask. $D_4$ as monomer is added under vigorous stirring and reaction is started by dipping into preheated oil bath. Phases are separated when mixture is cooled down to room temperature. The polymeric phase is poured into methanol.

Course of conversion and molecular weight are tracked over 24 h by taking samples every hour. Conversion is determined by $^{29}$Si(IG)-NMR in $CDCl_3$ and $M_n$ by GPC measurement using toluene as eluent and PDMS standards.

### 5.2.1 Reaction temperature

The reaction temperature is varied by altering the oil bath temperature. Investigated bath temperatures are room temperature (usually 20 – 22 °C), 40 °C, 65 °C, 81 °C and 90 °C. Samples are taken every hour to measure the conversion and average molecular weight $M_n$. Chart 5-11 shows how the different reaction temperatures impact the conversion of $D_4$.

Interestingly, polymerization reactions at 65 °C and above (95 °C and 81 °C), show only slight differences in the course of conversion. The higher temperatures show slightly steeper rise of conversion before reaching equilibrium. Generally, it can be seen that, the higher the temperature, the higher the conversion after the first hour.

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* The presented experiments have been performed in the framework of Lea Grefe's research practicum, University of Rostock.

Lower temperatures than 65 °C, 40 °C and room temperature, show significantly slower rates of conversion and both do not reach the equilibrium within the period of 7 h and 12 h ( conversions ~65 % at RT and ~75 % at 40 °C), respectively. After 24 h the ROP at room temperature reaches a conversion of 80 %, whereas the ROP at 40 °C reaches 89 %.

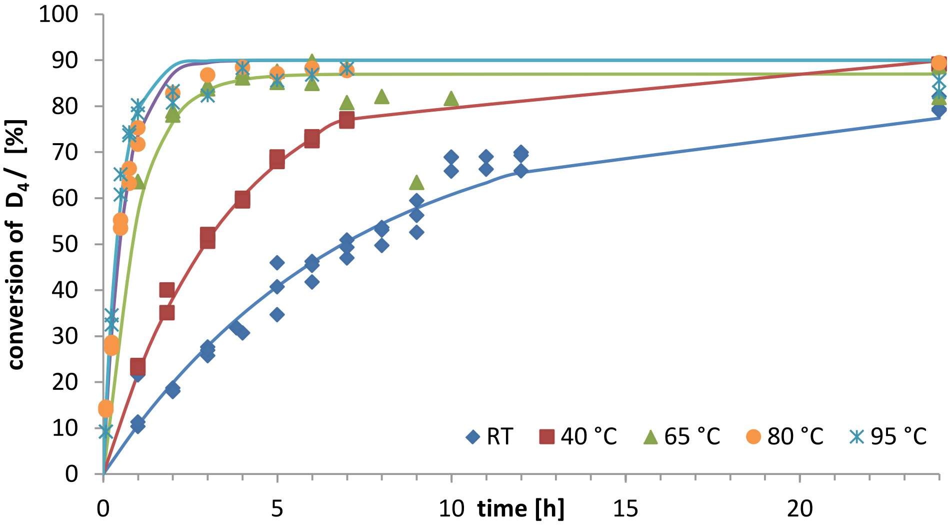

**Chart 5-11: Course of conversion polymerizations using different oil bath temperatures. For all presented polymerization reactions 2 mol% TBD, 200 mol% MeOH and acetonitrile (acetonitrile : $D_4$ = 1.5:1) are used. RT was = 23 °C. Conversion is calculated from $^{29}$Si(IG)-NMR.**

The change of reaction temperature does also have an impact on the average number molecular weight of the obtained polymers (Chart 5-12). Average molecular weights of the polydimethylsiloxanes can be compared, because they do not differ significantly in polydispersity.

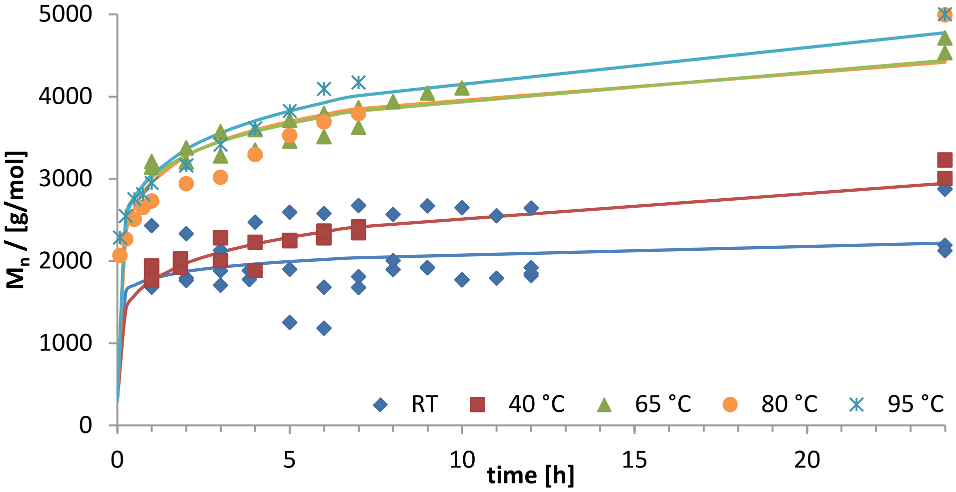

**Chart 5-12: Course of number averaged molecular weight of polymerizations using different oil bath temperatures. (200 mol%). For all presented polymerization reactions 2 mol% TBD, 200 mol% MeOH and acetonitrile (acetonitrile : D4 = 1.5:1) are used. RT was = 23 °C. $M_n$ is determined by GPC using toluene as eluent and PDMS standards.**

PDMS prepared at room temperature and 40 °C show significantly smaller molecular weights of ~2500 g/mol and ~3000 g/mol respectively compared to polymers obtained at higher temperatures (~4700 g/mol). Literature states that condensation reactions during ROP are observed during equilibration state.[23-24, 27] Therefore, the observed trend might be related to the fact that lower reaction temperatures lead to suppressed condensation reactions because of the slower polymerization speed. This assumption is supported by the fact that the molecular weight of the polymer prepared at room temperature reached equilibrium after 1 h at the latest, despite conversion is still increasing from 10 % to 80 %. Therefore, it is concluded that since the equilibrium is not reached in between 24 h, condensation reactions are not taking place. It is possible that during a later equilibration state condensation reactions can happen. But this leads also to the conclusion that alkoxylation reactions must take place since α-, ω-di(methoxydimethylsilyl) terminated PDMS is obtained.

Another explanation for this behavior might be that at lower temperatures hydrolysis reactions of the methoxy groups are suppressed and therefore molecular weight reaches a plateau. In terms of the final products, the PDMS prepared at 65 °C, 81 °C and 95 °C show only slight difference in their number average molecular weight after 24 h ranging from ~4500 g/mol to 5000 g/mol, which is not significant. This indicates that the higher reaction temperature does not affect the chain lengths of the resulting polymers.

Regarding the time course of conversions and number average molecular weights of the ring-opening-polymerizations at different temperatures, an optimum temperature can be determined. Despite fewer side reactions, temperatures below 40 °C are not suitable for the ROP of D4 with TBD, because they slow down the reaction to an extend where 90 % of $D_4$-conversion is not achieved within 24 h. The ring-opening-polymerizations at 65 °C, 81 °C and 95 °C did not differ strongly in conversion or number average molecular weight.

### 5.2.2 TBD concentration

Another reaction parameter which is investigated is the concentration of the base TBD which is used as co-initiator. It is assessed by examining different molar percentages (0.1 mol%, 0.5 mol%, 1 mol% and 2 mol%) in relation to the used amount of monomer.

A lower concentration of TBD affects the conversion speed in a decreasing way as it is shown in Chart 5-13. Lowering the TBD amount to 0.1 mol% leads to very slow reaction not reaching equilibrium state within the first seven hours of the experiment (conversion ~55 %). After 24 h conversion reaches ~80 %.

The usage of 0.5 mol%, 1 mol% and 2 mol% speeds up the reaction compared to 0.1 mol% in this order. With higher TBD concentrations the polymerization proceeded faster at the beginning of the reaction but at 5 h reaction time, those three experiments showed no significant difference in conversion anymore.

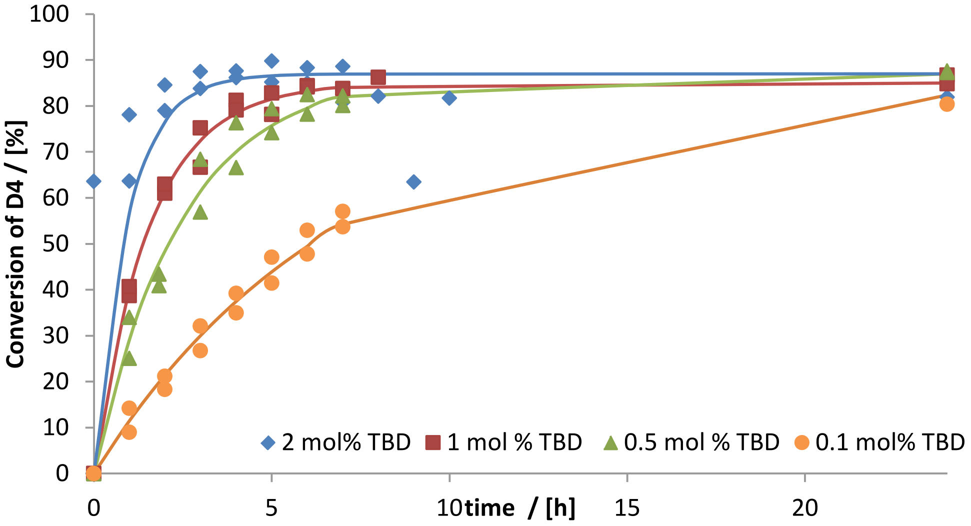

**Chart 5-13: Course of conversion of polymerization using different TBD concentrations and Methanol (200 mol%)in acetonitrile (acetonitrile : $D_4$ = 1.5:1) at 65 °C oil bath temperature. Conversion is calculated from $^{29}$Si(IG)-NMR.**

The time course of number average molecular weight over 24 h (c.f. Chart 5-14) shows that the lower the TBD concentration, the lower the value of $M_n$. This can be explained by a decreasing amount of side reactions, because conversion did not decrease to a comparable extend. Using less TBD could provide reaction conditions in which condensation reactions are slower than chain propagation and termination through alkoxylation.

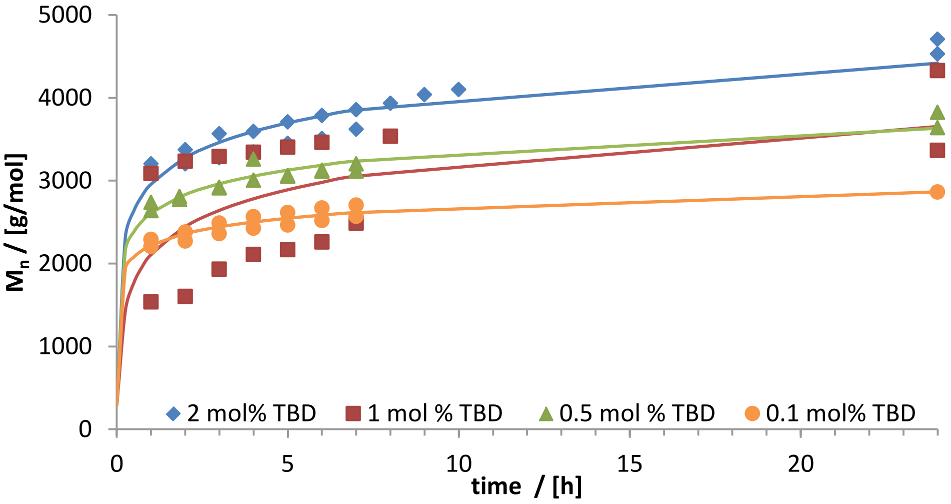

**Chart 5-14: Course of molecular weight $M_n$ during polymerization using different TBD concentrations and Methanol (200 mol%) in acetonitrile (acetonitrile : $D_4$ = 1.5:1) at 65 °C oil bath temperature. $M_n$ is determined by GPC using toluene as eluent and PDMS standards.**

Concluding from these experiments, 0.5 mol% of TBD yields a conversion >90 % of $D_4$ after 24 h and seem to lead to less side reactions. Hence, in an optimized reaction 0.5 mol% of TBD should be used.

### 5.2.3 Concentration of solvent

As already evaluated, acetonitrile serves as continuous phase in the mechanical stabilized emulsion polymerization (c.f. paragraph 3.2.1). It is now interesting to investigate whether the volume of acetonitrile may have an impact on the course of the reaction.

Therefore, three different acetonitrile volumes are assessed: $CH_3CN$ : D4 = 0.5 : 1, 1.5 : 1 and 0.5 : 1. When using 20 mL of $D_4$ this means in numbers 10 mL, 30 mL and 60 mL of acetonitrile respectively.

To better explain the obtained results, the solubility of $D_4$ in acetonitrile is calculated from $^1H$ NMR data to be 0.067 g $D_4$/g $CH_3CN$ at room temperature (~23 °C) (c.f. appendix A5.2.2).

With this knowledge, investigations in conversion and average molecular weight versus time are conducted.

Within the first two hours of the experiments the reaction profiles showed no difference. From then on, conversion remained in an equilibrium state (c.f. Chart 5-15).

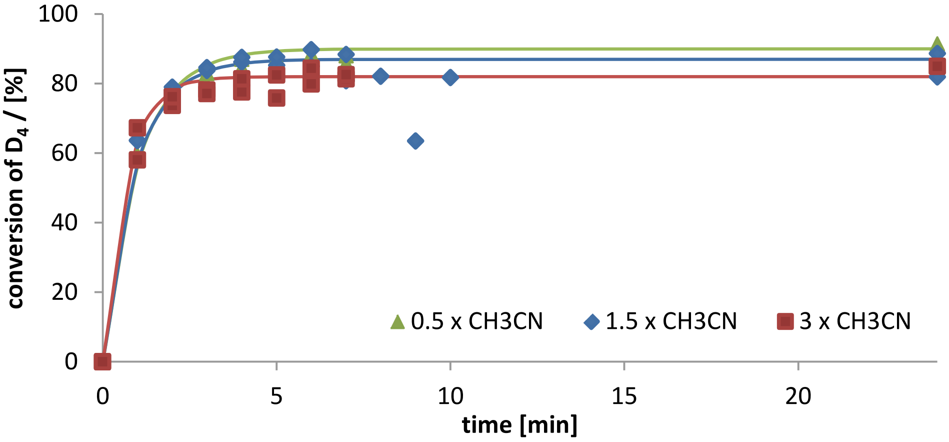

**Chart 5-15: Course of conversion of polymerization using different volumes of acetonitrile related to the volume of $D_4$. Polymerizations are conducted using 2 mol% TBD and 200 mol% methanol at 65 °C oil bath temperature. Conversion is calculated from $^{29}$Si(IG)-NMR.**

Hence, the concentration of acetonitrile does not have an apparent effect on the conversion. Since an increase in the amount of acetonitrile would lead to a dilution and therefore to a hampering of the reaction progress this leads to the conclusion that the ROP is located in the dispersed phase, or in other words within the $D_4$ droplets. This might be compared to a mini emulsion polymerization where initiation takes place in an emulsifier stabilized monomer droplet which functions as “microreactor” (c.f paragraph 2.5).[136]

The different average number molecular weights of the polymer during the reaction show that the more solvent was used, the higher was $M_n$. However, the differences between the average molecular weights are small and after 24 h (c.f. Chart 5-16) the differences between the molecular weights ranging from 4000 g/mol to 5000 g/mol are not significant anymore.

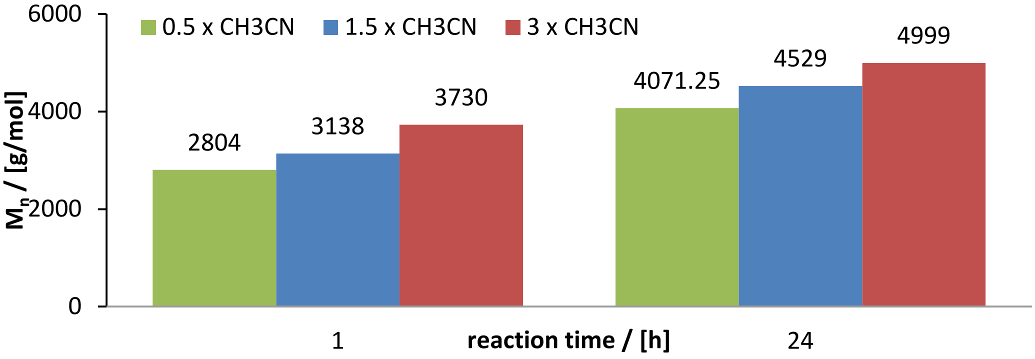

**Chart 5-16: Number averaged molecular weights after 24 h polymerizations using different volumes of acetonitrile related to the volume of $D_4$. Polymerizations are conducted using 2 mol% TBD and 200 mol% methanol at 65 °C oil bath temperature. $M_n$ is determined by GPC using toluene as eluent and PDMS standards.**

Regarding these results a solvent volume of 10 mL for 20 g of $D_4$ seems to be the best option for an optimized reaction, since less solvent means lower costs.

### 5.2.4 Investigation of optimized reaction parameters

Separate investigation of the reaction parameters show that following chosen conditions which are presented in Table 5-4 can be used for an optimized reaction set-up.

**Table 5-4: Comparison of initial and optimized reaction conditions.**

| Parameter | Optimized | Initially |
|---|---|---|
| Oil bath temperature | 65 °C | 65 °C |
| Amount of co-initiator | 0.5 mol% | 2 mol% |
| Solvent volume | acetonitrile : D4 = 0.5:1 | acetonitrile : D4 = 1.5:1 |

Therefore, an experiment using these optimized conditions combined is compared to the parameters which were used initially.

The results are shown in Chart 5-17. As it is expected considering the results of the separately investigated reaction parameters, conversion of $D_4$ increases slowlier than under the condition used initially. Nevertheless, a desired conversion higher than 90 % is reached within 24 h. At the same time, lower molecular weights were obtained (~2000 g/mol compared to ~4500 g/mol) indicating that less side reactions were taking place.

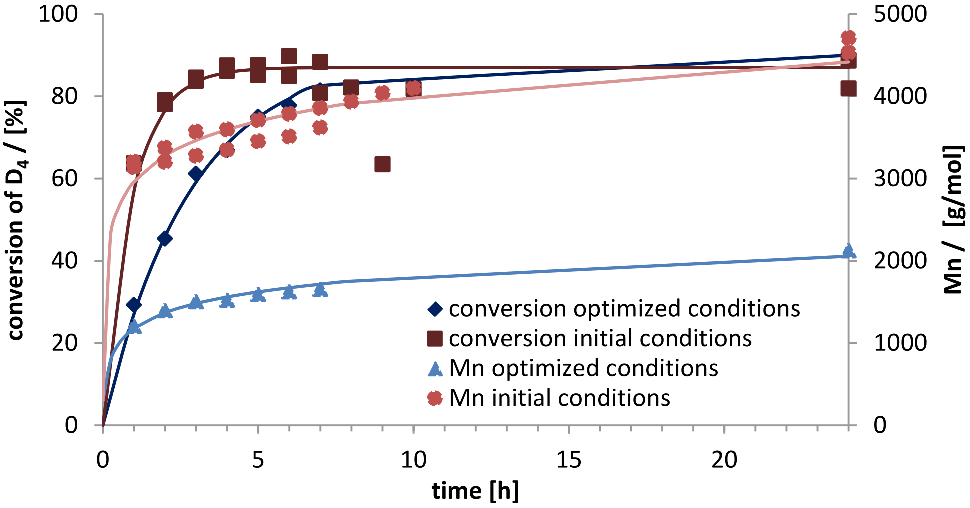

**Chart 5-17: Comparison of course of conversion of $D_4$ and of number average molecular weight using the optimized and initial reaction parameters described in Table 5-4. Methanol is used in an amount of 200 mol% related to the amount of $D_4$ for both polymerizations. Conversion is calculated from $^{29}$Si(IG)-NMR and $M_n$ is determined via GPC using toluene as eluent and PDMS standards.**

To investigate whether these effects stem from the combination of the optimized parameters or one parameter alone, the results of the polymerization using optimized conditions are compared to the ones where theses parameters were used separately as presented in Chart 5-18 and Chart 5-19.

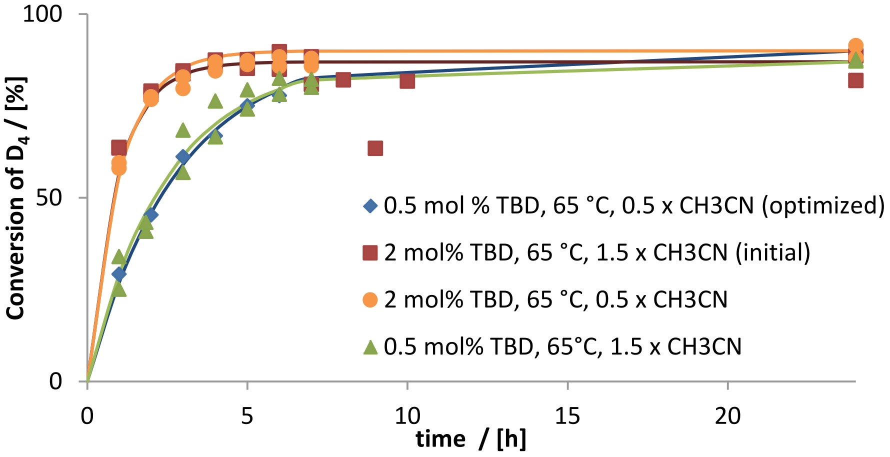

**Chart 5-18: Influence of co-initiator concentration and amount of solvent on conversion during course polymerization at 65 °C oil bath temperature. 200 mol% of MeOH are used. Conversion is calculated from $^{29}$Si(IG)-NMR.**

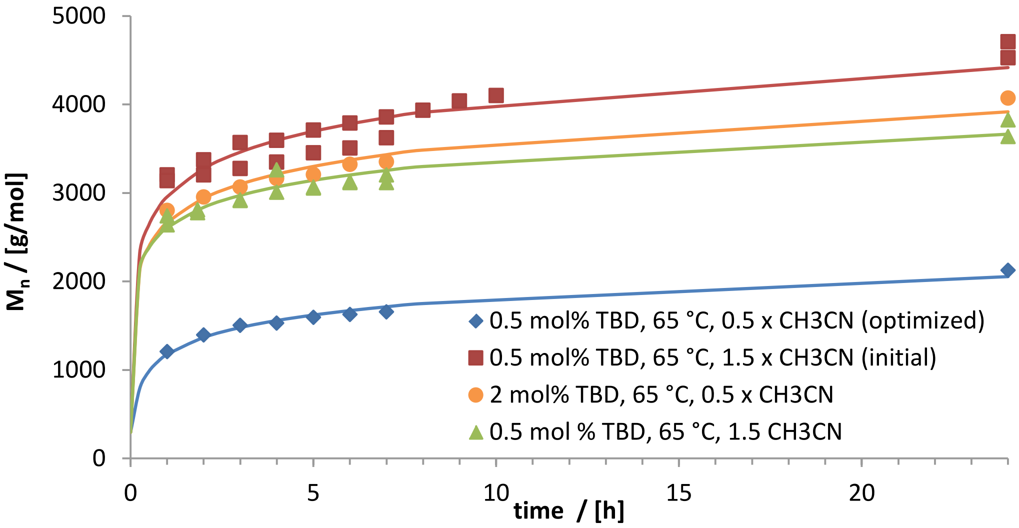

**Chart 5-19: Influence of co-initiator concentration and amount of solvent on molecular weight $M_n$ during course polymerization at 65 °C oil bath temperature. 200 mol% of MeOH are used. $M_n$ is determined via GPC using toluene as eluent and PDMS standards.**

This comparison supports the statement of subchapter 5.2.3 by showing that conversion is not affected by using less acetonitrile. Conversion is only affected by the amount of TBD used.

Conversely, $M_n$ is affected by the combination of the different parameters. Only changing the volume of acetonitrile at a TBD percentage of 2 % does not change $M_n$ significantly, neither does only changing the amount of TBD. But the combination of less TBD and less acetonitrile seems to decrease $M_n$ approximately to a half. This indicates that condensation reactions are suppressed under optimized reaction conditions.

## 5.3 Summary and conclusions

In this chapter, different hydroxy functional molecules are investigated as suitable initiators for ROP of $D_4$ in the presence of TBD.

When testing different alcohols, it is assumed that the basicity of alcohols is a measure for their activity in the polymerization process. This suggestion would have led to the consequence that *tert*-butanol would have been the most active alcohol. Since this is not the case and the activity of the tested alcohols decreases with increasing chain length and branching, it is proposed that the nucleophilicty of the alcohols, which is strongly influenced by sterical hindrance, is the key factor for their activity in ROP.

Additionally, water is tested in order to obtain silanol terminated PDMS. It is found that with increasing amount of water conversion decreases, suggesting an inhibition either of TBD or of the propagation reaction. At the same time, high molecular weight polymers are obtained stemming from uncontrolled polycondensation reactions taking place in equilibrium or maybe already during ROP itself.

As example for silanols trimethylsilanol is tested. In comparison to methanol and water, the usage of trimethylsilanol leads to significantly lower molecular weights. This can be related to the fact that in the case of trimethylsilanol no telechelic polymers with hydrolysable groups are obtained. Therefore, no hydrolyzation reactions are taking place due the lack of hydrolysable alkoxy groups. Hence, condensation reactions will take place to limited extend.

It is also demonstrated that with increasing concentration of the hydroxy compound, smaller molecular weights are obtained. Targeting molecular weight via set up of a regression line is not successful. This is hampered by the high standard deviations especially if low amounts of methanol are used stemming from a loss of methanol due to it its high vapor pressure at 65 °C.

Focusing on the usage of methanol in high concentrations, reaction parameters such as the concentration of TBD, reaction temperature and amount of solvent are investigated. It is shown that the concentration of TBD can be reduced to 0.5 mol% and the amount of solvent to half the volume of monomer. The results show slightly slower conversion over time. Anyhow, after 24 h still 90 % conversion is obtained. When looking at the course of $M_n$ it is obvious that lower molecular weight is obtained. The found optimized reaction conditions may have a positive effect on targeting molecular weight as well.

The optimization of reaction conditions leads to a decrease in manufacturing costs. Under initial conditions (2 mol% TBD, ratio $D_4$:$CH_3CN$ = 1:1.5) costs amount to 434.75 €/kg or 273.60 €/kg if the solvent phase is recycled five times. Using the described optimized conditions (0.5 mol% TBD, ratio $D_4$:$CH_3CN$ = 1:0.5) costs drop to 329.06 €/kg or 259.91 €/kg if the solvent phase is recycled. Not taken into account are production costs such as man power, energy costs, cleaning and transfer costs. Furthermore costs for hydroxy compounds which are needed as initiator and terminating agents are also not considered because their amount depends on the chosen molecular weight of the produced polymer. Details of the cost calculation are presented in the appendix A5.2.3.

# 6 Conclusion and Outlook

Within the scope of a screening of several nitrogen containing bases as initiators and co-initiators respectively for ring-opening polymerization of cyclic siloxanes, it was shown that N-heterocyclic carbenes are not suitable for the purposes of this work. NHCs, which act as initiators, have to be handled under moisture free, inert conditions, because they are very sensitive towards moisture and get inactivated easily. This makes them difficult to use in industrial processes. Although $CO_2$-protected NHCs are described, which decompose under slightly elevated temperatures under release of active NHCs and $CO_2$, the polymerization has to be performed under inert and moisture free conditions, which makes the process cost intensive. In the presented research the moisture sensitivity of the NHCs was advantageous since further quenching with an acid was not necessary.

Apart from these considerations first experiments with NHCs showed high conversions and high molecular weight polymers resulted from the polymerization. Investigations in order to obtain polymers with lower molecular weights by using solvents, decreasing the reaction temperature, increasing the concentration of alcohol lead to a decrease in molecular weight but also to a drastic decrease in conversion.

Investigations of amines, amides and guanidines as co-initiators where a hydroxy compound acts as initiator resulted into a new process setup. It was proven that reactions in acetonitrile led to strong increase in conversion in between 24 h of reaction time. Thereby acetonitrile increases the $pK_a$ value of the chosen base and solvates the formed ion pairs. Since both monomer and polymer are not miscible with the chosen solvent, polymerization takes place in a mechanical stabilized emulsion in which the monomer is dispersed in the solvent. It is assumed that the monomer droplets act as microreactors.

Since most of the tested initiators are not soluble in the monomer/polymer phase they do not need to be quenched via an acid. This bears the advantage that filtration of the polymer is not necessary. Furthermore, the solvent phase can be recycled for another polymerization without adding fresh co-initiator.

Thanks to this special polymerization set up also weaker bases such as amines and amides could serve as suitable co-initiators. In comparison to KOH which was used as state of the art it was demonstrated that bicyclic guanidines such as TBD and its derivatives showed best results in polymerization of $D_4$ with methanol regarding conversion of the monomer.

Further mechanistic investigations showed that contrary to the in literature proposed heterotelechelic $\alpha$-methoxydimethylsilyl-$\omega$-hydroxydimethylsilyl PDMS, homotelechelic $\alpha$-, $\omega$-di(methoxydimethylsilyl) PDMS is obtained. This could be traced back to condensation and alkoxylation in equilibrium with hydrolysis reactions. It is suggested that these side reactions are occurring in equilibrium state of the polymerization but this could not be proven yet and has to be further investigated. Equilibration reactions are not taking place. Back-biting reactions are taking place which was proven by GC-measurements of the final polymers. Macrocycles up to $D_{21}$ could be identified. Bishoff *et al.*[212] reported that backbiting reactions in a biphasic system where water serves as polar phase and the polymer is dissolved in toluene are suppressed because the hydroxy end-groups are located at the interphase. In a next step this could be also investigated for this biphasic process setup.

Up to this point only polymerization reactions of $D_4$ initiated by a combination out of TBD and methanol in acetonitrile have been investigated. It is also possible to used different alcohols whereby their reactivity is strongly depending on their nucleophilicity which is expressed by lower conversions with decreasing nucleophilicity.

Especially water as hydroxy compound was important in order to obtain silanol end-capped polymers, which was successful. Due to enhanced condensation reactions high molecular weights were obtained compared to methanol and increasing water concentration lead to decrease in conversion. The enhanced condensation reactions also lead to low reproducibility of the experimental results. A possible solution of these problems might be found in changing the experimental set up. Usage of lower reaction temperature or lower co-initiator concentration was promising (c.f. A6.2.1). Another solution might be usage of a two solvent system where the polymer phase is dissolved in toluene and as second solvent still acetonitrile is used in order to dilute the reaction system and slow down polymerization reactions.

In this context also the concept of the thermodynamic water activity $a_w$, which basically describes the hydration of a system, should be taken into account. The water activity does not depend on the water amount in the system but also on the properties of the reaction mixture such as polarity of the solvent used for example. The effect of $a_w$ on the activity of enzymes was studied by Halling *et al.* and it is described that some enzymes are reacting very sensitive towards changes of the $a_w$-value.[213-216] It might be that the thermodynamic water activity also has an impact on our polymerization, too and investigations in that direction should be undertaken.

In any case the concentration of water is a problem. With higher water amounts lower conversion was observed. A solution to overcome this might be dosing either water or monomer in course of the reaction. Especially first experiments where monomer was dosed were promising, whereas dosing of water led directly at the beginning of the reaction to strong increase in viscosity (c.f. A6.2.2). All the approaches have to be investigated further especially with regard to industrial application.

Anyhow, by adjusting the concentration of hydroxy compound the molecular weight can be controlled. With higher concentrations lower molecular weights are obtained. Yet targeting of molecular weight is not possible.

By investigation of reaction parameters optimal reaction conditions could be estimated regarding the amount of co-initiator, reaction temperature and the amount of solvent as well. Stirring speed was adjusted in a way that homogenous mixing of both phases was given and it was shown that an increase in reaction speed had no influence on the conversion or molecular weight. So far, the effect of the droplet size has not been assessed. Investigations in this direction should be undertaken via differential light scattering. This would bear the advantage that it would simplify a transfer into bigger scales since stirring speed is not a sufficient measure for droplet size distribution which is also depending on the stirring geometry, the rheological behavior of the reaction mixture as well as on the reactor. Furthermore, analysis via differential light scattering could also provide further information of the location of initiation and of chain propagation. Especially interesting would be also the location of condensation reactions. According to literature it is estimated, that the processes are located at the interphase. [144-145] It might be that the droplet size also has influence on the side reactions.

Apart from $D_4$ also $D_5$ and mixtures out of both were tested successfully tested as monomers. This is especially important for industry applications since it would be cost effective if not the pure monomer but monomer mixtures containing different cycles and eventually also short chained linear oligomers could be used. As general outcome it can be said that the polymerization of $D_5$ proceeds slower than the one of $D_4$ which is not surprising since this behavior is already described in literature and is related to the lower ring strain of $D_5$.[32] This has to be investigated further especially in means of kinetic investigations of higher cyclic monomers.

Since the synthesis of *α-, ω*-di(hydroxydimethylsilyl) end-capped polymers did not lead to controllable results yet the curing of *α-, ω*-di(dimethoxysilyly) end-capped polymers has to be optimized. Experiments in this direction will performed in a next step.

# 7 Summary

To sum up shortly:

A new process for the synthesis of linear siloxane polymers via ring-opening polymerization using guanidines, amidines and amines as co-initiators in the presence of a protic initiator has been established. The special characteristic of this process is its biphasic nature due to the usage of a polar, aprotic solvent in which both monomer and polymer are not miscible. This bears the advantage that the co-initiator does not need to be quenched and furthermore it can be recycled by recycling the whole solvent phase for another polymerization. The process was performed in scales up to 250 g of monomer. In this summer the process was also filed as patent application.

Characterization via ESI-TOF and MALDITOF as well as NMR studies of the obtained PDMS when polymerizing $D_4$ in the presence of TBD and methanol in this new process setup showed that in contrast to predicted heterotelechelic α-methoxydimethylsilyl-ω-hydroxydimethylsilyl PDMS homotelechelic α-, ω-di(methoxydimethylsilyl) PDMS are obtained. By performing mechanistic experiments the general polymerization mechanism proposed in literature could be confirmed and was extended by condensation, hydrolysis and alkoxylation reactions taking place in equilibrium state of polymerization. These side reactions led to the unexpected homotelechelic α-, ω-di(methoxydimethylsilyl) PDMS.

Moreover influencing parameters were assessed starting with screening of different alcohols, water and triorganosilanols as suitable initiators in the presence of TBD. Thereby reactivity of the alcohols decreases with increasing chain length and increasing branching due to lower nucleophilicity. This leads to slower reaction as well as lower molecular weight of the polymer.

Especially the usage of water as protic compound bears the advantage that α,ω-di(hydroxydimethylsilyl) PDMS is obtained as final product which can be directly used in curing reactions. Drawbacks are the enhanced condensation reactions leading to higher molecular weight in comparison to methanol and lower reproducibility.

By adjusting the amount of initiator, which additionally acts as terminating agent, also molecular weight of the final polymer can be adjusted. With higher amount of hydroxy compound lower molecular weights are obtained.

In a last step reaction parameters such as amount of co-initiator and solvent as well as reaction temperature have been investigated leading to an optimized reaction set up which leads also to lower costs due to reduced amounts of co-initiator and solvent.

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# Appendix

# Table of Appendix

# A1 List of Chemicals

| Name | Provider | Purity | Comments |
|---|---|---|---|
| (-)-Sparteine | Sigma Aldrich | | |
| 1-(o-Tolyl)biguanide | Sigma Aldrich | 98 % | |
| 1,3-Bis(2,4,6-trimethylphenyl)imidazolinium chloride | | | |
| 1,3-Butandiol | Fisher Scientific UK | | |
| 1,3-Divinyltetramethyldisiloxane | ABCR | 98 % | |
| 1,5,7-Triazabicyclo[4.4.0]dec-5-ene | Sigma Aldrich | 98 % | resublimated; stored under argon |
| 1,8-Bis(dimethylamino)naphthalene | Sigma Aldrich | 99 % | |
| 1,8-bis(tetramethylguanidino)naphthalene | Sigma Aldrich | $\geq$ 98 % | |
| 1,8-Diazabicyclo[5.4.0]undec-7-ene | Sigma Aldrich | 99 % | |
| 1-Decyl-3-methylimidazolium chloride | Iolitac | 98 % | |
| 1-Ethyl-3-methyl-imidazol-3-ium bis(trifluoromethylsulfonyl)amide | Iolitac | | |
| 1-Octyldodecanol (Eutanol G) | BASF | | |
| 2-Aminoethanol | Sigma Aldrich | 99 % | |
| 2-Iodbenzoic acid | Sigma Aldrich | 98 % | |
| 3-Aminopropyltriethoxysilane | ABCR | 98 % | |
| 3-Aminopropyltrimethoxysilane | Sigma Aldrich | 98 % | |
| Acetonitrile | | | Dried (PureSolv$^{TM}$), stored under argon over molecular sieves |
| Carbondisulfide | Sigma Aldrich | 98 % | |
| Chloroform | Acros Organics | | |
| Chrom(III)acetylacetonate | Acros Organics | 97 % | |
| Concentrated fluoroboric acid | Sigma Aldrich | | |
| Concentrated hydro chloric acid | Fisher Scientific UK | | |

| Name | Provider | Purity | Comments |
|---|---|---|---|
| Cyclohexylamine | Sigma Aldrich | $\geq$ 99.9 % | |
| Decamethylcyclopentasiloxane | Alfa Aesar | 97 % | |
| Dichloromethane | Acros Organics | | |
| Dicyclohexylcarbodiimide | Sigma Aldrich | 99% | |
| Di-n-propylamine | Alfa Aesar | 99 % | |
| Dioctyltinlaureate | ABCR | 95 % | |
| Ethyllactate | Sigma Aldrich | 98 % | |
| Glyoxal (40% in H2O) | Sigma Aldrich | | |
| Isopropanol (dry) | Acros Organics | Analytic grade | |
| L-Arginine | Sigma Aldrich | $\geq$ 98 % | |
| Magnesium sulfate | Sigma Aldrich | | |
| Methanol | Fisher Scientific UK | | |
| Methanol dry | Acros Organics | | |
| *N*,*N*,*N′*,*N′*-Tetramethylmethanediamine | Sigma Aldrich | 99 % | |
| Naphthalene | Sigma Aldrich | > 99 % | |
| n-Butanol | Fischer Scientific UK | | dried over neutral Alumina, stored under argon over moelcular sieves |
| N-Methylpyrrolidine | Sigma Aldrich | 97 % | |
| Octamethylcyclotetrasiloxane | TCI | > 98% | |
| Paraformaldehyde | Sigma Aldrich | 95 % | |
| Phosphazene base $P_2$-Et | Sigma Aldrich | $\geq$ 98 % | |
| Polydimethylsiloxane, trimethylsiloxy terminated, M.W. 14000 | Alfa Aesar | | |
| Polydimethylsiloxane, trimethylsiloxy terminated, M.W. 2000 | Alfa Aesar | | |
| Polydimethylsioxane, hydroxydimethylsiloxy terminated (DMS-S15) | Gelest | | |
| Potassium Hexamethyldisilazide | Sigma Aldrich | 95 % | Stored in Glove box |

| Name | Provider | Purity | Comments |
|---|---|---|---|
| Propanolamine | Sigma Aldrich | 99 % | |
| Sodium carbonate | | | |
| tert. Butanol | ROTH | | dried over neutral Alumina, stored under argon over molecular sieves |
| Tert.-butylamine | Sigma Aldrich | 98 % | |
| Tetrahydrofurane dry | Acros Organics | Analytic grade | |
| Toluene dry | Acros Organics | Analytic Grade | |
| Trimethylsilanol | Sigma Aldrich | 97.5 % | |
| Vinyltrimethoxysilane | sample of Henkel Co. KGaA | | |

# A2 Used Devices and Methods

## A2.1 Infrared spectroscopy (IR)

ATR infrared spectra of the samples were measured on Nicolet 6700 FT-IR (Thermo Electron). All samples were measured neat. Solid samples were pressed directly on to the IR-detector window. Maximum resolution is 0.5 $cm^{-1}$. Adsorption bands are given in wave numbers ($cm^{-1}$) and were measured in the range from 400 to 4000 $cm^{-1}$.

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

## A2.2 Nuclear magnetic resonance spectroscopy (NMR)

NMR spectra of the samples were measured on

Bruker AV 400 (Year 2005): Magnetic field = 9.4 T; Resonance frequency = 400 MHz
Bruker AV 300 (Year 2005): Magnetic field = 7.0 T; Resonance frequency = 300 MHz
Bruker Fourier 300 (Year 2012): Magnetic field = 7.0 T, Resonance frequency = 300 MHz)

Spectra shifts are reported as $\delta$-values in ppm relative to the deuterated solvent shift(s). Following solvents were used for referencing NMR spectra:

$d_1$-chloroform ($^1$H = 7.26 ppm, $^{13}$C = 77.00 ppm), $d_2$-methylene chloride ($^1$H = 5.32 ppm, $^{13}$C = 54.00 ppm), $d_8$-toluene ($^1$H = 2.08, 6.97, 7.01, 7.09 ppm, $^{13}$C = 137.48, 128.87, 127.96, 125.13, 20.43 ppm), DMSO ($^1$H = 2.50, 3,33 ppm; $^{13}$C = 39,52 ppm)

The abbreviations used to describe the multiplicity of the spectra peaks are: s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quadruplet), p (quintet), h (hexaplet), dd (doublet of doublets), and m (multiplet).

### A2.2.1 Exemplary assignment of NMR signals of key monomers and polymers

Octamethylcyclotetrasiloxane $D_4$

**$^1$H-NMR** (300 MHz, $CDCl_3$, 297.0 K, ppm) $\delta$ = 0.11 (s, $–[O–Si(C\underline{H}_3)_2]–$). **$^{13}$C-NMR** (75 MHz, $CDCl_3$, 297. K, ppm): $\delta$ = 0.94 (s, $–[O–Si(\underline{C}H_3)_2]–$). **$^{29}$Si-NMR** (59 MHz, $CDCl_3$, 297.0 K, ppm): $\delta$ = -19.18 (s, $–[O-\underline{Si}(CH_3)_2]–$).

Decamethylcyclotetrasiloxane $D_5$

**$^{1}$H-NMR** (300 MHz, CDCl$_3$, 297.0 K, ppm) $\delta$ = 0.10 (s, –[O–Si(C$\underline{H}_3$)$_2$]–);.**$^{13}$C-NMR** (75 MHz, CDCl$_3$, 297. K, ppm): $\delta$ = -1.39 (s, –[O–Si(C$\underline{H}_3$)$_2$]–);.); 1.06 (s, –[O–Si($\underline{C}$H$_3$)$_2$]–). **$^{29}$Si-NMR** (59 MHz, CDCl$_3$, 297.0 K, ppm): $\delta$ = -21.62 (s, –[O-$\underline{Si}$(CH$_3$)$_2$]–).

Homotelechelic α-,ω-di(methoxydimethylsilyl) PDMS (***P4.2***)

**$^{1}$H-NMR** (300 MHz, CDCl$_3$, 297.0 K, ppm) $\delta$ = 0.06 – 0.12 (m, –[O–Si(C$\underline{H}_3$)$_2$]–); 3.45 – 3.47 (s, C$\underline{H}_3$–O–Si(CH$_3$)$_2$–).**$^{13}$C-NMR** (75 MHz, CDCl$_3$, 297. K, ppm): $\delta$ = -1.39 (s, CH$_3$–O–Si($\underline{C}$H$_3$)$_2$–); 1.11 – 1.75 (m, –[O–Si($\underline{C}$H$_3$)$_2$]–); 49.76 (s, $\underline{C}$H$_3$–O–Si(CH$_3$)$_2$–). **$^{29}$Si-NMR** (59 MHz, CDCl$_3$, 297.0 K, ppm): $\delta$ = -22.5 – -21.48 (m, –[O-$\underline{Si}$(CH$_3$)$_2$]–); -11.47 (s, –$\underline{Si}$(CH$_3$)$_2$–O–CH$_3$).

Homotelechelic α-,ω-di(hydroxydimethylsilyl) PDMS (***DMS-15***)

**$^{1}$H-NMR** (300 MHz, CDCl$_3$, 297. K, ppm): $\delta$ = 0.05 – 0.16 (m, – [O–Si(C$\underline{H}_3$)$_2$]–). **$^{13}$C-NMR** (75 MHz, CDCl$_3$, 297. K, ppm): $\delta$ = 0.96 – 2.16 (m, –[O–Si($\underline{C}$H$_3$)$_2$]–). **$^{29}$Si-NMR** (59 MHz, CDCl$_3$, 297. K) [ppm]: $\delta$ = -22.76 – -21.12 (m, –[O–$\underline{Si}$(CH$_3$)$_2$]–); -11.35 (s, –$\underline{Si}$(CH$_3$)$_2$–OH).

Homotelechelic α-,ω-di(trimethylsily) PDMS (***P5.39***)

**$^{1}$H-NMR** (400 MHz, CDCl$_3$, 297.0 K) [ppm]: $\delta$ = -0.09 – 0.25 (m, –[O–Si(C$\underline{H}_3$)$_2$]–). **$^{13}$C-NMR** (100 MHz, CDCl$_3$, 297. K, ppm): $\delta$ = 0.87 – 1.61 (m, –[O-Si($\underline{C}$H$_3$)$_2$]–), 1.97 (s, (H$_3\underline{C}$)$_3$Si–). **$^{29}$Si-NMR** (80 MHz, CDCl$_3$, 297.0 K, ppm): $\delta$ = -22.55 – -21.96 (m, -[O-$\underline{Si}$(CH$_3$)$_2$] -); 7.21(s, (H$_3$C)$_3\underline{Si}$–).

In polymers with too high molecular weights signals assigned to terminating groups especially in $^{29}$Si are not observable.

### A2.2.2 Calculation of conversion

The conversion of monomer ($D_x$, with x = 4 or 5) is calculated via integration of the peak areas from $^{29}$Si-IG-NMR according to the following formula when alcohols or water were used in polymerization reaction. If $D_5$ is not used as monomer is belongs to the integral of the cyclic byproducts:

$$conversion = \frac{\int Polymer + \int terminating\ group + \int cyclic\ byproducts}{\int D_x + \int Polymer + \int terminating\ group + \int cyclic\ byproducts} \cdot 100\%$$

**Eq. A2-1**

The conversion of monomer is calculated via integration of the peak areas from $^{29}$Si-IG-NMR according to the following formula when triorganosilanols were used in polymerization reaction. Here the signals of the terminating group as well as the signal to the used triorganosilanol are not integrated due to the fact that they do not belong to the conversion of $D_x$ unless the terminating group is hydroxdimethylsilyl which was not observed in our reactions:

$$conversion = \frac{\int Polymer + \int cyclic\ byproducts}{\int D_x + \int Polymer + \int cyclic\ byproducts} \cdot 100\% \qquad \textbf{Eq. A2-2}$$

The conversion of monomer is calculated via integration of the peak areas from $^{29}$Si-IG-NMR according to the following formula when a combination of disiloxane and alcohol were used in polymerization reaction. Here the signals of the terminating group stemming from the disiloxane as well as the signal of the disiloxane alone are not integrated due to the fact that they do not belong to the conversion of $D_x$. In fact The signal deriving from $Si(CH_3)_2OR$ is integrated.

$$conversion = \frac{\int Polymer + \int cyclic\ by - products + \int Si(CH_3)_2OR}{\int D_x + \int Polymer + \int cyclic\ byproducts + \int Si(CH_3)_2OR} \cdot 100\% \qquad \textbf{Eq. A2-3}$$

Conversion of $D_x$ is determined by taking a sample after 24 h reaction time before stopping the reaction except when performing time-resolved measurements.

### A2.2.3 Determination of silanol content*

The NMR experiment is conducted on an Agilent (Varian) Mercury Plus 300 system according to the method described by Ho.[1]

## A2.3 Ionization techniques

Samples for mass spectrometry are dissolved in dichloromethane. Mass spectra are obtained by using Finngan MAT 95 (200 eV, EI-MS). For ESITOF measurements 6210 Time-of-Flight LC/MS (Agilent) is used. MALDITOF measurements are performed in THF on an ABI-4800MALDI-TOF/TOF instrument under positive reflection mode.†

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* Experiments were performed externally by Lindsay Murphy.

† MALDI-TOF experiments were performed externally by Dr. Dayong Sun.

## A2.4 Determination of melting point

Melting points are determined visually and measured on a Stuart SMP3 Melting Point Apparatus. The sample is filled into a melting point tube (~0.5 – 1 cm high). Measurement is started 15 °C below the expected melting point. Heating rate is 0.5 °C/min.

## A2.5 Gel permeation chromatography (GPC)

The determination of the molecular weight of the polymers is performed via GPC. For the separation a combination of three different columns is used: Styragel HR 4 (300 x 7,8 mm), Styragel HR 3 (300 x 7,8 mm), precolumn Styragel (30 mm) obtained from Waters. As a detector a light scattering detector is used. As eluent toluene is used with a flow rate of 1 mL/min. As standard PDMS is used.

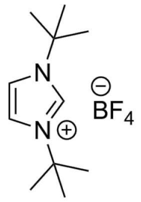
## A2.6 Elemental analysis

Measurements are performed with C/H/N/S – Microanalysator TruSpec CHNS (Leco). The sample is burnt with pure oxygen in a helium flow. The detection is performed with IR detectors.

# A3 Appendix to Chapter 3

## A3.1 N-Hetercyclic carbenes

### A3.1.1 Synthesis of 1, 3-di-tert-butyl-1H-imidazol-3-ium tetrafluorborate (*3.3a*)[2-3]

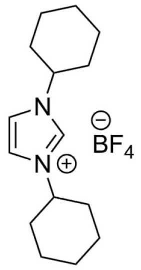


Paraformaldehyde (33.4 mmol) is submitted into a 50mL two-neck flask. 20 mL of toluene are added and a white suspension is formed. The suspension is cooled down to 3 °C and tert-butylamine (66.7 mmol) is added dropwise and the reaction mixture is stirred for further 15 min at 3 °C. The mixture heated up to 35 °C and a clear solution is formed. The solution is cooled down to 3 °C again and conc. HCl (33.4 mmol) is added dropwise. A white solid precipitates. Ice bath is removed and solution is stirred at RT for two hours. Then glyoxal solution (40 wt%, 33.4 mmol) is added and two colorless phases are formed. Solution is stirred overnight at 40 °C.

Solvent is distilled off "bulb-to-bulb" in an argon flow ($T_{head}$ = 80 °C). Then solution is cooled down to 50 °C and last solvent is removed in vacuo. The crude product is diluted in 25 mL water and filtered. $HBF_4$ (33.4 mmol) is added to the liquid. The white precipitate is filtered off and washed with water. Last traces of water are removed in vacuo and a beige powder is formed in a yield of 50 % (3.25 g).

**EA** (%, measured (calculated)), $C_{15}H_{20}N_2BF_4$: C 51.09 (49.47), H 7.77 (7.55), N 10.88 (10.49). **ESI-TOF/MS** (HRMS, g/mol measured (calculated)), $C_{11}H_{21}N_2^+$: 181.17 (181.17), $BF_4^-$: 86.01, 87.00 (86.01, 87.00). **$^1$H-NMR** (DMSO, 400 MHz, 297 K, ppm): δ = 8.99 (s, 1H, RN=C<u>*H*</u>-NR'), 8.05 (d, 2 H, RN–C<u>*H*</u>=C<u>*H*</u>–NR'), 1.60 (s, 18 H, tert-Butyl). **$^{13}$C-NMR** (DMSO, 100 MHz, 297 K, ppm): δ = 132.13 (s, RN=<u>*C*</u>H-NR'), 120.43 (s, RN–<u>*C*</u>H=<u>*C*</u>H–NR'), 59.63 (s, -<u>*C*</u>($CH_3$)$_3$), 29.05 (s, -<u>*C*</u>$H_3$). **IR (ATR):** ν ($cm^{-1}$) 3173.80 (w), 3152.92 (w), 3106.61 (w), 2984.42 (w), 2893.19 (w), 1546.94 (m), 1480.16 (w), 1408.93 (w), 1378.21 (m), 1292.81 (w), 1242.54 (w), 1206.46 (m), 1123.79 (m), 1029.72 (s), 996.42 (s), 832.80 (m), 753.76 (m), 649.33 (m), 616.90 (w), 519.79 (w).

### A3.1.2 Synthesis of 1, 3-di-cyclohexyl-1H-imidazol-3-ium tetrafluoroborate (***3.4a***)[2-3]



Paraformaldehyde (33.4 mmol) is submitted into a 50mL two-neck flask. 20 mL of toluene are added and a white suspension is formed. The suspension is cooled down to 3 °C and cyclohexylamine (66.7 mmol) is added dropwise. The reaction mixture was heated up to 47 °C and a clear solution is formed. Solution is cooled down to 3 °C again and conc. HCl (33.4 mmol) is added dropwise. A white soild precipitates. Ice bath is removed. Then aqueous glyoxal solution (40 wt%, 33.4 mmol) is added dropwise and two colorless phases are formed. Solution is stirred overnight at 40 °C.

Solvent is distilled "bulb-to-bulb" in an argon flow ($T_{head}$ ~ 80 °C). Then solution is cooled down to 50 °C and last solvent is removed in vacuo. The crude product is diluted in 20 mL water and filtered. $HBF_4$ (33.4 mmol) is added and white precipitation is formed which is filtrated and washed with water. Last traces of water are removed in compartment dryer (85 °C; 400 mbar). Yield: 8.84g (83%).

**EA** (%, measured (calculated)), $C_{15}H_{25}N_2BF_4$: C 57.22 (56.27), H 7.68 (7.87), N 8.92 (8.75). **ESI-TOF/MS** (HRMS, g/mol measured (calculated)), $C_{15}H_{25}N_2^+$: 233.20 (233.20), $BF_4^-$: 86.01, 87.00 (86.01, 87.00). **$^1$H-NMR** ($CD_2Cl_2$, 400 MHz, 24 °C, ppm): δ = 8.83 (s, 1H, RN=C<u>*H*</u>-NR‘), 7.33 (d, 2H, RN–C<u>*H*</u>=C<u>*H*</u>–NR‘), 4.32 – 4.24 (m, 2H, NC<u>*H*</u>), 2.20 – 2.13 (m, 4H, Cy), 1.95 – 1.88 (m, 4H, Cy), 1.77 – 1.62 (m, 6H, Cy), 1.53 – 1.41 (m, 4H, Cy), 1.32 – 1.21 (m, 2H, Cy). **13C-NMR** (CD2Cl2, 100 MHz, 24 °C, ppm): δ = 133.82 (s, RN=<u>*C*</u>H-NR‘), 120.60 (s, RN–<u>*C*</u>H=<u>*C*</u>H–NR‘), 60.79 (s, NC<u>*H*</u>), 33.89 (s, Cyclohexyl ortho), 25.49 (s, Cyclohexyl para), 25.19 (s, Cyclohexyl meta). **IR (ATR):** v (cm$^{-1}$) 3148.38 (w), 2933.37 (m), 2860.30 (w), 1554.32 (m), 1455.18 (w), 1432.45 (w), 1365.79 (w), 1269.76 (w), 1192.95 (w), 1160.70 (m), 1145.87 (w), 1119.41 (m), 1048.14 (s), 1019.41 (s), 895.64 (m), 848.29 (m) 757.57 (m), 649.82 (m), 520.20 (m), 441.18 (w).

### A3.1.3 Synthesis of 1,3-bis(1-adamantyl)-1H-imidazol-3-ium tetrafluoroborate (*3.5a*)[4]

Paraformaldehyde (7.5 mmol) and 1-adamantanamine (7.5 mmol) are submitted into a 25 mL two-neck flask. 7.5 mL Chloroform are added and a white suspension is formed. After stirring 1 h at RT the suspension is cooled down to 1 °C and another portion of 1-adamantanamine (7.5 mmol) is added. $HBF_4$ (7.5 mmol) and aqueous glyoxal solution (40 w%, 7.5 mmol) are added slowly. Solution is stirred overnight at 60 °C.

Next morning there is an orange-brown solution with second white and milky phase. Solution is cooled down to RT and saturated $Na_2CO_3$ solution is added. Phases are separated and the aqueous phase is extracted with methylene chloride. Organic layers combined and are dried over $Mg_2SO_4$ and solvent is removed in vacuo. The crude product is diluted in 3 mL of methylene chloride and 3mL diethylether is added. The product is filtered off and washed with ether. Yield: 2.24g (70%).

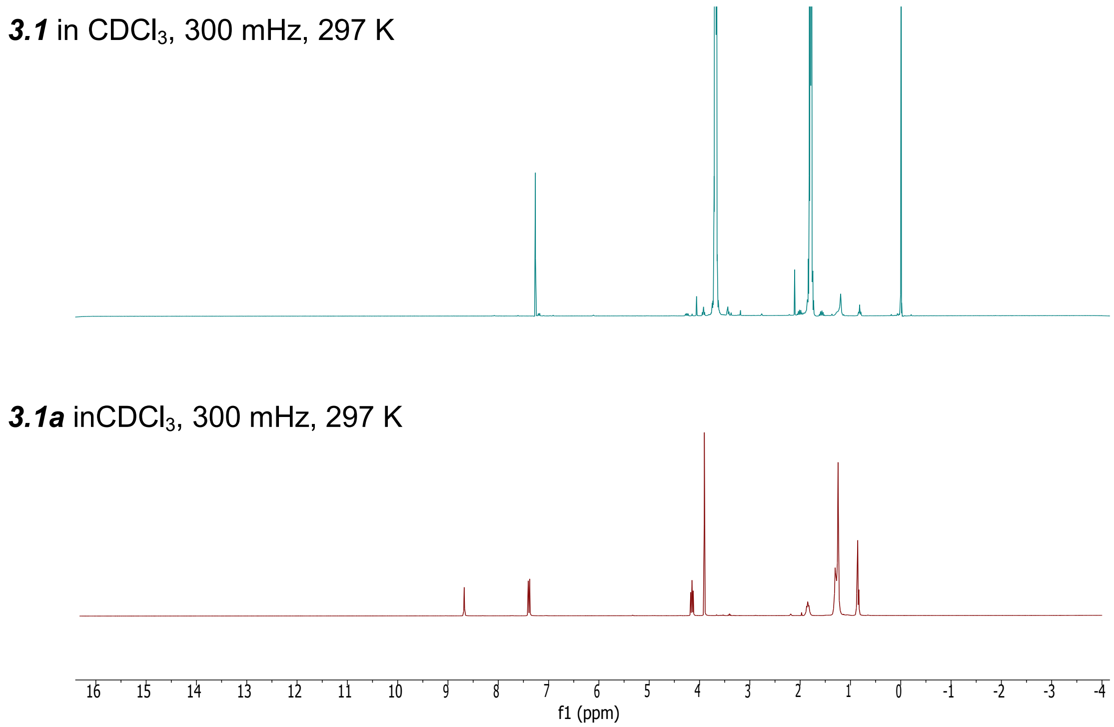
**EA** (%, measured (calculated)), $C_{23}H_{33}N_2BF_4$: C 65.98 (65.1), H 7.63 (7.84), N 6.76 (6.6). **ESI-TOF/MS** (HRMS, g/mol measured (calculated)), $C_{23}H_{33}N_2^+$: 337.26 (337.26), $BF_4^-$: 86,01, 87,00 (86,01, 87,00). **$^1$H-NMR** ($CD_2Cl_2$, 400 MHz, 24 °C, ppm): δ = 8.57 (s, 1H, RN=C*H*-NR'), 7.51 (d, 2H, RN–C*H*=C*H*–NR'), 2.31 – 1.78 (m, Adamantyl-). **$^{13}$C-NMR** ($CD_2Cl_2$, 100 MHz, 24 °C, ppm): δ = 130.34 (s, RN=*C*H-NR'), 119.57 (s, RN–*C*H=*C*H–NR'), 61.36 (s, quarternary C, adamantyl), 43.06 and 35.77 (s, CH2, adamantly), 30.16 (s, CH, adamantly). **IR (ATR):** ν ($cm^{-1}$) 3162.60 (w), 2910.27 (s), 2853.39 (m), 1544.21 (m), 1454.56 (m), 1366.39 (m), 1344.56 (m), 1309.10 (m), 1267.35 (w), 1193.13 (w), 1155.22 (s), 1107.20 (s), 1068.52 (s), 1019.13 (s), 832.92 (m), 814.42 (m), 759.92 (m), 693.72 (w), 654.40 (m), 633.96 (m), 520.07 (m), 459.34 (w).

## A3.1.4 Polymerization of $D_4$ by using NHCs as initiator

### A3.1.4.1 Preparation of NHCs

In the glove box KHMDS and the imidazolium salt are weighed in equimolar into an oven-dried, argon flushed Schlenk-tube. To this dry THF is added. The solution is stirred overnight at RT. The solution acts as stock solution of the initiator.

In following figures Figure A3-1 to Figure A3-6 the success of the deprotonation reaction is proven in $^1$H-NMR.



***3.1*** in $CDCl_3$, 300 mHz, 297 K

***3.1a*** in$CDCl_3$, 300 mHz, 297 K

**Figure A3-1: $^1$H-NMR of pure 3.1a and 3.1 (stock solution). The missing signal at 8.67 ppm in 3.1 is evidence for the success of the deprotonation.**

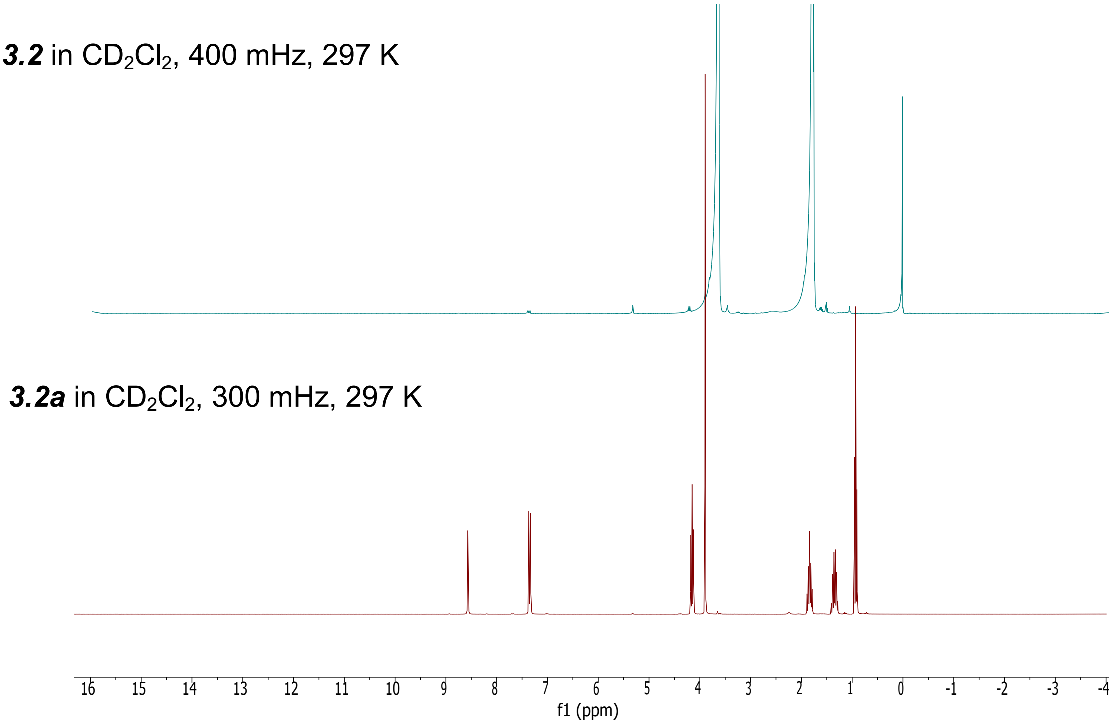


**Figure A3-2: $^1$H-NMR of pure 3.2a and 3.2 (stock solution). The missing signal at 8.56 ppm in 3.2 is evidence for the success of the deprotonation.**

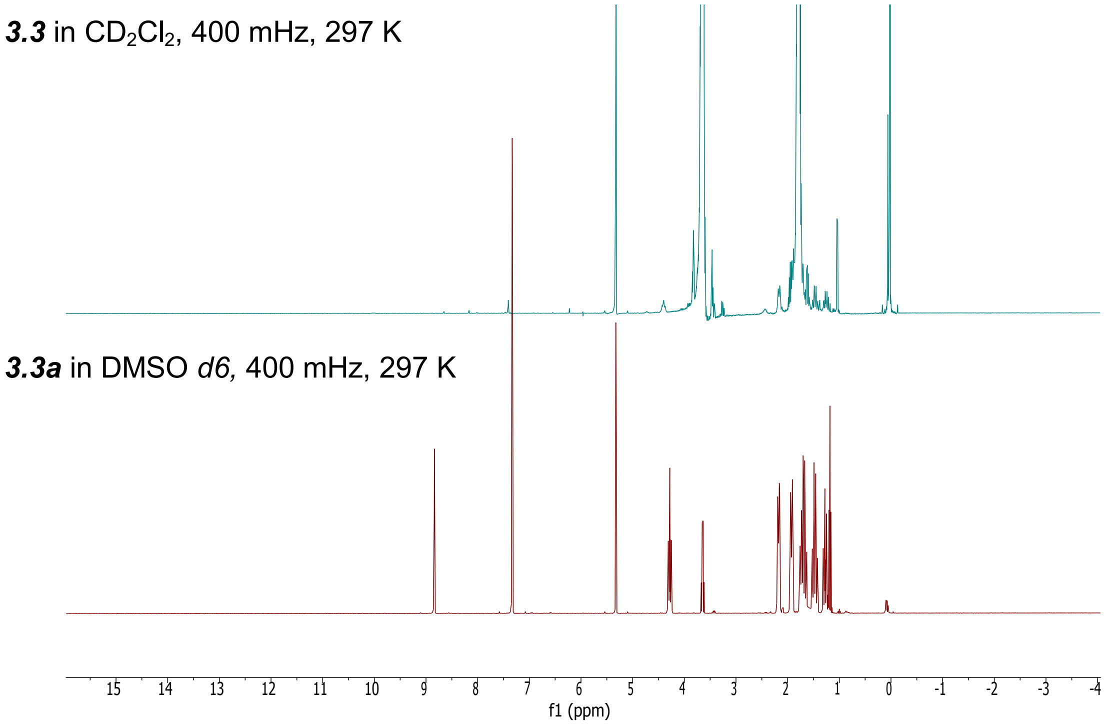
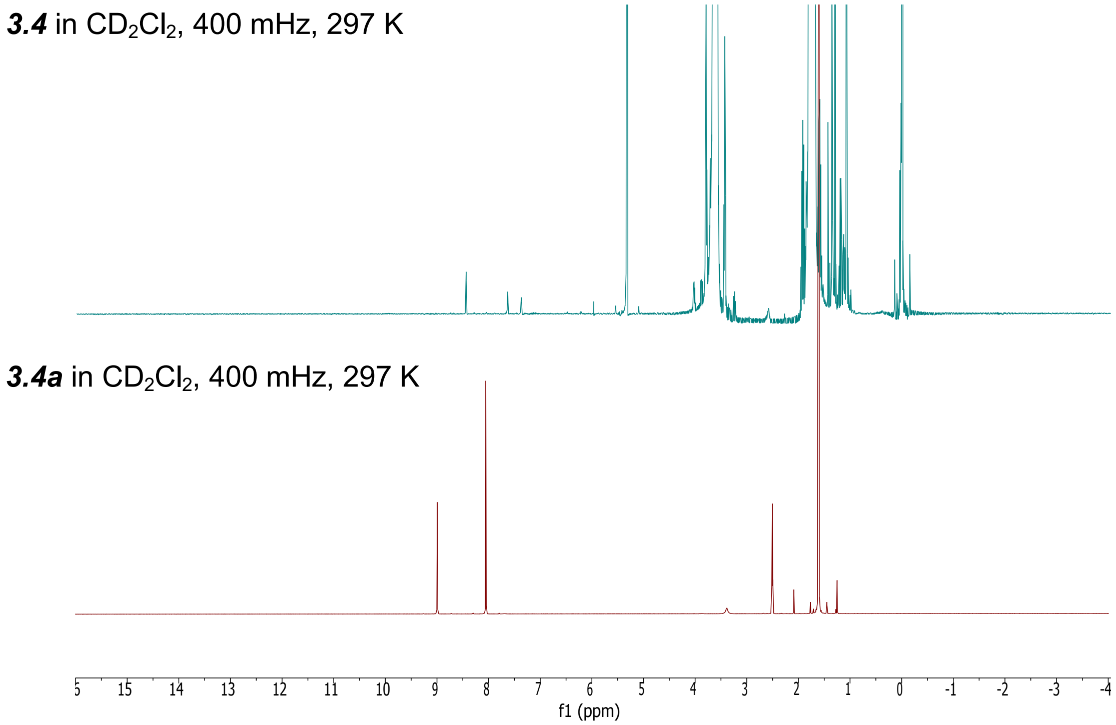


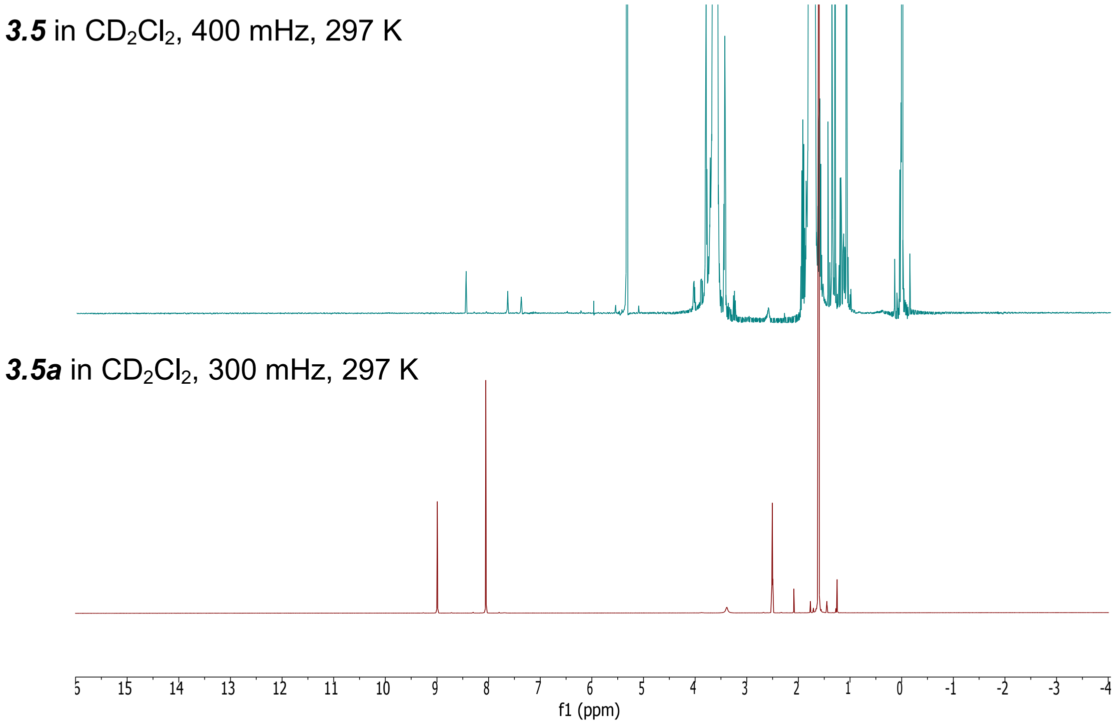
**Figure A3-3: $^1$H-NMR of pure 3.3a and 3.3 (stock solution). The missing signal at 8.99 ppm in 3.3 is evidence for the success of the deprotonation.**



***3.4*** in $CD_2Cl_2$, 400 mHz, 297 K

***3.4a*** in $CD_2Cl_2$, 400 mHz, 297 K

**Figure A3-4: $^1$H-NMR of pure 3.4a and 3.4 (stock solution). The missing signal at 8.83 ppm in 3.4 is evidence for the success of the deprotonation.**



***3.5*** in $CD_2Cl_2$, 400 mHz, 297 K

***3.5a*** in $CD_2Cl_2$, 300 mHz, 297 K

**Figure A3-5: $^1$H-NMR of pure 3.5a and 3.5 (stock solution). The missing signal at 8.57 ppm in 3.5 is evidence for the success of the deprotonation.**

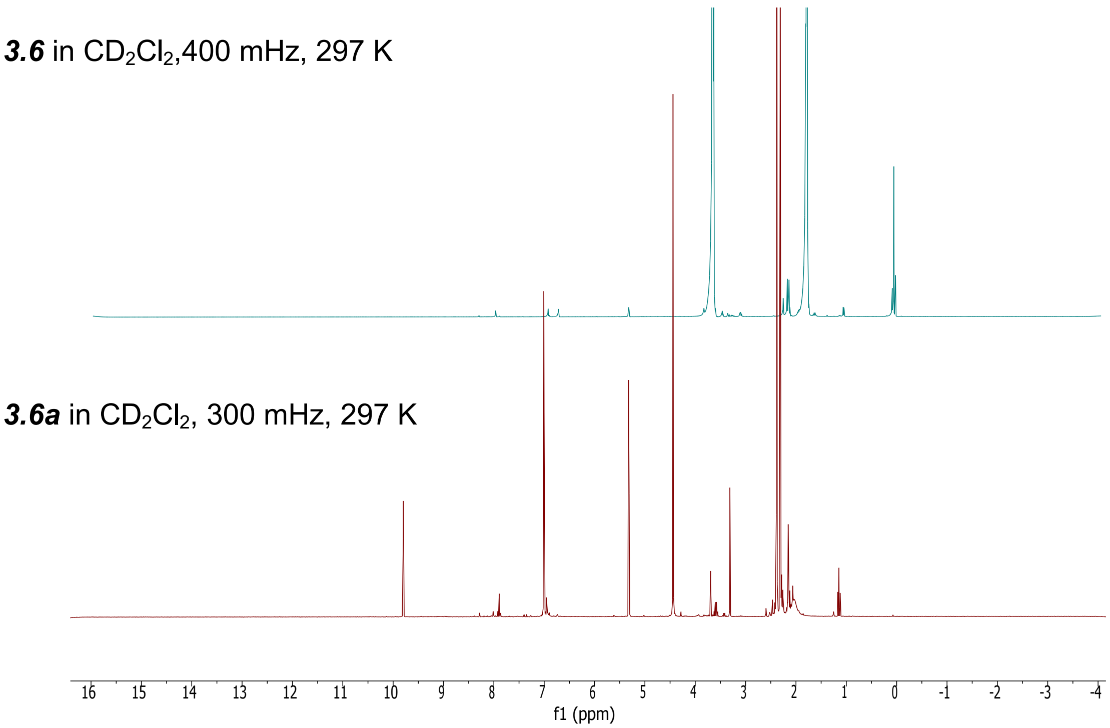


**Figure A3-6: $^1$H-NMR of pure 3.6a and 3.6 (stock solution). The missing signal at 9.79 ppm in 3.6 is evidence for the success of the deprotonation.**

### A3.1.4.2 Polymerization experiments

Into an oven-dried, argon flushed 50 mL-two-neck round bottomed flask equipped with a reflux condenser and septum D4 and NHC-solution are submitted. Alcohol and solvent are added and the reaction mixture is heated to the desired oil bath temperature. After 24 h reaction is stopped. Screened parameters are summarized in Table A3-1.

**Table A3-1: Summary of screened reaction parameters for ROP of $D_4$ utilizing NHC initiators. All experiments were performed twice.**

| Reaction | Initiator | | Substrate | | Co-initiator | | T | Solvent | |
|---|---|---|---|---|---|---|---|---|---|
| | | n [mmol] | | n [mmol] | | n [mmol] | [°C] | | V [mL] |
| P3.1 | **3.1** | 0.034 | $D_4$ | 32 | MeOH | 0.034 | 50 | - | - |
| P3.2 | **3.1** | 0.034 | $D_4$ | 32 | BnOH | 0.034 | 80 | - | - |
| P3.3 | **3.1** | 0.034 | $D_4$ | 32 | - | - | 80 | Tol | 30 |
| P3.4 | **-** | - | $D_4$ | 32 | BnOH | 0.034 | 80 | Tol | 30 |
| P3.5 | **3.1** | 0.034 | $D_4$ | 32 | MeOH | 0.034 | 50 | Tol | 10 |
| P3.6 | **3.1** | 0.034 | $D_4$ | 32 | MeOH | 0.034 | 50 | Tol | 30 |
| P3.7 | **3.1** | 0.034 | $D_4$ | 32 | BnOH | 0.034 | 80 | Tol | 10 |
| P3.8 | **3.1** | 0.034 | $D_4$ | 32 | BnOH | 0.034 | 80 | Tol | 30 |
| P3.9 | **3.1** | 0.034 | $D_4$ | 32 | BnOH | 0.034 | 80 | THF | 30 |
| P3.10 | **3.1** | 0.034 | $D_4$ | 32 | MeOH | 2.37 | 50 | - | - |
| P3.11 | **3.1** | 0.034 | $D_4$ | 32 | MeOH | 1.7 | 50 | Tol | 30 |
| P3.12 | **3.1** | 0.034 | $D_4$ | 32 | MeOH | 3.4 | 50 | Tol | 30 |
| P3.13 | **3.1** | 0.034 | $D_4$ | 32 | BnOH | 2.38 | 80 | - | - |
| P3.14 | **3.1** | 0.034 | $D_4$ | 32 | BnOH | 1.7 | 80 | Tol | 30 |
| P3.15 | **3.1** | 0.034 | $D_4$ | 32 | BnOH | 3.4 | 80 | Tol | 30 |
| P3.16 | **3.1** | 0.034 | $D_4$ | 32 | MeOH | 0.034 | 22 | - | - |
| P3.17 | **3.1** | 0.034 | $D_4$ | 32 | MeOH | 0.034 | 22 | Tol | 30 |
| P3.18 | **3.1** | 0.034 | $D_4$ | 32 | MeOH | 1.7 | 24 | Tol | 30 |
| P3.19 | **3.1** | 0.034 | $D_4$ | 32 | MeOH | 2.38 | 22 | - | - |
| P3.20 | **3.1** | 0.034 | $D_4$ | 32 | MeOH | 1.7 | 100 | Tol | 30 |
| P3.21 | **3.1** | 0.034 | $D_4$ | 32 | BnOH | 0.034 | 23 | - | - |
| P3.22 | **3.1** | 0.034 | $D_4$ | 32 | BnOH | 0.034 | 23 | Tol | 30 |
| P3.23 | **3.1** | 0.034 | $D_4$ | 32 | BnOH | 1.7 | 24 | Tol | 30 |
| P3.24 | **3.1** | 0,034 | $D_4$ | 32 | BnOH | 2.38 | 22 | - | - |
| P3.25 | **3.1** | 0.034 | $D_4$ | 32 | BnOH | 1.7 | 120 | Tol | 30 |
| P3.26 | **3.1** | 0.17 | $D_4$ | 160 | BnOH | 8.5 | 80 | Tol | 150 |
| P3.27 | **3.2** | 0.034 | $D_4$ | 32 | BnOH | 1.7 | 80 | Tol | 30 |
| P3.28 | **3.3** | 0.034 | $D_4$ | 32 | BnOH | 1.7 | 80 | Tol | 30 |
| P3.29 | **3.4** | 0.034 | $D_4$ | 32 | BnOH | 1.7 | 80 | Tol | 30 |
| P3.30 | **3.5** | 0.034 | $D_4$ | 32 | BnOH | 1.7 | 80 | Tol | 30 |
| P3.31 | **3.6** | 0.034 | $D_4$ | 32 | BnOH | 1.7 | 80 | Tol | 30 |

For polymerization ***P3.1***, ***P3.2***, ***P3.28*** and ***P3.29*** GPC samples were taken subsequently during course of reaction. For sample preparation sample is transferred into a vial and is diluted with toluene to concentration of 1 mg/mL.

The results for ***P3.28*** using **3.4** as initiator and ***P3.29*** using **3.5** as inititator are presented in following Chart A3-1.

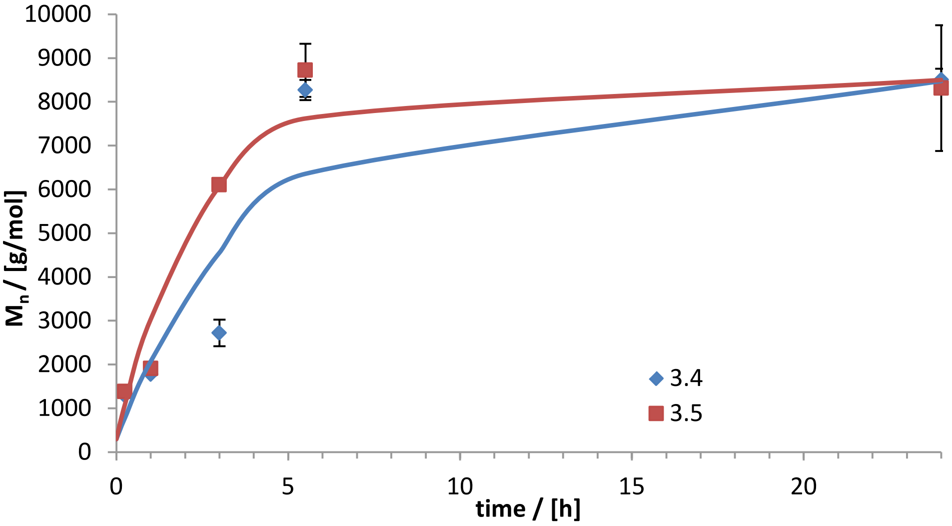


**Chart A3-1: Polymerization experiments using 0.1 mol% of 3.4 and 3.5 respectively and 5 mol% benzyl alcohol related to the amount of $D_4$. Experiments were carried out under inert, moisture free conditions at 80 °C oil bath temperature. Molecular weight determined by GPC using PDMS standards and toluene as eluent.**

## A3.2 Amines, amidines, guanidines

### A3.2.1 Screening of solvents

In general the polymerization experiments are carried out under inert gas in a moisture free atmosphere. First resublimed TBD (1.35 mmol) and dry methanol (1.35 mmol) are submitted into an argon flushed, flame-dried three neck flask quipped with reflux condenser, mechanical stirrer and a septum. They are dissolved in dry solvent (30 mL). After this $D_4$ (67.43 mmol), which was dried over molecular sieves, is added. The reaction is stirred with a mechanical or a magnetic stirrer at 65 °C oil bath temperature. The reaction is stopped after 24 h by removing the heat source. After cooling down to room temperature phases are separated. The polymer phase is washed with methanol. If the high viscosity of the product is too high it is dissolved in toluene. The polymer is dried in high vacuum (<1*10-3 mbar) at 80 °C.

Polymerization was performed without solvent, with toluene, tetrahydrofuran and acetonitrile.

### A3.2.2 Characterization of mechanical stabilized emulsion

To determine the dispersed and the continuous phase of the emulsion, the conductivity-method was applied and therefore conductivity of both phases alone and the resulting emulsion were tested (results shown in Table 5). For conductivity measurements a Knick Portamess 913 was used. Results are summarized in Table A3-2.

**Table A3-2: Conductivity measurements to determine dispersed and continuous phase of the emulsion.**

| | κ [µS] |
|---|---|
| acetonitrile (analytic grade) | 0.3 |
| $D_4$ (dry) | 0.0 |
| acetonitrile + 1 mL $H_2O$ (tap water) | 2.3 |
| emulsion: 120 mL acetonitrile + 84 mL $D_4$ (480 rpm) | 0.2 |
| emulsion: 120 mL acetonitrile + 1mL $H_2O$ (tap water) + 84 mL D4 (480 rpm) | 1.0 |

### A3.2.3 Recycling experiments

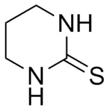
All polymerization are experiments are carried out under inert gas in a moisture free atmosphere at room temperature.

Initial Experiment **P3.32**: TBD and methanol are submitted into an argon-flushed, oven-dried three neck flask equipped with reflux condenser, mechanical stirrer and a septum. They are dissolved in dry acetonitrile (1.5 times the volume of $D_4$). While stirring (250 rpm) $D_4$, which was dried over molecular sieves, is added. Reaction is started by dipping into preheated oil bath (65 °C oil bath temperature). The reaction is stopped after 24 h by removing the heat source. After cooling down to room temperature phases are separated. The polymer phase is washed with methanol. The polymer is dried in high vacuum (<1*10-3 mbar) at 80 °C.

Recycling Experiment **P3.32a**: The solvent phase of **P32** is submitted into an argon-flushed, oven-dried three neck flask equipped with reflux condenser, mechanical stirrer and a septum. Methanol and $D_4$ are added while stirring at 250 rpm. Reaction is started by dipping into preheated oil bath (65 °C oil bath temperature). The reaction is stopped after 24 h by removing the heat source. After cooling down to room temperature phases are separated. The polymer phase is washed with methanol. The solvent phase of **P3.32a** is reused for recycling experiment **P3.32b.**

Recycling Experiment **P3.32b** – **P3.32e** are conducted as described for recycling experiment **P3.32a** by using the solvent phase of the previous experiment.

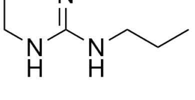
### A3.2.4 Synthesis of tetrahydro-2(1*H*)-pyrimidinethione (3.13a)[5-6]



1,3-Diaminopropane (0.015 mol), Ethanol (5 mL) and $H_2O$ (4 mL) were submitted into a two neck flask. The mixture was cooled down to 0 °C and $CS_2$ (0.014 mol) were added dropwise at this temperature. The biphasic mixture was heated to 100 °C oil bath temperature. During heating to 100 °C the two phases dissolved. The reaction mixture changed color to yellow and a white solid precipitated. After 18.5 h the reaction was stopped. While cooling down to room temperature the product crystallized. After cooling 1 h at 0 °C the product was filtered off and washed with 5 mL of diethyl ether. 1.039 g (63.89 %) of a white crystalline product are afforded.

**GC/MS** (EI, m/z (fragment, calculated))), 116 ($C_4H_8N_2S^+$, 116.04), 72 ($CS^+$, 59.99), 72 ($C_3H_8N_2^+$, 72.07), 44 ($CS^+$, 43.97).**$^1$H NMR** (300 MHz, $CDCl_3$, 297 K) [ppm] $\delta$ = 1.94 (p, $^1J_{H\text{-}H}$ = 5.9Hz, $^3J_{H\text{-}H}$ =11.8 Hz, 2H, –NH–CH$_2$–C$\underline{\mathit{H}_2}$–); 3.39 – 3.22 (m, 4H, –NH–C$\underline{\mathit{H}_2}$–CH$_2$); 6.76 (s, 2H, –N$\underline{\mathit{H}}$–CH$_2$–CH$_2$–).**$^{13}$C NMR** (75 MHz, $CDCl_3$, 297 K) [ppm] $\delta$ = 19.43 (–NH–$\underline{\mathit{C}}$H$_2$–CH$_2$–); 40.77 (–NH–CH$_2$–$\underline{\mathit{C}}$H$_2$–); 177.13 (–NH–$\underline{\mathit{C}}$S–NH–). **IR (ATR):** $\nu$ (cm$^{-1}$) 3157.16 (s), 3089.81 (s), 2996.92 (w) 2954.80 (m), 2943.03 (m), 2855.78 (m), 2759.69 (w), 2657.68 (m), 2525.62 (w), 1549.82 (s), 1477.90 (w), 1457.76 (w), 1427.16 (s), 1358.37 (s), 1312.56 (s), 1283.98 (w), 1233.68 (m), 1200.09 (w), 1191.18 (s), 1122.19 (w), 1089.23 (w), 1064.99 (s), 983.36 (w), 969,89 (m), 946.07 (m), 883.49 (w), 862.75 (w), 811.71 (s), 762.18 (s), 641.81 (s), 565.46 (s), 514.13 (s), 410.59 (s). **MP** (°C, (theoretical)) = 210.3 – 211.5 °C (210 – 212 °C).

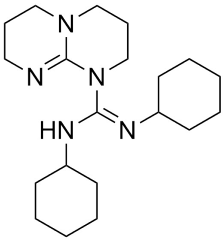
### A3.2.5 Synthesis of 1,4,5,6-tetrahydro-N-propyl-2-pyrimidinamine(3.13)[5-6]



***3.13a*** (6.64 mmol) and ethanol are submitted into a flame-dried, argon-flushed three neck flask equipped cooling condenser and a septum. Iodomethane (6.68 mmol) is added dropwise. Reaction mixture is heated to reflux temperature. While heating up ***3.13a*** dissolves and a clear and colorless mixture is obtained. After 1 h of refluxing reaction mixture changed to a yellow color and 1-aminopropane (6.52 mmol) is added dropwise. The color of the reaction mixture immediately changes from yellow to colorless. The reaction mixture is refluxed further overnight. KOH (6.46 mmol) is added carefully and the mixture is refluxed for another 60 min. White solid (KI) precipitates. The reaction is stopped and the reaction mixture is allowed to cool down to room temperature. The white solid is filtered off and washed with 2 mL of Ethanol. The organic phases are combined and the solvent is remove in high vacuum first at room temperature and then at 40 °C. A white solid formats. Yield: 1.049 g (115 %, traces of solvent lead to yield higher than 100%).

**GC/MS** (EI, m/z (fragment, calculated)): 141 ($C_7H_{15}N_3^+$, 141.13), 126 ($C_6H_{12}N_3^+$, 126.10), 112 ($C_5H_{10}N_3^+$, 112.09). **$^1$H-NMR** (400 MHz, $CD_2Cl_2$, 297 K, ppm) δ = 0.87 (t, $^1J_{H\text{-}H}$ = 7.4 Hz, 3H, $=N–CH_2–CH_2–C\underline{H}_3$); 1.48 (h, $^1J_{H\text{-}H}$ = 7.08 Hz, $^3J_{H\text{-}H}$ = 14.48 Hz, 2H, $=NH–CH_2–C\underline{H}_2–CH_3$); 1.70 – 1.79 (m, 2H, $–NH–CH_2–C\underline{H}_2–$); 3.01 (t, $^1J_{H\text{-}H}$ = 7.1 Hz, 2H, $=N–C\underline{H}_2–CH_2–CH_3$); 3.21 (t, $^1J_{H\text{-}H}$ = 5.9 Hz, 2H, $–NH–C\underline{H}_2–CH_2–$) .**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 297 K, ppm) δ = 11.86 $=N–CH_2–CH_2–\underline{C}H_3$); 21.62 ($–NH–CH_2–\underline{C}H_2–$); 23.19 ($=NH–CH_2–\underline{C}H_2–CH_3$); 40.16 ($–NH–\underline{C}H_2–CH_2–$); 43.19 ($=NH–\underline{C}H_2–CH_2–CH_3$); 153.78 (($–NH–\underline{C}(=N–C\underline{H}_2–CH_2–CH_3)–NH–$).

### A3.2.6 Synthesis of *N*,*N*'-dicyclohexyl-3,4,7,8-tetrahydro-2*H*-pyrimido[1,2-*a*]pyrimidine-1(6*H*)-carboximidamide (3.17)[7-8]



Into an oven-dried, argon-flushed flask 0.66 g TBD of (4.76 mmol) and 0.93 g of DCC (4.52 mmol) were submitted. When heated to 125 °C oil bath temperature a slightly yellow reaction mixture was formed. After 24 h the reaction was stopped. The dark brown reaction mixture was distilled at 75 – 80 °C. The product was afforded as a colorless, high viscous liquid (0.854 g; 54.7 %). After some days the product started to crystallize.

**GC/MS** (EI, m/z (fragment, calculated)): 207 ($C1_3H_{23}N_2$, 207.19), 136 ($C_9H_{14}N_2^+$, 136.11), 124 ($C_7H_{12}N_2^+$, 124.10), 83 ($C_6H_{11}^+$, 83.09).**$^1$H-NMR** (300 MHz, $CDCl_3$, 297 K, ppm) δ = 2.08 – 0.95 (m, 25H), 3.29 – 3.02 (m, 9H).**$^{13}$C-NMR** (75 MHz, $CDCl_3$, 297 K, ppm) δ = 21.23, 24.72, 24.48, 34.95, 38.65, 47.10, 55.77 139.82, 151.54. **MP** (°C, (theoretical)) = 68.8 – 69.7 °C (69 – 71 °C).

### A3.2.7 Screening of amines, amidines and guanidines

*Polymerization Procedure A*

In general the polymerization experiments are carried out under inert gas in a moisture free atmosphere. First co-initiator and methanol are submitted into an argon flushed, oven-dried three neck flask equipped with reflux condenser, mechanical stirrer and a septum. They are dissolved in dry acetonitrile (1.5 times the volume of $D_4$). While stirring (250 rpm) $D_4$, which was dried over molecular sieves, is added. Reaction is started by dipping into preheated oil bath (65 °C oil bath temperature). The reaction is stopped after 24 h by removing the heat source. After cooling down to room temperature phases are separated. If the high viscosity of the product is too high it is dissolved in toluene. The polymer phase is washed with methanol. The polymer is dried in high vacuum (<1*10-3 mbar) at 80 °C.

*Polymerization Procedure B*

In general the polymerization experiments are carried out under inert gas in a moisture free atmosphere. First co-initiator and methanol are submitted into an argon-flushed, oven-dried three neck flask equipped with reflux condenser, mechanical stirrer and a septum. They are dissolved in dry acetonitrile (1.5 times the volume of $D_4$). While stirring (250 rpm) $D_4$, which was dried over molecular sieves, is added. Reaction is started by dipping into preheated oil bath (65 °C oil bath temperature). The reaction is stopped after 24 h by removing the heat source. After cooling down to room temperature phases are separated. The polymer phase is washed with $H_2O$ and dried over $Na_2SO_4$. The polymer is stripped in high vacuum (<1*10-3 mbar) at 80 °C.

*Polymerization Procedure C*

In general the polymerization experiments are carried out under inert gas in a moisture free atmosphere. First co-initiator and methanol are submitted into an argon-flushed, oven-dried three neck flask quipped with reflux condenser, mechanical stirrer and a septum. They are dissolved in dry acetonitrile (1.5 times the volume of $D_4$). While stirring (250 rpm) $D_4$, which was dried over molecular sieves, is added. Reaction is started by dipping into preheated oil bath (65 °C oil bath temperature). The reaction is stopped after 24 h by removing the heat source. After cooling down to room temperature phases are separated. The polymer phase is washed with $H_2O$ and dried over $Na_2SO_4$. The polymer is stripped in high vacuum (<1*10-3 mbar) at 80 °C.

All experiments were performed twice. The reactions are summarized in Table A3-3.

**Table A3-3: Summary of screened reaction parameters for ROP of $D_4$ utilizing amines, amides and guanidines as coinitiators. All experiments were performed twice.**

| No | Coinitiator | n [mmol] | n ($D_4$) [mmol] | Acetonitrile V [mL] | ROH | n [mmol ] | Polymerization procedure |
|---|---|---|---|---|---|---|---|
| P3.33 | 3.7 | 1.35 | 67.43 | 30.0 | MeOH | 1.35 | A |
| P3.34 | 3.7 | 1.35 | 67.43 | 30.0 | MeOH | 134.85 | A |
| P3.35 | 3.7 | 1.35 | 67.43 | 30.0 | MeOH | 269.71 | A |
| P3.36 | 3.8 | 1.35 | 67.43 | 30.0 | MeOH | 134.85 | A |
| P3.37 | 3.8 | 1.35 | 67.43 | 30.0 | MeOH | 14.83 | A |
| P3.38 | 3.9 | 1.35 | 67.43 | 30.0 | MeOH | 134.85 | B |
| P3.39 | 3.10 | 0.34 | 16.86 | 7.5 | MeOH | 33.71 | B |
| P3.40 | 3.11 | 0.34 | 16.86 | 7.5 | MeOH | 0.34 | A |
| P3.41 | 3.12 | 1.35 | 67.43 | 30.0 | MeOH | 134.85 | B |
| P3.42 | 3.12 | 1.35 | 67.43 | 30.0 | $H_2O$ | 134.85 | C |
| P3.43 | 3.13 | 1.35 | 67.43 | 30.0 | MeOH | 134.85 | A |
| P3.44 | 3.14 | 1.35 | 67.43 | 30.0 | MeOH | 134.85 | A |
| P3.45 | 3.15 | 0.67 | 33.71 | 15.0 | MeOH | 134.85 | A |
| P3.46 | 3.16 | 1.35 | 67.43 | 30.0 | MeOH | 134.85 | A |
| P3.47 | 3.17 | 0.34 | 16.86 | 7.5 | MeOH | 134.85 | A |
| P3.48 | 3.18 | 1.35 | 67.43 | 30.0 | MeOH | 134.85 | A |
| P3.49 | 3.19 | 0.67 | 33.71 | 15.0 | MeOH | 67.43 | A |

In the following figures Figure A3-7 to Figure A3-17 $^{29}$Si(IG)-NMR results are presented in order to assess whether only methoxydimethylsilyl end-groups or additionally hydroxydimethylsilyl end-groups are formed.

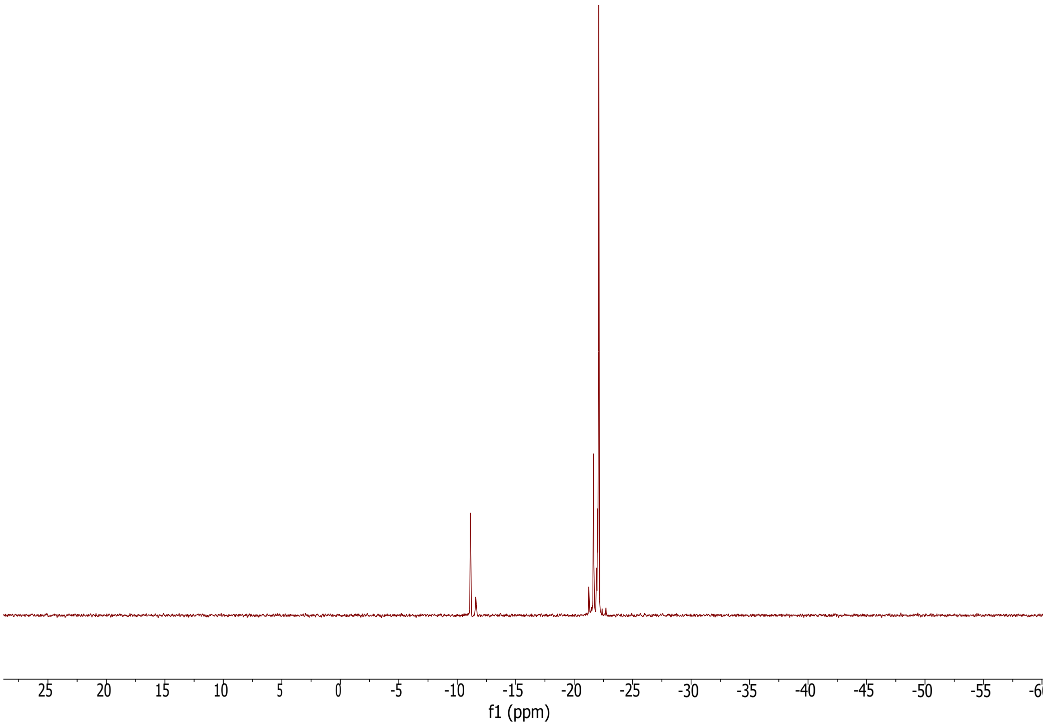


**Figure A3-7: $^{29}$Si(IG)-NMR of P3.34 (in CDCl$_3$, 59 mHz, 297 K).**

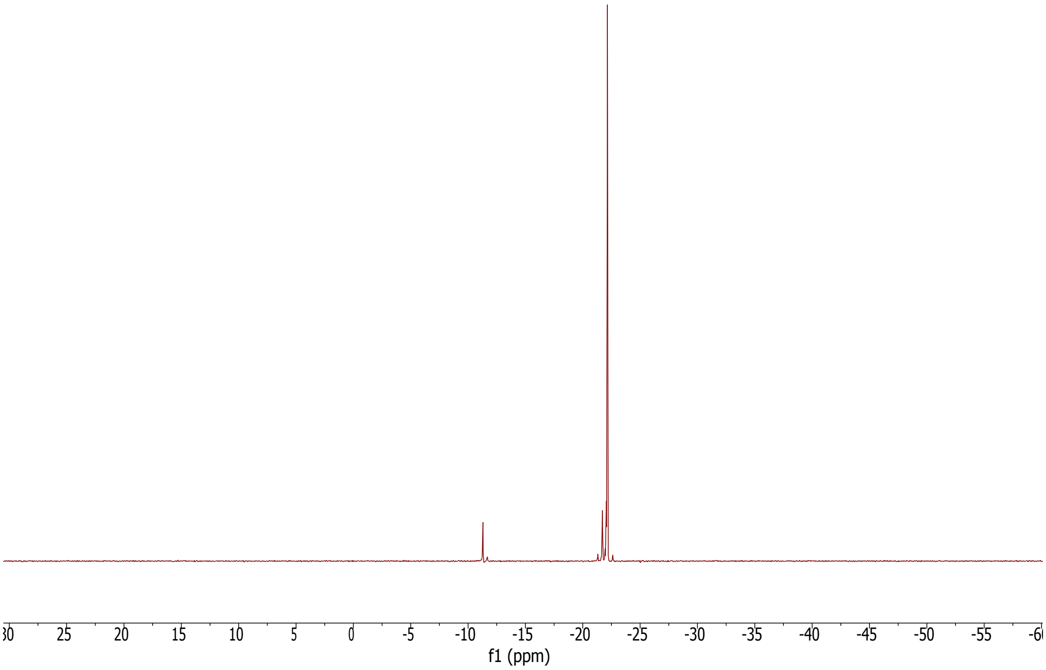


**Figure A3-8: $^{29}$Si(IG)-NMR of P3.36 (in CDCl$_3$, 80 mHz, 297 K).**

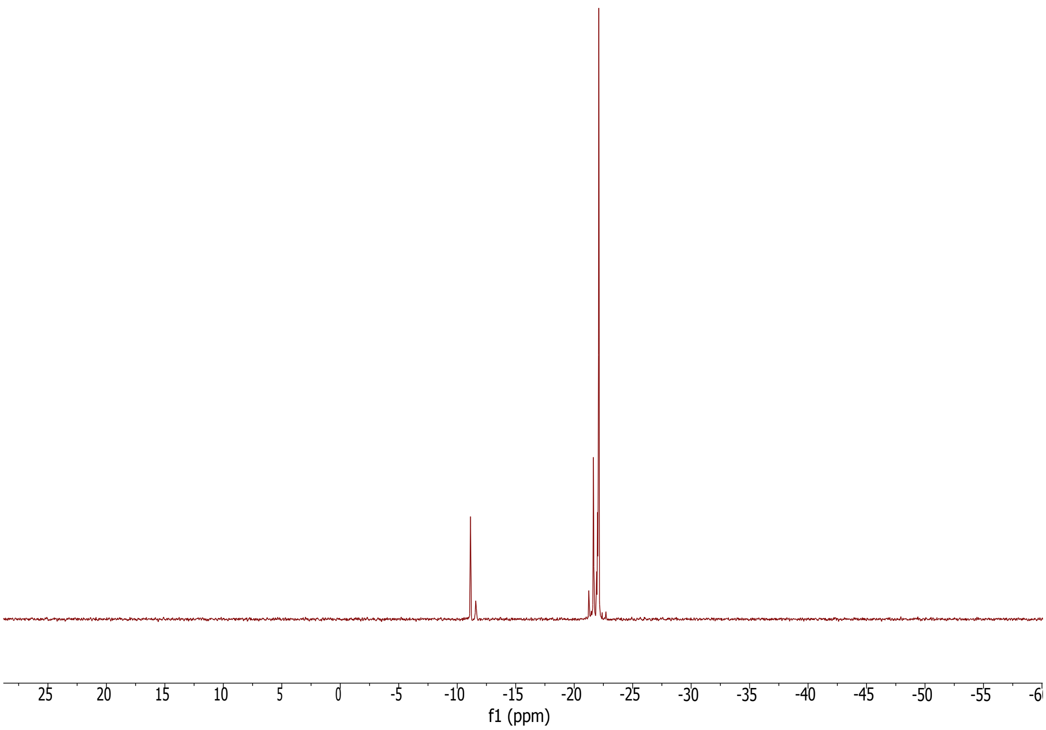


**Figure A3-9: $^{29}$Si(IG)-NMR of P3.38 (in CDCl$_3$, 59 mHz, 297 K).**

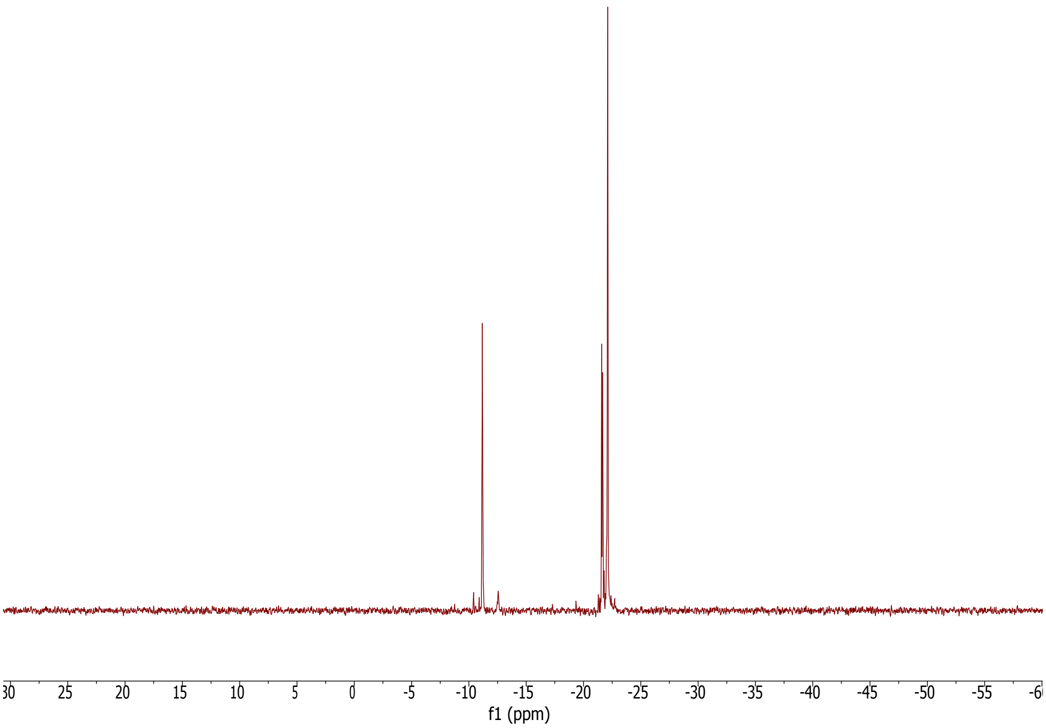


**Figure A3-10: $^{29}$Si(IG)-NMR of P3.39 (in CDCl$_3$, 59 mHz, 297 K).**

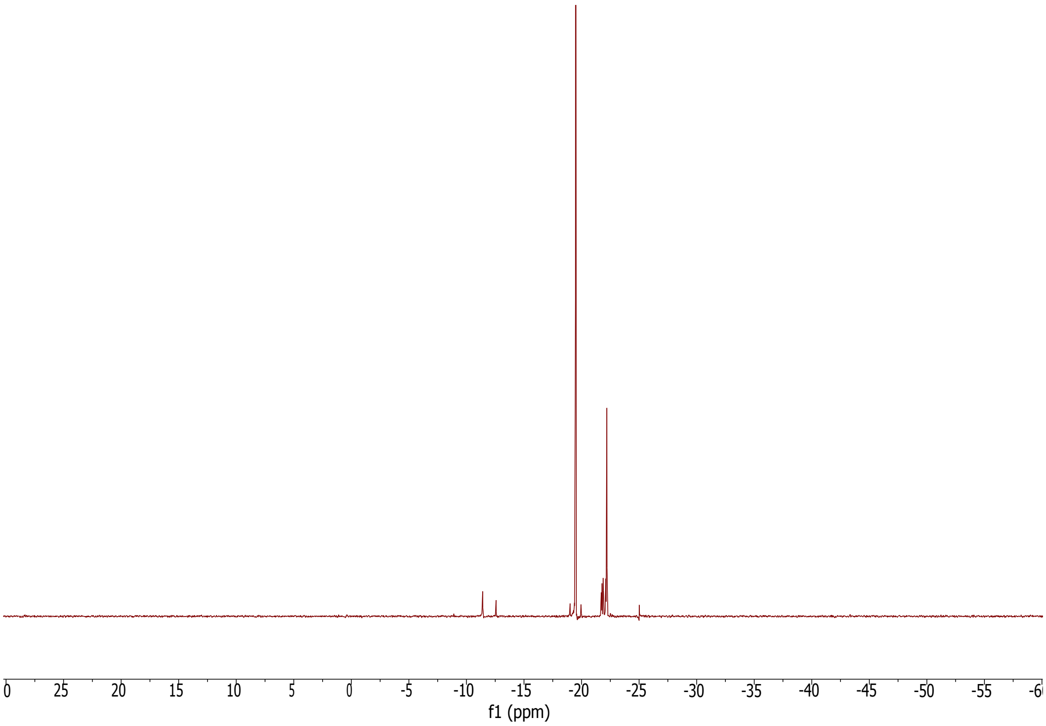


Figure A3-11: $^{29}$Si(IG)-NMR of P3.41 (in $CDCl_3$, 80 mHz, 297 K).

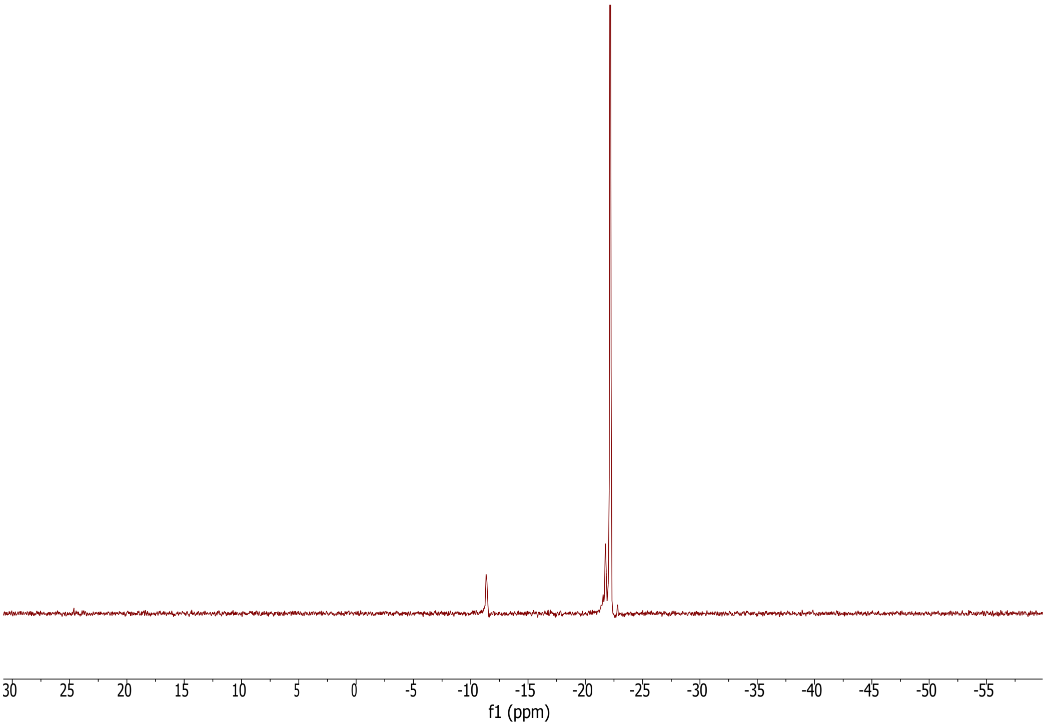


Figure A3-12: $^{29}$Si(IG)-NMR of P3.43 (in $CDCl_3$, 59 mHz, 297 K).

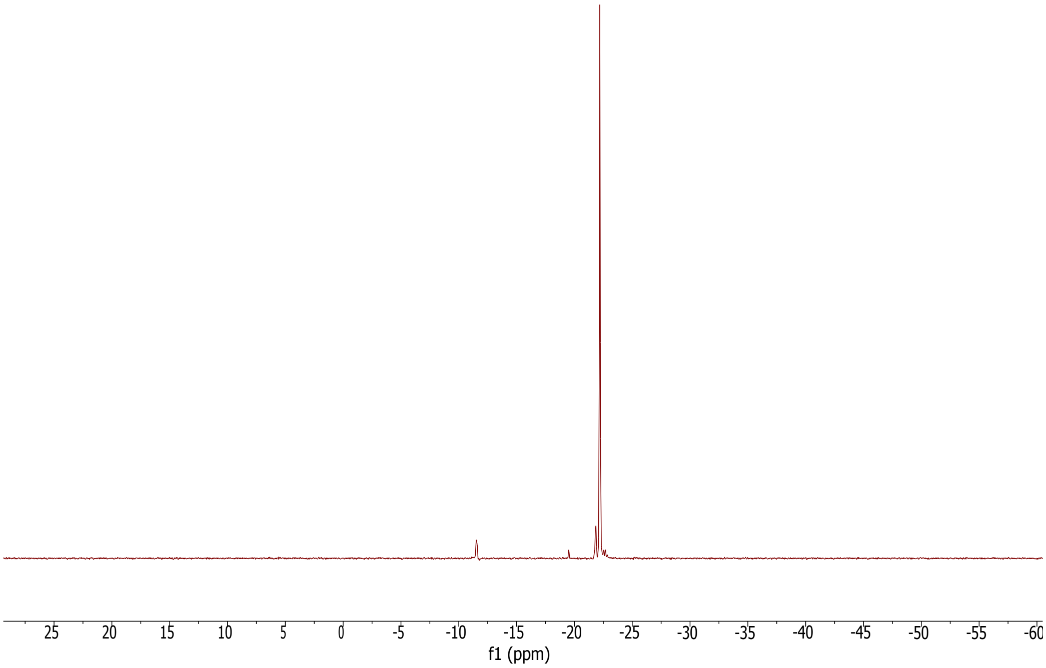


**Figure A3-13:** $^{29}$**Si(IG)-NMR of P3.44 (in CDCl$_3$, 80 mHz, 297 K).**

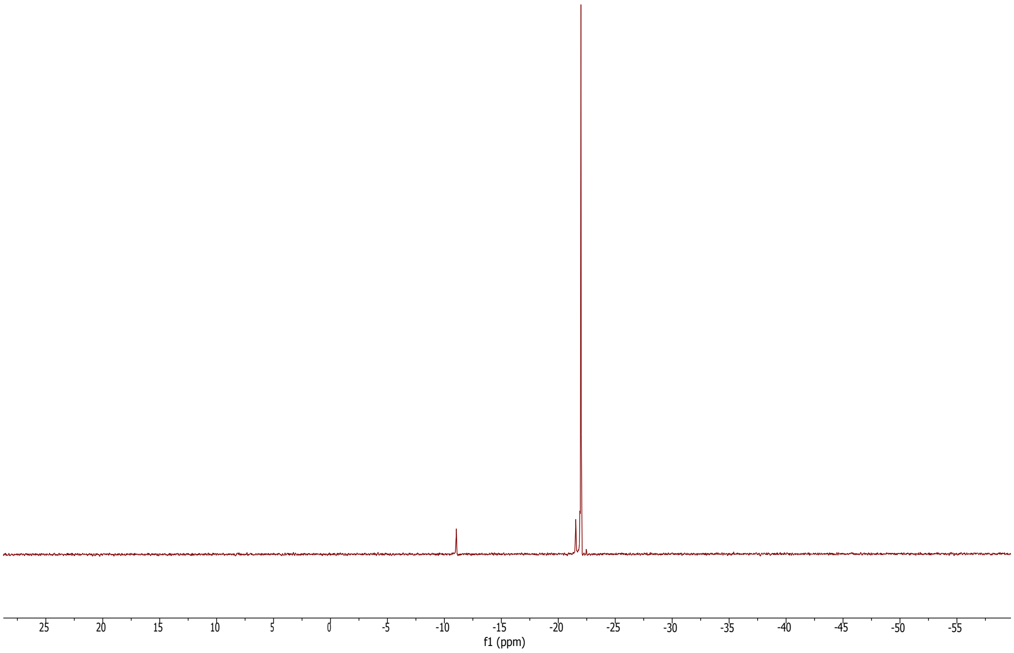


**Figure A3-14:** $^{29}$**Si(IG)-NMR of P3.45 (in CDCl$_3$, 80 mHz, 297 K).**

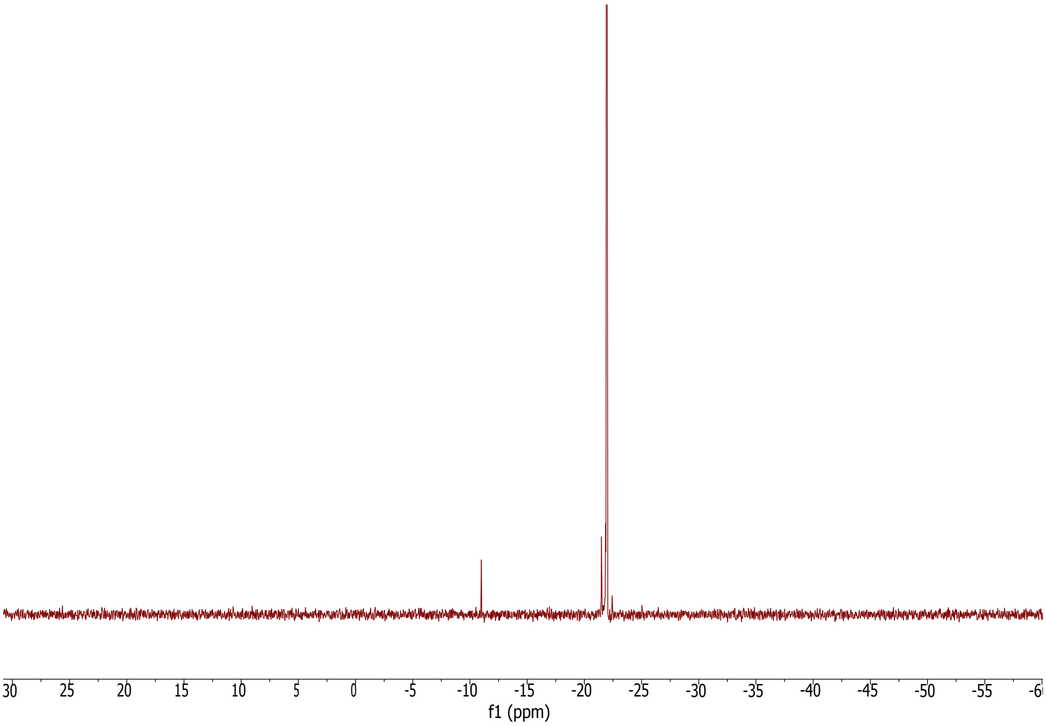


**Figure A3-15: $^{29}$Si(IG)-NMR of P3.47 (in $CDCl_3$, 80 mHz, 297 K).**

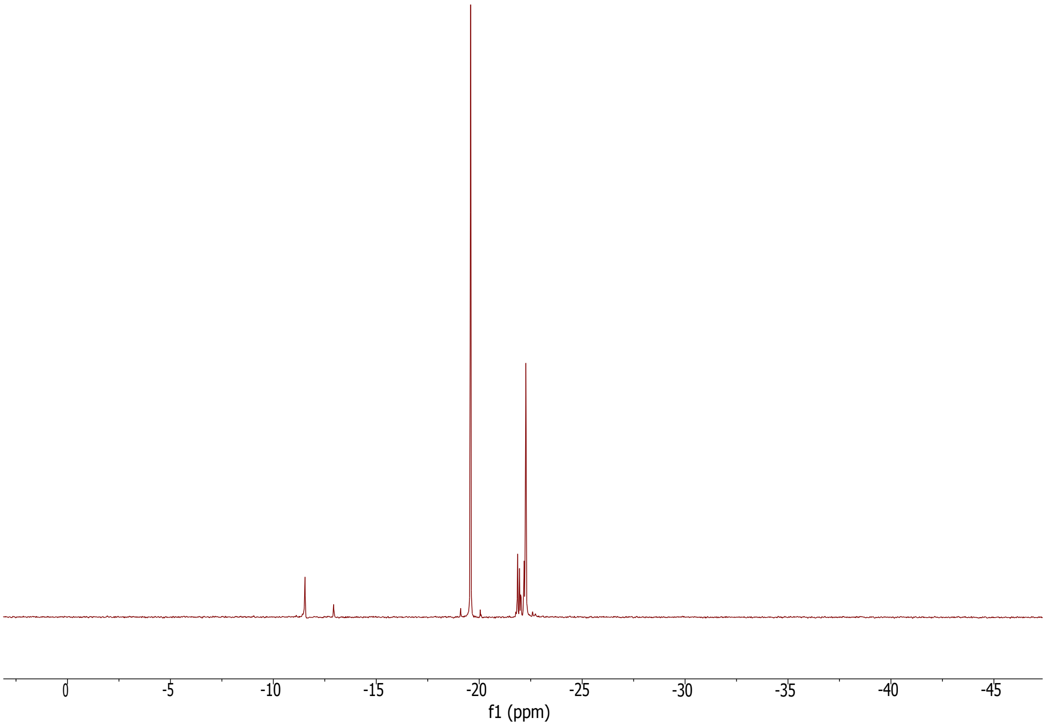


**Figure A3-16: $^{29}$Si(IG)-NMR of P3.48 (in $CDCl_3$, 80 mHz, 297 K).**

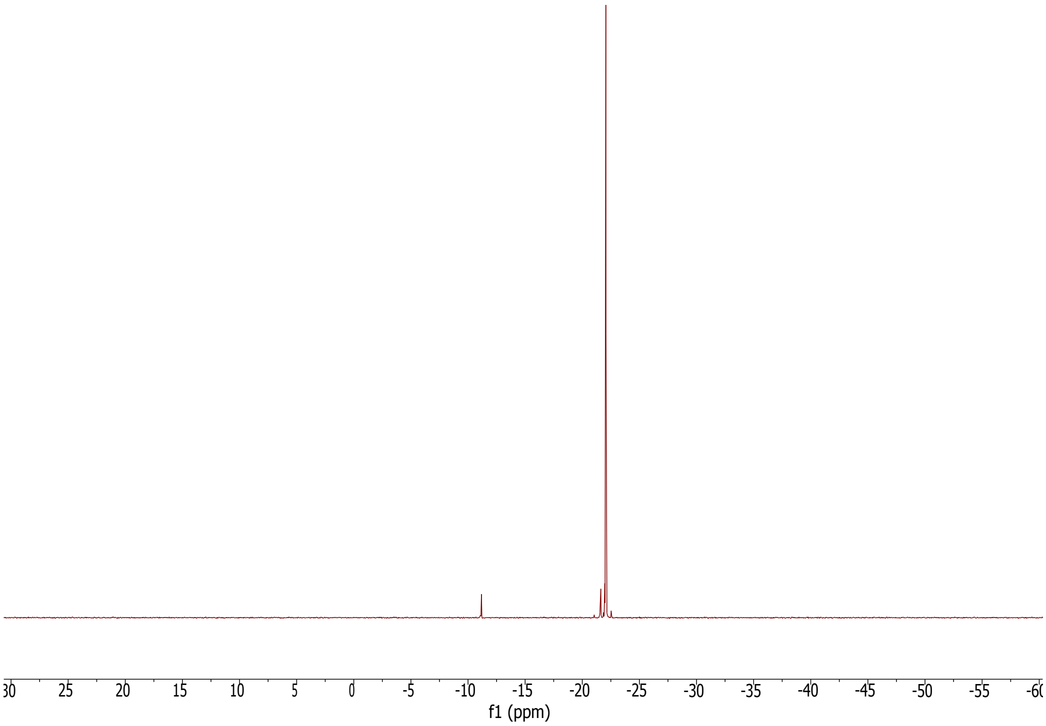


**Figure A3-17: $^{29}$Si(IG)-NMR of P3.49 (in $CDCl_3$, 80 mHz, 297 K).**

### A3.2.8 Time-resolved experiments

Polymerization reactions are conducted according to *Polymerization Procedure* A described in A3.2.7. Samples are taken subsequently during course of conversion for determination of molecular weight and conversion.

Sample preparation for samples taken throughout the reaction was done as follows: For GPC samples 0.5 mL of reaction mixture were transferred from the flask to into a vial and left to the side until phase separation took place. The solvent phase was removed and discarded. The polymer phase was then dissolved in toluene to a concentration of 1 mg/mL. For NMR samples 0.3 mL of reaction mixture are directly transferred from the flask into a NMR-tube and is dissolved in 0.3 mL of deuterated chloroform.

All experiments except P3.53 are performed twice. Reaction conditions are given in Table A3-4.Table A4-1

**Table A3-4: Summary of screened reaction parameters for ROP of $D_4$ utilizing amines, amides and guanidines as coinitiators. All experiments were performed twice.**

| No | Coinitiator | n [mmol] | n ($D_4$) [mmol] | Acetonitrile V [mL] | ROH | n [mmol ] |
|---|---|---|---|---|---|---|
| P3.50 | 3.7 | 1.35 | 67.43 | 30.0 | MeOH | 1.35 |
| P3.51 | 3.8 | 1.35 | 67.43 | 30.0 | MeOH | 134.85 |
| P3.52 | 3.14 | 1.35 | 67.43 | 30.0 | MeOH | 134.85 |
| P3.53 | 3.17 | 0.67 | 33.71 | 15.0 | MeOH | 67.43 |
| P3.54 | 3.19 | 0.67 | 33.71 | 15.0 | MeOH | 67.43 |

# A4 Appendix to Chapter 4

## A4.1 General reaction mechanism

### A4.1.1 Time resolved experiment P4.1

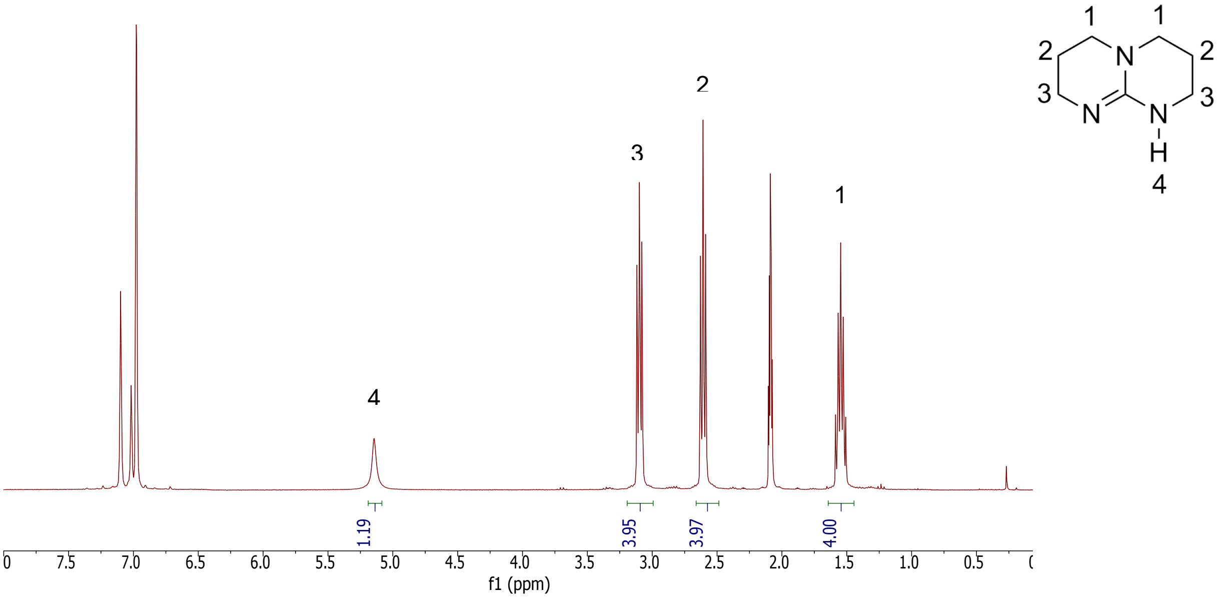
Polymerization is carried out under inert gas in a moisture free atmosphere. First TBD (1.35 mmol) and methanol (1.35 mmol) are submitted into an argon-flushed, oven-dried two neck flask equipped with reflux condenser, mechanical stirrer and a septum. While stirring (250 rpm) $D_4$ (67.43 mmol), which was dried over molecular sieves, is added. 0.2 mL of the mixture are taken and transferred into a oven-dried, argon-flushed Young-NMR-tube and 0.3 mL of deuterated toluene are added. To reaction mixture in the flask dry toluene (30 mL) is added and reaction is started by dipping into preheated oil bath (65 °C). The reaction is stopped after 24 h by removing the heat source. After cooling down to room temperature phases are separated. The polymer phase is washed with methanol. The polymer is stripped in high vacuum (<1*10-3 mbar) at 80 °C.

The Young-NMR tube is put into NMR-device which is preheated to 65 °C and NMR experiments ($^{1}$H, $^{29}$Si (IG) are performed every 2 h.

Parallel to this measurements samples (0.2 mL) for GPC-measurements are taken from the reaction in the flask and quenched with 2-Iod-Benzoic acid. After filtrating the samples are diluted with toluene up to concentration of 1 mg/mL.

In Figure A4-1 $^{1}$H-NMR of TBD is compared to TBDH$^{+}$. Thereby, the presented $^{1}$H-spectrum in Figure A4-1b is the starting NMR spectrum of ***P4.1*** directly after mixing all reactants and transferring the sample to the NMR device.

a) $^1$H-NMR of TBD (in toluene *d8*, 300 mHz, 297 K)



b) $^1$H-NMR directly after starting ROP focussing on TBDH$^+$ (in toluene *d8*, 400 mHz, 362 K)

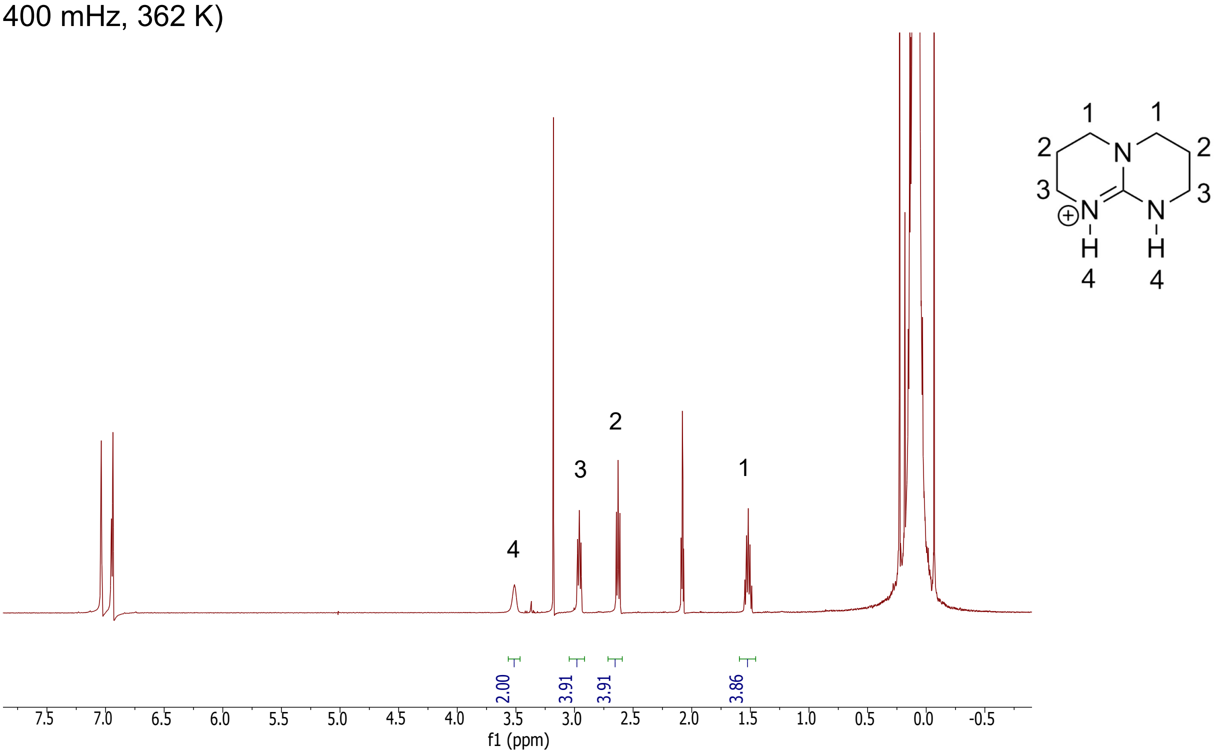


**Figure A4-1: Assignment of signals in $^1$H-NMR to a) TBD and b) TBDH$^+$.**

## A4.2 Analysis of terminating groups

### A4.2.1 Synthesis of homotelechelic α-, ω-di(methoxydimethylsilyl) PDMS (P4.2, P4.3 and P4.4)

According to _Polymerization Procedure A_ described in A3.2.7 polymerization reactions of P4.2, P4.3 and P4.4 are conducted using reaction parameters described in Table A4-1

**Table A4-1: Reaction parameters and characterization of the resulting polymers for end group analysis and as substrate for side reactions.**

| No | n (TBD) [mmol] | n ($D_4$) [mmol] | Acetonitrile V [mL] | n (MeOH) [mmol ] | Conversion [%] | $M_n$ [g/mol] | PDI |
|---|---|---|---|---|---|---|---|
| P4.2 | 135 | 674 | 350.0 | 270 | 90 | 3100 | 1.46 |
| P4.3 | 2.02 | 101.14 | 45.0 | 20.23 | 93 | 13900 | 1.64 |
| P4.4 | 2.02 | 101.14 | 45.0 | 404.56 | 94 | 4000 | 1.22 |

In Figure A4-2 HMBC spectrum ($^1H$, $^{29}Si$) is presented for P4.2:

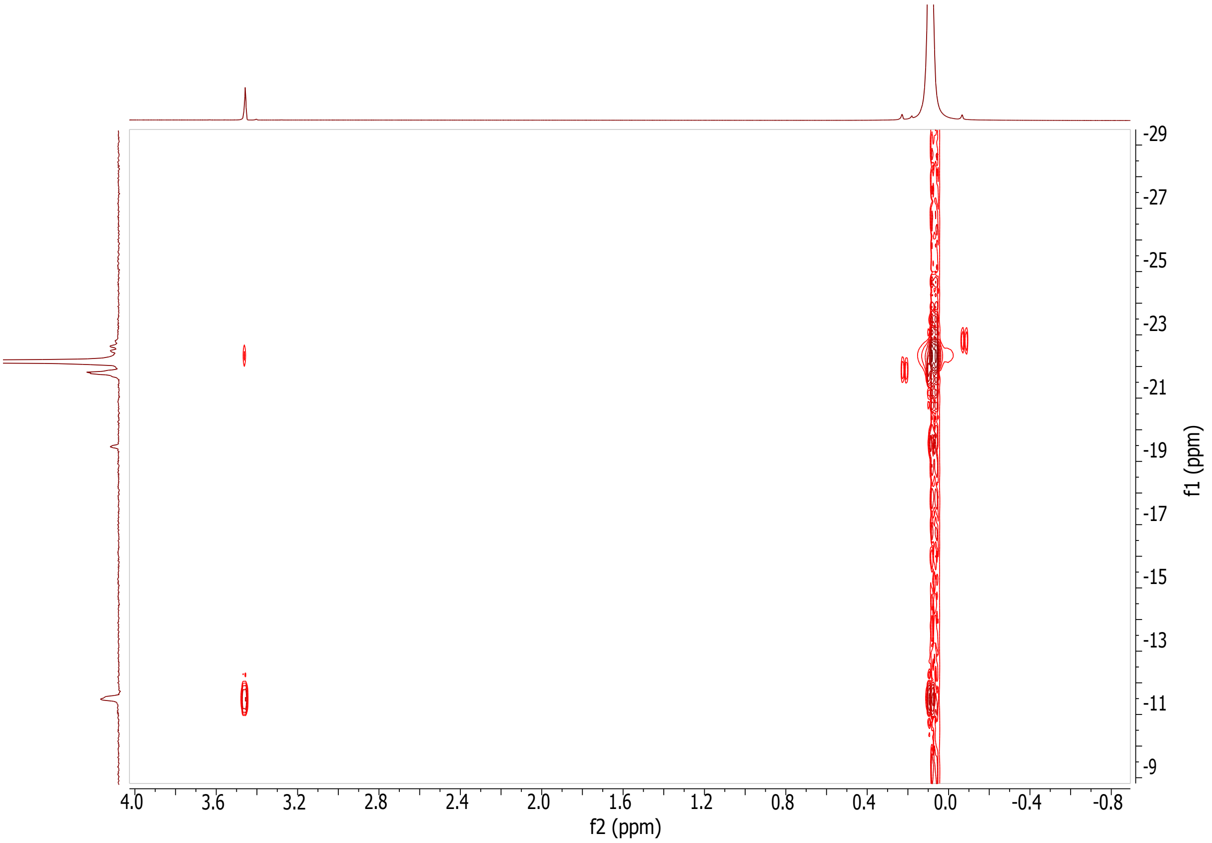


**Figure A4-2: HMBC spectrum ($^1H$, $^{29}Si$; 79.5 MHz in $CDCl_3$) of P4.2.**

MALDI-TOF results are presented in Figure A4-3.

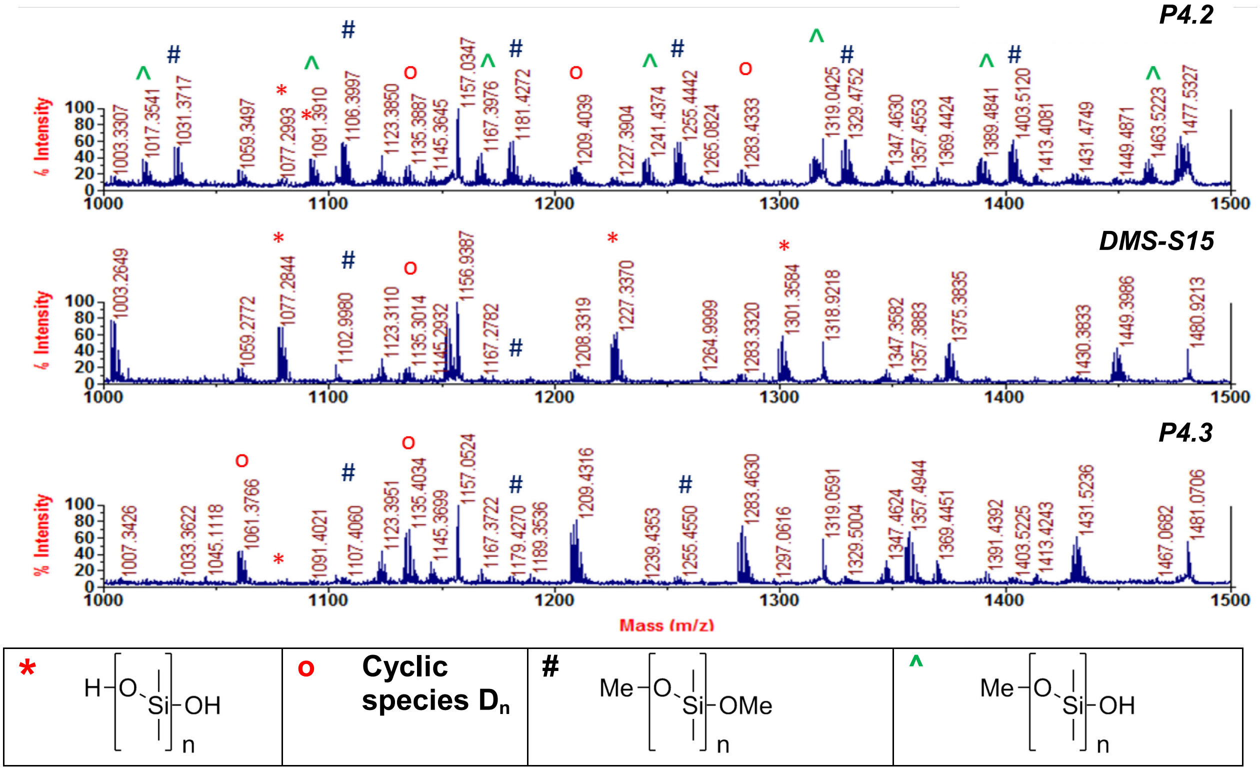


**Figure A4-3: MALDI-TOF results of polymers P4.2 and 4.3 for end-group analysis in comparison to a di(hydroxydimethylsilyl) PDMS (DMS-S15).***

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* MALDI-TOF measurements were performed by Dr. Dayong Sun.

## A4.3 Side reactions

### A4.3.1 Condensation and hydrolysis reactions

#### A4.3.1.1 Reactions with homotelechelic α-, ω-di(hydroxydimethylsilyl) PDMS

10 g of DMS-S15 (Si-OH terminated polymer of Gelest), TBD (1.44 mmol), the alcohol (for used alcohols and their amounts see Table A4-2) and 15 mL of acetonitrile are submitted into a flask equipped with a reflux condenser. Under vigorous stirring the biphasic reaction mixture is heated to 65 °C oil bath temperature by dipping into preheated oil bath. After 4 h reaction time the reaction is stopped and the acetonitrile layer is removed. The high viscous polymer phase is dissolved 35 mL of toluene. The polymer solution is then washed with all in all 250 mL of water. Phases are separated and the polymer phase is dried over $Na_2SO_4$. After filtration toluene is removed via rotary evaporation.

Used alcohols are presented in Table A4-2:

**Table A4-2: Tested alcohols in reactions with homotelechelic α-,ω-di(hydroxydimethylsilyl) PDMS.**

| No | ROH | n(ROH) [mmol] |
|---|---|---|
| P4.5 | --- | --- |
| P4.6 | --- | --- |
| P4.7 | Methanol | 12.12 |
| P4.8 | Methanol | 287.36 |
| P4.9 | 2-Octyldodecanol | 12.12 |

#### A4.3.1.2 Reactions with homotelechelic α-, ω-di(methoxydimethylsilyl) PDMS (P4.10)

10 g of **P4.4** (c.f. A4.2.1), TBD (0.06 mmol), $H_2O$ (12.12 mmol) and 15 mL of acetonitrile are submitted into a round bottomed flask equipped with a reflux condenser. Reaction is started by dipping into preheated oil bath ($T_{Oil}$ = 65 °C). After 4 h a first sample (***P4.10.1***) is taken and analyzed via GPC and NMR. After 24 h the reaction is stopped. The reaction mixture is allowed to cool down to room temperature and phases are separated. A sample of the polymer phase is taken (***P4.10.2***). The polymer phase which is dissolved in toluene is washed with ~200 mL of $H_2O$ and dried over $Na_2SO_4$. After filtration the solvent is removed via rotary evaporation and the high viscous polymer is dried further in high vacuum ($<10^{-3}$ mbar at 80 °C.

NMR spectra of the taken samples are presented in figures Figure A4-4 to Figure A4-7:

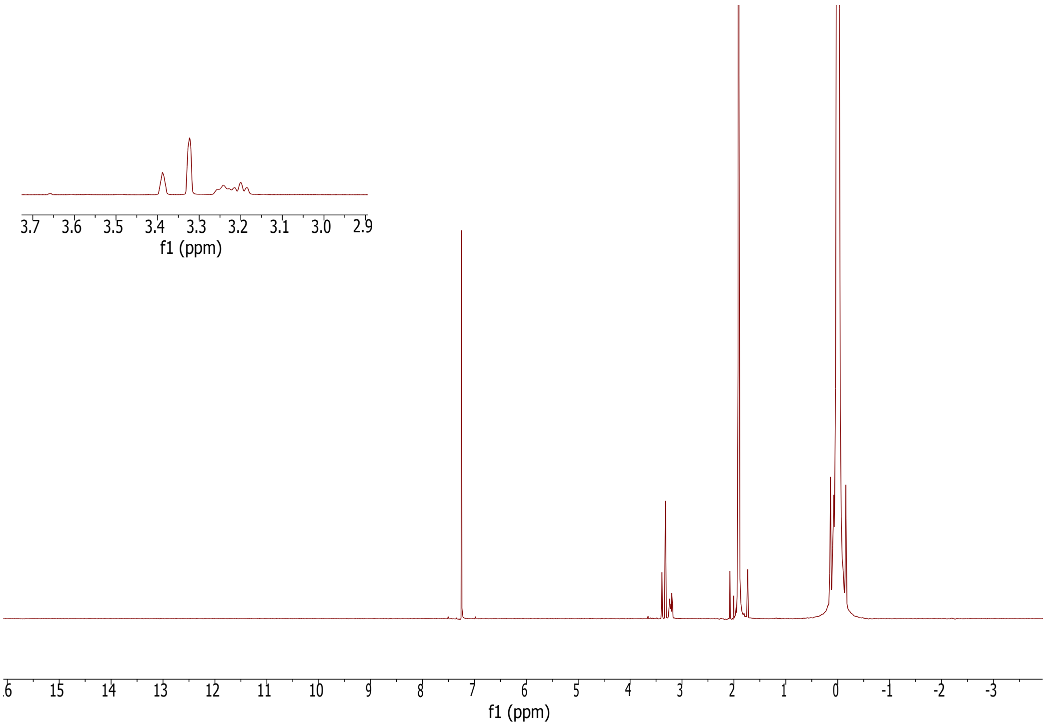


Figure A4-4: $^{1}$H-NMR of sample P4.10.1 (in $CDCl_3$, 400 mHz, 297 K).

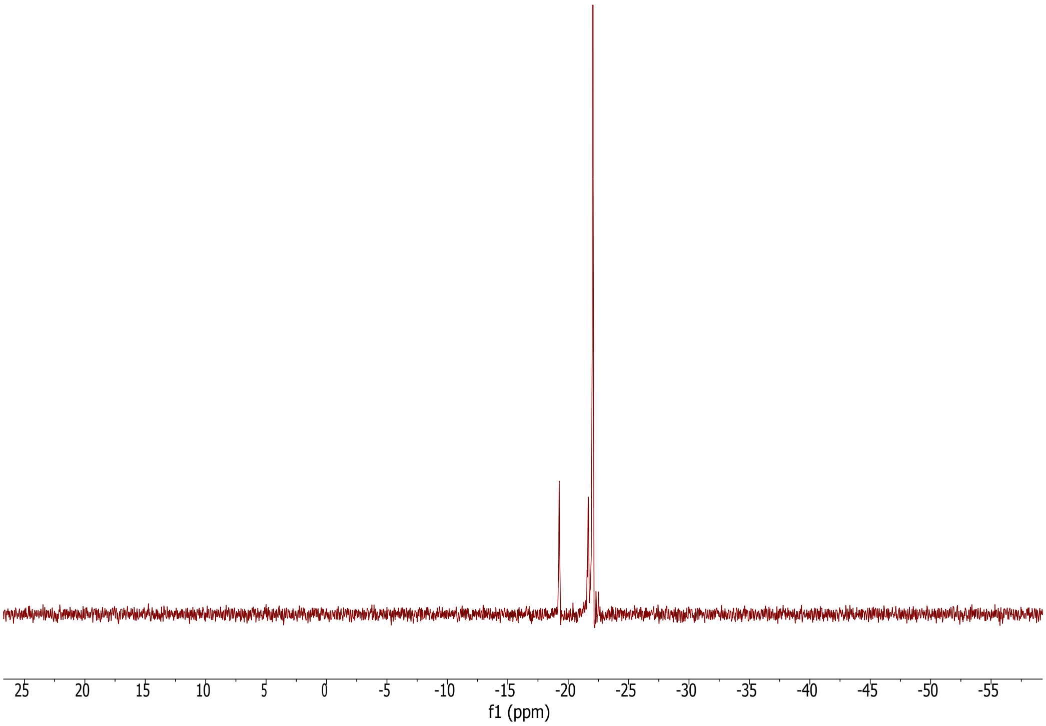


Figure A4-5: $^{29}$Si(IG)-NMR of sample P4.10.1 (in $CDCl_3$, 80 mHz, 297 K).

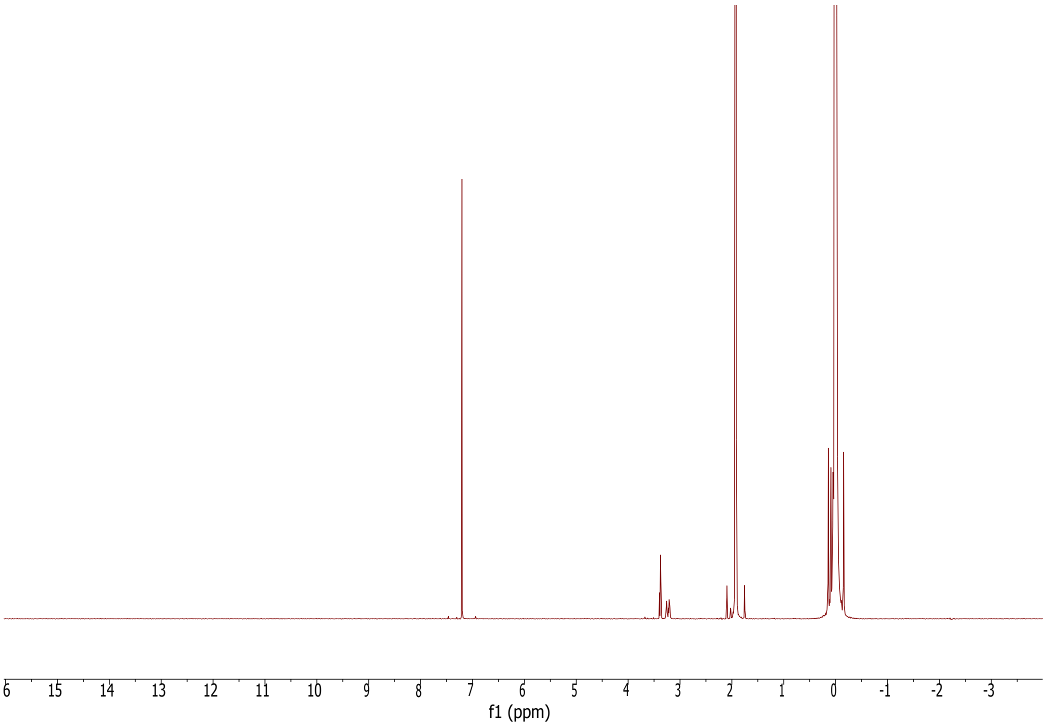


**Figure A4-6: $^1$H-NMR of sample P4.10.2 (in CDCl$_3$, 400 mHz, 297 K).**

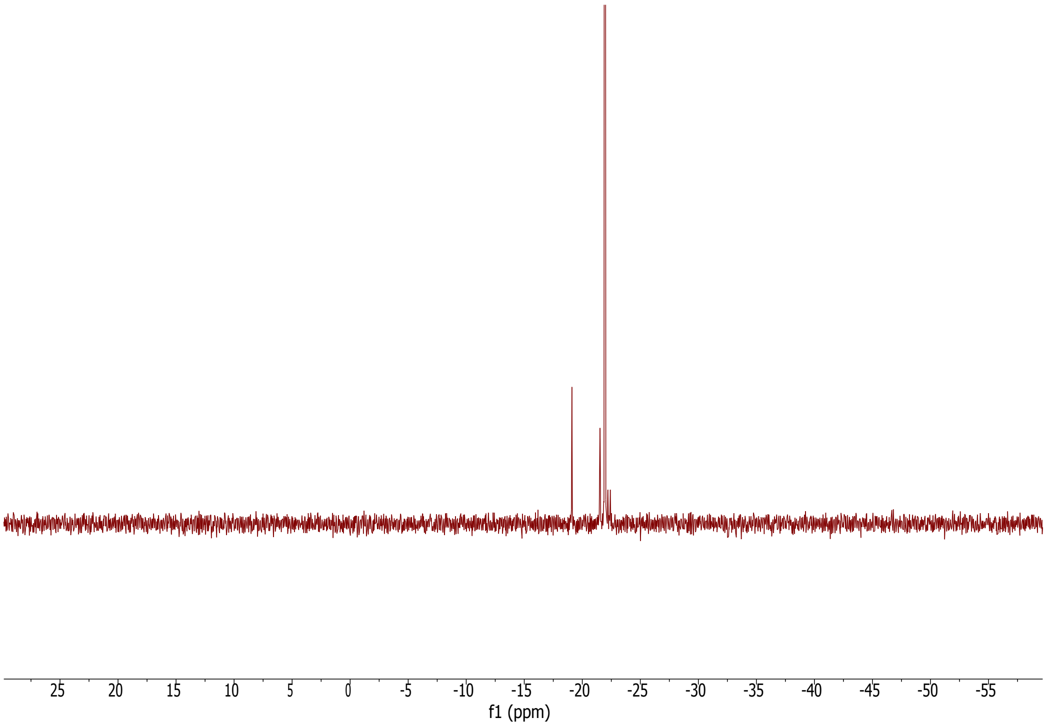


**Figure A4-7: $^{29}$Si(IG)-NMR of sample P4.10.2 (in CDCl$_3$, 80 mHz, 297 K).**

### A4.3.2 Usage of divinyltetramethyldisiloxane (P4.12)

Polymerization is carried out under inert gas in a moisture free atmosphere. First TBD (0.34 mmol) and methanol (67.43 mmol) and 1,3-divinyl31,1,3,3-tetramethyldisiloxane (2.76) are submitted into an argon flushed, oven-dried three neck flask equipped with reflux condenser, mechanical stirrer and a septum. They are dissolved in dry acetonitrile (7.5 mL). While stirring (250 rpm) $D_4$ (16.86 mmol), which was dried over molecular sieves, is added. Reaction is started by dipping into preheated oil bath (65 °C oil bath temperature). The reaction is stopped after 24 h by removing the heat source. After cooling down to room temperature phases are separated. The polymer phase is washed with methanol. The polymer is dried in high vacuum (<1*10-3 mbar) at 80 °C.

The amount of DVS is calculated according to Eq. A4-1and Eq. A4-2 in order to obtain a polymer with $M_n$ = 2000 g/mol if methanol would not be active in ROP.

$$n_{DVS} : n_{Monomer} = 1 : x \qquad \textbf{Eq. A4-1}$$

$$x = \frac{M_{target} - M_{DVS}}{M_{D4}} \qquad \textbf{Eq. A4-2}$$

**$^1$H-NMR** (400 MHz, CDCl$_3$, 297.0 K) [ppm]: $\delta$ = 0.29 – 0.03 (m,–[O–Si(C$\underline{H}_3$)$_2$]–); 3.48 ($\underline{H}_3$C–O–Si(CH$_3$)$_2$–); 5.75 (dd, J = 20.3, 4.0 Hz, $\underline{H}_2$C=CH–Si(CH$_3$)$_2$– trans position); 5.94 (dd, J = 14.9, 4.0 Hz, $\underline{H}_2$C=CH–Si(CH$_3$)$_2$– cis position); 6.14 (dd, J = 20.3, 14.9 Hz, H$_2$C=C$\underline{H}$–Si(CH$_3$)$_2$–).**$^{13}$C-NMR** (400 MHz, CDCl$_3$, 297. K) [ppm]: $\delta$ = -1.33 (s, CH$_3$–O–Si($\underline{C}$H$_3$)$_2$–); -0.50 (s, H$_2$C=CH–Si($\underline{C}$H$_3$)$_2$–); 0.932 – 1.75 (m, –[O–Si($\underline{C}$H$_3$)$_2$]–); 49.71 (s, $\underline{C}$H$_3$–O–Si(CH$_3$)$_2$–); -131.8 (s, H$_2\underline{C}$=CH–Si(CH$_3$)$_2$–); -139.5 (s, H$_2$C=$\underline{C}$H–Si(CH$_3$)$_2$–).**$^{29}$Si-NMR** (400 MHz, CDCl$_3$, 297.0 K) [ppm]: $\delta$ = -22.69 – -21.75 (m, –[O-$\underline{Si}$(CH$_3$)$_2$]–); -11.65 (s, –$\underline{Si}$(CH$_3$)$_2$–O–CH$_3$); -4.33 (s, H$_2$C=CH–$\underline{Si}$(CH$_3$)$_2$–).

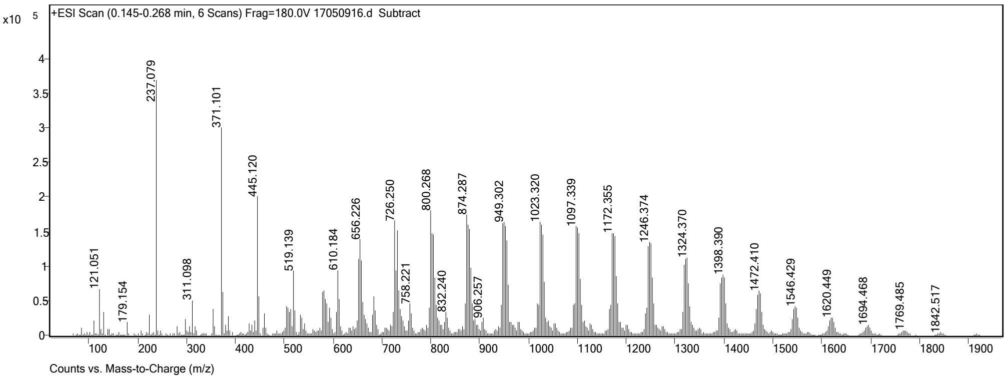


**Figure A4-8: ESITOF spectra of P4.12.**

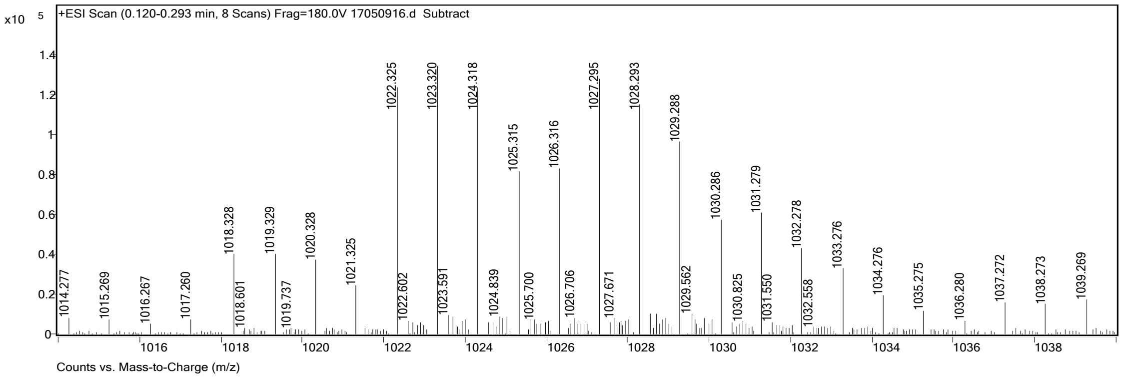


**Figure 4-9: ESITOF spectra of P4.12. Detail of signal group 1023.320 m/z.**

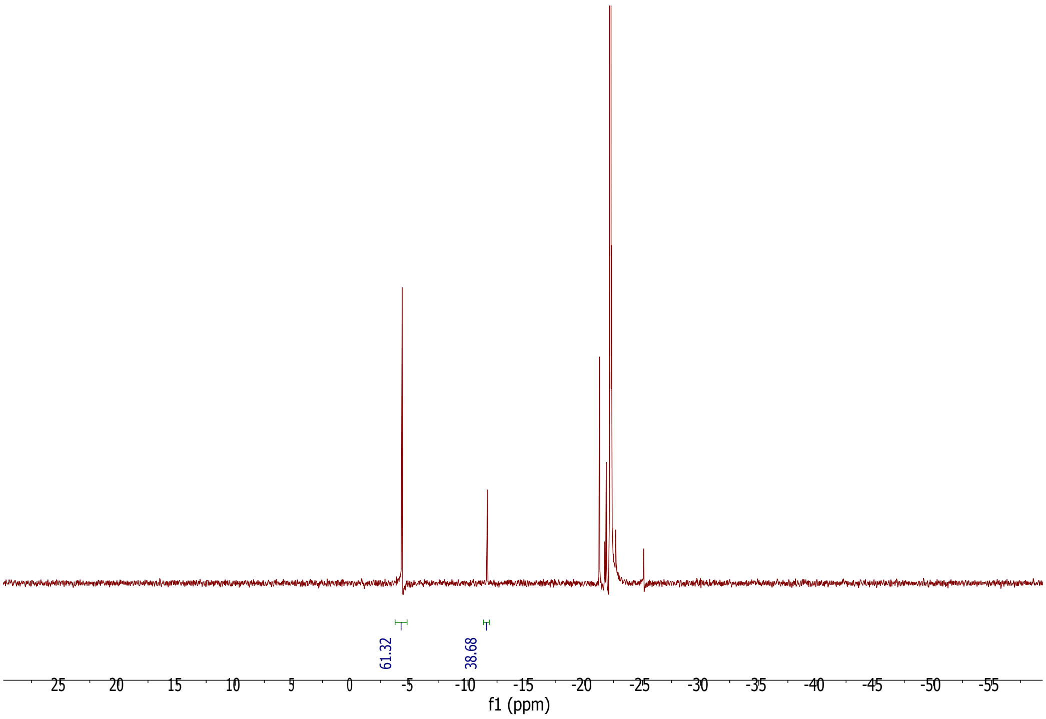


**Figure A4-10: $^{29}$Si(IG)-NMR of P4.12 (in CDCl$_3$, 80 mHz, 297 K).**

### A4.3.3 Equilibration reactions

**P4.13: PDMS 14000** (trimethylsilyl end-capped) (10 g) and **PDMS 2000** (trimethylsilyl end-capped) (10 g), both obtained from Alfa Aesar, are dried at least for 12 h over molecular sieves. Dry acetonitrile (30 mL) and TBD (2 wt%) are added. The reaction mixture is reacted 24 h at 65 °C. After cooling down to room temperature the acetonitrile layer is removed and the polymer phase is dissolved in toluene and filtered in order to remove the molecular sieves. The polymer phase is then washed with 30 mL of water and dried over $Na_2SO_4$. After filtration toluene is removed via rotary evaporation.

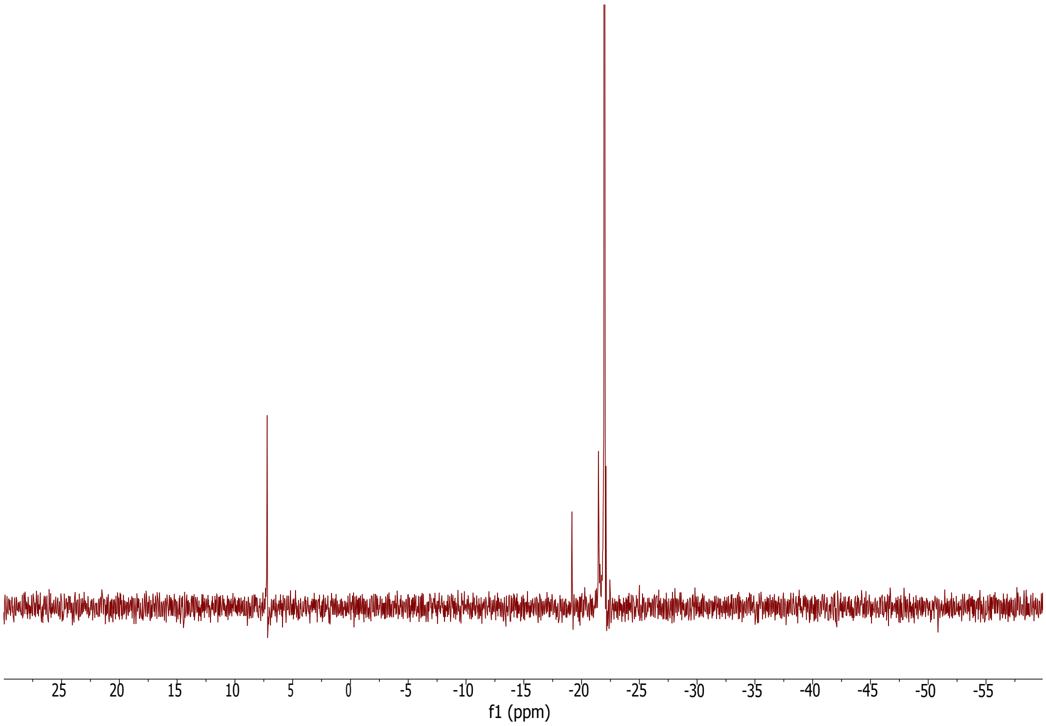


**Figure A4-11: $^{29}$Si(IG)-NMR of P4.13 measured in $CDCl_3$.**

**P4.14: PDMS 14000** (trimethylsilyl endcapped) (10 g) and **PDMS 2000** (trimethylsilyl endcapped), both obtained from Alfa Aesar, are dried at least for 12 h over molecular sieves. Dry acetonitrile, TBD (2 wt%) and methanol (287 mmol) are added. The reaction mixture is reacted 24 h at 65 °C. After cooling down to room temperature the acetonitrile layer is removed and the polymer phase is dissolved in toluene and filtered in order to remove the molecular sieves. The polymer phase is then washed with 100 mL of water and dried over $Na_2SO_4$. After filtration toluene is removed via rotary evaporation.

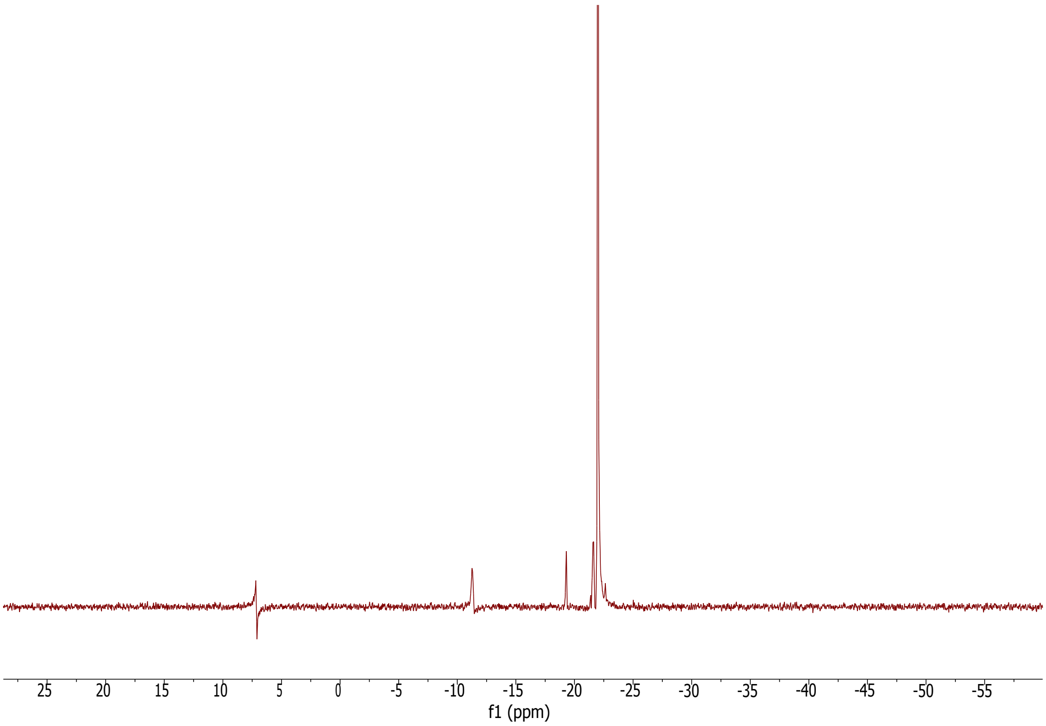


**Figure A4-12: $^{29}$Si(IG)-NMR of P4.14 measured in $CDCl_3$.**

### A4.3.3.1 GC Data of starting materials PDMS 2000 and PDMS 14000

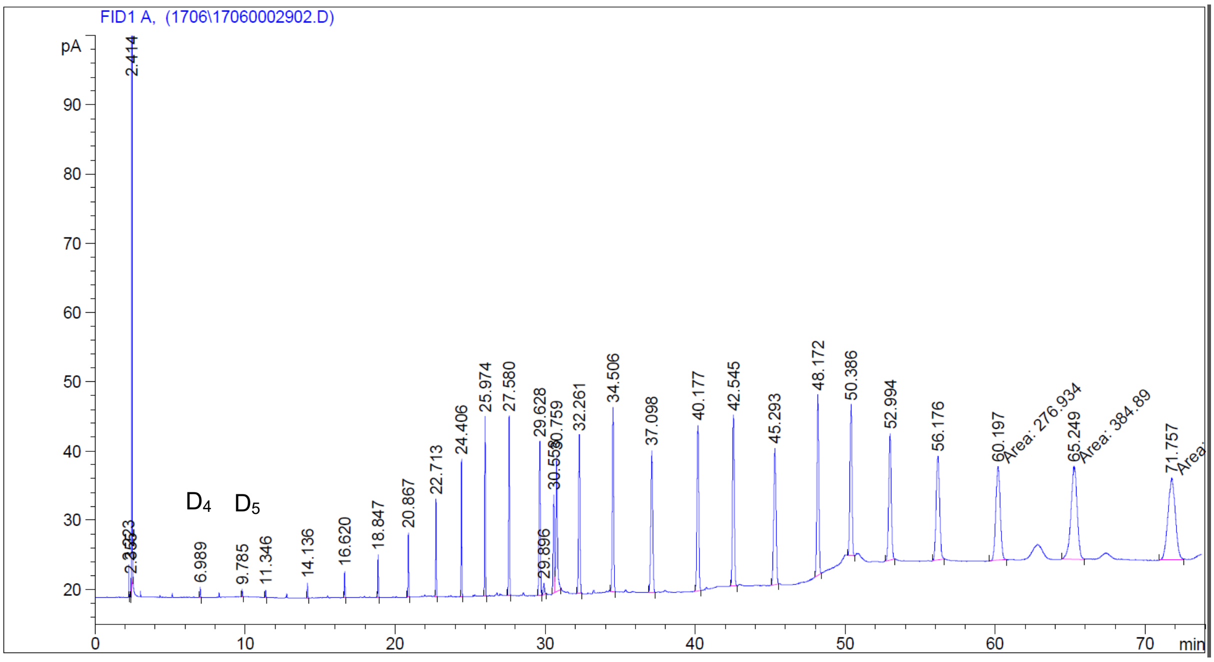


**Figure 4-13: GC spectrum of starting material PDMS 2000.**

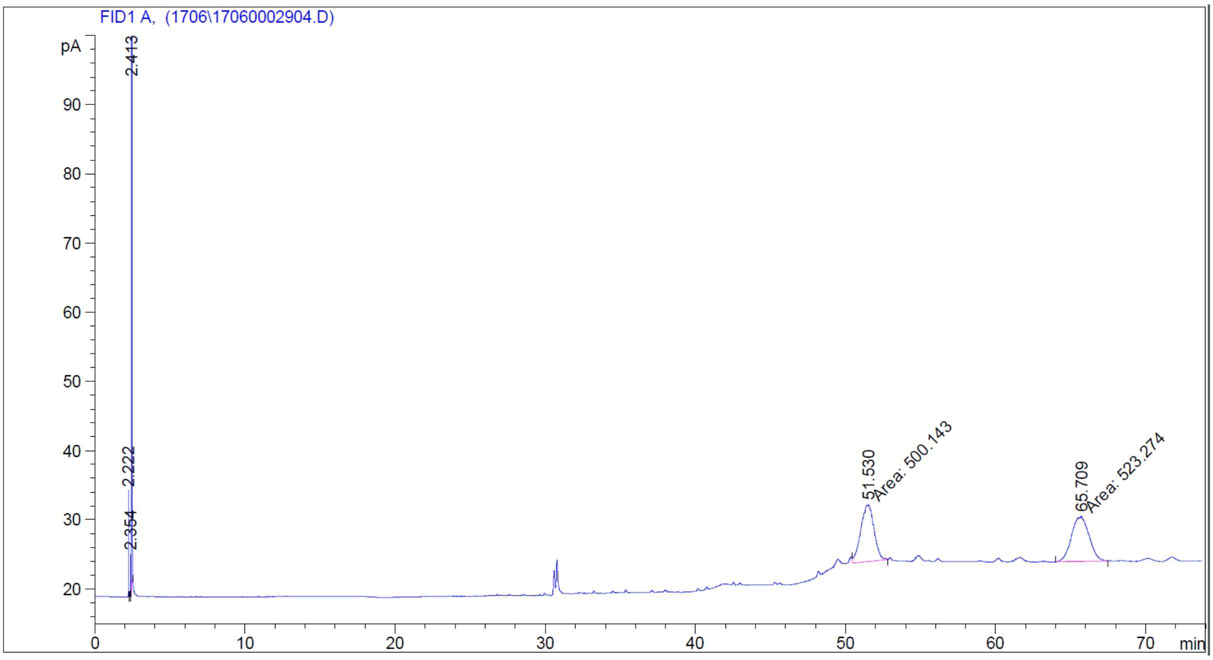
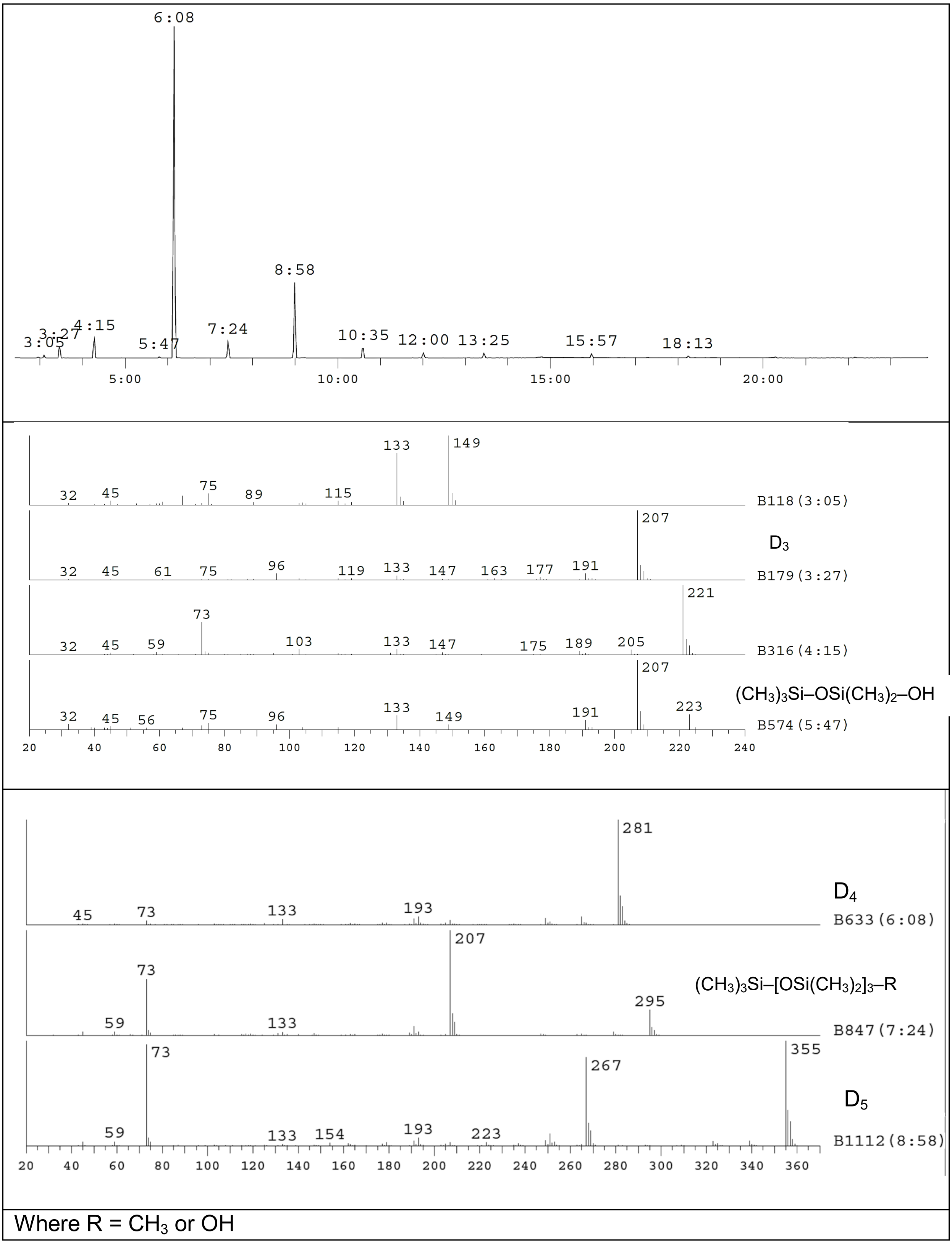


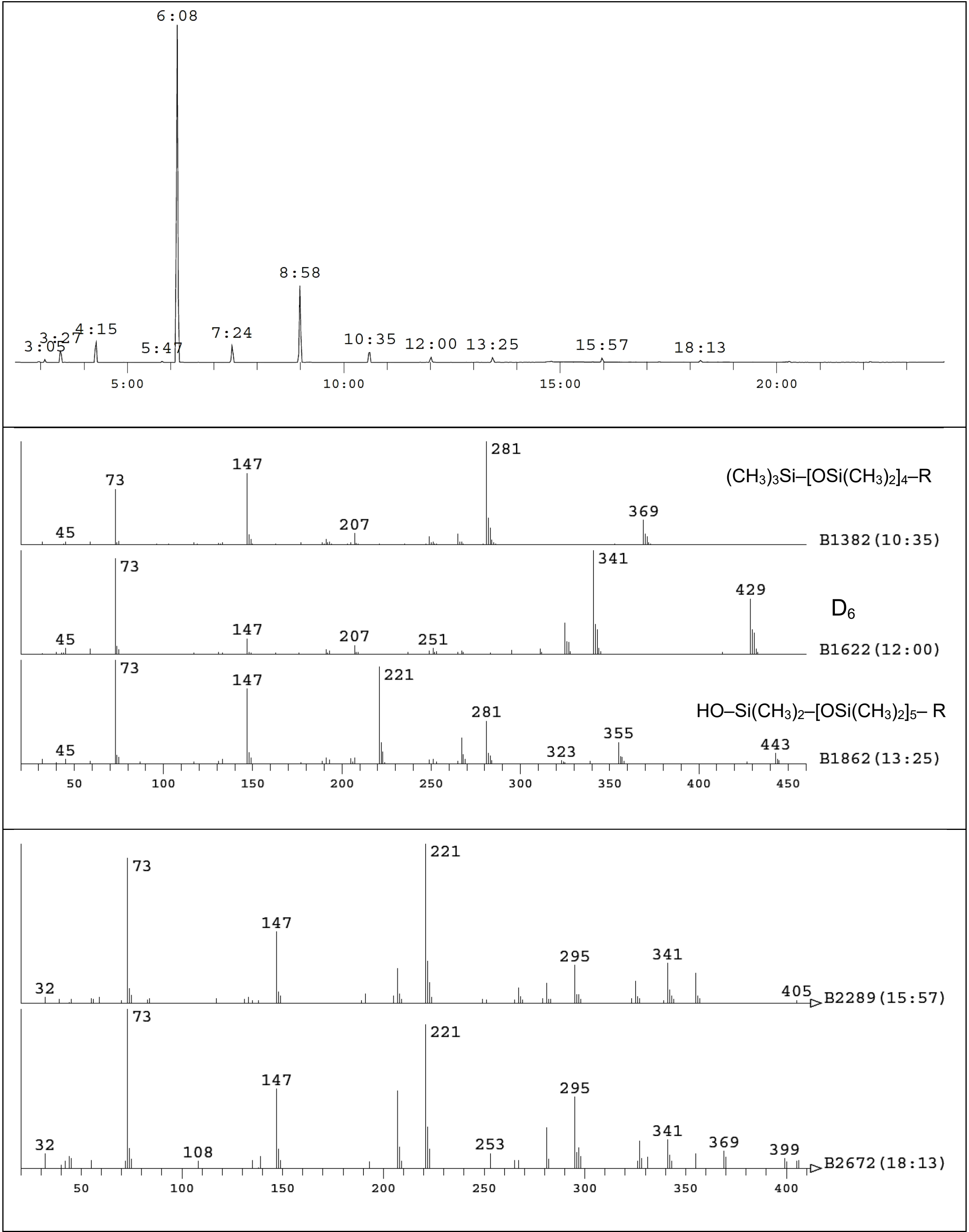
**Figure 4-14: GC spectrum of starting material PDMS 14000.**

### A4.3.3.2 GC-MS data of solvent phase of P4.13 and P4.14



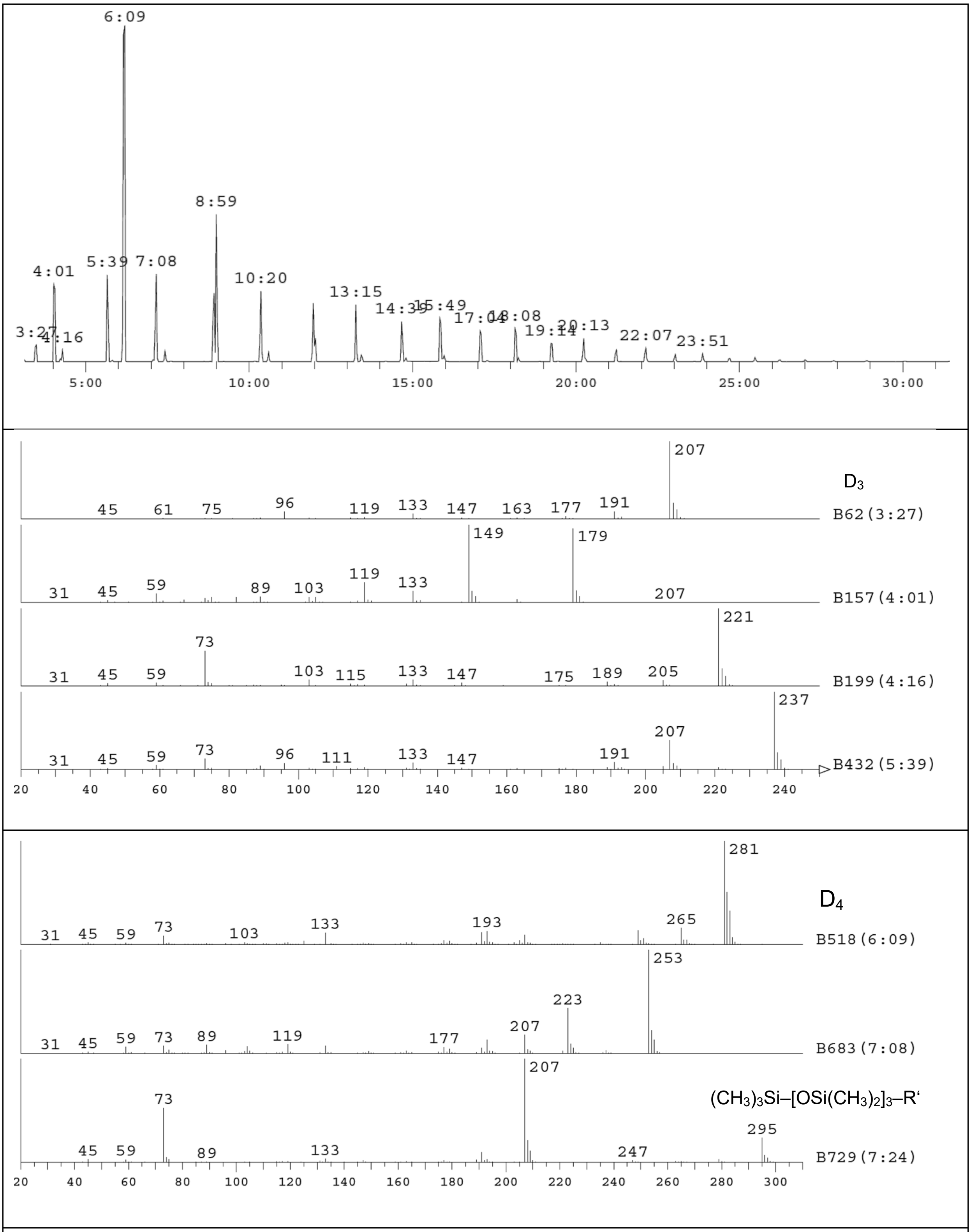
Where R = $CH_3$ or OH

**Figure 4-15: GC-MS spectra of solvent phase of P4.13 (Retention time: 3:05 – 8:58).**



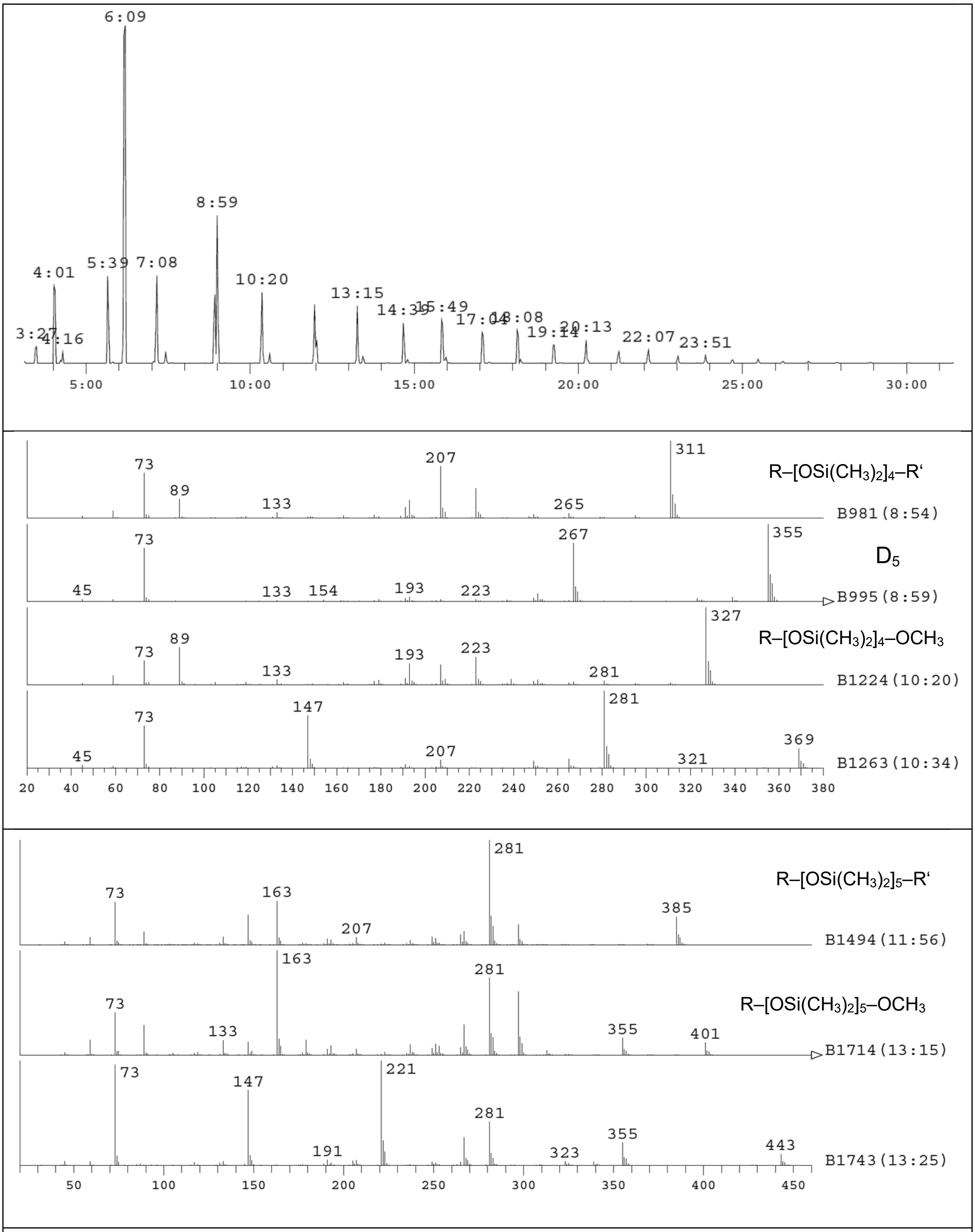
Where R = $CH_3$ or OH

**Figure 4-16: GC-MS spectra of solvent phase of P4.13 (Retention time: 10:35 – 18:13).**



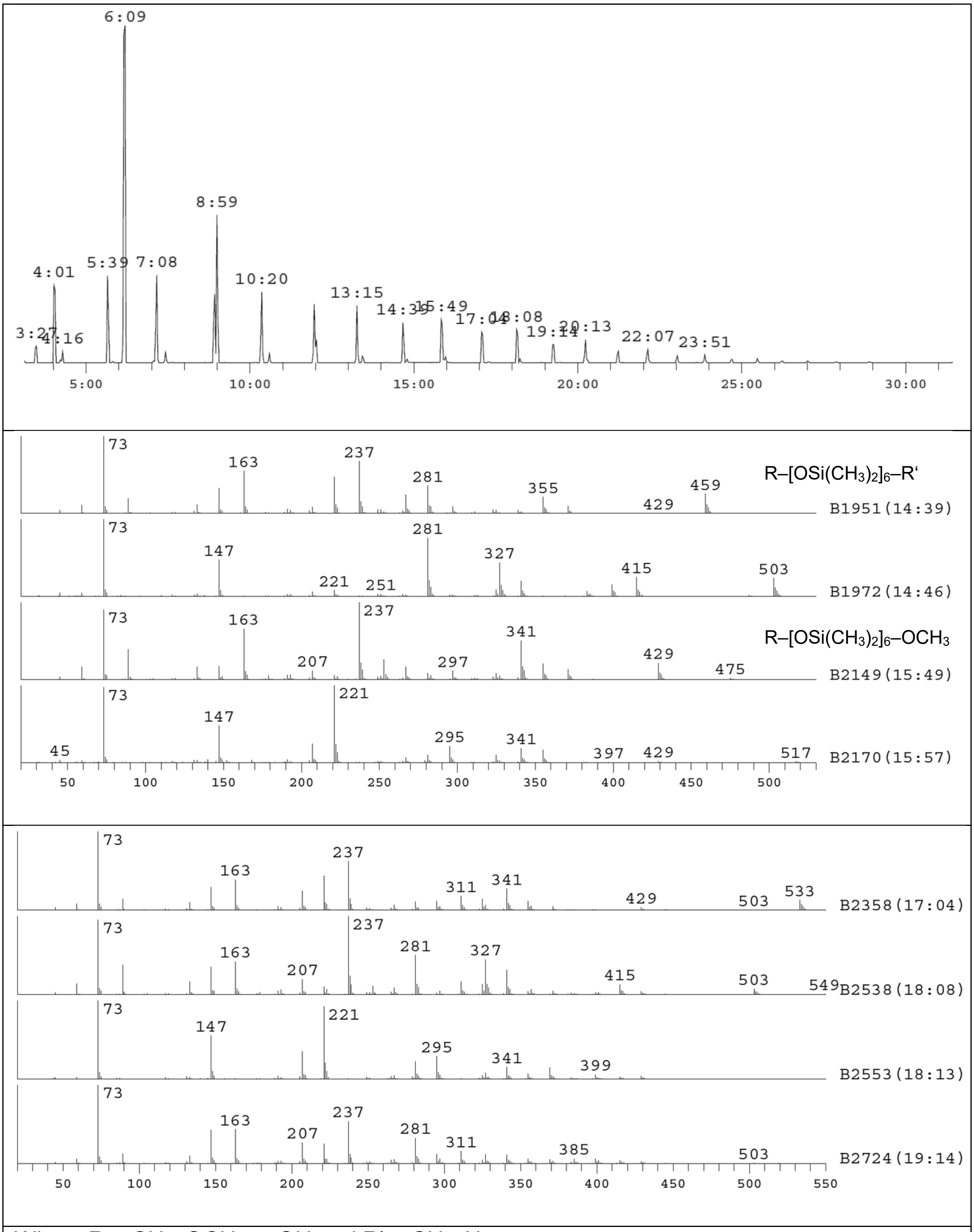
Where R = $CH_3$, $OCH_3$ or OH and R’ = $CH_3$, H

**Figure 4-17: GC-MS spectra of solvent phase of P4.14 (Retention time: 3:27 – 7:24).**



Where R = $CH_3$, $OCH_3$ or OH and R’ = $CH_3$, H

**Figure 4-18: GC-MS spectra of solvent phase of P4.14 (Retention time: 8:54 – 13:25).**



Where R = $CH_3$, $OCH_3$ or OH and R' = $CH_3$, H

**Figure 4-19: GC-MS spectra of solvent phase of P4.14 (Retention time: 14:39 – 19:14).**

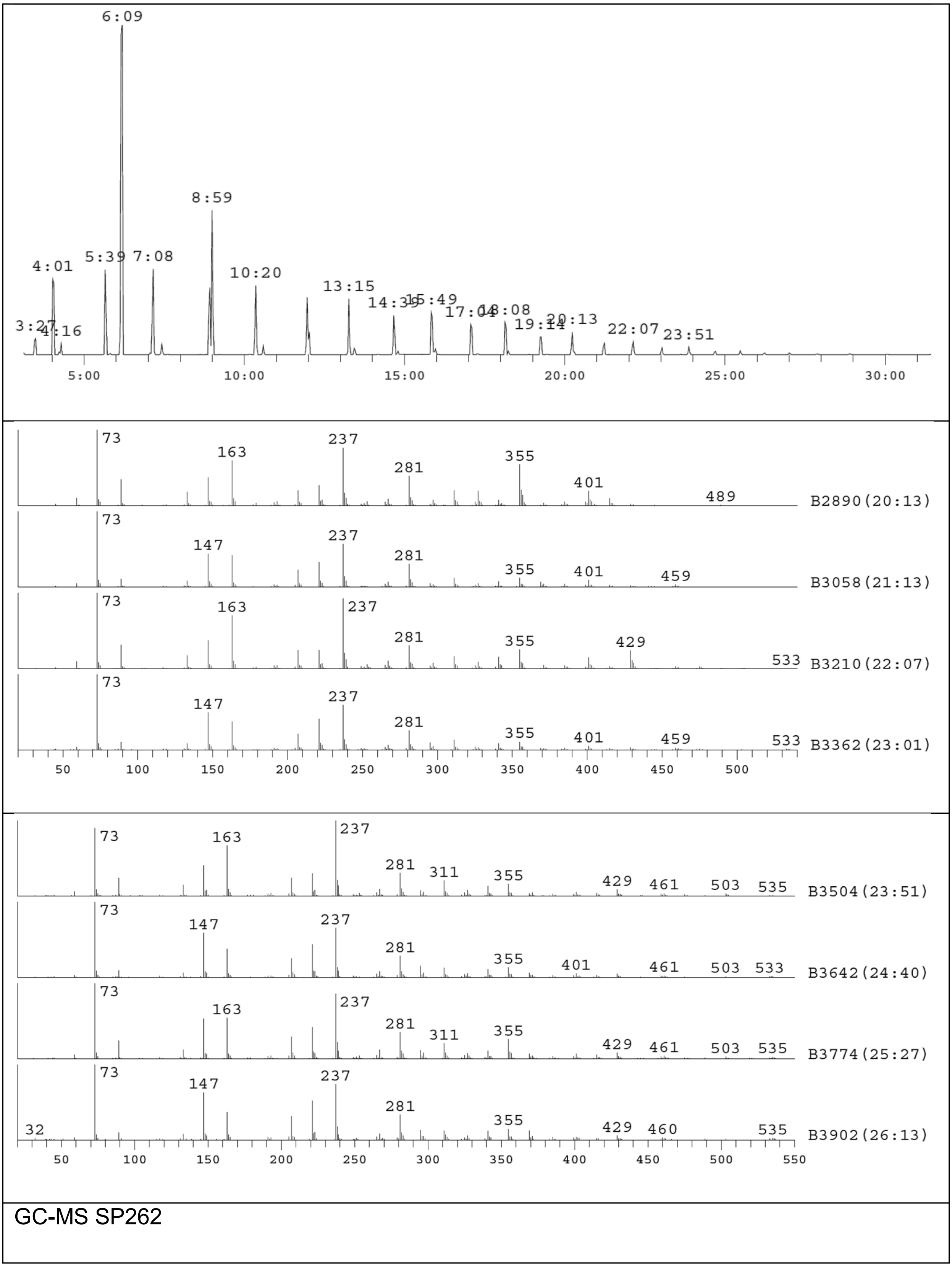


**Figure 4-20: GC-MS spectra of solvent phase of P4.14 (Retention time: 20:13 – 26:13).**

## A4.3.4 Kinetics

### A4.3.4.1 Determination of reaction order in monomer

*Polymerization Procedure D (for time-resolved experiments)*

In general the polymerization experiments are carried out under inert gas in a moisture free atmosphere. First coinitiator and methanol are submitted into an argon-flushed, flame-dried three neck flask equipped with reflux condenser, mechanical stirrer and a septum. They are dissolved in dry acetonitrile. While stirring $D_4$, which was dried over molecular sieves, is added. Reaction is started by dipping into preheated oil bath. The reaction is stopped after 24 h by removing the heat source. After cooling down to room temperature phases are separated. The polymer is stripped in high vacuum (<1*10-3 mbar) at 80 °C.

Samples are taken subsequently during course of conversion for determination of molecular weight and conversion.

Sample preparation for samples taken throughout the reaction is done as follows: For GPC samples 0.5 mL of reaction mixture are transferred from the flask into a vial and left to the side until phase separation took place. The solvent phase is removed and discarded. The polymer phase is then dissolved in toluene to a concentration of 1 mg/mL. For NMR samples 0.3 mL of reaction mixture are directly transferred from the flask into a NMR-tube and is dissolved in 0.3 mL of deuterated chloroform.

Polymerization reactions are conducted according to *Polymerization Procedure D* for 2 h. But the polymer is not worked up. Samples are taken subsequently during course of conversion for determination of molecular weight and conversion.

Sample preparation for samples taken throughout the reaction is done as follows: For GPC samples 0.5 mL of reaction mixture are transferred from the flask to into a vial and left to the side until phase separation takes place. The solvent phase is removed and discarded. The polymer phase is then dissolved in toluene to a concentration of 1 mg/mL. For NMR samples 0.3 mL of reaction mixture is transferred directly from the flask into a NMR-tube and is dissolved in 0.3 mL of deuterated chloroform in which Cr(III)acetylacetonate is dissolved (8 g/L).

Reaction parameters are summarized in Table A4-1. Experiments are performed twice.

**Table A4-1: Summary of reaction parameters of ROP experiments at different reaction temperatures.**

| No. | $T_{oil\ bath}$ [°C] | n ($D_4$) [mmol] | n (TBD) [mmol] | n (MeOH) [mmol] | V (Acetonitrile) [mL] | stirring speed [rpm] |
|---|---|---|---|---|---|---|
| P5.55 | 81 | 67.43 | 1.35 | 134.85 | 30 | 250 |
| P5.56 | 95 | 67.43 | 1.35 | 134.85 | 30 | 250 |
| P5.57 | 65 | 67.43 | 1.35 | 134.85 | 30 | 250 |
| P5.58 | 40 | 67.43 | 1.35 | 134.85 | 30 | 250 |
| P5.59 | RT | 67.43 | 1.35 | 134.85 | 30 | 250 |

### A4.3.4.2 Determination of reaction order in methanol

Polymerization reactions are conducted according to *Polymerization Procedure D* described in A4.3.4.1. But the polymer is not worked up. Samples are taken subsequently during course of conversion for determination of molecular weight and conversion.

Sample preparation for samples taken throughout the reaction was done as follows: For GPC samples 0.5 mL of reaction mixture were transferred from the flask to into a vial and left to the side until phase separation took place. The solvent phase was removed and discarded. The polymer phase was then dissolved in toluene to a concentration of 1 mg/mL. For NMR samples 0.3 mL of reaction mixture are directly transferred from the flask into a NMR-tube and is dissolved in 0.3 mL of deuterated chloroform.

**Table A1-2: Summary of reaction parameters of ROP for determination of reaction order in methanol.**

| No. | $T_{oil\ bath}$ [°C] | n ($D_4$) [mmol] | n (TBD) [mmol] | n (MeOH) [mmol] | V (Acetonitrile) [mL] | stirring speed [rpm] |
|---|---|---|---|---|---|---|
| P5.60 | 65 | 67.43 | 0.67 | 67.43 | 30 | 250 |
| P5.61 | 65 | 67.43 | 0.33 | 33.71 | 30 | 250 |

### A4.3.4.3 Determination of teaction order in coinitiator (TBD)

Polymerization reactions were conducted according to *Polymerization Procedure D* described in A4.3.4.1. But the polymer is not worked up. Samples are taken subsequently during course of conversion for determination of molecular weight and conversion.

Sample preparation for samples taken throughout the reaction is done as follows: For GPC samples 0.5 mL of reaction mixture are transferred from the flask into a vial and left to the side until phase separation takes place. The solvent phase is removed and discarded. The polymer phase is then dissolved in toluene to a concentration of 1 mg/mL. For NMR samples

0.3 mL of reaction mixture are transferred directly from the flask into a NMR-tube and is dissolved in 0.3 mL of deuterated chloroform.

**Table A1-3: Summary of reaction parameters of ROP for determination of reaction order in TBD.**

| No. | $T_{oil\ bath}$ [°C] | n ($D_4$) [mmol] | n (TBD) [mmol] | n (MeOH) [mmol] | V (Acetonitrile) [mL] | stirring speed [rpm] |
|---|---|---|---|---|---|---|
| P5.62 | 65 | 67.43 | 0.67 | 67.43 | 30 | 250 |
| P5.63 | 65 | 67.43 | 0.33 | 33.71 | 30 | 250 |

# A5 Appendix to Chapter 5

## A5.1 Hydroxy compound as part of the initiating system

### A5.1.1 Screening of hydroxy compounds

Polymerization Procedure E

In general the polymerization experiments are carried out under inert gas in a moisture free atmosphere. First TBD and alcohol are submitted into an argon-flushed, oven-dried three neck flask equipped with reflux condenser, mechanical stirrer and a septum. They are dissolved in dry acetonitrile. While stirring (250 rpm) $D_4$, which was dried over molecular sieves, is added. Reaction is started by dipping into preheated oil bath. The reaction is stopped after 24 h by removing the heat source. After cooling down to room temperature phases are separated. If viscosity of polymer is too high it is dissolved in toluene. The polymer phase is washed with water and dried over $Na_2SO_4$. The polymer is stripped in high vacuum (<1*10-3 mbar) at 80 °C.

For time-resolved experiments samples are taken subsequently during course of conversion for determination of molecular weight and conversion. Sample preparation for samples taken throughout the reaction is done as follows: For GPC samples 0.5 mL of reaction mixture are transferred from the flask to into a vial and left to the side until phase separation takes place. The solvent phase is removed and discarded. The polymer phase is then dissolved in toluene to a concentration of 1 mg/mL. For NMR samples 0.3 mL of reaction mixture are transferred directly from the flask into a NMR-tube and is dissolved in 0.3 mL of deuterated chloroform.

Experiments are summarized in Table A5-1:

**Table A5-1: Summary of reaction parameter screening different hydroxyl compounds (ROH). All Experiments were performed twice.**

| No | n (TBD) [mmol] | n ($D_4$) [mmol] | Acetonitrile V [mL] | ROH | n (ROH [mmol ] | $T_{oil\ bath}$ | Remark |
|---|---|---|---|---|---|---|---|
| P5.1 | 3.37 | 168.57 | 75.0 | nBuOH | 337.13 | 65 | Time resolved |
| P5.2 | 3.37 | 168.57 | 75.0 | i-PrOH | 337.13 | 65 | Time resolved |
| P5.3 | 3.37 | 168.57 | 75.0 | t-BuOH | 337.13 | 65 | Time resolved |
| P5.4 | 0.67 | 33.71 | 15.0 | t-BuOH | 67.43 | 100 | |
| P5.5 | 0.34 | 16.86 | 7.5 | 2-Aminoethanol | 0.34 | 65 | |
| P5.6 | 0.34 | 16.86 | 7.5 | 1,3-Butanediol | 0.34 | 65 | |
| P5.7 | 1.35 | 67.43 | 30 | Ethyllactate | 134.85 | 65 | |
| P5.8 | 1.35 | 67.43 | 30.0 | TMSOH | 134.85 | 65 | Time resolved |
| P5.9 | 1.35 | 67.43 | 30.0 | TMSOH | 67.43 | 65 | Time resolved |
| P5.10 | 1.35 | 67.43 | 30.0 | TMSOH | 13.49 | 65 | Time resolved |
| P5.11 | 1.35 | 67.43 | 30.0 | $H_2O$ | 674.43 | 65 | Time resolved |
| P5.12 | 1.35 | 67.43 | 30.0 | $H_2O$ | 269.60 | 65 | Time resolved |
| P5.13 | 1.35 | 67.43 | 30.0 | $H_2O$ | 134.85 | 65 | Time resolved |

$^1$H- and $^{29}$Si(IG)-NMR spectra are presented in the following Figure A5-1 - Figure A5-6.

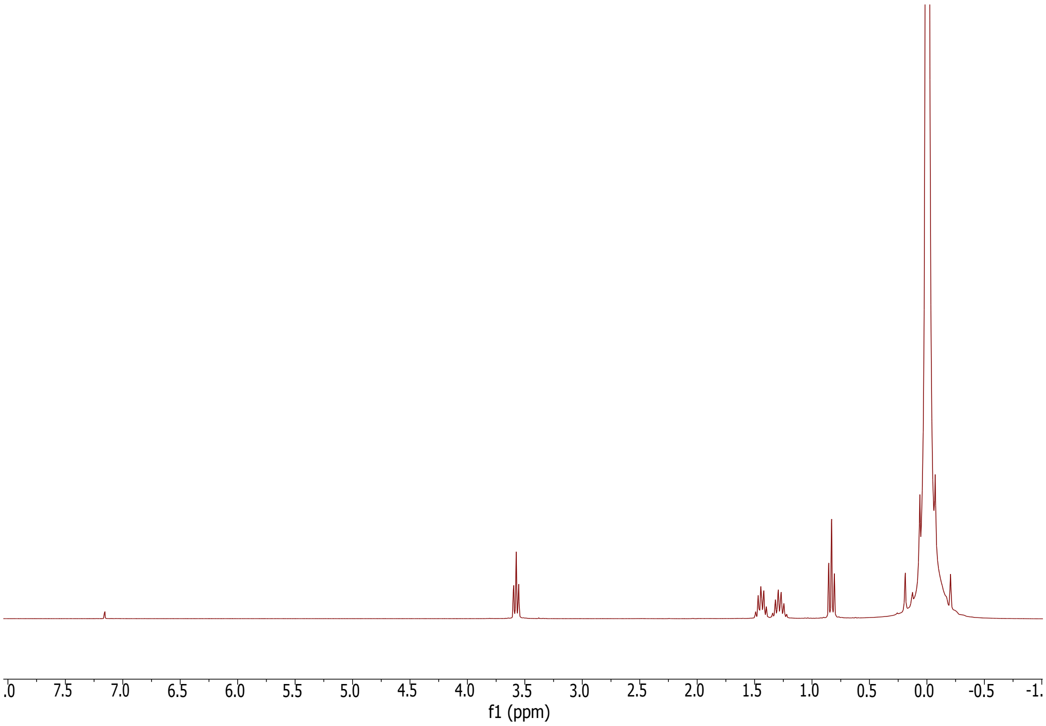


**Figure A5-1:** $^{1}$**H-NMR of P5.1 (in CDCl**$_3$**, 300 MHz, 297 K).**

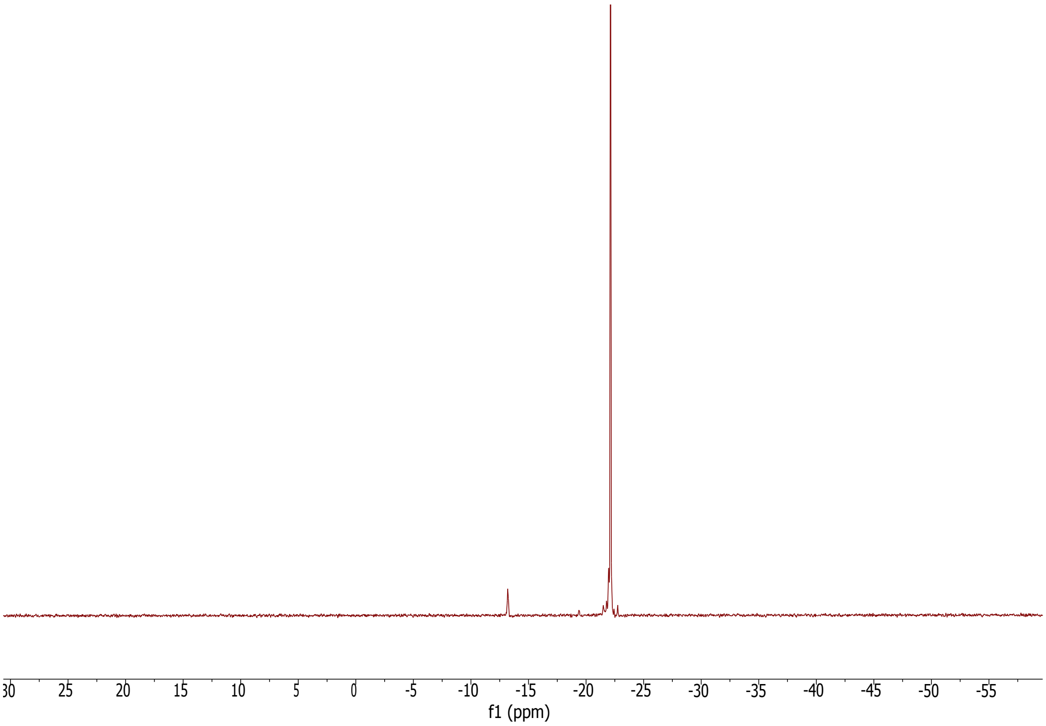


**Figure A5-2:** $^{29}$**Si(IG)-NMR of P5.1 (in CDCl**$_3$**, 59 mHz, 297 K).**

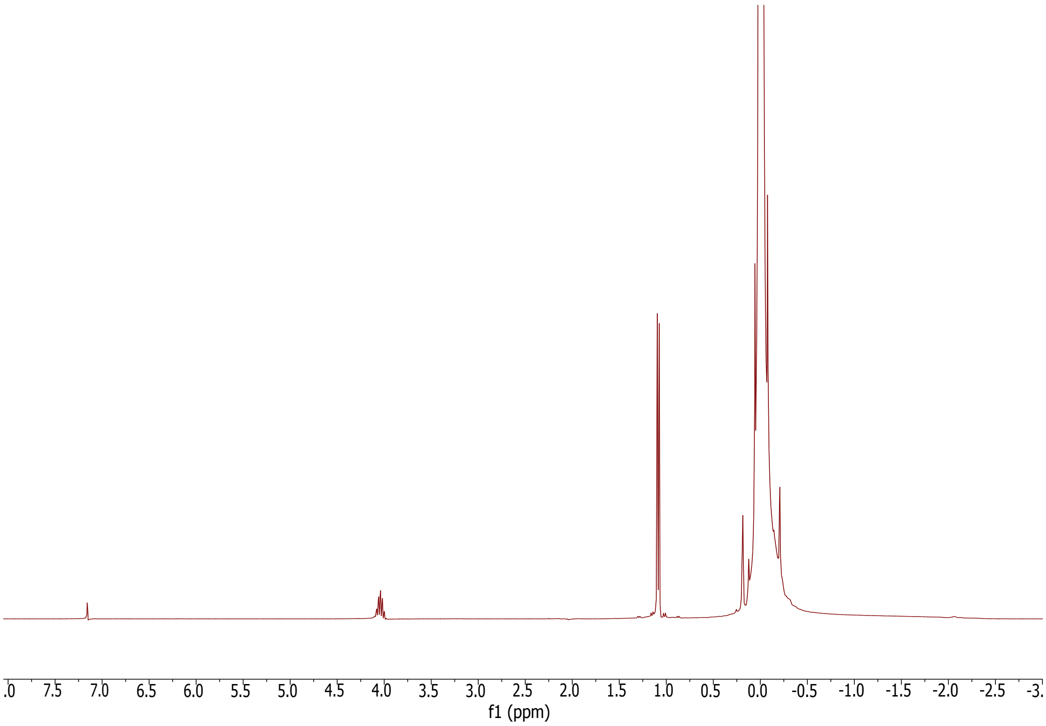


Figure A5-3: $^1$H-NMR of P5.2 (in $CDCl_3$, 300 MHz, 297 K).

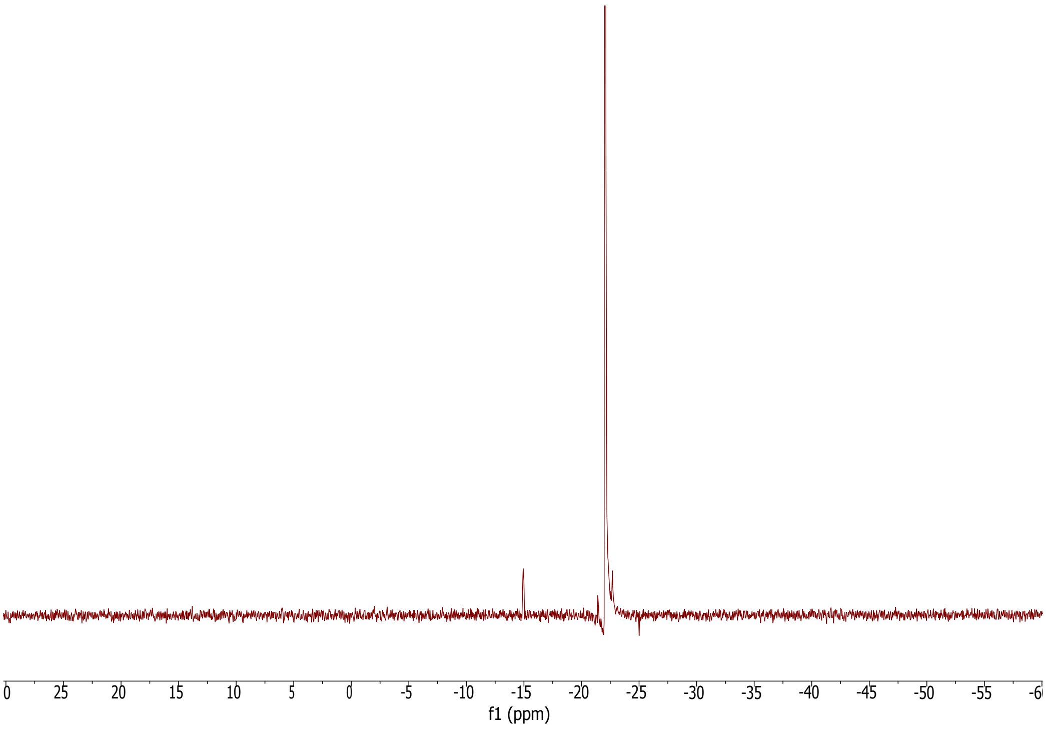


Figure A5-4: $^{29}$Si(IG)-NMR of 5.2 (in $CDCl_3$, 59 mHz, 297 K).

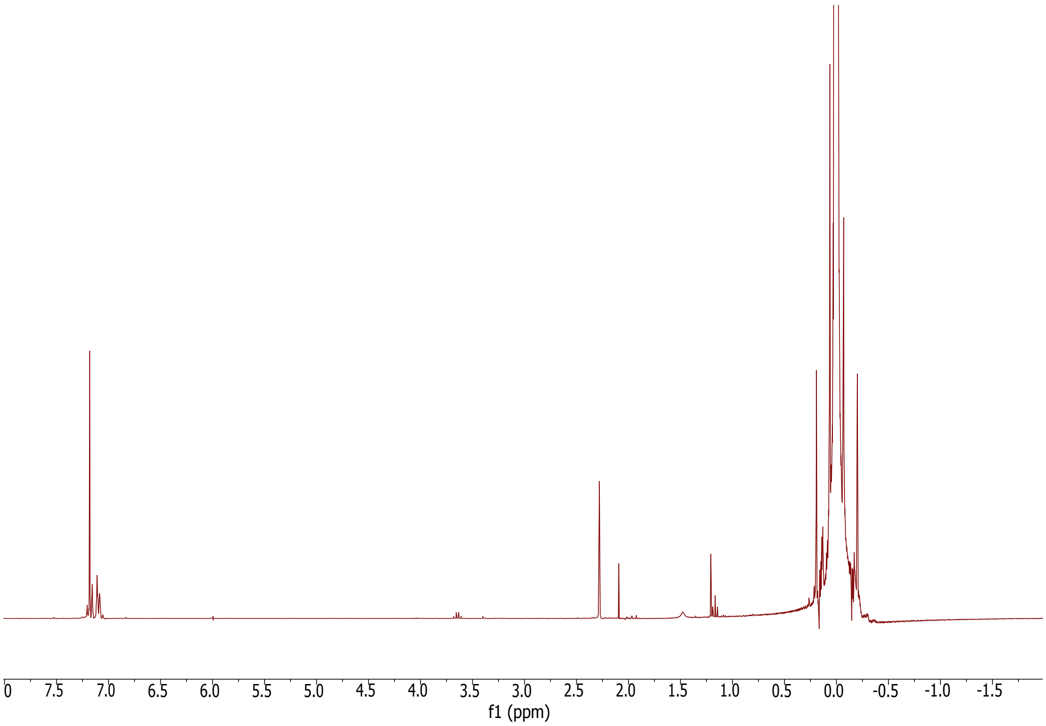


Figure A5-5: $^{1}$H-NMR of P5.3 (in $CDCl_3$, 300 MHz, 297 K).

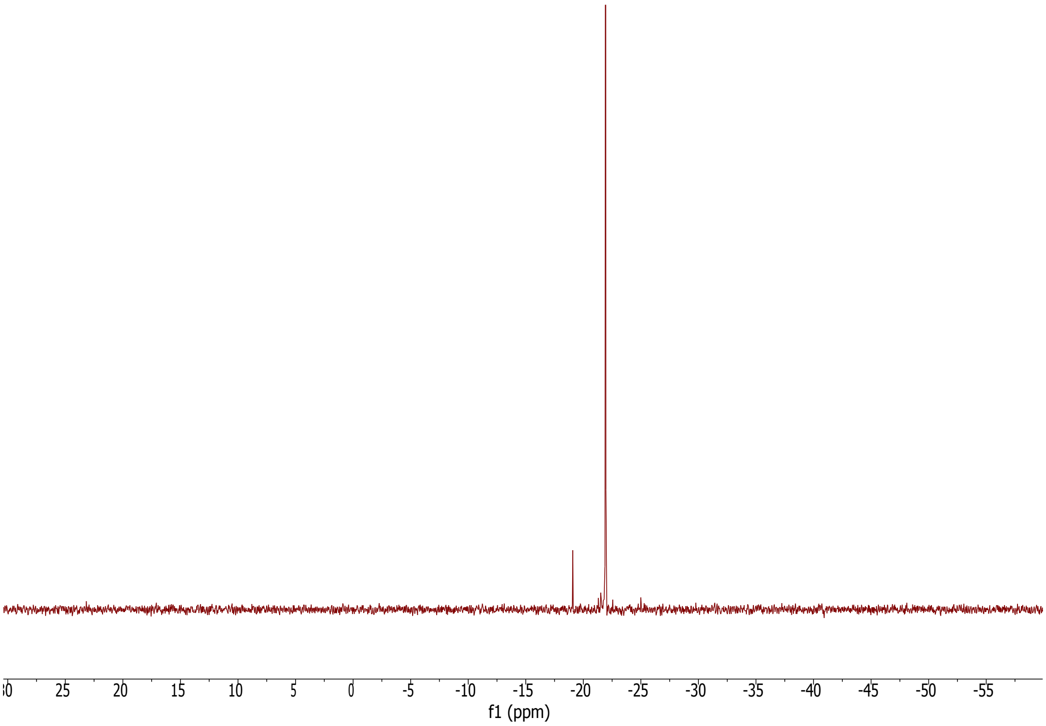


Figure A5-6: $^{29}$Si(IG)-NMR of 5.3 (in $CDCl_3$, 59 mHz, 297 K).

In Figure A5-7 to Figure A5-9 presented ESI-TOF measurements of Polymers P5.1 – P5.3 were performed by an external partner.*

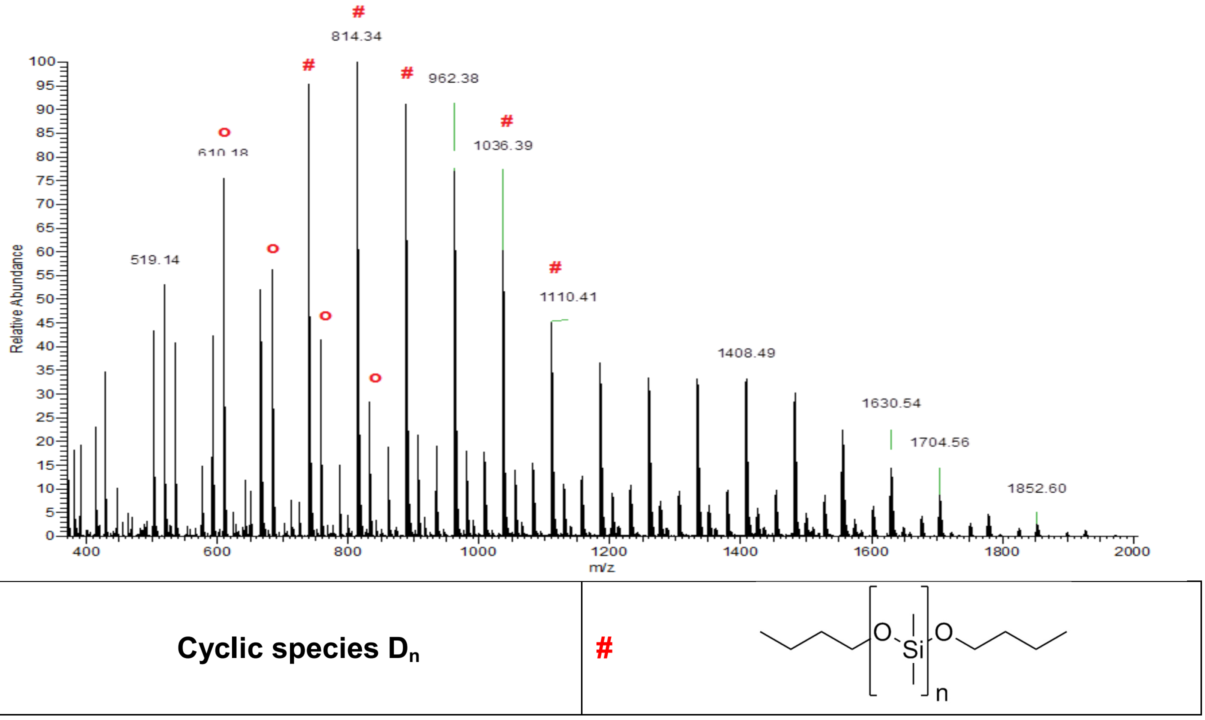


**Figure A5-7: ESITOF spectra of P5.1.**

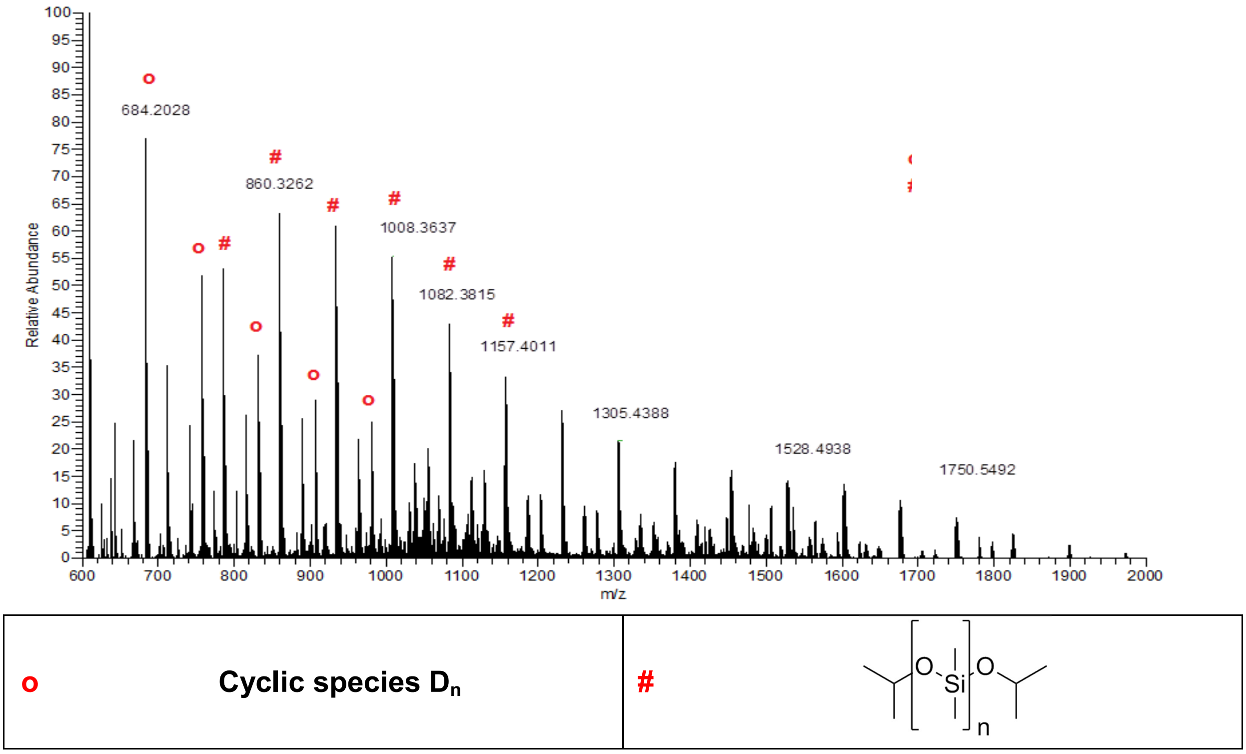


**Figure A5-8: ESITOF spectra of 5.2.**

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* Measurements were performed by Dr. Dayong Sun.

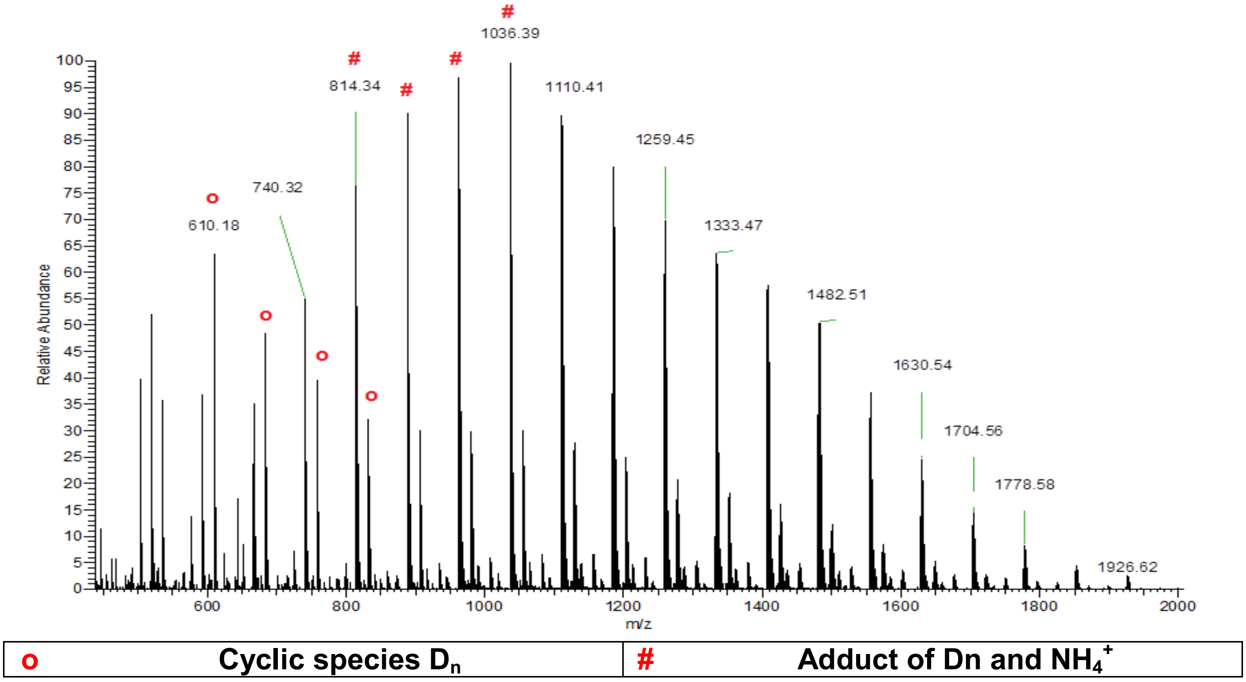

**Figure A5-9: ESITOF spectra of P5.3.**

## A5.1.2 Control of Molecular Weight

### A5.1.2.1 Reproducibility

All experiments are carried out according to Polymerization *Procedure A or B* described in A3.2.7. Experiments were repeated 4 times. Reaction parameters are summarized in Table A5-2.

**Table A5-2: Summary of reaction parameters for reproducibility experiments.**

| No | n (TBD) [mmol] | n ($D_4$) [mmol] | V (Acetonitrile) [mL] | ROH | n (ROH) [mmol ] | Procedure |
|---|---|---|---|---|---|---|
| P5.14 | 1.35 | 67.43 | 30.0 | MeOH | 2.70 | A |
| P5.15 | 1.35 | 67.43 | 30.0 | MeOH | 6.74 | A |
| P5.16 | 1.35 | 67.43 | 30.0 | 2-Octyldodecanol | 2.70 | B |
| P5.17 | 1.35 | 67.43 | 30.0 | 2-Octyldodecanol | 6.74 | B |

### A5.1.2.2 Water, methanol, triorganosilanol

The influence of the amount of hydroxyl compound is investigated. All experiments were carried out following Polymerization *Procedure A or B* described in A3.2.7. Experiments were performed 2 times. Reaction parameters are summarized in Table A5-3.

**Table A5-3: Summary of reaction parameters for investigating the influence of the amount of ROH on Mn.**

| No | n (TBD) [mmol] | n ($D_{4}$) [mmol] | Acetonitrile V [mL] | ROH | n (ROH) [mmol ] | Procedure |
|---|---|---|---|---|---|---|
| P5.18 | 0.34 | 16.86 | 7.5 | MeOH | 0.34 | A |
| P5.19 | 0.34 | 16.86 | 7.5 | MeOH | 0.67 | A |
| P5.20 | 0.34 | 16.86 | 7.5 | MeOH | 1.69 | A |
| P5.21 | 0.34 | 16.86 | 7.5 | MeOH | 3.37 | A |
| P5.22 | 0.34 | 16.86 | 7.5 | MeOH | 8.43 | A |
| P5.23 | 0.34 | 16.86 | 7.5 | MeOH | 16.86 | A |
| P5.24 | 0.34 | 16.86 | 7.5 | MeOH | 33.71 | A |
| P5.25 | 0.34 | 16.86 | 7.5 | MeOH | 67.43 | A |
| P5.26 | 1.35 | 67.43 | 30.0 | $H_2O$ | 1.35 | B |
| P5.27 | 1.35 | 67.43 | 30.0 | $H_2O$ | 2.70 | B |
| P5.28 | 1.35 | 67.43 | 30.0 | $H_2O$ | 6.74 | B |
| P5.29 | 1.35 | 67.43 | 30.0 | $H_2O$ | 13.48 | B |
| P5.30 | 1.35 | 67.43 | 30.0 | $H_2O$ | 33.71 | B |
| P5.31 | 1.35 | 67.43 | 30.0 | $H_2O$ | 134.85 | B |
| P5.32 | 1.35 | 67.43 | 30.0 | $H_2O$ | 269.60 | B |
| P5.33 | 1.35 | 67.43 | 30.0 | $H_2O$ | 674.43 | B |
| P5.34 | 1.35 | 67.43 | 30.0 | TMSOH | 1.35 | B |
| P5.35 | 1.35 | 67.43 | 30.0 | TMSOH | 2.70 | B |
| P5.36 | 1.35 | 67.43 | 30.0 | TMSOH | 6.74 | B |
| P5.37 | 1.35 | 67.43 | 30.0 | TMSOH | 13.48 | B |
| P5.38 | 1.35 | 67.43 | 30.0 | TMSOH | 33.71 | B |
| P5.39 | 1.35 | 67.43 | 30.0 | TMSOH | 134.85 | B |
| P5.40 | 1.35 | 67.43 | 30.0 | TMSOH | 269.60 | B |
| P5.41 | 1.35 | 67.43 | 30.0 | TMSOH | 674.43 | B |

### A5.1.2.3 Targeting molecular weight

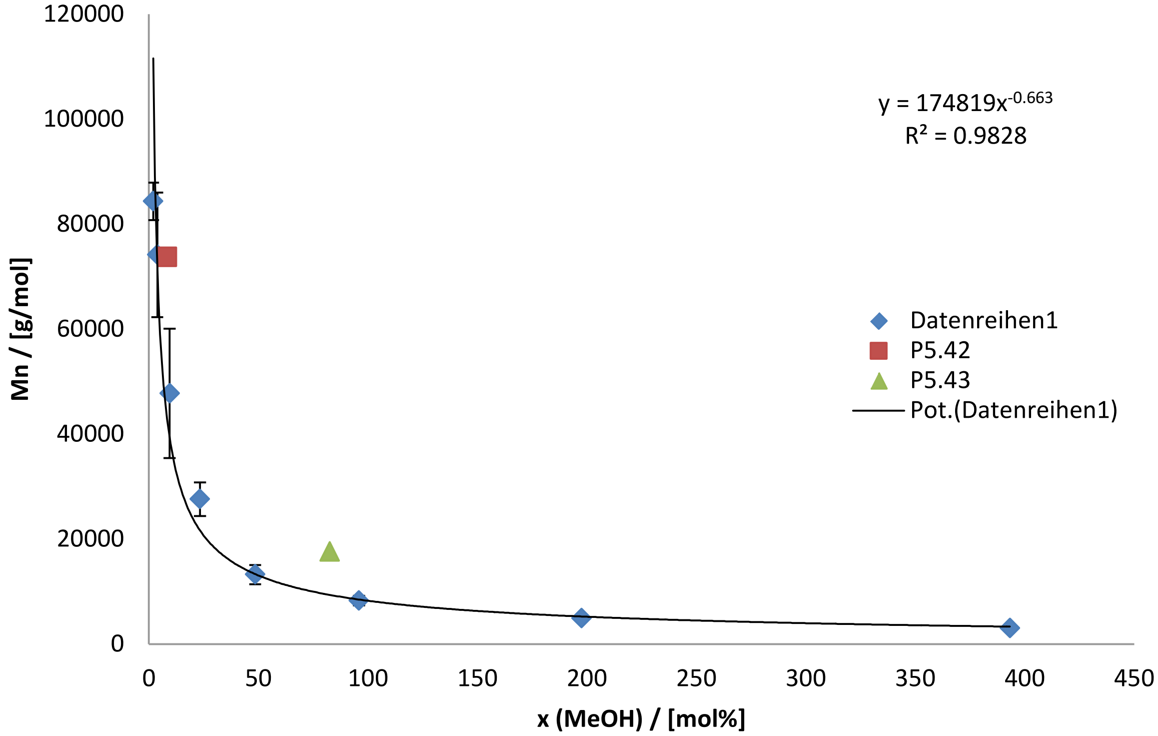

**Chart A5-1: Number averaged molecular weight of polymers depending on the used methanol concentration related to the amount of D4. Results are taken from polymerization experiments P5.18 – P5.25.**

P5.42 und P5.43 ar carried out following *Polymerization Procedure A*. According to Chart A5-1 the amount of methanol is calculated to target a certain molecular weight in polymer.

**Table A5-4: Experimental parameters and results of P5.42 and P5.43.**

| No | n (TBD) [mmol] | n ($D_{4)}$ [mmol] | Acetonitrile V [mL] | n (MeOH) [mmol ] | Conversion [%] | $M_n$ target [g/mol] | $M_n$ [g/mol] | PDI |
|---|---|---|---|---|---|---|---|---|
| P5.42 | 0.34 | 16.86 | 7.5 | 1.27 | 90 | 43000 | 73700 | 1.71 |
| P5.43 | 0.34 | 16.86 | 7.5 | 12.84 | 93 | 9000 | 17400 | 1.51 |

## A5.2 Investigation of reaction parameters

### A5.2.1 Polymerization experiments with varying reaction parameters

Experiments are performed according to *Polymerization Procedure D* described in A4.3.4.1

The screened parameter-combinations are shown in Table A5-5.

**Table A5-5: Summary of screened parameter-combinations.**

| No. | $T_{oil\ bath}$ [°C] | n ($D_4$) [mmol] | n (TBD) [mmol] | n (MeOH) [mmol] | V (Acetonitrile) [mL] | stirring speed [rpm] | Parameter changed |
|---|---|---|---|---|---|---|---|
| P5.44 | 81 | 67.43 | 1.35 | 134.85 | 30 | 250 | Reaction Temperature |
| P5.45 | 95 | 67.43 | 1.35 | 134.85 | 30 | 250 | |
| P5.46 | 40 | 67.43 | 1.35 | 134.85 | 30 | 250 | |
| P5.47 | RT | 67.43 | 1.35 | 134.85 | 30 | 250 | |
| P5.48 | 65 | 67.43 | 0.67 | 134.85 | 30 | 250 | TBD concentration |
| P5.49 | 65 | 67.43 | 0.33 | 134.85 | 30 | 250 | |
| P5.50 | 65 | 67.43 | 0.06 | 134.85 | 30 | 250 | |
| P5.51 | 65 | 67.43 | 1.35 | 134.85 | 60 | 250 | Amount of solvent |
| P5.52 | 65 | 67.43 | 1.35 | 134.85 | 10 | 250 | |
| P5.53 | 65 | 67.43 | 1.35 | 134.85 | 30 | 500 | Stirring speed |
| P5.54 | 65 | 67.43 | 0.66 | 134.85 | 10 | 250 | Optimized conditions |

### A5.2.2 Solubility of $D_4$

To quantify the solubility of $D_4$ in acetonitrile, 2.532 g of acetonitrile-d3 (121.44 mmol) and 2 g of $D_4$ (6.74 mmol) are mixed for 48 h and then put aside until phases separated. The amount of $D_4$ dissolved in the acetonitrile-d3-phase is quantified by adding 0.04321 g of naphthalene (0.337 mmol) as a standard to the analyzed 0.422 g of acetonitrile-phase using NMR. Calculations are done according to Eq. A5-1.

$$n_{D_4} = \frac{m_{Naph}}{M_{Naph}} \frac{I_{D_4}}{I_{Naph}} \frac{N_{Naph}}{N_{D_4}} \frac{p}{100\%}$$ **Eq. A5-1**

where n = number of moles [mol]
m = deployed mass [g]
M = molar mass [g/mol]
I = Integral
N = number of contributing nuclei
p = purity [%]

Exemplary NMR data for solubility measurements:

$^1$**H-NMR** ($CD_3CN$, 300 MHz, 297 K, ppm): δ = 0.14 (m, Si-C$\underline{H_3}$, $D_4$); 2.29 (s, $\underline{H_2}O$); 7.51, 7.89 (m, C$\underline{H}$ aromat, naphthalene).

### A5.2.3 Cost calculation

In the following a cost calculation is performed for the production for a 1 kg batch. Not included are costs such human resources, supplies (e.g. electricity etc.) and also chemicals which are needed for work up. Also the costs for hydroxy compounds which are needed as coinitiator and end-capping agent are neglected. Their amount depends on the molecular weight, which the polymer shall have:

**Standard conditions:** TBD = 2 mol% , acetonitrile:D4 = 1.5 : 1

**Optimized conditions:** TBD = 0.5 mol% ,acetonitrile = , acetonitrile:D4 = 0.5 : 1

| | **Raw materials** | | | **Standard** | | **Optimized** | |
|---|---|---|---|---|---|---|---|
| | **amount** | **pricing** | **Company** | **amount** | **costs** | **amount** | **costs** |
| **TBD** | 5 g | 34.30 € | Sigma[9] | 9.38 g | 64.35 € | 2.34 g | 16.09 € |
| **Acetonitrile** | 25 L | 1254.50 € | Acros[10] | 1.5 L | 75.25 € | 0.5 L | 25.09 € |
| **D4** | 0,5 L | 121.00 € | TCI[11] | 1.04 L | 251.68 € | 1.04 L | 251.68 € |

Assuming a conversion of 90%, based on the results when using methanol as initiator and when using standard conditions this results in costs of 434.75 €/kg. If the solvent phase is recycled five time costs are decreasing to 273.60 €.

Under optimized conditions a conversion of 89% was achieved. This results in material costs of 329.06 €/kg and when reusing the solvent phase five times the costs drop to 259.91 €/kg.

# A6 Appendix to Chapter 6

## A6.1 Determination of content of cyclic siloxanes

The determination of cyclic siloxanes in the isolated and worked up PDMS polymers is performed via GC-measurements by an external partner.*

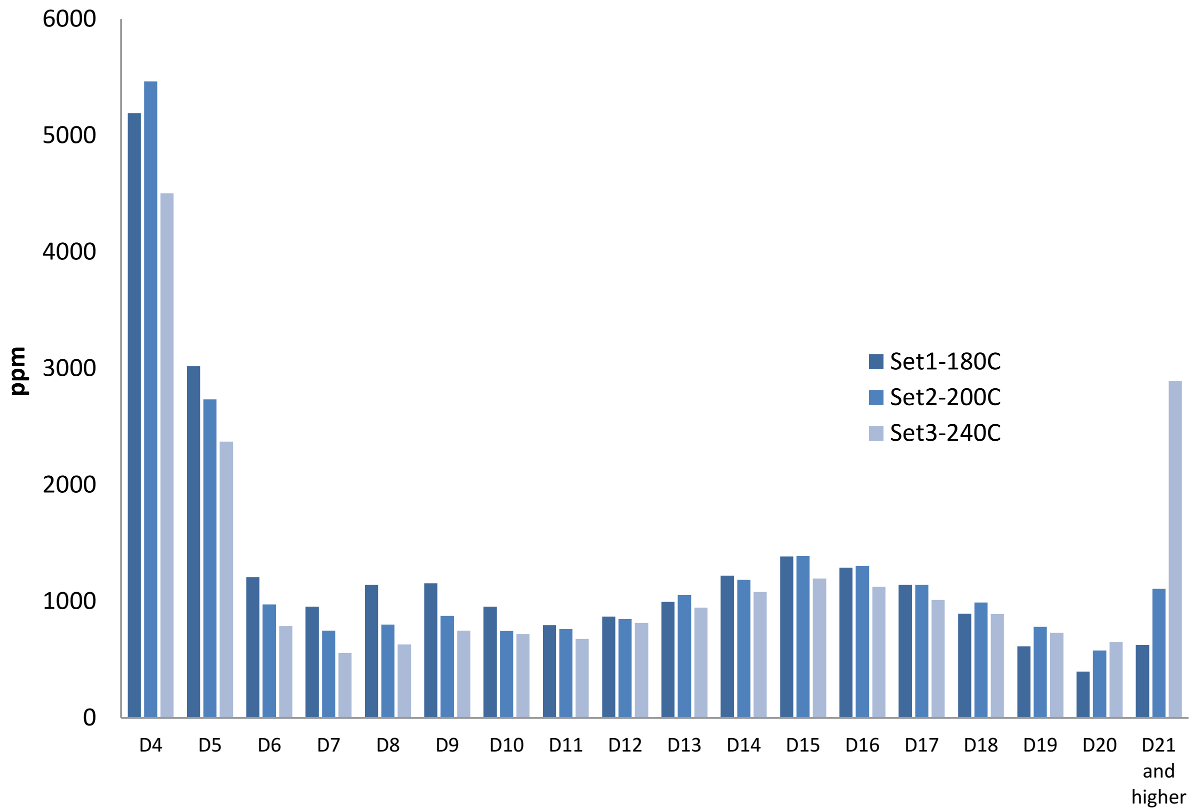

**Chart A6-1: Quantification of macrocycles in DMS-S15.**

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* Measurement were performed by Dr. Dayong Sun.

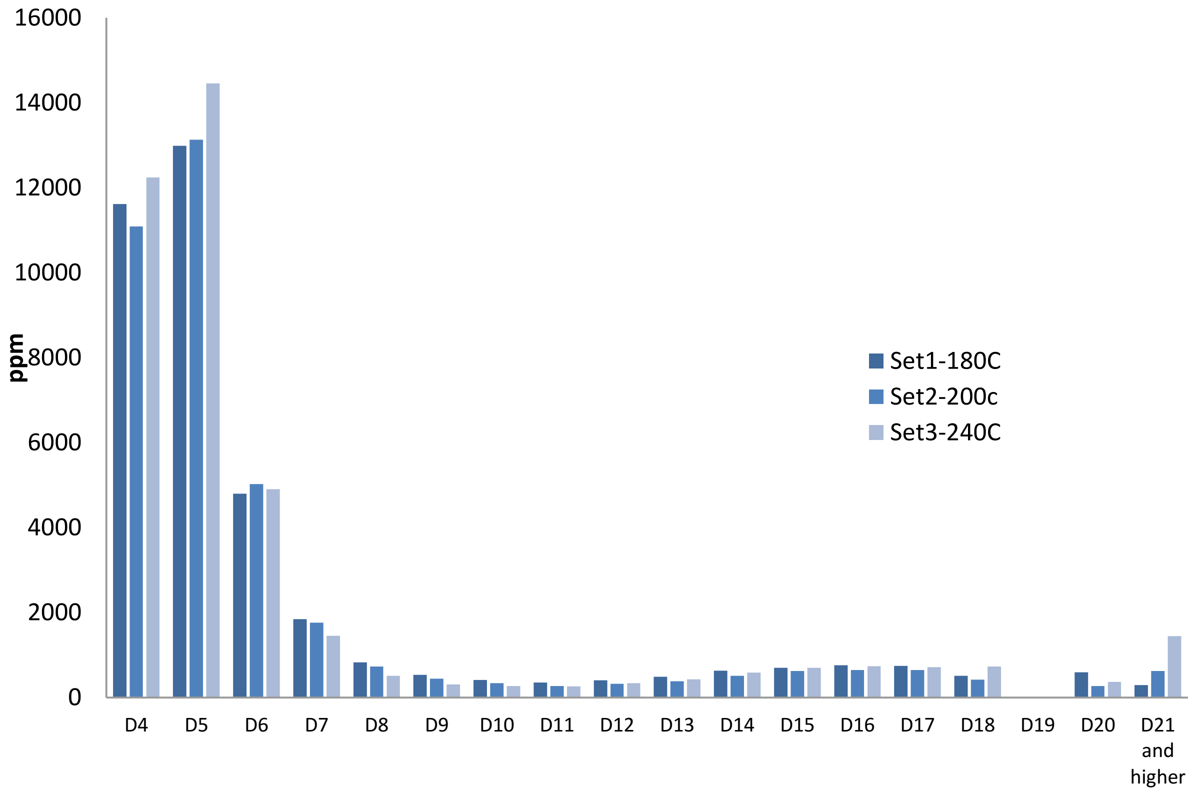

Chart A6-2: Quantification of macrocycles in P4.2.

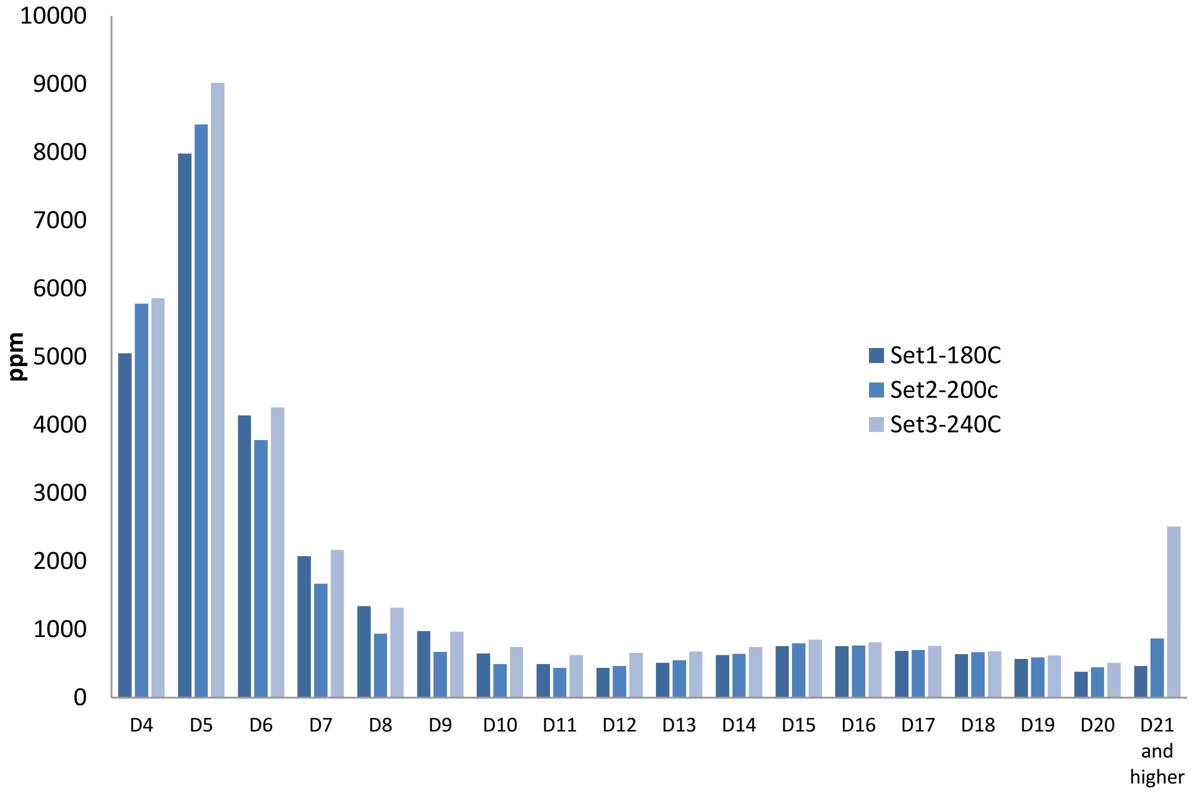

Chart A6-3: Quantification of macrocycles in P4.3.

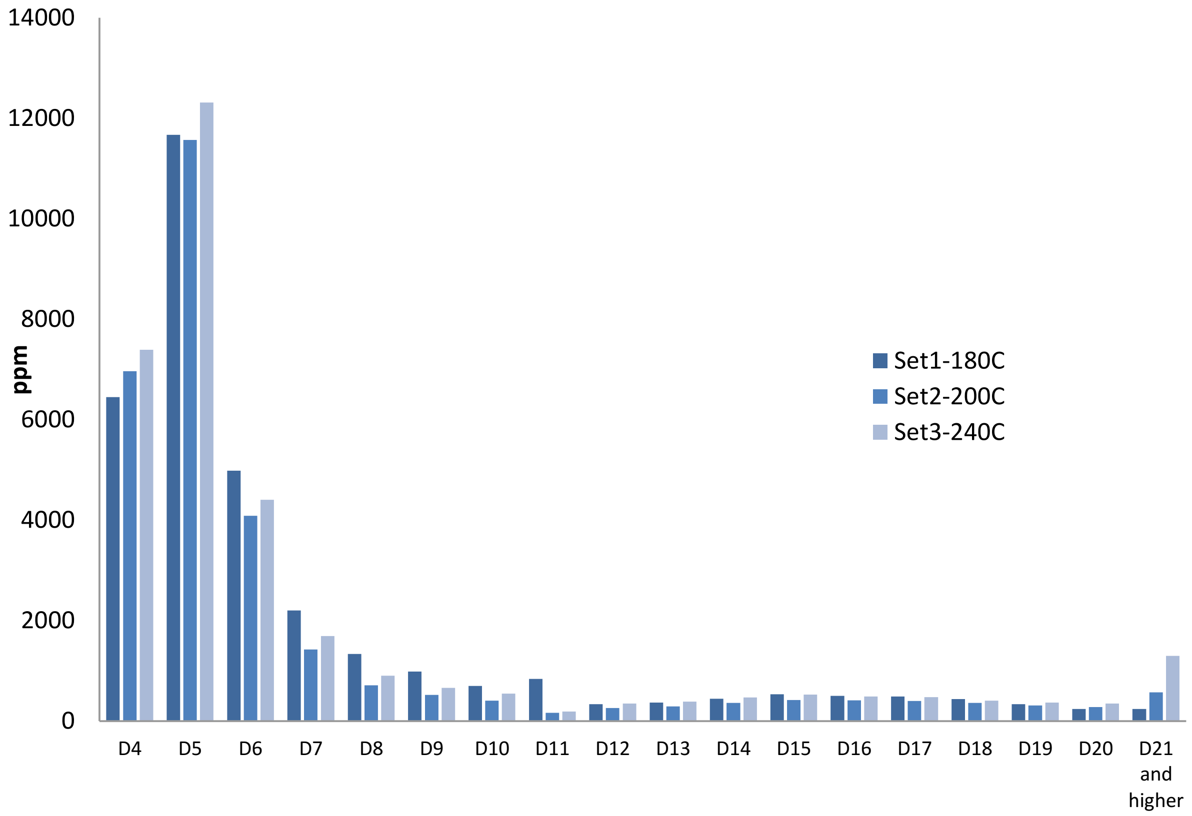

**Chart A6-4: Quantification of macrocycles in P5.1.**

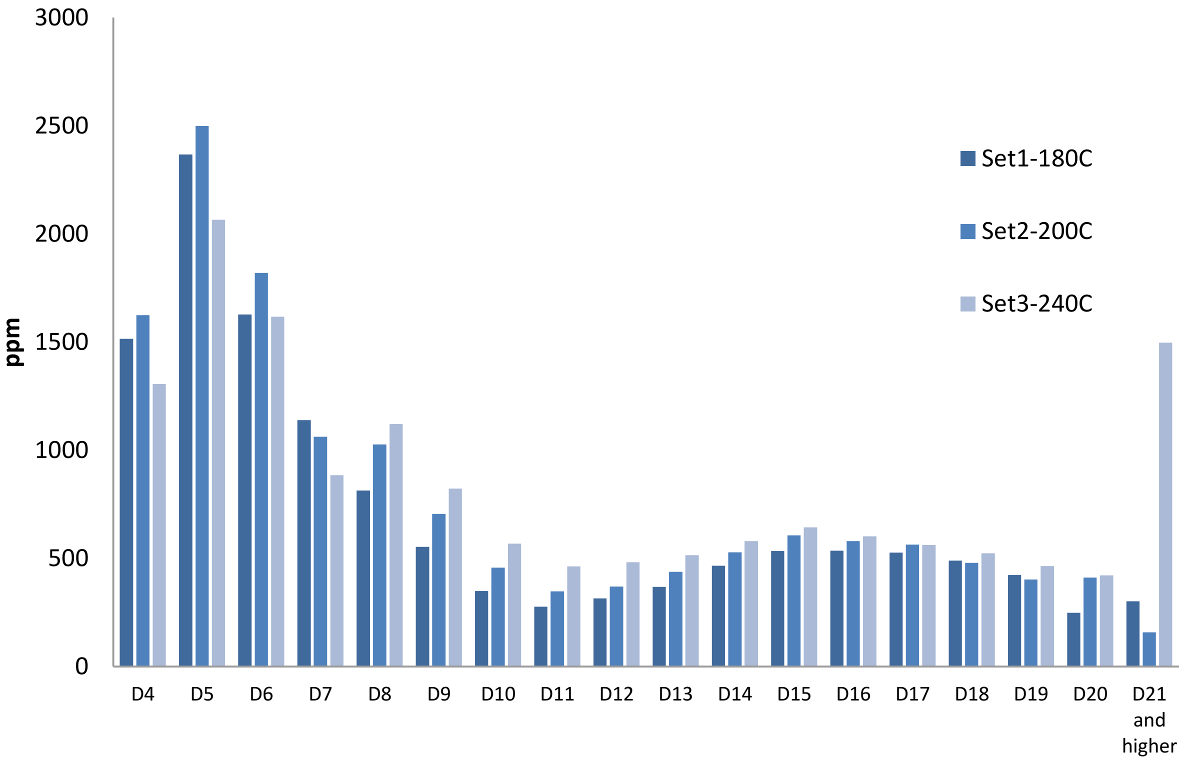

**Chart A6-5: Quantification of macrocycles in P5.2.**

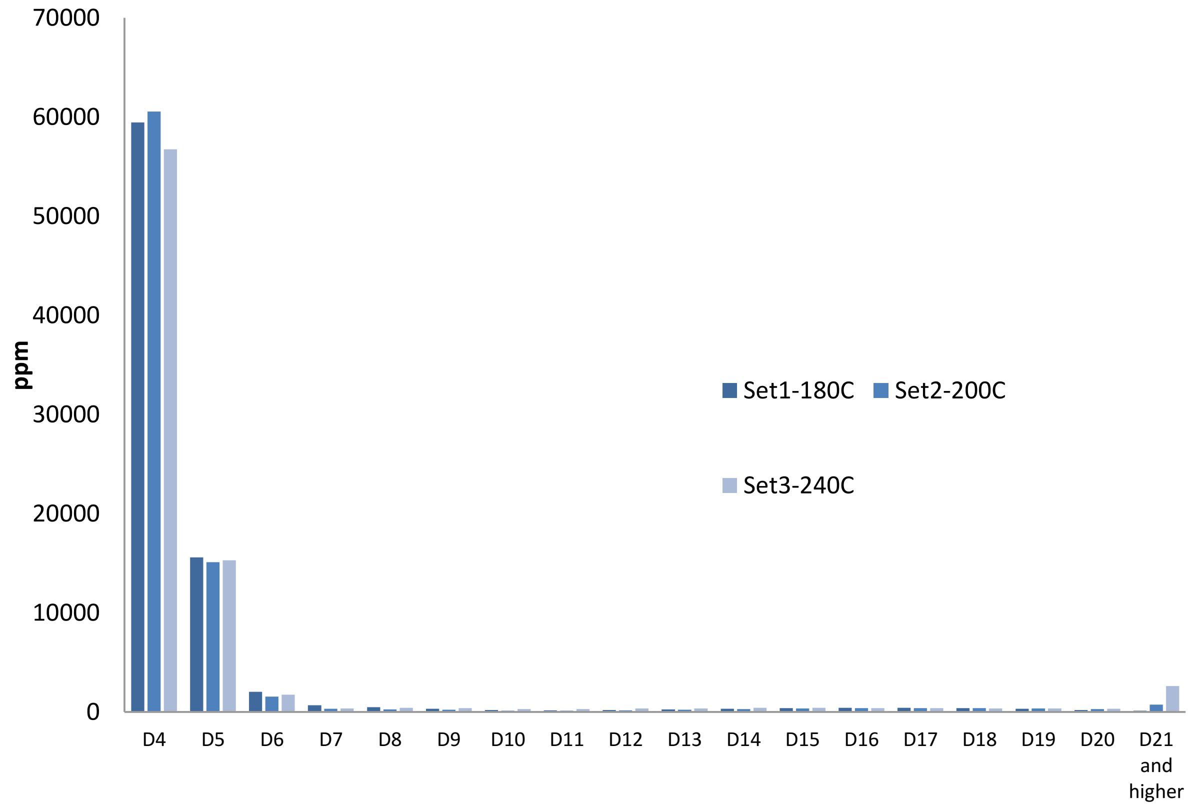

**Chart A6-6: Quantification of macrocycles in P5.3.**

## A6.2 Polymerization experiments with $H_2O$

### A6.2.1 Variation of TBD concentration and reaction temperature

Condensation reactions which are a strong side reaction of ROP if using water as initiator shall be inhibited in order to gain better control over molecular weight and more reproducible results. Polymerization reactions are performed according to *Polymerization procedure E.* Results are summarized in Table A6-1.

**Table A6-1: Summary of reaction parameters and results of ROP using either lower initiator concentration or lower reaction temperature.**

| No | n (TBD) [mmol] | n ($D_4$) [mmol] | Acetonitrile V [mL] | n ($H_2O$) [mmol ] | $T_{oilbath}$ | Conversion [%] | Mn | PDI |
|---|---|---|---|---|---|---|---|---|
| P6.1 | 1.35 | 67.43 | 30.0 | 67.43 | 65 | 94 | 52300 | 1.50 |
| P6.2 | 1.35 | 67.43 | 30.0 | 67.43 | 40 | 93 | 52100 | 1.39 |
| P6.3 | 1.35 | 67.43 | 30.0 | 67.43 | 23 | 60 | 18600* | 1.43* |
| P6.4 | 0.34 | 67.43 | 30.0 | 67.43 | 65 | 94 | 33500 | 1.43 |
| P6.5 | 0.07 | 67.43 | 30.0 | 67.43 | 65 | 85 | 22600 | 1.42 |

*unprocessed polymer

Both reducing the reaction temperature as well as reducing the amount of coinitiator result in lower molecular weights.

## A6.2.2 Dosing experiments

### A6.2.2.1 Dosing of monomer (P6.6)

The polymerization is carried out under inert gas in a moisture free atmosphere. First TBD (1.35 mmol) and water (134.85 mmol) are submitted into an argon-flushed, oven-dried three neck flask equipped with reflux condenser, mechanical stirrer and a septum. They are dissolved in dry acetonitrile (30 mL). While stirring (250 rpm) ~5 mL of $D_4$, which was dried over molecular sieves, is added. Reaction is started by dipping into preheated oil bath (65 °C). After 1 h a first sample is taken and another ~5 mL of $D_4$ are added to the reaction mixture. In this way two more portions of each ~5 mL are added to the reaction mixture after 2 and 3 h reaction time and samples are taken before. All in all 67.43 mmol of $D_4$ are added. The reaction is stopped after 24 h by removing the heat source. After cooling down to room temperature phases are separated. The polymer phase is dissolved in toluene. The polymer phase is washed with water and dried over $Na_2SO_4$. The polymer is stripped in high vacuum (<1*10-3 mbar) at 80 °C.

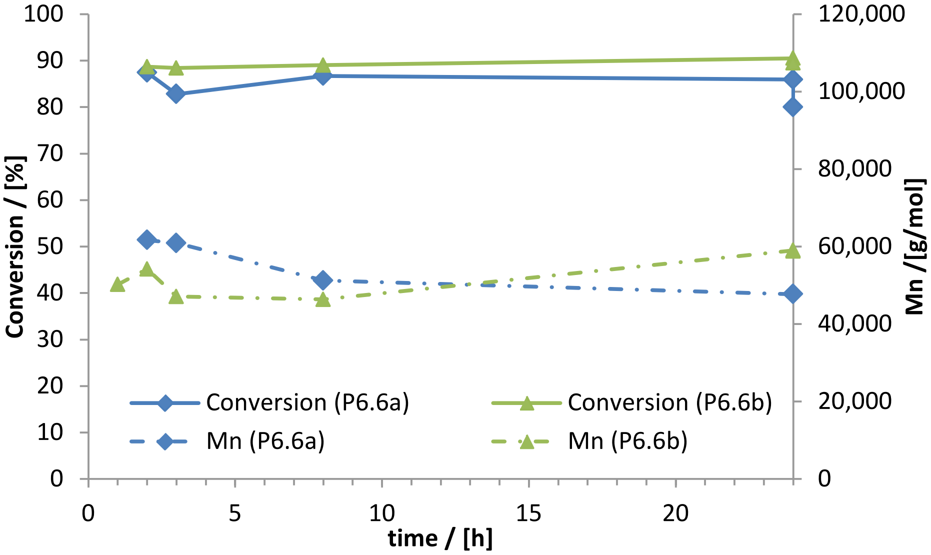

**Chart A6-7: Course of conversion and number averaged molecular weight of experiments P6.6 a and b.**

The results of these experiments summarized in Chart A6-7 show that conversion stays constant although $D_4$ is dosed in. This means that the added portion of $D_4$ can be consumed in between 1h. Unfortunately samples taken after the first hours could not be evaluated. Reproducibility seems to be a problem due to the fact that both polymers show a different course when tracking molecular weight. For ***P6.6a*** it seems that molecular weight breaks down from the beginning with is not explainable. However the experiments have to be repeated another time.

Compared to P5.31 (conversion = 92 %, Mn = 41500 g/mol) where same amounts of water were used conversion is in the same range but molecular weight especially regarding ***P6.6b*** is higher.

More experiments in this direction have to be undertaken in order to investigate whether dosing over longer periods would show similar results or whether dosing of higher amounts of $D_4$ would lead to even higher molecular weights. Last but not least reproducibility has to be checked by repeating this experiment several times as already mentioned.

#### A6.2.2.2 Dosing of water (P6.7)

The polymerization is carried out under inert gas in a moisture free atmosphere. First TBD (1.35 mmol) and water (~0.6 mL) are submitted into an argon-flushed, oven-dried three neck flask equipped with reflux condenser, mechanical stirrer and a septum. They are dissolved in dry acetonitrile (30 mL). While stirring (250 rpm) 67.43 mmol of $D_4$, which was dried over molecular sieves, is added. Reaction is started by dipping into preheated oil bath (65 °C). After 1 h a first sample is taken and another 0.6 mL $H_2O$ are added to the reaction mixture. In this way two more portions of each ~0.6 mL are added to the reaction mixture after 2 and 3 and samples are taken before. All in all 134.85 mmol of $H_2O$ are added. The reaction is stopped after 24 h by removing the heat source. After cooling down to room temperature phases are separated. The polymer phase is dissolved in toluene. The polymer phase is washed with water and dried over $Na_2SO_4$. The polymer is stripped in high vacuum (<1*10-3 mbar) at 80 °C.

Conversion was estimated was calculated top 93 % already after the first hour and remained constant compared to the sample taken after 24 h. The value has to be taken carefully. Due to the high viscosity of the polymer homogeneous sample taking could not be guaranteed.

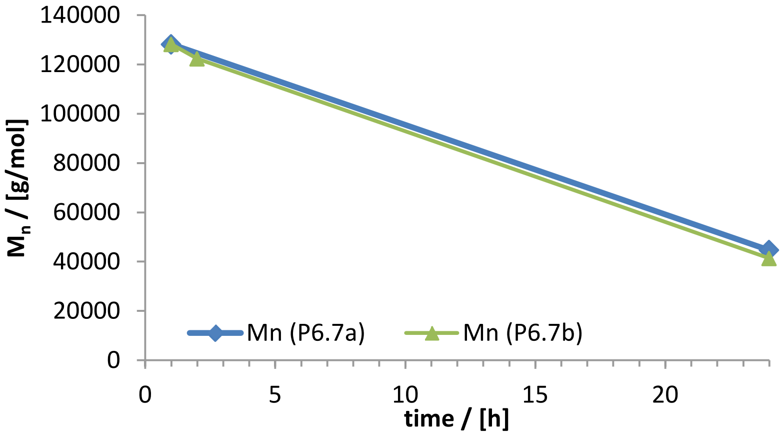

**Chart A6-8: Course of conversion and number averaged molecular weight of experiments P6.7 a and b.**

Interestingly it seems that molecular weight is decreasing continuously. But due to the high viscosity sample taking after the first two hour was not possible anymore. The trend might be not true and has to be investigated further. The breakdown of the polymer might be related to a polymer break down, but according to the high conversion no $D_4$ formats which would speak against backbiting reactions. But the formation of higher cyclic species has to be taken into account and was not yet checked on.

When comparing this results to P5.31 (conversion = 92 %, Mn = 41500 g/mol) than similar results are achieved.

More experiments in this direction have to be undertaken in order to investigate whether dosing over longer periods would show similar results, whether dosing of higher amounts of water would lead to even lower molecular weights. Last but not least reproducibility has to be checked by repeating this experiment several times.

## A6.3 Monomer mixtures

In general the polymerization experiments are carried out under inert gas in a moisture free atmosphere. First TBD and alcohol are submitted into an argon-flushed, oven-dried three neck flask equipped with reflux condenser, mechanical stirrer and a septum. They are dissolved in dry acetonitrile. While stirring (250 rpm) cyclic siloxanes are added. Reaction is started by dipping into preheated oil bath (65 °C). The reaction is stopped after 24 h by removing the heat source. After cooling down to room temperature phases are separated. The polymer phase is washed with methanol and stripped in high vacuum (<1*10-3 mbar) at 80 °C.

Reaction parameters and results are summarized in Table A6-2:

**Table A6-2: Summary of experiments using different monomer mixtures.**

| No | n (TBD) [mmol] | n (D$_{4)}$ [mmol] | n (D$_{5)}$ [mmol] | Acetonitrile V [mL] | n (MeOH) [mmol] | Conversion [%] | Mn [g/mol] | PDI |
|---|---|---|---|---|---|---|---|---|
| P6.8 | 0.54 | --- | 26.97 | 15.0 | 53.95 | 80 | 5000 | 1.33 |
| P6.9 | 0.28 | 3.37 | 10.79 | 7.5 | 28.32 | 71 | 5700 | 1.16 |
| P6.10 | 0.61 | 16.86 | 13.49 | 15.0 | 60.69 | 70 | 5000 | 1.43 |
| P6.11 | 0.65 | 26.97 | 5.39 | 15.0 | 64.73 | 88 | 8600 | 1.39 |

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| 12.04.2018 – 13.04.2018 | **Rhetorik**<br>Management-Institut Dr. A. Kitzmann, Münster |
| 28.06.2017 | **Von der Erfindung zum Patent**<br>Universitätsbibliothek Rostock / Deutsches Patent- und Markenamt; Rostock |
| 16.11.2016 | **Basics of Dealing with Intellectual Property**<br>Leibniz-Institut für Katalyse / Ascenion GmbH, Rostock |
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## Teilnahme an Workshops und Konferenzen

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| 08/2016 | **8th European Silicon Days**, Poznan, Polen. |
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## Publikationen

T. Köhler, L. Grefe, E. Mejia, U.Kragl, C. Despotopoulou, T. Hémery, J. Klein, Patent app. num. EP 18185931.5, European patent office, priority date 27.07.2018.
*“Process for the Polymerization of Cyclosiloxanes*”

A.Wanninger, H. E. Katerinopoulos, T. Köhler *et al*., SOFW Journal, 2015, 1-2, 50 – 58.
*„Sustainable Sources for Cosmetic Ingredients – Evaluation of the Biomass of Crete as a Model Region“.*

*A. Wanninger, T. Köhler, COSSMA,* ***2014****, 9, 26 – 27.*
*„Silikone – Multitalente für die Kosmetik?“*